

**EVALUATION OF STEADY-STATE SOIL
CONCENTRATIONS
FOR PERSISTENT ORGANIC POLLUTANTS (POPS)**

August, 1999

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is continually faced with regulatory issues concerning the migration of organic and inorganic chemical constituents to and through multimedia systems (water, soil, air, etc.). Each of these issues requires that the potential risk to human health and various ecosystems be evaluated. Recently, much of this attention has been focused on exposure to persistent organic pollutants (POPs). Historically, these POP compounds have been associated with application in an agricultural crop setting. These POP chemicals are of concern to the EPA due to their classification as "endocrine disruptors," which adversely impact the glandular system of the human body.

The purpose of this report is to present the results of a study conducted by HydroGeoLogic to investigate the behavior of a list of specified POPs, and to develop a predictive screening level methodology for use with other, similar chemical compounds. Detailed analysis was conducted for the following eleven POPs:

- Chlordane
- DDD
- DDE
- DDT
- Dicofol
- Dieldrin
- Endosulfan
- Furan
- Kepone
- Methoxychlor
- Toxaphene

The above compounds have historically been associated with usage as pesticides in agricultural settings. The analysis of these compounds primarily involved the design and execution of a series of long term simulations using Version 3.0 of the EPA's Pesticide Root Zone Model (PRZM-3). The intent of the individual simulations was to determine whether the listed POPs demonstrated a tendency to reach a steady state concentration in the upper soil horizon as a result of annual application, and, if so, to determine the time required for steady state concentrations to be achieved. Results of these simulations were used to support the development of a predictive screening level methodology which can be used for other POPs based on certain readily available chemical parameters. The screening level methodology, if used as described in this report, will allow rapid determination of whether a specific compound is likely to demonstrate a tendency to be persistent in the environment.

The remainder of this report will discuss the study methodology, the results of long term PRZM simulations for the listed POPs, the development of the screening level methodology, and a discussion of the uncertainty associated with application of the screening level methodology.

2.0 STUDY METHODOLOGY

The approach used to develop the screening level methodology involved the application of a detailed study methodology. Each portion of the study methodology will be described in more detail in subsequent sections of the report. The intent of this section is to briefly summarize the nature of the approach used for this investigation.

The basic backbone of this study involved detailed, long term simulations using PRZM-3. Simulations were conducted for each of the 11 study POPs at each of 32 sites distributed across the contiguous United States. The site selection process was designed to provide a group of simulation sites which were generally representative of the wide variety of cropping practices, climatology, and soils conditions in agricultural regions. Simulations assumed an annual unit (1 kg/ha) application of a specific POP, and were conducted for a minimum of 100 years.

PRZM-3 simulations considered the annual pesticide application as the source term, and erosion, runoff, volatilization, decay, and leaching as the primary loss terms. For persistent compounds (those which exhibit a tendency to increase in concentration over time), the magnitude of the loss terms increases as the concentration increases in the upper layer of the soil. Since the assumed application rate is constant, many compounds eventually reach a steady-state condition where the annual loss term matches the source term. Simulation results were analyzed to determine 1) whether a specific compound exhibited a tendency to reach a steady state concentration, and if so, 2) what the magnitude of the steady state concentration was, and 3) how much time was required for steady-state conditions to be achieved.

Following completion of the base simulations, a series of sensitivity analyses were conducted to determine which of the input variables in the PRZM-3 simulations had the most effect on computed soil concentrations. A rigorous statistical analysis was then conducted to determine the best method to predict steady state concentrations and time required to reach steady state conditions. The results of the sensitivity analyses were used to guide the development of the predictive screening level methodology and the subsequent uncertainty analyses. The uncertainty analysis was performed to help assess the limitations of the screening level methodology.

3.0 BASE SIMULATIONS

3.1 PRZM-3 MODEL

The Pesticide Root Zone Model (PRZM-3) is a one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone (EPA, 1998). It has two major components - hydrology (and hydraulics) and chemical transport. The hydrologic component for calculating runoff and erosion is based on the Soil Conservation Service (SCS) Curve Number (CN) technique and Modified Universal Soil Loss Equation (MUSLE). Evapotranspiration is divided among evaporation from crop interception, evaporation from soil, and transpiration by the crop. Water movement is simulated by the use of generalized soil parameters, including field capacity, wilting point, and saturation water content. The chemical transport component can simulate pesticide application on the soil or on the plant foliage. Dissolved, adsorbed, and vapor-phase concentrations in the soil are estimated by simultaneously considering the processes of pesticide uptake by plants, surface runoff, erosion, degradation or transformation, volatilization, foliar washoff, advection, dispersion, and chemical advection due to sorption.

3.2 SITE SELECTION PROCESS

The site selection process was designed to allow identification of sites in geographically diverse locations for which detailed PRZM-3 simulations could be conducted. Since the POPs investigated in detail are historically associated with pesticide usage in agricultural settings, the sites selected were chosen from areas of primary agricultural production. Simulations were conducted for four major crops: corn, cotton, soybeans, and wheat. Figures 3.1 through 3.4 show crop distribution maps for each of these crops in the United States. These figures were based on data published in the National Resource Conservation Service (NRCS) 1992 National Resources Inventory (NRI). The darker shadings refer to successively higher percentages of land in a given county which is dedicated to production of the respective crops. Using these maps, and a map of average annual precipitation (see Figure 3.5), eight sites were selected for each crop type, resulting in a total of 32 sites identified for detailed simulations.

While the PRZM-3 simulations were one dimensional, the sites were selected on a county basis. PRZM-3 input files were generated using parameter values that were determined to be the most representative of average conditions across a selected county. More information on how this was done is presented in Section 3.4.

Figure 3.6 shows the sites that were selected for detailed PRZM-3 simulations. Table 3.1 presents summary information for these sites.

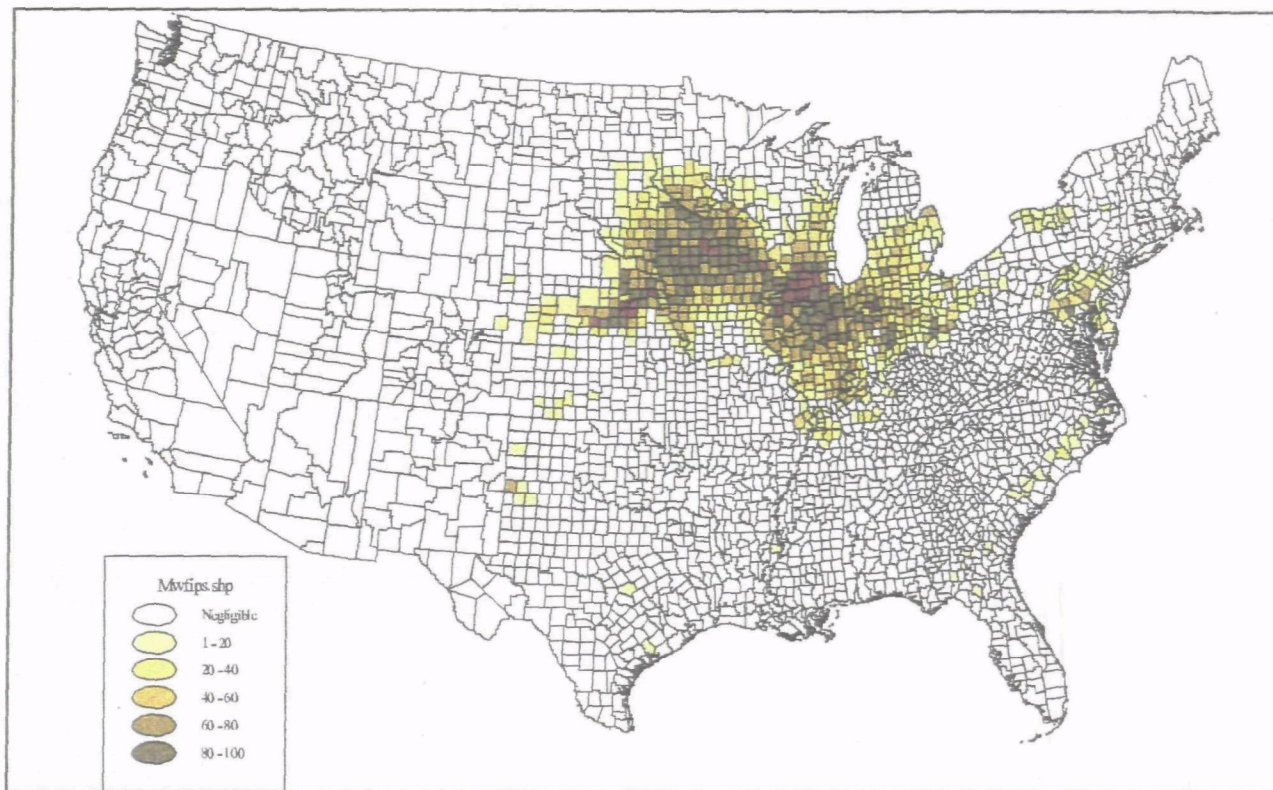


Figure 3.1 Crop Distribution by % Land Use for Corn, from 1992 NRI data.

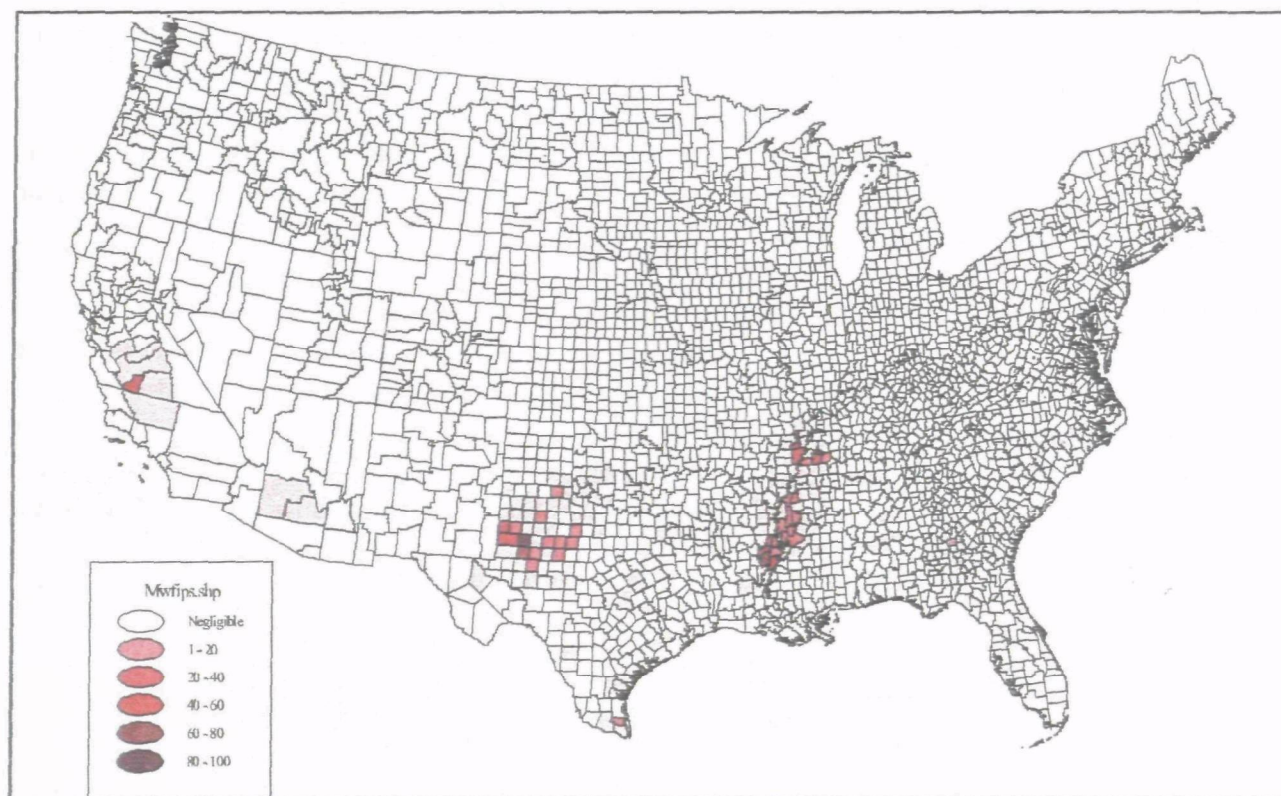


Figure 3.2 Crop Distribution by % Land Use for Cotton, from 1992 NRI data.

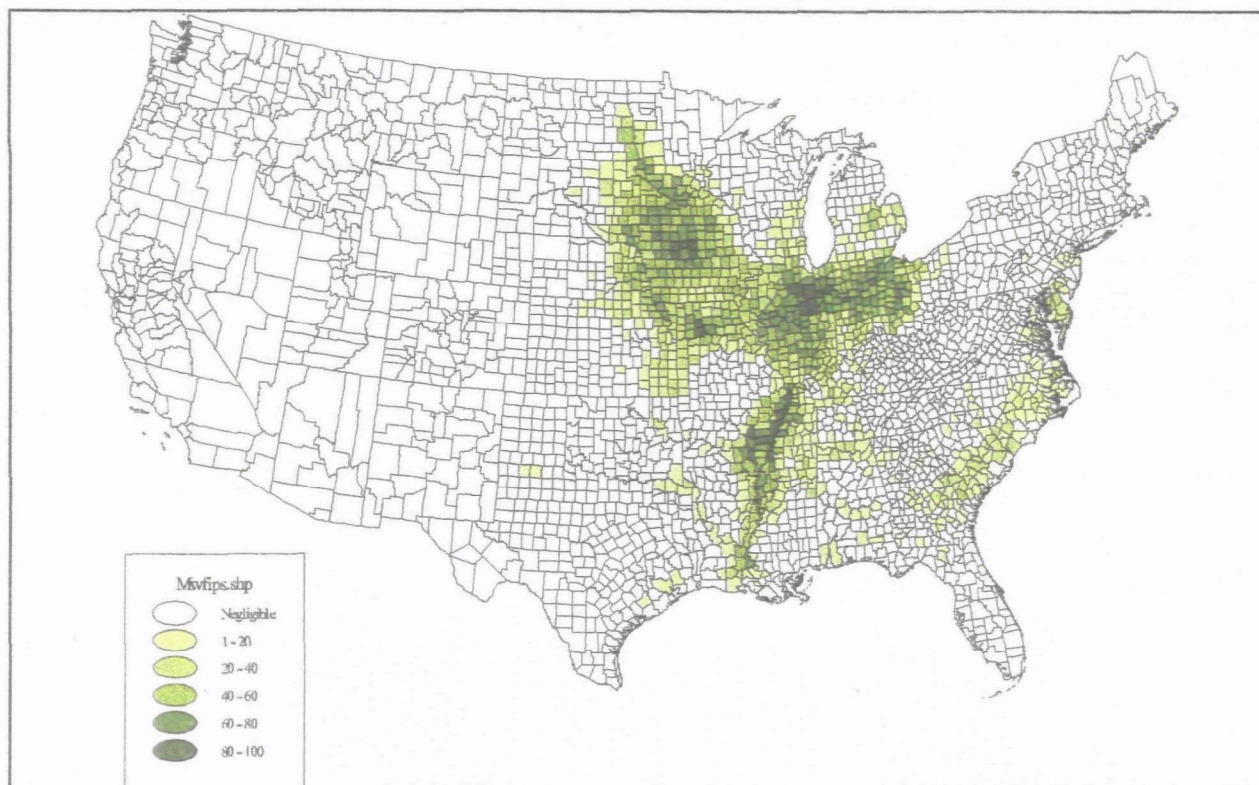


Figure 3.3 Crop Distribution by % Land Use for Soybeans, from 1992 NRI data.

