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Fate and transport of organics in soil: model predictions and experimental results

Brian D. Symons, Ronald C. Sims, William J. Grenney

ABSTRACT: Laboratory batch reactors were used to generate quantitative information about the fate of polynuclear aromatic hydrocarbon (PNA) compounds in soil systems. First-order degradation rates and equilibrium partition coefficients determined in laboratory studies were used in the Vadose Zone Interactive Processes (VIP) mathematical model to predict the fate and behavior of the PNA compounds as a function of time and soil depth. Predicted model results were compared with independent laboratory soil column studies for model validation. The VIP model provided a good approximation of the degradation and transport of the seven PNA compounds evaluated after 6 months of incubation in soil. Sensitive parameters in the VIP model included degradation rates and initial soil concentrations. *J. Water Pollut. Control Fed.*, **60**, 1684 (1988).

KEYWORDS: leachate, soil, organic chemicals, (polynuclear aromatic hydrocarbons), mathematical model, fate, (transport process), degradation, (vadose zone).

A validated mathematical model provides a tool for integrating and interpreting the complex physical, chemical, and biological factors affecting degradation, immobilization, and transformation of organic compounds in soils. A validated unsaturated zone model is important for predicting the potential for groundwater contamination from organic compounds applied to soils in the vadose zone.

The Regulatory and Investigative Treatment Zone model (RITZ) was presented for use in banning specific hazardous wastes from land treatment.¹ The model is based on an approach for simulating the fate of pesticides in soils.² An expanded RITZ model has incorporated features that increase its utility for evaluating the soil treatability of a waste.³ A description of the Vadose Zone Interactive Processes (VIP) model (the expanded RITZ model, RITZE) and experimental results using three polynuclear aromatic (PNA) compounds was presented.⁴ Results indicated that the VIP model closely simulated fate and behavior of three PNA compounds—anthracene, fluoranthene, and naphthalene—in soil columns. Other work provided a basis for the laboratory model validation examination using a complex environmental waste mixture.⁴

Laboratory validation for the complex waste was based on an approach described elsewhere.⁵ This paper describes

the usefulness of the VIP model and the model construct. Implementation of the laboratory validation is reviewed and model performance is compared with acceptance criteria. Laboratory validation is a precursor to a currently conducted field validation of the model.⁶ Laboratory evaluation in a more controlled environment provided a link between verification of model algorithms and field validation.

The acceptance criteria used in this laboratory validation were presented⁷ for use in validating the Pesticide Root Zone Model (PRZM). It was indicated that, for screening applications, a model should replicate field data (concentration profile, total mass, flux past root zone, soil-water content, and storage) within an order of magnitude and site specific applications within a factor of two. Optimally, under controlled conditions in the laboratory, the VIP model should replicate laboratory data with much less variability than would be expected in a field validation.

Model Description

The VIP model is a mechanistic model developed as a predictive tool for numerically integrating and describing the physical, chemical, and biological processes in the soil unsaturated zone. It integrates degradation and immobilization processes of organic compounds in the vadose zone. The U. S. Environmental Protection Agency³ (EPA) is using the VIP (formerly RITZE) model as a predictive tool for land treatment demonstrations.

Model input. An organic constituent applied to the soil is acted on by degradation and immobilization mechanisms, which are in turn affected by soil, waste, site, and operational factors. Table 1 presents factors and specific input information related to degradation and immobilization required by the VIP model.

Model output. The model output predicts constituent concentration at incremental depths in the soil profile at different times during the waste application period. Specific outputs include

- mass balance describing the mass of constituent remaining, degraded, leached, and volatilized;
- constituent concentration profiles for the water, oil, air, and soil phases;

Table 1—Design/operational variables required for use in the VIP Model.³

Soil properties	Environmental properties	Waste properties
Porosity	Constituent concentration, ppm	Van't Hoff-Arrhenius temperature coefficient
Bulk density, g/cm ³	Weight fraction of oil, kg/kg	Site temperature, °C
Moisture coefficient	Weight fraction of water, kg/kg	Mean daily recharge rate, m ³ /m ² · d
Saturated hydraulic conductivity, m/d	Waste density, g/cm ³	
Initial constituent concentration, water, air, and soil, g/m ³	Oil density, g/cm ³	
	Constituent detection limit, g/m ³	
Operational factors	Biodegradation information	Immobilization information
Plow zone depth, m	Constituent decay rate, d ⁻¹	K _o = partitioning of constituent between water and oil (waste) phases
Treatment zone depth, m	Oil decay rate, d ⁻¹	K _d = partitioning of constituent between water and soil phases
Waste application rate, g waste/100 g soil		K _n = partitioning of constituent between water and air phases
Application period, days		
Application frequency, days		

- fractional proportion of air, water, and oil in the soil pore space; and
- constituent concentration in the groundwater.

