Experimental Measurement of Mass Fluxes During Simultaneous Volatilization and Leaching of Contaminated Soils and Risk Assessment Implications

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Background

Subsurface contamination by mixtures of hazardous organic compounds is a widespread problem in soil and ground water at industrial and military sites in the U.S. and abroad (NRC 1994, 1997, Siegrist and Van Ee 1994, U.S.EPA 1997). Organic contaminants of concern (COCs) commonly include volatile organic chemicals (VOCs) such as tetrachloroethene (PCE), trichloroethene (TCE), and benzene (Ben), and semivolatile organic chemicals (SVOCs) such as naphthalene (Nap), phenanthrene (Phen), and pyrenes (Pyr) (Table 1).

While varied exposure scenarios can present serious current or future health risks at many contaminated sites, baseline risk is often governed by inhalation exposures to toxic organics that volatilize from contaminated soils, and by ingestion exposures from toxic organics that leach from wastes and soils into ground water used for drinking water (Figure 1). The incremental risk due to such a current or future exposure is often estimated using site characterization data and transport models. As shown in the following equations for carcinogenic risk, the estimated mass flux of contaminants to a receptor leads to exposure concentrations (CA or CW) that are directly related to risk:

$$\text{Risk} = \text{CDI}*\text{CPF} \quad [1]$$

$$\text{CDI}_{ih} = \text{CA} * (\text{IHR}*\text{ET}*\text{EF}*\text{ED}) / (\text{BW}*\text{AT}) \quad [2]$$

$$\text{CDI}_{ig} = \text{CW} * (\text{IGR}*\text{EF}*\text{ED}) / (\text{BW}*\text{AT}) \quad [3]$$

where, CDI = chronic daily intake (mg/kg/d), CPF = cancer potency factor $(\text{mg/kg/d})^{-1}$ (U.S. EPA 1989). Chronic daily intakes from inhalation (CDI_{ih}) or drinking water ingestion (CDI_{ig}) are based on the average chemical concentration in air (CA, mg/m^3) and water (CW, mg/L) over the duration of exposure. The other terms in eqn. 2 and 3 (with the typical values prescribed for benzene inhalation shown in brackets) are: IHR = inhalation rate [15.2 m^3/d], IGR = ingestion rate [L/d], ET = exposure time [18.4 hr/d], EF = exposure frequency [365 d/yr], ED = exposure duration [30 yr], BW=body weight [71.8 kg], and AT= averaging time [27375 d].

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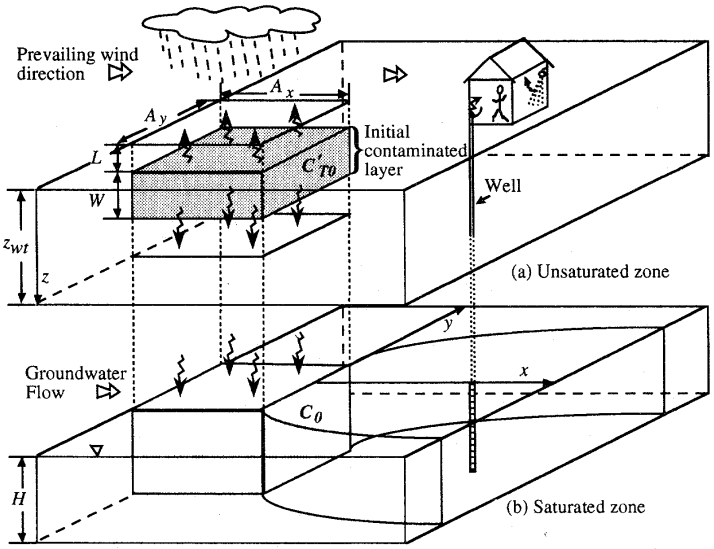


Figure 1. Illustration of VOC contaminated soil with the source term and volatilization and leaching fluxes from it (shown by the arrows) (Labieniec et al. 1996).

Table 1. Examples of Prevalent and Problematic Volatile Organic Chemicals.

