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## **Data Analysis for Preliminary Conceptual Model Design, Vadose Zone Monitoring System (VZMS), McClellan AFB 1997 Annual Report**

P.T. Zawislanski and C.M. Oldenburg

**Earth Sciences Division**

January 1998

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**Earth Sciences Division  
Ernest Orlando Lawrence Berkeley National Laboratory  
Berkeley, CA 94720**

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**January 5, 1998**

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## **1.0 INTRODUCTION**

Vadose zone investigations are being performed at site S-7 in IC 34, at McClellan AFB. At this location (Fig. 1), a Vadose Zone Monitoring System (VZMS) (LBNL, 1996) is being used to collect subsurface data including hydraulic potential, soil gas pressure, moisture content, water chemistry, gas chemistry, and temperature. Although each individual data set is useful in improving the characterization of this contaminated site, the overall purpose of data collection is to provide input for the conceptual and numerical modeling of VOC transport in the vadose zone and the exchange of contaminants between the vadose zone and groundwater. In this report we submit a summary and preliminary analysis of the data collected through the end of 1997 and present it in the context of input for the impending modeling. This report merges findings from both the first and second half of 1997 and is presented as an "annual" report in lieu of two semi-annual reports, due to the fact that insufficient data had been collected up to mid-June to allow a meaningful analysis.

## **2.0 MODELING STRATEGY FOR ENHANCED VZMS DATA ANALYSIS**

### **2.1 Introduction**

As part of the analysis of data collected from the VZMS, we will be carrying out numerical simulations of two-phase multicomponent flow and transport. The purpose of the numerical simulations is to quantify interpretations, test hypotheses, and perform sensitivity and uncertainty analyses so that a better understanding of the physical system can be developed. The approach we take is to use all of the available data for the site including VZMS temporal data to build a plausible conceptual model. This conceptual model is then implemented into a numerical model by which we can simulate the evolution of the system over time. Forward calculations to simulate temporal changes in moisture content, gas phase pressure, contaminant concentrations, and temperature can be carried out and results compared against measurements from the VZMS. Differences between the model and the actual system as measured by the field data can be reduced by adjusting the least certain parameters in the model and running the forward calculation again in a history matching mode. We can then test hypotheses and investigate key questions such as whether VOCs are being transported downwards and the rates of transport of VOCs. The enhanced data analysis is carried out using the three-dimensional multiphase (gas, aqueous, NAPL) and multicomponent (air, water, VOC) integral finite difference simulator T2VOC (Falta et al., 1995; 1992a; 1992b) for flow and transport, and ITOUGH2 (Finsterle, 1993) for sensitivity and uncertainty analyses. In this section,

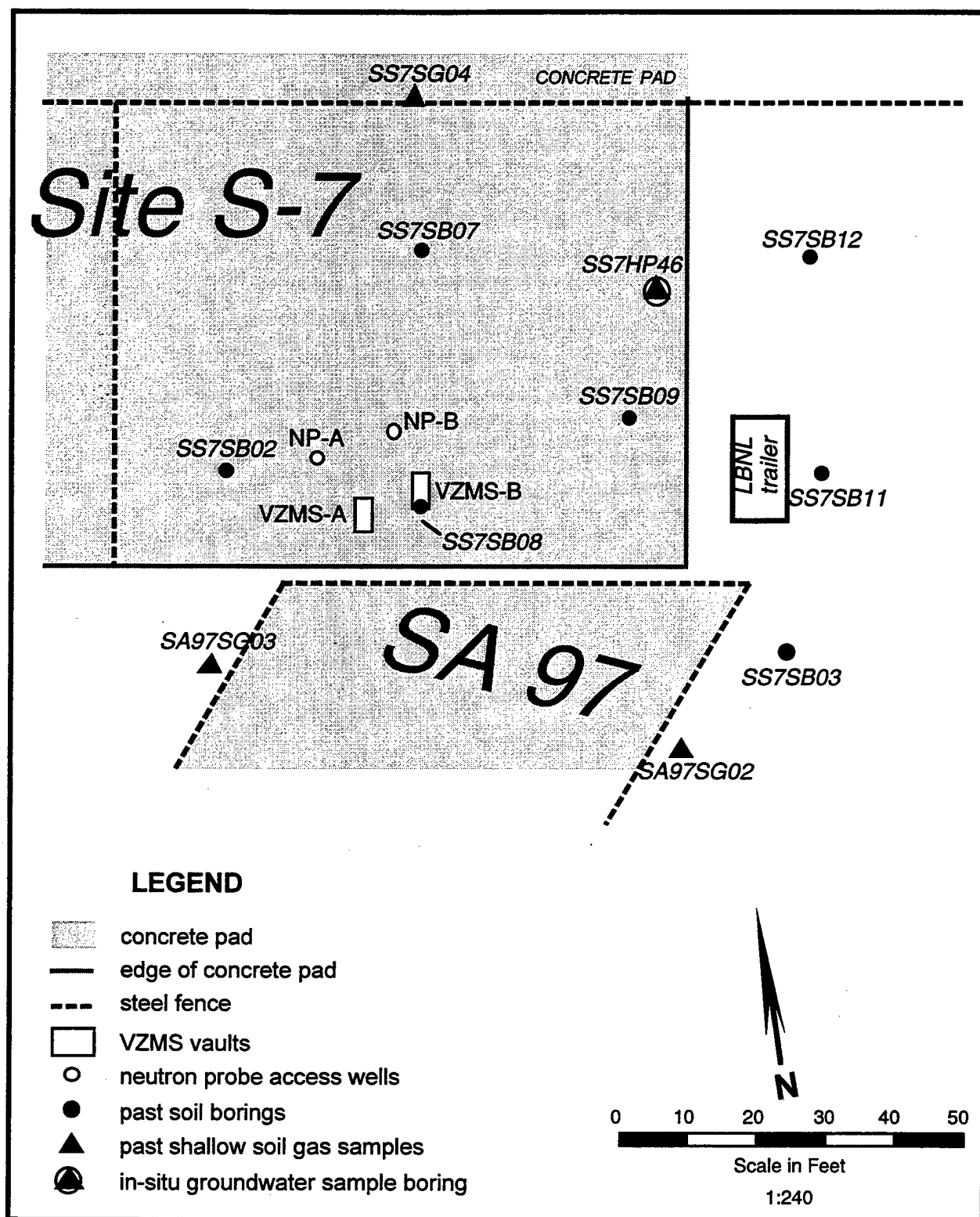


Figure 1. Location of VZMS installations relative to existing and former structures at Site S-7, including locations of previously drilled boreholes and soil-gas sampling points.

we present the general methodology and approach for using these computational tools for the enhanced data analysis which will begin later this year.

## **2.2 Model Development**

### **2.2.1 Conceptual Model**

The main challenge in the numerical simulation of natural systems is the development of a defensible conceptual model. The conceptual model is an abstraction of a natural system that captures the key physical and chemical processes in the system. For the system at S-7 in IC 34 where the VZMS is installed, the conceptual model consists of a thick ( $\approx 110$  ft) section of dry to moist alluvial sediments variably contaminated by VOCs. The system is bounded at the top by a paved surface at atmospheric pressure and ambient temperature. The bottom of the system is at the water table. Water infiltrates at the top during rainfall events, while drying occurs at the top at other times. 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. The numerical model will allow for contaminant migration by liquid and gas phase fluxes as well as by diffusion.

### **2.2.2 Domain**

The region within the boundaries of the conceptual model comprises the domain, which should be chosen to be consistent with the available data in terms of length and time scales. For example, with two VZMS boreholes approximately 8 ft apart with data collected at relatively short intervals, we envision a domain that encompasses the boreholes for their full vertical extent ( $\approx 110$  ft) as well as an extension to the water table. We have the choice of carrying out (i) independent one-dimensional simulations for each borehole, (ii) an averaged one-dimensional simulation for both boreholes, (iii) two-dimensional simulations of a cross-section with the boreholes on either side, or (iv) a three-dimensional simulation of a domain encompassing both boreholes, but not extending farther away laterally from the boreholes than the distance between the two boreholes. With any one of these conceptualizations, the dominant flow and transport are assumed to be vertical. Time scales for the system will be on the order of weeks and months, consistent with the data collection frequency. Because we restrict the model to the area very near the boreholes, we can use lithologic logs and core properties as good approximations of the properties of the system. Some simple interpolation will be done for the areas between the boreholes for the two- and three-dimensional cases. Based on the VZMS data collected to date which show contaminant concentrations varying between the two boreholes, our preliminary simulations are going to be based on domain (i),

namely one-dimensional systems for each borehole. As we gain experience with the system, we may move to one of the other conceptualizations.

### **2.2.3 Characterization**

The most important properties that we define for the system are the porosity, permeability, and characteristic curves that describe capillary pressure and relative permeability as a function of liquid saturation. Hydrostratigraphic units with common properties will be defined based on the lithologic logs and measured data (LBNL, 1996, Appendices B and D), as well as on empirical correlations based on grain-size distributions (Shepherd, 1989; Vereecken, 1995). The spacing between the defined hydrostratigraphic units will be some compromise between the detailed spacing afforded by the lithologic logs ( $\approx 1.5$  ft) and the spacing between the 13 VZMS instrumented levels (5 to 10 ft). Although permeability measurements have not been made, reasonable estimates for the purposes of initial simulations can be made based on grain-size analysis (Shepherd, 1989). In addition, laboratory measurements of saturated permeability and moisture characteristic curves will be made on samples which will be collected in 1998. Neutron probe and VZMS data will be used to characterize the sections in terms of moisture content and contaminant distribution.

