APPENDIX C

Limited Validation of the Jury Infinite Source and Jury Finite Source Models (EQ, 1995)

LIMITED VALIDATION OF THE JURY INFINITE SOURCE AND JURY REDUCED SOLUTION FINITE SOURCE MODELS FOR EMISSIONS OF SOIL-INCORPORATED VOLATILE ORGANIC COMPOUNDS

by

Environmental Quality Management, Inc.
Cedar Terrace Office Park, Suite 250
3325 Chapel Hill Boulevard
Durham, North Carolina 27707

Contract No. 68-D30035
Work Assignment No. 1-55
Subcontract No. 95.5
PN 5099-4

Janine Dinan, Work Assignment Manager

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF SOLID WASTE AND EMERGENCY RESPONSE
WASHINGTON, D.C. 20460

July 1995

DISCLAIMER

This project has been performed under contract to E.H. Pechan & Associates, Inc. It was funded with Federal funds from the U.S. Environmental Protection Agency under Contract No. 68-D30035. The content of this publication does not necessarily reflect the views or policies of the U.S. Environmental Protection Agency nor does mention of trade names, commercial products, or organizations imply endorsement by the U.S. Government.

CONTENTS

APPENDICES

FIGURES

TABLES

ACKNOWLEDGMENT

This report was prepared for the U.S. Environmental Protection Agency by Environmental Quality Management, Inc. of Durham, North Carolina under contract to E.H. Pechan & Associates, Inc. Ms. Annette Najjar with E.H. Pechan & Associates, Inc. served as the project technical monitor and Craig Mann with Environmental Quality Management, Inc. managed the project and was author of the report. Janine Dinan of the U.S. Environmental Protection Agency's Toxics Integration Branch provided overall project direction and served as the Work Assignment Manager.

SECTION 1

INTRODUCTION

In December 1995, the U.S. Environmental Protection Agency (EPA) Office of Solid Waste and Emergency Response published the Draft Technical Background Document (TBD) for Soil Screening Guidance (U.S. EPA, 1994). This document provides the technical background behind the development of the Soil Screening Guidance for Superfund, and defines the Soil Screening Framework. The framework consists of a suite of methodologies for developing Soil Screening Levels (SSLs) for 107 chemicals commonly found at Superfund sites. An SSL is defined as "a chemical concentration in soil below which there is no concern under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) for ingestion, inhalation, and migration to ground water exposure pathways...." (U.S. EPA, 1994).

The SSL inhalation pathway considers exposure to vapor-phase contaminants emitted from soils. Inhalation pathway SSLs are calculated using air pathway fate and transport models. Currently, the models and assumptions used to calculate SSLs for inhalation of volatiles are updates of risk assessment methods presented in the Risk Assessment Guidance for Superfund (RAGS) Part B (U.S. EPA, 1991). The RAGS Part B methodology employs a reverse calculation of the concentration in soil of a given contaminant that would result in an acceptable risk-level in ambient air at the point of maximum long-term air concentration.

Integral to the calculation of the inhalation pathway SSLs for volatiles, is the soil-to-air volatilization factor (VF) which defines the relationship between the concentration of contaminants in soil and the volatilized contaminants in air. The VF (m^3/kg) is calculated as the inverse of the ambient air concentration at the center of a ground-level, nonbouyant area source of volatile emissions from soil. The equation for calculating the VF consists of two parts: 1) a volatilization model, and 2) an air dispersion model.

The volatilization model mathematically predicts volatilization of contaminants fully incorporated in soils as a diffusion-controlled process. The basic assumption in the mathematical treatment of the movement of volatile contaminants in soils under a concentration gradient is the applicability of the diffusion laws. The changes in contaminant concentration within the soil as well as the loss of contaminant at the soil surface by volatilization can then be predicted by solving the diffusion equation for different boundary conditions.

As noted in the TBD, Environmental Quality Management, Inc. (EQ) under a subcontract to E. H. Pechan conducted a preliminary evaluation of several soil volatilization models for the U.S. EPA Office of Emergency and Remedial Response (OERR) that might be suitable for addressing both infinite and finite sources of emissions (EQ, 1994). The results of this study indicated that simplified analytical solutions are presented in Jury et al. (1984 and 1990) for both infinite and finite emission sources. These analytical solutions are mathematically consistent and use a common theoretical approximation of the effective diffusion coefficient in soil. Under a subcontract with E. H. Pechan for OERR, EQ performed a limited validation of the Jury Infinite Source emission model (Jury et al., 1984, Equation 8) and the Jury Reduced Solution finite source emission model (Jury et al., 1990, Equation B1), hereinafter known as the Jury volatilization models.

This document reports on several studies in which volatilization of contaminants from soils was directly measured and data were obtained necessary to calculate emissions of contaminants using the Jury Infinite Source model and the Jury Reduced Solution finite source model. These data are then compared and analyzed by statistical methods to determine the relative accuracy of each model.

1.1 PROJECT OBJECTIVES

The primary objective of this project was to assess the relative accuracy of the Jury volatilization models using experimental emission flux data from previous studies as a reference data base.

1.2 TECHNICAL APPROACH

The following series of tasks comprised the technical approach for achieving the project objectives:

1. Review the theoretical basis and development of the Jury volatilization models to verify the applicable model boundary conditions and variables, and to document model assumptions and limitations.

2. Perform a literature search and survey (not to exceed nine contacts) for the purpose of determining the availability of acceptable emission flux data from experimental and field-scale measurement studies of volatile organic compound (VOC) emissions from soils. Acceptable data must have undergone proper quality assurance/quality control (QA/QC) procedures.

3. Determine if the emission flux measurement studies referred to in Task No. 2 also provided sufficient site data as input variables to the volatilization models. Again, acceptable variable input data must have undergone proper QA/QC procedures.

4. Review, collate, and normalize emission flux measurement data and volatilization model variable data, and compute chemical-specific emission rates for comparison to respective measured emission rates.

5. Perform statistical analysis of the results of Task No. 4 to establish the extent of correlation between measured and modeled values and perform parametric analysis of key model variables.

SECTION 2

REVIEW OF THE JURY VOLATILIZATION MODELS

The Jury Reduced Solution finite source volatilization model calculates the instantaneous emission flux from soil at time, t, as:

$$J_s = C_o\, e^{-m}\, (D_E/p\ t)^{1/2}\, \left[1\ -\exp(-L^2/4\, D_E\ t)\right] \tag{1}$$

where J_s = Instantaneous emission flux, μg/cm^2 -day

C_o = Initial soil concentration (total volume), μg/cm^3-soil

μ = Degradation rate constant, 1 /day

t = Time, days

D_E = Effective diffusion coefficient, cm^2 /day

L = Depth from the soil surface to the bottom of contamination, cm

and,

$$DE\ =\ \left[(a^{10/3}\ D_g^a\ K_H\ +\ Q1^{10/3}\ D_i^w)/f^{\,2}\right]/(\rho_b\ f_{oc}\ K_{oc}\ +\ Q\ +\ a\,K_H) \tag{2}$$

where D_E = Effective diffusion coefficient, cm^2 /day

a = Soil volumetric air content, cm^3/cm^3

$D_g{}^a$ = Gaseous diffusion coefficient in air, cm^2/day

K_H = Henry's law constant, unitless

Θ = Soil volumetric water content, cm^3/cm^3

D_i^w = Liquid diffusion coefficient in pure water, cm^2/day

ϕ = Total soil porosity, unitless

ρ_b = Soil dry bulk density, g/cm^3

f_{oc} = Soil organic carbon fraction

K_{oc} = Organic carbon partition coefficient, cm^3/g.

The model assumes no boundary layer at the soil-air interface, no water flux through the soil, and an isotropic soil column contaminated uniformly to some depth L. The initial and boundary conditions for which Equation 1 is solved are:

$$c\ =\ C_0 \text{ at } t = 0,\ 0\ \le\ x\ \le\ L$$

$$c\ =\ 0 \text{ at } t = 0,\ x\ \succ\ L$$

$$c = 0 \text{ at } t \succ 0,\ x = 0$$

where c and C_o are, respectively, the soil concentration and initial soil concentration (g/cm^3-total volume), x is the distance measured normal to the soil surface (cm), and t is the time (days).

The average flux over time (J_s^{avg}) is computed by integrating the time-dependent flux over the exposure interval.

The Jury Infinite Source volatilization model calculates the instantaneous emission flux from soil at time, t, as:

$$J_s = C_0 \, (D_E / \pi t)^{1/2} \tag{3}$$

where J_s = Instantaneous emission flux, μg/cm^2-day

C_o = Initial soil concentration (total volume), μg/cm^3-soil

t = Time, days

D_E = Effective diffusion coefficient, cm^2/day (Equation 2).

The model assumes no boundary layer at the soil-air interface, no water flux through the soil, and an isotropic soil column contaminated uniformly to an infinite depth. The boundary conditions for which Equation 3 is solved are:

$$c = C_0 \text{ at } t \geq 0,\ x = \infty$$

$$c = O \text{ at } t > 0,\ x = 0$$

The average flux over time (J_s^{avg}) is calculated as:

$$J_s^{avg} = C_0 \, (4 \, D_E \, / \pi t)^{\ 1/2} \tag{4}$$

2.1 FINITE SOURCE MODEL DERIVATION

The Jury Reduced Solution finite source model is derived from the methods presented by Mayer et al. (1974), and Carslaw and Jaeger (1959). Mayer et al. (1974) considered a system where pesticide is uniformly mixed with a layer of soil and volatilization occurs at the soil surface. If diffusion is the only mechanism supplying pesticide to the surface of an isotropic soil column, and if the diffusion coefficient, D_E, is assumed to be constant, the general diffusion equation is:

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D_E} \frac{\partial c}{\partial t} = O \tag{5}$$

where c = Soil concentration, g/cm^3 - total volume

x = Distance measured normal to soil surface, cm

D_E = Effective diffusion coefficient in soil, cm^2/d

t = Time, days.

If the pesticide is rapidly removed by volatilization from the soil surface and is maintained at a zero concentration, the initial and boundary conditions which also allow for diffusion across the lower boundary at x = L are identical to those of Equation 1.

Recognizing the analogy between the heat transfer equation (Fourier's Law) and the transfer of matter under a concentration gradient (Fick's Law), Mayer et al. (1974) employed the heat transfer equation of Carslaw and Jaeger (1959, page 62, Equation 14) to solve the diffusion equation given these initial and boundary conditions as:

$$C = C_o/2)\{2 \operatorname{erf}\left[x/2(D_E t)^{1/2}\right] - \operatorname{erf}\left[(x-L)/2(D_E t)^{1/2}\right] - \operatorname{erf}\left[(x+L)/2(D_E t)^{1/2}\right]\} \quad (6)$$

The flux is obtained by differentiating Equation 6 with respect to x, determining $\partial c/\partial x$ at x = O. and multiplying by D_E. The result is:

$$J_s = D_E \left[\partial c/\partial x\right]_{x=o} = \left[D_E\, C_o/(\pi D_E t)^{1/2}\right]\left[1 - \exp(-L^2/4\, D_E t)\right] \quad (7)$$

Note that Equation 7 is equivalent to the Jury Reduced Solution given in Equation 1 with the exception of the first-order degradation expression $(e^{-\mu t})$.

Jury et al. (1983 and 1990) expanded upon the work of Carslaw and Jaeger (1959) and Mayer et al. (1974) by developing an analytical solution for Equation 5 which includes water flux through the soil column and a soil-air boundary layer. In addition, the Jury et al. solution also includes a theoretical approximation of the effective diffusion coefficient (Equation 2) which was not included in Mayer et al. (1974). Given these conditions, the flux equation from Jury et aI (1983) is given as:

$$J_s = -D_E\,(\partial c_T/\partial x) + V_E\, C_T \quad (8)$$

where C_T = Soil total concentration

x = Depth normal to soil surface

V_E = Effective solute convection velocity.

The minus sign is used because the x direction is positive downward.

Given the initial and boundary conditions:

$c = C_o$ at $t=0,\ 0 \leq x \leq L$

$c = O$ at $t=0,\ x > L$

$c = O$ at $t>0,\ x = 0$

$J_s = -hC_G$ at $t>0,\ x = 0$

where h = Transport coefficient across the soil-air boundary layer of thickness d ($h = D_g^a/d$)

C_G = Vapor-phase concentration ($C_G = K_H\, C_l$), The Jury et al. (1983) analytical solution for the volatilization flux is:

$$J_s(t,L) = + \frac{1}{2} C_o V_E \left[\mathrm{erfc} \left(\frac{V_E t}{2(D_E t)^{1/2}} \right) - \mathrm{erfc} \left(\frac{L + V_E t}{2(D_E t)^{1/2}} \right) \right]$$

$$+ \frac{1}{2} C_o (2H_E + V_E) \exp \left(\frac{H_E (H_E + V_E) t}{D_E} \right) \tag{9}$$

$$x \left[\exp \left(\frac{H_E L}{D_E} \right) \mathrm{erfc} \left(\frac{L + (2H_E + V_E) t}{2(D_E t)^{1/2}} \right) - \mathrm{erfc} \left(\frac{(2H_E + V_E) t}{2(D_E t)^{1/2}} \right) \right]$$

where H_E Is the transport coefficient across the boundary layer divided by the gasphase partition coefficient, $H_E = h/(\rho_b f_{oc} K_{oc}/K_H + \Theta/K_H + a)$.

Jury et al. (1990) explains that compounds with large values of K_H are insensitive to the thickness of the soil-air boundary layer (i.e., as $H_E \rightarrow \infty$). Therefore, for the case where $H_E \rightarrow \infty$ and in the absence of water flux ($V_E = 0$) Equation 9 is reduced to Equation 1 where the approximation

$$\mathrm{erfc}\,[x] = \frac{1}{(\pi)^{1/2}} \frac{e^{-x^2}}{x} \tag{10}$$

is used to expand the error function for large values of x (Carslaw and Jaeger, 1959).

The Jury Reduced Solution given in Equation 1 is therefore a reduced form of the analytical solution given in Equation 9 for the conditions of zero water flux and no soil-air boundary layer. As such, the Jury Reduced Solution (discounting degradation) is equivalent to the Mayer et al. (1974) solution for diffusion across both the upper and lower boundaries (Equation 7).

2.2 INFINITE SOURCE MODEL DERIVATION

The Jury Infinite Source volatilization model (Equation 3) is derived from Mayer et al. (1974) Equations 3 and 4. Mayer et al. (1974) employed the heat transfer equation of Carslaw and Jaeger (19SS, page 97, Equation 8) to solve the diffusion equation given the boundary conditions:

$$c = C_o \text{ at } t = 0,\ 0 \le x \le L$$

$$c = 0 \text{ at } t \succ 0,\ x = 0$$

$$\partial c / \partial x = 0 \text{ at } x = L$$

The Mayer et al. (1974) solution for the volatilization flux is:

$$J_s = D_E \left[\partial c / \partial x \right]_{x=0} = D_E C_o / (\pi D_E t)^{1/2} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 L^2 / D_E t) \right] \tag{11}$$

Therefore, Equation 11 is the analytical solution for a finite emission source, but accounts only for diffusion across the upper boundary.

The summation expression in Equation 11 decreases with increasing L and decreasing D_E and t. If this term is small enough to be negligible, Equation 11 reduces to:

$$J_s = D_E C_o/(\pi D_E\ t)^{1/2} \tag{12}$$

Use of Equation 12 will result in less than 1 percent error if $t < L^2/18.4\ D_E$ (Mayer et al., 1974) .

Jury et al. (1984 and 1990) gave the solution for the semi-infinite case in Equation 3 where

$C = C_o$ at $t \geq 0,\ x = \infty$ as:

$$J_s = C_o(D_E/\pi\ t)^{1/2}$$

Equation 3 is equivalent to the semi-infinite solution of Mayer et al. (1974) as given in Equation 12 and provides a bounding estimate of the maximum volatilization flux but does not account for source depletion. As with Equation 12, use of Equation 3 on a finite system will result in less than 1 percent error if $t < L^2/18.4\ D_E$. For the purposes of calculating SSLs based on volatilization from soils, let t be set equal to the exposure interval. If $t < L^2/18.4\ D_E$, Equation 1 should be used to calculate the volatilization factor. As an alternative, an estimate of the average emission flux over the exposure interval, $<J_s>$, can be obtained from a simple mass balance:

$$< J_s > = C_o\ L/t \tag{13}$$

where C_o = Initial soil concentration (total volume), µg/cm^3-soil

L = Depth from soil surface to the bottom of contamination, cm

t = Exposure interval, days.

2.3 SUMMARY OF MODEL ASSUMPTIONS AND LIMITATIONS

The Jury Reduced Solution finite source volatilization model is analogous to the mathematical solution for heat flow in a solid such that the region $0 < x < L$ is initially at constant temperature, the region $x > L$ is at zero, and the surface $x = 0$ is maintained at zero for $t > 0$ (Carslaw and Jaeger, 1959). As such, the model's applicability to diffusion processes is limited to the initial and boundary conditions upon which the model is derived. The following represents the major model assumptions for these conditions:

1. Contamination is uniformly incorporated from the soil surface to depth L.
2. The soil column is isotropic to an infinite depth (i.e., uniform bulk density, soil moisture content, porosity and organic carbon fraction).
3. Liquid water flux is zero through the soil column (i.e., no leaching or evaporation).
4. No soil-air boundary layer exists.
5. The soil equilibrium liquid-vapor partitioning (Henry's law) is instantaneous.
6. The soil equilibrium adsorption isotherm is instantaneous, linear, and reversible.