Model assumptions. Model assumptions were required to determine input parameters for soil, site, waste, and operational factors, and for inputs related to degradation and immobilization processes. Some of these assumptions were made to simplify soil system and numerical equation complexity. The soil is assumed to be a homogeneous system with constant porosity, bulk density, and chemical characteristics. Waste is a mixture of oil, water, specific organic constituents, and inert matter. The applied waste has constant characteristics of density and composition throughout the application period. Steady-state conditions are assumed during any month or season (for example, constant recharge rate and site temperature). Waste is applied periodically to the soil system in which only four phases exist: soil, water, air, and oil. The oil is completely mixed in and does not penetrate below the zone of waste application.

Biodegradation is the primary decay mechanism. Photodegradation and other abiotic decay mechanisms are insignificant. Biodegradation of waste constituents and oil follows first order kinetics as expressed by a decay coefficient. Immobilization reactions are governed by constant soil pore velocity, diffusion, and dispersion with depth. Mass transfer rates between the soil, oil, air, and water phases are virtually instantaneous.

Detailed description and listings of the VIP model can be found elsewhere.^{3,4,6,7}

Laboratory Validation of the Model

A specific design scenario was developed for a laboratory validation of the model. It is based on current design and management practices in the petroleum refining industry for land treatment of petroleum refinery wastes that are known to contain hazardous organic constituents. Validation using land treatment of petroleum refinery wastes was selected because the 1984 amendments to the Resource Conservation and Recovery Act (RCRA) prohibit

land disposal of hazardous wastes beyond specific dates unless EPA determines that a land disposal method protects human health and the environment. Laboratory experiments were designed to test the hypothesis that migration of hazardous constituents from the application zone would not occur for as long as the petroleum wastes remained hazardous.⁸

The American Petroleum Institute⁹ (API) has sponsored studies to determine the range of site, waste, and operating conditions found at petroleum refinery land treatment facilities. Based on these studies, waste, site, and operating conditions were determined.

Waste description. The hazardous waste was a composite of three types of petroleum refinery wastes, including API separator sludge, dissolved air flotation float, and slop oil emulsion solids. Equal volumes of each type of waste were mixed before soil application. The composite waste was analyzed for total oil and grease, total solids, volatile organic constituents, base neutral/acid extractable organic constituents, and metals. The average oil and grease content of the composite waste was 18.9% by weight, the average solids content was 14.5% by weight, and thus, the water content was 66.6%. Waste density was 1.02 g/cm³. Polynuclear aromatic hydrocarbon (PNA) compounds were selected for this validation because they occur in petroleum and other industrial wastes, and represent a class of compounds with toxic and mutagenic potential. These compounds were identified and quantified in the composite petroleum waste using EPA Method 8310, high performance liquid chromatography (HPLC). Table 2 lists the concentrations of PNA compounds detected in the composite waste.

Soil characterization. Two different soil types were used, Kidman sandy loam and Nunn clay loam. Soils were obtained from uncontaminated agricultural land located near Kaysville, Utah, and Fort Collins, Colo. To preserve the *in-situ* soil profile for soil column studies, soils were collected in 15-cm increments to a depth of 1.5 m. Each 15-cm soil increment was sieved separately through a 2 mm (#10) sieve before use in batch degradation or soil column

Table 2—Average initial PNA constituent concentrations in the waste.

Compound	Average $\mu\text{g/g}$	Standard deviation	Coefficient of variation	Number of samples
PNA:				
Naphthalene	161	44.3	0.276	9
Acenaphthylene	<100			
Acenaphthene	203	85.5	0.421	18
Fluorene	65.5	14.2	0.217	18
Phenanthrene	605	110	0.182	18
Anthracene	80.3	17.5	0.218	18
Fluoranthene	3 590	674	0.188	18
Pyrene	5 390	1 230	0.228	18
Benzo(a)anthracene	1 087	301	0.277	18
Chrysene	303	96.2	0.318	18
Benzo-				
(b)fluoranthene	—			
Benzo-				
(k)fluoranthene	86.9	25.5	0.294	18
Benzo(a)pyrene				
Dibenzo-				
(a,h)anthracene	—			
Benzo(g,h,i)perylene	18.5	2.22	0.120	3
Indeno(1,2,3-				
cd)pyrene	39.8	16.0	0.403	18
Oil and grease	209 000	26 600	0.142	36

studies. Table 3 presents measured physical, chemical, and biological characteristics of the upper 15 cm for the two soils.

Analytical procedures for PNA compounds. Soil samples collected for PNA analysis were frozen until extraction was begun. An aliquot was weighed out and extracted in methylene chloride, using sonication. The methylene chloride solvent extract was back-extracted with water at a basic pH to remove phenolic interferences. The base neutral fraction was concentrated and passed through alumina gel to remove additional interfering substances. The resulting extract was then analyzed for the compounds of interest. Leachate samples did not require sonication.

Extracted samples were analyzed for PNA compounds using HPLC and following EPA method 8310.¹⁰ The compounds were separated using a water:acetonitrile solvent gradient. Detection was achieved using a fixed wavelength (254 nm) UV detector.