### **2.2.4 Discretization and Boundary and Initial Conditions**

The domain will be discretized into an appropriate number of layers depending on the hydrostratigraphic units. A simple Cartesian grid will suffice for one-dimensional calculations. We envision somewhere between 50-100 layers. The top of the system will have an atmosphere boundary block that maintains atmospheric pressure, while the bottom will be at the water table and remain fully saturated. The boundary conditions at the top and bottom may vary with time consistent with rainfall events and pressure changes, and this specification can be easily made in T2VOC. Whether or not we choose to enforce a time-varying boundary condition or choose to average over some time frame depends on the time scale of the simulation. Initial conditions for contaminant concentrations will be set based on the first reliable set of measurements from the VZMS.

## **2.3 Simulation Methods**

The enhanced data analysis will be made with the T2VOC (Falta et al., 1995) and ITOUGH2 codes (Finsterle, 1993). These two codes are part of the TOUGH2 family of codes developed at Lawrence Berkeley National Laboratory (Pruess, 1987; Pruess, 1991).

### 2.3.1 T2VOC

T2VOC models the subsurface flow and transport of three phases (aqueous, gas, and NAPL) and three components (water, air, VOC) as well as heat. Transport occurs by gas- and liquid-phase advection and gas-phase diffusion. The particular VOC to be modeled is selected by specification of appropriate physical properties in the input file. In this way, any VOC component can be modeled for which some fundamental physical properties can be defined. Relative permeability and capillary pressure functions are also defined in the input file. While able to model the complex physical processes associated with multiphase flow in the subsurface, T2VOC retains the conceptual simplicity of the integral finite difference method (IFDM) upon which it is based. In the IFDM, there is little of the mathematical abstraction associated with other methods (e.g., the finite element method), and sparse gridding can be used for quick approximate or preliminary calculations. One of the most powerful features of T2VOC is the residual formulation and fully-coupled solution technique that is capable of efficient solution of highly nonlinear flow problems (Oldenburg and Pruess, 1995).

### 2.3.2 ITOUGH2

ITOUGH2 is the inverse modeling, sensitivity, and uncertainty analysis code that uses TOUGH2 for forward modeling. With ITOUGH2, we can perform inverse modeling using T2VOC to fit, for example, simulated gas-phase pressures to observations by changing the permeability field. In addition, ITOUGH2 can be used to perform sensitivity and uncertainty analysis. For example, ITOUGH2 allows the user to conveniently assess the effects on the simulated results of changes in input parameters thus indicating the sensitivity of input parameters. With ITOUGH2 we can also generate, for example, a range of predictions of contaminant concentrations based on Monte Carlo simulations of the system assuming a distribution of permeability as opposed to fixed values. These powerful capabilities allow defensible predictions based on a realistic assessment of the certainty of input properties.

## 2.4 Summary

Enhanced data analysis will be carried out in FY98 in the form of numerical simulations of the unsaturated zone at S-7 in IC 34. A conceptual model based on the data collected at the site will be implemented in the numerical model T2VOC. Forward calculations based on initial conditions measured by the VZMS will be performed and compared against measurements in a history matching mode. Model adjustments will be made to minimize the differences between model results and measured data. Through simulation and numerical experiment, we expect to be able to

test hypotheses and interpretations based on VZMS data collection. For example, we plan to test whether VOCs are being transported more strongly by gas phase diffusion or by gas phase advection, and we can make an assessment of the likelihood that VOCs are being transported downward through the section and the rates of VOC transport. By using ITOUGH2, we may be able to assess which variables control particular processes most strongly, and therefore determine which variables are most important to measure more carefully. In summary, the enhanced data analysis will allow us to fully exploit the detailed data being collected by the VZMS.

### **3.0 SUMMARY OF INPUT PARAMETERS**

#### **3.1 Determination of Moisture Content from Neutron Probe Data**

Neutron logging provides a one-dimensional distribution of moisture content in the formation. Due to the presence of casing and backfill material, as well as the spatial variability of geologic properties of the medium, this information is largely qualitative, although relative percentage change in moisture content at any one point can be quantified. Therefore, this tool is best used to measure changes in the moisture distribution, whether due to evaporation or rainfall infiltration. However, in conjunction with moisture content data from cores, a calibration of neutron counts to moisture content is possible. In this section, available data are used to construct a generic calibration curve for neutron probe measurements and previously presented neutron count data are transformed into estimates of absolute moisture contents.

Neutron logging is being performed at the site using a CPN 503DR Hydroprobe consisting of a 50 mCi Am-Be neutron source and a He detector of thermal neutrons. An obstruction in Well NP-A at 25 ft has prevented the logging of this hole below that depth. Well NP-B is logged to a depth of 98 ft. Thus far, the data have been presented as ratios of readings taken in the borehole to readings taken in a standard Hydroprobe shielded casing.

During the drilling of boreholes for the installation of the VZMS system in December 1995, split-spoon samples of the formation were collected. These samples were subsequently used to measure physical properties of the formation, including moisture content, porosity, bulk density, and particle size distribution. Although a continuous core was collected, only certain depth intervals were analyzed. These intervals were selected based on being representative of major lithologies in the vadose zone. The samples were collected from boreholes into which soil water samplers, tensiometers, gas probes, and thermistors were subsequently installed. Boreholes used for neutron probe access pipe installation were not cored because of their small, 4-inch, diameter.

Therefore, some error will be introduced by comparing moisture data from one borehole to neutron readings from another, even though they are within a few feet of each other.

Fig. 2 shows previously presented neutron probe data (LBNL, 1997a,b,c), expressed as normalized counts. The data collected in December 1995 suggests distinctly lower moisture content from all subsequent readings, which show almost no change relative to each other. This is puzzling because one would not expect such a uniform increase in moisture content throughout the vadose zone, especially given the range of particle size distributions, going from >95% sand to >65% silt+clay. Unfortunately, the neutron log generated on 12/19/95 cannot be corroborated by other readings, since no other readings were taken between 12/95 and 2/97. Therefore, it is possible that either the neutron probe generated erroneous readings or that operator error resulted in the incorrect calibration of the probe.

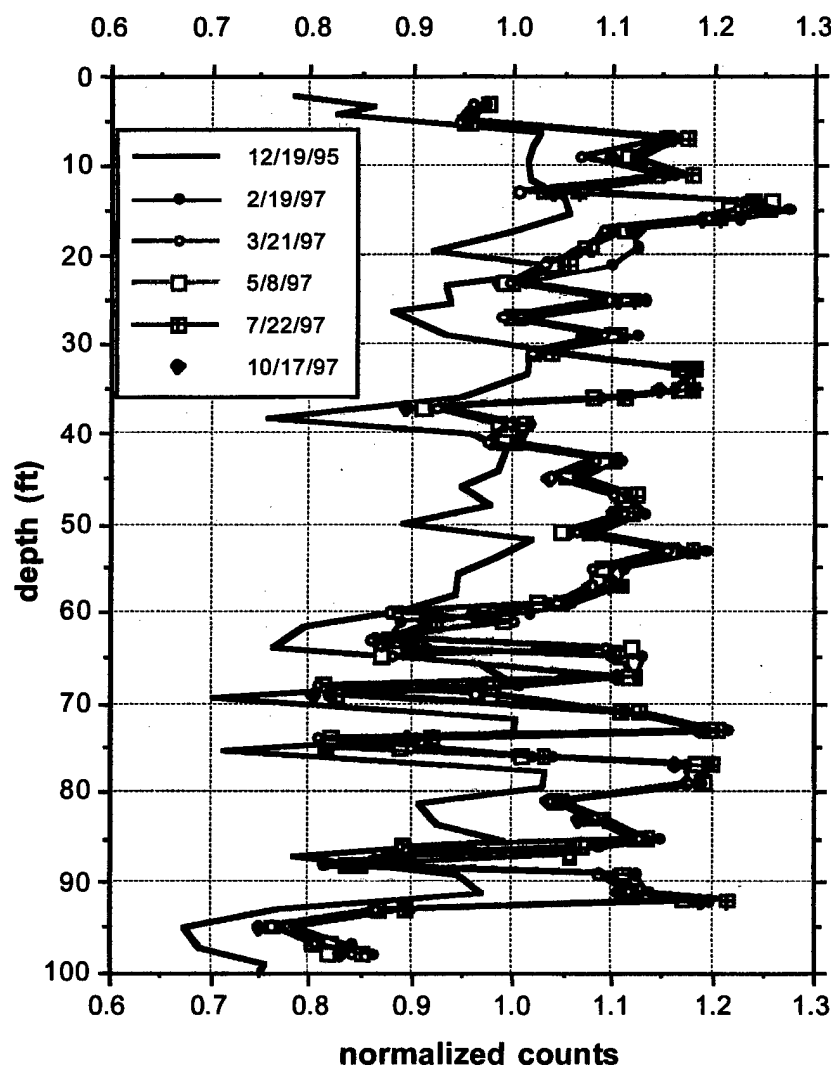
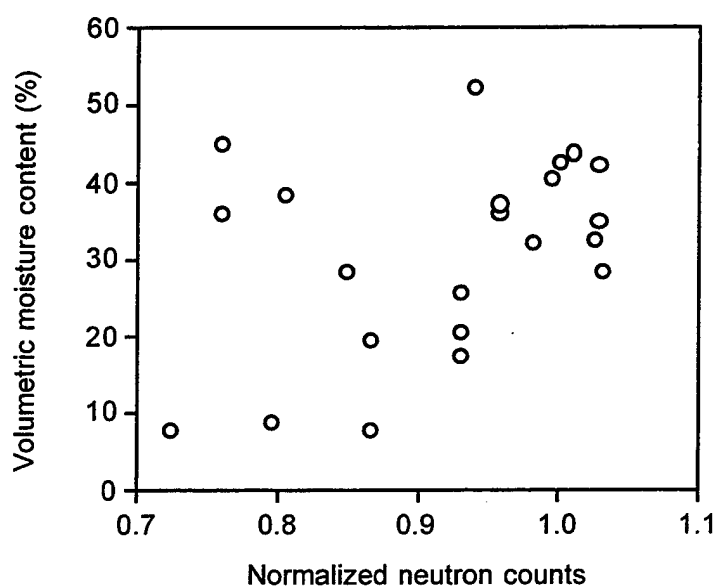
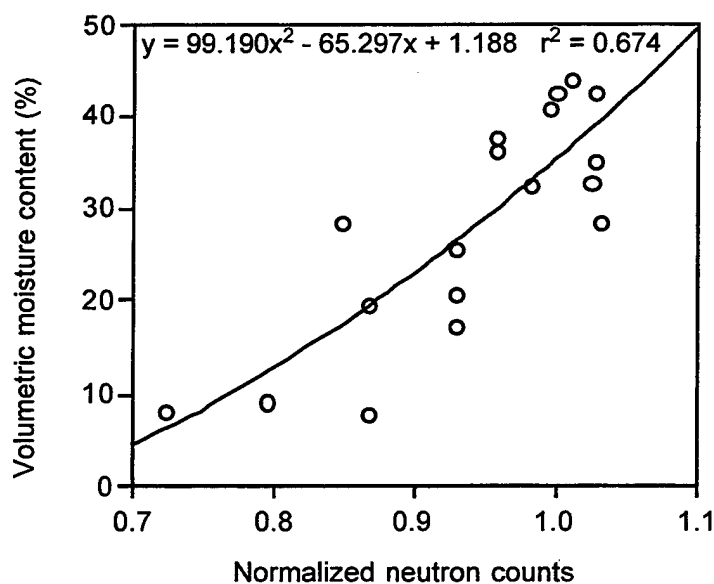


