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## Spatial distributions of perchloroethylene reactive transport parameters in the Borden Aquifer

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[1] We determined the descriptive statistical and spatial geostatistical properties of the perchloroethene  $\ln K_d$  and the  $\ln k$  of a 1.5 m thick by 10 m horizontal transect of the Borden aquifer near the location of the Stanford-Waterloo (SW) tracer experiment. The  $\ln K_d$  distribution is not normal and is right skewed because of a few high values that occur localized in two regions of the transect. In contrast, the  $\ln k$  data can be characterized by a normal distribution. A linear regression of  $\ln K_d$  on  $\ln k$  yields a statistically significant positive correlation, also shown at small lags in the cross correlogram. No significant vertical or horizontal trend in the  $\ln K_d$  data was detected. The semivariogram ranges of  $\ln k$  and  $\ln K_d$  differ from one another in the vertical direction ( $0.33 \pm 0.06$  m and  $0.20 \pm 0.04$  m, respectively) and are much less than the horizontal ranges (a few meters). Despite significant effort the horizontal range of  $\ln K_d$  remains poorly characterized because of limitations of the sample locations. Many of the characteristics described above do not match those assumed in prior theoretical studies that examined the importance of various aquifer characteristics on SW tracer transport. We suggest that there is knowledge to be gained by revisiting the conclusions of these prior studies in light of the new information presented here.

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### 1. Introduction

[2] The Stanford-Waterloo (SW) experiment [Mackay *et al.*, 1986b; Roberts *et al.*, 1986] is one of a few well-characterized reactive solute transport field experiments that exist against which to test and develop our conceptual understanding of reactive contaminant transport [e.g., Freyberg, 1986; Roberts *et al.*, 1986a; Sudicky, 1986; Goltz and Roberts, 1988; Rajaram and Gelhar, 1991; Quinodoz and Valocchi, 1993; Miralles-Wilhelm and Gelhar, 1996; Brusseau and Srivastava, 1997; Cushey and Rubin, 1997]. In the SW experiment, conducted in the early 1980s, dissolved apolar organic solutes were injected below the water table as a pulse, creating a small plume within the unconfined sandy aquifer. Their concentrations were monitored in three dimensions relative to nonreactive chloride and bromide tracers over a period of approximately two years. A subset of the organic solutes were naturally transformed during the experiment. Perchloroethylene (PCE) and

carbon tetrachloride (CT) were the persistent organic compounds. Of these two, PCE was the most retarded. The sorbing organic solute plumes exhibited two unexpected transport behaviors [Roberts *et al.*, 1986]: (1) the solute plumes decelerated with travel distance (apparent retardation factors increased) [Roberts *et al.*, 1986] exhibiting what has been termed a “macrokinetic” behavior [Miralles-Wilhelm and Gelhar, 1996]; and (2) the longitudinal spreading of the sorbing organic solutes was greater than for the nonreactive solutes at the same travel distance.

[3] Some uncertainty in the quantification of SW plume spreading has been expressed, for example because of incomplete plume capture for some compounds at some sampling events and because of the limitations inherent in the sampling and interpolation of heterogeneous concentrations [Miralles-Wilhelm and Gelhar, 1996; Ball *et al.*, 1997]. Solute spreading was estimated originally using two-dimensional depth-integrated data [Freyberg, 1986; Roberts and Mackay, 1986] and, more recently, using a fully three dimensional process [Rajaram and Gelhar, 1991; Miralles-Wilhelm, 1993; Miralles-Wilhelm and Gelhar, 1996]. Despite the uncertainties, both methods determined that the longitudinal organic solute spreading was greater than that of the conservative tracers at the same travel distance for distances greater than  $\sim 5$  m: by a factor of three in the two-dimensional analysis [Brusseau and Srivastava, 1997], and a factor between two and three for the nondegraded solutes (CT and PCE) in the three-dimensional analyses (i.e., compare longitudinal spreading presented by Miralles-Wilhelm [1993] for CT and PCE to that computed by

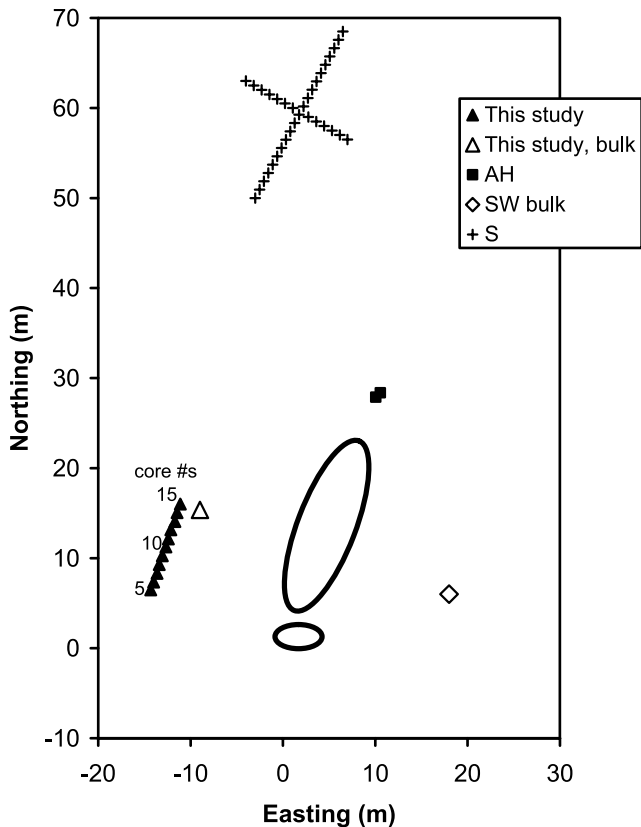
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**Figure 1.** Cores of this study (numbers shown), collected at the same depth interval (1.5–3.0 m below ground surface) and adjacent to the location of the SW natural gradient tracer test. The PCE plume boundaries in the SW experiment [Mackay *et al.*, 1986b], during which groundwater flow was toward the north-northeast, are shown schematically. The large oval approximates the 0.1  $\mu\text{g/L}$  PCE contour after 633 days, and the small oval represents the initial contaminant distribution (1 day after injection) [Mackay *et al.*, 1986b]. Core lines labeled S mark the samples analyzed by Sudicky [1986], Woodbury and Sudicky [1991], and Robin *et al.* [1991]. The SW bulk sediment was collected by Curtis *et al.* [1986] and was also used for study by Ball and Roberts [1991a]. Cores labeled AH are those used by Allen-King *et al.* [1998].

Rajaram and Gelhar [1991] for the conservative tracer at the same distance). Importantly, the trends described for the first and second spatial moments above were: exhibited by both PCE and CT; identified by both methods of analysis; and exhibited for combinations of sampling date and compound that were deemed ‘reliable’ (complete plume capture) by Miralles-Wilhelm and Gelhar [1996] in their critical reevaluation of plume sampling completeness. Therefore, although the value of the increase in spreading for the sorbing solutes appears to differ between studies, the trend cannot be refuted.

[4] Laboratory studies have shown that sorption is rate limited at the grain scale; a process that can be simulated by intragranular diffusion [Ball and Roberts, 1991b]. Batch-measured sorption rates have been used successfully to predict transport in dynamic laboratory column experi-

ments [Young and Ball, 1994]. However, several plume simulation studies have concluded that the macrokinetic behavior of the organic solutes in the field cannot be caused by the observed grain-scale rate-limited sorption alone [Goltz and Roberts, 1988; Quinodoz and Valocchi, 1993; Miralles-Wilhelm and Gelhar, 1996; Brusseau and Srivastava, 1997; Ball *et al.*, 1998; Cushey and Rubin, 1998].

[5] The importance of published Borden (or Borden-like) permeability heterogeneity [Sudicky, 1986; Woodbury and Sudicky, 1991] has been explored extensively. For example, Cushey and Rubin [1997] successfully matched measured with modeled plume behavior through simulation of transport with a heterogeneous permeability field combined with rate-limited sorption. However, their simulations did not incorporate sorption heterogeneity. Several studies have explored the effects of assumed correlation between the  $\ln k$  and  $\ln K_d$  in addition to heterogeneous  $\ln k$  [Quinodoz and Valocchi, 1993; Burr *et al.*, 1994; Miralles-Wilhelm and Gelhar, 1996; Brusseau and Srivastava, 1997]. Burr *et al.* [1994] demonstrated that correlated  $\ln k$  and  $\ln K_d$  in a heterogeneous aquifer can result in an apparent increasing (or decreasing) trend in the retardation factor with travel distance despite the fact that sorption was modeled as an instantaneous process. They and others [Brusseau and Srivastava, 1997; Cushey and Rubin, 1997] highlight the importance of ergodicity by showing that single realizations of heterogeneous  $\ln k$  and  $\ln K_d$  fields reproduced the SW plume deceleration when the contaminant was “injected” into a relatively low  $K_d$  zone in the simulation. However, Brusseau and Srivastava [1997] demonstrated that such a simulation cannot also match the second moment in the same realization unless a spatial trend in the  $K_d$  field is also assumed. (They assumed an increase in PCE  $K_d$  from 0.47 mL/g at the injection point to 0.79 mL/g at a distance of 10.5 m, the approximate travel distance experienced by the PCE plume center of mass in the field experiment.)

[6] There are two unproven assumptions about the aquifer underlying the simulations described above: (1) the studies that incorporated heterogeneity in the  $\ln K_d$  field assumed that  $\ln K_d$  is negatively correlated to  $\ln k$  [Burr *et al.*, 1994; Miralles-Wilhelm and Gelhar, 1996; Brusseau and Srivastava, 1997]; and (2) a horizontal spatial trend in  $K_d$  is assumed [Brusseau and Srivastava, 1997]. The simulations showed that plume spreading is very sensitive to the spatial correlation between  $\ln k$  and  $\ln K_d$ , but because the spatial distribution of  $\ln K_d$  for an organic solute in the Borden aquifer and its correlation to  $\ln k$  were not known, these studies by necessity assumed spatial distributions for  $\ln K_d$ . Assuming a negative correlation between the two attributes also results in an  $\ln K_d$  field that has the same spatial statistical properties as the  $\ln k$  field, a feature which also has not been demonstrated.