Contaminant	Properties: MW or AW solubility	ATSDR 1997 ranking[1]	Prevalence at NPL sites (no. of sites)[2]	Reference values[3]	
				MCLs (ug/L)	Soil SSL's (mg/kg)
Tetrachloroethene (PCE)	166 g 200 mg/L	33	771 of 1430	5 – MCL	11 – vapor inh. 0.003 – GW migr.
Trichloroethene (TCE)	135 g 1100 mg/L	15	852 of 1430	5 – MCL	5 – vapor inh. 0.003 – GW migr.
Methyl chloroform (TCA)	133 g 1330 mg/L	79	696 of 1430	200 – MCL	1200 – vapor inh. 0.1 – GW migr.
Carbon tetrachloride (CT)	154 g 792 mg/L	46	326 of 1416	5 – MCL	0.3 – vapor inh. 0.003 - GW migr.
Toluene (Tol)	92 g 526 mg/L	61	869 of 1416	1000 – MCL	650 – vapor inh. 0.6 – GW migr.
Naphthalene (Nap.)	128 g 31 mg/L	72	536 of 1430	1000 – RfD	N/A – vapor inh. 4 – GW migr.
Phenanthrene (Phen.)	178 g 1.6 mg/L	10 (PAH's)	600 of 1430 (PAH's)	-	-

[1] Agency for Toxic Substances and Disease Registry. 1997 Priority List of Hazardous Substances. Division of Toxicology, U.S. Dept. of Health and Human Services. Nov. 1997.

[2] ToxFAQs. 1999. Agency for Toxic Substances and Disease Registry. http://www.atsdr.cdc.gov. April 1999.

[3] Reference values for cleanup are based on maximum contaminant levels (MCLs), reference dose (RfDs), or EPA soil screening levels (SSLs). SSL's are given for key exposure routes: vapor inh. = vapor inhalation, part. inh. = particulate inhalation, and GW migr. = ground water migration. Soil Screening Guidance: Technical Background Document. U.S. EPA OSWER. EPA/540/R-95/128. May 1996.

Risk reduction from an estimated baseline risk at most contaminated sites is achieved through reduction in contaminant mass and a concomitant reduction in the contaminant flux that creates exposures to receptors. Predicting the degree of treatment needed to achieve a desired reduction in risk is based on back-calculation (or iterative calculation) to set an acceptable residual contaminant level that will yield mass fluxes that, upon mixing into receiving mediums, do not exceed health-based exposure concentrations (e.g., CA or CW). There are numerous intermedia and multimedia transport models being used for risk assessment and in some cases, the prediction of the risk reduction benefits of *in situ* treatment (Labieniec et al. 1996, 1997, Sheldon 1999). However, experimental validation of the mass fluxes that occur during simultaneous leaching and volatilization of VOCs from contaminated soils have been lacking. Moreover, their use for assessing *in situ* treatment has yet to be evaluated. To remedy this situation, an experimental research project has been initiated at the Colorado School of Mines. Highlights of this work are presented herein while additional details may be found in published papers and forthcoming journal articles (Sheldon et al. 1997, 1998, Sheldon 1999, Sheldon et al. 1999a,b,c).

Research Highlights

Assembly and Testing of a Multimedia Lysimeter. A novel multimedia lysimeter was developed to simulate volatilization and leaching processes in VOC contaminated soil as depicted in Figure 1. The lysimeter apparatus is comprised of an unsaturated soil block (30 cm cubed) underlain by a micro-porous plate and hanging water column to control soil water content (Figure 2). A dynamic vapor flux chamber is located above the surface of the soil block along with an artificial rainmaker to disperse precipitation onto the soil at a prescribed interval. The airflow rate, humidity, temperature, rainfall, and soil water content are controlled to match desired field environmental conditions. After carefully packing the lysimeter with a soil matrix, a known amount of contaminants are added in an aqueous solution during upflow saturation. Following an equilibration period, drainage of the lysimeter to a baseline unsaturated soil water content is accomplished and the mass of contaminants recovered in the leachate is determined. The initial VOC mass and concentration in the lysimeter is then determined by difference. A continuous airflow is then initiated along with intermittent rainfall events. During the following days, the VOC concentrations in the air flow moving above the soil surface and in the leachate from the soil are measured by sampling and gas chromatography. To support multimedia modeling efforts, lysimeter environmental parameters are monitored continuously and recorded by a datalogging system (e.g., air flow rate, temperature and humidity; soil temperature and water content; and leachate flow rate and volume). Two multimedia lysimeters were fabricated and tested. Simultaneous leaching and volatilization results for replicate experiments with 1,1,1-trichloroethane in a sand matrix confirmed the reproducibility of triplicate experimental runs.

