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Project Summary

Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites

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The volatilization of hazardous organics from hazardous waste land treatment systems was evaluated in laboratory and field studies using complex petroleum refining hazardous wastes. Laboratory experiments were conducted using two soils and an inert construction sand to investigate the emission flux rates of seven volatile constituents, i.e., benzene, toluene, ethylbenzene, p-, m-, o-xylene, and naphthalene, from API Separatory Sludge and Slop Oil Emulsion Solids wastes in column and flask laboratory units. Emission flux rates were monitored as a function of waste application rate, application method (surface versus subsurface), soil type and soil physical characteristics. Field experiments were conducted at an active petroleum refinery hazardous waste land treatment site to which a combined API Separator Sludge/DAF bottom sludge was surface applied.

Pure constituent collection and quantification in both laboratory and field studies were carried out using an emission flux chamber and split stream Tenax^{TM} sorbent tube concentration system. Suggested operating procedures in terms of purge flow rates, split stream sampling rates, sample collection volumes for minimal contaminant sorbent tube breakthrough, etc., are presented.

Measured laboratory and field data were compared to the Thibodeaux-Hwang Air Emission Release Rate (AERR) model in an effort to validate this state-of-the-art land treatment emission model. Once specific data are collected which describe the physical environment of the land treatment system, prediction of pure constituent air emissions from surface application and tilling can be provided by the model, within a factor of two to ten, even for complex hazardous wastes applied to complex soil systems.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Land treatment may be defined as the engineered usage of the upper soil zone for the treatment and ultimate disposal of waste materials at a rate and to an extent that the land used for disposal will not be irretrievably removed from beneficial use sometime in the future. The characteristics of waste constituents and their interactions within the land treatment system lead to a classification of loading limitations based on: (1) the loss of waste components due to volatility or leachability as affected by soil and micrometerological site conditions, (2) movement of components from the land treatment area due to their limited degradation, transformation, and/or immobilization, or (3) accumulation of non-assimilable components to levels that limit the future beneficial use of the land treatment area.

The primary emphasis in the monitoring and evaluation of land treatment facilities has been related to rates of degradation of biodegradable waste constituents and to the impact of land disposal activities on surface and groundwater systems. However, the 1984 RCRA Amendments acknowledge the potential for air emissions from hazardous waste Treatment, Storage and Disposal Facilities (TSDFs) in Section 201 and specify that EPA promulgate regulations for the monitoring and control of air emissions at hazardous waste TSDFs within 30 months of the enactment of these amendments.

The full report provides results of a laboratory and field evaluation of a sampling system used for the collection of data describing the magnitude and extent of the volatilization component of hazardous constituent transport at hazardous waste land treatment facilities. Data from laboratory and field scale validation of the Thibodeaux-Hwang AERR model, which describes the volatilization rates of hazardous organic waste constituents from land treatment systems, are also presented.

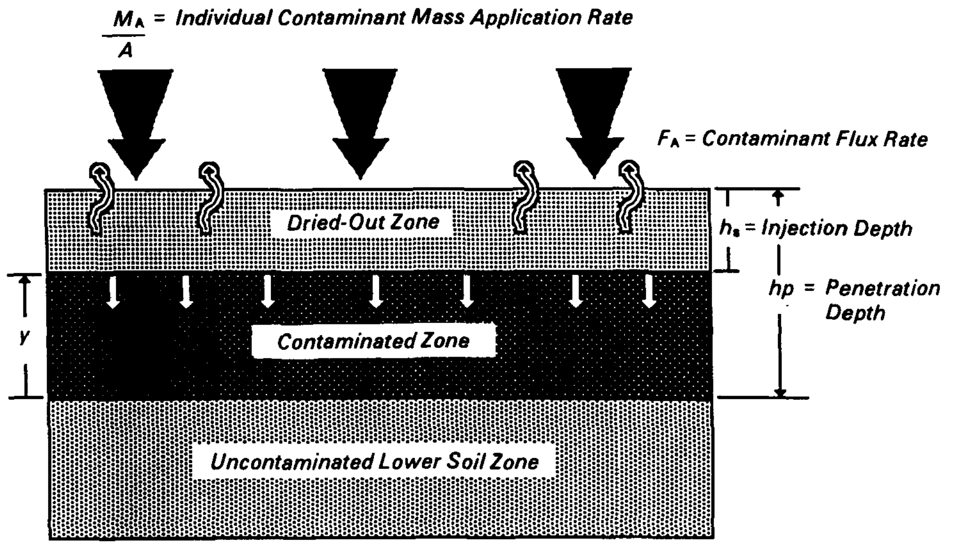

Figure 1. *Theoretical contaminant behavior described by the Thibodeaux-Hwang AEER model. Adapted from Thibodeaux and Hwang (1982).*