[7] The rationale supplied for assuming a negative  $\ln k$ - $\ln K_d$  correlation was either the work of Robin *et al.* [1991], who observed a weak negative correlation between  $\ln k$  and the  $\text{Sr}^{2+}$   $\ln K_d$  in the Borden aquifer, and/or theoretical arguments that assume greater surface area with smaller grain size [Burr *et al.*, 1994; Miralles-Wilhelm and Gelhar, 1996; Brusseau and Srivastava, 1997]. However, apolar organic solute sorption is controlled primarily by interactions with carbonaceous matter (noncarbonate, carbon con-

taining material) [Allen-King *et al.*, 2002, and references reviewed therein] and not interactions with charged mineral surfaces in saturated (water wet) sediments in which organic mineral interactions are weak [Schwarzenbach *et al.*, 2003]. While carbonaceous matter content can be greater for more fine-grained sediment, it is not necessarily so. Therefore the expectation that the PCE  $K_d$  should be negatively correlated to grain size or behave similarly to a cation sorption behavior ( $\text{Sr}^{2+}$ ) is not supported by geochemical principles. In fact, there exists evidence to the contrary for the Borden aquifer. Ball and Roberts [1991a] observed a positive trend between the PCE  $K_d$  and grain size for fine to very coarse sand size grains sieved from the Borden aquifer (location in Figure 1). More specifically, Allen-King *et al.* [1998] observed a weak positive correlation between  $\ln$  PCE  $K_d$  and  $\ln k$  (estimated by correlation to grain size) for high-resolution subsamples taken from a single core in the Borden aquifer. For the same data set, these workers [Allen-King *et al.*, 1998] also report that the vertical integral scale of  $\ln k$  is larger (7 cm) than the value determined for  $\ln K_d$  (5.2 cm). These studies [Ball and Roberts, 1991a; Allen-King *et al.*, 1998] imply that the negative correlation assumed in previous simulation studies is incorrect and suggest that the geostatistics that describe  $\ln K_d$  may not be the same as those describing  $\ln k$ . However, these studies provide a limited data set from which to draw insights on vertical  $\ln K_d$  variability and no information on the horizontal geostatistical properties of  $\ln K_d$ .

[8] Assumption (2), that there is a positive horizontal trend in  $K_d$  with travel distance, is related but not identical to the finding of importance of ergodicity on plume transport. Brusseau and Srivastava [1997] derive support for this assumption by reinterpreting Durant's [1986] depth-integrated core sample data from the approximate centerline of the initial 12 m of SW plume travel. In these data they [Brusseau and Srivastava, 1997, p. 128] identify a trend of increasing  $K_d$  that is "of sufficient magnitude to potentially influence the transport of the organic solutes." Later work by Ball and Roberts [1991b] showed that the time required for Borden sand grains of various sizes to equilibrate ranges from days to months, thus equilibrium can require much longer than the 3 day contact time used by Durant [1986]. Therefore the apparent variability between core samples reported by Durant includes differences in the  $K_d$  that would have been measured at equilibrium and the degree to which these data represent nonequilibrium. Because the latter is not known, a significant aquifer trend in  $K_d$  cannot be supported by Durant's [1986] data.

[9] Finally, the decomposition of HCA to PCE during the SW experiment [Curtis, 1991] also contributed to the apparent PCE spreading in the experiment. Ball *et al.* [1997] used a one-dimensional homogenous approximation of the aquifer incorporating field-derived sorption mass transfer rates (greater than the laboratory-observed values) to show that HCA decomposition contributed very modestly to the zeroth and first PCE plume moments. This result arises from the relatively rapid half-life of HCA transformation, estimated as 40 days [Ball *et al.*, 1997]. During 40 days, the PCE plume would have traveled a distance less than the initial pulse width of the experiment. However, because HCA is more retarded than PCE [Mackay *et al.*, 1986a; Roberts *et al.*, 1986], decomposition of the remain-

ing HCA contributed to apparent tailing in the PCE plume [Ball *et al.*, 1997]. This process has not been incorporated into quantitative simulations of the PCE plume that also model aquifer heterogeneity.

[10] Because the assumptions about the  $\ln K_d$  field required to simulate both the first and second moments of the field experiment accurately are not supported by available observations, the conclusions concerning the importance of various processes on plume transport are also drawn into question. This situation highlights a significant knowledge gap and underscores a need for more complete information about the chemical property heterogeneity of the reference Borden aquifer. Aquifer attributes differing from those assumed will produce different plume transport effects. For example, a positive  $\ln k$ - $\ln K_d$  correlation diminishes spreading for sorbing compared to nonreactive tracers [Bosma *et al.*, 1993; Rabideau and Miller, 1994], opposite the result observed in the SW experiment. Additionally, imperfect correlation diminishes spreading to a greater extent than perfect positive correlation [Bellin and Rinaldo, 1995]. Therefore understanding of plume spreading processes must include accurate representation of the heterogeneity of  $\ln K_d$  and its correlation to  $\ln k$ .

[11] The goal of this study was to examine the natural distributions of reactive transport properties,  $K_d$  and  $k$ , for PCE in the Borden aquifer. Specific tasks in our study were to characterize and model the univariate distribution of values for PCE  $\ln K_d$ , the regression-based correlation between PCE  $\ln K_d$  and  $\ln k$ , and the two-point bivariate autocorrelation and cross correlation of the PCE  $\ln K_d$  and  $\ln k$  in the Borden aquifer. For expediency, the  $k$  values were determined using air permeametry. Our samples were purposefully collected adjacent to the location of the SW experiment (Figure 1) to facilitate consideration of the potential impact of our findings on its interpretation.

## 2. Methods and Materials

### 2.1. Sampling

[12] The samples used in this study were collected from a series of eleven 1.5 m long by 5.08 cm outer diameter cores spaced one meter apart along the approximate direction of groundwater flow (Figure 1). The Borden aquifer material is generally well sorted, fine- to coarse-grained sand with occasional lenses of granules or pebbles and small, discontinuous beds and lenses of silt. Information on the geology of the Borden site is available from Burwasser and Cairns [1974], Fitzgerald [1982], and Bohla [1986]. The cores were collected adjacent to the SW transport experiment [Mackay *et al.*, 1986b] to insure that uncontaminated core material was procured for our study and to stay away from subsequent contamination of the region of the aquifer used in the original transport study by later experiments [e.g., King and Barker, 1999]. The cores were extracted according to the method of Starr and Ingleton [1990] from approximately the same vertical depth interval into which the SW natural gradient experiment plume was injected. The ends of each core were sealed with wax and the cores were stored at 4°C until use. The elevation of the ground surface along the line of coring fluctuates; depth corrections are thus made using a survey of the ground surface elevation so that accurate subsurface sample locations

can be obtained. The vertical datum for this study is 221.257 meters above mean sea level (masl) and is referred to herein as the ground surface. Physically, this elevation is the lowest surface elevation along the transect and occurs at core 15.

[13] Cores were opened by removing a 90° arc of the aluminum casing lengthwise from the core, causing as little sediment disturbance as possible. The exposed sediment was leveled and subcores used to measure permeability were collected horizontally (relative to the ground surface) by inserting 1.3 cm outer diameter stainless steel tubes immediately adjacent to one another down the center of the core. Material surrounding each subcore was saved. All samples were dried immediately and completely in a 40°C oven (prior to permeability analysis).

[14]  $K_d$  determinations were made every 3 cm vertical spacing for cores 10–15 and at a lower density of one measurement every 6 cm vertical spacing for cores 5–9. The denser sample spacing was used on approximately half of the cores to maximize the number of vertical lags available for spatial analysis while moderating the number of the more labor intensive  $K_d$  measurements. Within the depth interval 1.50–2.95 m, “undisturbed” subcore permeability is reported for 841 samples. There are missing permeability measurements due to a variety of reasons that include: unavailable core from unevenness of the ground or lost material at the end of a core segment, sample lost or disturbed in the permeability subcoring process, inaccurate  $k$  measurements, or other reasons as specified below. For all cores except numbers 5, 6, 9, and 10, there are less than a dozen samples missing from the target sample interval. Twenty-five  $k$  measurements are missing from core 6 due to inadvertent use of inconsistent (and incorrect) sample spacing over a portion of the core. An exceptionally large number of permeability measurements from cores 9 and 10 are not reported (47 and 34, respectively) because the undisturbed air permeameter measurements were inadvertently made while the sediment was still damp and are therefore not accurate. For 60 of these samples, and an additional 10 samples from other cores, the sample  $k$  were estimated using the sample ‘repacked’ into the subcore tube. These ‘repacked’  $k$  estimates are not included in the primary statistical data analysis, but are included in estimations of the correlation and cross correlation between  $\ln k$  and  $\ln K_d$ . The sample spacing used for core 5 is described below and resulted in 38 ‘missing’  $k$  measurements. Sparse additional measurements available from some cores in the interval above 1.5 m or below 2.95 m depth (1.45–1.50 m or 2.95–3.00 m) for either parameter are included in the data sets used for descriptive statistics for each property. The uneven spacing and the missing information, in particular, caused considerable (and unavoidable) computational difficulties for the spatial statistics.

## 2.2. Permeability

[15] Because of the ease and speed of collection, air permeameter measurements were made in preference to methods using water as the fluid. An air minipermeameter was built and calibrated using pressure transducers, similar to the design specified by *Davis et al.* [1994], where a falling plunger forces air through a sample. The permeability determined for air flowing through the sample encased in the subcore tube was calculated after *Springer et al.* [1998].