Batch degradation studies. Batch reactors containing soil from the waste incorporation zone (the top 15 cm of soil) were used to establish the rate and extent of degradation for the complex waste/soil mixture. Each reactor consisted of a 600-mL glass beaker containing 200-g dry-weight of non-acclimated soil and 2 g of waste acclimated soil from an active petroleum land treatment facility. The moisture content of the Kidman sandy loam and Nunn clay loam was maintained at 11.1 and 23.9% by weight (one-third bar matric potential), respectively. The beakers were covered with polyethylene film to retard evaporation but allow gas transfer. The beakers were incubated in the dark at $20^\circ\text{C} \pm 2^\circ\text{C}$.

The waste mixture was applied to Kidman sandy loam and Nunn clay loam at concentrations of 2, 4, and 8% by oil and grease (O & G) content. Waste-soil mixtures were

incubated at 20°C and extracted and analyzed in triplicate for PNA compounds and O & G concentrations to determine changes in concentration over time of incubation in soil. One control reactor (soil without waste addition) was also evaluated at each sampling event. Waste application occurred only at the beginning of the study. Every 2 weeks beakers were aerated with a glass stirring rod, and moisture was added. Triplicate reactors of each waste loading rate/soil type combination were sacrificed each month of the 8-month study.

Data from the batch degradation studies were used to determine first order degradation constants for PNA compounds and for O & G. Table 4 presents first order degradation rate constants for each soil type and waste loading rate evaluated. The 95% confidence limits were determined for compounds with sufficient data. Concentrations of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene were below the detection limit after 1 month, which yielded insufficient data for determination of degradation constants.

Partition coefficient studies. Laboratory studies were conducted to evaluate the partitioning of PNA compounds between waste and water followed by partitioning of a constituent present in the aqueous phase between the soil and the aqueous phase. This study was based on procedures described elsewhere.³

The procedure required spiking the waste with the constituents of interest so that they would partition in sufficient quantities to be detected in all phases. Spiked waste was mixed with distilled water in a reactor for 24 hours

Table 3—Physical, chemical, and biological characteristics of the upper 15 cm of soil.

Characteristics	Kidman sandy loam	Nunn clay loam
Physical		
Percent sand	56	35
Percent silt	29	31
Percent clay	15	34
Texture	sandy loam	clay loam
Moisture retention, percent water	24.5	39.0
0 bar		
.33 bar	13.0	23.6
15 bar	5.0	11.2
Porosity	0.39	0.38
Bulk density, g/cm^3	1.61	1.51
Soil moisture coefficient ¹¹	4.90	8.52
Chemical		
pH	8.1	8.1
EC, mhos/cm	0.5	0.4
Organic carbon, percent	0.51	1.1
CEC, meq/L	11.7	18.8
Biological		
Bacteria, cfu/g	2.3×10^4	2.2×10^7
Actinomyces, cfu/g	3×10^5	3.1×10^3
Fungi, cfu/g	4.3×10^2	3.1×10^3

^a Colony forming units.

Table 4—Experimentally determined PNA compound first order degradation constants.

Compound	Kidman sandy loam, <i>k</i> (per day)			Nunn clay loam, <i>k</i> (per day)		
	2% O & G	4% O & G	8% O & G	2% O & G	4% O & G	8% O & G
Naphthalene	>0.014	>0.019	>0.013	—	—	>0.016
Acenaphthylene	>0.014	>0.014	—	—	—	—
Acenaphthene	>0.019	>0.056	>0.054	>0.007	>0.021	>0.043
Fluorene	>0.045	>0.068	0.007	>0.023	>0.045	0.015
Phenanthrene	>0.117	>0.118	0.016	>0.099	>0.120	>0.023
Anthracene	>0.052	>0.075	0.013	>0.027	>0.051	>0.073
Fluoranthene	0.037	0.027	0.021	0.045	0.047	0.041
Pyrene	0.016	0.014	0.014	0.022	0.021	0.020
Benzo(a)anthracene	0.009	0.011	0.008	0.005	0.004	0.003
Chrysene	0.017	0.012	0.009	0.009	0.007	0.006
Benzo(k)fluoranthene	0.003	—	—	0.005	0.005	0.003
Benzo(g,h,i)perylene	0.003	0.005	0.004	0.0004	0.003	—
Indeno(1,2,3-cd)pyrene	0.007	0.011	0.005	0.010	0.011	0.012
Oil and grease	0.004	0.003	0.004	0.004	0.004	0.004

and subsequently centrifuged. The aqueous phase was analyzed to determine the waste to water partition coefficient (K_o). A portion of the aqueous phase was retained and mixed with both types of soil—Kidman sandy loam and Nunn clay loam. The aqueous and solid phases of this second mixture were then analyzed to determine the soil to water partition coefficient (K_d). The partition coefficient studies were completed by using various ratios of waste to water (K_o) and soil to water (K_d). Partition coefficients were determined for each individual set of data points, and an average partition coefficient was computed. If the constituents were below detection limits in any of the media tested, the coefficient was not calculated. Table 5 summarizes the average K_o , K_d , and K_h values.

