APPENDIX C

WORK PLAN FOR DISTRIBUTION COEFFICIENT COLUMN STUDY

Introduction

The primary objective of this study is to measure the distribution coefficient (K_d) for perchlorate in the soil samples that are scheduled to be collected from the borings completed as part of the additional investigation. Estimation of this parameter will be performed by conducting batch and column tests. This study was designed to support groundwater flow and chemical transport modeling by better understanding the site- and chemical-specific input parameters used in the modeling effort. The report describes the theoretical basis and procedures for field and laboratory work for obtaining the distribution coefficient for perchlorate in soil samples collected from the two additional monitoring well locations at NASA JPL.

Definition and Significance of Distribution Coefficients

As groundwater migrates through geologic media, certain geochemical reactions occur between the chemicals in groundwater and the geologic media. These interactions determine the relative rates at which chemicals migrate with respect to the advective front of groundwater. The primary process associated with the attenuation of chemicals in groundwater, with respect to groundwater modeling simulations, are diffusion, biodegradation, and sorption. Distribution coefficients are used to quantify sorption reactions (i.e., adsorption and anion exchange) between the chemicals and the geologic media.

The distribution coefficient of a specific chemical may be defined as the ratio of the mass sorbed on a geologic medium to the mass remaining in solution:

$$K_d = \frac{q_e}{C_e} \tag{1}$$

where:
K_d	=	distribution coefficient (mL/g)
q_e	=	mass of the chemical on the solid phase (or surface loading) per unit mass of solid phase (mg/g) at equilibrium
C_e	=	mass of the chemical in solution per unit volume of the liquid phase (mg/L) at equilibrium

and

$$q_e = \frac{(C_e - C_i)V}{m} \tag{2}$$

where:
C_i	=	initial chemical concentration in the liquid phase (mg/L)
V	=	volume of the liquid (L)
m	=	mass of the solid (g)

The quantification of the distribution coefficient is based on the assumption that chemical equilibrium is reached between the solid and aqueous phases. Although there is little direct evidence that a true chemical equilibrium is reached during a short term experiment, a lack of change in chemical concentrations during such an experiment conducted over several days suggests that a steady state has been attained.

The relationship between the distribution coefficient of a specific chemical and the parameters pertinent to the evaluation and prediction of the fate of that chemical in a geologic medium may be described by the following equations (Fetter, 1993):

$$D\frac{\partial C_e}{\partial x^2} - V\frac{\partial C_e}{\partial x} = R\frac{\partial C_e}{\partial t} \qquad\qquad R = 1 + \frac{\rho_b K_d}{\theta_e} \qquad\qquad (3)\ (4)$$

where:

x	=	distance (m)
t	=	time (s)
D	=	dispersion coefficient (m^2/s)
V_s	=	seepage velocity (m/s)
R	=	retardation factor
θ_e	=	effective porosity (m^3/m^3)
ρ_b	=	bulk density of the solid (g/cm^3)

It should be noted that applying laboratory-determine distribution coefficient values to a real hydrogeologic system must be done with caution because only the sorption reactions between the chemicals and the migrating groundwater are quantified. For example, geochemical reactions that result from interaction of the migrating groundwater with another aqueous phase of a differing chemistry can profoundly change the rate of chemical movement relative to the rate of groundwater movement. In addition, the equilibrium conditions experienced in the laboratory may not be realistic in natural situations because of the time dependence or the kinetics of the specific reactions that are involved. Also, migrating solutions always follow the more permeable paths of least resistance. These paths tend to allow less time for reactions to occur and less soil surface exposure to the migrating groundwater, and may preclude the attainment of local chemical equilibrium. Therefore, the distribution coefficient is directly applicable to problems involving chemical migration in geologic media.

Sorption reactions depend on the thermodynamic activity of the contaminants in solution. Because competing ion and ion complexation effects may influence the distribution coefficient for a particular chemical, groundwater representative of the sample collection area should be used during laboratory studies. The sorption of chemicals also is influenced, or controlled, by geologic media and by solution pH, Eh, and temperature. Therefore, site-specific materials must be used in the distribution coefficient measurements. Precautions should be taken to preserve the site-specific materials so that their properties are not significantly altered prior to laboratory testing. In the event that groundwater from the study are cannot be obtained for used in the study, deionized (DI) water (with a chemical spike) can serve as a substitute.