[16] For a group of test samples taken from three different cores,  $k$  determinations used air and water successively as the measurement fluid to allow direct comparisons between the two measurements for our system. This information facilitates comparisons to prior Borden aquifer studies that determined saturated hydraulic conductivity. Two of the cores (adjacent to core line) were taken solely for side investigations of this type, and do not contribute any additional data to this study. The third core (number 5) contributes  $k$  and  $K_d$  data. Air permeametry in this comparison trial was conducted according to the method described above, except that 2.5 cm stainless steel tubes were used to obtain subcore samples (instead of the 1.3 cm tubes used for all the other  $k$  data collected). Following the air permeameter measurement, the sample was installed in a constant head permeameter, purged with CO<sub>2</sub> for twenty minutes to displace air from the pores [after *Sudicky*, 1986], and de-aired (in line boiled, cooled) water was used to saturate the sample. Data were collected at head differences of 5, 10, 15, and 20 cm for each sample.

[17] A linear regression of the permeability values observed using the two fluids was determined ( $\ln k = 0.98 k_w + 0.25$ , where  $k_w$  is the value resulting from water permeameter measurement, see also Figure S1 in the auxiliary material<sup>1</sup>). Near the mean  $\ln k$  for our data set, this equation can be approximated as  $k_w \sim 0.57 k$ . The offset between the two permeability observations is within the numeric offset range observed by *Springer et al.* [1998], who compared permeability measurements made with both fluids for a range of samples. The consistent offset indicates a systematic bias that, regardless of the mechanism, does not affect the spatial statistics (other than the mean) in which we are interested. Unless specified otherwise, the values reported in our manuscript are those measured directly using the air permeameter.

[18] Because it is impossible to obtain replicate subcores to estimate the uncertainty of the sampling and permeability measurement process in our study, we use the data from the air versus water permeametry method comparison experiments for this purpose. The mean square (MS) residuals (determined from the best fit regression of the  $\ln k_w$  as a function of  $\ln k$ ) are used to estimate the variance of  $\ln k$  attributable to measurement error as 0.03. This corresponds to a relative error of 18% of the average  $\ln k$  measurement in the sample set (expressed by the coefficient of variation defined as the root MS residuals divided by the mean).

[19] The  $\ln k$  for samples repacked into the subcore tubes replace “missing” measurements for the samples noted in the prior section. In order to establish the difference that resulted from repacking the samples, we repacked and measured  $\ln k$  for 98 samples for which we had already measured the undisturbed sample  $\ln k$ . We found that the repacked samples reproduced the mean value for the undisturbed sample set well ( $\ln k$  (cm<sup>2</sup>) = -14.8 and -14.9, respectively). However, repacking the samples significantly reduced variability (repacked sample  $\ln k$   $\sigma^2$  = 0.049 compared to undisturbed sample  $\ln k$   $\sigma^2$  = 0.30). All of the coarser samples experienced significant reduction in observed  $\ln k$ . Therefore, for samples in which no undis-

<sup>1</sup>Auxiliary material is available at <ftp://ftp.agu.org/apend/wr/2005WR003977>.

turbed  $k$  measurement is available, we use twice the observed  $k$  for repacked coarse samples and we used the repacked value directly for all of the other samples. Because of the high uncertainty that this approximation introduces, we used these estimates only in the work that examines the cross correlation between  $\ln k$  and  $\ln K_d$ .

[20] The complete  $k$  data set is tabulated in the auxiliary material (Table S1). In addition, we supply information on each subcore physical dimension (diameter and length), measurement temperature, and sample porosity. The latter indicates sample expansion that occurred with subcoreing.

### 2.3. Sorption

[21] The PCE  $K_d$  was determined using a batch technique, similar to *Allen-King et al.* [1998], in which approximately 7 g pulverized sediment, 3.35  $\mu\text{g}$  PCE, and 4 mL synthetic groundwater were combined in 5 mL Wheaton glass ampoules. The sediment was pulverized in our experiments to obtain sorption equilibrium rapidly. *Ball and Roberts* [1991b] determined that PCE sorption equilibrium (within one standard deviation of the ‘ultimate’  $K_d$  value obtained during a much longer contact period for the unpulverized sample) was obtained for a pulverized test Borden sample within 72 hours of contact time. Further, they [*Ball and Roberts*, 1991b] found that pulverization did not otherwise affect the equilibrium PCE  $K_d$  observed. Therefore, in our experiments, the ampoules were rotated for 72 hours after PCE addition prior to centrifugation and measurement of the PCE solution concentration by gas chromatography with electron capture detection. We assume that the resulting  $K_d$  values provide a good estimate of the equilibrium condition.

[22] The resulting average equilibrium PCE concentration in the aqueous phase for all samples was 466  $\mu\text{g/L}$  ( $\sigma = 102 \mu\text{g/L}$ ). The dominant mode of sorption (i.e., adsorption versus partitioning) is known to depend on concentration [*Allen-King et al.*, 2002]; the transition from adsorption at low concentrations to partitioning at higher concentrations occurs at approximately 10 mg/L for PCE in Borden sand [*Allen-King and Mackay*, 2000]. Thus the dominant sorption mechanism in this study is comparable to that operating in the SW experiment, in which the initial PCE concentration was approximately 30  $\mu\text{g/L}$ .

[23] The apparent sorption distribution coefficient is calculated using a mass balance that incorporates the total PCE mass and final solution concentrations, the estimated PCE mass in the vial, and the sample and water masses [after *Ball and Roberts*, 1991a]. The initial mass of PCE added to each ampoule ( $M_o$ ) is determined by interspersing multiple hexane-filled vials with the samples during PCE additions and immediately analyzing the amount of PCE in the hexane. Volume of air ( $V_a$ ) is estimated by difference,  $V_T - V_w - (m_s/\rho_s)$  where  $V_T$  is the average total ampoule volume and  $\rho_s$ , the particle density, is 2.71 g/mL [*Ball et al.*, 1990]. The Henry’s Law constant ( $H$ ) is calculated for the estimated average laboratory temperature of 22°C using the data from *Gossett* [1987] to yield a dimensionless  $H$  value of 0.610 for PCE.

[24] Two types of replicate experiments are analyzed in conjunction with  $M_o$  and control samples in order to quantify confidence in  $K_d$  measurements. Replicates of selected samples (generally analyzed on the same day) or homogenized bulk Borden material (referred to as “bulk

replicates” throughout the rest of the text and analyzed as part of several groups to account for day-to-day variation) are analyzed in a subset of batches to quantify error on  $K_d$  measurements.

[25] Standard error propagation techniques [e.g., *Meyer*, 1975] are used to quantify the relative error ( $\varepsilon_{K_d}$ ) of  $K_d$  (equation (A1)) for each sample. When mass fraction sorbed is below approximately 0.3, relative error in  $K_d$  increases sharply [*Ball and Roberts*, 1991a]. The PCE mass fraction sorbed at equilibrium ranged from 0.11 to 0.89 (mean = 0.35,  $\sigma = 0.13$ ) over all the samples. The resulting  $\varepsilon_{K_d}$  estimated for the samples consequently range from 0.02 to 0.68 (mean  $\varepsilon_{K_d} = 0.18$ , standard deviation of  $\varepsilon_{K_d} = 0.095$ , median  $\varepsilon_{K_d} = 0.16$ ) with the highest relative errors generally associated with the lowest  $K_d$  values. Of the only nine samples in the total  $K_d$  data set with  $\varepsilon_{K_d} > 0.40$ , all are within the 10 smallest  $K_d$  values. Because the average variability attributable to the measurement error is small (e.g., for a typical sample squared standard error =  $S_{K_d}^2 = (0.16 \times 0.45)^2 = 0.0052$ ) compared to the variance of the total data set (0.37), we will treat the relative error on  $K_d$  as constant (homogeneous variance) for our geostatistical analyses.

[26] The complete  $K_d$  data set is tabulated in the auxiliary material (Table S2). In addition, we supply contextual information for each measurement including: dissolved and sorbed concentrations, initial PCE mass and the estimated relative error.

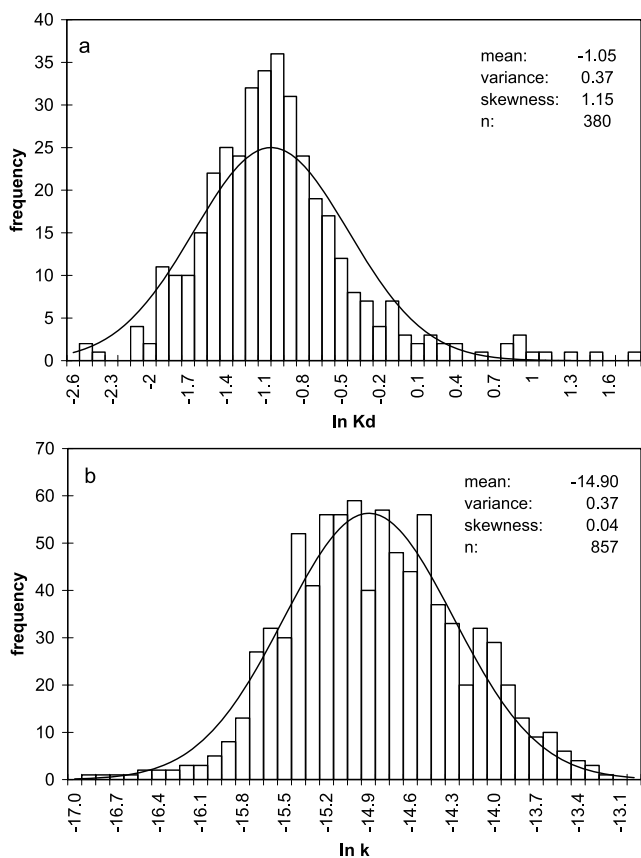
## 3. Results and Discussion

### 3.1. Descriptive Statistics for $K_d$ and $k$

[27] The 380 observed PCE  $K_d$  ranged from 0.08 to 5.60 mL/g with a geometric mean of 0.35 mL/g and an arithmetic mean 0.45 mL/g. The arithmetic mean  $K_d$  observed in our study (0.45 mL/g) is comparable to that obtained by others [*Ball and Roberts*, 1991a] with depth-integrated samples from the same aquifer when the effect of solution concentration is taken into account. We can quantitatively compare our results to the measurements of *Ball and Roberts* [1991a] by computing the  $K_d$  at  $C = 466 \mu\text{g/L}$  (the average  $C$  of batch experiment systems in our study) from their reported Freundlich isotherm parameters ( $K_f = 1.3$ ,  $n = 0.81$ ) as  $K_d = K_f C^{n-1} = 0.41 \text{ mL/g}$ . This value is within our experimental error on  $K_d$ .