Thibodeaux-Hwang AERR Model

Use of a "dried-out" zone to model air emissions from land treatment of petroleum wastes has been carried out by Thibodeaux and Hwang (1982) and represents the state-of-the-art description for the volatilization of organics from land treatment operations. Their model assumes an isothermal soil column, no capillary action through the soil layer, no adsorption in the soil pore space, and no biodegradation of applied organics within the soil column. This description of vapor movement through the soil/waste matrix is applicable to surface or subsurface waste application events through the use of surface injection depth, h_s, and depth of penetration or plow slice depth, h_p (Figure 1). Under steady-state conditions, the time for the initial mass applied to the soil to completely volatilize into the soil pore space, t_e, and the mass flux rate of each component, F_A, are determined through a mass balance of each component assuming Fickian diffusion through the soil column. With an air phase concentration at the air/soil interface equal to 0, the following relationship for evaporation time can be developed:

$$t_e=\frac{M_A\cdot(h_p+h_s)}{2A\cdot D_A\cdot C_A^*} \qquad (1)$$

while mass flux rate is given as:

$$F_A=\frac{D_A\cdot C_A^*}{\left(h_s^2+\frac{2D_A\cdot t\cdot A\cdot(h_p-h_s)\cdot C_A^*}{M_A}\right)^{1/2}} \qquad (2)$$

where: t=time after component application.

The component pore-space concentration, C_A^*, is related to the component concentration within the applied oil by equating the rate of movement through the oil phase to that through the dry soil column. The concentration of the component in the air and oil phases within the soil pore space is related by a modified Henry's Law constant with units of cm^3 oil/cm^3 air. The expression for the concentration of the component in the soil vapor phase in terms of its initial concentration within the oil then becomes:

$$C_A^*=\frac{H_{C'}}{1+H_{C'}\cdot\frac{D_A\cdot Zo}{Do\cdot a_s\cdot y\cdot(h_p-y)}}\cdot C_{io} \qquad (3)$$

Estimating an average value for the lengthening dry zone diffusion path, $y\cdot(h_p-y)$, by the integral of $y\cdot(h_p-y)$ from 0 to h_p-h_s divided by h_p-h_s yields:

$$C_A^*=\frac{H_{C'}}{1+H_{C'}\cdot\frac{6\cdot D_A\cdot Zo}{Do\cdot a_s\cdot(h_p^2+h_p\cdot h_s-2h_s^2)}}\cdot C_{io} \qquad (4$$

If the land treatment unit is tilled a time t less than the volatilization life time of the hazardous constituents o interest, the equations above must b modified for the new geometry whic results. The mass of contaminant los during the period prior to tilling, M_{At}, i determined from the integration o Equation 2 from t=0 to t=time of tilling resulting in Equation 5:

$$M_{At}=\frac{M_A}{(h_p-h_s)}\cdot\left[\left(h_s^2+\frac{2D_A\cdot A\cdot t\cdot(h_p-h_s)\cdot C_A^*}{M_A}\right)^{1/2}-h_s\right] \qquad (5$$

The mass remaining after time t $M_{Ar}=M_A-M_{At}$, is then used in Equations 1 and 2 above to determine th evaporation time and mass flux rate fo the residual mass from the tilled soil assuming uniform mass distributio within a soil column of dimension h_p=tilling depth and h_s=0.

With the use of Equations 1 through 5 the rate of organic emissions from lan treatment sites before and after tillin can be determined once the followin three sets of parameters are measured

1) soil parameters including bulk density, particle diameter and particle density; 2) compound parameters including air and oil molecular diffusivity and modified Henry's Law constant; and 3) operational parameters including surface injection and penetration or plow splice depth, tilling depth, surface area of application, mass application rate, and time. Further details of model development and its application to laboratory and field data are presented in the full report, along with example calculations for theoretical emission rates.

Laboratory Procedures

Sampling System Evaluation

Sampling is a key step in the measurement and detection of contaminants for evaluation and analysis of models used for predicting their fate in the environment. The flux chamber investigated in this study (Figure 2) was a modification of a design developed for the U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, by Radian Corporation (Schmidt and Balfour 1983, Balfour et al. 1983). It consisted of a 68.7 × 68.7 cm square exterior dimension (effective emission surface area=4560 cm^2), clear acrylic double-domed skylight modified for isolation flux sampling as shown in Figure 2. The acrylic double-dome interior was lined with opaque, adhesive Teflon™ tape to provide a non-adsorbing, non-reactive interior surface. Teflon™ was used for all bulk head fittings and purge gas inflow and outflow lines to provide an inert surface in all areas of the chamber. Bulk head openings were provided for influent and effluent lines as well as for temperature and chamber interior pressure measurements.