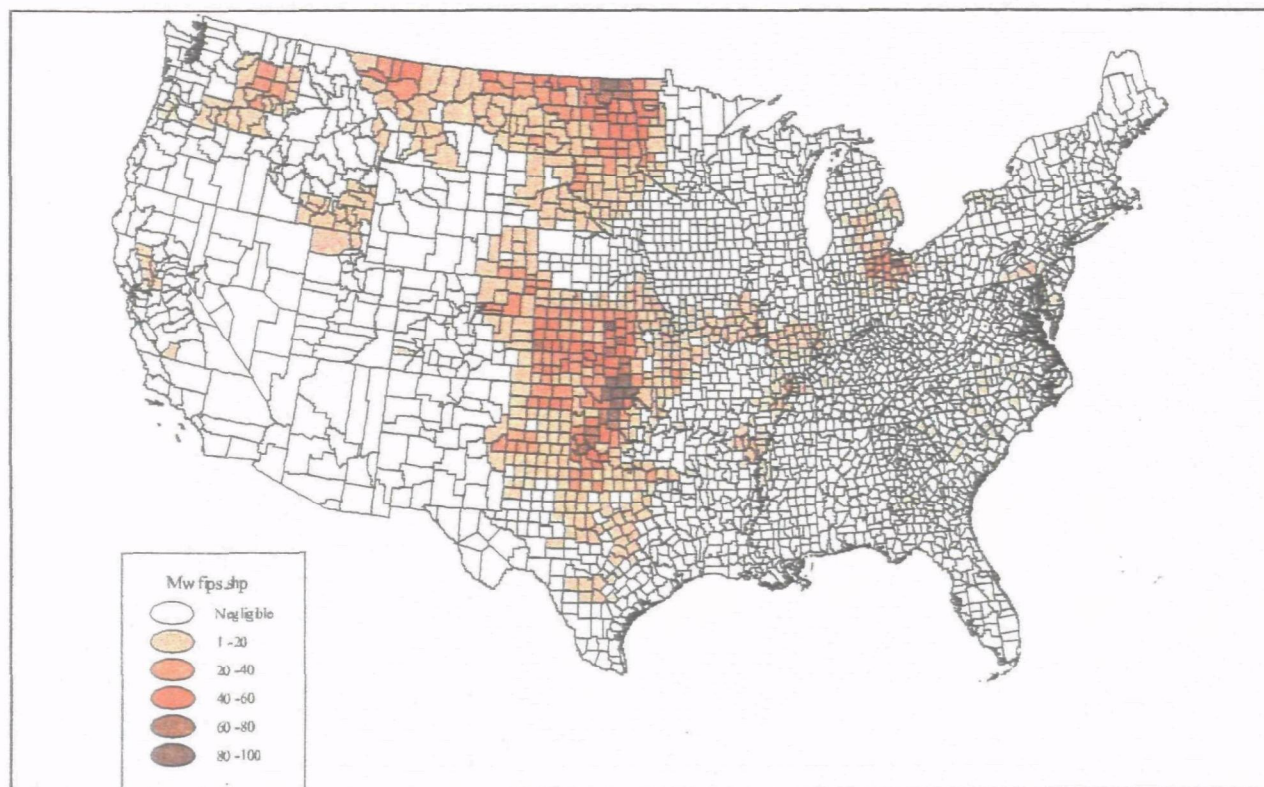


Figure 3.4 Crop Distribution by % Land Use for Wheat, from 1992 NRI data.

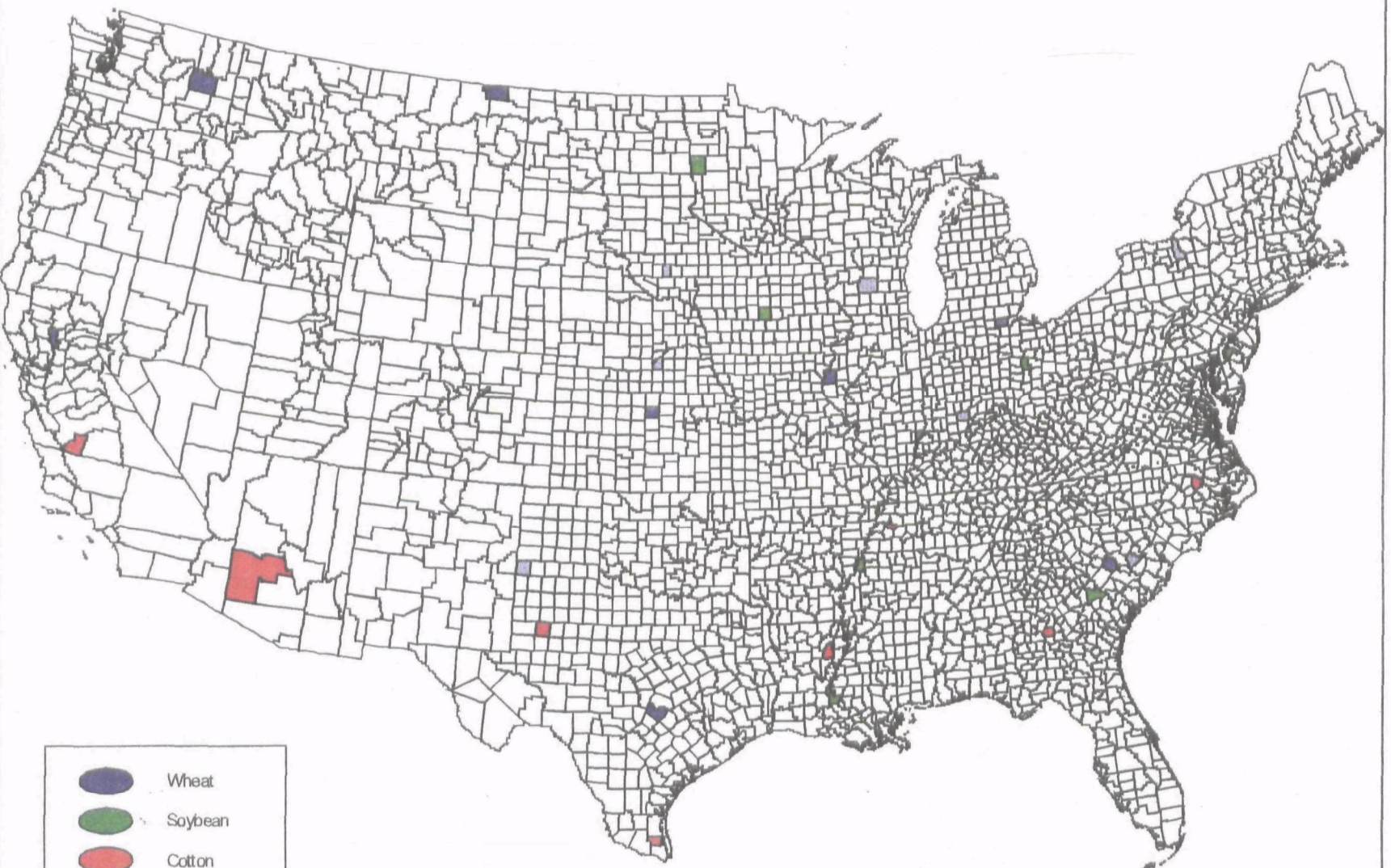


Figure 3.6 32 Sites Selected for Detailed PRZM-3 Simulations.

Table 3.1
Summary Information for 32 Sites Selected for Detailed PRZM-3 Simulations

Site #	County, State	Crop	Soil Name	HSG	Met Station
1	Jackson, IN	Corn	Peoga	C	Louisville, KY
2	Kent, MD	Corn	Matapeake	B	Wilmington, DE
3	Hamilton, NE	Corn	Holder	B	Grand Island, NE
4	Cayuga, NY	Corn	Honeoye	B	Syracuse, NY
5	Sumter, SC	Corn	Norfolk	B	Columbia, SC
6	Hanson, SD	Corn	Clarno	B	Sioux Falls, SD
7	Parmer, TX	Corn	Olton	C	Amarillo, TX
8	Dane, WI	Corn	Plano	B	Madison, WI
9	Maricopa, AZ	Cotton	Momoli	B	Phoenix, AZ
10	Kings, CA	Cotton	Armona	C	Fresno, CA
11	Dooly, GA	Cotton	Tifton	B	Macon, GA
12	Franklin, LA	Cotton	Calhoun	D	Jackson, MS
13	Edgecombe, NC	Cotton	Goldsboro	B	Raleigh-Durham, NC
14	Crockett, TN	Cotton	Loring	C	Memphis, TN
15	Dawson, TX	Cotton	Amarillo	B	Midland, TX
16	Willacy, TX	Cotton	Raymondville	D	Brownsville, TX
17	Burke, GA	Soybeans	Dothan	B	Augusta, GA
18	Wabash, IL	Soybeans	Roby	C	Evansville, IN
19	Hamilton, IA	Soybeans	Brownton	C/D	Des Moines, IA
20	Pointe Coupee, LA	Soybeans	Commerce	C	Baton Rouge, LA
21	Clay, MN	Soybeans	Bearden	C	Fargo, ND
22	Tunica, MS	Soybeans	Sharkey	D	Memphis, TN
23	Salem, NJ	Soybeans	Mattapex	C	Wilmington, DE
24	Union, OH	Soybeans	Blount	C	Columbus, OH
25	Sutter, CA	Wheat	Capay	D	Sacramento, CA
26	Hancock, IL	Wheat	Virden	B/D	Burlington, IA
27	Mitchell, KS	Wheat	Harney	B	Concordia, KS
28	Daniels, MT	Wheat	Cherry	C	Williston, ND

Table 3.1 (continued)
Summary Information for 32 Sites Selected for Detailed PRZM-3 Simulations

Site #	County, State	Crop	Soil Name	HSG	Met Station
29	Fulton, OH	Wheat	Mermill	B/D	Toledo, OH
30	Lexington, SC	Wheat	Nason	C	Columbia, SC
31	Travis, TX	Wheat	Houston Black	D	Austin, TX
32	Lincoln, WA	Wheat	Bagdad	B	Spokane, WA

3.3 PESTICIDE CHEMICAL DATA

Table 3.2 shows the chemical data used for detailed PRZM-3 simulations for each of the study POPs. These data were obtained from a variety of sources as documented in the table.

Table 3.2
Chemical Data for Investigated POPs

POP	D _a (cm ² /day)	K _h (dim)	ENPY (kcal/mole)	K _w (day ⁻¹)	K _s (day ⁻¹)	half-life (soil, days)	K _{oc} (cm ³ /g)
Chlordane	1019.52	1.99E-03	20	1.03E-07	0.00	∞	7.76E+05
DDD	1347.84	1.63E-04	20	1.29E-04	6.85E-05	10,117	7.76E+05
DDE	1244.16	8.55E-04	20	0.00	0.00	∞	4.37E+06
DDT	1183.68	3.31E-04	20	1.01E-03	1.64E-04	4,226	3.89E+06
Dicofol	3473.28 ¹	4.1E-07 ¹	20	1.68E-01 ³	1.68E-01 ³	4	6.06E ₄ +03
Dieldrin	1080	6.19E-04	20	1.73E-04	1.73E-04	4006	1.20E+05
Endosulfan	993.6	4.58E-04	20	6.44E-01	2.05E-04	3380	3.55E+03
Furan	8985.6	0.2207	6.56 ²	0.00	0.00	∞	1.00E+01
Kepone	6912	1.04E-06	20	0.00	0.00	∞	1.41E+04
Methoxychlor	1347.84	6.46E-04	20	1.92E-03	1.89E-03	367	7.94E+04
Toxaphene	1002.24	2.45E-04	20	2.68E-04	1.92E-04	3609	2.04E+04

¹from the SPARC (Sparc Performs Automated Reasoning in Chemistry) properties calculator

²from the Handbook of Chemistry and Physics, 79th Edition, 1995-96

³from the NRCS ARS Pesticide Properties Database for pH of 7

⁴from the NRCS ARS Pesticide Properties Database (selected value by ARS)

Note: D_a = vapor phase molecular diffusivity coefficient
K_h = Henry's constant
ENPY = enthalpy of vaporization
K_w = liquid phase decay rate
K_s = solid phase decay rate
K_{oc} = organic carbon coefficient

Values for D_a and K_h were obtained from the EPA Region VI Delisting Spreadsheets (except as noted). Values for ENPY were obtained from the PRZM-3 User's Manual (except as noted). Values for K_w and K_s were calculated based on 25 °C and rate constants from the Hazardous Waste Identification Rule (HWIR) publication (EPA, 1995) (except as noted). Values for K_{oc} were taken from the HWIR publication (except as noted).

3.4 DESIGN OF SIMULATIONS

For each selected site, a generic PRZM-3 input file was generated. This generic file was then modified as required to reflect the chemical data for a specific POP. The generic input file was generated using the capabilities of the Pesticide Assessment Tool for Rating Investigations of Transport (PATRIOT) (Imhoff et al, 1993). PATRIOT is a decision support system that allows the user to interact with a series of databases (including rainfall, soils, cropping, and pesticides).

In order to generate the generic PRZM-3 input data set for each site, the PATRIOT system was used to identify the most predominant soil type for the crop of interest, and to identify the nearest meteorological station. The option to generate a PRZM (version 2) input file was then selected. This file was then modified as required to reflect the changes in the input data requirements for the PRZM-3 model. PATRIOT was used to define the following variables in the final versions of the input files used for detailed simulations: crop emergence, maturation, and harvest dates; the curve number (CN) data used for runoff calculations; total depth of soil core; and soil horizon data including bulk density, initial soil water content, field capacity, wilting point, and percent organic carbon.

Other sources of data were used to build the generic PRZM-3 input files, including the PRZM-3 User's Manual and the soils database included within the NRCS 1992 National Resources Inventory. Once completed, the generic input files for each site were then modified for each POP, using the chemical data in Table 3.2. Appendix A provides documentation for the major assumptions made and for the sources of data used for the base PRZM-3 simulations.