Figure 2. Normalized neutron counts measured in Well NP-B over the period 12/95 to 10/97.

Moisture content data from core analysis were compared with neutron probe readings at equivalent depths. In Fig. 3a, all of the data are shown, while in Fig. 3b four outliers were removed. A second-order polynomial fit ( $r^2 = 0.674$ ) appears to represent the relationship fairly well. The removal of the outliers is reasonable since some of the moisture content and bulk density measurements provided by the contract lab (BSK & Associates, shown in LBNL, 1996) were clearly outside a reasonable range. For instance, in some cases the volumetric moisture content was calculated as being equal to porosity, suggesting full saturation of the medium, a result which contradicts field observations.



**a.**



**b.**

Figure 3. (a) Volumetric moisture content in soil cores and corresponding normalized neutron counts, both collected in 12/95; (b) same relationship, without outliers.

The most apparent feature of the volumetric moisture–neutron count relationship in Fig. 3b is the steepness of the slope over a very narrow range of normalized neutron count values. In effect, very large changes in moisture content would be detected as very small changes in neutron counts. For instance, a quadrupling of moisture content from 10% to 40% results in the normalized neutron count increasing from 0.75 to 1.05. Such a response characteristic is to be expected due to the presence of both a PVC casing and concrete backfill. It has long been recognized that the nature of the access borehole can significantly affect neutron thermalization (Amoozegar et al., 1989). PVC casing, which is the material most often used in environmental applications, is not well suited for neutron logging because of its high chlorine content. Chlorine has a very large capture cross-section for thermal neutrons (Celata et al., 1996) and greatly reduces the thermal neutron count, thereby reducing sensitivity. Concrete grout has the advantage over other backfill materials of having a more or less constant moisture content with time, but a high moisture content nonetheless, resulting in a high background neutron count.

When the polynomial regression is applied to data sets shown in Fig. 2, it becomes apparent that the 12/19/95 data set is erroneous, because the calculated volumetric moisture contents for many depth intervals in all the subsequent data sets exceed the measured porosity values, sometimes by 20-25%, giving impossible saturation values of 1.2 or even higher. Therefore, it can be concluded that the normalized neutron counts collected on 12/19/95 are too low. Although there is no way to rectify these data, it can be safely assumed that the overall moisture content over a depth of 100 ft in such a hydrogeologic setting is not likely to consistently increase at all depths. Thus, an adjustment to the standard neutron count for that date was made, an adjustment which amounted to approximately 7% of the original value, thereby defining the lower boundary on the uncertainty of this calibration. The results of this adjustment are shown in Fig. 4. The adjusted data from 12/19/95 nearly overlaps data from subsequent sample dates. Most of the apparent departures from the trend are due to the fact that the 12/19/95 readings were not always taken at the exact same depths as the subsequent readings. Some other differences, such as those observed at a depth of 80 to 85 ft, may be due to actual changes in moisture content.

Once the adjusted normalized neutron counts are used in a comparison with the lab-measured moisture content data, a similar regression with slightly different coefficients is generated (Fig. 5). This regression was used to convert all of the normalized neutron counts to volumetric moisture content. Fig. 6 shows a comparison of those results for 12/19/95 for both neutron probe access holes with the laboratory-measured moisture contents. The agreement is in general quite good but this is not surprising since most of the lab results shown here were used in the calibration and the generation of the polynomial regression. The discrepancy between NP-A and NP-B in the top 15 ft

of the sediment profile could be caused by slight lithological differences and/or related moisture conditions, which could also be affected by shallow seepage.

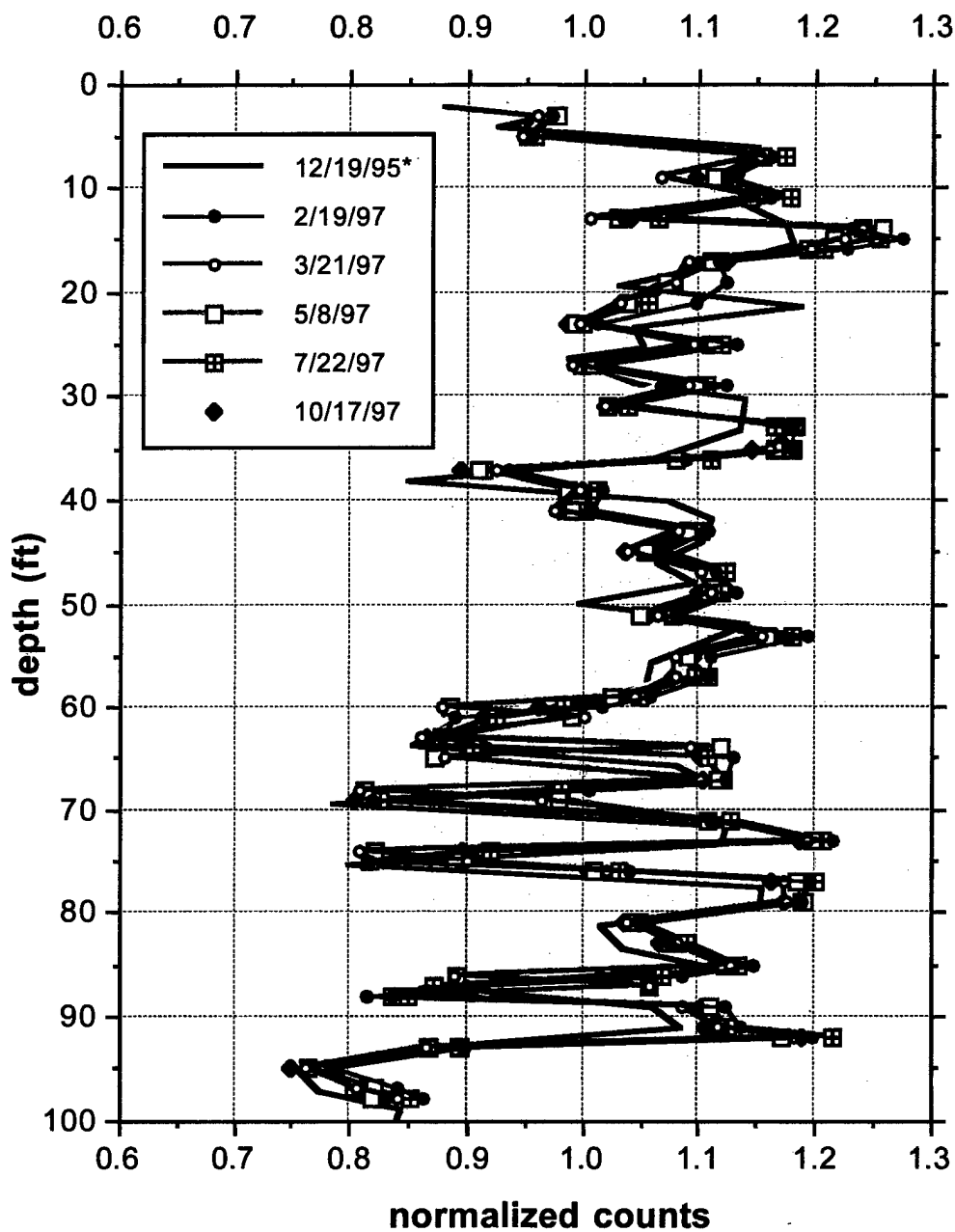


Figure 4. Normalized neutron counts measured in Well NP-B over the period 12/95 to 10/97, with adjusted data from 12/95.