Solid Sorbent Collection/ Concentration System Evaluation

Solid sorbent evaluation included the analysis of collection and recovery efficiency of pure compounds and their mixtures identified as major volatile components of petroleum refinery wastes using Tenax™ and charcoal sorbent tubes. These compounds included benzene, toluene, ethylbenzene, p-, m-, o-xylene, and naphthalene. Spike recovery analyses provided data for this evaluation. Tenax™ data were collected utilizing U.S. EPA EMSL/RTP standard operating procedures for the spiking of Tenax™ cartridges with a known mass of an organic constituent via the flash evaporation method. Data were collected for compound mass injection levels ranging from 0.09 to 250 μg/sorbent tube. Charcoal sorbent tube recovery data were obtained for the same pure volatile compounds used in the Tenax™ studies according to standard NIOSH methods. The effects of sampling stream moisture content on the collection and recovery efficiency of the charcoal tubes were also investigated. Finally, the combined flux chamber/sorbent tube sampling train was evaluated in terms of sampling train collection and recovery efficiency using mixtures of the pure compounds of interest.

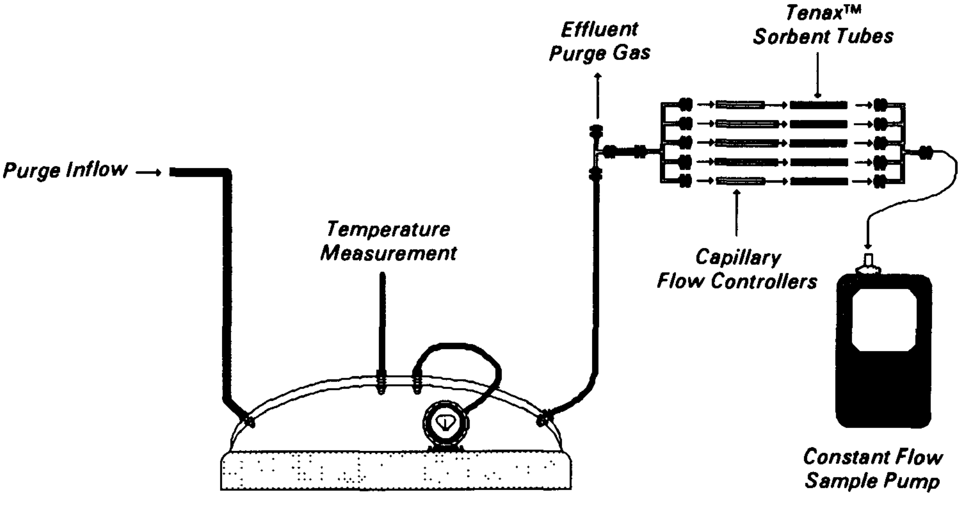

Figure 2. Schematic of Isolation Flux Chamber/solid sorbent tube sampling system.

Due to difficulties in consistently recovering naphthalene from the charcoal tubes at efficiencies greater than 50 percent, only Tenax™ traps were used for breakthrough volume evaluation studies. Injected mass levels of 1.1 to 120 μg were used at collection temperatures of 20-22°C and 32-35°C. A purge flow rate of 200 ml/min, comparable to that used in laboratory and field emission measurements, was used in these experiments for time periods of 5 minutes to 2 hours.

Flux Chamber Pressure and Mixing Studies

The flow regime within the flux chamber is of critical importance as component emission rate calculations are based on the assumption that emission measurements from the chamber effluent are representative of a completely-mixed chamber volume. In addition, adequate flow and turbulence must be provided to assure no component mass accumulation within the chamber that may affect the component's flux from the soil surface into the lower atmosphere. Counter to the desire for maximizing flow and turbulence within the flux chamber is the need for minimizing positive pressure development within the chamber as it may cause emission suppression and possibly flux reversal during emission sampling.

The impact of purge flow rate on chamber pressure build-up was evaluated by monitoring chamber interior pressure (with respect to ambient) as a function of purge flow. Pressure measurements were made over a range of purge flows from 0.7 to 4 liters/min as suggested in Radian protocol (Schmidt and Balfour 1983, Balfour et al. 1983).

Mixing within the flux chamber as a function of purge flow rate was evaluated using standard tracer techniques. The flash vaporization technique was used to vaporize liquid acetone used as a tracer. Flow curves were evaluated to provide a quantitative description of chamber mixing conditions in terms of dimensionless indicator retention time parameters and the Morril dispersion index.

Flux Chamber/Sorbent Tube Collection/Recovery Evaluation

Contaminant collection and recovery efficiency for the combined flux chamber/solid sorbent sampling train was evaluated at 22°C ± 2°C to indicate the effect if any the flux chamber had on observed mass recovery efficiency results for the Tenax™ sorbent collection/concentration tubes. The flux chamber was configured with a four position Tenax™ sorbent split-stream sampling system placed in the effluent purge gas line. Compound recovery data using the flux chamber/sorbent tube sampling train were collected for compound mass injection levels ranging from 0.5 to 90 μg/tube. Chamber purge flow was maintained at 4 liters/minute and sampling continued for three theoretical chamber retention times to ensure representative chamber volume sampling.