[28] Within the Borden aquifer, using similar vertical sampling intervals and the same solute, the present study and that of *Allen-King et al.* [1998] produce nearly identical  $K_d$  ranges. This parity of results is not unexpected given the similar conditions of the experiments. However, we note that *Allen-King et al.* [1998] examined only a single core of aquifer material. Comparison between these studies demonstrates that much of the variability occurs vertically.

[29] The above values translate to a mean  $\ln K_d$  of  $-1.05$  with a range of  $-2.55$  to  $1.72$  and a variance of 0.37. The distribution of  $\ln K_d$  is right skewed (skewness coefficient = 1.16) with a tail containing 10 important high  $\ln K_d$  observations (Figure 2a). The normal distribution function is not consistent with either the arithmetic  $K_d$  data or the  $\ln$ -transformed data, although the natural log transformed data is the better fit of the two. A  $\chi^2$  test with William’s



**Figure 2.** Histograms of (a)  $\ln K_d$  and (b)  $\ln k$  data. Measured units of  $K_d$  and  $k$  are mL/g and  $\text{cm}^2$ , respectively. Bin labels are the maximum sample values that can be included in each bin. Statistics for  $\ln k$  are reported for the undisturbed sample data set only (see section 2.1). A normal curve is included for reference.

correction [Sokal and Rohlf, 1981] produced a  $\chi^2$  test statistic (49.1) greater than the critical value (27.9) leading to the rejection of the null hypothesis that the normal distribution fits the  $\ln K_d$  data ( $\chi^2$  test,  $p = 0.0018$ ).

[30] A lognormal distribution fits the permeability data collected in our study reasonably well ( $\chi^2$  test,  $p = 0.077$ ). The observed  $\ln k$  ranges between  $-16.98$  and  $-13.27$ , with a mean of  $-14.90$  and a variance of  $0.37$  (Figure 2b). Converting the mean  $\ln k$  to account for the offset between measurements made with air and water as the mobile fluid shows that our results are comparable to values reported in prior Borden permeability studies (Table 1). The relatively modest differences between the mean  $\ln k$  observed in this study and those of the other two studies may be as much a result of the differences in the methods of data collection as true differences in permeability. Our study measured permeability using air as the mobile fluid in aquifer subcores in which in situ sedimentary structures were retained with some unavoidable sample expansion. The expansion is a likely contributor to the higher mean value measured in our study. In addition, the other two studies listed in Table 1 [Sudicky, 1986; Turcke and Kueper, 1996] measured hydraulic conductivity using a falling head permeameter test on homogenized samples extracted from vertical depth intervals approximately four times larger than those that we studied.

[31] The descriptive statistics presented in this paper are based on the entire data sets collected because the  $\ln K_d$  data set in particular is relatively small. In order to ensure that autocorrelation did not affect the results, we repeated the analysis with 10 randomly selected subsets of data for each property (adopting the strategy of Woodbury and Sudicky [1991]) and compared the results to those from entire data set. The subsets of the  $\ln k$  data consisted of 6% of the entire data set (50 points). The t test results indicate that the means of all 10 of the  $\ln k$  data subsets are not significantly different from that obtained from the total data set ( $p \geq 0.05$ ). The variance of the  $\ln k$  data subsets range from 0.26

**Table 1.** Comparison of Borden  $\ln k$  and  $\ln K_d$  Statistics From Different Studies

Study	Chemical	Mean	Variance	Vertical Range, <sup>a</sup> m	Vertical Sample Spacing, m	Horizontal Range, <sup>a</sup> m	Horizontal Times Vertical Transect Dimensions, m
<i>Comparisons of <math>\ln k</math> [<math>\ln (\text{cm}^2)</math>]</i>							
Sudicky [1986]		-16.12	0.38	0.36	0.05	7.4	19 × 1.75
Woodbury and Sudicky [1991] <sup>b,c</sup>		-16.17	0.36	0.48	0.05	21.5	19 × 1.75
Robin et al. [1991] <sup>b,c,d</sup>		-16.12	0.38	0.42	0.05	22.5	19 × 1.75
Turcke and Kueper [1996] <sup>e</sup>		-16.46	0.59	0.47	0.05	14.4	10 × 2.95
Allen-King et al. [1998] <sup>b</sup>		-16.52	0.19	0.21	0.02	na	na
This study <sup>f</sup>		-15.46	0.37	0.33	0.015	2.7 <sup>g</sup>	10 × 1.5
<i>Comparisons of <math>\ln K_d</math> [<math>\ln (\text{mL/g})</math>]</i>							
Allen-King et al. [1998]	PCE	-0.54	0.39	0.15	0.02	na	na
This study	PCE	-1.05	0.37	0.20	0.03	4.0 <sup>g</sup>	10 × 1.5

<sup>a</sup>Practical range (3 times integral scale or correlation length) reported for studies that used an exponential model to fit the data.

<sup>b</sup>Converted from observed saturated hydraulic conductivity assuming that the viscosity and density of water are 1002  $\mu\text{Pa s}$  (at 20°C [Lide, 1997]) and 1000 g/L, respectively.

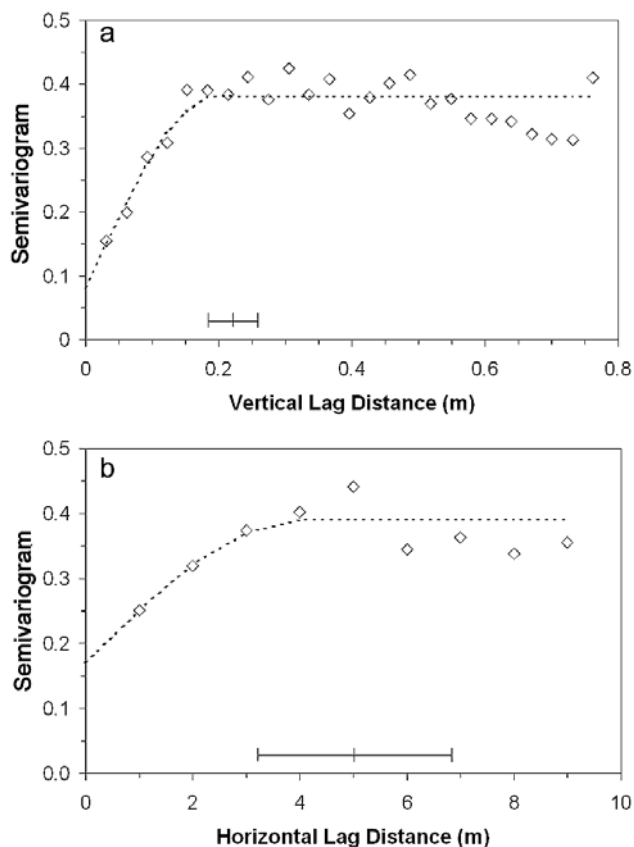
<sup>c</sup>Same data as Sudicky [1986]. Geostatistics reported for their section A-A'.

<sup>d</sup>Their model 2 results for A-A'.

<sup>e</sup>Located 60 m north-northeast from the site of the Woodbury and Sudicky [1991] site.

<sup>f</sup>This value is adjusted using the equation that resulted from air-water permeametry comparison as described in section 2.

<sup>g</sup>Unreliable or very uncertain result.



**Figure 3.** Variograms of  $\ln K_d$  data in the (a) vertical and (b) horizontal directions. Diamonds represent the semivariogram values; the dashed line is the spherical model determined using nonlinear least squares regression. The 95% confidence limits for the sill and range are marked. (a) Only data points from the same core are paired. Nugget = 0.08, sill = 0.38, and range = 0.20. (b) Horizontal bandwidth is 7.6 cm. Nugget = 0.17, sill = 0.39, and range = 4.0.

to 0.55 (average 0.38) and the skewness coefficient is near zero and alternates in sign with data subset, indicating a lack of skewness.

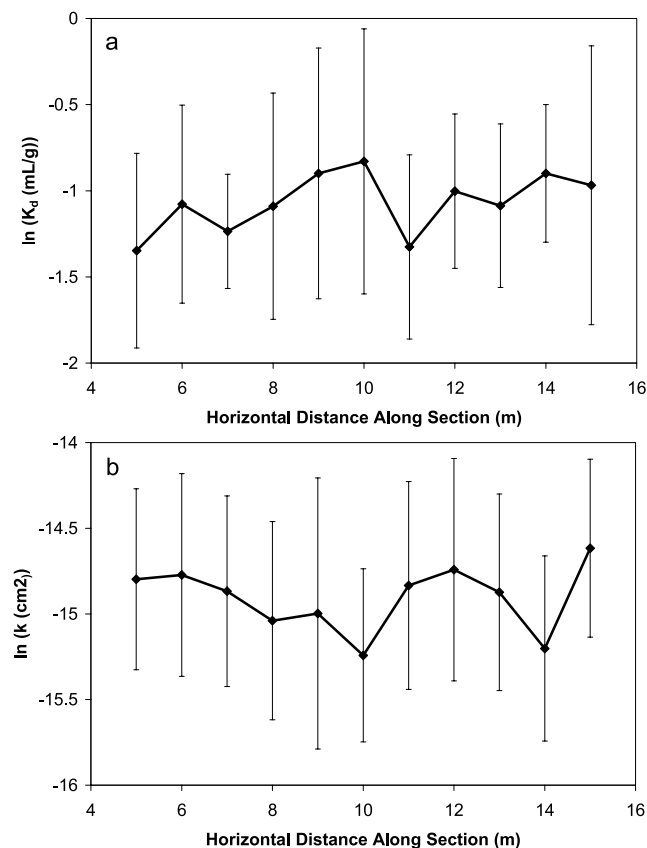
[32] The subsets of  $\ln K_d$  consisted of 14% of the entire data set (also 50 data points). The random selection process was designed to select samples with equal probability from any of the cores (i.e., without biasing the data subsets with more samples from cores for which greater numbers of measurements are contained in the entire dataset). The mean of only one of the 10  $\ln K_d$  data subsets is significantly different from the entire data set ( $p = 0.05$ ). The variance ranged from 0.16 to 0.58 for the data subsets, with an average value of 0.36. Positive skewness, an important characteristic of the entire  $\ln K_d$  data set, was also observed in each of the  $\ln K_d$  data subsets. We conclude that autocorrelation in the data sets has a minimal effect on the mean and variance presented for the entire dataset.