Since study simulations were designed to be at least 100 years long, the option to use the 10 year record in the PATRIOT rainfall database was not used. Instead, once a meteorological station had been identified, the data for that station were downloaded from the EPA's Center for Exposure Assessment Modeling (CEAM) site. The met stations selected are shown in Table 3.1. Most stations had 36 years of data; the available data for each station were successively appended to provide a meteorology input file with 100 years of data.

The PRZM-3 irrigation option was selected for corn sites 3 and 7; cotton sites 9, 10, and 16; and wheat site 25. Irrigation was chosen for these sites based on United States Department of Agriculture maps showing percent of cropland in irrigation by county for 1992 (see web site address "<http://www.nhq.nrcs.usda.gov/land/meta/m2289.html>").

Pesticide applications were assumed to be 1.0 kg/ha, applied on the same date to the same crop for every year of the simulations. All pesticides were assumed to be soil applied, using a default incorporation depth of 4 cm. The processes of biodegradation and plant uptake of pesticides were not considered.

3.5 RESULTS OF SIMULATIONS

The results of the PRZM-3 simulations are presented in this section. Soil concentrations are presented throughout as average concentrations over the top 15 cm of the soil column. The 15 cm depth was judged to be reasonable to support risk assessments in which primary exposure routes are ingestion and dermal contact. The leaching of POPs below the 15 cm depth was considered to be a loss term, although that does not necessarily imply transport to the groundwater system.

HydroGeoLogic wrote a simple post processor which parsed the PRZM-3 output file and extracted the total, adsorbed, dissolved, and gaseous concentrations for the top 15 cm at the end of every month. Graphs of total concentration vs time were prepared and investigated. Simulations beyond 100 years were then conducted where required to allow concentrations to reach steady state. These were conducted by repeating the original simulation (from 0 to 100 years), but with initial soil pesticide concentrations set equal to the concentrations predicted at time = 100 years. At every site, the modeled soil compartment thickness was 1 cm over the depth range from which concentration data were investigated.

Figure 3.7 shows typical simulation results for toxaphene. The figure shows end of month average soil concentration versus time. The results shown are taken from Site 1, but are representative of the behavior of toxaphene at all sites. Similarly, all other results shown in this section are typical for the respective POPs and are taken from Site 1.

Figure 3.7 demonstrates typical behavior for the more "well-behaved" POPs of those investigated in detail. Initially, the sum of all of the loss terms associated with erosion, runoff, volatilization, decay, and leaching is much lower than the annual unit source term. Average soil concentrations increase rapidly, but the increase in concentration leads to higher loss terms, which are each a function of soil concentration. Eventually, the annual loss term approximately balances the annual source term, and steady state concentrations are achieved.

From Figure 3.7, it appears that steady state concentrations are achieved sometime after about 60 years, but because of the monthly variation in concentration it is not immediately clear what we mean by steady state. It was determined that an objective means to determine "time to reach steady state" was required, so that simulation results could be processed objectively and consistently.

The methodology adopted to determine the time required for steady state conditions to be achieved involved plotting the percent change in the moving average of the computed soil concentration data. Theoretically, when the value of the percent change in moving average reaches zero, steady state conditions have been achieved. Durations of from one to five years for the moving average computation were considered. Figure 3.8 shows these data for the toxaphene plot presented in Figure 3.7 for one year and five year moving averages. Successively longer moving average periods reduce the "noise" in the data and produce smoother and more consistent curves. A moving average period of five years was adopted in the subsequent determination of time required to reach steady state conditions for all POPs at all sites. Based on this moving average period, the time required for toxaphene concentrations shown in Figure 3.7 to reach steady state conditions (hereinafter designated T_{ss}) is 74.08 years, at which time the average concentration is 4.77 mg/kg.

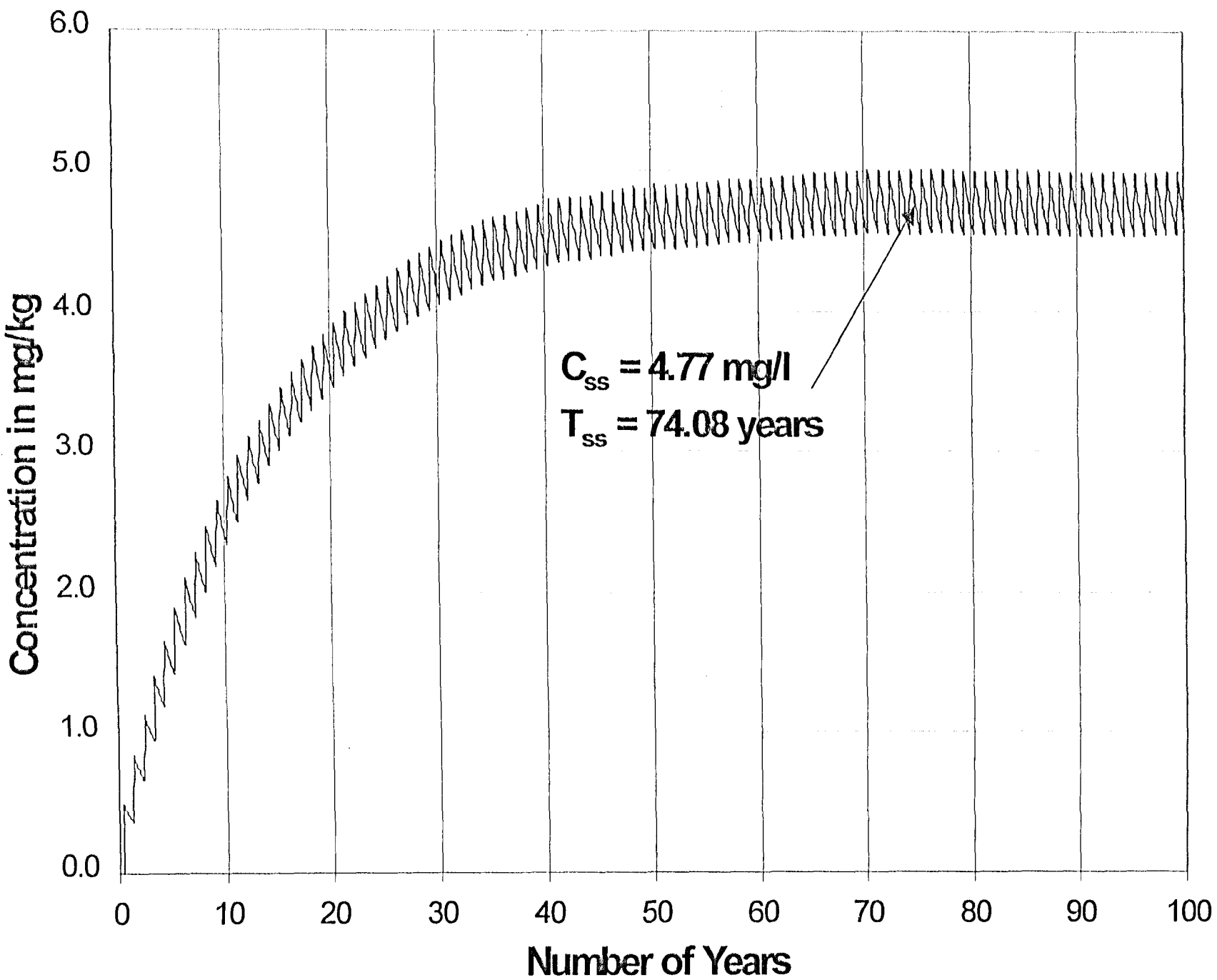


Figure 3.7 Typical PRZM-3 Simulation Results - Toxaphene.

Figure 3.8 Time Required to Reach Steady State - Toxaphene.

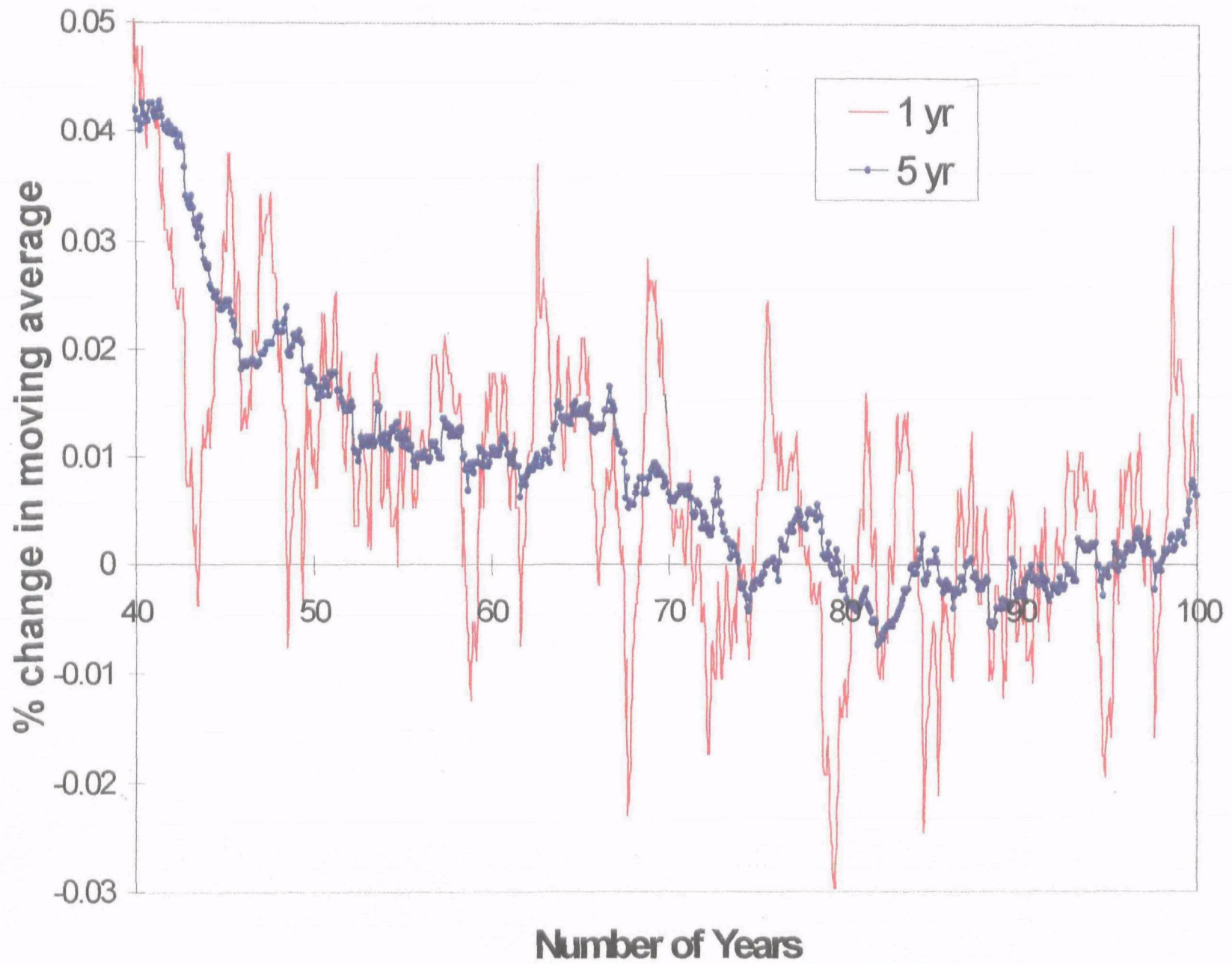


Figure 3.9 Typical PRZM-3 Simulation Results - Chlordane.