Controlled Volatilization and Leaching Experiments. Using the multimedia apparatus, twelve (12) volatilization and leaching experiments have been performed involving four chemicals and three soil types (Tables 2 and 3) (Sheldon et al. 1999a). To illustrate the nature of the data obtained, results with three chemicals in a sand matrix are presented in Figure 2. As illustrated therein, the experimental results yield the time dependent mass loss of initial contaminant due to both volatilization into the overlying air flow as well as into the rainfall induced leachate. Differences in the rate and extent of intermedia mass transfer are evident and are related to differences in the transport properties of the target compound and the soil matrix (e.g., K_{oc} and

K_H, and porosity and f_{oc}, respectively). Based on the complete experimental dataset, the volatilization mass transport is shown to be directly related to the VOC K_H and the media air-filled porosity, and inversely related to the VOC K_{oc} and media f_{oc}. The leaching mass transport is directly related to the VOC's C_w and the water content of the soil media and inversely related to the VOCs K_{oc} and media's f_{oc}.

Multimedia Transport and Risk Modeling. With the properties of the VOCs and environmental characteristics of the lysimeter, multimedia transport models are being used to predict the VOC concentrations in the vapor and leachate exiting the lysimeter during an experiment. Models that have been employed to date include SOILMOD, VLEACH, and EMSOFT (Sheldon 1999, Sheldon et al. 1999b). The model predictions are then compared to the experimentally observed results. For this comparison, the experimentally measured volatilization and leaching rates represent "truth," and the discrepancy between the measured quantities and the corresponding model predictions can be considered "errors".