### 3.2. Spatial Distributions of $\ln K_d$ and $\ln k$

[33] Vertical and horizontal variograms of the  $\ln K_d$  data from this study (Figure 3) were fitted with a spherical model. The common practice of limiting the maximum lag to one half the longest lag sampled is not followed in

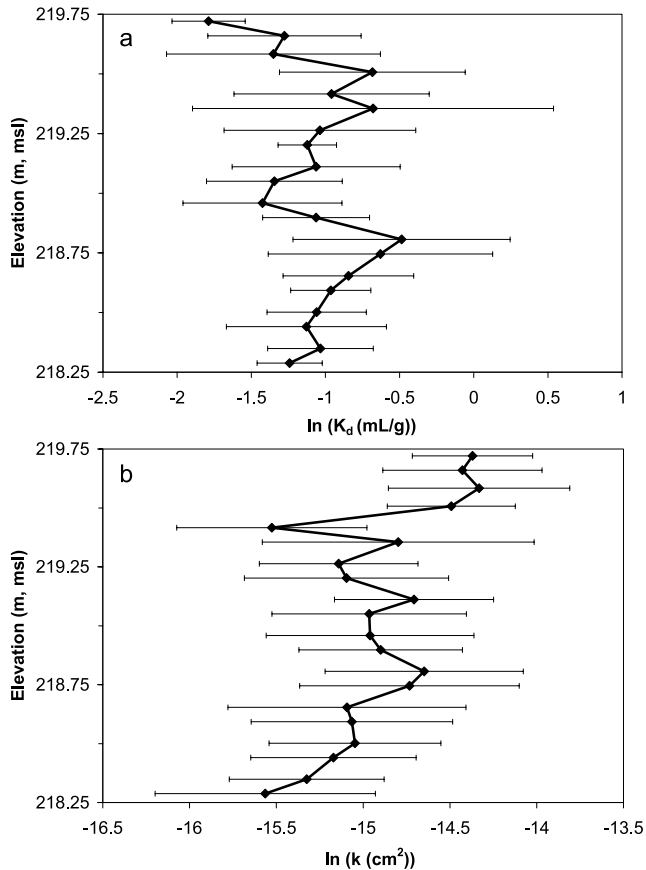
this case, due to the already limited number of lags available and the fact that there are a number of horizontal variograms (one for each vertical elevation) that can be stacked (averaged) to improve the quality of the estimates at each lag. The ranges obtained from the spherical models are  $0.20 \text{ m} \pm 0.04 \text{ m}$  in the vertical direction and  $4.0 \text{ m} \pm 2.2 \text{ m}$  in the horizontal direction ( $\pm 95\%$  confidence interval, CI). Whereas the vertical range is relatively well defined by the number and spacing of samples obtained, the large uncertainty in the horizontal range arises from the wide spacing of the cores that poorly defines the horizontal correlation over short length scales and the limited number of samples (cores) in the longitudinal direction, resulting in at most 10 points used to define the variogram. It is clear that cores spaced less than one meter apart are desirable to reduce uncertainty in defining the shape and range of the horizontal variogram. The limited total length of the transect measured is less than three times the length of the estimated range for  $\ln K_d$ ; consequently, correlation over longer horizontal scales may remain uncaptured.

[34] No significant trends  $\ln K_d$  were detected in either the vertical ( $p = 0.28$ ) or horizontal ( $p = 0.13$ ) directions for the extent of sediment characterized (Figures 4a and 5a). A slight trend in the vertical ( $p = 0.002$ ) but not the horizontal ( $p = 0.97$ )  $\ln k$  was observed (Figures 4b and 5b). To test for vertical trend, the means were computed for samples from particular and relatively evenly spaced depths, and these mean values were tested for a significant trend. Horizontal trend analysis used core average values.



**Figure 4.** Horizontal data used to test for trends in (a)  $\ln K_d$  and (b)  $\ln k$ . No significant trend exists for either parameter. Error bars represent  $\pm 1\sigma$ .





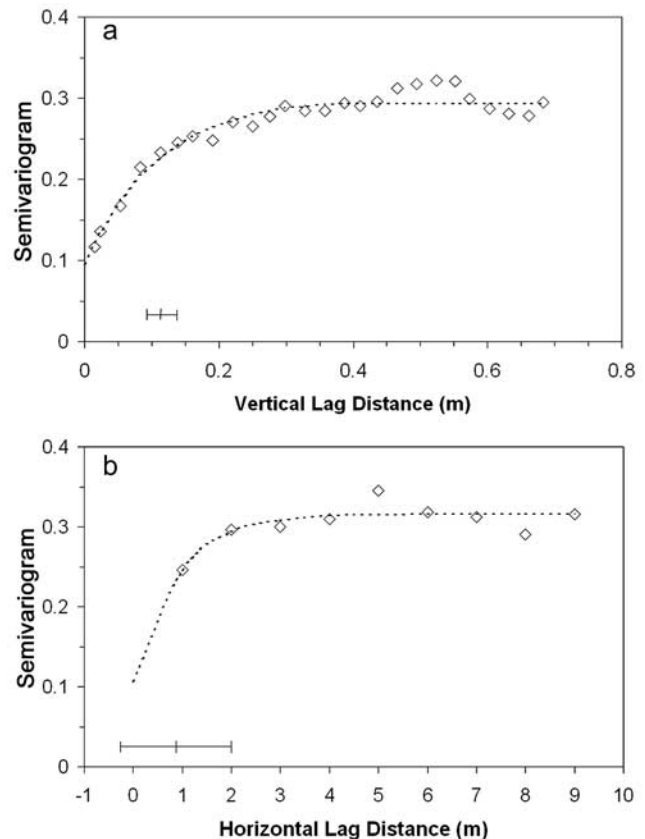
**Figure 5.** Vertical data used to test for trends in (a)  $\ln K_d$  and (b)  $\ln k$ . A significant trend was observed for  $\ln k$ . Error bars represent  $\pm 1\sigma$ .

[35] *Brusseau and Srivastava* [1997] based their simulation constraints on *Durant's* [1986] core-averaged  $K_d$  measurements, which are equivalent to arithmetic mean values. Therefore we also examined the arithmetic mean values computed for our transect in the longitudinal direction and found no obvious trend in the data. (It is inappropriate to test these values using ANOVA because the variance is not homogeneous.) However, we note that the arithmetic average values span the range comparable to the range quoted by *Brusseau and Srivastava* [1997]. Our data may suggest that localized trends are present over much shorter distances (e.g., a factor of 2 increase in  $\ln K_d$  is apparent from core 7 to core 10). However, to our knowledge, the effect of such small-scale trends on transport has not been explored.

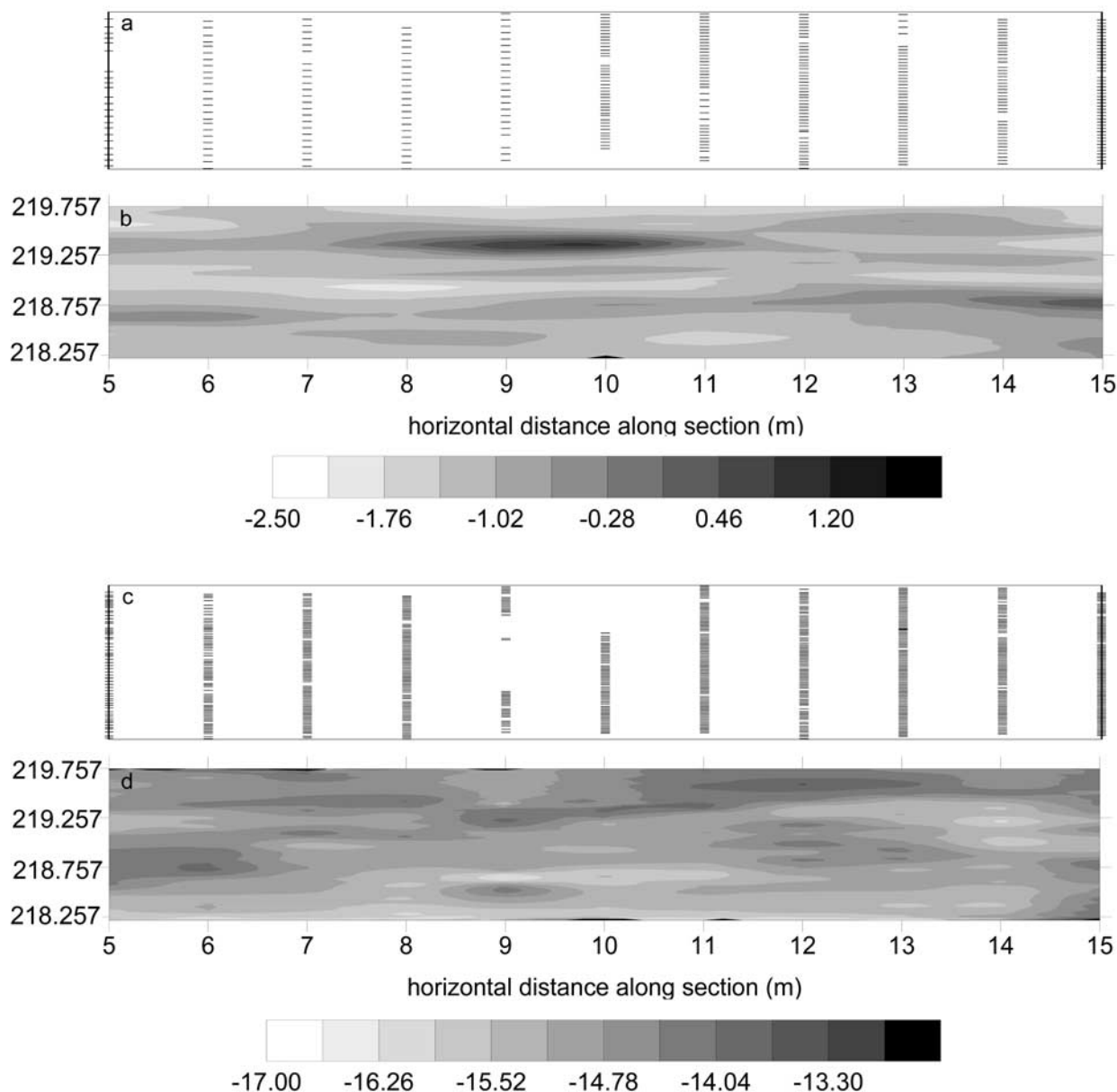
[36] The  $\ln k$  variograms are best fit (using least squares regression) to exponential functions with vertical and horizontal integral scales ( $\pm 95\%$  CI) of  $0.11 \text{ m} \pm 0.02 \text{ m}$  and  $0.91 \text{ m} \pm 1.12 \text{ m}$ , respectively (Figure 6). The practical or effective ranges (to which we will refer as simply the range hereafter) are  $0.33 \text{ m}$  and  $2.7 \text{ m}$  in the vertical and horizontal directions, respectively. The vertical trend was subtracted prior to the generation of the vertical variogram to ensure first-order stationarity. As with the  $\ln K_d$ , the horizontal variogram was not truncated. As for the  $\ln K_d$ , the uncertainty in the horizontal range is very large. Furthermore, while the vertical range agrees well with prior studies (Table 1), the horizontal range is much smaller than that