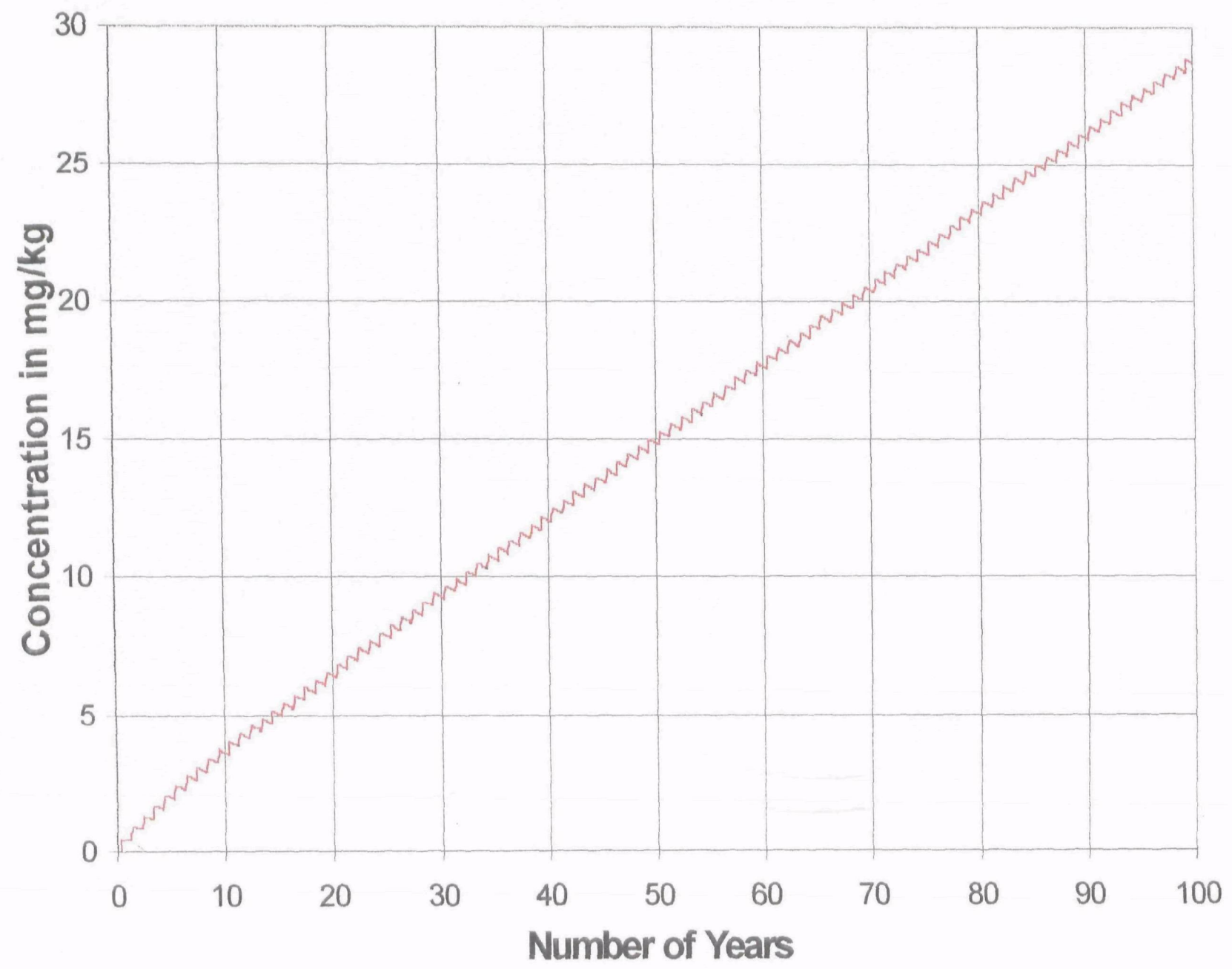
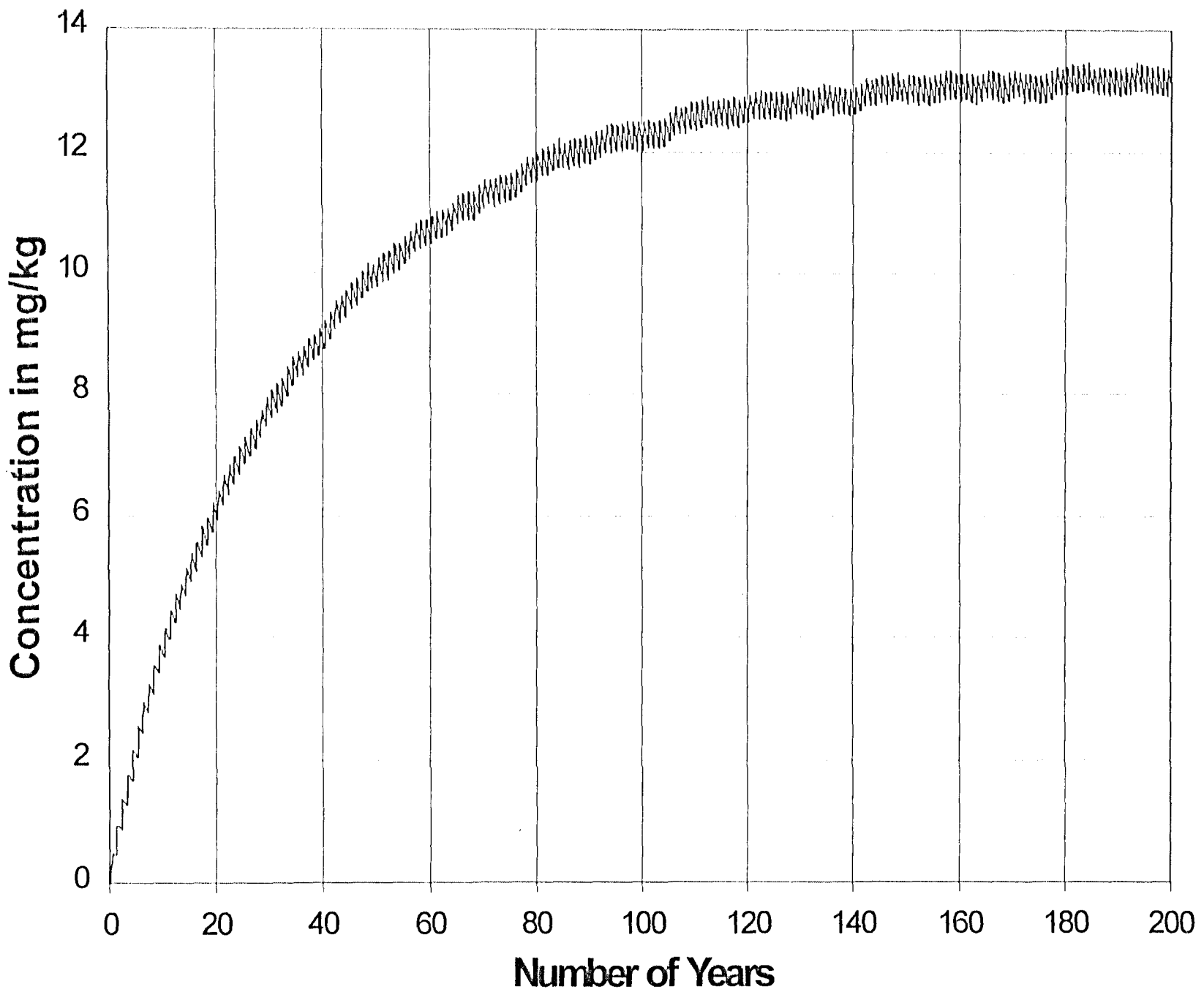


Figure 3.10 Typical PRZM-3 Simulation Results - DDD.



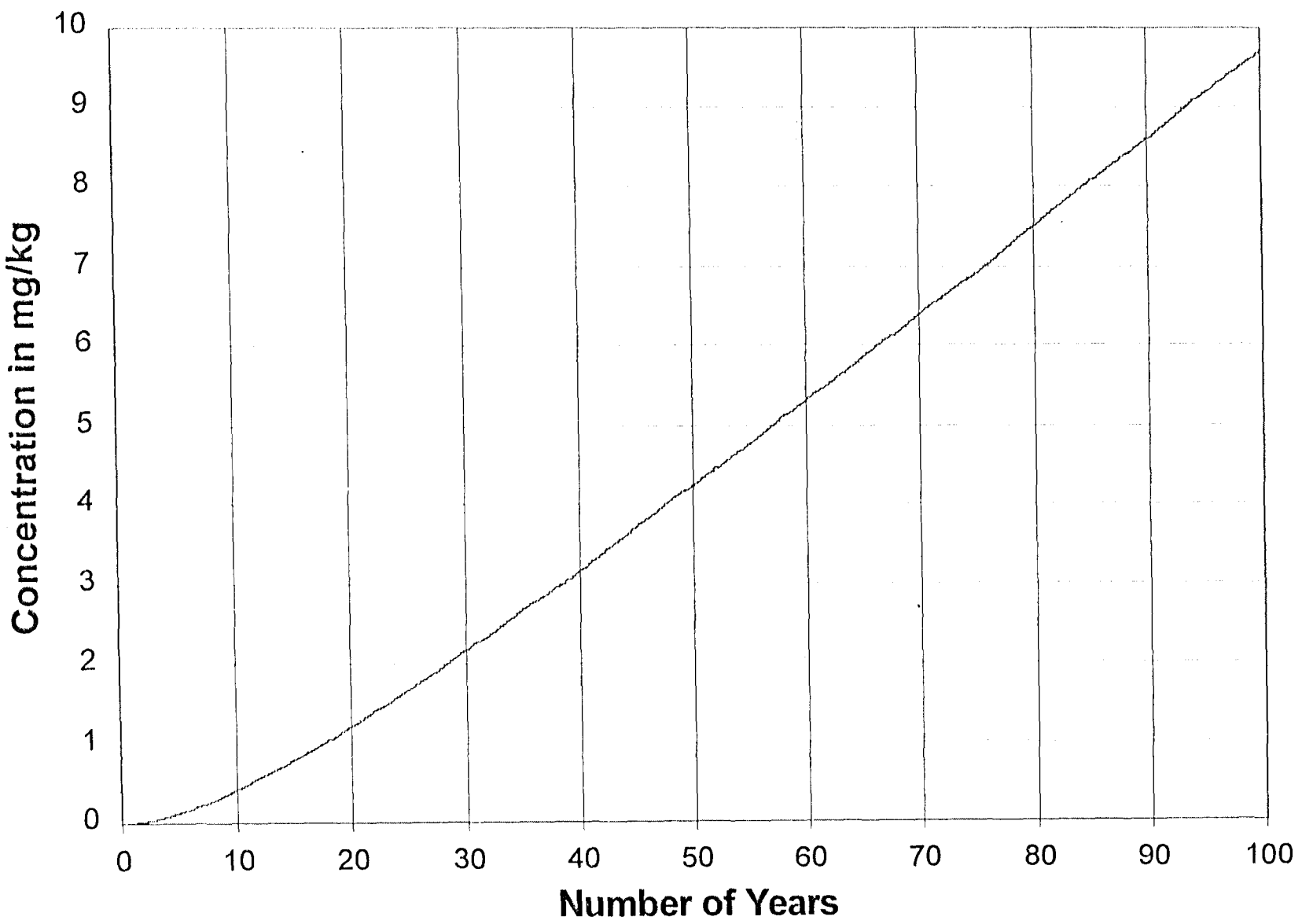
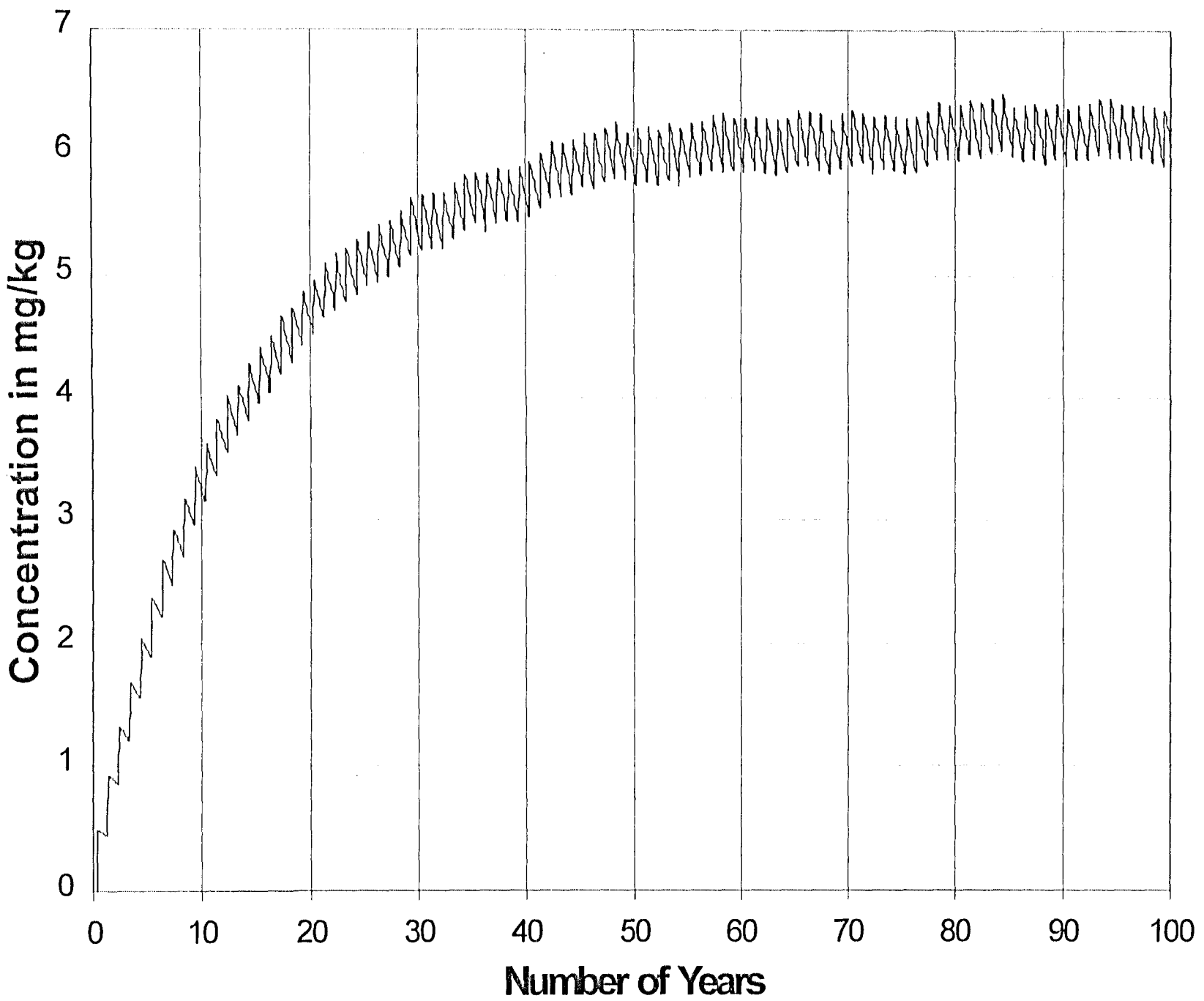


Figure 3.11 Typical PRZM-3 Simulation Results - DDE.

Figure 3.12 Typical PRZM-3 Simulation Results - DDT.