All of the neutron count data, converted to volumetric moisture content, are shown in Fig. 8. Although there are some depth intervals in which moisture content does vary from month to month, all of these changes fall within  $\pm 5\%$  of the mean value. The uncertainty associated with these neutron probe measurements is generally considered to be between 2% and 4% (or between 1 to 2 standard deviations). Therefore, most, if not all of the observed fluctuations fall within or very close to the noise range.

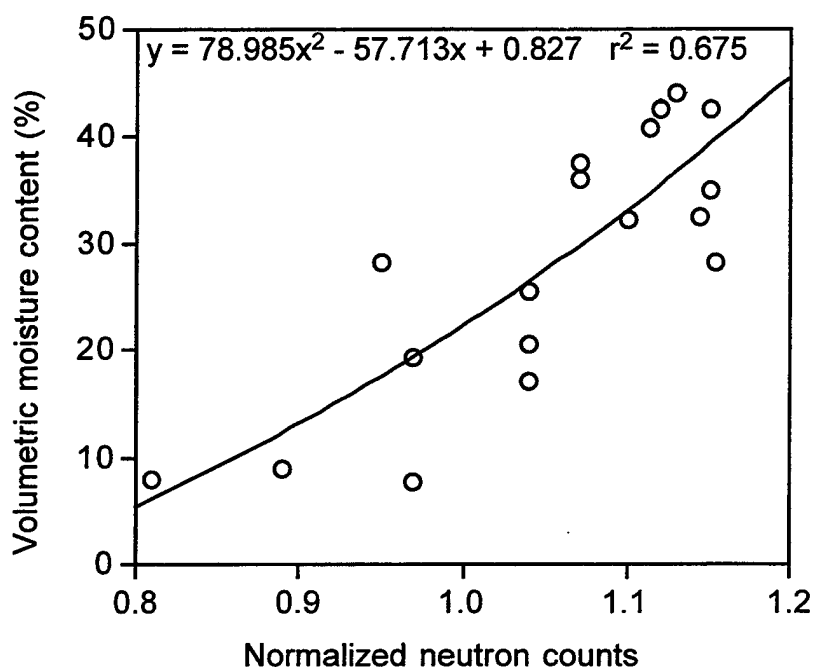


Figure 5. Volumetric moisture content in soil cores and corresponding normalized neutron counts, both collected in 12/95, without outliers, neutron counts normalized to corrected standard count.

The polynomial regression generated by comparing field data with laboratory results should be considered highly approximate for reasons described above. However, the resultant volumetric moisture content data will be useful in both the conceptual and numerical modeling of the system, as described in Section 2. The uncertainty in the volumetric moisture data is likely to be far less than that associated with estimates, and even measurements, of unsaturated permeability.

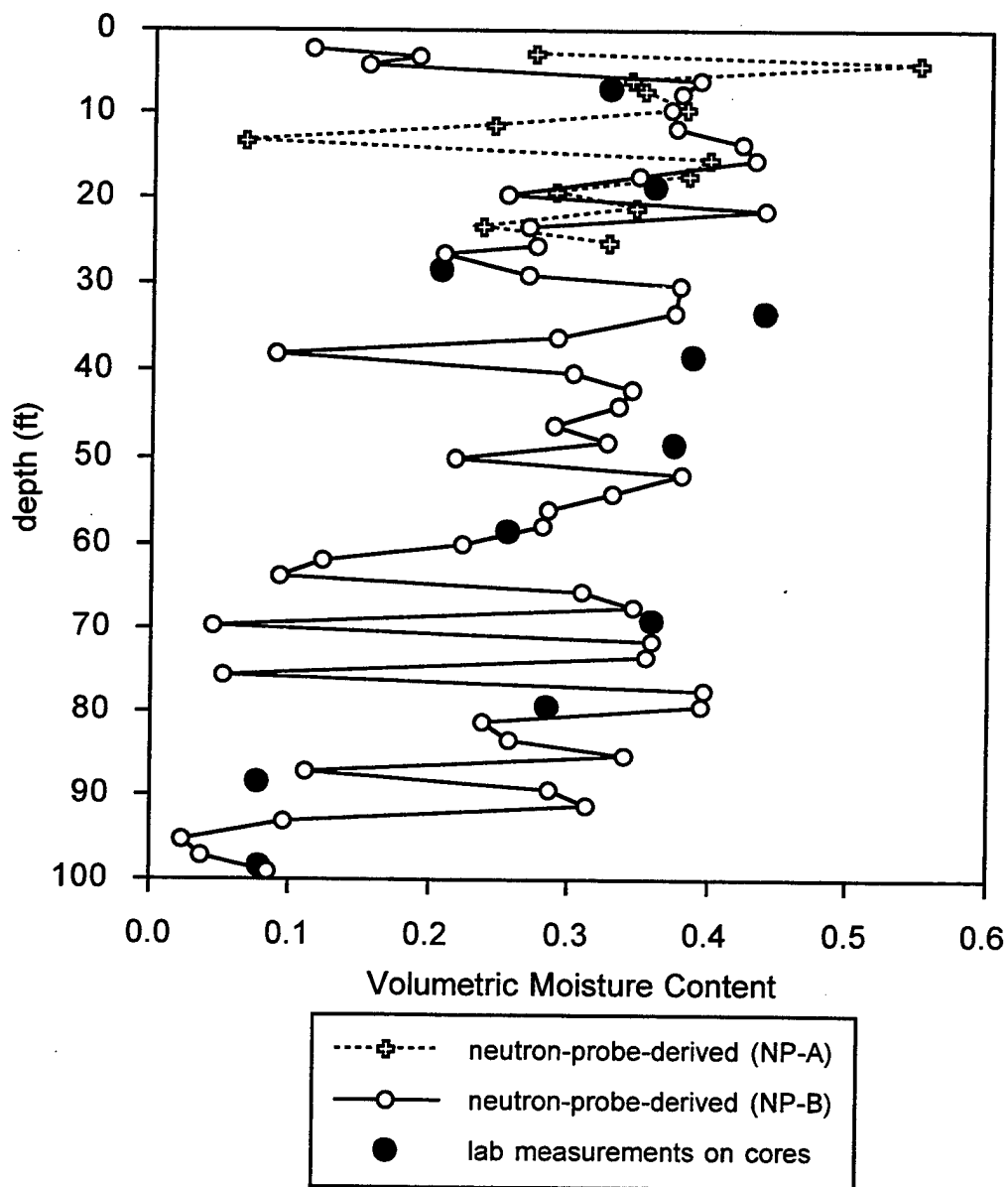


Figure 6. Comparison of neutron-probe-derived volumetric moisture content with laboratory-measured values. Data and samples collected in 12/95.