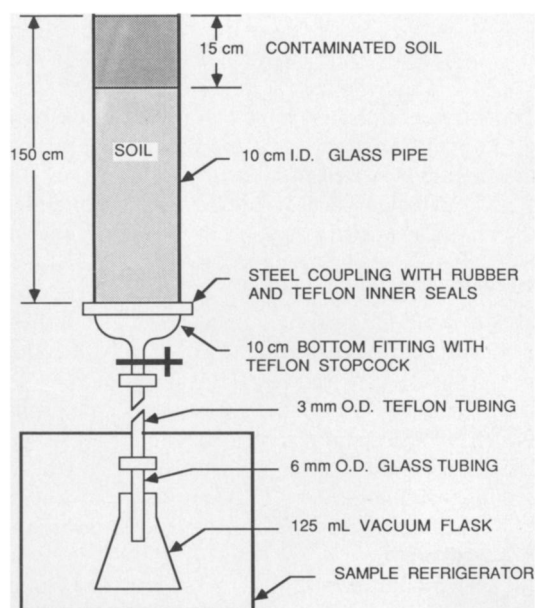
Table 5—Summary of PNA partition coefficients determined experimentally.

Compound	Log K_o , g/m ³ /g/m ³	K_d	
		Kidman, mL/g	Nunn, mL/g
Naphthalene	3.00	22.8	32.3
Acenaphthylene	BDL ^a	BDL	BDL
Acenaphthene	3.6	103.0	150.0
Fluorene	3.29	62.5	87.9
Phenanthrene	3.29	160.0	163.0
Anthracene	3.21	125.0	215.0
Fluoranthene	BDL	BDL	BDL
Pyrene	3.32	59.6	183.0
Benzo(a)anthracene	3.34	199.0	189.0
Chrysene	3.30	175.0	212.0
Benzo(b)fluoranthene	BDL	49.1	BDL
Benzo(k)fluoranthene	BDL	86.8	271.0
Benzo(a)pyrene	BDL	18.2	69.0
Benzo(g,h,i)perylene	BDL	18.9	77.2
Indeno(1,2,3-cd)pyrene	BDL	BDL	BDL

^a Below detection limit.

Soil column studies. Soil columns containing the upper 150 cm of soil were used to evaluate PNA compound mobility. Twenty borosilicate glass columns, 150 cm long by 5 cm diameter, contained the 150-cm soil profile. A steel coupling with a polytetrafluoroethylene seal coupled a glass cap fitted with a polytetrafluoroethylene stopcock to the bottom of the glass pipe. Figure 1 shows the soil column construction. Ten grams of clean glass wool were packed into the bowl of the glass cap to prevent soil from washing out the bottom of the column.

Sieved soil was packed in the glass columns in 7.5-cm sections to a height of 137 cm. Following placement of the soil, columns were saturated with deionized water and allowed to drain. Fifteen centimeters of contaminated

**Figure 1—Soil column construction.**

waste/soil mixture were placed over the clean soil profile. The contaminated soil was a mixture of clean soil, 1% waste acclimated soil, and sufficient waste to result in loading rates of 2, 4, and 8% oil and grease. Two control columns were packed with 15 cm of 1% acclimated soil mixed with clean soil. Triplicate soil columns for each soil type and application rate were constructed.

The soil columns were located in an enclosed, dark, ventilated room with an average temperature of $20^{\circ}\text{C} \pm 2$. The average pan evaporation rate was 0.152 cm/d. The upper 15 cm of the soil column was aerated by tilling, and moisture was adjusted every 2 weeks by water application to 11.1% and 23.9% by weight for the Kidman sandy loam and the Nunn clay loam, respectively.

The equivalent of 4 cm of water was applied to each soil column every month, excluding water applied to compensate for evaporation. As water was applied, leachate from each column was collected in a 125-mL flask. Samples were refrigerated at 4°C until analyzed.

Soil columns were operated and sampled for 6 months, after which they were destructively sampled. Samples were taken at depths of 30, 60, 90, and 120 cm and in the zone of incorporation (the upper 15 cm of soil). Only soil from the zone of incorporation was composited and subsampled. A soil sample from each depth was analyzed for PNA compounds, beginning at the zone of waste incorporation and proceeding downward through each column

until no PNA compounds were detected in the sample, at which time analyses for that column were discontinued.

Extracted samples were analyzed for PNA compounds using HPLC and following EPA method 8310. Compounds were separated using a water:acetonitrile solvent gradient. Detection was achieved using a fixed wavelength (254 nm) UV detector.

Comparison of Model Predictions with Observed Laboratory Results

Data from soil and waste analyses and degradation and partitioning studies were used as input data for VIP model validation. Results from the VIP model were compared with observed laboratory data to determine whether predictions met acceptance criteria.

Model input data. The initial PNA compound concentrations in the composite petroleum refinery waste were calculated based on initial concentrations measured in waste/soil mixtures (Table 2).