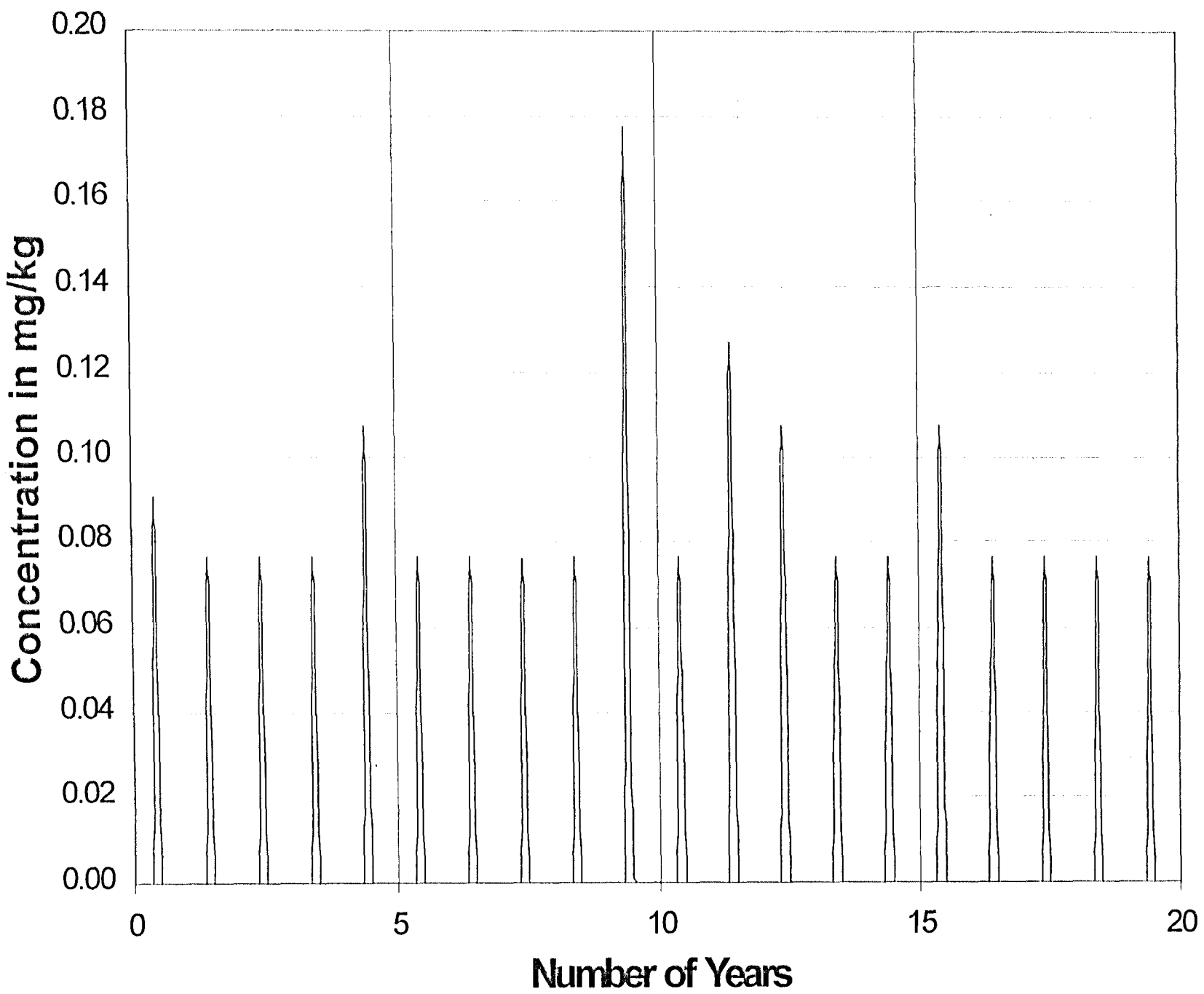


Figure 3.13 Typical PRZM-3 Simulation Results - Dicofol

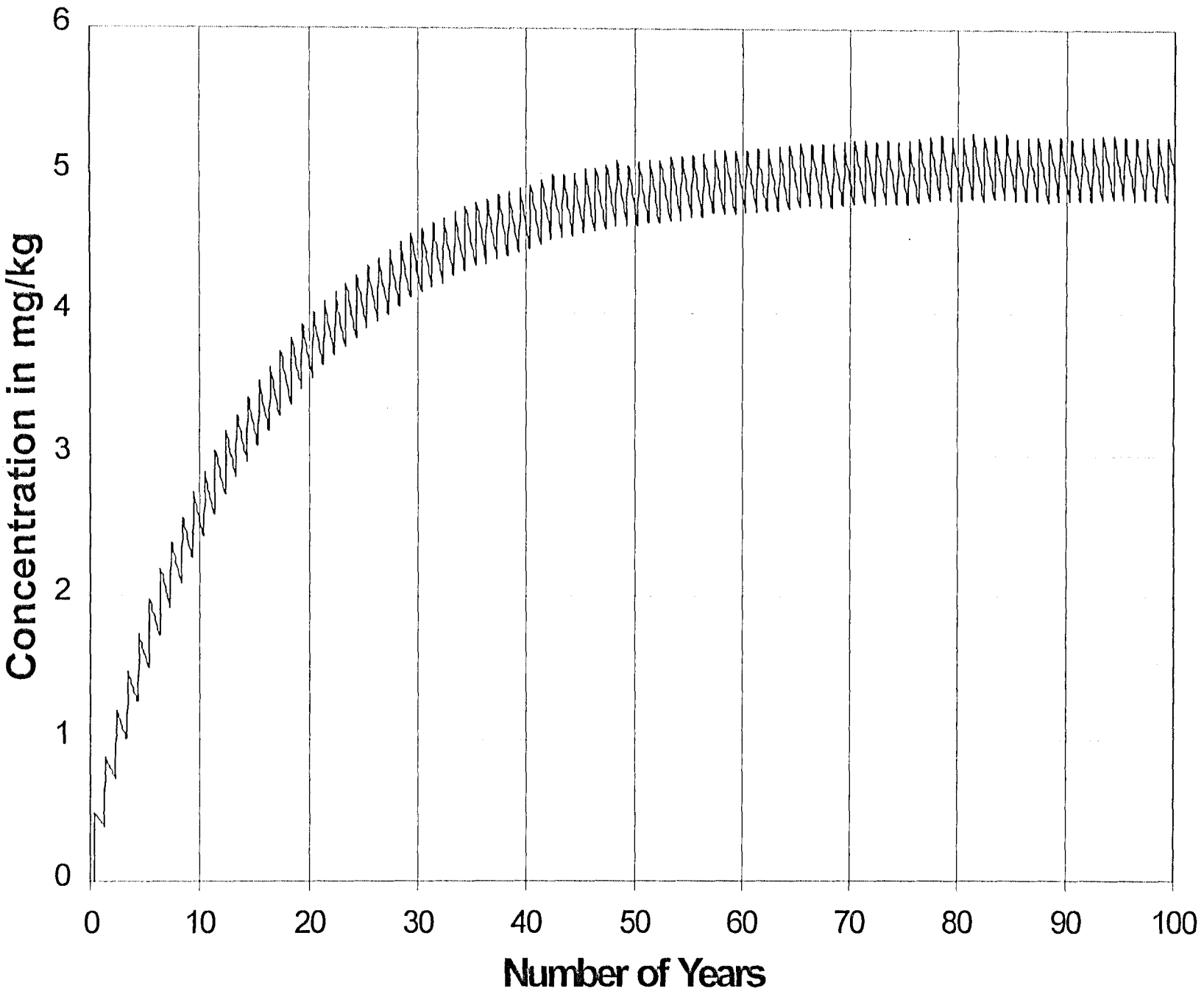


Figure 3.14 Typical PRZM-3 Simulation Results - Dieldrin

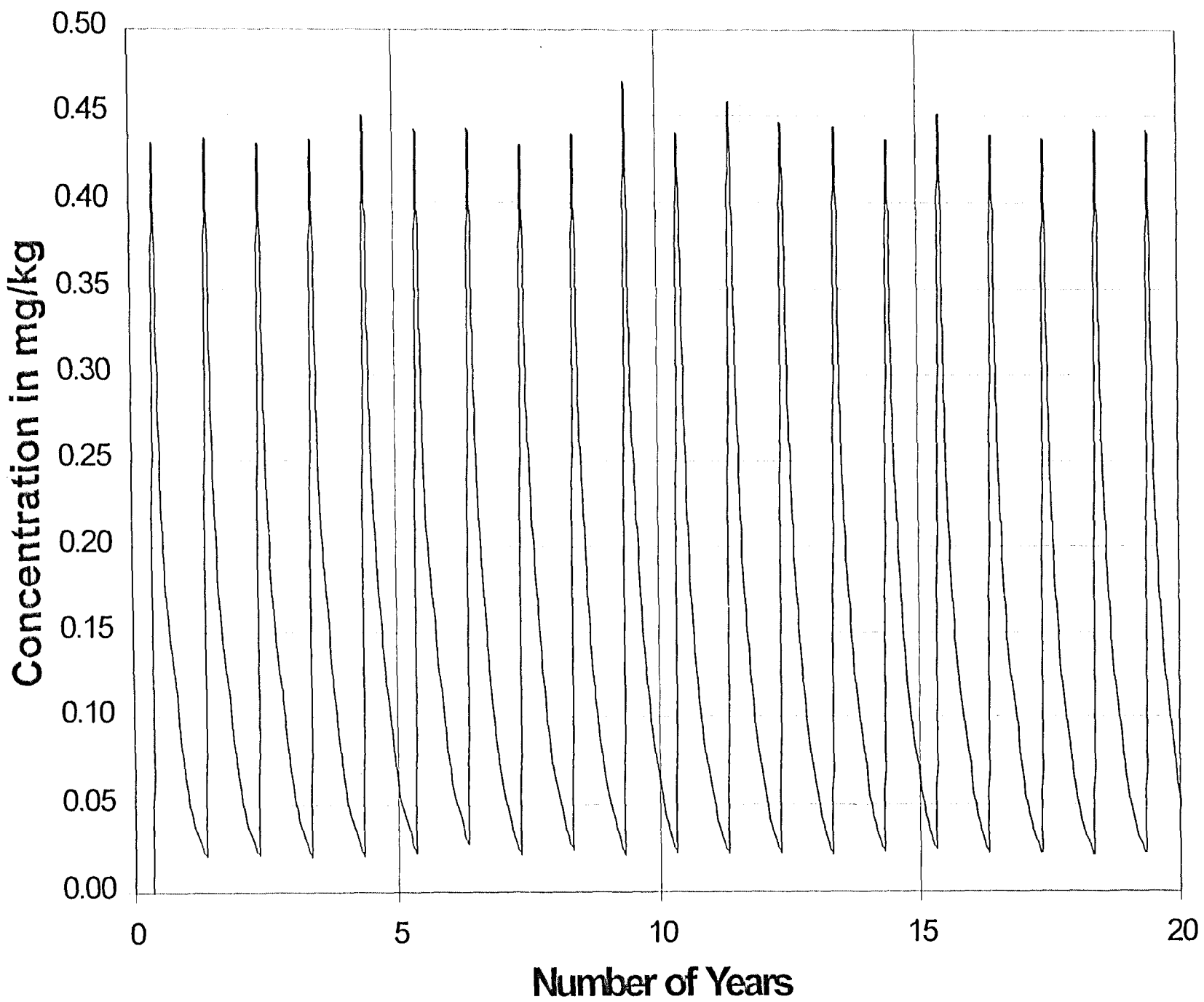
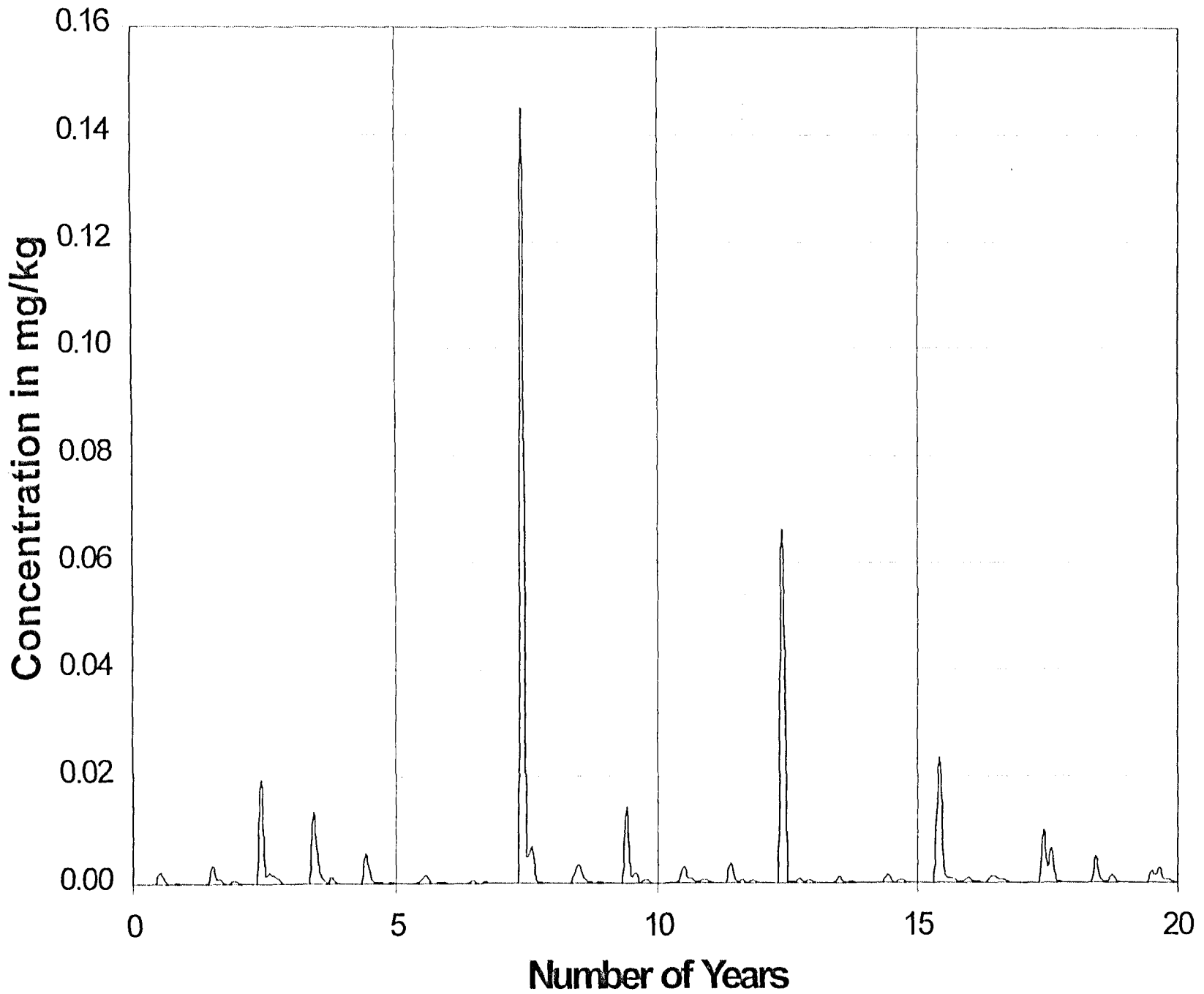


Figure 3.15 Typical PRZM-3 Simulation Results - Endosulfan

Figure 3.16 Typical PRZM-3 Simulation Results - Furan



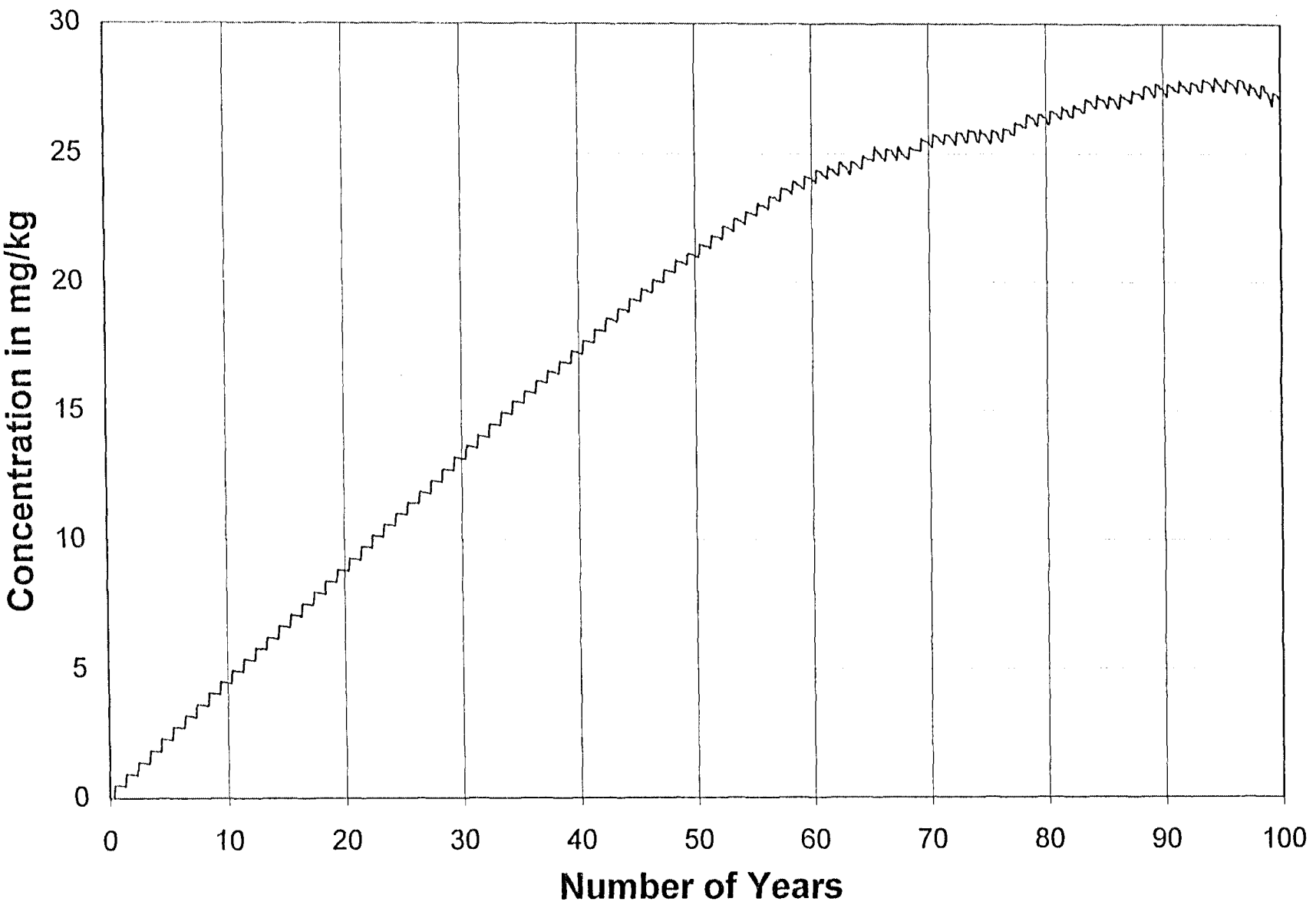


Figure 3.17 Typical PRZM-3 Simulation Results - Kepone.