Laboratory Model Evaluation Studies

Model evaluation was carried out using modular, beaded glass process pipe microcosm systems (Figure 3), and ground-glass Erhlenmeyer flask screening apparatus (Figure 4) in conjunction with Tenax™ sorbent sampling/concentration systems. Measured versus predicted pure compound emission rates using two listed hazardous wastes from the petroleum refining industry, an API Separator Sludge and Slop Oil Emulsion Solids, were compared under a range of soil, waste loading, and waste application conditions. Constituent analyses were conducted on methanol extracts of samples of the waste used in each laboratory experiment. The extract procedure used was a modification of Method 5030 "Purge-and-Trap Method," with analysis via purge and trap/GC-FID detection. The pure compounds of interest were quantified in the complex wastes via standard spike recovery analysis procedures.

A range of soil types were evaluated in the study to identify soil characteristics found to significantly affect constituent volatilization. Soil parameters evaluated included media texture, media particle size distribution, particle density, and bulk density. Soil chemical parameters evaluated included soil organic carbon and specific organic constituents by methanol extraction/purge and trap analysis using a modified Method 5030 procedure.

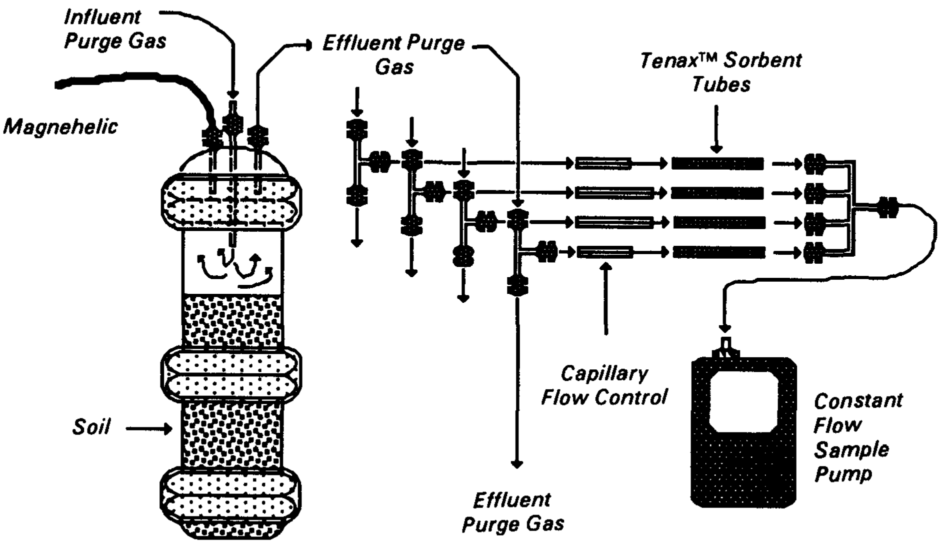

Figure 3. Laboratory microcosm apparatus used in laboratory AERR model validation studies.

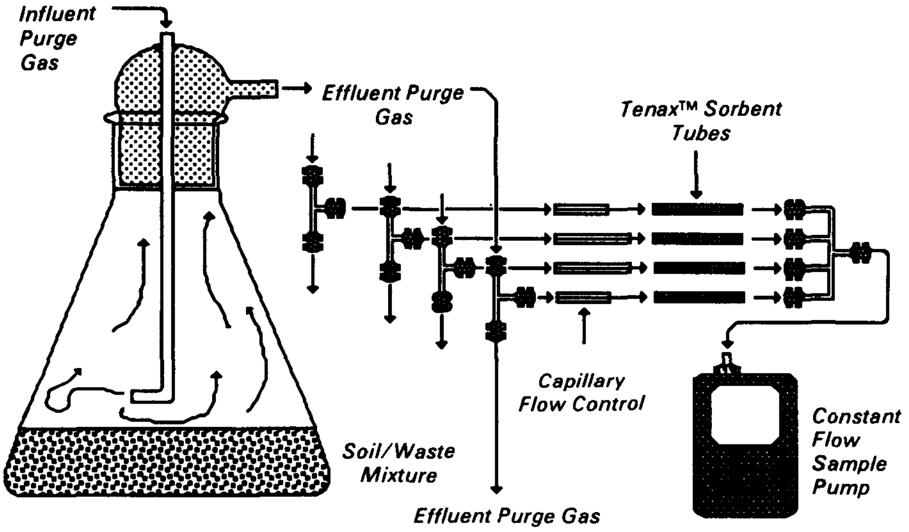

Figure 4. Screening flask apparatus used in laboratory AERR model validation studies.

Microcosm Experiments

The application rates used in these studies were based on a weight percent of waste applied with respect to the top 15.24 cm (6 inches) of soil in the microcosms. If subsurface injection was simulated, the appropriate amount of soil was added to the unit immediately following waste application to provide the desired soil depth above the point of application. Purge gas was maintained constant at 300 to 500 ml/min/microcosm during the volatilization experiments. The sorbent traps were sampled at a rate of 50 to 200 ml/min/trap for a period not exceeding five minutes to minimize breakthrough of the benzene. Breakthrough traps were used in the first five sampling events to allow the quantification of any breakthrough which occurred. The sampling and analysis procedures were repeated at selected time intervals following waste addition corresponding to the predicted log decay in emission rates of volatile organics from the soil systems. Blank and spike traps were used throughout the sampling period to maintain QA/QC standards during these studies.