determined in prior studies. Correlation over longer horizontal scales remains uncaptured.

[37] The near-equal sills in the vertical and horizontal directions for both  $\ln k$  and  $\ln K_d$  indicate a lack of zonal anisotropy, i.e., the horizontal and vertical variability are approximately equal. Not only is the variance the same horizontally and vertically for each property, in this specific study the variance is the same between properties (Table 1). The large vertical to horizontal difference in the ranges, however, confirms strong geometric anisotropy. Thus the range over which the values of an individual parameter are related varies depending on the horizontal or vertical direction. In the case of  $\ln K_d$ , the horizontal range is 20 times that of the vertical direction; for  $\ln k$  the range is eight times the vertical. Close examination of analogue sedimentary deposits exposed nearby (at the Borden site) (D. R. Gaylord, unpublished data, 2005) reveals that the cross-sectional depiction in Figure 7 portrays the dominantly horizontal geometries of bounding surfaces (surfaces of erosion, nondeposition or abrupt change in textural character) that characterize the heterogeneous Borden strata on a number of scales.



**Figure 6.** Variogram of detrended  $\ln k$  data in the (a) vertical and (b) horizontal directions. Diamonds represent the semivariogram values; the dashed line is the exponential model determined by nonlinear least squares regression. The 95% confidence limits for sill and range are marked. (a) Only data points from the same core are paired. Nugget = 0.09, sill = 0.30, and integral scale = 0.11. (b) Horizontal bandwidth is 3 cm. Nugget = 0.11, sill = 0.32, and integral scale = 0.91.



**Figure 7.** Contoured (b)  $\ln K_d$  and (d)  $\ln k$  fields with (a and c) post plots of sampled points. Vertical axis is elevation in masl. Each dash on the post plots represents one sample. Each shade on the contour plots represents  $0.37 \ln K_d$  or  $\ln k$  units, equal to the variance. The  $\ln K_d$  and  $\ln k$  values at unsampled locations are estimated via kriging with input parameters estimated from the semivariograms.

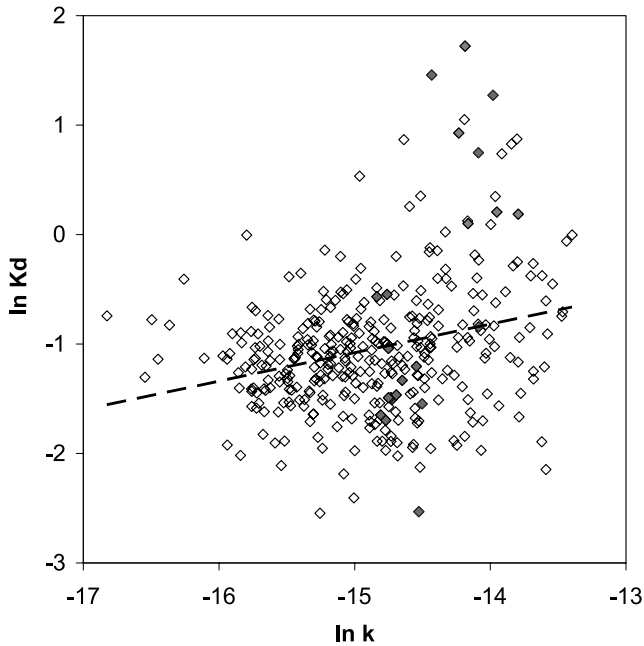
[38] The semivariogram parameters are used to generate a contour plot of a cross section of the subsurface, estimating the  $\ln K_d$  and  $\ln k$  at unsampled points via kriging (Figure 7). The  $\ln K_d$  cross section reflects the circumstance that much of the section is relatively uniform (Figure 7b), with all but one of the upper 5% of  $\ln K_d$  values ( $>0.09$ ) clustered into zones that are apparently continuous across several cores located in either the central region at approximately 219.4 masl or at 218.4 masl at the north end of the transect. Most of the samples with  $0.09 > \ln K_d > -0.28$  (an additional 4% of the samples) are also associated with these regions or clustered together. The appearance of the high  $\ln K_d$  values (constituting the skewed right tail on the histogram) in only a few localized zones within a background of relatively lower values may

have contributed to the enhanced spreading and macrokinetic behaviors observed for the reactive solutes in the SW original tracer experiment.

[39] The contoured cross section of the  $\ln k$  transect appears in Figure 7d. The  $\ln k$  cross section is more heterogeneous than the  $\ln K_d$  cross section. For example, while the highest  $\ln K_d$  values appear in only a few zones, the highest  $\ln k$  values ( $>-14.02$  and constituting 8.5% of the data set) appear in all of the cores and at multiple elevations separated by many lower valued samples in most cores.

### 3.3. Correlation Between $\ln K_d$ and $\ln k$

[40] A linear regression of the  $\ln K_d$  on  $\ln k$  exhibits a statistically significant positive correlation with a great deal



**Figure 8.** Scatterplot of  $\ln K_d$  versus  $\ln k$  exhibits weak positive correlation. Shaded points indicate that  $\ln k$  value is estimated from the repacked sample measurement (section 2.1). Dashed line indicates regression result that includes the repacked sample results.

of noise (Figure 8). These observations are consistent with prior work that used samples from a single core [Allen-King *et al.*, 1998]. The linear regression parameters for the dataset including the estimated (repacked)  $\ln k$  values ( $n = 366$ , see section 2.1 for description of repacked  $\ln k$ ) are slope = 0.26 and intercept = 2.82. (Both are significantly different from zero with  $p = 2.0 \times 10^{-7}$  and  $1.3 \times 10^{-4}$ , respectively.) For the dataset not including the repacked sample results ( $n = 342$ ), the slope is shallower (0.198) and the intercept = 1.88. (Both are also significantly different than zero,  $p = 1.5 \times 10^{-5}$  and 0.0055, respectively.) The unfortunate loss of undisturbed sample  $\ln k$  measurements that correspond to about half of the highest  $\ln K_d$  samples ( $\ln K_d > \sim 0$ ) adds significant uncertainty to the assessment of the magnitude of correlation between the two at zero lag. However, the trend is clearly positive. Therefore we conclude that the negative correlation used in prior modeling studies to match the SW transport experiment trends is not correct.

[41] The autocorrelation and the cross-correlation functions (ACF and CCF, respectively) are estimated in the vertical and horizontal directions; all computations are performed on the log-transformed variables. The data is filtered to obtain 360 points in the profile for which both  $\ln k$  and  $\ln K_d$  values are available and this data set is used for both the ACF and CCF analysis; it is noted that in addition to the undisturbed sample  $\ln k$  measurements, the  $\ln k$  estimates based on repacked samples were used for the ACF and CCF determinations. The ACFs (not shown) give analogous information to the variograms. The results are presented to complement the CCF result since both are based on a data subset that is modestly different than that used for the variograms. The filtering process produced a

cross section of  $\ln k$  and a corresponding cross section of  $\ln K_d$  values wherein the points were uniformly spaced but with many ‘missing’ values, particularly in the region of cores 5–9 which were sampled less frequently for  $K_d$ . Missing values pose a significant challenge for most software and consequently, the autocorrelation and cross-correlation functions (ACF and CCF respectively) are calculated by hand in a spreadsheet.