7. Initial soil concentration is in dissolved form (i.e., no residual-phase contamination).

8. Diffusion occurs simultaneously across the upper boundary at x = 0 and the lower boundary at x = L.

The model is therefore limited to surface contamination extending to a known depth and cannot account for subsurface contamination covered by a layer of clean soil. Also, the model does not consider mass flow of contaminants due to water movement in the soil nor the volatilization rate of nonaqueous-phase liquids (residuals). Finally, the model does not account for the resistance of a soil-air boundary layer for contaminants with low Henry's law constants.

The Jury Infinite Source volatilization model is analogous to the mathematical solution for heat flow in a semi-infinite solid. The major model assumptions are the same as those of the Jury Reduced Solution finite source model except that the contamination is assumed to be uniformly incorporated from the soil surface to an infinite depth, and that diffusion occurs only across the upper boundary.

In general, both models describe the vapor-phase diffusion of the contaminants to the soil surface to replace that lost by volatilization to the atmosphere. Each model predicts an exponential decay curve over time once equilibrium is achieved. In actuality, there is a high initial flux rate from the soil as surface concentrations are depleted. The lower flux rate characteristics of the latter portion of the decay curve are thus determined by the rate at which contaminants diffuse upward. This type of desorption curve has been well documented in the literature. It is important to note that both models do not account for the high initial rate of volatilization before equilibrium is attained and will tend to underpredict emissions during this period. Finally, each model is most applicable to single chemical compounds fully incorporated into isotropic soils. Effective solubilities and activity coefficients in multicomponent systems are not addressed in the determination of the effective diffusion coefficient nor is the effect of nonlinear soil adsorption and desorption isotherms. However, because of the complexities involved with theoretical solutions to these effects, their contribution to model accuracy is difficult to predict, especially in multicomponent systems.

SECTION 3

MODEL VALIDATION

To achieve the project objective, EQ executed a literature search and a survey of professional environmental investigation/research firms as well as regulatory agencies to obtain experimental and field data suitable for comparing modeled emissions with actual emissions. The literature search uncovered several papers and bench-scale experimental studies concerned with the volatilization and vapor density of pesticides and chlorinated organics incorporated in soils (Farmer et al., 1972, 1974, and 1980; Spencer and Cliath, 1969 and 1970; Spencer, 1970; and Jury et al., 1980).

3.1 VALIDATION OF THE JURY INFINITE SOURCE MODEL

From the literature search, one bench-scale study was found that approximated the boundary conditions of the Jury Infinite Source model and met the data requirements for this project, Farmer et al., (1972). The Farmer et al. (1972) study reports the experimental emissions of lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer) and dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, exo-5, 8-dimethanonapthalene) incorporated in Gila silt loam.

The objective of the survey of professional firms and regulatory agencies was to find pilot-scale or field-scale studies of volatilization of organic compounds using the U.S. EPA emission isolation flux chamber. The candidate flux chamber studies must also have provided adequate data for input to the volatilization models.

Flux chamber studies were chosen to provide pilot-scale or field-scale measurement data needed for model validation. Flux chambers have been widely used to measure flux rates of VOCs and inorganic gaseous pollutants from a wide variety of sources. The flux chamber was originally developed by soil scientists to measure biogenic emissions of inorganic gases and their use dates back at least two decades (Hill et al., 1978). In the early 1980's, EPA became interested in this technique for estimating emission rates from hazardous wastes and funded a series of projects to develop and evaluate the flux chamber method. The initial work involved the development of a design and approach for measuring flux rates from land surfaces. A test cell was constructed and parametric tests performed to assess chamber design and operation (Kienbusch and Ranum, 1986 and Kienbusch et al., 1986). A series of field tests were performed to evaluate the method under field conditions (Radian Corporation, 1984 and Balfour, et al., 1984). A user's guide was subsequently prepared summarizing guidance on the design, construction, and operation of the EPA recommended flux chamber (Keinbusch, 1985). The emission isolation flux chamber is presently considered the preferred in-depth direct measurement technique for emissions of VOCs from land surfaces (EPA, 1990).

EQ contacted several environmental consulting firms as well as State and local agencies. In addition, the EPA data base of emission flux measurement data was reviewed (EPA, 1991a). Although several flux measurement studies were found, only one applicable study was identified with adequate QA/QC documentation and the necessary input data for the Jury Infinite Source model (Radian Corporation, 1989).

From Farmer et al. (1972) the influence of pesticide vapor pressure on volatilization was measured by comparing the volatilization from Gila silt loam of dieldrin with that of lindane. Volatilization of dieldrin and lindane was measured in a closed airflow system by collecting the volatilized insecticides in ethylene glycol traps. Ten grams of soil were treated with either 5 or 10 μg/g of C-14 tagged insecticide in hexane. The hexane was evaporated by placing the soils in a fume hood overnight. Sufficient water was then added to bring the initial soil water content to 10 percent. For the volatilization studies, the treated soil was placed in an aluminum pan 5 mm deep, 29 mm wide, and 95 mm long. This produced a bulk density of 0.75 g/cm^3. The aluminum pan was then introduced into a 250 mL bottle which served as the volatilization chamber. A relative humidity of 100 percent was maintained in the incoming air stream to prevent water evaporation from the soil surface. Air flow was maintained at 8 mL/s equivalent to approximately 0.018 miles per hour. The temperature was maintained at 30°C. The soil was a Gila silt loam, which contained 0.58 percent organic carbon.

The volatilized insecticides were trapped in 25 mL of ethylene glycol. Insecticides were extracted into hexane and anhydrous sodium sulfate was added to the hexane extract to remove water. Aliquots of the dried hexane were analyzed for lindane and dieldrin using liquid scintillation. The extraction efficiencies for lindane and dieldrin were 100 and 95 percent, respectively. The concentrations of volatilized compounds were checked using gas-liquid chromatography. All experiments were run in duplicate.

To ensure that the initial soil concentrations of lindane and dieldrin were in dissolved form, the saturation concentration (mg/kg) of both compounds under experimental conditions was calculated using the procedures given in U.S. EPA (1994):

$$C_{sat} = \frac{S}{\rho_b} \left(f_{oc} K_{oc} \rho_b + \Theta + K_H a \right) \tag{14}$$

where S is the pure component solubility in water. C_{sat} for lindane and dieldrin were calculated to be 34 mg/kg and 12 mg/kg, respectively. Therefore, the initial soil concentrations of 10 and 5 mg/kg were below saturation for both compounds.

Table 1 gives the values of each variable employed to calculate the emissions of lindane and dieldrin using the Jury Infinite Source volatilization model (Equation 3). The potential for loss of contaminant at the lower boundary at each time-step was checked to see if $t > L^2/18.4\ D_E$. If this condition was true at any time-step, the boundary conditions of the infinite source model were violated. In such a case, emissions were also calculated using the finite source model of Mayer et al. (1974) as presented in Equation 11. The difference between the predictions of both models were compared at each time-step and a percent error was calculated for the infinite source model. The instantaneous emission flux values predicted by Equation 3 and Equation 11 (where applicable) were plotted against the measured flux values for dieldrin and lindane at both 5 and 10 ppmw.

Figure 1 shows the comparison of the predicted and measured values of dieldrin at an initial soil concentration of 5 ppmw. For dieldrin, the boundary conditions of the infinite source model were not violated until the last time-step. A best curve was fit to both the measured and predicted values. As expected, both curves indicate an exponential decrease in emissions with time.

The ratio of the modeled emission flux to the measured emission flux was determined as a measure of the relative difference between the modeled and measured values. The natural log of this ratio was then analyzed by using a standard paired Student's t-test. This analysis is equivalent to assuming a lognormal distribution for the emission flux and analyzing the logtransformed data for differences between modeled and measured values.

TABLE 1.
VOLATILIZATION MODEL INPUT VALUES FOR LINDANE AND DIELDRIN

Variable	Symbol	Units	Value	Reference/Equation
Initial soil concentration	C_o	mg/kg	5 and 10	Farmer et al. (1972)
Soil depth	L	cm	0.5	Farmer et al. (1972)
Soil dry bulk density	ρ_b	g/cm^3	0.75	Farmer et al. (1972)
Soil particle density	ρ_s	g/cm^3	2.65	U.S. EPA (1988)
Gravimetric soil moisture content	w	percent	10	Farmer et al. (1972)
Water-filled soil porosoty	Θ	cm^3/cm^3	0.075	$w\rho_s$
Total soil porosity	ϕ	cm^3/cm^3	0.717	$1-(\rho_b/\rho_s)$
Air-filled soil porosity	a	cm^3/cm^3	0.642	ϕ - Θ
Soil organic carbon	f_{oc}	fraction	0.0058	Farmer et al. (1972)
Organic carbon partition coefficient	K_{oc}	cm^3/g	1380	U.S. EPA (1994)
Diffusivity in air (Lindane)	D_g^a	cm^2/d	1521	U.S. EPA (1994)
Diffusivity in air (Dieldin)	D_g^a	cm^2/d	1080	U.S. EPA (1994)
Diffusivity in water (Lindane)	D_i^w	cm^2/d	0.480	U.S. EPA (1994a)
Diffusivity in water (Dieldrin)	D_i^w	cm^2/d	0.410	U.S. EPA (1994a)
Henry's law constant (Lindane)	K_H	unitless	1.40 E-04	U.S. EPA (1994)
Henry's law constant (Dieldrin)	K_H	unitless	2.75 E-06	U.S. EPA (1994)
Degradation rate constant (Lindane and Dieldrin)	μ	1/day	0	Default to eliminate effects of degradation

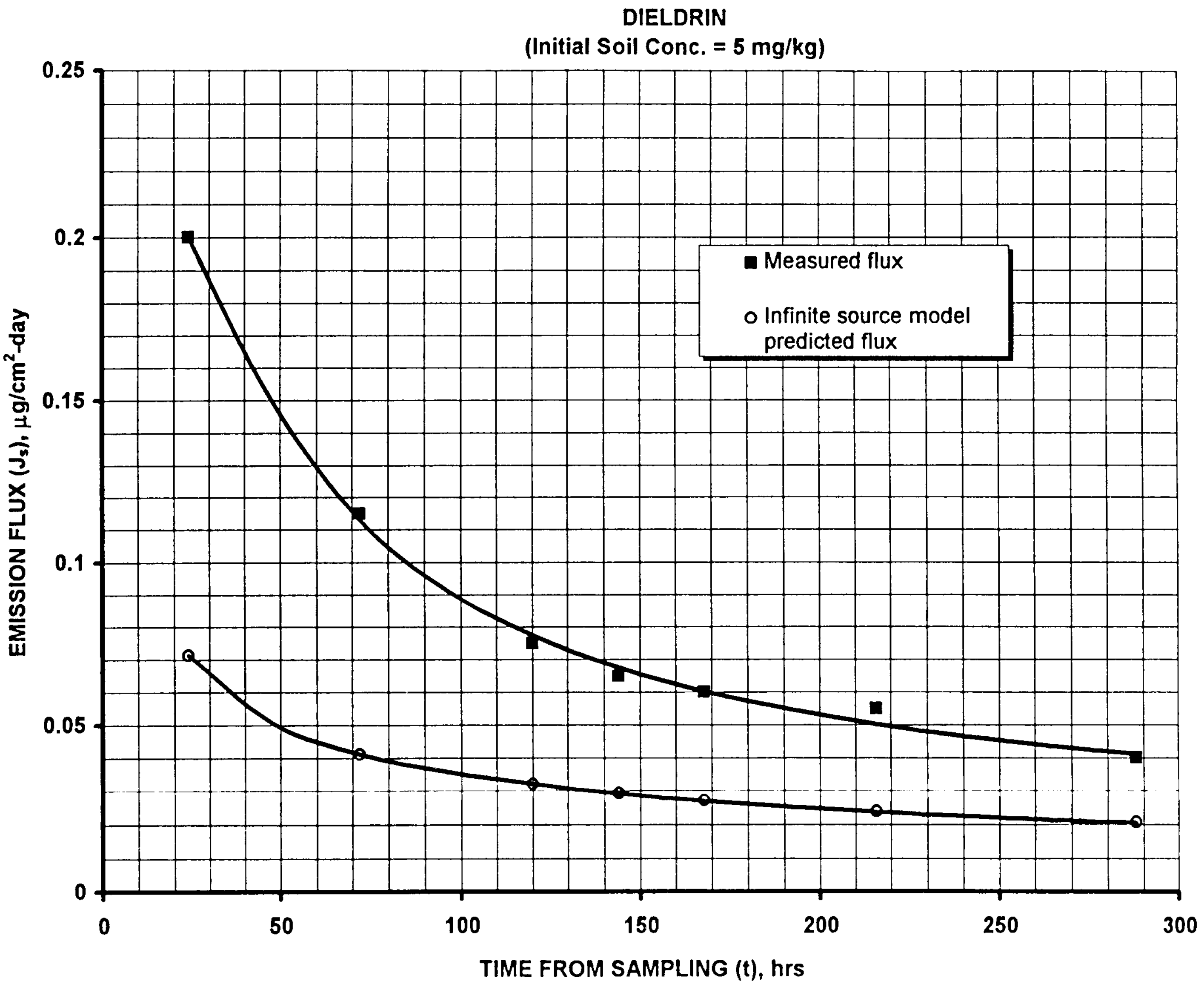

Figure 1
Predicted And Measured Emission Flux Of Dieldrin Versus Time (C_o = 5 ppmw)

The data were also analyzed by using standard linear regression techniques (Figure 2). Again, the data were assumed to follow a lognormal distribution. A simple linear regression model was fit to the log-transformed data and the Pearson correlation coefficient was determined. The Pearson correlation coefficient is a measure of the strength of the linear association between the two variables.

From a limited population of four observations, the correlation coefficient was calculated to be 0.994 with a mean ratio of modeled-to-measured values of 0.42. The actual significance (p-value) of the paired Student's t-test was p = 0.0001. The lower and upper confidence limits were calculated to be 0.38 and 0.48, respectively. On average, this indicates that at the 95 percent confidence limit, the modeled emission flux is between 0.38 and 0.48 times the measured emission flux.

Figure 3 shows the modeled and measured flux values of dieldrin at an initial soil concentration of 10 ppmw, while Figure 4 shows the relationship of the log-transformed data and the upper and lower confidence limits. At 10 ppmw, the correlation coefficient was 0.974 with a mean ratio of 0.45, p-value of 0.0001, and a 95 percent confidence interval of 0.37 to 0.54.

As can be seen from Figures 1 and 3, the model underpredicts the emissions during the initial stages of the experiment. This is to be expected in that during this phase, contaminant is evaporating from the soil surface. The apparent discrepancy between measured and predicted values decreases with time as equilibrium is achieved and diffusion becomes the rate-limiting factor.

For lindane, the boundary conditions of the infinite source model were violated after the first time-step (i.e., $t > L^2/18.4\ D_E$ at 24 hours). Therefore, the Mayer et al. (1974) finite source model was used to derive a percent error at each succeeding timestep. At an initial soil concentration of 5 ppmw, the infinite source model predicted 114 percent total mass loss of the finite source model over the entire time span of the experiment. At a concentration of 10 ppmw, the infinite source model predicted 107 percent total mass loss of the finite source model.

Figures 5 and 6 show the comparison of modeled to measured values of lindane at initial soil concentrations of 5 and 10 ppmw, respectively. Likewise, Figures 7 and 8 show the comparisons of the log-transformed data. At an initial soil concentration of 5 ppmw, the correlation coefficient between modeled and measured values was 0.997 with a mean modeled-to-measured ratio of 0.81, a p-value of 0.3281, and a 95 percent confidence interval of 0.46 to 1.44. At an initial soil concentration of 10 ppmw, the correlation coefficient was calculated to be 0.998, the mean ratio 0.73, the p-value 0.1774, and the confidence interval 0.41 to 1.28.

The p-values for dieldrin are considerably lower than those of lindane. This is due to the very narrow confidence interval around the modeled values. In the case of dieldrin, Equation 3 did not predict a loss of contaminant at the lower boundary until the last time-step (i.e., $t > L^2/18.4\ D_E$ at 12 days). This results in a nearly perfect straight line when the log-transformed data are plotted. For dieldrin, therefore, Equations 3 and 11 predict identical values until the last timestep.

Table 2 summarizes statistical analysis for the bench-scale comparative validation of the Jury Infinite Source volatilization model. In general, the data support good agreement between modeled and measured values and show relatively narrow confidence intervals and high correlation coefficients.