The distribution ratio of a contaminant may be measured by either a batch or column experiment in the laboratory. The following sections discuss the theoretical basis of these measurements.

Theoretical Basis for Batch Studies: Adsorption Isotherms. Measured distribution coefficient values for the solid-liquid partitioning of chemicals by adsorption are valid only for the specific conditions of the experiments, including the chemical compositions of both solid and liquid phases and the initial

concentrations of the chemicals. Estimation of solid-liquid partitioning at chemical concentrations different form those used for measuring K_d may be valid only within small concentration ranges. When the concentration ranges for K_d extrapolation are large, the partitioning between solid and liquid may not be linear with concentrations. Nonlinear solid-liquid partitioning in groundwater systems is commonly described by the adsorption isotherms of Langmuir and Freundlich (Fetter, 1993). The Langmuir isotherm is described by the following equation:

$$qe = \frac{K_L A_m C_e}{1 + K_L C_e} \qquad \text{or, in the linear form} \qquad \frac{C_e}{q_e} = \frac{1}{K_L A_m} + \frac{C_e}{A_m} \qquad (5)\ (6)$$

Where: K_L =   Langmuir constant related to the binding energy (L/mg)
           A_m =   the maximum amount of solute that can be adsorbed by the solid (mg/kg)

In the linear form, the values of K_L and A_m may be determined from the intercept and slope of the straight line, respectively, on a plot of C_e/Q_e (or $1/K_d$) versus C_e.

The Langmuir isotherm is based on several assumptions (Rai et al., 1984), including:

1. There is a finite number of adsorption sites and all sites are equivalent.

2. Adsorption at a given site is independent of whether or not the neighboring sites are occupied.

3. Adsorption is limited to monolayer coverage of the sites.

The assumption of equivalent surface sites may be invalid in many geologic systems where the lithologies consist of two or more major minerals with nonuniform adsorption sites and adsorption characteristics (Aggarwal et al., 1991). In such cases, the Freundlich adsorption isotherm may be used.

The Freundlich isotherm can be expressed as follows:

$$q_e = K_f C e^{1/n} \qquad \text{or, in linear form:} \qquad \log q_e = \log K_F + 1/n \log C_e \qquad (7)\ (8)$$

Where K_F and n are constants and n is generally greater than or equal to 1. When n is equal to 1, the partitioning is linear with concentration and the Freundlich isotherm becomes the same as the distribution coefficient. In the linear form, the values of K_F and $1/n$ may be determined from the intercept and slope of a linear curve on a plot of $\log q_e$ versus $\log C_e$.

Therefore, if the K_d values are measured for at least three to five initial concentrations, a Langmuir or Freundlich relationship can be derived by regression. These constants may then be used to predict the partitioning of the contaminants between solid and aqueous phases at a give aqueous concentration. However, due to the nonlinear nature of the isotherms, extrapolation of the Freundlich adsorption isotherms to concentrations much lower than those used for the experimental studies may not be reliable (Kinniburgh and Jackson, 1981).

Theoretical Basis for Column Studies. Data from column experiments are represented as breakthrough curves, which are plots of relative contaminant concentrations in the column effluent, $C_{eff/inf}$ (ratio of the concentration at time t and the initial concentration), versus time or number of pore volumes displaced through the column. The magnitude of the retardation factor for the transport of a contaminant in the column may be approximated from the following analytical solution of the equation describing the relationship between the distribution coefficient and fate and transport parameters (van Genuchten and Wierenga, 1986):

$$C_e(x,t) = \frac{1}{2} erfc\left[\frac{(Rx)-(V_s t)}{2(DRt)^{1/2}}\right]$$ (9)

Which, for a finite column length can be rearranged as

$$C_{eff/inf} = \frac{1}{2} erfc\left[\left(\frac{P}{4RT}\right)^{1/2}(R-T)^{1/2}\right]$$ (10)

Where: erfc =   complement of the error function
           x   =   distance (m)
           t   =   time (s)
           V_s =   seepage velocity (m/s)
           D   =   dispersion coefficient (m^2/s)
           P   =   Peclet number
           T   =   number of pore volumes displaced

The Peclet number is described by the following equation:

$$P = \frac{vd}{D}$$ (11)

Where: v   =   linear velocity (m/s)
           D   =   average particle diameter (m)

For the case when R = T, erfc [0] = 1. The previous equation can be reduced to:

$$C_{eff/inf} = 0.5$$ (12)

Therefore, the retardation factor in a column study is approximately equal to the number of pore volumes required to achieve a 50% breakthrough. The distribution coefficient, therefore, can be calculated from Equation 4.