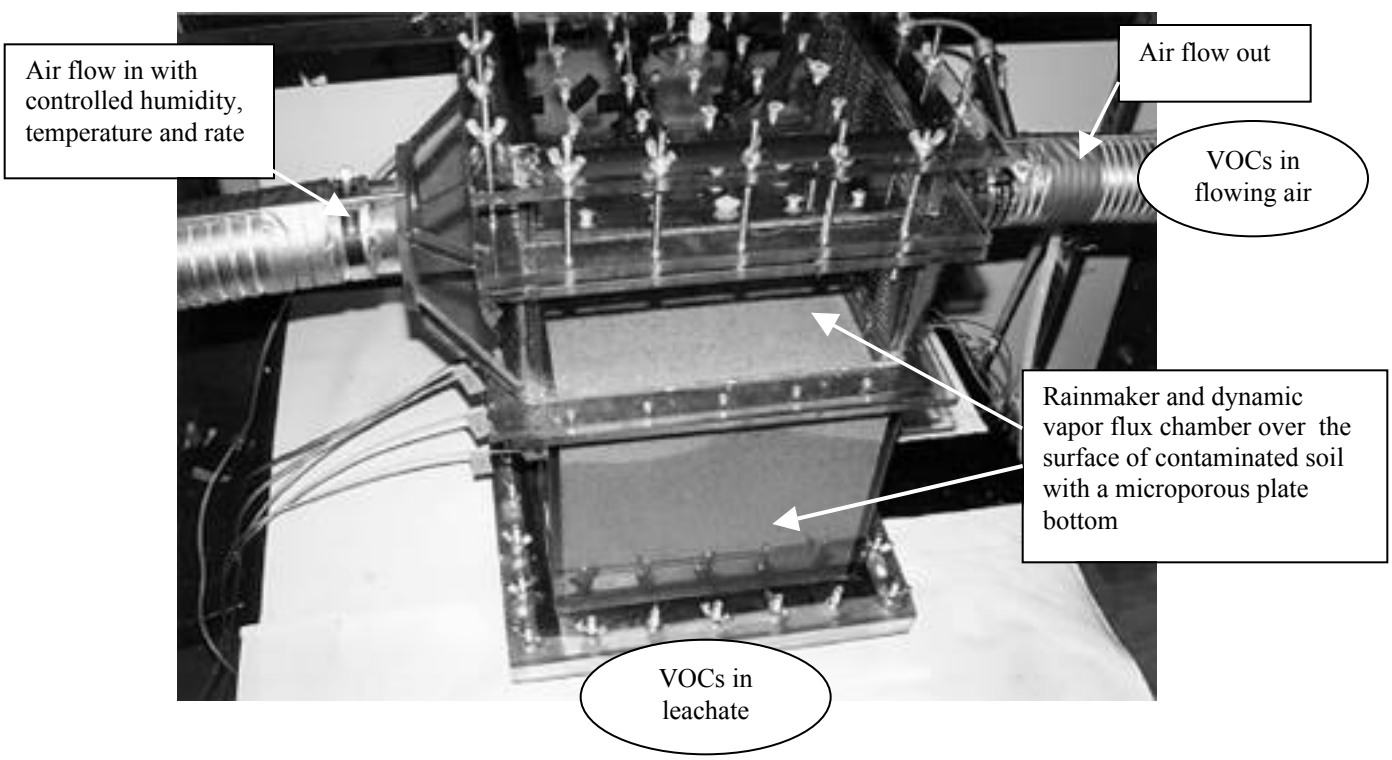


Figure 2. Photograph of the multimedia lysimeter apparatus established at CSM.

Table 2. Soil media used during experiments in the multimedia lysimeter apparatus.

Test soils	Type	Porosity (v/v)	Organic carbon content (dry wt.%)
Matrix 1	Sand	0.438	0.0169
Matrix 2	Silty sand	0.453	0.225
Matrix 3	Heterogeneous Created by patchwork layering of #1 and #2	Mixed	0.0169 or 0.225

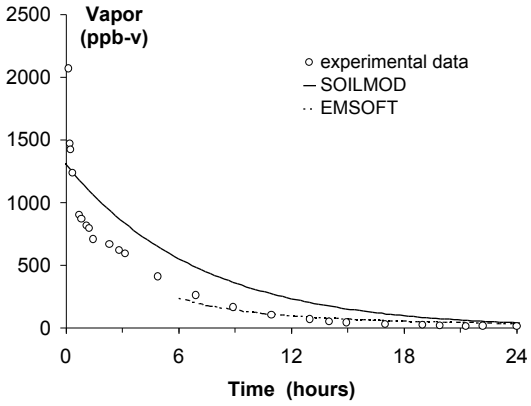
Table 3. Chemicals tested in the multimedia lysimeter apparatus[1].

Chemical	Mol. wt. (gmol)	Vapor pressure (Pa)	Solubility (mg/L)	K_{oc} (mL/g)	K_H (unitless)
1,1,1-Trichloroethane	133.4	16,490	1,330	135	0.676
trans-1,2-Dichloroethene	96.9	45,300	6,300	38	0.285
Tetrachloroethene	165.8	2,462	200	265	0.835
Toluene	92.1	3,804	526	140	0.272
Trichloroethene	131.4	6,307	1,100	94	0.308

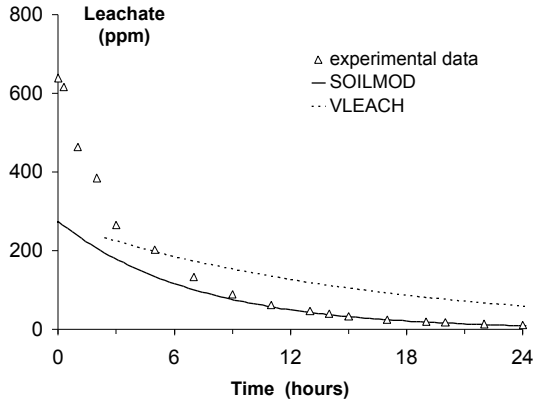
[1]Each experiment was carried out at an air flow rate of 0.16 m/s, temperature of 21C, and relative humidity of 60%. Rainfall rate was 1 cm/d yielding a soil water content of 0.13 to 0.19 v/v (baseline to peak following a rain event). The initial bulk chemical concentration ranged from ~10 to 200 mg/kg for the different VOCs on media.