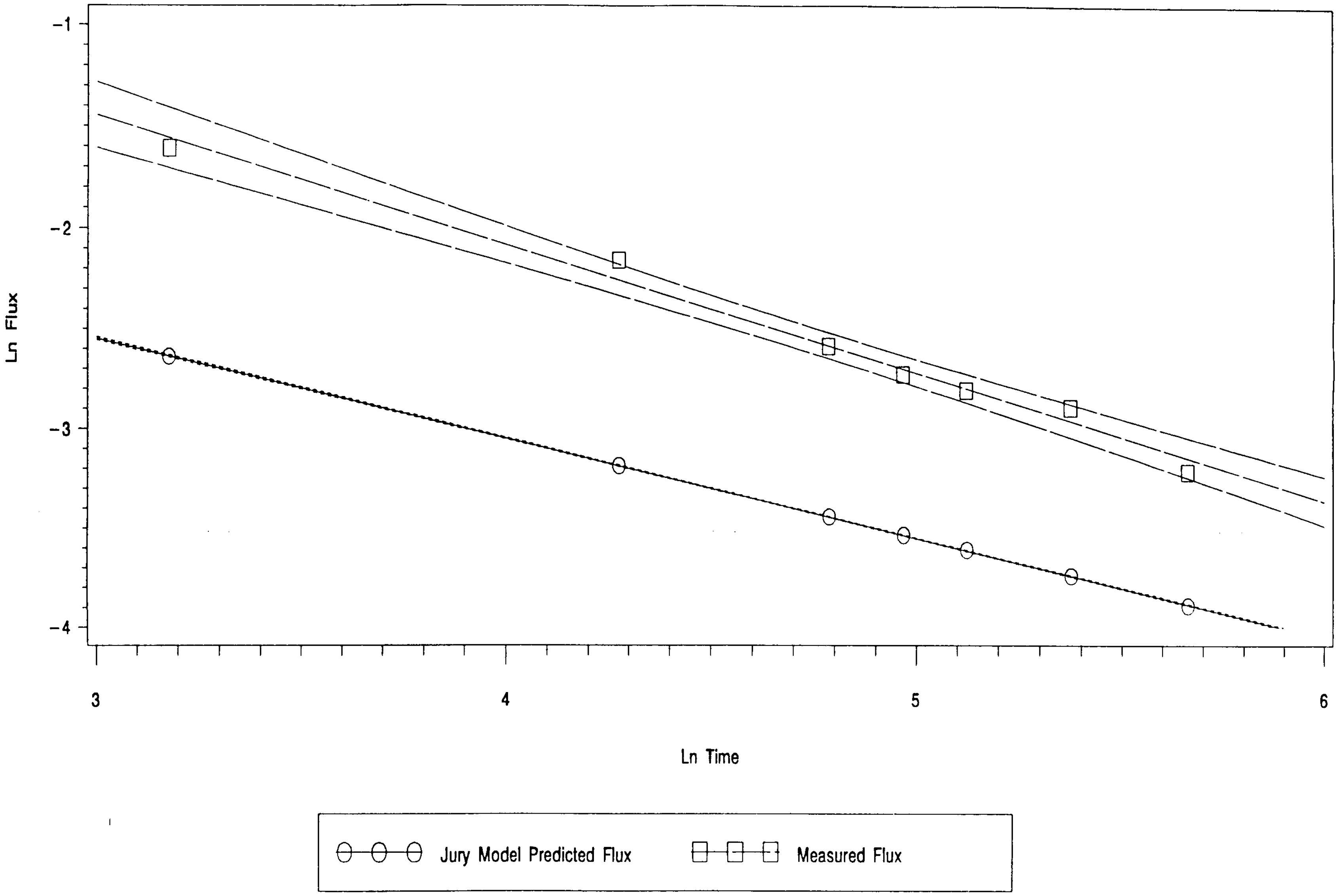

Figure 2
Predicted And Measured Emission Flux Of Dieldrin Versus Time (C_o = 10 ppmw)

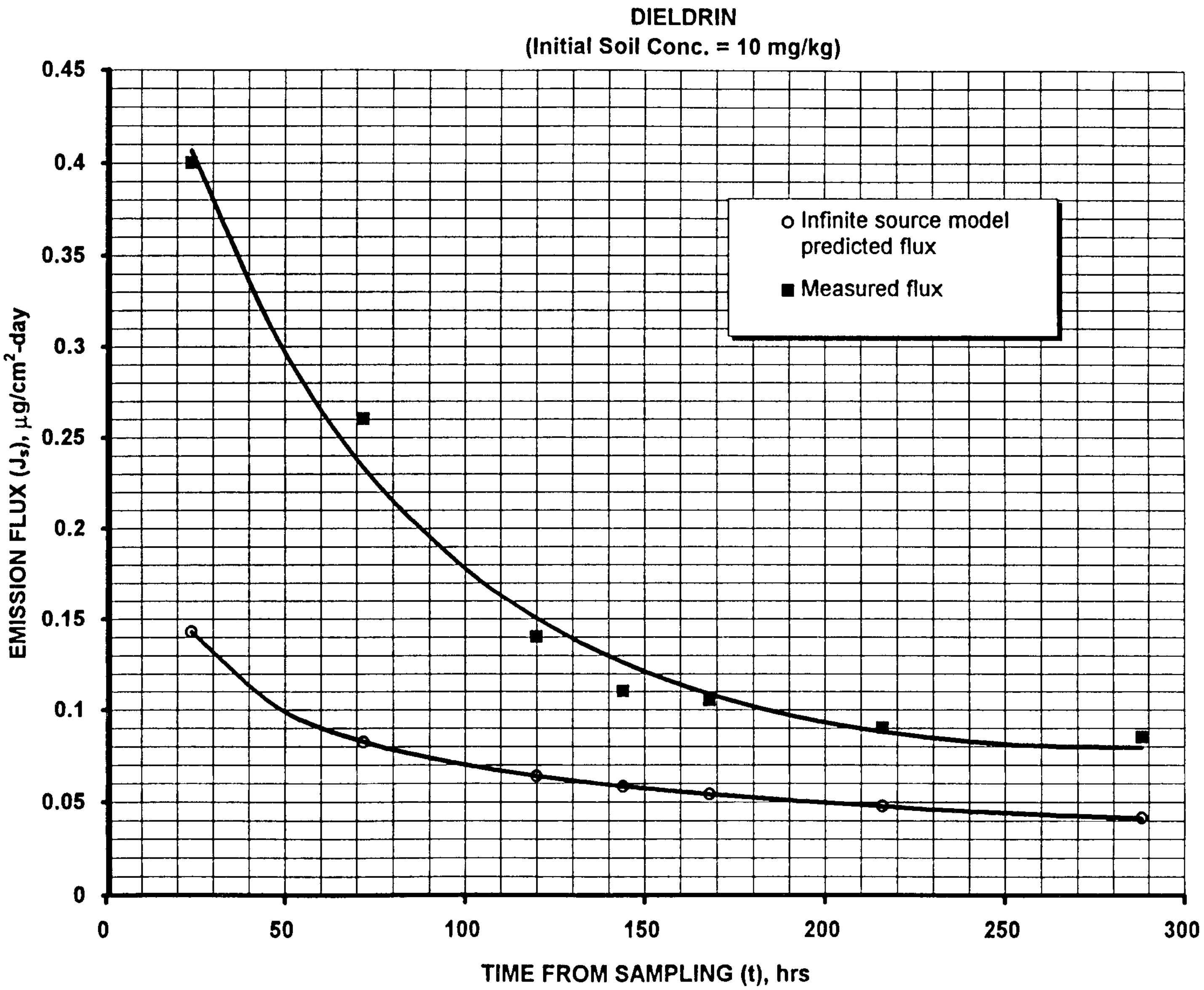

Figure 3
Predicted And Measured Emission Flux Of Dieldrin Versus Time (C_o = 10 ppmw)

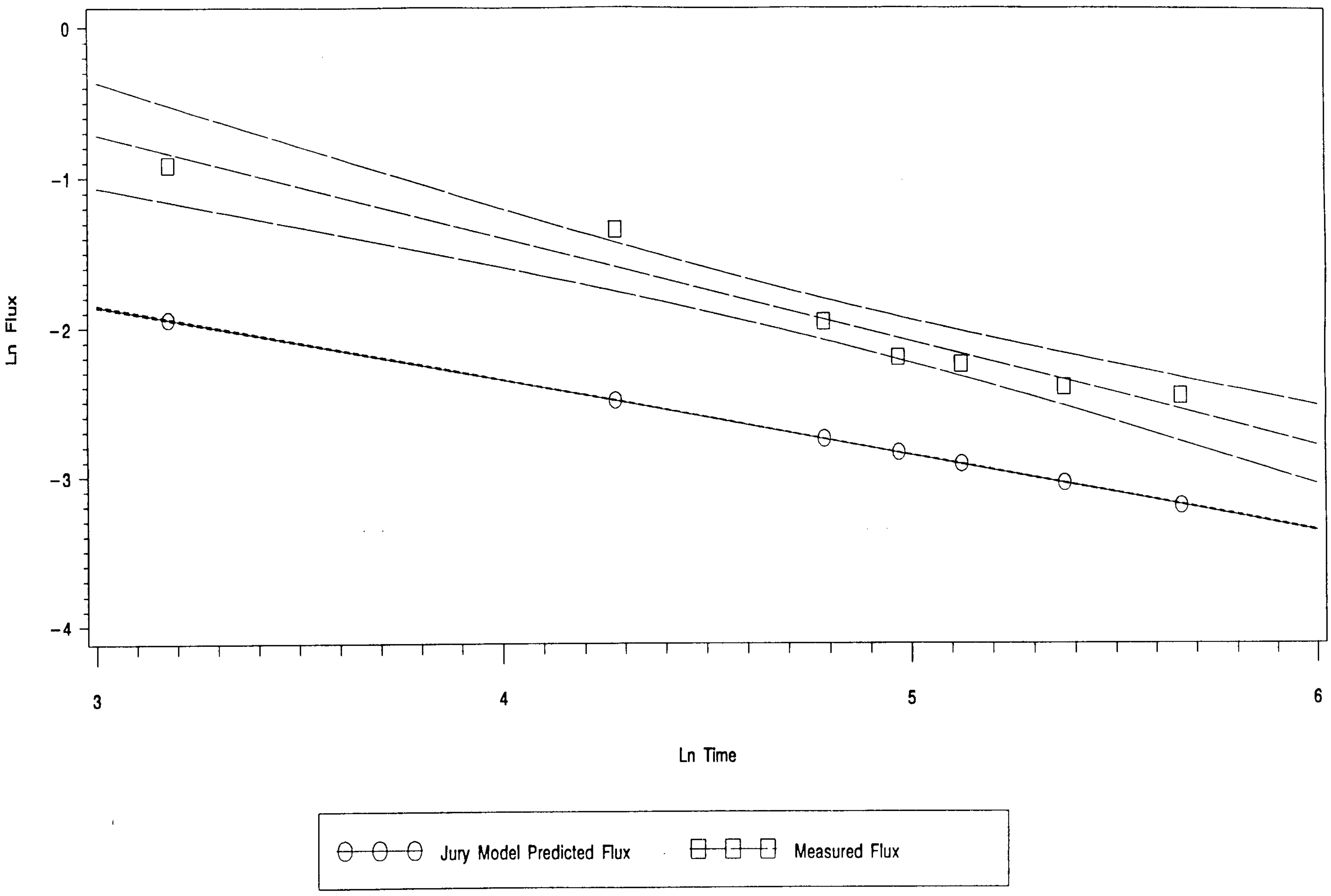

Figure 4
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Dieldrin (C_o = 10 ppmw)

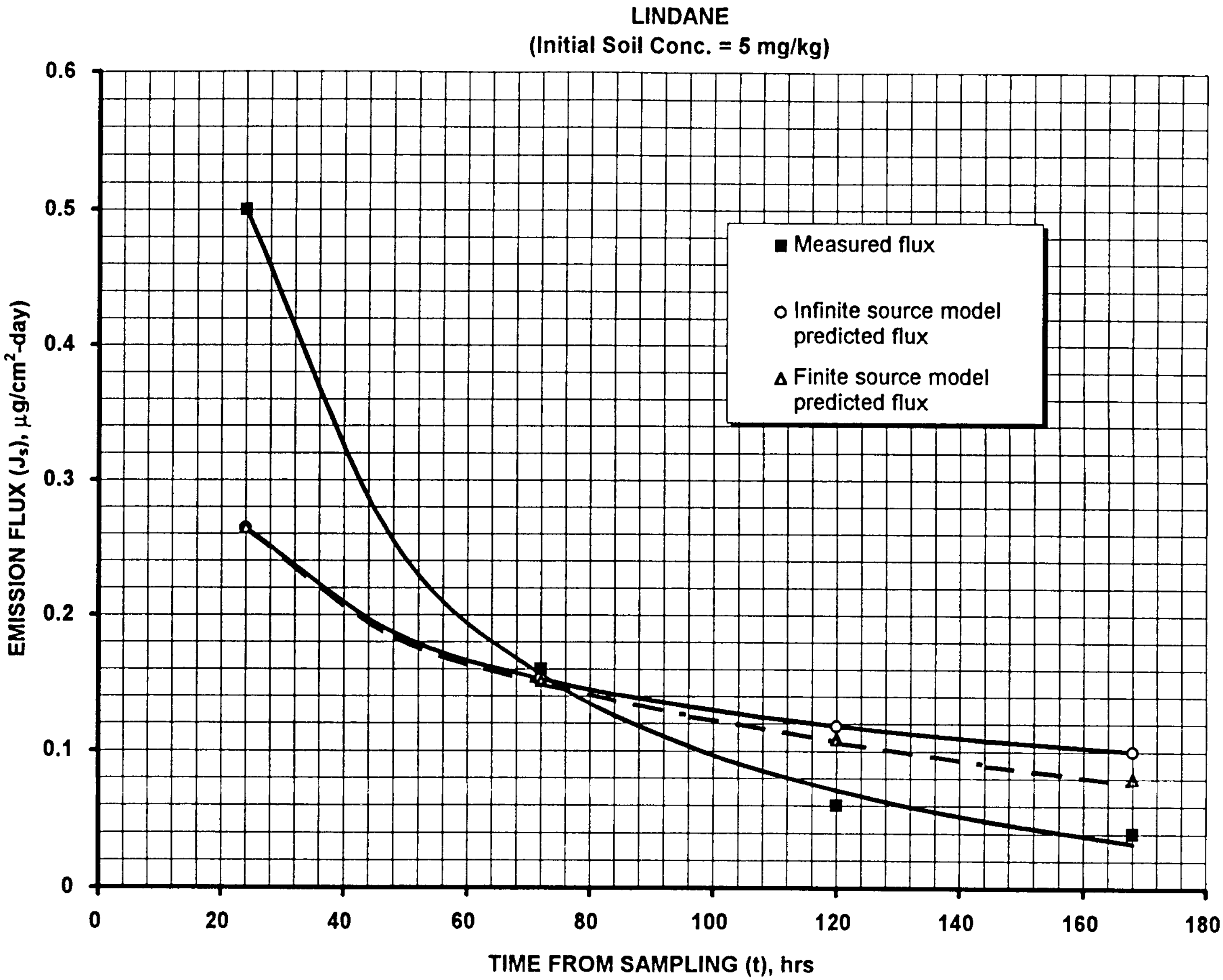

Figure 5
Predicted And Measured Emission Flux Of Lindane Versus Time (Co = 5 ppmw)

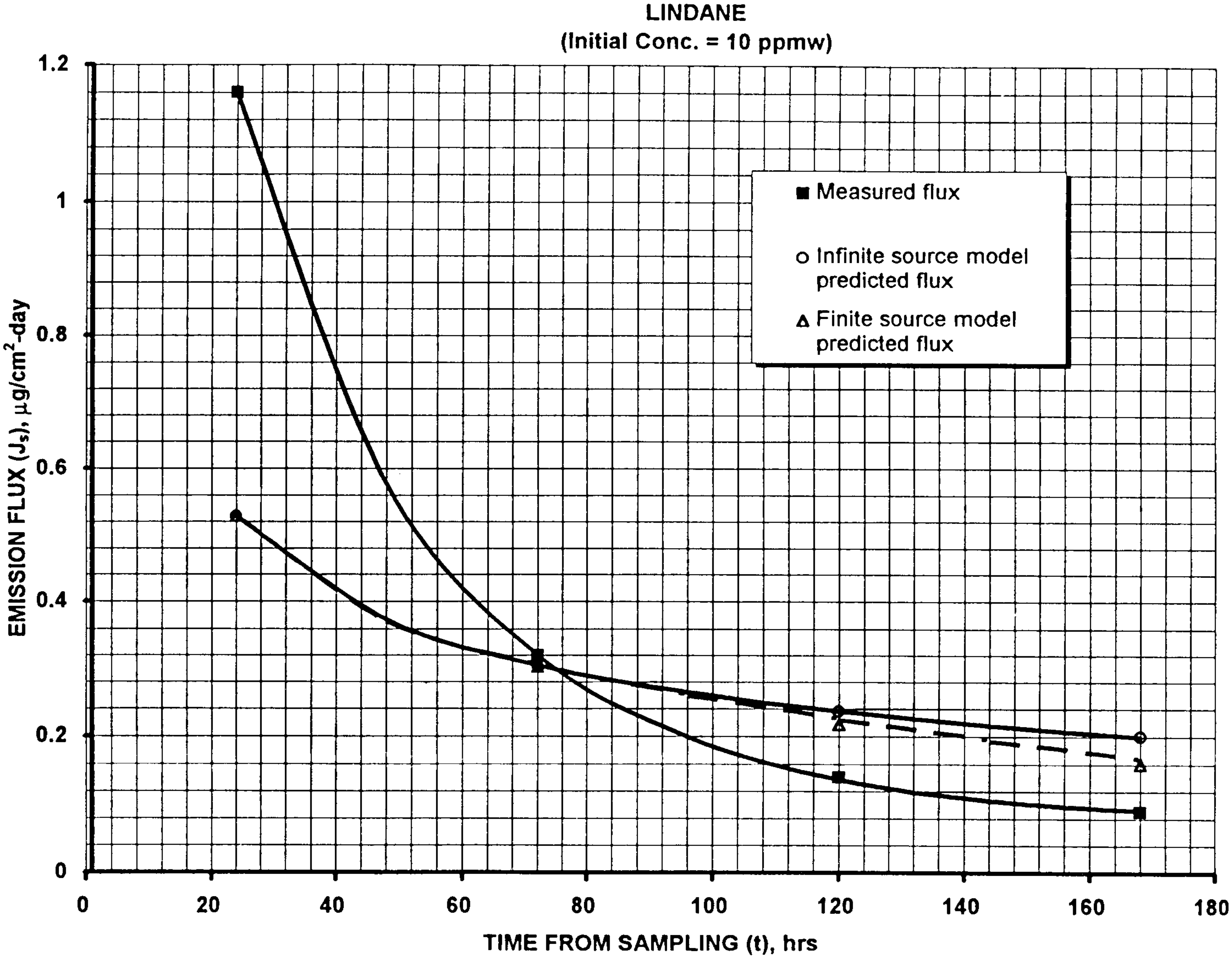

Figure 6
Predicted And Measured Emission Flux Of Lindane Versus Time (C_o = 10 ppmw)