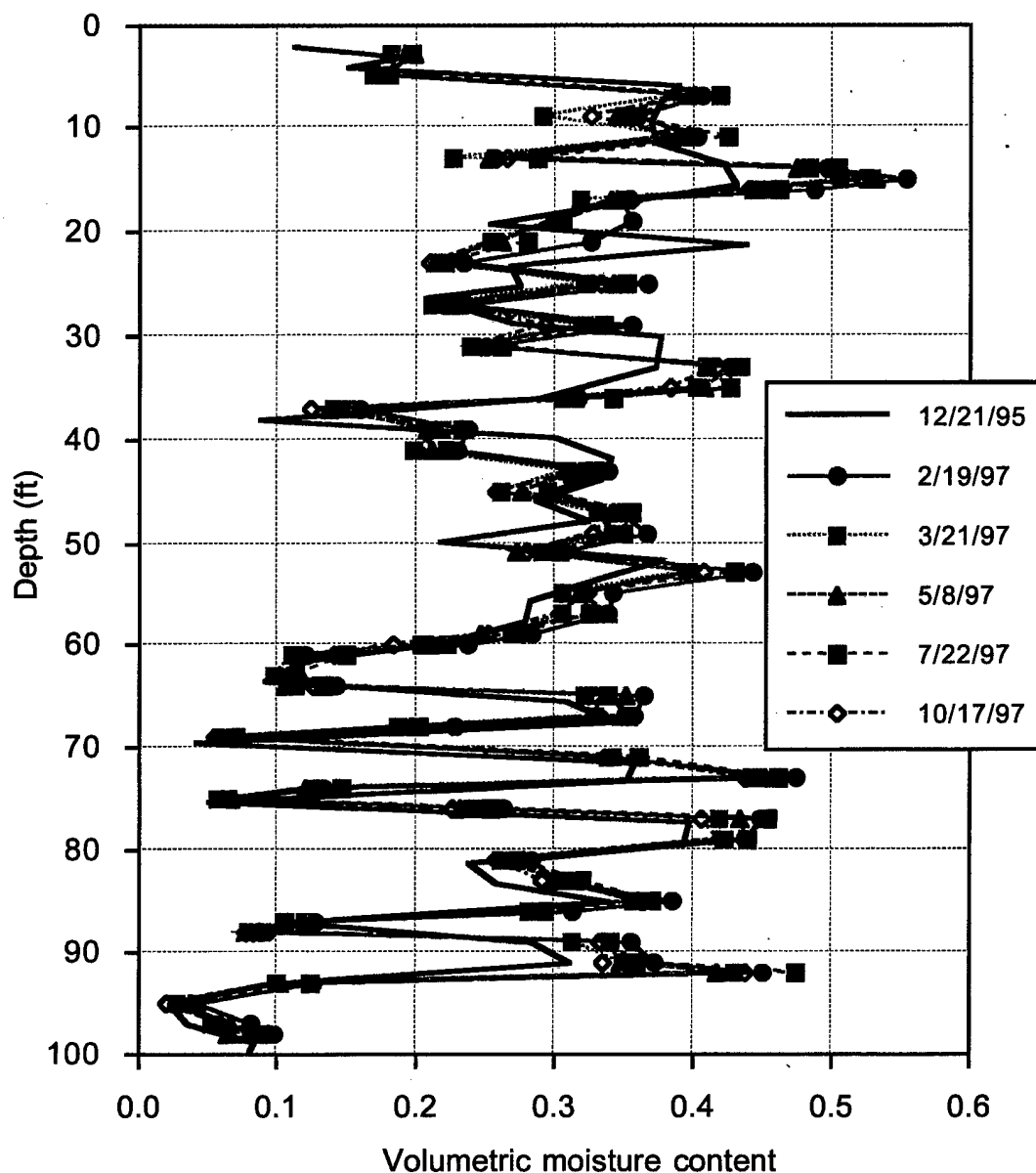


Figure 7. Volumetric moisture content in well NP-B, as derived from neutron probe measurements, 12/95-10/97.

### 3.2 Atmospheric and Formation Temperature

Formation temperature is being measured using in-situ thermistors. The data are collected electronically in real time and the measured resistance is converted to temperature in °C using calibrations generated in the laboratory prior to installation. As expected, the magnitude of air temperature changes is rapidly dampened with depth, due to the very high heat capacity of the formation (Hillel, 1980). Thus, discernible temperature changes are recorded only in the top 18 ft

of the formation, though there are no thermistors between 18 ft and 30 ft, so that it is not possible to define the depth at which temperature is effectively constant. Diurnal changes in air temperature do not result in quantifiable changes in formation temperature, not even at the shallowest depth of 6 ft.

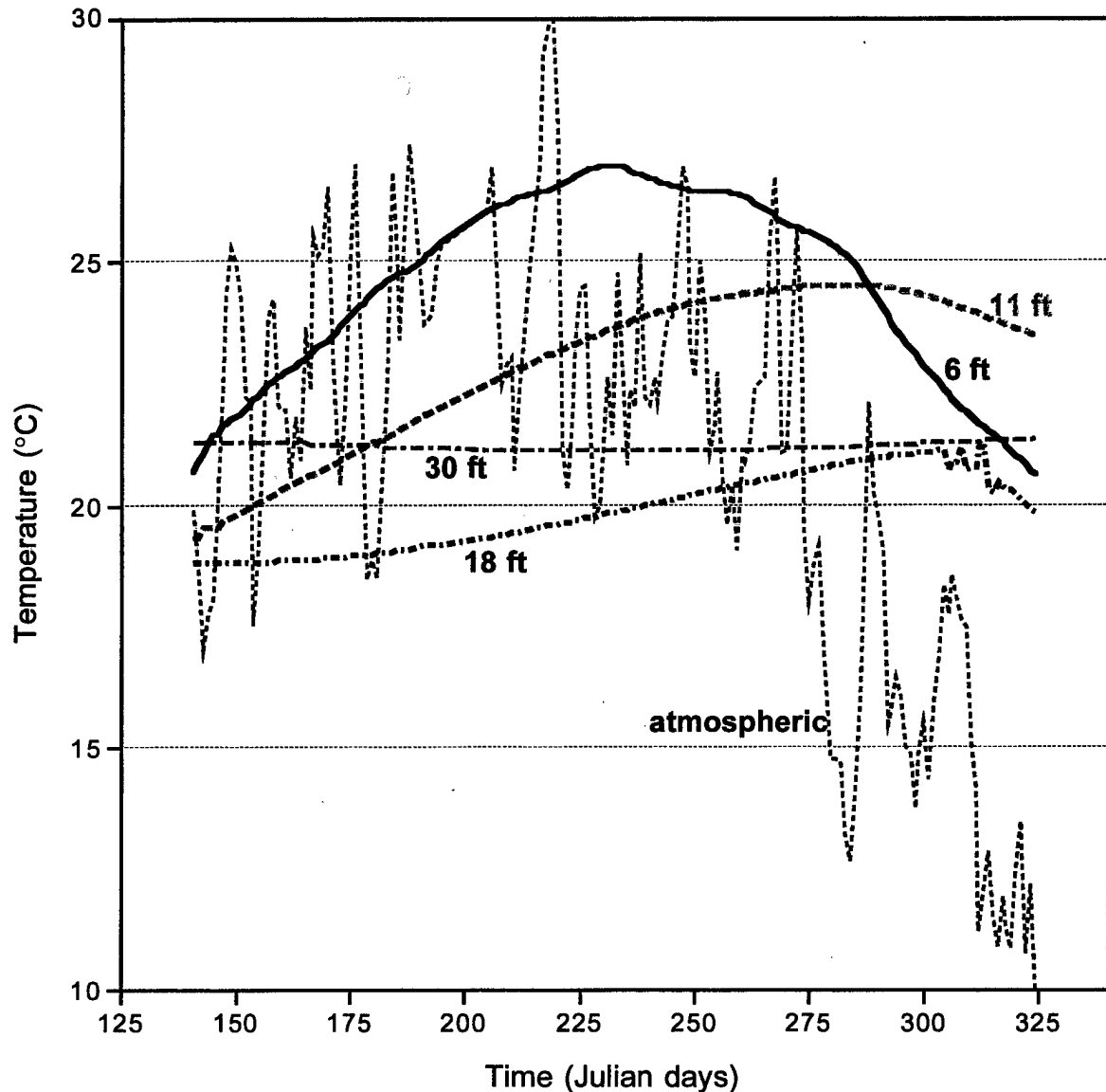


Figure 8. Formation and air temperature in Well B, from 5/21/97 to 11/20/97.

Formation temperature, sampled arbitrarily at or near noon on each day from 5/21/97 through 11/20/97 in Well B, and average daily air temperature are shown in Fig. 8. Air temperature was not measured on site, but was downloaded from the California Irrigation Management Information System (CIMIS) and was collected at a nearby weather station in Fair Oaks. Only data from the top

four monitoring levels are shown since deeper levels showed no change over this period. As expected, the magnitude and lag decrease and increase, respectively, with depth. Due to heat storage effects, temperature at the 11 ft and 18 ft depths continues to rise long after air temperature decreases in the fall. This results in a reversal of the thermal gradient between 6 ft and 30 ft, i.e., temperature is higher at greater depths.

While the effect of diurnal air temperature changes is negligible at the monitored depths, there is some minor influence on the formation temperature at, and presumably above, 6 ft due to daily and weekly air temperature fluctuations. At this point it is not clear whether it is necessary to include such detail in numerical modeling.

### 3.3 Atmospheric and Formation Pressure

Gas-phase pressure is being measured using the same probes as used for gas sampling. These are allowed to equilibrate with the subsurface environment and the pressure is measured using dedicated pressure transducers at the ground surface. Overall, gas-phase pressures are very close to atmospheric pressure, but display a slight lag and dampening relative to diurnal atmospheric pressure fluctuations. Both effects are to be expected given that the gas samplers are measuring pressure at depth, and serve to confirm that none of the samplers are leaking at the ground surface. Although formation gas-phase pressure at all levels responds to changes in atmospheric pressure, attention here is focused on the top four levels (6 ft, 11 ft, 18 ft, and 30 ft) as those encompass the part of the formation which is most contaminated and in which gas-phase flow would most significantly affect movement of VOCs.

Daily average gas-phase pressures measured from 5/21/97 through 11/20/97 are shown in Figure 9. By eliminating diurnal effects, it becomes clear that formation pressures follow atmospheric pressure quite closely and that gas-phase pressure gradients are barely discernible. The absolute differences amongst the pressure readings at various depths may simply be due to composite error in transducer calibration, since the uncertainty in the transducer calibration is  $\pm 0.004$  bar. The reader should note that 0.005 bar is equivalent to 5 cm of water head. In fact, day-to-day changes in formation pressures often exceed apparent pressure differences between monitored levels. The lag between atmospheric pressure fluctuations and formation gas-phase pressure changes is shown in Figs. 10 and 11. In each figure, a one-week period between 11/6/97 and 11/13/97 is shown. In Fig. 10 all of the collected data, i.e., on a four-hour interval, is presented, while in Fig. 11, only an average daily value is shown, with a smoothed interpolation between points. Due to the diurnal fluctuations, the lag, though discernible, is difficult to quantify in Fig. 10. On the other hand, once the data are averaged in Fig. 11, a lag of 6 to 13 hours between

atmospheric pressure and formation pressure can be estimated. This type of information will be particularly useful when calibrating the parameters for a numerical model which would incorporate gas-phase pressure gradients and resultant gas flow.