Environmental properties selections were based on air temperature and mean daily recharge rates measured in the soil column studies. The average daily air temperature measured in the soil column studies from October 14, 1985 to August 26, 1986 was 22.3°C with a maximum of 26.0°C and a minimum of 18.5°C . An average air temperature of 20°C was selected for the model predictions.

Table 6—Predicted and measured PNA concentrations ($\mu\text{g/g}$): Kidman sandy loam.

Compound	Depth, cm	Measured			Predicted		
		2% O & G	4% O & G	8% O & G	2% O & G	4% O & G	8% O & G
Fluoranthene	7.5	0.61	1.22	4.98	0.334	4.632	27.685
	15	—	—	—	0.343	4.819	27.960
	22.5	—	—	—	0.009	0.189	0.275
	30	<0.6	<0.6	1.57	0	0.005	0
	60	<0.6	<0.6	<0.6	0	0	0
	150	<0.6	<0.6	<0.6	0	0	0
Pyrene	7.5	13.25	55.47	263.67	25.989	77.999	154.990
	15	—	—	—	26.638	80.494	156.040
	22.5	—	—	—	0.652	2.490	1.050
	30	<1.0	<1.0	38.56	0.011	0.081	0.010
	60	<1.0	<1.0	<1.0	0	0	0
	150	<1.0	<1.0	<1.0	0	0	0
Benzo(a)anthracene	7.5	6.34	52.95	195.95	19.830	27.884	96.587
	15	—	—	—	20.027	28.313	96.969
	22.5	—	—	—	0.197	0.431	0.381
	30	<0.5	<0.5	<0.5	0	0	0
	150	<0.5	<0.5	<0.5	0	0	0
Benzo(k)fluoranthene	7.5	2.84	10.37	28.18	4.848	16.907	34.541
	15	—	—	—	4.944	17.374	34.759
	22.5	—	—	—	0.097	0.469	0.218
	150	<0.5	<0.5	0.5	0	0	0
Ildeno(1,2,3-cd)pyrene	7.5	1.55	3.47	6.49	1.067	1.036	6.231
	15	—	—	—	1.068	1.037	6.232
	22.5	—	—	—	0	0	0
	150	<0.5	<0.5	<0.5	0	0	0

Because saturated and unsaturated hydraulic conductivities were not measured, mean daily recharge rates were estimated from soil column leaching data. Mean daily recharge rates for Kidman soil at 2, 4, and 8% O & G were 0.0016, 0.0029 and 0.0010 m³/m²·d, respectively. Van't Hoff-Arrhenius temperature coefficients were neither measured nor available in the literature, and thus were assumed to be 1.0.

Predicted model results and observed laboratory results. Tables 6 and 7 present the observed laboratory and predicted model results after 6 months of soil treatment. Model predictions for only 7 of the 16 PNA compounds evaluated were compared because of incomplete data for degradation constants and constituent concentrations in the soil. Target detection limits for base/neutral organic compounds³ were used as detection limits for model predictions. Detection limits for laboratory results were determined by an analytical laboratory that conducted all HPLC analyses for PNA compounds.

Discussion

The acceptability of the VIP model was evaluated by comparing measured and predicted concentration as a function of depth as presented in Tables 6 and 7. Model ability to predict mobility and degradation was evaluated. Mobility was defined as the depth a constituent would penetrate into the soil profile. Degradation was defined as

constituent concentration in the zone of waste incorporation after 6 months. Concentration versus depth data from the soil column analyses were insufficient to compare constituent concentrations of PNA compounds at depths other than in the zone of waste incorporation.

Mobility. None of the PNA compounds measured in soil samples removed from the soil columns were present above detectable limits at a depth greater than 30 cm below the soil surface. The VIP model predicted that none of the PNA constituents would be measured in concentrations greater than 0.005 µg/g below 30 cm from the soil surface. The model predicted higher mobility of constituents applied to Kidman sandy loams at the 4% O & G loading because of the significantly higher recharge rate used for the Kidman soil. Analysis of concentration versus depth data from the soil column study indicated that no constituents penetrated more than 15 cm below the zone of incorporation, 30 cm below the soil surface.

The VIP model predicted PNA compound mobility within the analytical limits of the soil column study. Because the laboratory columns were sampled at the zone of waste incorporation and depths of 30, 60, 90, 120, and 150 cm, the degree of accuracy was ±15 cm. Concentrations predicted by the model were in 7.5-cm increments with an incremental accuracy of ±3.8 cm. Detection limits for model predictions were within detection limits attained in the soil column study analyses. Detection limits for

Table 7—Predicted and measured PNA concentrations (µg/g): Nunn clay loam.