Initial soil data collected for each microcosm included the soil depth above the application point, h_s, and total depth and weight of soil in the microcosms. Data relating to the physical conditions of the microcosm systems were collected at each sampling time and included air and soil temperature, height of the capillary rise observed above the injection point, and depth of the waste wetting front below the soil surface, h_p. Measurements of h_p and h_s were determined in laboratory experiments by visual identification of the wetting fronts.

Screening Flask Experiments

The application rates used in these studies were based on a weight percent of waste applied with respect to 200 g of the field soil placed within each test unit. Sampling and analyses procedures were repeated at selected time intervals following waste addition in a manner identical to those of the microcosm units.

Field Procedures

The ultimate objective of this research project was to provide field evaluation of the Thibodeaux-Hwang AERR model for the prediction of volatile organic emissions from land treatment facilities. Field studies involved the use of the emission isolation flux chamber for the collection and concentration of volatile organics emitted from a land treatment facility during typical land treatment activities.

Waste/Soil Characterization Methods

Waste samples at flux chamber locations were collected in 15.24 cm (6 inch) × 68.6 cm (27 inch) × 10.2 cm (4 inch) sheet metal pans placed on either side of the flux chamber sampling locations, perpendicular to the long axis of the land treatment application area. These sample collection pans were used for mass application rate measurements, and for sample collection for physical/chemical property and specific constituent concentration measurements. The collection pans were immediately analyzed on-site gravimetrically for application rate determinations using a top loading balance. The two pans at each sampling site were composited and aliquot waste samples were subsequently collected for density, viscosity and specific constituent measurements.

Composite soil samples for particle size distribution, particle density, oil and grease, and specific constituent analyses were manually collected with a trowel from the surface to a 15 cm depth. The magnitude of h_p prior to tilling was determined by visual identification of the bottom of the wetting front during collection of the composite soil samples. The plow splice depth, h_p, following tilling was estimated by visual observation of subsurface soil conditions at each sampler location following each tilling event.

Waste Application/Tilling Methods

The test plot used in field experiments was approximately 6 m by 182 m in area and was divided lengthwise in half. Waste application was carried out via gravity feed from a tank truck equipped with a slotted application pipe approximately 3 m in length and 8 cm in diameter. Each side of the application area received a full truck load of waste corresponding to approximately 880 gallons. Tilling of one half of the application plot at a time was carried out using a rototiller. Initial tilling was conducted approximately 24 hours after waste application. The test plot was retilled approximately 155 hours after waste application due to rainfall that had occurred following the first tilling event. Tiller depth was variable, ranging from approximately 17 to 23 cm.

Flux Chamber Field Sampling Procedures

Sampling was conducted at the field plot using six sampling flux chambers. Four distinct sampling phases were conducted: 1) background sampling of the test site prior to tillage (BBT), 2) background sampling of the test site following tillage and prior to waste application (BAT), 3) specific constituent emission sampling following waste addition (WBT), and 4) specific constituent emission sampling following two tilling operations (WAT, WST).

Sampling chambers were systematically placed to provide a representative estimate of emissions from the entire application site both during background and specific constituent emission sampling. A systematic random sampling of the application area, entailing a plot grid and a random numbers table, was used to select sampling locations. Once placed at a sampling location, sampling was conducted at that same location during background and specific constituent sampling to preserve spatial continuity of the collected data. Sample collection frequency was based on a logarithmic time scale in anticipation of results following the trends predicted by the Thibodeaux-Hwang AERR model.

Thermocouple temperature probes were used for 0.6 cm (1/4 inch) and 5 cm (2 inch) soil depth and chamber air temperature measurements. Temperature readings were also collected for soil and ambient temperatures prior to chamber placement in the land application area. The chambers were forced into the soil such that the bottom of the Teflon™ lined acrylic dome rested on, and the aluminum dome rim made a tight seal with the soil surface. A pressurized high-purity breathing air purge gas was passed through the flux chambers via a constant volume sampling pump operated at rates of 2 to 6 liters/minute for three retention volumes (≈15 minutes) prior to sample collection with the sorbent traps. Purge gas flow adjustment was made via a micro-valve flow controller.

Large temperature differentials were observed between the flux chamber interior air space and ambient air temperature that reached a maximum of 49.5°C during initial background sampling and 33.7°C during sampling following waste application. Flux chamber shading was utilized in all WAT and WST sampling events in order to evaluate the effect shading had on chamber air and soil temperatures and compound emission flux rates. Flux chamber shading was accomplished utilizing wooden 2 × 2's supporting a sheet of plywood angled to shade the entire flux chamber.