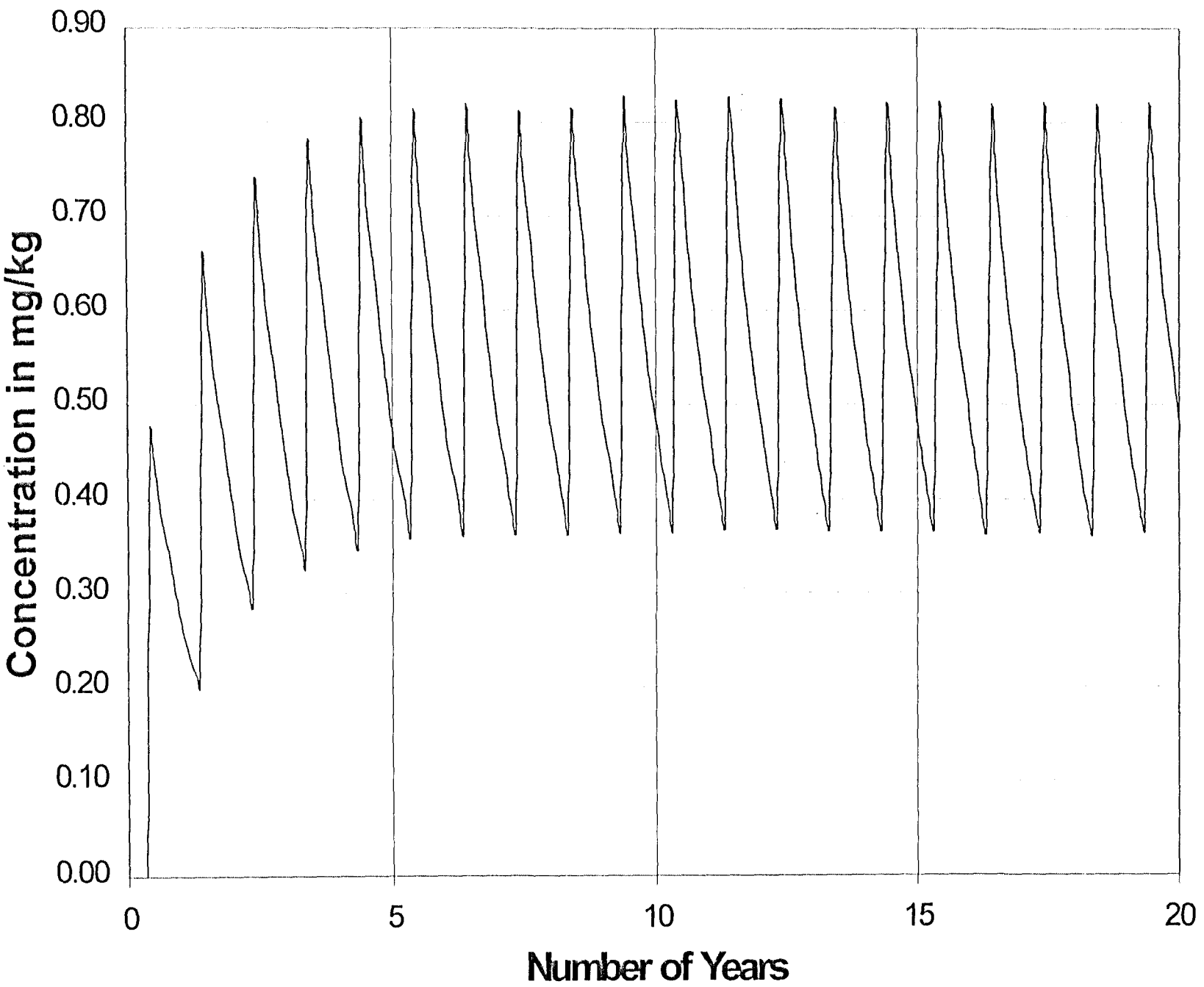


Figure 3.18 Typical PRZM-3 Simulation Results - Methoxychlor.

The magnitude of the steady state concentration (hereinafter designated C_{ss}) is therefore assumed to be 4.77 mg/kg. (Note that while C_{ss} and T_{ss} data are typically reported quite precisely, this is an artifact of the software used to generate these numbers. The accuracy of these data are probably limited to 1 or 2 significant figures; for the above example, it would therefore be acceptable to assume that $C_{ss} = 4.8$ mg/l and $T_{ss} = 74$ years.)

Inspection of Figure 3.7 and Figures 3.9 through 3.18 demonstrates that there are several types of behavior among the investigated POPs (a discussion of each compound is presented later). The most persistent compounds are chlordane and DDE. These compounds did not show a tendency to reach steady state, even for simulations as long as 400 years. Both of these POPs have high K_d values (indicating a strong tendency to remain in the solid phase) and zero K_s values. Computed concentrations at the end of the initial 100 year simulation for chlordane and DDE are presented in Table 3.3.

Table 3.3
Computed Concentrations in mg/kg at t=100 years: Chlordane and DDE

Site	Chlordane	DDE
1	28.74	9.69
2	31.38	10.57
3	26.23	8.60
4	29.13	9.58
5	24.01	8.67
6	32.59	12.40
7	28.87	9.60
8	33.37	11.07
9	24.94	9.43
10	27.03	9.00
11	24.73	9.63
12	26.28	8.64
13	28.53	10.33
14	26.14	8.69
15	25.10	10.04
16	29.18	9.58
17	24.26	9.24
18	29.38	10.91
19	32.89	11.11
20	29.17	9.59
21	32.38	12.29
22	29.08	9.59
23	30.47	10.17
24	27.55	9.14
25	26.97	9.06
26	32.90	12.51
27	30.21	10.30
28	29.71	11.50
29	29.91	12.11
30	27.77	9.04
31	30.38	9.92
32	31.05	10.63

The POPs DDD and kepone are also strongly persistent. However, these compounds show a tendency to reach steady state concentrations after an extended period of time, often in excess of 100 years. Values of C_{ss} and T_{ss} for these compounds are presented in Table 3.4.

Table 3.4
 C_{ss} and T_{ss} : DDD and Kepone

Site	DDD		Kepone	
	C_{ss} , mg/kg	T_{ss} , yrs	C_{ss} , mg/kg	T_{ss} , yrs
1	12.65	116.25	27.69	97.33
2	13.13	95.42	21.67	60.50
3	10.69	108.67	22.59	84.25
4	12.17	95.58	51.99	161.33
5	11.09	97.67	13.16	54.08
6	15.97	113.58	82.52	228.42
7	12.51	140.92	20.91	81.58
8	13.43	84.75	74.41	199.58
9	12.98	162.5	7.11	28.00
10	11.29	161.75	14.97	67.08
11	13.04	134	5.69	23.17
12	9.56	76.25	37.20	135.58
13	13.35	112.17	44.91	148.50
14	9.96	98.42	16.97	62.75
15	12.77	109.58	31.42	95.00
16	12.04	141.58	19.95	82.08
17	12.18	112.67	3.14	12.42
18	14.69	138.08	22.34	72.42
19	13.84	86.42	> 156	> 400
20	11.93	97.75	30.36	97.75
21	15.39	102.42	> 173	> 400
22	11.91	98.75	36.87	126.08
23	12.69	95.67	32.31	95.92
24	11.43	93.08	44.33	140.17
25	11.73	114.83	20.27	70.92
26	15.56	100.58	104.34	293.83
27	12.81	87.58	66.31	189.75
28	14.49	104.67	25.93	87.83
29	14.6	100.67	78.54	241.58
30	10.75	85.83	26.12	91.58
31	11.94	84.83	59.09	185.50
32	12.61	74.17	58.96	174.17

The next group of POPs demonstrated a consistent tendency to reach steady state conditions in less than 100 years. This group includes DDT, dieldrin, methoxychlor, and toxaphene. In addition, the magnitude of the C_{ss} for a specific POP did not show as much variation from site to site as for the more persistent POPs. Values of C_{ss} and T_{ss} for these compounds are presented in Table 3.5.

Table 3.5
 C_{ss} and T_{ss} : DDT, Dieldrin, Methoxychlor, and Toxaphene

Site	DDT		Dieldrin		Methoxychlor		Toxaphene	
	C_{ss} , mg/kg	T_{ss} , yrs	C_{ss} , mg/kg	T_{ss} , yrs	C_{ss} , mg/kg	T_{ss} , yrs	C_{ss} , mg/kg	T_{ss} , yrs
1	5.98	52.25	5.00	74.50	0.56	13.58	4.77	74.08
2	6.19	48.75	5.40	58.50	0.58	11.67	5.19	54.75
3	4.87	44.83	4.55	63.92	0.51	11.67	4.40	65.58
4	4.96	27.58	5.30	57.42	0.64	13.50	4.93	57.42
5	5.51	52.33	4.31	83.58	0.47	11.83	3.97	67.33
6	7.80	68.42	5.76	75.83	0.67	13.42	5.25	73.75
7	5.85	75.42	5.02	75.42	0.55	12.33	4.85	69.67
8	6.60	42.67	5.92	63.58	0.70	12.42	5.49	63.58
9	5.94	63.83	4.63	92.00	0.47	16.17	3.64	33.75
10	4.95	62.25	4.65	81.33	0.51	16.50	4.40	61.75
11	6.13	63.92	4.58	83.00	0.48	12.42	3.24	27.58
12	4.47	36.25	4.11	95.58	0.52	10.75	4.23	56.33
13	6.53	63.92	5.16	74.42	0.59	11.67	4.78	79.67
14	4.64	61.00	4.38	62.08	0.48	9.50	4.26	62.08
15	6.52	62.58	4.32	80.42	0.47	12.92	4.01	66.17
16	5.48	65.92	5.06	76.75	0.57	15.42	4.88	74.50
17	5.46	44.58	4.23	62.50	0.42	11.58	2.14	15.42
18	6.98	59.42	5.27	85.83	0.59	13.67	4.96	63.58
19	6.99	49.75	5.82	49.75	0.70	12.67	5.34	60.83
20	5.83	53.25	5.08	61.75	0.60	13.58	4.90	71.67
21	7.58	63.50	5.78	65.83	0.68	13.75	5.09	76.58
22	5.90	62.08	5.04	62.42	0.59	12.00	4.77	70.50
23	6.30	58.50	5.24	59.58	0.60	11.67	5.00	57.75
24	5.73	55.42	4.85	68.50	0.58	10.50	4.55	69.42
25	5.71	69.08	4.68	69.92	0.53	12.33	4.44	68.08
26	7.63	61.75	5.93	77.75	0.67	11.83	5.32	77.75
27	6.38	47.58	5.28	64.83	0.60	15.83	4.86	66.42
28	7.42	63.33	5.08	81.42	0.57	14.42	4.56	64.67
29	7.10	69.58	5.32	69.58	0.59	14.83	4.78	66.58
30	5.28	48.75	4.71	50.17	0.58	11.58	4.64	59.67
31	5.98	47.83	5.11	48.83	0.60	10.17	4.86	64.42
32	6.38	38.17	5.43	72.42	0.63	11.08	4.98	80.00

Finally, a group of compounds exhibited no tendency to reach steady state conditions. For these compounds, the loss terms were sufficient to reduce the average concentration in the top 15 cm to zero (or nearly to zero in the case of endosulfan). This group includes dicofol, endosulfan, and furan. Since these compounds exhibited no tendency towards persistence (at least as defined for this study), computed concentration results are not presented here.

Following is a brief discussion of the PRZM-3 simulation results for each compound, presented in order of persistence behavior (as discussed above):

Chlordane

Chlordane simulations, even those carried out as far as 400 years, produced concentration vs time plots that were nearly linear (similar to Figure 3.9). Chlordane had one of the highest K_{oc} (and consequently, K_d) values of the investigated POPs, indicating a strong tendency to remain in the solid or adsorbed phase. Since its solid phase decay rate (K_s) is zero, soil concentrations continue to increase year after year. Note that chlordane has a relatively high K_h value among the investigated POPs; volatilization losses were typically the highest loss term in the PRZM-3 simulations. However, because the compound remains primarily in the solid phase, computed volatilization losses were relatively minor.

DDE

DDE was the only one of the investigated POPs for which the PRZM-3 parent daughter simulation capabilities were employed. The results of these simulations were not included in the development of the predictive screening level methodology, but are reported here for purposes of project documentation.

We assumed that DDT degradation would produce decay products of 40% DDD and 40% DDE (DDD was included in the parent daughter simulations to preserve mass balance). Since the DDT K_s value is $1.64E-04/\text{day}$ (see Table 3.2), the simulated rate for production of solid phase DDE from degradation of DDT was therefore $0.40(1.64E-04/\text{day})$ or $6.56E-05/\text{day}$. Similarly, the simulated rate for production of liquid phase DDE from degradation of DDT was therefore $0.40(1.01E-03/\text{day})$ or $4.04E-04/\text{day}$. The K_s and K_w rates for DDE are both zero.