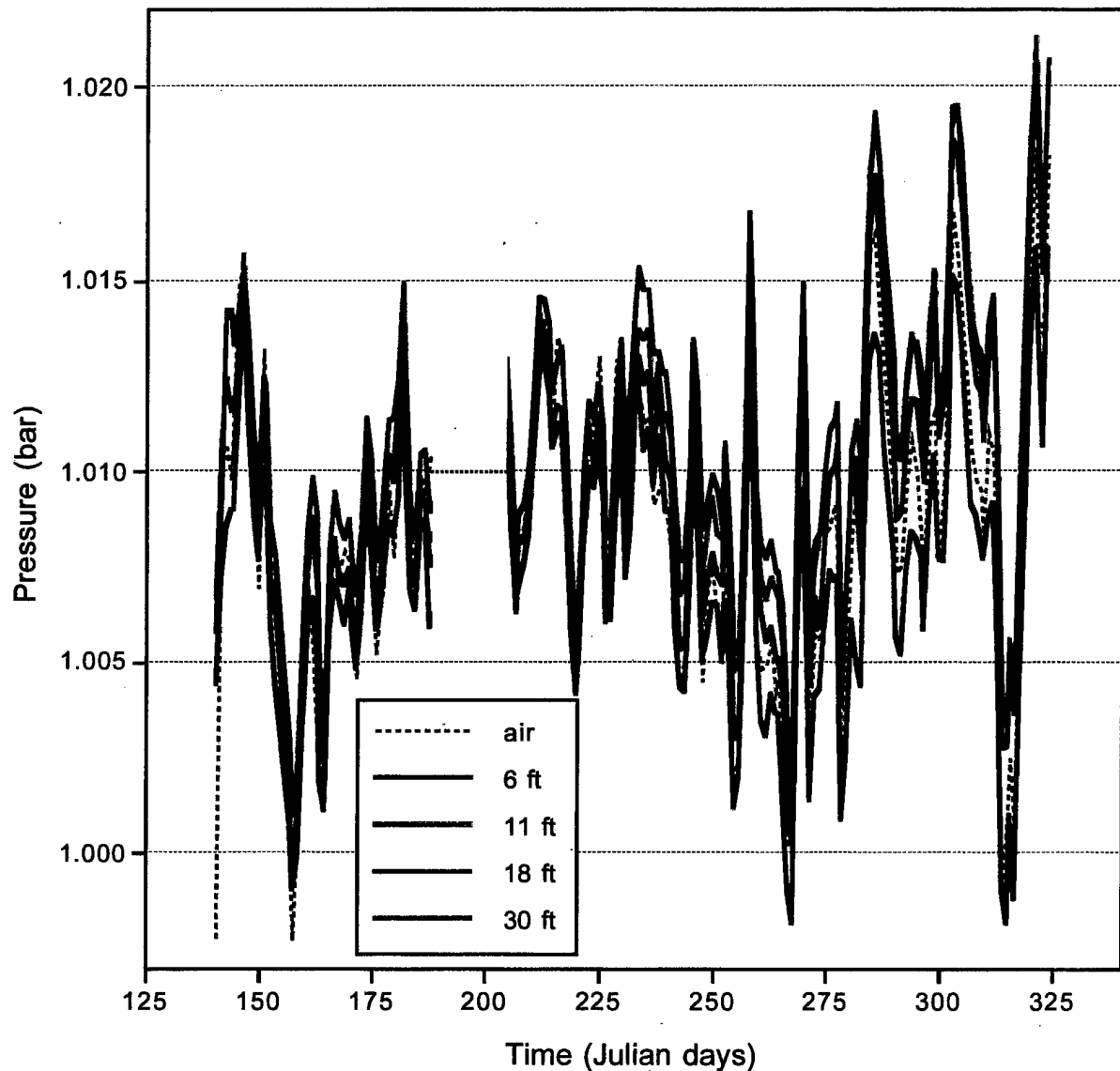


Figure 9. Daily average formation and air pressure in Well B, from 5/21/97 to 11/20/97.

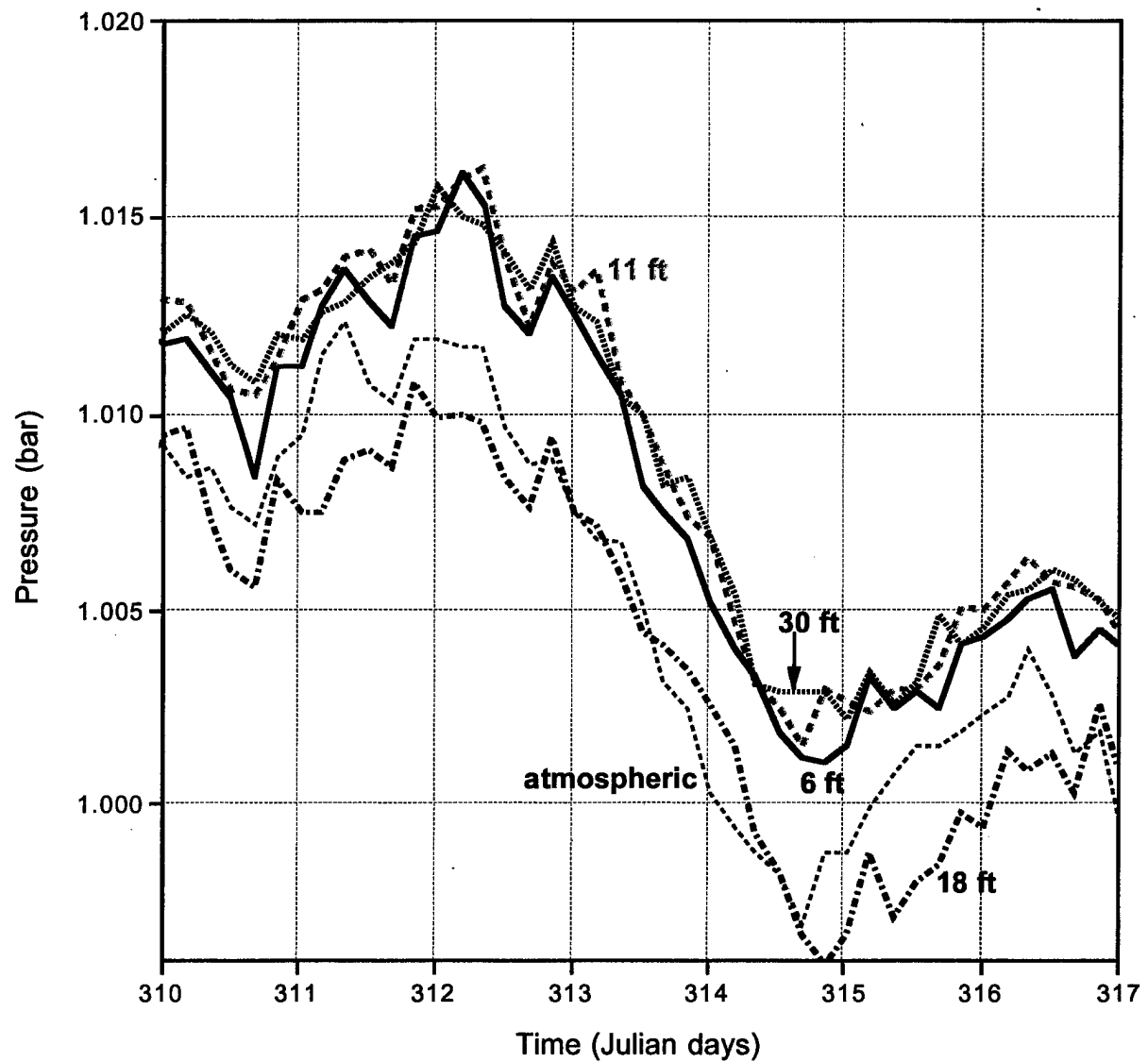


Figure 10. Formation and air pressure in Well B, from 11/6/97 to 11/13/97, data collected on a 4-hour interval.