Sample Collection

As discussed in the Work Plan, an attempt will be made to collect one saturated and unsaturated soil samples from each of the proposed additional monitoring locations during drilling. One unsaturated soil sample will be collected from a depth that is relatively close to the water table. A saturated soil sample will be collected from each of the depths associated with proposed screen intervals within the monitoring wells, with a maximum of five saturated soil samples per location. The samples will be collected using a split-spoon sampler that will be deployed in the well after the augers and casing have been tripped during drilling, which will be performed using mud rotary. The inherent difficulties of split-spoon sample collection at the proposed depths may inhibit sample collection, so it is likely that less than five saturated soil samples per location will be collected. An attempt will be made to collect as much soil as possible at each location.

After collection, each of the soil samples will be placed into a five-gallon bucket and transported overnight to Battelle's laboratories in Columbus, Ohio. Upon arrival, the sample containers will be stored within their containers in a 4ºC walk-in cold room until used in the batch and column tests.

When a soil sample is collected for analysis for a distribution coefficient, a composite sample will be placed in two one-gallon zip-loc bags and shipped to an off-site analytical lab for analysis of physical parameters, including grain size analyses, bulk density, effective porosity, fraction organic carbon, and vertical and horizontal hydraulic conductivity. These parameters will be used to assist in the continued development of the site conceptual model and in the hydrogeologic modeling investigation. In addition, a sufficient volume of sample will be shipped to an offsite analytical laboratory for analysis of perchlorate and any other important inorganic parameters critical to the measurement of the distribution coefficient.

Due to the drilling method, it is unlikely that groundwater samples will be collected at the time of drilling. However, if the wells are completed and developed within a reasonable timeframe following sample collection (<2 weeks) groundwater samples may be collected from each sampled depth interval for use in the batch and column studies. In this event, two 2.5 gallon cubitainers will be filled and shipped back to the laboratory, where they will be stored in a 4ºC walk-in cold room until use in the laboratory scale studies. In addition, once development of the wells is complete, an initial round of groundwater samples will be collected from each of the screened intervals and analyzed for the parameters included in the Sampling and Analysis Plan (see Appendix A), including VOCs, perchlorate, and water quality parameters.

Experimental Methods

An attempt will be made to perform both batch and column experiments during this investigation. The volume of soil sample collected during the field investigation will determine the number and type of experiments that are conducted. The following sections describe the methodology associated with both of these methods.

Batch Experiments. The ASTM D 4319-83, "Standard Test Method for Distribution Ratios by the Short-Term Batch Method", will be slightly modified and used to determine the sorption affinity of perchlorate to the geologic media. This method is a short-term laboratory method primarily intended for ionic species subject to migration in porous material. However, this method may not exactly simulate sorption characteristics that would occur in undisturbed settings, and the application of the method's results to long-term field behavior is not known. The ASTM D 4319-83 method does provide procedures for estimating the distribution coefficient for a given set of hydrogeologic conditions.

The geologic samples collected in the field will be crushed, homogenized, and sieved through a No. 4 sieve screen before being stored in appropriate containers. Groundwater collected for the investigation will be filtered through a 0.45-µm pore size filter membrane to remove any soil particles, particulates, and other settled materials. In the event groundwater is not able to be collected, laboratory DI water will be used. Any water used in the experiment will be stored at 4ºC until the experiments are ready to begin. If native groundwater is used, the pH will be recorded prior to each experiment and the alkalinity (as bicarbonate) and sulfate concentrations will be analyzed and used to determine anionic effects on sorption of perchlorate.

In the event that perchlorate concentrations in the native groundwater are too low, or laboratory DI water is used, stock solutions of perchlorate will be prepared by separately spiking known amounts of reagent-grade perchlorate into a carrier solvent. Immediately before use, the working solutions of the perchlorate will be prepared by dispensing known amounts of stock solutions into the filtered groundwater or DI water. A microsyringe will be used to spike the stock solution into the groundwater/DI water, which will

be contained in a series of headspace-free containers while undergoing a gentle stirring motion. Once the stock solutions are dispensed, the containers will be capped and the stirring motion will be continued for an additional 30 to 60 seconds.