A comparison of preliminary modeling results to the model predictions for time-weighted concentrations revealed deviations ranging from –51 to 184% relative error (Table 4). When evaluating the reliability of a given model, the possible range of error for its use in a generic model application, in theory, should be predictable based on past model performance (e.g., based on experimental comparisons such as completed in this work) provided the existing database is sufficient to statistically represent the population of possible model errors.

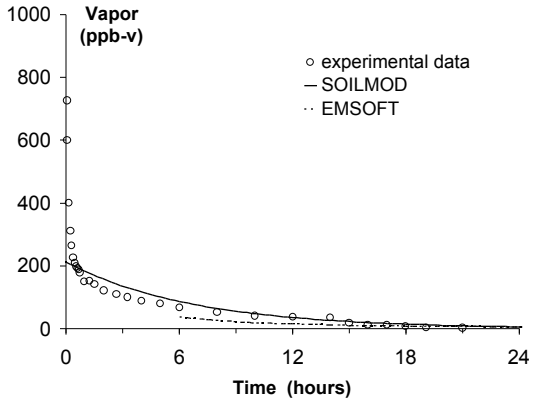
We are using the results from our experiments in conjunction with predictions from multimedia modeling efforts to develop frequency distributions for the deviations in a selected model's predictions compared to the experimentally observed behavior. The number of error observations developed from this research project is believed to be sufficiently large to fit a conditional parametric probability distribution for error in each model. These distributions are used to represent concentration term uncertainty in probabilistic human health risk calculations. Sensitivity analyses are used to compare the sensitivity of risk predictions to uncertainty in the modeled concentration term versus the uncertainty in human exposure factors like body weight and contact rates.



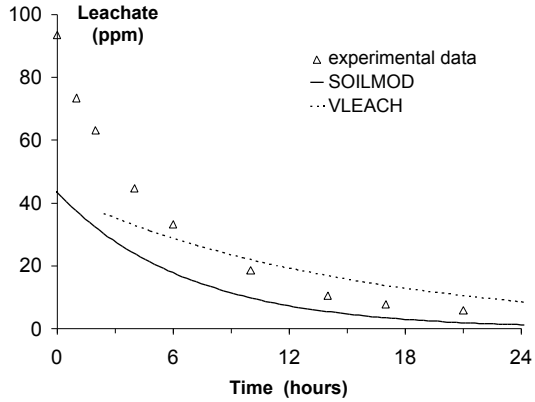
(a) 1,1,1-TCA Volatilization



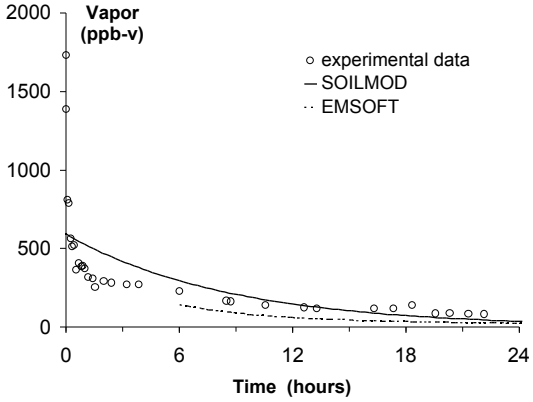
(b) 1,1,1-TCA Leaching



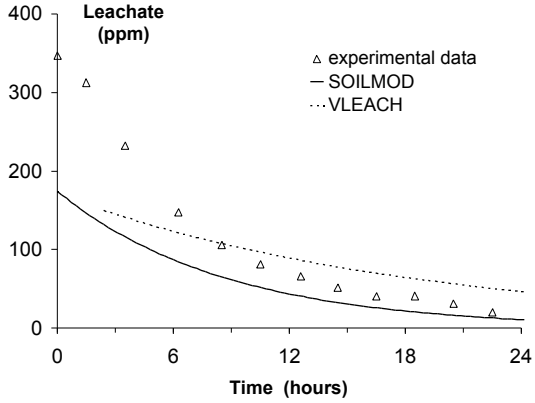
(c) PCE Volatilization



(d) PCE Leaching



(e) Toluene Volatilization



(f) Toluene Leaching

Figure 3. Experimental results for three chemicals during simultaneous volatilization and leaching in a sand matrix as compared to model predictions made using SOILMOD, EMSOFT, and VLEACH (Sheldon 1999).