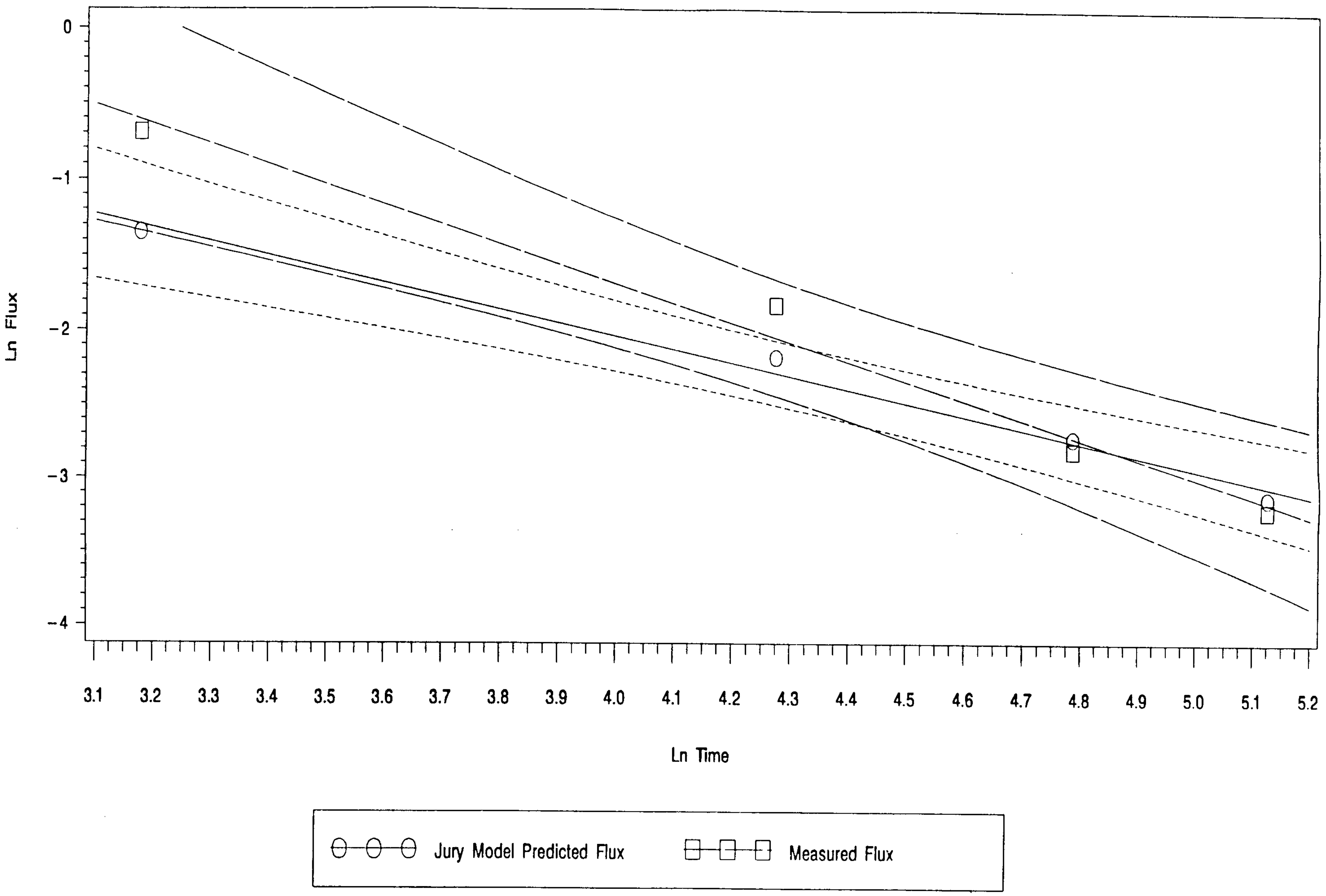

Figure 7
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Lindane (C_o = 5 ppmw)

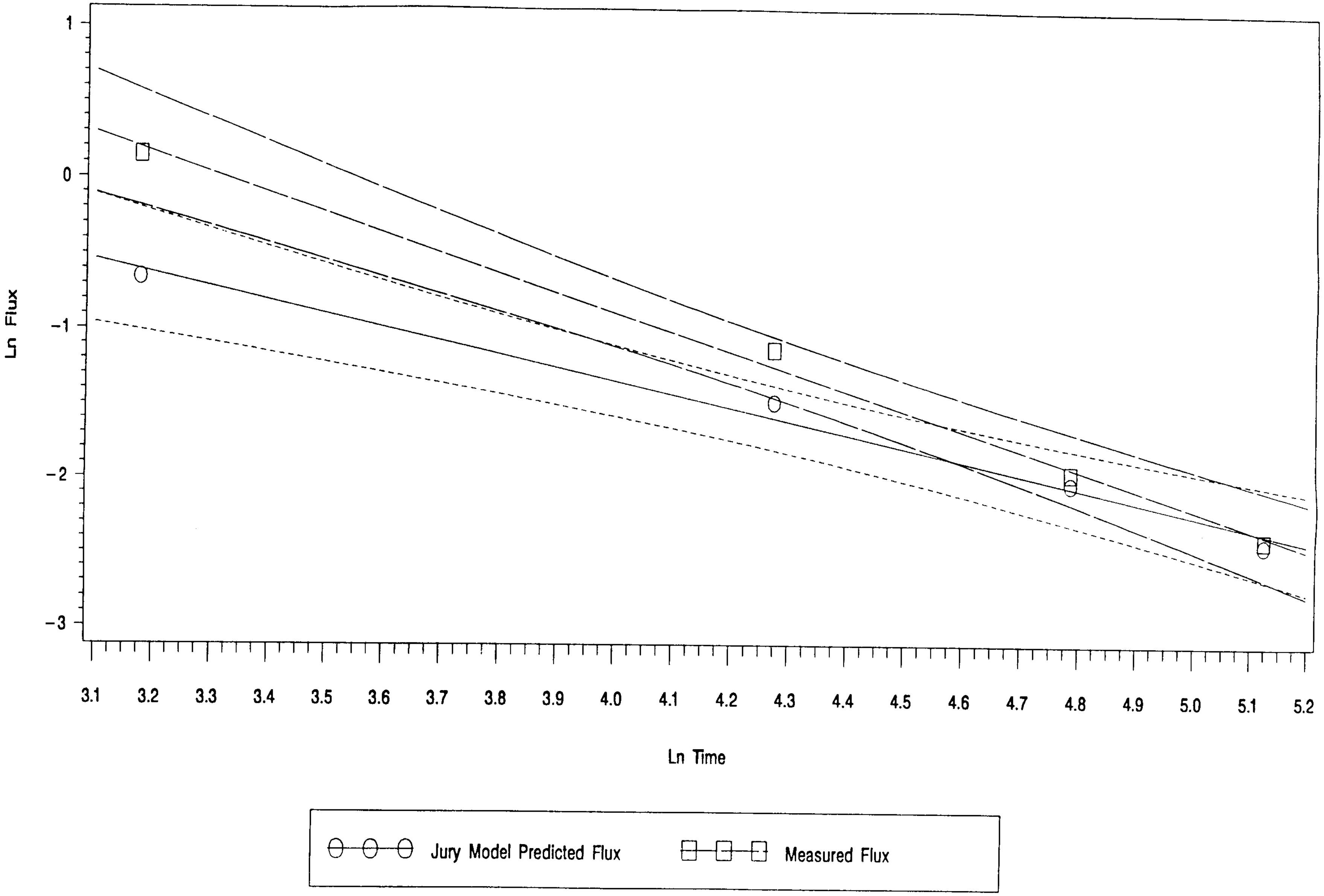

Figure 8
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Lindane (C_o = 10 ppmw)

TABLE 2.
SUMMARY OF THE BENCH-SCALE VALIDATION OF THE JURY INFINITE SOURCE MODEL

Chemical	N	Correlation coefficient	Mean ratio: Modeled-to-measured	p-value	95% confidence interval
Lindane (5 ppmw)	4	0.997	0.81	0.3281	(0.46, 1.44)
Lindane (10 ppmw)	4	0.998	0.73	0.1774	(0.41, 1.28)
Dieldrin (5 ppmw)	7	0.994	0.42	0.0001	(0.38, 0.48)
Dieldrin (10 ppmw)	7	0.974	0.45	0.0001	(0.37, 0.54)

Appendix A contains the spreadsheet calculations for the bench-scale validation of the Jury Infinite Source volatilization model.

From Radian Corporation (1989), a pilot-scale study was designed to determine how different treatment practices affect the rate of loss of benzene, toluene, xylenes, and ethylbenzene (BTEX) from soils. The experiment called for construction of four piles of loamy sand soil, each with a volume of approximately 4 cubic yards (7900 pounds), a surface area of 8 square meters, and a depth of 0.91 meters. Each test cell was lined with an impermeable membrane and the soil in each cell was sifted to remove particles larger than three-eighth inch in diameter. The contaminated soil for each pile was prepared in batches using 55-gallon drums. In the "high level" study, each soil batch was brought to 5 percent moisture content and 6 liters of gasoline added. Additional water was then added to bring the soil to 10 percent moisture by weight. The drums were capped and sat undisturbed overnight. The drums were then opened the next day and shoveled into the test cell platform. Twenty-two soil batches were prepared for each soil pile. Each batch consisted of 360 pounds of soil and 6.0 liters of fuel. Therefore, each soil pile contained 7900 pounds of soil and 132 liters of gasoline. Each soil pile was then subjected to one of the following management practices:

- A control pile that was not moved or treated
- An "aerated" or "mechanically mixed" pile
- A soil pile simulating soil venting or vacuum extraction
- A soil pile heated to 38°C.

Losses due to volatilization during the mixing and transfer process and during a 28 hour holding time in the test bed before initial sampling reduced the residual BTEX in soil. For the purpose of this validation study, however, these losses caused initial soil concentrations of benzene, toluene, and ethylbenzene to be below or within a factor of two of their respective single component saturation concentrations. Because the mixed pile, vented pile, and heated pile were subject to mechanical disturbances or thermal treatment, only the control pile data were used in this study.

In general, the test schedule called for collection of soil samples and air emission loss measurements during the first, sixth, and seventh weeks Soil samples were collected randomly within specified grid areas by composite core collection to the maximum depth of the pile. Emission losses were measured similarly using an emission isolation flux chamber as specified in Kienbusch (1985). Only data for which soil samples and flux chamber measurements were taken on the same day were used for this study.

Analysis of BTEX in soil samples was accomplished by employing the EPA 5030 extraction method and the EPA 8020 analytical method. The BTEX method was modified to reduce the sample hold time to one day in an effort to improve the accuracy of the method. Five soil samples were submitted in duplicate. The relative percent differences (RPD) ranged from 8.0 to 48.9 percent. The average RPD for the five samples was 26.8 percent. In addition, EPA QC sample analysis indicated average percent recoveries ranging from 89 percent for m-xylene to 119 percent for toluene. The pooled coefficient of variation (CV) for all the BTEX analysis was 10.5 percent. Spiked sample recoveries (eight samples) ranged from 75 percent for m-xylene to 168 percent for toluene. The average spike recoveries ranged from 108 percent for benzene to 146 percent for toluene. Finally, both system blanks and reagent blanks indicated no contamination was found in the analytical system.

It should be noted that the standard method used for BTEX analysis was observed to have contributed to the variabilities in soil concentrations. The EPA acceptance criteria based on 95 percent confidence intervals from laboratory studies are roughly 30 to 160 percent for the BTEX compounds during analysis of water samples. The necessary extraction step for soil samples would increase this already large variability.

Analysis of vapor-phase organic compounds via the emission isolation flux chamber was accomplished using a gas chromatograph (GC). Gas samples were collected from the flux chamber in 100 mL, gas-tight syringes and analyzed by the GC in laboratory facilities adjacent to the test site. During the study, a multicomponent standard was analyzed daily to assess the precision and daily replication of the analytical system. The results of the analysis indicated a good degree of reproducibility with coefficients of variation ranging from 5.1 to 16.3 percent.

From these data, instantaneous emission fluxes were calculated for benzene, toluene, and ethylbenzene corresponding to each time period at which flux chamber measurements were made. Table 3 gives the values of each variable employed to calculate emissions of each compound using the Jury Infinite Source model and the Mayer et al. (1974) finite source model. Appendix A contains the spreadsheet data for benzene, toluene, and ethylbenzene at initial soil concentrations of 110 ppm, 880 ppm, and 310 ppm, respectively.

It should be noted that the fraction of soil organic carbon (f_{oc}) was not available from Radian (1989). For this reason, the default value for f_{oc} of 0.006 from U.S. EPA (1994) was used for all calculations.

Figures 9, 10, and 11 show the comparison of modeled and measured emission fluxes of benzene, toluene, and ethylbenzene, respectively. The Radian Corporation study noted that the second measured value in each figure represented a data outlier, possibly due to the formation of a soil fissure, reducing the soil path resistance and increasing the emission flux.

Table 4 presents the results of the statistical analysis of the comparison of modeled and measured values. For both benzene and ethylbenzene, measured values were below the detection limits after the fifth observation; measured values for toluene were below the detection limit after the seventh observation.