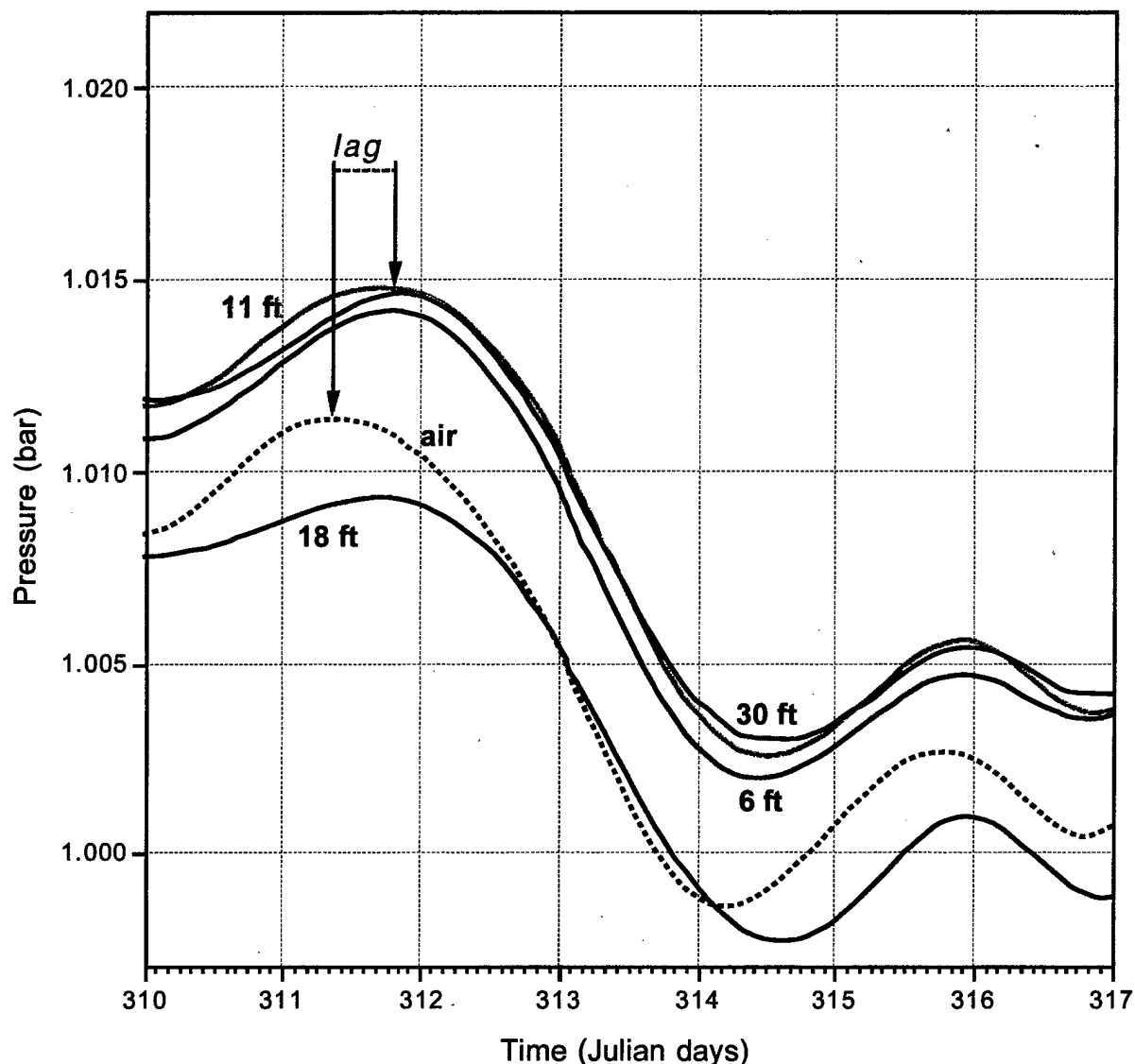


Figure 11. Average daily formation and air pressure in Well B, from 11/6/97 to 11/13/97, interpolated and smoothed.

Liquid-phase pressure measurements are being performed using a new design of an air-pocket tensiometer in which a porous tip is connected to a two-cell transducer with a constant water level above the porous tip. The cumulative tensiometer data collected to date suggests that, with the exception of the deepest sample points (at 112 ft and 109 ft in Wells A and B, respectively), and possibly two other points in Well A, the matric potential in the formation is more negative than the air-entry pressure of the porous stainless steel cups of the tensiometers (-500 to -600 mbar, equivalent to approximately -5 to -6 m water column). These observations are corroborated by the small number of lysimeters which yield water and the very small volume of water which they

yield. Conventional shallow tensiometers, with ceramic porous cups with air-entry pressures of 1 bar, as well as psychrometers, will be installed in an additional borehole in the near future. It is anticipated that these tools will provide more quantitative data on the formation matric potential.

### 3.4 Gas-Phase and Liquid-Phase VOC Concentrations

The gas phase is being sampled via in-situ gas samplers consisting of a 7.62 cm long, 100  $\mu$ m-pore size porous metal cylinder with welded top and bottom flanges. A 1/4 in diameter stainless steel tube extends out from the top flange and is connected using Swagelok™ compression fittings to a 1/4 in Teflon tube that goes up to the ground surface. In order to purge the gas collected in the gas probe, a photo-ionization detector (PID-580) is used. The sampler is purged until the PID reading is stable. The PID is then disconnected and a gas sample is collected by applying a vacuum through an absorbent tube. A calibrated volumetric pump is used for this purpose and the exact time and volume collected are recorded. The absorbent tube is sealed with brass Swagelok™ compression fittings lined with Teflon gaskets. This sampling method does not require refrigeration and the sample holding time is 25 days. EPA TO14 analyses are performed by the Environmental Measurements Laboratory of LBNL.

Liquid-phase VOCs are sampled using two-chamber suction lysimeters designed for use at depths greater than 7-8 m. One 1/4-in and one 1/8-in tube connect the lysimeter to the surface. A miniature check valve separates the lower chamber from the upper chamber. A 0.5  $\mu$ m porous stainless steel cylinder permits the collection of the sample which is drawn by vacuum through the check valve into the upper chamber. To withdraw a water sample from the soils into the suction lysimeter, a vacuum is applied to the tube connected to the top of the upper chamber. In order to bring the water sample to the surface, dry, purified gas, either N<sub>2</sub> or Ar, is used to pressurize the upper chamber, forcing the water sample up through the second tube that connects the bottom of the upper chamber to ground surface. The check valve closes, preventing liquid from being forced back into the lower chamber.

Data gathered to date indicate that TCE and cis-1,2-DCE are by far the predominant contaminants, with two distinctive TCE peaks, one near the depth of 6 ft and another above the water table, but only one distinctive cis-1,2-DCE peak at 6 ft. In addition, Freon 123a was identified at and up to 25 ft above the groundwater table. The quantification of this recently confirmed compound is pending. Due to the relative dryness of the formation, few liquid samples are collected on a regular basis. On the other hand, soil-gas is successfully drawn at all sample points during all sampling intervals. Therefore, there is a large disparity between the amount of

data on liquid-phase versus gas-phase VOC concentrations. The available concentration data were used in an analysis to determine whether the gas-phase VOCs and liquid-phase VOCs are close to equilibrium. Henry's Law relates equilibrium inter-phase concentrations of a compound via an empirically or theoretically derived proportionality constant, known as the "Henry's law constant,"

$$P_x / [x_{aq}] = K_{H,x}$$

where,  $P_x$  is the partial pressure of compound  $x$  in the gas phase [atm],  $[x_{aq}]$  is the concentration of compound  $x$  in the liquid phase [mol m<sup>-3</sup>], and  $K_{H,x}$  is the Henry's law constant for compound  $x$  [atm m<sup>3</sup> mol<sup>-1</sup>]. Henry's law constants for TCE and cis-1,2-DCE were drawn from the literature and are presented in Table 1.  $K_H$  values for TCE, which represent both experimental and theoretical results, fall in a fairly narrow range. Additional data on cis-1,2-DCE  $K_H$ 's will be identified in the near future.

*Table 1. Henry's law constants for TCE and cis-1,2-DCE derived from the literature.*

<i>Compound</i>	<i>K<sub>H</sub> used</i>	<i>Sources</i>	<i>Other K<sub>H</sub> values</i>	<i>Other sources</i>
TCE	0.01	Domenico and Schwartz (1990)	0.0116 0.0128 0.0093	Mackay and Shiu (1981); Neely (1976); Dilling (1977)
cis-1,2-DCE	0.0075	Mackay and Shiu (1981); Dilling (1977)	none	none

Gas-phase TCE and cis-1,2-DCE data collected from Well B on 4/4/97 and 10/23/97 were used to calculate their anticipated equilibrium liquid-phase concentrations using the  $K_H$  values shown in Table 1. A comparison of the results of these calculations with concentrations measured in pore waters collected at those times is shown in Figs. 12 and 13. Although the measured liquid-phase data are very sparse, there is in general good agreement between the calculated and measured values, suggesting that the compounds in question are close to equilibrated between the liquid and gas phase. The one exception are the low measured liquid-phase concentrations on 4/4/97 at a depth of 6 ft, compared with the very high gas-phase concentrations. This could be due to either very steep concentration gradients at this depth, or due to the collection of small-volume pore water samples which may not have been fully representative of the surrounding formation.

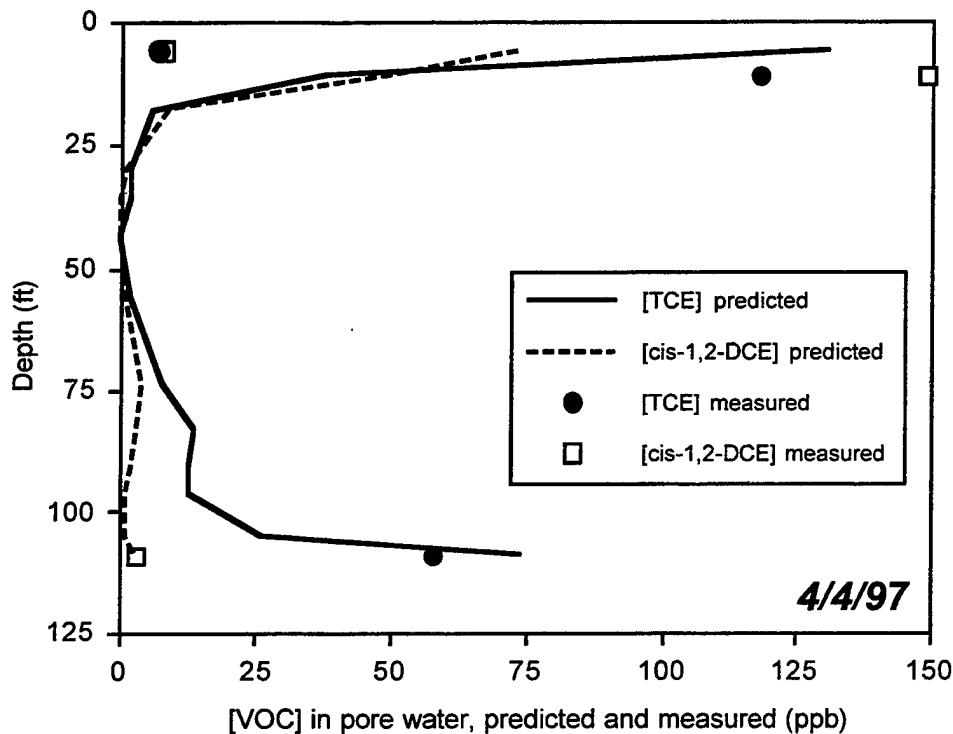


Figure 12. TCE and cis-1,2-DCE concentrations in the liquid phase, measured and predicted values derived from gas-phase data via Henry's Law, 4/4/97, Well B.