Compound	Depth, cm	Measured			Predicted		
		2% O & G	4% O & G	8% O & G	2% O & G	4% O & G	8% O & G
Fluoranthene	7.5	<0.6	0.81	30.06	0.103	0.131	0.535
	15	—	—	—	0.105	0.132	0.541
	22.5	—	—	—	0	0	0.006
	30	<0.6	<0.6	<0.6	0	0	0
	150	<0.6	<0.6	<0.6	0	0	0
Pyrene	7.5	6.67	57.26	226.28	9.972	22.897	45.684
	15	—	—	—	10.082	23.133	46.068
	22.5	—	—	—	0.111	0.237	0.385
	30	<1.2	<1.2	3.30	0	0	0
	150	<1.2	<1.2	<1.2	0	0	0
Benz(a)anthracene	7.5	5.87	56.66	251.92	43.547	103.570	242.210
	15	—	—	—	44.003	104.580	244.140
	22.5	—	—	—	0.457	1.012	1.931
	30	<0.6	<0.6	<0.6	0	0.006	0.011
	60	<0.6	<0.6	<0.6	0	0	0
	150	<0.6	<0.6	<0.6	0	0	0
Benzo(k)fluoranthene	7.5	3.30	9.48	34.17	3.491	6.910	19.419
	15	—	—	—	3.518	6.963	19.545
	22.5	—	—	—	0.027	0.053	0.126
	150	<0.5	<0.5	<0.5	0	0	0
Ildeno(1,2,3-cd)pyrene	7.5	1.43	2.85	8.11	0.652	1.064	1.585
	15	—	—	—	0.652	1.064	1.585
	22.5	—	—	—	0	0	0
	150	<0.6	<0.6	<0.6	0	0	0

Table 8—Comparison of measured and predicted concentrations in the ZOI: Kidman sandy loam.

Compound	Loading, percent O & G	Concentration, µg/g		
		Measured (M)	Predicted (P)	Ratio (P):(M)
Fluoranthene	2	0.61	0.334	0.55
Pyrene	2	13.25	25.989	1.96
Benzo(a)anthracene ^a	2	6.34	19.830	3.13
Chrysene	2	0.98	1.228	1.25
Benzo(k)fluoranthene	2	2.84	4.848	1.71
Benzo(g,h,i)perylene ^a	2	7.50	0.985	0.13
Indeno(1,2,3-cd)Pyrene	2	1.55	1.067	0.69
Fluoranthene ^a	4	1.22	4.632	3.80
Pyrene	4	55.47	77.999	1.41
Benzo(a)anthracene	4	52.95	27.884	0.53
Chrysene	4	9.21	6.447	0.70
Benzo(k)fluoranthene	4	10.37	16.907	1.63
Benzo(g,h,i)perylene ^b	4	15.80	1.355	0.09
Indeno(1,2,3-cd)Pyrene ^a	4	3.47	1.036	0.30
Fluoranthene ^a	8	4.98	27.685	5.56
Pyrene	8	263.67	154.990	0.59
Benzo(a)anthracene ^a	8	195.95	96.587	0.49
Chrysene	8	35.89	22.310	0.62
Benzo(k)fluoranthene	8	28.18	34.541	1.23
Benzo(g,h,i)perylene ^a	8	22.65	3.441	0.15
Ideno(1,2,3-cd)pyrene	8	6.49	6.231	0.96

^a Differs by greater than a factor of 2.^b Differs by greater than a factor of 10.**Table 9—Comparison of measured and predicted concentrations in the ZOI: Nunn clay loam.**

Compound	Loading, percent O & G	Concentration µg/g		
		Measured (M)	Predicted (P)	Ratio (P):(M)
Fluoranthene ^a	2	0.60	0.103	0.17
Pyrene	2	6.67	9.972	1.49
Benzo(a)anthracene ^a	2	5.87	43.547	7.42
Chrysene ^a	2	0.96	5.893	6.14
Benzo(k)fluoranthene	2	3.30	3.491	1.06
Benzo(g,h,i)perylene ^a	2	7.26	1.678	0.23
Indeno(1,2,3-cd)pyrene ^a	2	1.43	0.652	0.46
Fluoranthene ^a	4	0.81	0.131	0.16
Pyrene ^a	4	57.26	22.897	0.40
Benzo(a)anthracene	4	56.66	103.570	1.83
Chrysene	4	10.72	16.685	1.56
Benzo(k)fluoranthene	4	9.48	6.910	0.73
Benzo(g,h,i)perylene ^a	4	16.11	2.088	0.13
Indeno(1,2,3-cd)pyrene ^a	4	2.85	1.064	0.37
Fluoranthene ^b	8	30.06	0.535	0.02
Pyrene ^a	8	226.28	45.684	0.20
Benzo(a)anthracene	8	251.92	242.210	0.96
Chrysene	8	39.92	37.939	0.95
Benzo(k)fluoranthene	8	34.17	19.419	0.57
Benzo(g,h,i)perylene ^a	8	29.54	7.273	0.25
Ideno(1,2,3-cd)pyrene ^a	8	8.11	1.585	0.20

^a Differs by greater than a factor of 2.^b Differs by greater than a factor of 10.

PNA compounds in soils in the soil column study were between $0.5 \mu\text{g/g}$ and $1.2 \mu\text{g/g}$. The detection limit used for all phases in the model was $0.005 \mu\text{g/g}$.