Table 4. Preliminary experimental results and model predictions for sandy soil (matrix 1).

Model and phase	Chemical	Experimental result (ppb or ppm)	Model prediction (ppb or ppm)	Relative error (%)	Normalized relative error[1]
EMSOFT -- vapor	1,1,1-Trichloroethane	53 ppb-v	74 ppb-v	39	1.39
	Tetrachloroethene	29 ppb-v	17 ppb-v	-40	0.60
	Toluene	125 ppb-v	61 ppb-v	-51	0.49
	trans-1,2-Dichloroethene	330 ppb-v	584 ppb-v	77	1.77
SOILMOD -- vapor	1,1,1-Trichloroethane	170 ppb-v	255 ppb-v	50	1.50
	Tetrachloroethene	57 ppb-v	64 ppb-v	12	1.12
	Toluene	169 ppb-v	176 ppb-v	4	1.04
	trans-1,2-Dichloroethene	662 ppb-v	1062 ppb-v	60	1.60
VLEACH -- water	1,1,1-Trichloroethane	58 ppm	165 ppm	184	2.84
	Tetrachloroethene	20 ppm	28 ppm	36	1.36
	Toluene	85 ppm	112 ppm	32	1.32
	trans-1,2-Dichloroethene	624 ppm	1005 ppm	61	1.61
SOILMOD -- water	1,1,1-Trichloroethane	82 ppm	88 ppm	7	1.07
	Tetrachloroethene	26 ppm	20 ppm	-24	0.76
	Toluene	107 ppm	87 ppm	-19	0.81
	trans-1,2-Dichloroethene	826 ppm	941 ppm	14	1.14

[1] Value = model result/experimental observation.

Uncertainty in concentration term predictions that are made using intermedia or multimedia models is a reflection of the quality of model performance. The statistics of a normalized relative error distribution can be used to represent each model's performance. For example, an expected value for bias in a generic model result is indicated by the distribution median. The expected value for bias calculated for all four evaluated models in this study represents an under-prediction of concentration in the receiving medium (i.e., all 50th percentile normalized relative error values are less than one). Combined variability and bias for a generic model prediction is represented by calculated quantile values. A conservative estimate of possible model under-prediction of the true concentration values can be obtained from the 10th percentile normalized relative error value. For example, the 10th percentile value for the EMSOFT fitted distribution is 0.118. An estimate for a possible actual air concentration correction factor is obtained by the inverse of the normalized relative error value. Thus, for EMSOFT, an upperbound estimate for the possible actual air concentration is 8.47 times the average predicted value (i.e., the correction factor equals 0.118^{-1}). The statistical uncertainty in the correction factor that exists due to the relatively small sample size can be evaluated by calculating upper and lower confidence limits for the quantile of interest. Second-order random variables govern variability and bias in the distribution quantiles. The estimated upperbound possible actual air concentration correction factor corresponding with the second-order uncertainty estimate is 24.5 (i.e., 0.0408^{-1}). Similar calculations can be made for the other models, but EMSOFT represents the worst performer among the models evaluated to date.

Source Term Error and Uncertainty. Error and uncertainty in quantifying the average concentration or total mass of contaminant in the soil region of interest before or after treatment (also known as the "source term") can propagate into human health risk estimates through either transport calculations during intermedia transfer modeling or from exposure calculations for direct soil contact (Siegrist and Van Ee 1994). An experimental study of VOC source term quantification was completed using trichloroethene (TCE) in soil matrix 1 (Siegrist et al. 1999). For this study, the lysimeter was contaminated in the same fashion as during the other volatilization and leaching experiments to yield a known mass of TCE in the soil within the lysimeter. After equilibration but before any volatilization or leaching, nine thin-tube sampling probes were driven into the soil simultaneously and then each was retrieved with the relatively undisturbed soil within it (Figure 3). Using a micro-coring device, duplicate subsamples were taken at each of three depths and a plug of soil was extruded into hexane solvent contained within a Teflon-faced, solid cap glass vial. From each of the soil subsamples in hexane, five subsamples of each hexane extractant were later taken and for each of these, five separate VOC analyses were made (Figure 4).