[42] The autocovariance function for  $\ln k$  ( $A_{\ln k-\ln k}(\bar{h})$ ) is estimated from

$$A_{\ln k-\ln k}(\bar{h}) = \frac{1}{n_p} \sum_{i_p=1}^{n_p} \left[ \ln k'(\bar{x}) \ln k'(\bar{x} + \bar{h}) \right]_{i_p} \quad (1)$$

and the ACF ( $R_{\ln k-\ln k}(\bar{h})$ ), from

$$R_{\ln k-\ln k}(\bar{h}) = A_{\ln k-\ln k}(\bar{h}) / \text{var}(\ln k) \quad (2)$$

where  $\bar{h}$  is the lag or separation distance in the horizontal or vertical direction,  $\bar{x}$  is the position vector,  $\ln k'(\bar{x})$  is the perturbation of  $\ln k$ ,  $\text{var}(\ln k)$  is the variance of  $\ln k$ ,  $i_p$  is the  $i$ th pair of points and  $n_p$  is the total number of pairs of points separated by lag distance  $\bar{h}$ . The perturbation,  $\ln k'(\bar{x})$ , is the difference between each observation,  $\ln k(\bar{x})$ , and the mean,  $\langle \ln k \rangle$ :

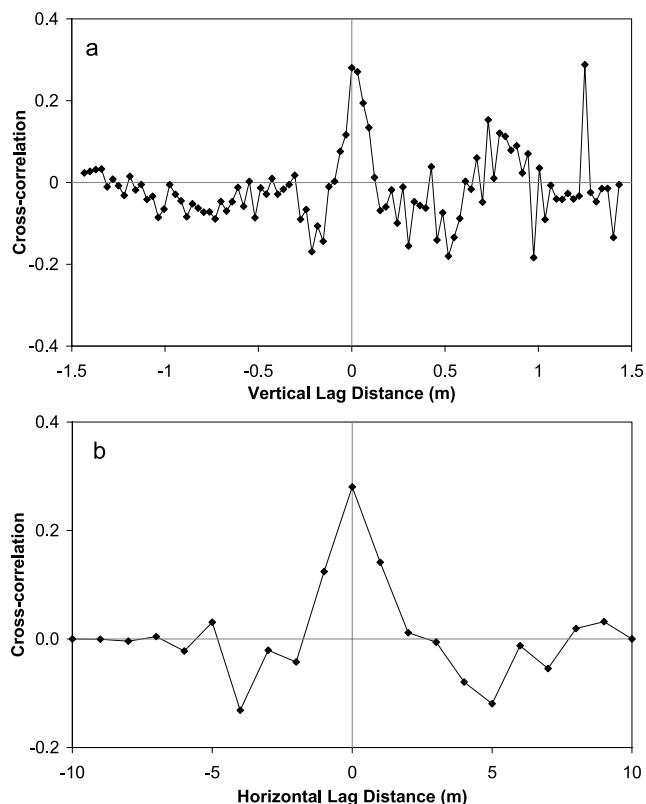
$$\ln k'(\bar{x}) = \ln k(\bar{x}) - \langle \ln k \rangle \quad (3)$$

For the purpose of calculating the ACF and the CCF we use the means of the entire data sets (e.g., values in Table 1) instead of the means of the 360 point profile and, as a result, the perturbations do not add up to zero. Similarly, we use the entire data set to evaluate the variance and, as a result, the ACF can sometimes be out of the normal range  $(-1, 1)$ .

[43] Because of the large number of missing points, the error on the covariance (and correlation) estimates is difficult to quantify. However the error is known to increase with lag, where fewer pairs of points are available for estimating the covariances. This increasing error with lag can be palliated somewhat by the common practice of multiplying the covariance functions with a triangular window defined by the following weighting function:

$$w\left(\frac{\bar{h}}{h}\right) = 1 - \left| \frac{\bar{h}}{h} / \frac{\bar{h}}{h_{\max}} \right| \quad (4)$$

[Robin *et al.*, 1991, and references therein]. For evenly spaced data series, this triangular window is obtained simply by using the number of points in the series (a constant) in equation (1) instead of the number of pairs of points, which decreases with lag. The estimator given above without triangular weighting is nonbiased, but it is biased when the triangular weighting is applied. (The expected value of a nonbiased estimator is the value of the population parameter.) The practical implication is that nonbiased estimates can be averaged (or stacked, or pooled) to produce better estimates whereas biased estimates cannot. Since the calculations were carried out by hand, the ACFs were stacked in each direction before applying a triangular



**Figure 9.** Cross correlograms in the (a) vertical and (b) horizontal directions.

window. Software that produces ACFs via the Fast Fourier Transform will generally produce this biased estimator. The ACF for  $\ln K_d$  is calculated using the same methodology as that used for  $\ln k$ .

[44] Exponential decay functions were fitted to the positive values of autocorrelation functions as a means of summarizing the data. In the vertical direction, the correlation lengths (given by the decay constant) for  $\ln k$  and  $\ln K_d$  are 0.10 m and 0.05 m, respectively, and these translate to practical ranges of 0.30 m and 0.15 m, respectively. A relatively smooth decay of the ACFs (without “hole”) indicates that periodicity could not be detected. In the horizontal direction, the correlation lengths for  $\ln k$  and  $\ln K_d$  are 0.8 m and 1.25 m, respectively. (The practical ranges are 2.4 m and 3.75 m, respectively). However, the ACFs show that the core spacing is too large to properly assess horizontal correlation. The summary statistics are intended here only as descriptive statistics with no intention to infer process. The ranges derived from this analysis are comparable to those determined from the semivariogram analysis, confirming that the slight differences in the data sets used for the analyses do not result in important and unintended biases.

[45] The cross-covariance function between  $\ln k$  and  $\ln K_d$  is estimated from

$$A_{\ln k - \ln K_d} \left( \frac{-}{h} \right) = \frac{1}{n_p} \sum_{i_p=1}^{n_p} \left[ \ln k' \left( \frac{-}{x} \right) \ln K_d' \left( \frac{-}{x+h} \right) \right]_{i_p} \quad (5)$$

and the cross-correlation function, from

$$R_{\ln k - \ln K_d} \left( \frac{-}{h} \right) = A_{\ln k - \ln K_d} \left( \frac{-}{h} \right) / \sqrt{\text{var}(\ln k) \text{var}(\ln K_d)}. \quad (6)$$

As in the ACF computation, a triangular window is applied after stacking the available estimates.

[46] The vertical CCF (Figure 9a) shows a positive peak centered around lag zero, indicating that the correlation between the two variables is positive and not offset; that is, an increase (or decrease) in one variable relative to the mean corresponds to an increase (or decrease) of the other variable at the same location. Two additional peaks appear at positive lags. Although it is difficult to ascertain its significance based on this data set, the first peak, near lag 0.75 m indicates that an increase in  $\ln k$  at one location corresponds to an increase in  $\ln K_d$  about 0.75 m down the profile. The second peak consists of a single point at lag 1.25 m and is not considered significant because of the large error in cross correlation associated with large lags. Similarly, the negative CCF values of both vertical and horizontal CCFs are not considered significant, because of their small values relative to the estimation error, particularly at large lags. The vertical CCF shows weak signs of periodicity at positive lags (roughly sinusoidal shape) but the quality of the data cannot ascertain this trend.

[47] The horizontal CCF (Figure 9b) shows a positive peak at lag zero, indicating that the correlation between the two variables is positive and not offset. The cross correlation decreases quickly on either side of the origin to near zero, indicating, similarly to the horizontal ACFs, that the core spacing was too large to properly assess the horizontal cross correlation.

#### 4. Concluding Remarks

[48] The SW and associated studies at the Borden site continue to offer a benchmark to use in developing conceptual models of contaminant transport. The data collected in our study provide information about the descriptive statistics and spatial geostatistics of  $\ln K_d$  for a two-dimensional vertical slice of the Borden aquifer. Our findings include the following: (1) a positive correlation between  $\ln k$  and  $\ln K_d$  at zero and small lags (less than 0.2 m vertically and less than 1 m horizontally); (2) differences between the two property distributions (skewed right for  $\ln K_d$  and normal for  $\ln k$ ); (3) different geostatistics that best describe their vertical spatial distributions; and (4) the occurrence of most high  $K_d$  values adjacent to one another in only two localized regions while the high  $k$  values are spread throughout the transect. Unfortunately, the statistics describing the horizontal autocorrelation behavior of  $\ln K_d$  and its cross correlation to  $\ln k$  remain very uncertain, despite a high level of effort, because of limitations in the sample distribution.

[49] Because observations 1–4 contrast with the assumptions used in prior simulation studies (described in the Introduction), we conclude that additional analysis is required to establish the determinants (or probable determinants) of the macrokinetic and enhanced spreading behaviors observed for the organic solutes in the SW experiment. In addition to simulation studies that include

more realistic representations of the geochemical complexities of the aquifer, more extensive sampling at the SW field site is needed to reduce uncertainty in the horizontal geostatistics that describe  $\ln K_d$ .

## Appendix A

[50] The relative error on  $K_d$  is computed using error propagation techniques as:

$$\varepsilon_{K_d}^2 = \frac{S_{M_o}^2}{M_s^2} + \frac{S_{C_w}^2 M_a^2}{C_w^2 M_s^2} + \frac{S_{H+X}^2 M_a^2}{M_s^2 H^2} + \frac{S_{V_a}^2 M_a^2}{M_s^2 V_a^2} + \frac{S_{C_w}^2 M_w^2}{M_s^2 C_w^2} + \frac{S_{C_w}^2}{C_w^2} \quad (\text{A1})$$

where the  $S_i$  are the standard errors on the  $i$  terms in the sorption equation,  $C_w$  is the dissolved PCE concentration,  $M_k$  are the total mass in each of the  $k$  phases (water, sorbed, air), and other variables are as previously defined. The solution concentration standard error,  $S_{C_w}$ , is determined from the calibration data [Sokal and Rohlf, 1981]. The standard errors on the gravimetrically determined terms (mass of solids, volume of water) are much smaller than those on the concentration-related terms and so are neglected. The standard error of the headspace volume measured on replicate ampoules is 0.106 mL. Equation (A1) represents the main sources of error in the  $K_d$  measurements: that associated with the  $M_o$ , error due to uncertainty on  $C_w$  and  $V_a$ , and error due to the difference between the actual (unknown)  $H$  controlling PCE mass in air and the estimated value. Additional day-to-day sources of experimental errors are not separated from one another, but instead grouped with the recognized unquantified error on  $H$  following the logic of [Ball and Roberts, 1991a] to create the resulting term  $(H + X)$ , where  $X$  represents the errors from unidentified sources. The standard error on  $H + X$  is determined from the measured relative error on  $K_d$  obtained from the several experiments with the ‘bulk’ sample; the  $\varepsilon_{K_d} \approx \sigma_{K_d, \text{bulk}}/K_{d, \text{bulk}} = 0.17$ , where the  $K_d$  variance of the bulk replicates ( $\sigma_{K_d, \text{bulk}}^2$ ) is 0.0029 and the average  $K_d$  of the bulk replicates ( $K_{d, \text{bulk}}$ ) is 0.32. Because the bulk sample was created by pulverizing and then homogenizing a larger aquifer sample, we attribute variations between replicates to unquantified day-to-day experimental error rather than to sample variability. Solving for  $\varepsilon_{H+X}$  produces 0.345, which is used in equation A.1 to calculate relative error on  $K_d$  for each sample. When a high mass fraction of PCE is sorbed, uncertainty on  $C_w$  dominates error; when sorption is low, however, most of the error is due to uncertainty on  $V_a$  and  $H + X$ .