TABLE 3.
VOLATILIZATION MODEL INPUT VARIABLES FOR BENZENE, TOLUENE, AND ETHYLBENZENE

Variable	Symbol	Units	Value	Reference/Equation
Initial soil concentration	C_o	mg/kg		Radian (1989)
- benzene			110	
- toluene			880	
- ethylbenzene			310	
Soil Depth	L	cm	91	Radian (1989)
Soil dry bulk density	ρ_b	g/cm^3	1.5	Radian (1989)
Soil particle density	ρ_s	g/cm^3	2.65	U.S. EPA (1988)
Gravimetric soil moisture content	w	percent	10	Radian (1989)
Water-filled soil porosoty	Θ	cm^3/cm^3	0.150	$w\rho_b$
Total soil porosity	ϕ	cm^3/cm^3	0.434	$1-(\rho_b/\rho_s)$
Air-filled soil porosity	a	cm^3/cm^3	0.284	$\phi - \Theta$
Soil organic carbon	f_{oc}	Fraction	0.006	U.S. EPA (1994) default value
Organic carbon partition coefficient	K_{oc}	cm^3/g		
- benzene			57	U.S. EPA (1994)
- toluene			131	U.S. EPA (1994)
- ethylbenzene			221	U.S. EPA (1994)
Diffusivity in air	D_g^a	cm^2/s		
- benzene			0.0870	U.S. EPA (1994)
- toluene			0.0870	U.S. EPA (1994)
- ethylbenzene			0.0750	U.S. EPA (1994)
Diffusivity in water	D_i^w	cm^2/s		
- benzene			9.80 E-06	U.S. EPA (1994a)
- toluene			8.60 E-06	U.S. EPA (1994a)
- ethylbenzene			8.64 E-06	U.S. EPA (1994a)
Henry's law constant	K_H	Unitless		
- benzene			0.22	U.S. EPA (1994)
- toluene			0.26	U.S. EPA (1994)
- ethylbenzene			0.32	U.S. EPA (1994)
Degradation rate constant	μ	1/day	0	Default to eliminate effects of degradation

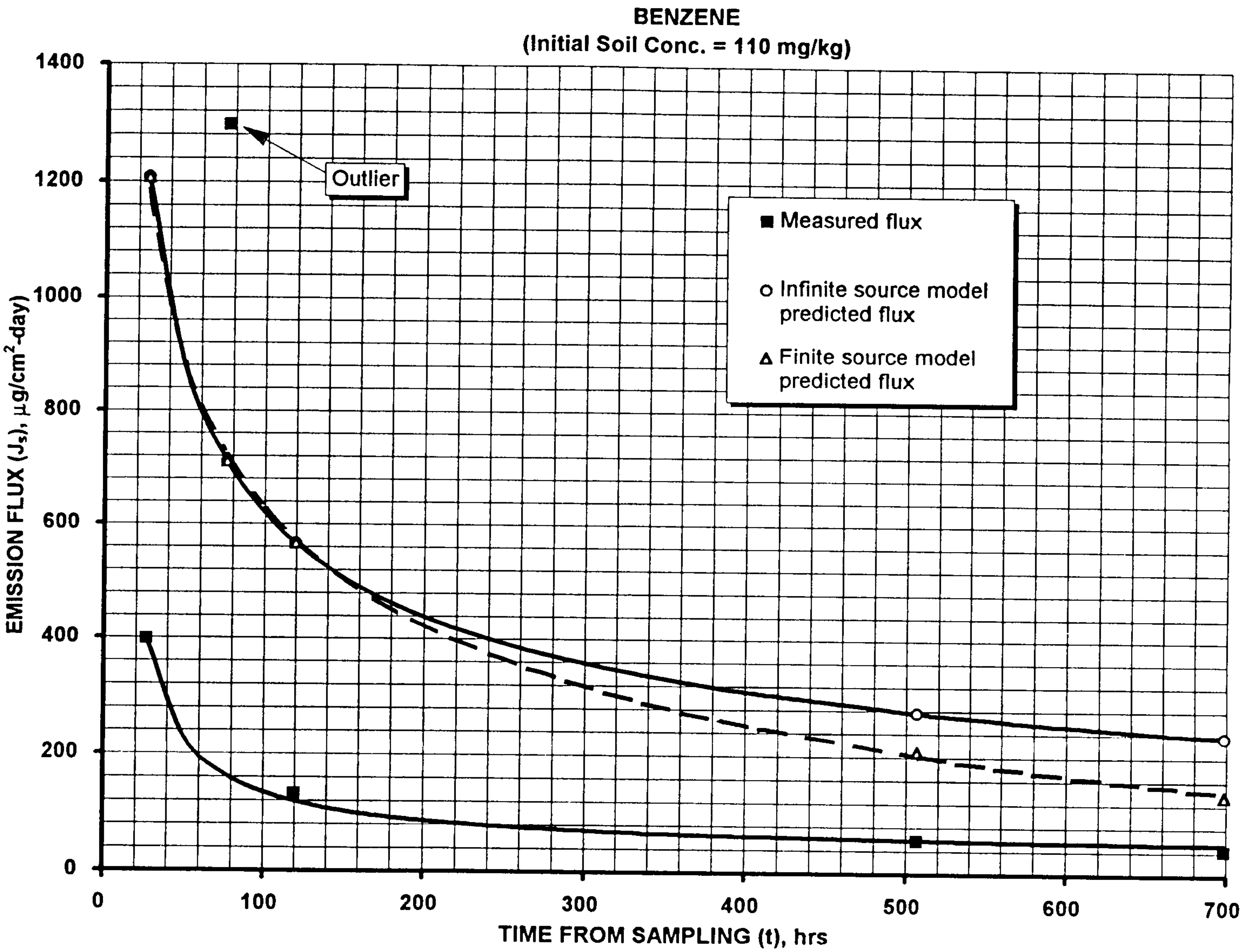

Figure 9
Predicted And Measured Emission Flux Of Benzene (C_o = 110 ppmw)

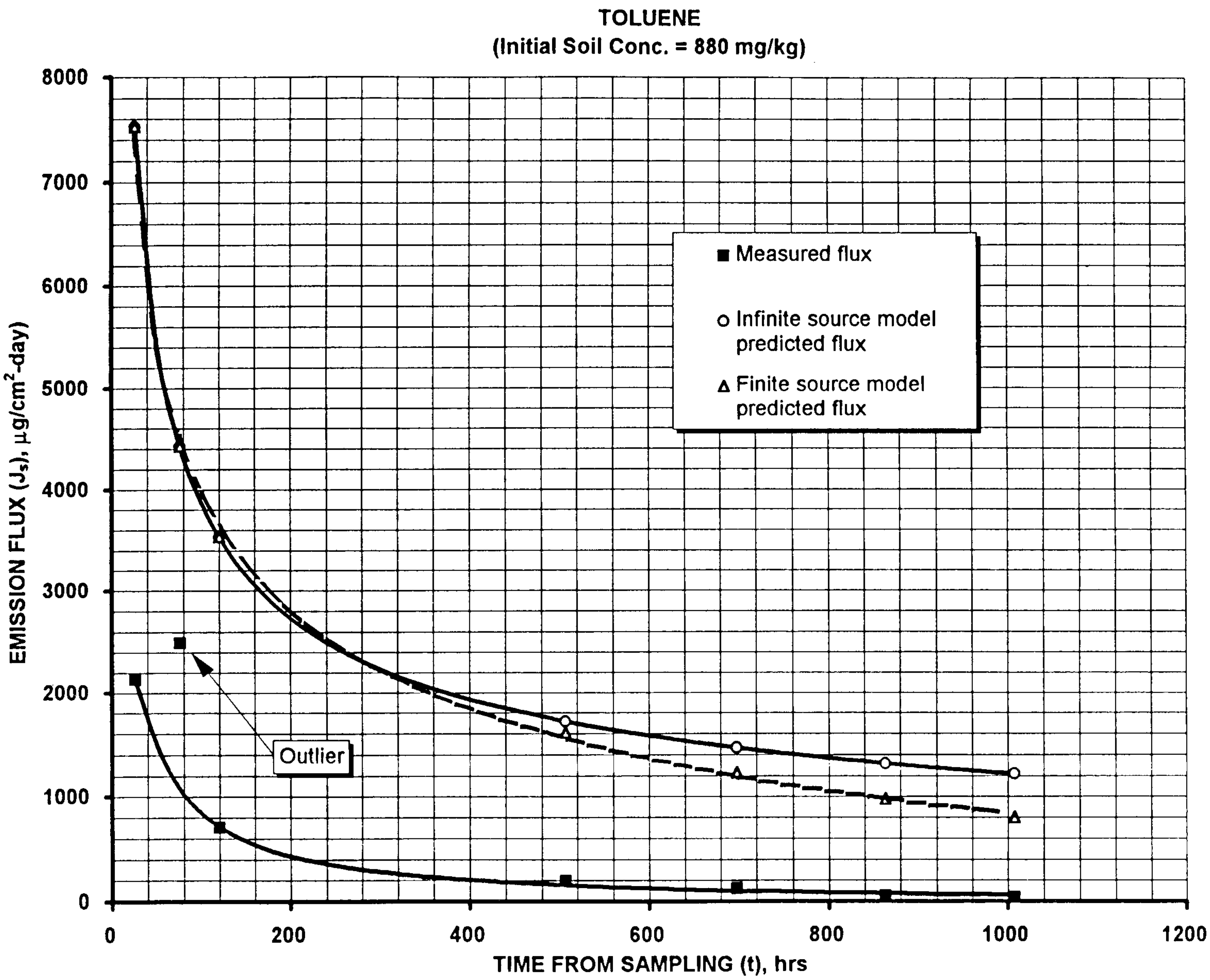

Figure 10
Predicted And Measured Emission Flux Of Toluene (C_o = 880 ppmw)

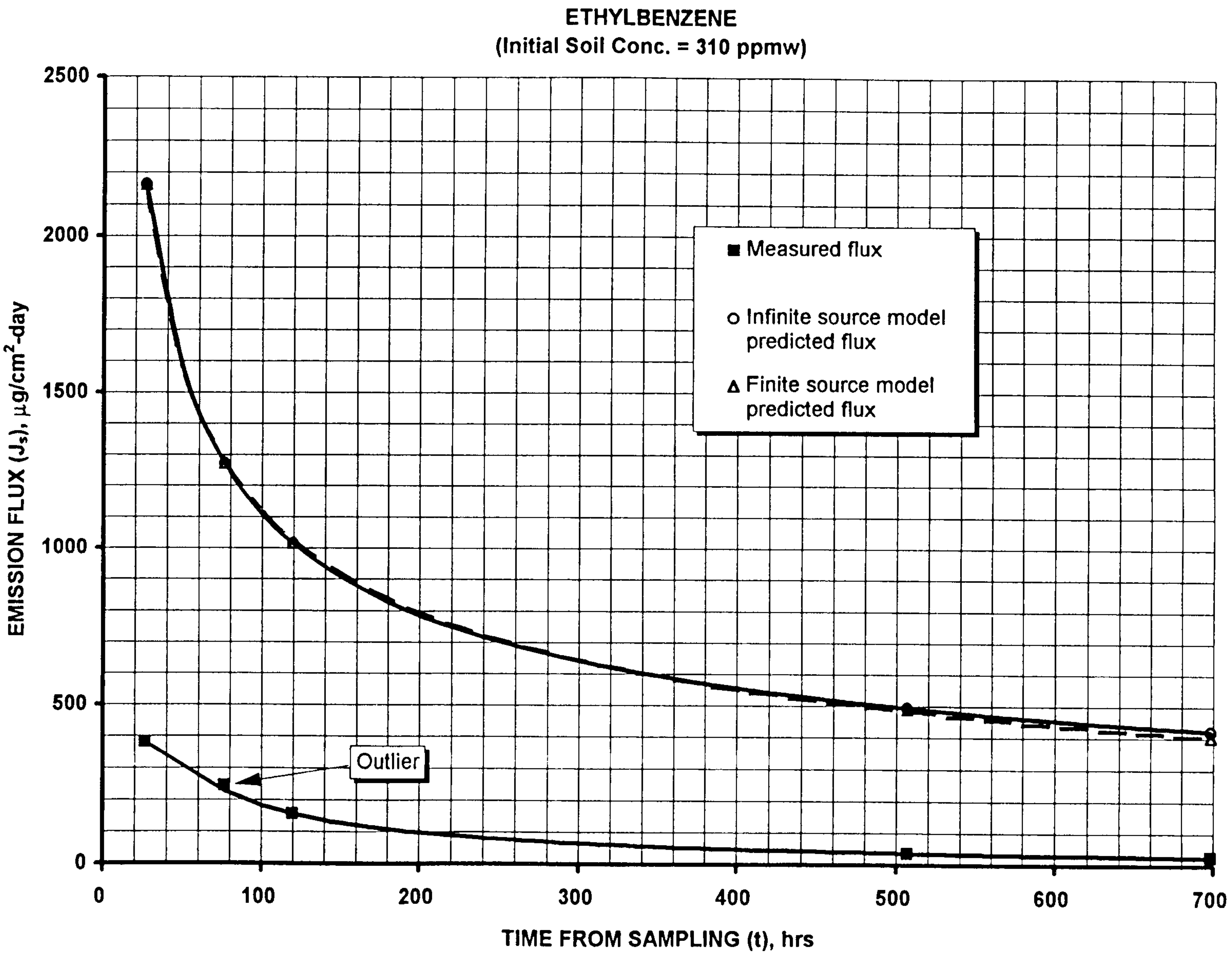

Figure 11
Predicted And Measured Emission Flux Of Ethylbenzene (C_o = 310 ppmw)

TABLE 4.
SUMMARY OF STATISTICAL ANALYSIS OF PILOT-SCALE VALIDATION

Chemical	N	Correlation coefficient	Mean ratio: Modeled-to-measured	p-value	95% confidence interval
Benzene (110 ppm)	5	0.982	2.5	0.0149	(1.4, 4.5)
Toluene (880 ppm)	7	0.988	6.3	0.0002	(3.9, 10.4)
Ethylbenzene (310 ppm)	5	0.999	7.8	0.0008	(4.9, 12.4)

Figures 12, 13, and 14 show the comparison of the log-transformed data for the modeled and measured emission fluxes of benzene, toluene, and ethylbenzene, respectively. As can be seen from Table 4, correlation coefficients ranged from 0.982 for benzene to 0.999 for ethylbenzene, while p-values and 95 percent confidence intervals indicate a significant statistical difference between modeled and measured values.

The boundary conditions of the infinite source model were violated after the first timestep for benzene, and after the third time-step for both toluene and ethylbenzene. The infinite source model predicted 134 percent, 117 percent, and 103 percent of the total mass loss of the finite source model for benzene, toluene, and ethylbenzene, respectively.

In general, the predicted values were higher than the measured values throughout the time-span of the experiment for all three compounds. It is also interesting to note that during the initial stage of the experiment the predicted values were considerably higher than measured values even when contaminant loss at the soil surface due to evaporation was expected. Although the relative differences between predicted and measured values are not excessive (i.e., the highest modeled-to-omeasured mean ratio is within a factor of approximately 10), they are considerably higher than those of the bench-scale studies.

Any one or a combination of the following could account for the larger discrepancies between measured and predicted values in the pilot-scale study:

1. Although the initial soil concentrations of the three compounds were below or within a factor of two of their respective single component saturation concentrations, they may have been greater than the component concentrations for which a residual-phase of gasoline existed. If this were the case, measured emissions may have been in part due to the presence of nonaqueous-phase liquids (NAPL) which would have violated the model's assumptions of equilibrium partitioning.

2. Soil mixing processes and transfer to the test bed may have resulted in heterogenous incorporation of the contaminants. If surface concentrations were reduced due to incomplete mixing, measured emissions would have been reduced during the initial stages of the experiment.

3. Sampling and/or analytical variability may have resulted in under reporting of emission fluxes and/or over reporting of initial soil concentrations.

4. Contaminants sorbed to the test bed liner may have acted to reduce emissions.

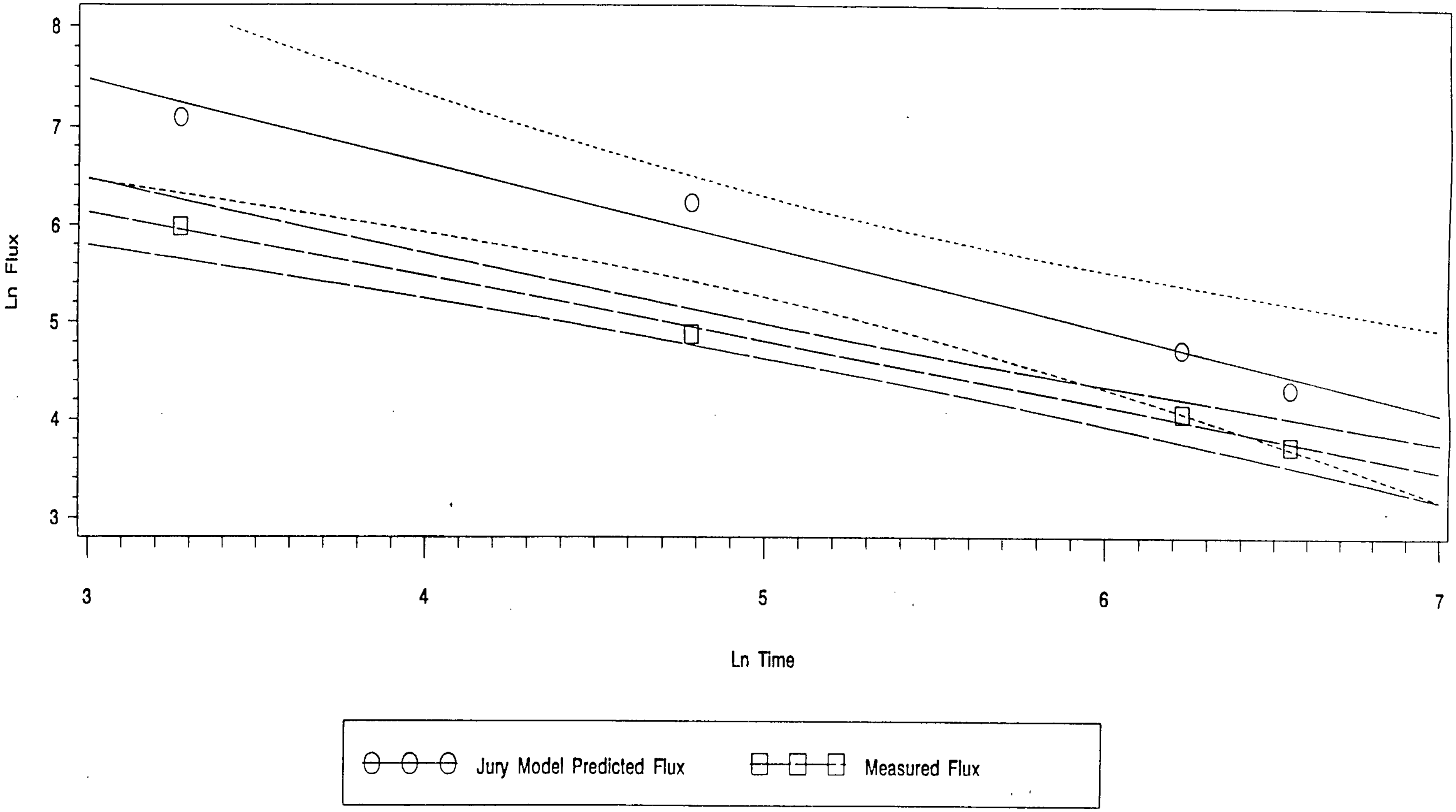

Figure 12
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Benzene (C_o = 110 ppmw)