The source term mass estimated by the discrete samples was biased low and depending on how spatial interpolation was completed, it accounted for only 5 to 15% of that present in the lysimeter. This is consistent with previously reported findings of Jenssen and Siegrist (1990). In addition, when estimating the average TCE concentration in the lysimeter, the variability was high. A nested analysis of variance revealed that the variances associated with sample location-depth and subsamples per location were dominant (>95%) with limited variance contributed by the hexane extraction or the GC analysis components (<5%) (Figure 5). The high bias and spatial variability is believed to be do to rapid vapor and aqueous phase losses that occurred during sample handling of the unsaturated sandy soil (with low TOC) despite the careful practices used.

The results of this study support the use of a mass-balance approach (versus traditional discrete soil sampling and analysis) to quantify the source term for the purposes of the lysimeter volatilization and leaching experiments described above. The results are also insightful regarding the potential magnitude of bias and variability to be encountered during soil sampling and analysis for characterization at VOC sites, even when extremely careful practices are used. Errors in source term characterization can impact risk assessment decision making by increasing the estimated exposure concentration term uncertainty.

Multimedia Reliability Evaluation for Human Health Risk Assessment. Multimedia model reliability for human health risk assessment applications is a function of both the form of the modeling error distribution and the tolerances for modeling error established by decision performance goals. Using decision performance goal diagrams, we are evaluating the effect on probabilistic risk predictions, of concentration term uncertainty due to modeling error. By comparing statistics of a cancer risk probability distribution calculated using uncertain concentration information to the risk distribution calculated for the same scenario using perfect concentration information, we identify threshold tolerances for concentration term uncertainty in human health risk assessments. A model reliability evaluation methodology has been developed and implemented for a previously reported but limited model validation study.