Field blank and spike traps were used in conjunction with breakthrough traps to provide quality control information for the field sampling. The blanks were collected by exposing them to ambient conditions for approximately 15 seconds, the approximate time required for sorbent tube placement in the sampling manifolds. Additionally, soil and waste samples were split with the U.S. EPA Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, Oklahoma, for oil and grease, and specific constituent quantification using identical sample processing and analytical procedures for comparison purposes to ensure quality control for these measurement methods. All other measurements were conducted in at least duplicate to provide statistical information regarding measurement precision for comparison with original QA/QC goals established for the study.

Parameter Calculation/ Estimation Methods

A limited theoretical base exists for the determination of many of the soil/

Table 1. Specific Organic Constituents of Hazardous Wastes Used in the Study

	Mass (µg/g Waste)			
Compound	Mean	St. Dev.	C.V. (%)	n
SLOP OIL				
Benzene	5421	2403	44	16
Toluene	7696	1953	25	18
Ethylbenzene	1639	657	40	18
p-Xylene	3399	928	27	18
m-Xylene	8500	1910	22	18
o-Xylene	3365	1108	33	18
Naphthalene	1621	687	42	16
SEPARATOR SLUDGE				
Benzene	2350	648	28	6
Toluene	2487	899	36	8
Ethylbenzene	605	212	35	9
p-Xylene	1686	467	28	8
m-Xylene	3641	607	17	8
o-Xylene	2194	654	30	9
Naphthalene	2306	692	30	9
FIELD WASTE				
UTAH WATER RESEARCH LABORATORY (UWRL) Analyses (GC)				
Benzene	249.2	29.7	12.0	10
Toluene	631.7	50.0	8.0	10
Ethylbenzene	22.0	1.2	6.0	10
p-Xylene	33.2	4.6	14.0	10
m-Xylene	181.2	14.9	8.0	10
o-Xylene	56.0	3.0	5.0	10
Naphthalene	124.6	8.8	7.0	10
RSKERL Analyses (GC/MS)				
Benzene	278			
Toluene	687			
Ethylbenzene	36			
p-Xylene & m-Xylene	238			
o-Xylene	81			
Naphthalene	108			

waste/compound parameters critical to emission estimation using the Thibodeaux-Hwang AERR model. Consequently, correlation equations were used, when appropriate, for the estimation of parameters that could not be easily or accurately determined experimentally.

Compound effective soil air diffusion coefficients, D$_A$, were estimated utilizing the method presented by Farmer et al. (1973). The effective Henry's Law constant, H$_C$', was determined from solubility, solvent:octanol, solvent:water, and solubility characteristics of the individual compounds of interest using correlation equations from Lyman et al. (1982). The complex waste was modeled as a hexane solvent system as hexane was shown to be a prominent component of the waste from GC/MS analyses. Compound oil diffusion coefficients were estimated using a modification of the Wilke-Chang equation, and temperature corrections for waste viscosity, compound vapor pressure and oil and air diffusion coefficients were made using standard procedures (Lyman et al. 1982).

Results and Discussion

Waste Analyses

Pure constituent waste concentrations are indicated in Table 1 for complex hazardous wastes used in both laboratory and field studies. Data indicate that the laboratory wastes were significantly higher in pure volatile constituents than the waste collected in the field study. This result emphasizes the necessity for accurate waste characterization due to the significant effect waste generation and handling practices have on final waste composition. Results from analysis of the field waste indicate that two independent laboratories can duplicate volatile constituent waste analyses if strict QA/QC procedures are used.

Tenax™ Evaluation

Laboratory Tenax™ and Tenax™/chamber recovery efficiency values ranged from 61 to 94 percent, while field spike results indicated recovery values from 57 to 137 percent for the seven pure compounds of interest. Due to the wide variation in field results, no statistically significant difference existed between these results.

Tenax™ breakthrough results are presented in Table 2. These results indicate the major effect collected mass and temperature have on compound breakthrough and suggest that breakthrough data provided by EPA protocol for use of Tenax™ sorbent tubes for ambient monitoring are not appropriate for the high mass levels expected from land treatment emissions.

Flux Chamber Evaluation

Interior chamber pressure development was found to be greater than 0.25 cm (0.1 inch) of water at a purge flow of 1 liter/min for the chamber design used in this study. Mixing results suggested, however, that even at purge flow rates below 1 liter/min, the chamber air approached theoretical complete-mixed conditions. Operation of the isolation chamber sampling system is possible at low purge flow rates without a downstream purge pump or at high purge flow rates with a downstream purge pump to overcome pressure increases inside the chamber.

Laboratory Model Evaluation

Both upper and lower contaminated zone boundary movement was observed in laboratory studies, and was shown to follow a linear relationship of depth versus log(time). An effort was made to accommodate these variable boundary conditions by using mean values of h$_p$ and h$_s$ over discrete time increments of 0 to 1, 1 to 10 and 10 to 100 hours.