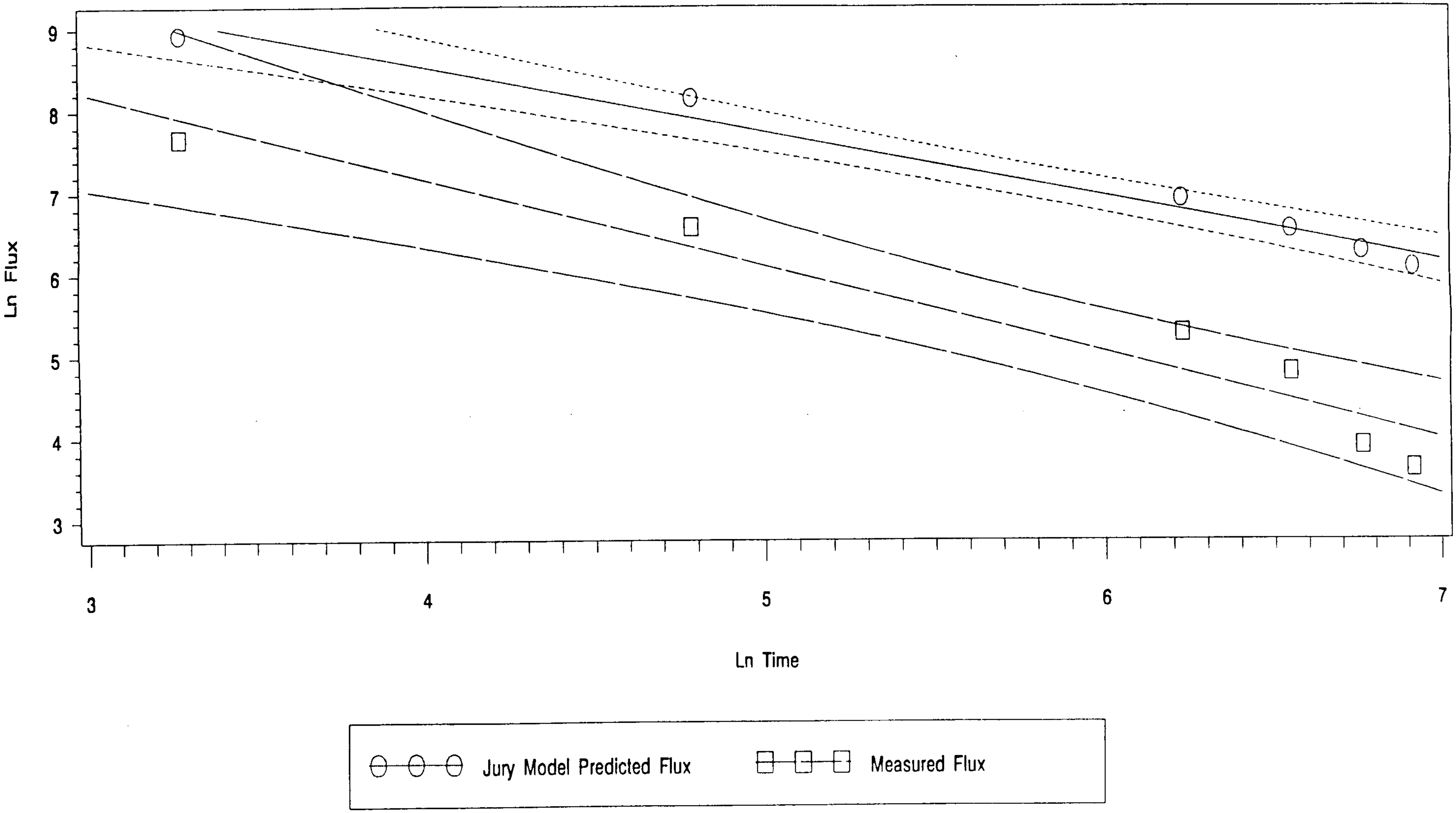

Figure 13
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Toluene (C_o = 880 ppmw)

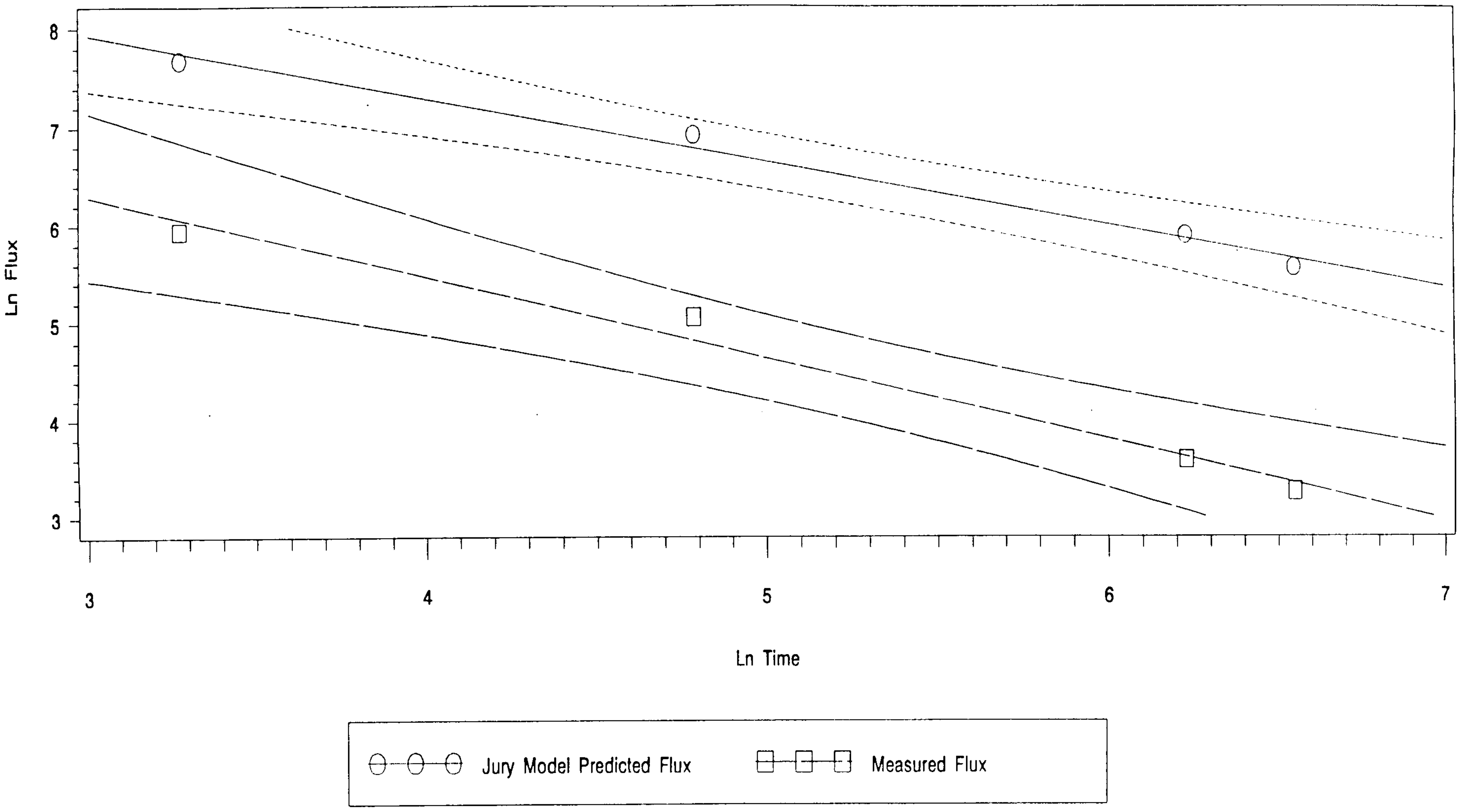

Figure 14
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Ethylbenzene (C_o = 310 ppmw)

5. Variability in the relative humidity of the air above the test bed may have induced surface water evaporation in between flux chamber samples. Water evaporation would have moved contaminants to the surface by convection and depleted soil concentrations in between sampling events.

6. The model is not as accurate for compounds with relatively high Henry's law constants.

From these observations, it appears more likely that the larger discrepancies between modeled and measured emissions in the pilot-scale study are due to experimental conditions. Sufficient uncertainty exists as to whether all model boundary conditions were maintained during the experiment. For this reason, the results of the pilot-scale validation should be considered less reliable than those of the bench-scale validation. This conclusion suggests that controlled studies should be considered for validation of model predictions for compounds with relatively high Henry's law constants.

3.2 VALIDATION OF THE JURY REDUCED SOLUTION FINITE SOURCE MODEL

From the literature search, one bench-scale study was found that replicated the boundary conditions of the Jury Reduced Solution model (Equation 1). Jury et al. (1980) reports the emissions of the herbicide triallate [S-(2,3,3-trichloroallyl) diisopropyithiocarbamate] incorporated in San Joaquin sandy loam. This study replicated the model boundary conditions in that a clean layer of soil underlayed the contaminated soil allowing diffusion across the lower boundary as well as the upper boundary.

Volatilization of triallate was measured in a closed volatilization chamber (Spencer et al., 1979). The air chamber above the soil was 2 mm deep and 3 cm wide, matching the width of the evaporating surface. An average air flow rate of 1 liter per minute was maintained across the surface equivalent to a windspeed of 1 km/h. Triallate was applied by atomizing the material in hexane onto the air-dry autoclaved soil. The soil was mixed and allowed to equilibrate in a vented fume hood. The soil was then transferred to the chamber and wetted from the bottom. To prevent water evaporation at the soil surface, the chamber was maintained at 100 percent relative humidity and a temperature of 25°C.

The volatilized triallate was trapped daily on polyurethane plugs and extracted and analyzed as described in Grover et al. (1978). The volatilization of triallate at an initial soil concentration of 10 ppmw was measured over a 29 day period in the absence of water evaporation. Calculation of the saturation concentration (C_{sat}) confirmed that the initial concentration of 10 ppmw was in dissolved form. Table 5 gives the values of each variable employed to calculate emissions of triallate using the Jury Reduced Solution volatilization model.

Figure 15 shows the comparison of the predicted and measured values for triallate at an initial soil concentration of 10 ppmw. The data plots indicate very good agreement between modeled and measured values. Figure 16 shows the comparison of the log-transformed data and confidence intervals. From the population of 32 observations, the correlation coefficient was calculated to be 0.998 with a mean modeled-to-measured ratio of 1.11. The p-value was calculated at 0.0001, and the confidence interval was 1.07 to 1.16.

TABLE 5.
VOLATILIZATION MODEL INPUT VALUES FOR TRIALLATE

Variable	Symbol	Units	Value	Reference/Equation
Initial soil concentration	C_o	mg/kg	10	Jury et at. (1980)
Soil depth	L	cm	10	Jury et at. (1980)
Soil dry bulk density	ρ_b	g/cm^3	1.34	Jury et at. (1980)
Soil particle density	ρ_s	g/cm^3	2.65	U.S. EPA (1988)
Gravimetric soil moisture content	w	percent	21	Calculated from Jury et al. (1980)
Water-filled soil porosoty	Θ	cm^3/cm^3	0.279	Jury et at. (1980)
Total soil porosity	ϕ	cm^3/cm^3	0.494	Jury et at. (1980)
Air-filled soil porosity	a	cm^3/cm^3	0.215	Jury et at. (1980)
Soil organic carbon	f_{oc}	fraction	0.0072	Calculated from Jury et al. (1980)
Organic carbon partition coefficient	K_{oc}	cm^3/g	3600	Jury et at. (1980)
Diffusivity in air	D_g^a	cm^2/d	3888	Jury et at. (1980)
Diffusivity in water	D_i^w	cm^2/d	0.432	Jury et at. (1980)
Henry's law constant	K_H	unitless	1.04 E-03	Jury et at. (1980)
Degradation rate constant	μ	1/day	0	Default to eliminate effects of degradation

The degree of agreement between modeled and measured emission flux values for triallate may be due to soil adsorption studies conducted to experimentally derive the organic carbon partition coefficient specific to the San Joaquin sandy loam used in the experiment. With experimentally derived values of K_{oc}, more accurate phase partitioning was possible resulting in an experimental-specific value of the effective diffusion coefficient (Equation 2). Appendix B contains the spreadsheet calculations for the bench-scale validation of the Jury Reduced Solution finite source volatilization model.