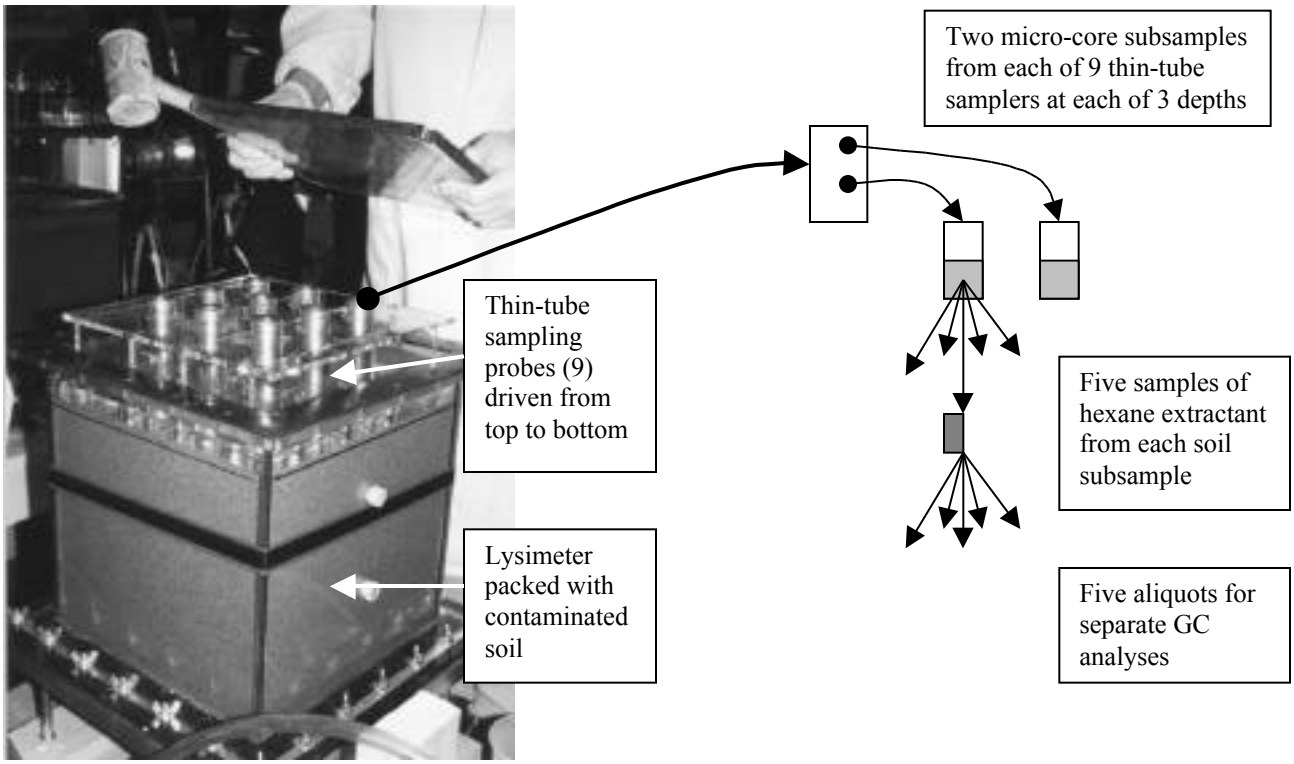


Figure 4. Photograph of a lysimeter during a source term characterization experiment.

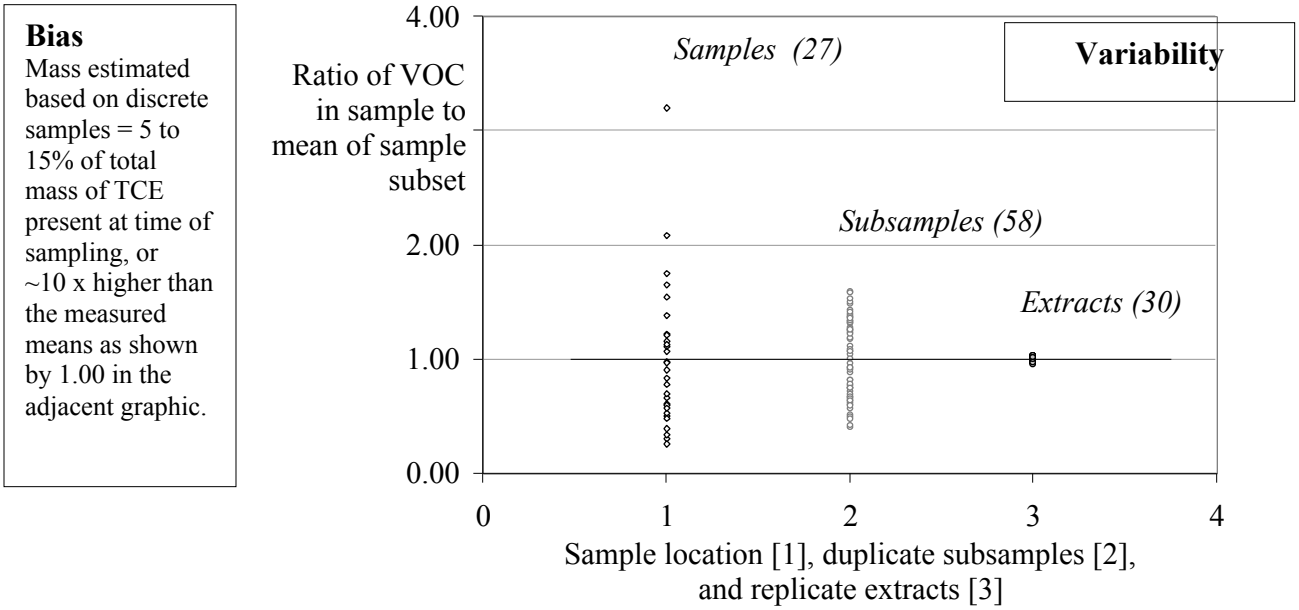


Figure 5. Bias and variability results for source term characterization of TCE in sand.

With the requisite data furnished from the laboratory experimentation, a full model reliability evaluation was completed as described in Sheldon (1999).

Future Studies

Studies are ongoing and planned to explore mass fluxes with other chemicals and soil materials and also before and after in situ treatment by chemical oxidation and other techniques.

Acknowledgements

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