Degradation. Concentrations of constituents in the zone of incorporation were used to evaluate model ability to predict constituent degradation and persistence. This evaluation was possible because of the low volatility of PNA compounds and low mobility of the same compounds as indicated by soil column results and model predictions. The PNA compounds, once applied to the soil, primarily remain in the zone of waste incorporation where biological processes can degrade them.

Tables 8 and 9 summarize the measured and predicted concentrations of constituents in the zone of incorporation (ZOI) after 6 months. Ratios (the last column in Tables 8 and 9) less than 2 and greater than 0.5 indicate that the predicted concentration is within a factor of 2 of the observed concentration. Ratios greater than 1.0 indicate that the model over-predicted the final concentration in the zone of waste incorporation. Ratios less than 1.0 indicate that the model under-predicted the final concentration.

The model did not consistently over- or under-predict the constituent concentrations after 6 months for all compounds (Figure 2). In 27 of 42 cases (64%), the model under-predicted the constituent concentration after 6 months. In 21 of 42 cases (50%), the model over- or under-predicted the final concentration by more than a factor of two, but in two of these cases the concentration was

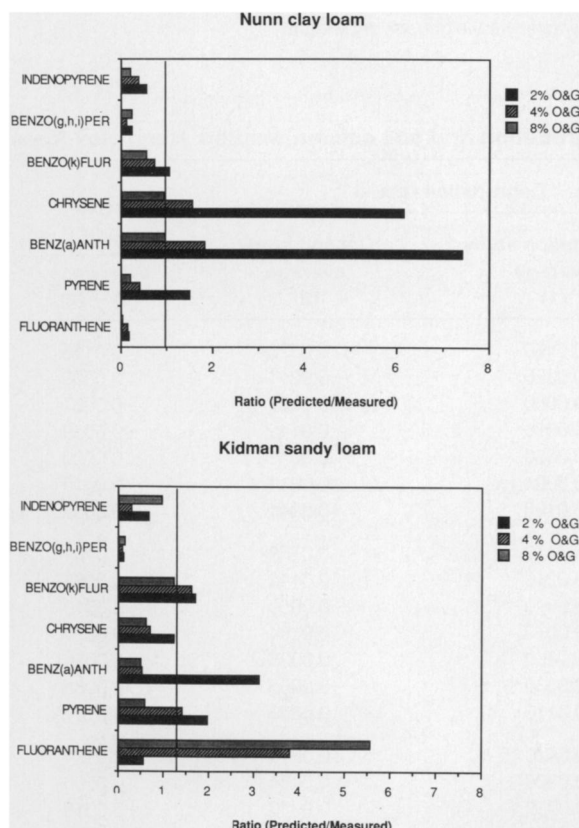


Figure 2—Ratio of PNA concentrations predicted by the VIP model to PNA concentrations observed in laboratory columns.

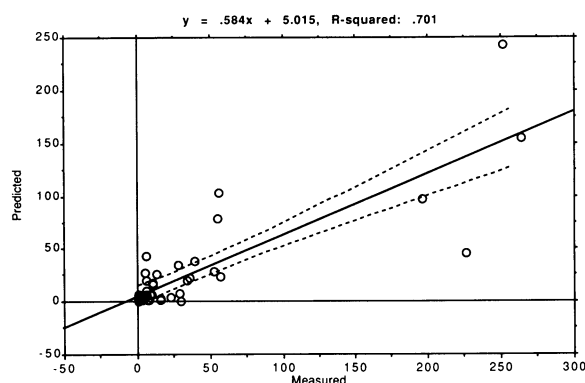


Figure 3—Linear regression of predicted versus measured concentrations in the ZOI 6 months after waste application.

under-predicted by a factor greater than 10. The model consistently under-predicted the constituent concentration of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.

Figure 3 is a plot of the predicted concentrations in the zone of incorporation after 6 months as a function of the concentrations measured in the soil column studies. Figure 3 also gives the 95% confidence interval and the equation of the best fit line through the data by the least-squares method. Ideally, the slope of the line should be 1.0, the y-intercept should be 0.0, and the coefficient of correlation should be 1.0. The slope of the line, 0.584, indicates a tendency for the model to under-predict observed results as indicated previously. The coefficient of determination, R-squared, was 0.701, which is well above 0.0924, the lower limit required to show a correlation for approximately 40 points. Although the y-intercept is 5.015, this is only 1.9% of the maximum value. The data is statistically within acceptable limits, but the results indicate a tendency to underestimate the observed concentration.

Sources of error. Sensitivity analyses of the VIP model indicated that the accuracy of the degradation rates and initial waste concentrations used as inputs in model predictions can have a significant effect on the difference between measured and predicted results.

Tables 10 and 11 present a comparison of the differences between the degradation rates calculated from batch degradation studies and used as inputs in the VIP model and the degradation rates observed in the soil columns. An error of only 5% in a degradation rate of $0.020/\text{d}$ will yield errors in the final concentration greater than 16%, after 180 days, assuming first order kinetics. Differences calculated in Tables 10 and 11 are highly variable, between -0.0116 and $+0.0191 \text{ d}^{-1}$. This can account for much of the variability observed between measured and predicted results.