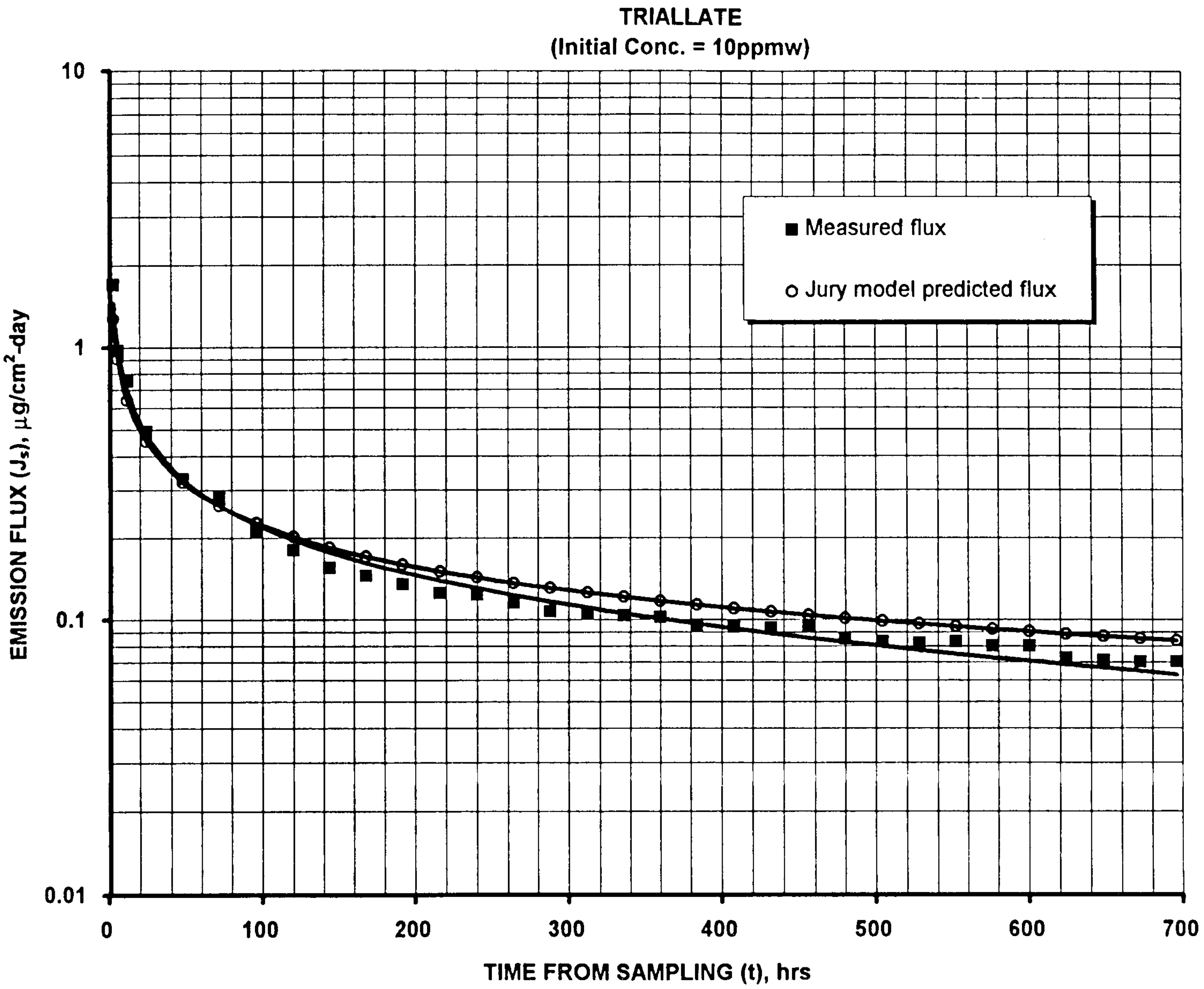

Figure 15
Predicted And Measured Emission Flux Of Triallate Versus Time

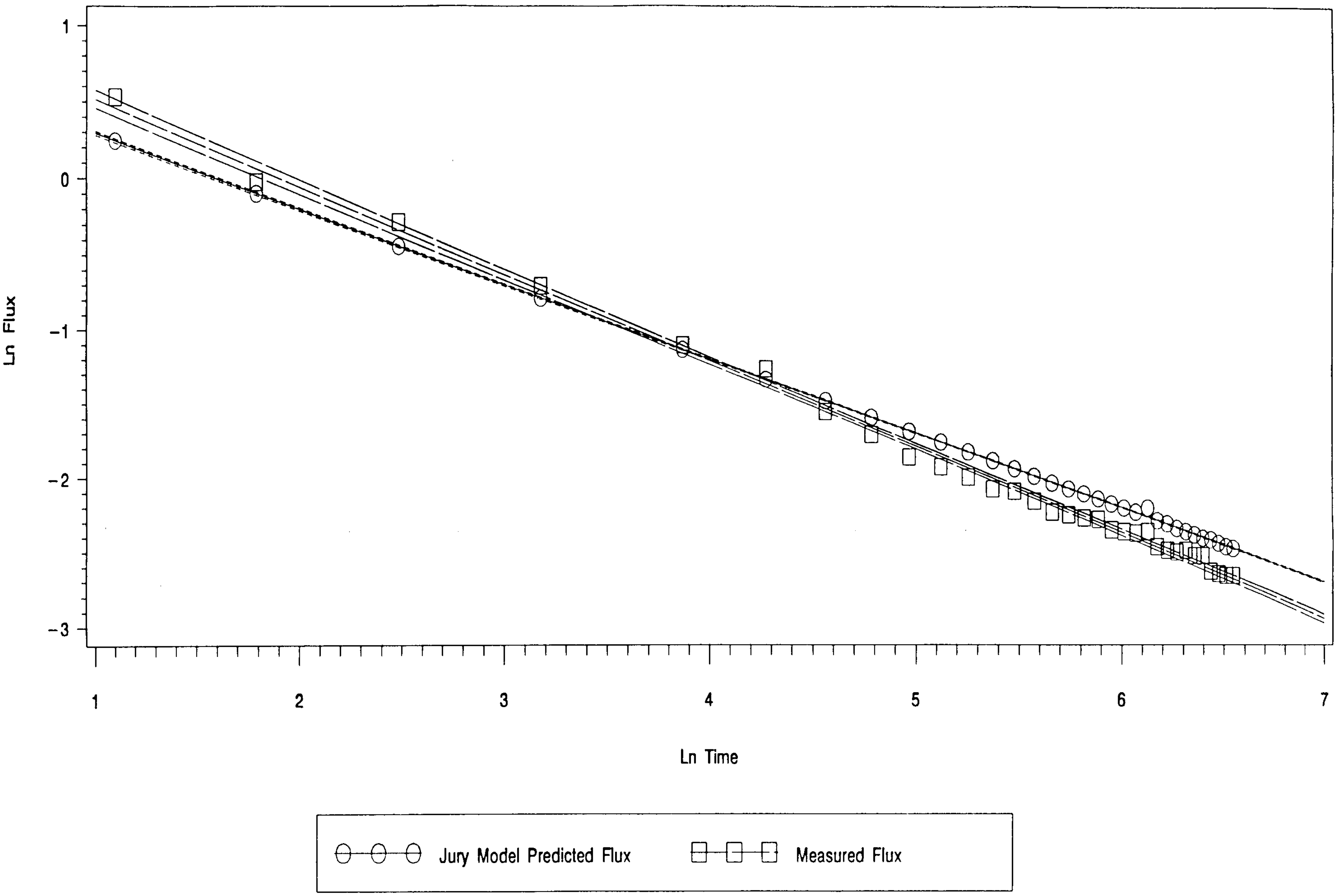

Figure 16
Comparison Of Log-Transformed Modeled And Measured Emission Flux Of Triallate

SECTION 4

PARAMETRIC ANALYSIS OF THE JURY VOLATILIZATION MODELS

This section presents the results of parametric analysis of the key variables of the Jury volatilization models (Equations 1 and 3). The Jury volatilization models are applicable for the case of no boundary layer resistance at the soil-air interface and no water flux through the soil column. Because the models are equivalent to the Mayer et al. (1974) solutions to the general diffusion equation (Equation 5), the parametric observations of Mayer et al. (1974) and Farmer, et al. (1980) are also directly applicable.

Jury et al. (1983) established the relationship between vapor and solute diffusion and adsorption by defining total phase concentration partitioning as it relates to the effective diffusion coefficient. The effective diffusion coefficient is a theoretical expression of the combination of soil parameters and chemical properties which govern the rate at which soil contaminants move to the surface to replace those lost by evaporation. As such, the effective diffusion coefficient is the rate-limiting factor governing the general diffusion equation in soils given the initial and boundary conditions for which the models are applicable. The remainder of this section discusses the key soil and nonsoil parameters used in the expression of the effective diffusion coefficient and the general diffusion equation.

4.1 AFFECTS OF SOIL PARAMETERS

In this section, the experimental results of Farmer, et al. (1980) are discussed as they relate to the effect of soil water content, soil bulk density, air-filled soil porosity, and temperature on diffusion in soil.

Soil Moisture Content

Farmer, et al. (1980) indicates that the effect of soil moisture content on the volatilization flux of contaminants through soils is exponential. Increasing soil water content decreases the pore spaces available for vapor diffusion and will decrease volatilization flux. In contrast, increasing soil water content has also been shown to increase the volatility of pesticides in soil under certain conditions (Gray, et al., 1965; and Spencer and Cliath, 1969 and 1970). In essence, the soil water content affects the contaminant adsorption capacity by competing for soil adsorption sites. Under these conditions, an increase in soil moisture above a certain point will tend to desorb contaminants, increasing the flux dependent on the relative water and contaminant adsorption isotherms.

Bulk Density

Soil compaction or bulk density also determines the porosity of soil and thus affects the diffusion through the soil. Experimental results from Farmer et al. (1980) indicate that soil bulk density also has an exponential effect on volatilization flux through the soil. From previous considerations of the effect of soil water content, a higher bulk density will have similar effects to that of an increased soil moisture content.

Soil Air-Filled Porosity

The effects of soil water content and soil bulk density on volatilization can be contributed to their effect on the air-filled porosity, which in turn is the major soil factor controlling volatilization. The effect of air-filled porosity is manifested in the expression of the effective diffusion coefficient. The effective diffusion coefficient, however, does not depend only on the amount of air-filled pore space. The presence of liquid film on the solid surfaces not only reduces porosity, but also modifies the pore geometry increasing tortuosity and the length of the gas passage. The Jury et al. (1983) expression of the effective diffusion coefficient uses the model of Millington and Quirk (1961) to account for the porosity and the tortuosity of soil as a porous medium.

Soil Temperature

The effect of soil temperature on the volatilization flux is multifunctional. The diffusion in air, D_g^a, is theoretically related to temperature, T, and the collision integral, Ω, in the following manner (Lyman, et al., 1990):

$$D_g^a \text{ (proportional to) } \frac{T^{0.5}}{\Omega(T)} \tag{15}$$

The exponential coefficient for temperature varies from 1.5 to 2 over a wide range of temperatures. Barr and Watts (1972) found that 1.75 gave the best values for gaseous diffusion. Farmer, et al. (1980) estimates the effective diffusion coefficient at temperature T_2 as:

$$D_2 = D_1 \, (T_2 \, / T_1)^{0.5} \tag{16}$$

where D_2 = Diffusion coefficient at T_2

D_1 = Diffusion coefficient at T_1

T = Absolute temperature.

A temperature increase will effect the vapor pressure function of the Henry's Law constant, which causes an increase in the vapor concentration gradient across the soil layer. In actual fact, temperature gradients will exist across the soil due primarily to seasonal variations. Vapor diffusion is influenced by such gradients; however, these effects of fluctuating soil temperatures will tend to cancel one another over time.

4.2 AFFECTS OF NONSOIL PARAMETERS

The nonsoil variables in the Jury volatilization models include the initial soil concentration, C_o, the Henry's law constant (K_H), the soil/water partition coefficient, (K_D) and the depth of contaminant incorporation (L).

Initial Soil Concentration

The effect of change in the initial soil concentration is linear; i.e., an increase in C_o of 100 percent causes an increase in the emission rate of 100 percent. Probably the greatest degree of uncertainty in the value of C_o is likely to be either insufficient soil sampling to adequately characterize site soil concentrations, or the variability in percent recovery of contaminants as it applies to existing sampling and analysis methods for organic compounds in soils. Typically, present extraction and analysis method recovery variability increases the likelihood of underprediction of the emission rate (i.e., more contaminant is present in the soil than is reported by sampling and analysis methods).

Henry's Law Constant and Soil/Water Partition Coefficient

Jury et al. (1984) showed that a given chemical can be grouped into three main categories depending on the ratio K_D/K_H. These categories are defined as a function of which phase dominates diffusion. A Category I chemical is dominated by the vapor-phase, a Category III chemical by the liquid-phase, and Category II chemicals by vapor-phase diffusion at low soil water content and liquid-dominated at high water content. Desorption from the solid-phase to the liquid-phase is a function of the soil/water partition coefficient, while volatilization from the liquid to the vapor-phase is a function of the Henry's law constant. Therefore, the interstitial vapor density, and thus emission flux, is directly proportional to K_H and inversely proportional to K_D. Because the Jury volatilization models do not account for a soil-air boundary layer, the effects of K_H and K_D are exponential for all three categories of chemicals.

Depth of Contaminant Incorporation

The Jury Reduced Solution finite source model accounts for diffusion across both the upper and lower boundaries. Therefore for chemicals with high effective diffusion coefficients, the residual soil concentration will decrease rapidly. In this regard, the emission flux curve will become asymptotic more rapidly than for the semi-infinite case (Equation 3). The exponential term $[1 - \exp(-L^2/4\, D_E t)]$ in Equation 1 accounts for diffusion across the lower boundary such that the term decreases rapidly with time for small values of L and large values of D_E.

SECTION 5

CONCLUSIONS

From the results of this study, it can be concluded that for the compounds included in the experimental data, both models showed good agreement with measured data given the conditions of each test. Each model demonstrated superior agreement with bench-scale measured values and to a lesser extent the infinite source model with pilot-scale data. The results indicate high correlation coefficients across all experimental data with mean modeled-to-measured ratios as low as 0.37 and as high as 7.8.

From a review of test conditions, it was concluded that the bench-scale studies better approximated the initial and boundary conditions of the infinite source model. This is evident in the lower modeled-to-measured mean ratios and narrow 95 percent confidence intervals. Although the pilot-scale study data showed reasonable agreement with predicted values, questions remain as to whether the test conditions were in agreement with model assumptions and accurately replicated all model boundary conditions. Overall, each model provided reasonably accurate predictions.

Clearly, this validation study is limited by the range of conditions simulated, the assumptions under which the models operate, and the initial and boundary conditions of each model. Important limitations include:

1. The duration of the experiments examined range from 7 to 36 days. Model performance for longer periods could not be validated.

2. Both models assume no mass flow of contaminants due to water movement in the soil. Mass flow due to capillary action or redistribution of contaminates due to rain events may be significant if applicable to site-specific condition.

3. The models are valid only if the effective diffusion coefficient in soil is constant. This assumes isotropic soils and completely homogeneous incorporation of contaminants. In reality, soils are usually heterogeneous, with properties that change with depth (e.g., fraction of organic carbon, water content, porosity, etc.). The user will need to carefully consider the characterization of soil properties before assigning model input parameters.

4. The equilibrium partitioning relationships used in the models are no longer valid for pure-phase chemicals or when high dissolved concentrations are present. Therefore, the models should not be used when these conditions exist.

5. The models do not consider the effects of a soil-air boundary layer on the volatilization rate. For chemicals with Henry's law constants less than approximately 2.5×10^{-5}, volatilization is highly dependent on the thickness of the boundary layer (Jury et al., 1984). A boundary layer will restrict volatilization if the maximum flux through the boundary layer is small compared to the rate at which the contaminant moves to the surface. In this case, the volatilization rate is inversely proportional to the boundary layer thickness.

6. In the case of the infinite source model, validation for chemicals with relatively high Henry's law constants requires that the depth of contamination be sufficient to prevent loss at the lower boundary over the duration of the experiment, i.e., $L > (18.4\ D_E\ t)^{1/2}$. Although this study indicates that the Jury Infinite Source model exhibited a relatively small maximum error (i.e., 134% of the Mayer et al. finite source model total mass loss for benzene), any future validation studies should

maintain a sufficient depth of incorporation to prevent violation of the model boundary conditions.

7. No experimental data could be found in the literature for validation of the Jury Reduced solution finite source model for compounds with high Henry's law constants.

Emission rates predicted by the Jury Infinite Source volatilization model and the Jury Reduced Solution finite source volatilization model indicate good correlation to measured emission rates under controlled conditions, but predicted values for field conditions would be subject to error because the boundary conditions and environmental conditions are not as well defined as they are in the laboratory. Nonetheless, results of this study indicate that both models should make reasonable estimates of loss through volatilization at the soil surface given the boundary conditions of each model.

REFERENCES

Balfour, W. D., B. M. Eklund, and S. J. Williamson. Measurement of Volatile Organic Emissions from Subsurface Contaminants. In *Proceedings of* the *National Conference on Management of Uncontrolled Hazardous Waste Sites*. September 1984, pp. 77-81. Hazardous Materials Control Research Institute, Silver-Springs, Maryland.

Barr, R. F. and H. F. Watts. 1972. Diffusion of Some Organic and Inorganic Compounds in Air. J. Chem. *Eng. Data* 17:45-46.

Carslaw, H. S., and J. C. Jaeger. 1959. *Conduction of Heat in Solids.* zd Edition Oxford University Press, Oxford.

Environmental Quality Management, Inc. 1994. *A Comparison of Soil Volatilization Models in Support of Superfund Soil Screening Level Development. U.S.* Environmental Protection Agency, Contract No. 68-D30035, Work Assignment No. 0-25.

Farmer, W. J., K. Igue, W. F. Spencer, and J. P. Martin. 1972. Volatility of Organochlorine Insecticides from Soil. I and II Effects. *Soil Sci. Soc. Amer. Proc.* 36:443-450.

Farmer, W. J., and J. Letey. 1974. *Volatilization Losses of Pesticides From Soils.* Office of Research and Development. EPA-660/2-74/054.

Farmer, W. J., M. S. Yang, J. Letey, and W. F. Spencer. 1980. *Land Disposal of Hexachlorobenzene Wastes.* Office of Research and Development. EPA-600/2-80/119.

Gray, R. A., and A. J. Weierch. 1965. Factors Affecting the Vapor Loss of EPTC from Soil. *Weeds* 13:141-147.

Grover, R., W. F. Spencer, W. J. Farmer, and T. D. Shoup. 1978. Triallate Vapor Pressure and Volatilization from Glass Surfaces. *Weed Sci.,* 26:505-508.

Hill, F. B., V. P. Aneja, and R. M. Felder. 1978. A Technique for Measurement of Biogenic Sulfur Emission Fluxes. *J. Env. Sci. Health* AIB (3), pp. 199-225.

Howard, P. H., R. S. Boethling, W. F. Jarvis, W. M. Meylan, and E. O. Michaelenko. 1991. *Handbook* of *Environmental Degradation Rates.* Lewis Publishers, Chelsea, Michigan.

Jury, W. A., R. Grover, W. F. Spencer, and W. J. Farmer. 1980. Modeling Vapor Losses of Soil-lncorporated Triallate. *Soil Science Society Am. J.,* 44:445-450.

Jury, W. A., W. F. Spencer, and W. J. Farmer. 1983. Behavior Assessment Model of Trace Organics in Soil: I. Model Description. *J. Environ. Qual.*, Vol. 12, No. 4:558:564.

Jury, W. A., W. J. Farmer, and W. F. Spencer. 1984. Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity. *J. Environ. Qual.,* Vol. 13, No. 4:567-572.

Jury, W. A., D. Russo, G. Streile, and H. El Abd. 1990. Evaluation of Volatilization by Organic Chemicals Residing Below the Soil Surface. *Water Resources Res.*, Vol. 26, No. 1:13-20.

Kienbusch, M. *Measurement* of *Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber - User's Guide*. Report to EPA-EMSL, Las Vegas under EPA Contract No. 68-02-3889, Work Assignment No. 18, December 1985.

Kienbusch, M. and D. Ranum. 1986. *Validation of Flux Chamber Emission Measurements on Soil Surface* - Draft Report to EPA-EMSL, Las Vegas, Nevada.

Kienbusch, M., W. D. Balfour, and S. Williamson. *The Development of an Operations Protocol for Emission Isolation Flux Chamber Measurements on Soil Surfaces.* Presented at the 79th Annual Meeting of the Air Pollution Control Association (Paper 86-20.1), Minneapolis, Minnesota, June 22-27, 1986.

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1990. *Handbook* of *Chemical Property Estimation Methods.* American Chemical Society, Washington, D.C.

Millington, R. J., and J. M. Quirk. 1961. Permeability of Porous Solids. *Trans. Faraday* Soc. 57:1200-1207.

Radian Corporation. *Soil Gas Sampling Techniques* of *Chemicals* for *Exposure Assessment - Data Volume.* Report to EPA-EMSL, Las Vegas under EPA Contract No. 68-02-3513, Work Assignment No. 32, March 1984.

Radian Corporation. *Short-term Fate and Persistence* of *Motor Fuels in Soils.* Report to the American Petroleum Institute, Washington, D.C. July 1989.

Spencer, W. F., M. Cliath, and W. J. Farmer. 1969. Vapor Density of Soil Applied HEOD as Related to Soil Water Content, Temperature, and HEOD Concentration. *Soil Sci. Soc. Amer. Proc.* 33:509-511.

Spencer, W. F., and M. Cliath. 1970. Vapor Density and Apparent Vapor Pressure of Lindane (γ-BHC). *J. Agr. Food Chem. 18*:529-530.