Data observed in laboratory surface application experiments followed the linear relationship of flux versus 1/time$^{1/2}$ as indicated in the Thibodeaux-Hwang AERR model (Figure 5), however subsurface application results generally

Table 2. *Tenax Sorbent Tube Breakthrough Volumes as a Function of Temperature and Mass Injection Level*

Mass Level	Benzene	Toluene	Ethylbenzene	p-Xylene	m-Xylene	o-Xylene	Naphthalene
19-23°C Tenax Breakthrough Volumes (l) for a Given Percent Recovery on First Trap of Two Trap Series							
120.0 μg							
90% Recovery	0.20	5.08	25.01	32.55	25.84	21.03	*
50% Recovery	3.15	14.68	110.6	150.0	115.1	91.78	*
50.0 μg							
90% Recovery	1.87	*	*	*	*	*	*
50% Recovery	4.90	*	*	*	*	*	*
Mass Range:	8.5-15.0 μg	10-15.3 μg	9.7 μg	13.4 μg	29.8 μg	11.2 μg	18.0 μg
90% Recovery	3.02	25.41	*	*	*	*	*
50% Recovery	7.79	49.52	*	*	*	*	*
Mass Range:	1.8-2.0 μg	2.2 μg	1.1 μg	1.8 μg	4.2 μg	1.9 μg	2.4 μg
90% Recovery	5.27	*	*	*	*	*	*
50% Recovery	28.10	*	*	*	*	*	*
28-32°C Tenax Breakthrough Volumes (l) for a Given Percent Recovery on First Trap of Two Trap Series							
20.0 μg							
90% Recovery	0.28	0.20	11.31	12.08	10.97	12.77	*
50% Recovery	0.60	2.50	22.22	22.48	24.09	25.44	*
50.0 μg							
90% Recovery	0.71	0.22	14.28	14.87	15.24	14.90	*
50% Recovery	1.79	5.96	24.88	25.43	27.05	28.54	*
15.0 μg							
90% Recovery	1.21	17.35	*	*	*	*	*
50% Recovery	3.54	33.20	*	*	*	*	*
1.1-4.2 μg							
90% Recovery	4.50	19.22	*	*	*	*	*
50% Recovery	13.67	40.35	*	*	*	*	*

*=>>24 liters

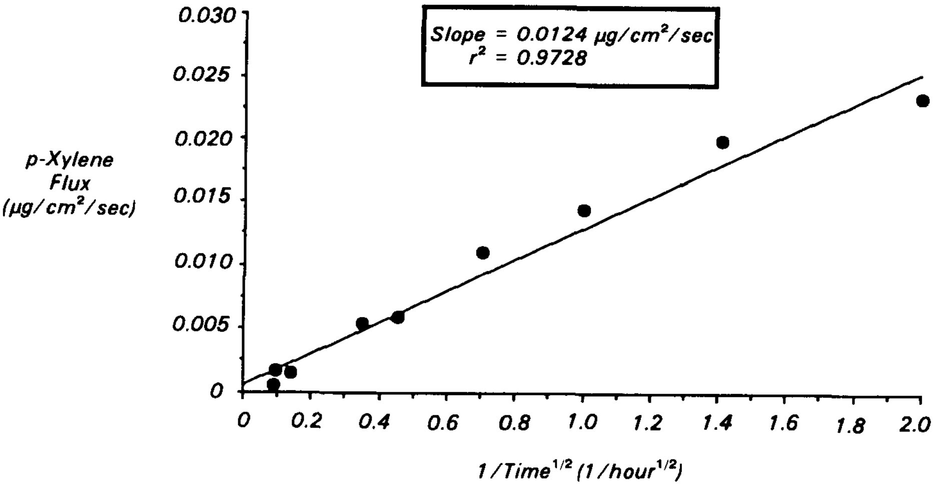

Figure 5. Slop oil surface application to Durant clay loam, Run #8, Position #5.

did not (Figure 6). The increase then decrease in emission rates in the subsurface experiments, as indicated in Figure 6, could be attributed to the variable upper boundary condition with time, along with unsteady-state diffusion during the development of an upper uncontaminated soil zone compound concentration gradient following waste application. Subsurface application resulted in from one to four orders of magnitude reduction in compound flux rates as compared to surface application experiments, and soil versus sand data suggested some reduction in compound emissions due to adsorption to soil organic matter.

Compound flux data for the emission flasks and the surface application microcosm experiments correlated well for most waste/soil mixtures evaluated. The screening flask method appears to hold promise as a simple method for the determination of waste/soil volatilization potential.

Field Model Evaluation

Results of field blank, spike and replicate data suggest the need for strict QA/QC procedures to ensure adequately prepared, stored and analyzed sorbent tubes. Oil and grease data for field samples analyzed by both the Utah Water Research Laboratory (UWRL) and the RSKERL showed a variability of less than 20 percent between samples, indicating the validity of these analyses methods.