Simulation results for DDE indicate a high degree of persistence, similar to chlordane. In fact, the K_{oc} value for DDE was the highest of the POPs investigated. This compound demonstrates a strong tendency to remain in the solid phase and not decay. The highest loss term for this compound in PRZM-3 simulations was typically erosion.

DDD

DDD, like DDE, is a daughter product of DDT. However, DDD has historically been used as a pesticide. Therefore, it was simulated in a fashion similar to all of the other investigated POPs. DDD has a K_{oc} value equal to that of chlordane, but, unlike chlordane, it has a nonzero K_s value of $6.85E-04/\text{day}$. While this value is relatively low, the decay loss term was typically the highest for this compound in the PRZM-3 simulations. The low rates of decay account for the long T_{ss} values for this compound.

Kepone

Kepone is another compound that exhibited long T_{ss} values for many sites. It has a zero decay rate for both solid and liquid phases. Unlike DDD, however, kepone has a relatively low K_{oc} value, which means it is relatively more likely to be in the liquid or gaseous phase. Of the true loss terms considered, volatilization losses were typically highest in the PRZM-3 simulations. However, because kepone is more readily transported through the soil column in the liquid phase than some of the other POPs, some of the "loss" for this compound is associated with leaching.

As shown in Table 3.4, values of C_{ss} and T_{ss} for kepone at sites 19 and 21 were not determined. These two sites had the highest percent organic carbon of any of the simulated sites, and the high K_d values for kepone produced strongly persistent behavior. Simulations were carried out to 400 years for both sites, at which point steady state conditions had not yet been achieved.

DDT

DDT was simulated as a parent with no daughter products in order to determine its ultimate concentration in the upper soil profile. While DDT has one of the higher K_{oc} values investigated, it also has K_s , K_w , and K_h values that allow losses that are higher than the more persistent POPs investigated. The decay losses were typically the highest losses in the PRZM-3 simulations. As shown in Table 3.5, DDT was one of the most consistent POPs investigated, with a fairly narrow range of C_{ss} and T_{ss} values.

Dieldrin

Dieldrin simulations indicate behavior similar to that of DDT. Again, the chemical parameters for dieldrin suggest a compound that will be persistent, but not strongly so, and subject to a wide range of loss processes. For dieldrin, the highest loss term was decay, followed by volatilization losses which typically were about half the decay losses. This compound, like DDT, behaved in a very consistent fashion from site to site.

Methoxychlor

Methoxychlor, as shown in Figure 3.18, is at the lower end of what might be considered the range of possible persistent behaviors. Soil concentrations of methoxychlor typically increase for several years, but quickly reach a steady state condition where the loss terms match the application rate. Methoxychlor has a relatively low K_{oc} value and the highest K_s value of all of the "persistent" POPs investigated. The highest loss term for methoxychlor was typically decay.

Toxaphene

Toxaphene is similar to DDT and dieldrin in its behavior from site to site, with a tendency to reach steady state conditions at consistent values of C_{ss} and T_{ss} . This POP has a relatively low K_{oc} value, and typically was subjected to losses in the solid, liquid, and gaseous phases. Its primary loss mechanism is associated with decay.

Dicofol

Dicofol had one of the lowest K_{oc} values investigated, and also had the highest K_s and K_w rates of any of the POPs. Its decay losses were the highest of any POP investigated, and these losses were sufficient to prevent any accumulation of chemical from year to year.

Endosulfan

Endosulfan behavior is somewhat similar to that of methoxychlor. In fact, at all sites, the computed minimum concentrations never reached zero after the first year or two. However, because its loss terms are relatively high, it is not judged to behave as a "persistent" pesticide. The endosulfan K_{oc} value is lower than methoxychlor, and the decay term for the liquid phase significantly higher. The highest loss term for endosulfan in the PRZM-3 simulations was decay.

Furan

Furan is not a persistent POP, at least as defined for this study. Its minimum concentration reaches zero every year at all sites, and it exhibits no tendency to accumulate in the top soil layer. Furan has the lowest K_{oc} value of all of the POPs investigated (by over two orders of magnitude). Although its solid and liquid phase decay rates are zero, it has a very high K_h value. It was the only POP investigated that had volatilization as its highest loss term.

4.0 SENSITIVITY ANALYSIS

Following completion of the base PRZM-3 simulations described in Section 3, a sensitivity analysis was conducted. The purpose of the sensitivity analysis was to determine which of the parameters in the PRZM-3 input files had the greatest effect on computed POP concentrations. The sensitivity analysis was performed by conducting and analyzing additional PRZM-3 simulations as described in this section.

Based on the base simulation results, it was determined to design the sensitivity analysis using dieldrin and kepone. These two POPs were chosen for additional analysis because they both exhibited the tendency toward steady state behavior of interest to this study. However, the chemical nature of these two compounds (at least with respect to their K_h , K_w , K_s , and K_{oc} values) were different enough to warrant investigating both.

Sensitivity analyses were conducted at four sites. One site was chosen for each of the four crops simulated in this study. The intent was to pick sites that would represent a wide range in climatological conditions across the country. The four sites selected were site number 4 (corn; Cayuga County, NY; cool and wet); site number 9 (cotton, Maricopa County, AZ; hot and dry); site number 22 (soybeans, Tunica County, MS; hot and wet); and site number 28 (wheat, Daniels County, MT, cool and dry).

A total of 21 PRZM-3 input parameters were modified (one parameter per simulation). Each parameter selected for inclusion in the sensitivity analysis was increased and decreased by 50% in separate simulations, and the resultant impact on computed soil concentrations tabulated. It should be noted that for two parameters (runoff CN and maximum percent coverage for a crop) it did not make physical sense to follow the $\pm 50\%$ variation. Runoff CNs were allowed to vary to the minimum and maximum values listed in the PRZM-3 User's Manual for a given hydrologic soil group. The minimum and maximum percent coverages were assumed to be 80 and 100, respectively (the base simulations assumed 95% coverage). For the purposes of this analysis, computed concentrations at $t = 50$ years were compared to the base simulation to determine the relative impact a particular parameter had on concentration.

Results of the sensitivity analyses for dieldrin are shown in Table 4.1, and for kepone in Table 4.2. The results indicate that the most sensitive parameters included K_h , K_s , K_d , and CN. These parameters were included in the attempt to develop a predictive screening level methodology described in Section 5.

Table 4.1
Results of Sensitivity Analyses for Dieldrin

PRZM-3 Parameter	Site #4: Corn Cayuga County, NY concentration in mg/kg, t=50yrs			Site #9: Cotton Maricopa County, AZ concentration in mg/kg, t=50yrs			Site #22: Soybeans Tunica County, MS concentration in mg/kg, t=50yrs			Site #28: Wheat Daniels County, MT concentration in mg/kg, t=50yrs		
	50%	100%	150%	50%	100%	150%	50%	100%	150%	50%	100%	150%
ANETD	5.128	5.128	5.122	4.377	4.393	4.691	4.876	4.879	4.879	4.825	4.837	4.846
USLEK	5.270	5.128	5.030	4.404	4.393	4.381	4.962	4.879	4.819	4.848	4.837	4.827
USLELS	5.271	5.128	5.030	4.404	4.393	4.381	4.957	4.879	4.825	4.849	4.837	4.827
USLEP	5.270	5.128	N/A	4.404	4.393	N/A	4.962	4.879	N/A	4.849	4.837	N/A
SLP	5.139	5.128	5.120	4.394	4.393	4.391	4.885	4.879	4.874	4.839	4.837	4.836
HL	5.150	5.128	5.105	4.393	4.393	4.391	4.889	4.879	4.874	4.838	4.837	4.837
CINTP	5.129	5.128	5.127	4.391	4.393	4.392	4.883	4.879	4.875	4.839	4.837	4.835
AMXDR	5.135	5.128	5.121	4.737	4.393	4.474	4.880	4.879	4.879	4.835	4.837	4.839
HTMAX	5.128	5.128	5.128	4.393	4.393	4.393	4.879	4.879	4.879	4.837	4.837	4.837
USLEC	5.269	5.128	5.029	4.404	4.393	4.381	4.961	4.879	4.818	4.849	4.837	4.827
MNGN	5.106	5.128	5.142	4.389	4.393	4.394	4.868	4.879	4.889	4.835	4.837	4.839
DAIR	5.371	5.128	4.962	4.835	4.393	4.147	5.147	4.879	4.723	5.233	4.837	4.654
HENRYK	5.371	5.128	4.962	4.834	4.393	4.147	5.146	4.879	4.723	5.232	4.837	4.654
ENPY	5.128	5.128	5.128	4.393	4.393	4.393	4.879	4.879	4.879	4.837	4.837	4.837
PCDEPL	N/A	5.128	N/A	4.095	4.393	4.804	N/A	4.879	N/A	N/A	4.837	N/A
RATEAP	N/A	5.128	N/A	4.393	4.393	4.393	N/A	4.879	N/A	N/A	4.837	N/A
DWRATE	5.128	5.128	5.128	4.394	4.393	4.392	4.879	4.879	4.879	4.838	4.837	4.836
DSRATE	8.149	5.128	3.669	7.230	4.393	3.050	7.846	4.879	3.462	7.814	4.837	3.416
KD	4.951	5.128	5.228	4.290	4.393	4.450	4.729	4.879	4.977	4.635	4.837	4.998
COVMAX	5.128	5.128	5.128	4.394	4.393	4.393	4.881	4.879	4.879	4.838	4.837	4.836
CN	5.492	5.128	4.981	4.487	4.393	4.251	5.155	4.879	4.813	4.872	4.837	4.81
% deviation from base simulation												
Parameter	50%	100%	150%	50%	100%	150%	50%	100%	150%	50%	100%	150%
ANETD	0.00	-	-0.12	-0.36	-	6.78	-0.06	-	0.00	-0.25	-	0.19
USLEK	2.77	-	-1.91	0.25	-	-0.27	1.70	-	-1.23	0.23	-	-0.21
USLELS	2.79	-	-1.91	0.25	-	-0.27	1.60	-	-1.11	0.25	-	-0.21
USLEP	2.77	-	N/A	0.25	-	N/A	1.70	-	N/A	0.25	-	N/A
SLP	0.21	-	-0.16	0.02	-	-0.05	0.12	-	-0.10	0.04	-	-0.02
HL	0.43	-	-0.45	0.00	-	-0.05	0.20	-	-0.10	0.02	-	0.00
CINTP	0.02	-	-0.02	-0.05	-	-0.02	0.08	-	-0.08	0.04	-	-0.04
AMXDR	0.14	-	-0.14	7.83	-	1.84	0.02	-	0.00	-0.04	-	0.04
HTMAX	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00
USLEC	2.75	-	-1.93	0.25	-	-0.27	1.68	-	-1.25	0.25	-	-0.21
MNGN	-0.43	-	0.27	-0.09	-	0.02	-0.23	-	0.20	-0.04	-	0.04
DAIR	4.74	-	-3.24	10.06	-	-5.60	5.49	-	-3.20	8.19	-	-3.78
HENRYK	4.74	-	-3.24	10.04	-	-5.60	5.47	-	-3.20	8.17	-	-3.78
ENPY	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00
PCDEPL	N/A	-	N/A	-6.78	-	9.36	N/A	-	N/A	N/A	-	N/A
RATEAP	N/A	-	N/A	0.00	-	0.00	N/A	-	N/A	N/A	-	N/A
DWRATE	0.00	-	0.00	0.02	-	-0.02	0.00	-	0.00	0.02	-	-0.02
DSRATE	58.91	-	-28.45	64.58	-	-30.57	60.81	-	-29.04	61.55	-	-29.38
KD	-3.45	-	1.95	-2.34	-	1.30	-3.07	-	2.01	-4.18	-	3.33
COVMAX	0.00	-	0.00	0.02	-	0.00	0.04	-	0.00	0.02	-	-0.02
CN	7.10	-	-2.87	2.14	-	-3.23	5.66	-	-1.35	0.72	-	-0.56