Spencer, W. F., T. D. Shoup, M. M. Cliath, W. J. Farmer, and R. Haque. 1979. Vapor Pressures and Relative Volatility of Ethyl and Methyl Parathion. *J. Agric. Food Chem.*, 27:273-278.

Spencer, W. F. 1970. Distribution of Pesticides Between Soil, Water and Air. In *Pesticides in the Soil: Ecology, Degradation and Movement.* A symposium, February 25-27, 1970. Michigan State University.

U.S. Environmental Protection Agency. 1988. *Superfund Exposure Assessment Manual.* Office of Emergency and Remedial Response. EPA-540/1-88-001.

U.S. Environmental Protection Agency. 1990. *Procedures for Conducting Air Pathway Analyses for Superfund Activities, Interim Final Documents: Volume 2 - Estimation of Baseline Air Emissions at Superfund Sites.* Office of Air Quality Planning and Standards. EPA-450/1-89-002a.

U.S. Environmental Protection Agency. 1991. *Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part B).* Office of Emergency and Remedial Response. Publication No. 9285.7-01B.

U.S. Environmental Protection Agency. 1991a. *Database of Emission Rate Measurement Projects - Technical Note.* Office of Air Quality Planning and Standards. EPA-450/1 -91 003.

U.S. Environmental Protection Agency. 1994. *Technical Background Document for Soil Screening Guidance - Review Draft.* Office of Solid Waste and Emergency Response. EPA-540/R-94/102.

U.S. Environmental Protection Agency. 1994a. *CHEMDAT8 Data Base of Compound Chemical and Physical Properties.* Office of Air Quality Planning and Standards Technology Transfer Network, CHIEF Bulletin Board. Research Triangle Park, North Carolina.

APPENDIX A

VALIDATION DATA FOR THE JURY INFINITE SOURCE MODEL

DIELDRIN 5 PPM
(1 of 2)

Chemical	Sample Point	Initial soil conc.,	Initial soil conc.,	Emitting area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility	Soil organic carbon,	Saturation conc.,	C_o>C_{sat}	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(μg/m^2 -	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		Kg/L	Kg/L	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	min)	(cm^3/g)
Dieldrin	1	5	5.00E-06	27.55	0.5	GilaSlit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	200	10900
Dieldrin	2	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	115	10900
Dieldrin	3	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	75	10900
Dieldrin	4	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	65	10900
Dieldrin	5	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	60	10900
Dieldrin	6	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	55	10900
Dieldrin	7	5	5.00E-06	27.55	0.5	Gila Slit Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	40	10900

DIELDRIN 5 PPM
(2 of 2)

Chemical	Soil/water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux emission flux	Time, t	t > L^2/14.4 D$_E$	Infinite source model emission flux
	K_D	D_g^a	D_i^w	D_E	K_H	ϕ	a		Cumulative		
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	(µg/cm^2-day)	(hours)	(Yes/No)	(µg/cm^2-day)
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.2000	24	No	0.0714
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.1150	72	No	0.0412
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0750	120	No	0.0319
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0650	144	No	0.0292
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0600	168	No	0.0270
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0550	216	No	0.0238
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0400	288	No	0.0206

DIELDRIN 10 PPM
(1 of 2)

Chemical	Sample Point	Initial soil conc.,	Initial soil conc.,	Emitting area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility,	Soil organic carbon,	Saturation conc.,	$C_o > C_{sat}$	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(ng/cm^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(g/cm^3)	(g/cm^3)	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-day)	(cm^3/g)
Dieldrin	1	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0 1870	0.0058	12	No	400	10900
Dieldrin	2	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	260	10900
Dieldrin	3	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	140	10900
Dieldrin	4	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	110	10900
Dieldrin	5	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	105	10900
Dieldrin	6	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0 1870	0.0058	12	No	90	10900
Dieldrin	7	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	0.1870	0.0058	12	No	85	10900

DIELDRIN 10 PPM
(2 of 2)

Chemical	Soil/ water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	t > $L^2/14.4\ D_E$	Infinite source model emission flux
	K_D	D_g^a	D_i^w	D_E	K_H	ϕ	a		Cumulative		
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	(µg/cm^2-day)	(hrs)	(Yes/No)	(µg/cm^2-day)
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.4000	24	No	0.1428
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.2600	72	No	0.0825
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.1400	120	No	0.0639
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.1100	144	No	0.0583
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.1050	168	No	0.0540
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0900	216	No	0.0476
Dieldrin	63.22	0.0125	4.74E-06	1.32E-08	0.00011	0.7170	0.6420	0.0850	288	No	0.0412

LINDANE 5 PPM
(1 of 2)

Chemical	Sample Point	Initial soil conc.	Initial soil conc.	Emitting area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility,	Soil organic carbon,	Saturation conc.,	$C_o>C_{sat}$	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}			K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(g/cm$^{3)}$	(g/cm$^{3)}$	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	(ng/cm^2-day)	(cm^3/g)
Lindane	1	5	5.00E-06	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	500	1380
Lindane	2	5	5.00E-06	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	160	1380
Lindane	3	5	5.00E-06	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	60	1380
Lindane	4	5	5.00E-06	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	40	1380

LINDANE 5 PPM
(2 of 2)

Chemical	Soil/water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	$t > L^2/14.4\ D_E$	Infinite source model emission flux	Finite source model emmision flux	Infinite source model error
	K_D	D_g^a	D_i^w	D_E	K_H	ϕ	a		Cumulative				
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	($\mu g/cm^{2-}$day)	(hours)	(Yes/No)	($\mu g/cm^{2-}$day)	($\mu g/cm^{2-}$day)	(percent)
Lindane	8.00	0.0176	5.57E-06	1.80E-07	0.00014	0.7170	0.6420	0.5000	24	No	0.2641	0.2641	0.0000
Lindane	8.00	0.0176	5.57E-06	1.80E-07	0.00014	0.7170	0.6420	0.1600	72	Yes	0.1525	0.1510	0.9604
Lindane	8.00	0.0176	5.57E-06	1.80E-07	0.00014	0.7170	0.6420	0.0600	120	Yes	0.1181	0.1086	8.7891
Lindane	8.00	0.0176	5.57E-06	1.80E-07	0.00014	0.7170	0.6420	0.0400	168	Yes	0.0998	0.0797	25.2965

LINDANE 10 PPM
(1 OF 2)

Chemical	Sample Point	Initial soil conc.,	Initial soil conc.,	Emitting area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility,	Soil organic carbon,	Saturation conc.,	C_o>C_{sat}	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(ng/cm^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(g/cm^3)	(g/cm^3)	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-day)	(cm^3/g)
Lindane	1	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	1160	1380
Lindane	2	10	1.00E-05	27.55	0.5	Gila Silt Loarn	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	320	1380
Lindane	3	10	1.00E-05	27.55	0.5	Gila Silt Loam	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	140	1380
Lindane	4	10	1.00E-05	27.55	0.5	Gila Silt Loarn	0.75	2.65	0.10	0.0750	4.2000	0.0058	34	No	90	1380

LINDANE 10 PPM
(2 of 2)

Chemical	Soil/water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	$t > L^2/14.4\ D_E$	Infinite source model emission flux	Finite source model emmision	Infinite source model error
	K_D	D_g^a	D_i^w	D_E	K_H	ϕ	a	($\mu g/cm^2$	Cumulative		($\mu g/cm^2$	($\mu g/cm^2$	
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	-day)	(hours)	(Yes/No)	-day)	-day)	(percent)
Lindane	8.00	0.0176	5.57E-.06	1.80E-07	0.00014	0.7170	0.6420	1.1600	24	No	0.5282	0.5282	0.0000
Lindane	8.00	0.0176	5.57E-.06	1.80E-07	0.00014	0.7170	0.6420	0.3200	72	Yes	0.3049	0.3020	0.9604
Lindane	8.00	0.0176	5.57E-.06	1.80E-07	0.00014	0.7170	0.6420	0.1400	120	Yes	0.2362	0.2171	8.7891
Lindane	8.00	0.0176	5.57E-.06	1.80E-07	0.00014	0.7170	0.6420	0.0900	168	Yes	0.1996	0.1593	25.296

BENZENE 110 PPMW
(1 of 2)

Chemical	Sample Point	Initial soil conc.,	Initial soil conc.,	Flux chamber surface area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility,	Soil organic carbon,	Saturation conc.,	C_o>C_{sat}	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(µg/cm^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(Kg/L)	(Kg/L)	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-day)	(cm^3/g)
Benzene	3	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	2760	57
Benzene	4	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	9000	57
Benzene	5	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	910	57
Benzene	6	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	400	57
Benzene	7	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	290	57
Benzene	8	110	1.10E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	1780	0.006	862	No	0	57

BENZENE 110 PPMW
(2 of 2)

Chemical	Soil/water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	H	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	$t > L^2/14.4\ D_E$	Infinite source model emission flux	Finite source model emmision flux	Infinite source model error
	K_D	D_g^a	D_l^w	D_E		K_H	ϕ	a	(μg/cm^2	Cumulative		(μg/cm^2	(μg/cm^2	
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(atm-m^3/mol)	(unitless)	(unitless)	(unitless)	-day)	(hours)	(Yes/No)	-day)	-day)	(percent)
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	397	26.40	No	1207	1207	0.0000
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	1296	76.25	Yes	710	710	0.0002
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	131	119.73	Yes	567	567	0.0253
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	58	506.83	Yes	275	209	31.5053
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	42	698.55	Yes	235	135	73.9743
Benzene	0.34	0.0870	9.80E-06	2.14E-03	0.00543	0.22263	0.4340	0.2840	0	863.17	Yes	211	92	128.3941

TOLUENE 880 PPMW
(1 OF 2)

Chemical	Sample Point	Initial soil conc.	Initial soil conc.	Flux chamber surface area	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility	Soil organic carbon,	Saturation conc.,	$C_o>C_{sat}$	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o		(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(μg/m^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(kg/L)	(kg/L)	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-min)	(cm^3/g)
Toluene	3	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	14800	131
Toluene	4	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	17300	131
Toluene	5	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	4910	131
Toluene	6	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	1340	131
Toluene	7	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	830	131
Toluene	8	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	340	131
Toluene	9	880	8.80E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	558	0.006	522	Yes	260	131

TOLUENE 880 PPMW
(2 OF 2)

Chemical	Soil/water part. coeff., K_D (cm^3/g)	Diffusivity in air, D_g^a (cm^2/s)	Diffusivity in water, D_l^w (cm^2/s)	Effective diffusion coefficient, D_E (cm^2/s)	H (atm-m^3/mol)	Henry's law constant, K_H (unitless)	Total soil porosity, ϕ (unitless)	Air-filled soil porosity, a (unitless)	Measured emission flux ($\mu g/cm^{2}$-day)	Time, t Cumulative (hours)	$t > L^2/14.4\ D_E$ (Yes/No)	Infinite source model emission flux ($\mu g/cm^{2}$-day)	Finite source model emmision flux ($\mu g/cm^{2}$-day)	Infinite source model error (percent)
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	2131	26.40	No	7524	7524	0.0000
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	2491	76.25	No	4427	4427	0.0000
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	707	119.73	No	3533	3533	0.0001
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0 00637	0.26117	0.4340	0.2840	193	506.83	Yes	1717	1613	6.4806
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	120	698.55	Yes	1463	1231	18.8541
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	49	863. 17	Yes	1316	978	34.5481
Toluene	0.79	0.0870	8.60E-06	1.30E-03	0.00637	0.26117	0.4340	0.2840	37	1007.17	Yes	1218	800	52.2568

ETHYLBENZENE 310 PPMW
(1 of 2)

Chemical	Sample Point	Initial soil conc.	Initial soil conc.	Flux chamber surface	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravimetric soil moisture,	Water-filled soil porosity,	Solubility	Soil organic carbon,	Satura-tion conc.,	$C_o>C_{sat}$	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o	area	(L)		ρ_b	ρ_s	w	Θ	S	f_{oc}	C_{sat}		(μg/cm^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(g/cm$^{3)}$	(g/cm$^{3)}$	(wt. fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-min)	(cm^3/g)
Ethylbenzene	3	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	2640	221
Ethylbenzene	4	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	1700	221
Ethylbenzene	5	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	1080	221
Ethylbenzene	6	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	250	221
Ethylbenzene	7	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	180	221
Ethyibenzene	8	310	3.1 0E-04	1300	91	Loamy Sand	1.5	2.65	0.10	0.1500	173	0.006	257	Yes	0	221

ETHYLBENZENE 310 PPMW
(2 of 2)

Chemical	Soil/ water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	$t > L^2/14.4\ D_E$	Infinite source model emission flux	Finite source model emmision flux	Infinite source model error
	K_D	D_g^a	D_l^w	D_E	K_H	ϕ	a	(μg/cm^{2-}	Cumulative		(μg/cm^{2-}	(μg/cm^{2-}	
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	day)	(hours)	(Yes/No)	day)	day)	(percent)
Ethylbenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	380	26.40	No	2162	2162	0.0000
Ethylbenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	245	76.25	No	1272	1272	0.0000
Ethylbenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	156	119.73	No	1015	1015	0.0000
Ethylbenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	36	506.83	Yes	493	488	1.0596
Ethylbenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	26	698.55	Yes	420	402	4.6357
Ethyibenzene	1.33	0.0750	7.80E-06	8.64E-04	0.32021	0.4340	0.2840	0	863.17	Yes	373	343	10.0850

APPENDIX B

VALIDATION DATA FOR THE JURY REDUCED SOLUTION FINITE SOURCE MODEL

TRIALLATE 10 PPM
(1 OF 2)

Chemical	Sample Point	Initial soil conc.	Initial soil conc.	Emitting	Soil Depth	Soil Type	Soil bulk density,	Soil particle density,	Gravi-metric soil moisture, w	Water-filled soil porosity,	Solubility	Soil organic carbon,	Saturation conc.,	$C_o > C_{sat}$	Measured emission flux	Organic carbon part. coeff.,
		C_o	C_o	area	(L)		ρ_b	ρ_s	(wt.	Θ	S	f_{oc}	C_{sat}		(µg/cm^2	K_{oc}
		(mg/kg)	(g/g)	(cm^2)	(cm)		(Kg/L)	(Kg/L)	fraction)	(unitless)	(mg/L)	(fraction)	(mg/kg)	(Yes/No)	-day)	(cm^3/g)
Triallate	1	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	1.700	3600
Triallate	2	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.975	3600
Triallate	3	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.750	3600
Triallate	4	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.490	3600
Triallate	5	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.330	3600
Triallate	6	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.280	3600
Triallate	7	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.210	3600
Triallate	8	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.180	3600
Triallate	9	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.155	3600
Triallate	10	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.145	3600
Triallate	11	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.135	3600
Triallate	12	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.125	3600
Triallate	13	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.123	3600
Triallate	14	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.115	3600
Triallate	15	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.107	3600
Triallate	16	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.105	3600
Triallate	17	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.103	3600
Triallate	18	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.102	3600
Triallate	19	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.095	3600
Triallate	20	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.094	3600
Triallate	21	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.093	3600
Triallate	22	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.094	3600
Triallate	23	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.085	3600
Triallate	24	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.083	3600
Triallate	25	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.082	3600
Triallate	26	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	1 05	No	0.083	3600
Triallate	27	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.00.72	105	No	0.080	3600
Triallate	28	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.00.72	105	No	0.080	3600
Trlallate	29	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.00.72	105	No	0.072	3600
Triallate	30	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0 071	3600
Triallate	31	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0 070	3600
Triallate	32	10	1.00E-05	30	10	San Joaquin Sandy Loam	1.34	2.65	0.21	0.2787	4.00	0.0072	105	No	0.070	3600

TRIALLATE 10 PPM
(2 OF 2)

Chemical	Soil/ water part. coeff.,	Diffusivity in air,	Diffusivity in water,	Effective diffusion coefficient,	Henry's law constant,	Total soil porosity,	Air-filled soil porosity,	Measured emission flux	Time, t	Jury finite source model emission flux
	K_D	$D_g{}^a$	$D_l{}^w$	D_E	K_H	ϕ			Cumulative	
	(cm^3/g)	(cm^2/s)	(cm^2/s)	(cm^2/s)	(unitless)	(unitless)	(unitless)	(μg/cm^{2}·day)	(hours)	(μg/cm^{2}·day)
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	1.700	3	1.278
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.975	6	0.904
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.750	12	0.639
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.490	24	0.452
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.330	48	0.320
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.280	72	0.261
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.210	96	0.226
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.180	120	0.202
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.155	144	0.184
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.145	168	0.171
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.135	192	0.160
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.125	216	0.151
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.123	240	0.143
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.115	264	0.136
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.107	288	0.130
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.105	312	0.125
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.103	336	0.121
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.102	360	0.117
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.095	384	0.113
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.094	408	0.110
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.093	432	0.107
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.094	456	0.104
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.085	480	0.101
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.083	504	0.099
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.082	528	0.096
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.083	552	0.094
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.080	576	0.092
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.080	600	0.090
Triailate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.072	624	0.085
Trialiate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.071	648	0.087
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0.070	672	0.085
Triallate	25.92	0.0450	5.00E-06	4.14E-08	0.00104	0.4943	0.2156	0 070	696	0.084