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## References

Allen-King, R. M., and D. M. Mackay (2000), Exploiting natural chemical heterogeneity within a sedimentary deposit to probe controls on non-

- linear non-ionic organic pollutant sorption, paper presented at 220th National Meeting, Am. Chem. Soc., Washington, D. C.
- Allen-King, R. M., R. M. Halket, D. R. Gaylord, and M. J. L. Robin (1998), Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-based approach, *Water Resour. Res.*, *34*, 385–396.
- Allen-King, R. M., P. Grathwohl, and W. P. Ball (2002), New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks, *Adv. Water Resour.*, *25*, 985–1016.
- Ball, W. P., and P. V. Roberts (1991a), Long-term sorption of halogenated organic chemicals by aquifer material, 1. Equilibrium, *Environ. Sci. Technol.*, *25*, 1223–1237.
- Ball, W. P., and P. V. Roberts (1991b), Long-term sorption of halogenated organic chemicals by aquifer material, 2. Intraparticle diffusion, *Environ. Sci. Technol.*, *25*, 1237–1249.
- Ball, W. P., C. Buehler, T. C. Harmon, D. M. Mackay, and P. V. Roberts (1990), Characterization of a sandy aquifer material at the grain scale, *J. Contam. Hydrol.*, *5*, 253–295.
- Ball, W. P., G. P. Curtis, and P. V. Roberts (1997), Physical/chemical processes affecting the subsurface fate and transport of synthetic organic materials, in *Subsurface Restoration*, edited by C. H. Ward, J. A. Cherry, and M. R. Scaff, pp. 27–58, Ann Arbor Press, Chelsea, Mich.
- Ball, W. P., M. N. Goltz, P. V. Roberts, A. J. Valocchi, and M. L. Brusseau (1998), Comment on “Field-scale transport of nonpolar organic solutes in 3-D heterogeneous aquifers,” *Environ. Sci. Technol.*, *32*, 2654–2655.
- Bellin, A., and A. Rinaldo (1995), Analytical solutions for transport of linearly adsorbing solutes in heterogeneous formations, *Water Resour. Res.*, *31*, 1505–1511.
- Bohla, J. (1986), A sedimentological investigation of a progradational fore-shore sequence: C.F.B. Borden, M.S. thesis, Univ. of Waterloo, Waterloo, Ontario, Canada.
- Bosma, W. J. P., A. Bellin, S. van der Zee, and A. Rinaldo (1993), Linear equilibrium adsorbing solute transport in physically and chemically heterogeneous porous formations: 2. Numerical results, *Water Resour. Res.*, *29*, 4031–4043.
- Brusseau, M. L., and R. M. Srivastava (1997), Nonideal transport of reactive solutes in heterogeneous porous media: 2. Quantitative analysis of the Borden natural-gradient field experiment, *J. Contam. Hydrol.*, *28*, 115–155.
- Burr, D. T., E. A. Sudicky, and R. L. Naff (1994), Nonreactive and reactive solute transport in three-dimensional heterogeneous porous-media: Mean displacement, plume spreading, and uncertainty, *Water Resour. Res.*, *30*, 791–815.
- Burwasser, G. J., and B. D. Cairns (1974), Quaternary geology of the barrie area (western half), southern Ontario, map, scale 1:50,000, Ontario Div. of Mines, Toronto, Ontario, Canada.
- Curtis, G. P. (1991), Reductive dehalogenation of hexachloroethane and carbon tetrachloride by aquifer sand and humic acid, Ph.D. dissertation, Stanford Univ., Stanford, Calif.
- Curtis, G. P., P. V. Roberts, and M. Reinhard (1986), A natural gradient experiment on solute transport in a sandy aquifer: 4. Sorption of organic solutes and its influence on mobility, *Water Resour. Res.*, *22*, 2059–2067.
- Cushey, M. A., and Y. Rubin (1997), Field-scale transport of nonpolar organic solutes in 3-D heterogeneous aquifers, *Environ. Sci. Technol.*, *31*, 1259–1268.
- Cushey, M. A., and Y. Rubin (1998), Response to comment on “Field-scale transport of nonpolar organic solutes in 3-D heterogeneous aquifers,” *Environ. Sci. Technol.*, *32*, 2654–2656.
- Davis, J. M., J. L. Wilson, and F. M. Phillips (1994), A portable air-minipermeameter for rapid in situ field measurements, *Ground Water*, *32*, 258–266.
- Durant, M. G. (1986), Spatial variability of organic solute sorption in the Borden aquifer, engineer thesis, Stanford Univ., Stanford, CA.
- Fitzgerald, W. D. (1982), Post glacial history of the Minesing Basin, Ontario, M.S. thesis, Univ. of Waterloo, Waterloo, Ontario, Canada.
- Freyberg, D. L. (1986), A natural gradient experiment on solute transport in a sand aquifer: 2. Spatial moments and the advection and dispersion of nonreactive tracers, *Water Resour. Res.*, *22*, 2031–2046.
- Goltz, M. N., and P. V. Roberts (1988), Simulations of physical nonequilibrium solute transport models: Application to a large-scale field experiment, *J. Contam. Hydrol.*, *3*, 37–63.
- Gossett, J. M. (1987), Measurement of Henry’s law constants for C1 and C2 chlorinated hydrocarbons, *Environ. Sci. Technol.*, *21*, 202–208.

- King, M. W. G., and J. F. Barker (1999), Migration and natural fate of a coal tar creosote plume 1. Overview and plume development, *J. Contam. Hydrol.*, *39*, 249–279.
- Lide, D. R. (Ed.) (1997), *CRC Handbook of Chemistry and Physics*, 78th ed., CRC Press, Boca Raton, Fla.
- Mackay, D. M., W. P. Ball, and M. G. Durant (1986a), Variability of aquifer sorption properties in a field experiment on groundwater transport of organic solutes: Methods and preliminary results, *J. Contam. Hydrol.*, *1*, 119–132.
- Mackay, D. M., D. L. Freyberg, and P. V. Roberts (1986b), A natural gradient experiment on solute behavior in a sand aquifer: 1. Approach and overview of plume movement, *Water Resour. Res.*, *22*, 2017–2029.
- Meyer, S. L. (1975), *Data Analysis for Scientists and Engineers*, John Wiley, Hoboken, N. J.
- Miralles-Wilhelm, F. (1993), Stochastic analysis of sorption and biodegradation in three-dimensionally heterogeneous aquifers, Ph.D. thesis, Mass. Inst. of Technol., Cambridge.
- Miralles-Wilhelm, F., and L. W. Gelhar (1996), Stochastic analysis of sorption macrokinetics in heterogeneous aquifers, *Water Resour. Res.*, *32*, 1541–1549.
- Quinodoz, H. A., and A. J. Valocchi (1993), Stochastic analysis of the transport of kinetically sorbing solutes in aquifers with randomly heterogeneous hydraulic conductivity, *Water Resour. Res.*, *29*, 3227–3240.
- Rabideau, A. J., and C. T. Miller (1994), Two-dimensional modeling of aquifer remediation influenced by sorption nonequilibrium and hydraulic conductivity heterogeneity, *Water Resour. Res.*, *30*, 1457–1470.
- Rajaram, H., and L. W. Gelhar (1991), Three-dimensional spatial moment analysis of the Borden tracer test, *Water Resour. Res.*, *27*, 1239–1251.
- Roberts, P. V., and D. M. Mackay (Eds.) (1986), A natural gradient experiment on solute transport in a sand aquifer, *Tech. Rep. 292*, 153 pp., Dep. of Civ. Eng., Stanford Univ., Stanford, Calif.
- Roberts, P. V., M. N. Goltz, and D. M. Mackay (1986), A natural gradient experiment on solute transport in a sand aquifer: 3. Retardation estimates and mass balances for organic solutes, *Water Resour. Res.*, *22*, 2047–2058.
- Robin, M. J. L., E. A. Sudicky, R. W. Gillham, and R. G. Kachanoski (1991), Spatial variability of strontium distribution coefficients and their correlation with hydraulic conductivity in the Canadian Forces Base Borden aquifer, *Water Resour. Res.*, *27*, 2619–2632.
- Schwarzenbach, R. P., P. M. Gschwend, and D. M. Imboden (2003), *Environmental Organic Chemistry*, 2nd ed., 1313 pp., John Wiley, Hoboken, N. J.
- Sokal, R. R., and F. J. Rohlf (1981), *Biometry: The Principles and Practice of Statistics in Biological Research*, 2nd ed., W. H. Freeman, New York.
- Springer, D. S., H. A. Loaiciga, S. J. Cullen, and L. G. Everett (1998), Air permeability of porous materials under controlled laboratory conditions, *Ground Water*, *36*, 558–565.
- Starr, R. C., and R. A. Ingleton (1990), A new method for collecting core samples without a drilling rig, *Ground Water Monit. Rem.*, *12*, 91–95.
- Sudicky, E. A. (1986), A natural gradient experiment on solute transport in a sand aquifer: Spatial variability of hydraulic conductivity and its role in the dispersion process, *Water Resour. Res.*, *22*, 2069–2082.
- Turcke, M. A., and B. H. Kueper (1996), Geostatistical analysis of the Borden aquifer hydraulic conductivity field, *J. Hydrol.*, *178*, 223–240.
- Woodbury, A. D., and E. A. Sudicky (1991), The geostatistical characteristics of the Borden aquifer, *Water Resour. Res.*, *27*, 533–546.
- Young, D. F., and W. P. Ball (1994), A-priori simulation of tetrachloroethene transport through aquifer material using an intraparticle diffusion-model, *Environ. Prog.*, *13*, 9–20.

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