Field emission rate data were found to support the validity of the diffusion assumption for describing soil volatilization from land treatment systems, as most measured data followed the linear flux versus 1/time$^{1/2}$ relationship with r^2 values greater than 0.7. Measured versus theoretical compound emission flux rates compared quite well for WBT sampling events once spatial and temporal corrections for waste application rate, soil characteristics (bulk density, porosity, moisture content, plow splice depth), and soil temperature conditions at the 5 cm (2 inch) soil depth were made. Measured flux values were within a factor of two to ten of Thibodeaux-Hwang model predictions for most data during WBT sampling, while measured data diverged to one to two orders of magnitude from predicted rates some 70 to 170 hours following waste application in the WAT and WST sampling events. This increased divergence from predicted values with time indicates the possibility of compound

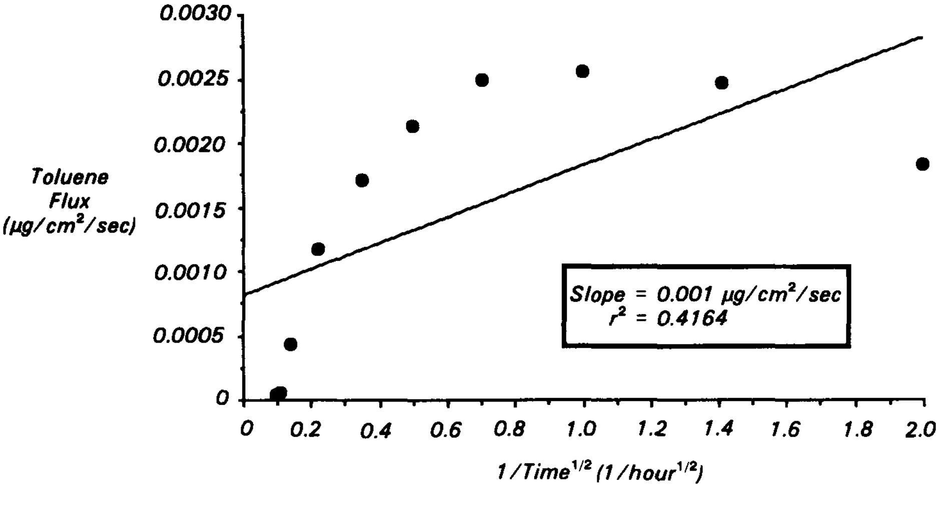

Figure 6. *Separator sludge subsurface application to 30 mesh sand, Run #4, Position #5.*

biodegradation/adsorption within the soil column that is not accounted for in the Thibodeaux-Hwang AERR model.

Conclusions and Recommendations

Experience utilizing the isolation flux chamber/split stream sampling system with Tenax™ solid sorbent collection/concentration tubes in flask, microcosm and field studies for the RCRA volatile organic profile observed in three petroleum refining wastes suggests the system is simple and straightforward and can provide continuity in sampling protocol over a wide range of sampling activities with little modification between source configurations. From analysis of the chamber/Tenax™ sorbent collection system it can be concluded that:

1. Mean recoveries from the chamber/Tenax™ sorbent collection system for the seven aromatic compounds of interest in this study can be expected to range from 61 to 94 percent.
2. Tenax™ breakthrough volumes are a strong function of collected mass as well as temperature. Ambient air protocol breakthrough volumes are not appropriate for source emission sampling from land treatment facilities.
3. Sampling systems must be operated at purge flow rates less than 1 liter/min or in conjunction with a downstream purge pump to minimize chamber internal pressures and potential soil emission suppression.

Both laboratory and field model validation studies indicated the general validity of the Thibodeaux-Hwang AERR model for describing volatile emissions from land treatment facilities. The following conclusions can be made based on model verification results:

1. Owing to the unsteady-state nature of contaminant emissions in the subsurface application experiments caused by variable boundary conditions and soil vapor phase concentration gradient development following waste application, the Thibodeaux-Hwang AERR model cannot be used to accurately predict flux rates during this initial unsteady-state period.
2. The temporal variation in both h_p and h_s are of such a magnitude that this variation should be included in future Thibodeaux-Hwang AERR model refinements.
3. Surface versus subsurface application experiments indicated a one to four order of magnitude decrease in flux rates when wastes are subsurface applied. This reduction is more significant for soils than sand indicating the importance of soil organic matter to soil vapor emission attenuation.
4. Site specific information for waste application rates, and site and time specific data for soil physical and temperature characteristics are required to provide accurate correlation between measured and predicted compound emission flux rates.
5. The validity of the modeling approach in field studies, especially immediately following waste application events indicates that a simple diffusion based modeling approach, as used in the Thibodeaux-Hwang AERR model, is valid for describing hazardous organic air emission rates from complex hazardous waste land treatment systems

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The complete report, entitled "Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites," (Order No. PB 86-233 939/AS; Cost: $16.95, subject to change) will be available only from:

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