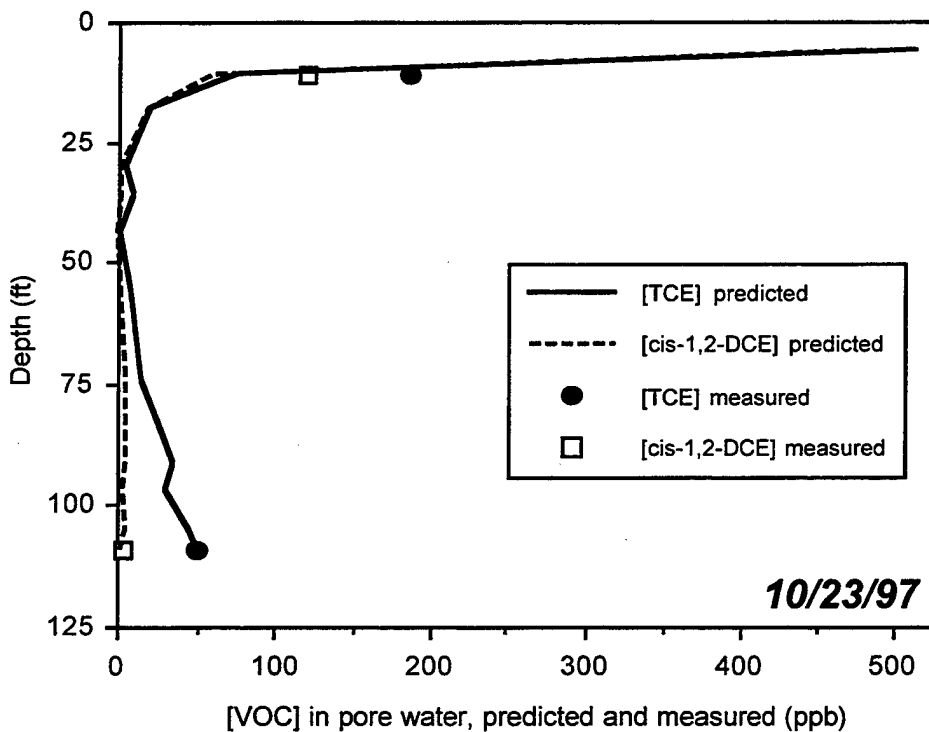


Figure 13. TCE and cis-1,2-DCE concentrations in the liquid phase, measured and predicted values derived from gas-phase data via Henry's Law, 10/23/97, Well B.

The apparent equilibrium between the liquid and gas phase has important implications to both the conceptual and numerical modeling of the system, in that it will allow for the estimation of liquid-phase VOC concentrations based on readily available gas-phase concentrations.

#### **4.0 SUMMARY**

Data collected over the last year have helped define initial conditions, boundary conditions, and many of the parameters necessary for the conceptual and numerical modeling of the system. The apparent stability of the hydrologic system over this time period, based on both the relative dryness of the formation as well as a lack of significant changes in moisture content distribution, is suggestive of the potential predominance of the gas phase in VOC transport through the profile. The semi-quantitative equilibrium between liquid-phase and gas-phase VOCs is further evidence of a fairly static system. The nearly uniform response of formation gas-phase pressure to atmospheric pressure is indicative of a hydrologic system in good communication with the atmosphere, signifying a low probability of the presence of any perched water. In fact, the short response lag of the system to atmospheric pressure changes is evidence for a strong and continuous connection via the gas phase. Seasonal reversals in the temperature gradient may create fluxes in the gas-phase on a limited spatial scale, especially in the top 20 ft, where VOC concentration gradients are the steepest.

Ongoing and future data collection, with special attention to changes induced by seasonal storm events, will further enhance the understanding of the system and provide additional input to the modeling effort.

## REFERENCES

- Amoozegar, A., K.C. Martin, and M.T. Hoover. 1989. Effect of access hole properties on soil water content determination by neutron thermalization. *Soil Sci. Soc. Am J.* 53:330-335.
- Celata, C.M., M. Amman, R. Donahue, K. Leung, P.N. Luke, L.T. Perkins, P.T. Zawislanski. 1996. A new intense neutron generator and high resolution detector for well logging applications. *Proc. of 1996 IEEE Nuclear Science Symposium*, Nov. 2-9 1996, Anaheim, CA, p. 29.
- Dilling, W.L. 1977. Interphase processes: II. Evaporation rates of chloro methanes, ethanes, ethylenes, propanes, and propylenes from dilute aqueous solutions. Comparison with theoretical predictions. *Environ. Sci. Technol.* 11:405-409.
- Domenico, P.A. and F.W. Schwartz. 1990. *Physical and Chemical Hydrogeology*. New York, John Wiley and Sons, Inc. 824 p.
- Falta, R. W., K. Pruess, I. Javandel, and P. A. Witherspoon. 1992a. Numerical modeling of steam injection for the removal of nonaqueous phase liquids from the subsurface 1. Numerical formulation., *Water Res. Res.*, 28:433-449.
- Falta, R. W., K. Pruess, I. Javandel, and P. A. Witherspoon. 1992b. Numerical modeling of steam injection for the removal of nonaqueous phase liquids from the subsurface 2. Code validation and application. *Water Res. Res.* 28:451-465.
- Falta, R. W., K. Pruess, S. Finsterle, and A. Battistelli. 1995. T2VOC User's Guide, Lawrence Berkeley Laboratory Report, LBL-36400, Berkeley, California (March 1995).
- Finsterle, Stefan. 1993. ITOUGH2 Users Guide Version 2.2, Lawrence Berkeley Laboratory Report, LBL-34581, Berkeley, California (August 1993).
- Hillel, D. 1980. *Fundamentals of Soil Physics*. Academic Press, Inc. Orlando, Florida. 413 p.
- LBNL, 1996. *Vadose Zone Monitoring System Installation Report for McClellan AFB*. Prepared by Zawislanski, P.T., B. Faybishenko, A. James, B. Freifeld, and R. Salve, for Department of the Air Force, McClellan AFB, October, 1996.
- LBNL, 1997a. Monitoring and Data Analysis for the Vadose Zone Monitoring System (VZMS), McClellan AFB. Prepared by Zawislanski, P.T., R. Salve, B. Freifeld, H.S. Mountford, R. Dahlquist, A. James, S. Rodriguez, and B. Faybishenko, Quarterly Status Report to the Department of the Air Force, McClellan AFB, May 28, 1997.
- LBNL, 1997b. Monitoring and Data Analysis for the Vadose Zone Monitoring System (VZMS), McClellan AFB. Prepared by Zawislanski, P.T., R. Salve, B. Freifeld, H.S. Mountford, R. Dahlquist, S. Rodriguez, and B. Faybishenko, Quarterly Status Report to the Department of the Air Force, McClellan AFB, August 22, 1997.
- LBNL, 1997c. Monitoring and Data Analysis for the Vadose Zone Monitoring System (VZMS), McClellan AFB. Prepared by Zawislanski, P.T., H.S. Mountford, R. Dahlquist, S. Rodriguez, and R. Salve, Quarterly Status Report to the Department of the Air Force, McClellan AFB, December 5, 1997.

- Mackay, D., and W.Y. Shiu. 1981. Critical review of Henry's law constants for chemicals of environmental interest. *J. Phys. Chem. Ref. Data*. 10:1175-1199.
- Neely, W.B. 1976. Predicting the flux of organics across the air/water interface. National Conference on Control of Hazardous Material Spills. New Orleans.
- Oldenburg, C.M, and K. Pruess. 1995. Dispersive transport dynamics in a strongly coupled groundwater brine flow system. *Water Res. Res.* 31: 289-302.
- Pruess, K. 1987. TOUGH User's Guide, Nuclear Regulatory Commission, Report NUREG/CR-4645 (June 1987) (also Lawrence Berkeley Laboratory Report, LBL-20700, Berkeley, California (June 1987).
- Pruess, K. 1991. TOUGH2 - A General Purpose Numerical Simulator for Multiphase Fluid and Heat Flow, Lawrence Berkeley Laboratory Report, LBL-29400, Berkeley, California (May 1991).
- Shepherd, R.G. 1989. Correlations of permeability and grain size. *Ground Water*. v 27.
- Vereecken, H. 1995. Estimating the unsaturated hydraulic conductivity from theoretical models using simple soil properties, *Geoderma*, 65:81-92.

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