The batch experiments will consist of mixing a series of working solutions containing a known concentration of perchlorate with an accurately weighed dose of the site soils that were collected in the field. Except in those cases where otherwise specified, the amount of soil used on a wet scale basis will yield a soil to solution ratio of about 1:8 (i.e., 7.5 g of soil to 60 mL of solution). The vials containing the soil/perchlorate mixture will be kept headspace free. All batch tests will be performed using a leaktight closure on the sampling container which will prevent the solutions from being exposed to the atmosphere.

The vials will be placed in an orbital shaker to maximize the reaction between solids and liquids. A series of sample vials containing only the working solutions will also be placed in the orbital shaker and used as control samples. The reaction will be allowed to continue at room temperature until equilibrium is reached. The time required to reach equilibrium will be determined by sampling sacrificial reaction vials at several different time intervals. Equilibrium will be considered attained if little or no change in perchlorate concentration is detected from one sampling event to the next. Upon reaching equilibrium, any sample bottles remaining in the sample set will have their contents removed and the solutions containing the perchlorate/soil mixtures will be filtered through 0.45-μm filter membranes to remove any residual soil particles. Prior to being sent to an off-site laboratory for analysis, the pH of the filtered solutions (and the control samples) will be measured. The filtered solutions will then be placed in an appropriate sample bottle containing an appropriate amount of 1 $\underline{N}$ HNO_3 as a preservative to yield 0.01 molar HNO_3.

Column Experiments. Column experiments may be performed provided a significant amount of the native site soils and groundwater can be collected during field activities. In the event that only a small (i.e. less than 1,000 g) quantity of site soils is available, only soil batch tests will be performed. Should a sufficient volume of soil be available for a given sample, multiple column studies may be conducted. The column experiments for perchlorate will be carried out in a packed column. The column assembly for the packed column experiments will be constructed of glass, Teflon, and stainless steel. The soil samples will be sieved through a series of sieve screens. The fraction of less than 28-mesh to greater than 60-mesh will be first rinsed with groundwater/DI water to remove fines and then wet packed into two separate glass columns equipped with Teflon screw caps at the inlet and outlet ends of the column. During the column packing, extreme care will be taken to avoid trapping any air bubbles in the soil beds. The soil will be secured in the column with stainless steel screen (200 mesh), and the solid dry weight, bed height, bed volume, and pore volume of each column will be noted and calculated. The filtered groundwater/DI water will be pumped upflow through the column at room temperature by a peristaltic pump at approximately 1 mL/min for at least 24 hours before a test solution containing perchlorate at a concentration similar to that observed in native groundwater is introduced into the columns. The perchlorate concentration in the feed will be maintained by storing the feed in a collapsible 20-L Tedlar bag with a solution outlet. The perchlorate concentration in the influent and effluent of the columns will be determined by taking solution samples at the sampling ports near the inlet and outlet of the columns and submitting them to an offsite laboratory for analysis. The alkalinity, pH, and sulfate concentration of the column inlet and outlet water will also be sampled and analyzed to determine if any sorption of perchlorate by anionic constituents occurs during the column tests. These measurements will provide the data necessary for calculating the distribution coefficient of the soil in the column.

References

Aggarwal, P.K., T.R. Powell, G.L. Headington, and A.J. Pollack. 1991. *An Experimental Study of Radionuclide Adsorption on Glacial Deposits from Southeastern Illinois*, Report Prepared by Battelle Memorial Institute for Chem-Nuclear Systems Inc.

Fetter, C.W. 1993. *Contaminant Hydrogeology*, Macmillan Publishing Co., New York, NY.

Kinniburgh, D.G. and M.L. Jackson. 1981. "Cation Adsorption by Hydrous Metal Oxides and Clays," in *Adsorption of Inorganics at Solid-Liquid Interfaces*, M.A. Anderson and A.J. Rubin, Eds., Ann Arbor Sci., Ann Arbor, MI.

Rai, D., J. Zachara, A. Schwab, R. Schmidt, D. Girvin, and J. Rogers. 1984. *Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Vol. I: A Critical Review*, Report EA-3356 to EPRI, Battelle Pacific Northwest Laboratories, Richland, WA.

Van Genuchten, M.T. and P.J. Wierenga. 1986. Solute Dispersion Coefficients and Retardation Factors," in A. Klute, Ed., *Methods of Soil Analysis*, Part I, 2nd ed., American Society of Agronomy, Inc., Madison, WI.