Initial and final concentrations measured in the soil can also vary significantly. The initial soil concentrations in batch degradation studies differed by 7.2 to 252% from initial soil concentrations measured in the soil columns. This variability may be caused by non-representative sampling, incomplete mixing, or variability in the applied waste itself. The accuracy of the HPLC analyses used to detect the PNA compound is also affected by interferences

Table 10—Observed degradation rates from batch degradation and soil column studies: Kidman sandy loam.

Compound	Loading rate, percent O & G ^a	Degradation rate, d ⁻¹		Difference (1) – (2)
		Degradation study average (1)	Column study average (2)	
Fluoranthene	2	0.0370	0.0378	-0.0008
Pyrene	2	0.0160	0.0234	-0.0074
Benzo(a)anthracene	2	0.0090	0.0188	-0.0098
Chrysene	2	0.0170	0.0226	-0.0056
Benzo(k)fluoranthene	2	0.0030	0.0107	-0.0077
Benzo(g,h,i)perylene	2	0.0030	-0.0012	0.0042
Indeno(1,2,3-cd)pyrene	2	0.0070	0.0027	0.0043
Fluoranthene	4	0.0270	0.0366	-0.0096
Pyrene	4	0.0140	0.0179	-0.0039
Benzo(a)anthracene	4	0.0110	0.0087	0.0023
Chrysene	4	0.0120	0.0127	-0.0007
Benzo(k)fluoranthene	4	0.0000	0.0096	-0.0096
Benzo(g,h,i)perylene	4	0.0050	-0.0054	0.0104
Indeno(1,2,3-cd)pyrene	4	0.0110	0.0055	0.0055
Fluoranthene	8	0.0210	0.0326	-0.0116
Pyrene	8	0.0140	0.0132	0.0008
Benzo(a)anthracene	8	0.0080	0.0056	0.0024
Chrysene	8	0.0090	0.0078	0.0012
Benzo(k)fluoranthene	8	0.0000	0.0004	-0.0004
Benzo(g,h,i)perylene	8	0.0040	0.0008	0.0032
Indeno(1,2,3-cd)pyrene	8	0.0050	0.0086	-0.0036

^a % O & G = initial percent oil and grease in the waste/soil mixture, waste wet weight/soil dry weight.

Table 11—Observed degradation rates from batch degradation and soil column studies: Nunn clay loam.

Compound	Loading rate, % O & G	Degradation rate, d ⁻¹		Difference (1) – (2)
		Degradation study average (1)	Column study average (2)	
Fluoranthene	2	0.0450	0.0335	0.0115
Pyrene	2	0.0220	0.0211	0.0009
Benzo(a)anthracene	2	0.0050	0.0137	-0.0087
Chrysene	2	0.0090	0.0149	-0.0059
Benzo(k)fluoranthene	2	0.0050	0.0041	0.0009
Benzo(g,h,i)perylene	2	0.0004	-0.0011	0.0015
Indeno(1,2,3-cd)pyrene	2	0.0100	0.0041	0.0059
Fluoranthene	4	0.0470	0.0369	0.0101
Pyrene	4	0.0210	0.0142	0.0068
Benzo(a)anthracene	4	0.0040	0.0059	-0.0019
Chrysene	4	0.0070	0.0104	0.0034
Benzo(k)fluoranthene	4	0.0050	0.0025	0.0025
Benzo(g,h,i)perylene	4	0.0030	-0.0055	0.0085
Indeno(1,2,3-cd)pyrene	4	0.0110	0.0003	0.0107
Fluoranthene	8	0.0410	0.0219	0.0191
Pyrene	8	0.0200	0.0134	0.0066
Benzo(a)anthracene	8	0.0030	0.0043	-0.0013
Chrysene	8	0.0060	0.0066	-0.0006
Benzo(k)fluoranthene	8	0.0030	-0.0015	0.0045
Benzo(g,h,i)perylene	8	0.0000	-0.0032	0.0032
Indeno(1,2,3-cd)pyrene	8	0.0120	0.0047	0.0073

from other organic compounds present in the complex waste mixture.

Conclusions and Recommendations

A laboratory validation of the VIP model demonstrated the following:

- A laboratory soil column study is a feasible method for validation of a fate and transport model before field validation.
- The VIP model predicted the depth of penetration of seven PNA compounds within the limits of acceptance.
- The VIP model provided a good approximation of the concentration of a constituent after 6 months, within a factor of two in half of the cases.
- Variability in degradation rates and initial soil concentrations significantly affected the final concentrations of PNA compounds after 6 months.

The laboratory validation provided a basis for assessing the model in a field situation. Because many of the spatially and temporally variable factors such as soil characteristics, temperature, and recharge rate were constant in this study, even greater variability should be expected in field experiments and even greater care must be taken to accurately determine the input values used in a field validation study.

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