Table 4.2
Results of Sensitivity Analyses for Kepone

PRZM-3 Parameter	Site #4: Corn Cayuga County, NY concentration in mg/kg, t=50yrs			Site #9: Cotton Maricopa County, AZ concentration in mg/kg, t=50yrs			Site #22: Soybeans Tunica County, MS concentration in mg/kg, t=50yrs			Site #28: Wheat Daniels County, MT concentration in mg/kg, t=50yrs		
	50%	100%	150%	50%	100%	150%	50%	100%	150%	50%	100%	150%
ANETD	20.60	20.60	20.55	7.114	6.757	4.119	20.50	20.55	20.49	21.03	20.69	20.17
USLEK	21.68	20.60	19.86	6.798	6.757	6.721	21.33	20.55	19.97	20.90	20.69	20.50
USLELS	21.68	20.60	19.86	6.796	6.757	6.719	21.28	20.55	20.03	20.91	20.69	20.51
USLEP	21.68	20.60	N/A	6.798	6.757	N/A	21.33	20.55	N/A	20.91	20.69	N/A
SLP	20.69	20.60	20.54	6.763	6.757	6.753	20.60	20.55	20.50	20.72	20.69	20.68
HL	20.76	20.60	20.43	6.757	6.757	6.752	20.65	20.55	20.50	20.71	20.69	20.68
CINTP	20.65	20.60	20.56	6.792	6.757	6.751	20.59	20.55	20.51	20.63	20.69	20.75
AMXDR	20.65	20.60	20.55	4.939	6.757	5.168	20.56	20.55	20.54	20.84	20.69	20.49
HTMAX	20.60	20.60	20.60	6.757	6.757	6.757	20.55	20.55	20.55	20.69	20.69	20.69
USLEC	21.68	20.60	19.86	6.798	6.757	6.721	21.33	20.55	19.97	20.91	20.69	20.51
MNGN	20.44	20.60	20.71	6.745	6.757	6.764	20.43	20.55	20.63	20.65	20.69	20.72
DAIR	20.73	20.60	20.47	6.836	6.757	6.682	20.72	20.55	20.39	21.31	20.69	20.15
HENRYK	20.73	20.60	20.47	6.836	6.757	6.682	20.72	20.55	20.39	21.31	20.69	20.15
ENPY	20.60	20.60	20.60	6.757	6.757	6.757	20.55	20.55	20.55	20.69	20.69	20.69
PCDEPL	N/A	20.60	N/A	13.53	6.757	4.103	N/A	20.55	N/A	N/A	20.69	N/A
RATEAP	N/A	20.60	N/A	6.757	6.757	6.757	N/A	20.55	N/A	N/A	20.69	N/A
DWRATE	N/A	20.60	N/A	N/A	6.757	N/A	N/A	20.55	N/A	N/A	20.69	N/A
DSRATE	N/A	20.60	N/A	N/A	6.757	N/A	N/A	20.55	N/A	N/A	20.69	N/A
KD	21.17	20.60	19.82	3.446	6.757	10.120	18.05	20.55	19.99	13.22	20.69	22.47
COVMAX	20.61	20.60	20.59	6.751	6.757	6.752	20.56	20.55	20.55	20.67	20.69	20.70
CN	23.44	20.60	19.42	6.105	6.757	8.311	19.63	20.55	19.81	20.51	20.69	20.59
% deviation from base simulation												
Parameter	50%	100%	150%	50%	100%	150%	50%	100%	150%	50%	100%	150%
ANETD	0.00	-	-0.24	5.28	-	-39.04	-0.24	-	-0.29	1.64	-	-2.51
USLEK	5.24	-	-3.59	0.61	-	-0.53	3.80	-	-2.82	1.01	-	-0.92
USLELS	5.24	-	-3.59	0.58	-	-0.56	3.55	-	-2.53	1.06	-	-0.87
USLEP	5.24	-	N/A	0.61	-	N/A	3.80	-	N/A	1.06	-	N/A
SLP	0.44	-	-0.29	0.09	-	-0.06	0.24	-	-0.24	0.14	-	-0.05
HL	0.78	-	-0.83	0.00	-	-0.07	0.49	-	-0.24	0.10	-	-0.05
CINTP	0.24	-	-0.19	0.52	-	-0.09	0.19	-	-0.19	-0.29	-	0.29
AMXDR	0.24	-	-0.24	-26.91	-	-23.52	0.05	-	-0.05	0.72	-	-0.97
HTMAX	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00
USLEC	5.24	-	-3.59	0.61	-	-0.53	3.80	-	-2.82	1.06	-	-0.87
MNGN	-0.78	-	0.53	-0.18	-	0.10	-0.58	-	0.39	-0.19	-	0.14
DAIR	0.63	-	-0.63	1.17	-	-1.11	0.83	-	-0.78	3.00	-	-2.51
HENRYK	0.63	-	-0.63	1.17	-	-1.11	0.83	-	-0.78	3.00	-	-2.51
ENPY	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00	0.00	-	0.00
PCDEPL	N/A	-	N/A	100.24	-	-39.28	N/A	-	N/A	N/A	-	N/A
RATEAP	N/A	-	N/A	0.00	-	0.00	N/A	-	N/A	N/A	-	N/A
DWRATE	N/A	-	N/A	N/A	-	N/A	N/A	-	N/A	N/A	-	N/A
DSRATE	N/A	-	N/A	N/A	-	N/A	N/A	-	N/A	N/A	-	N/A
KD	2.77	-	-3.79	-49.00	-	-49.77	-12.17	-	-2.73	-36.10	-	8.60
COVMAX	0.05	-	-0.05	-0.09	-	-0.07	0.05	-	0.00	-0.10	-	0.05
CN	13.79	-	-5.73	-9.65	-	23.00	-4.48	-	-3.60	-0.37	-	-0.48

Site 9: Dieldrin - Sensitivity at T = 50 Years
Parameter: HENRYK

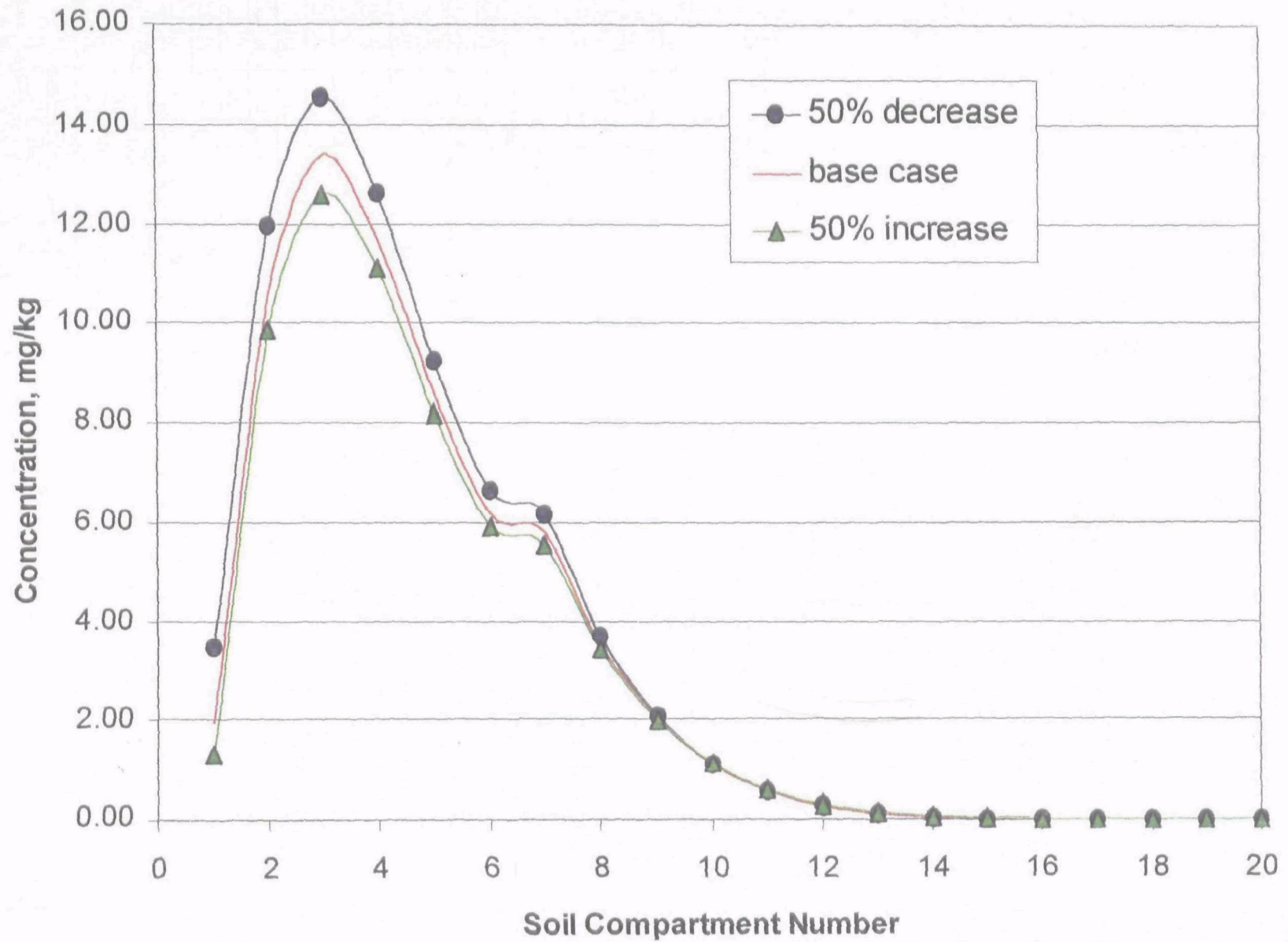


Figure 4.1 Sensitivity Analysis Results for Kh: Concentration Profiles for Dieldrin at Site 4.

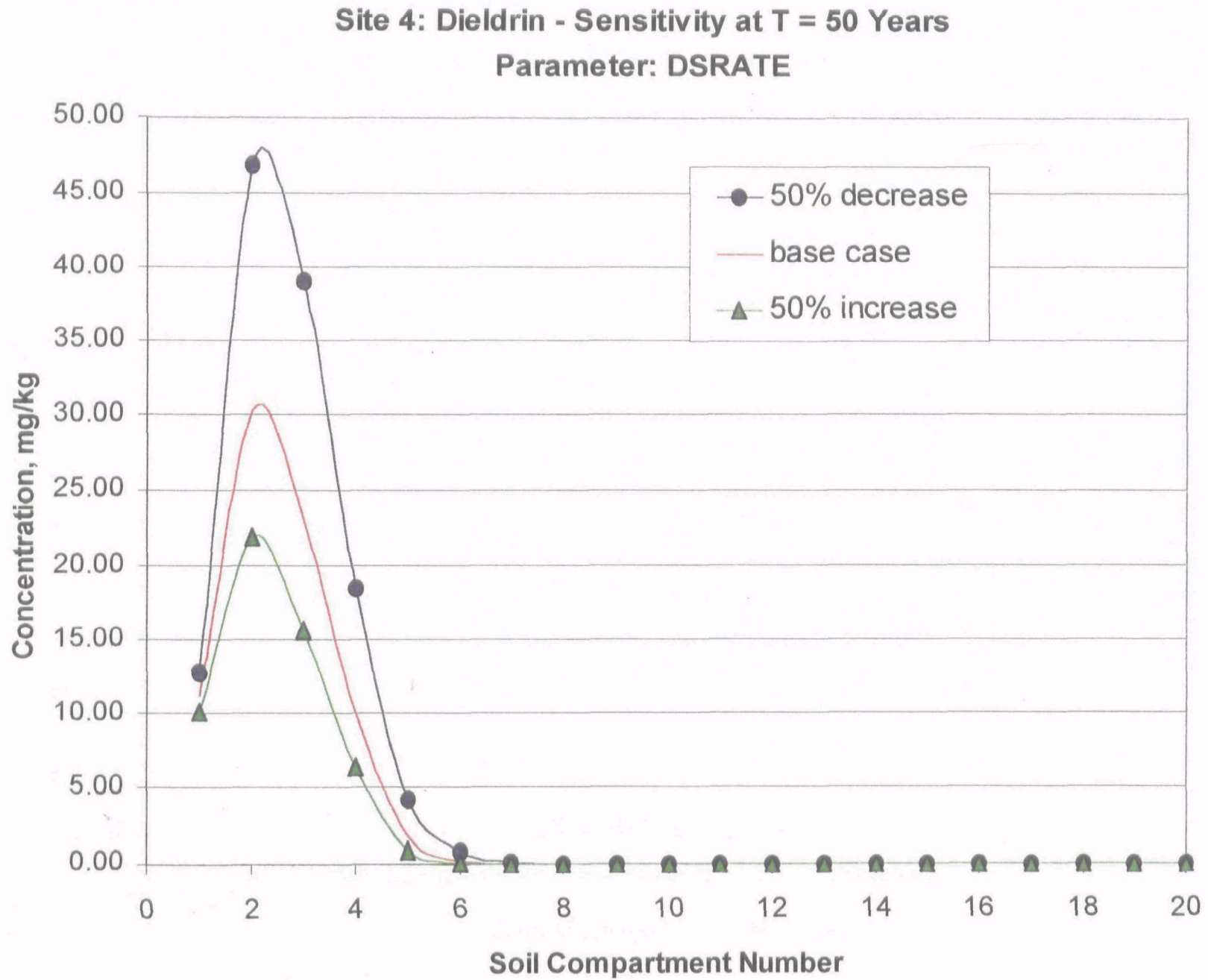


Figure 4.2 Sensitivity Analysis Results for Ks: Concentration Profiles for Dieldrin at Site 9.

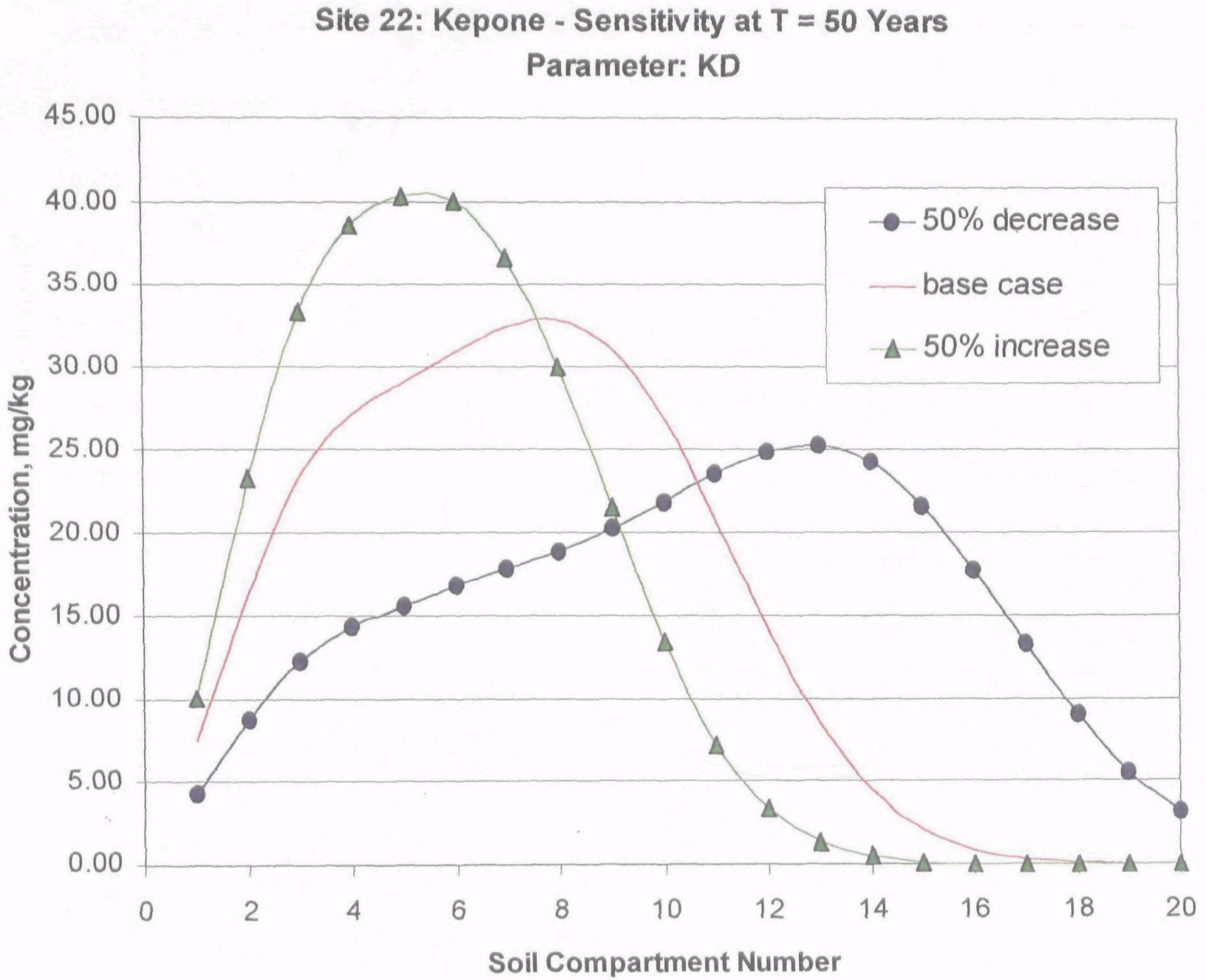


Figure 4.3 Sensitivity Analysis Results for Kd: Concentration Profiles for Kepone at Site 22.

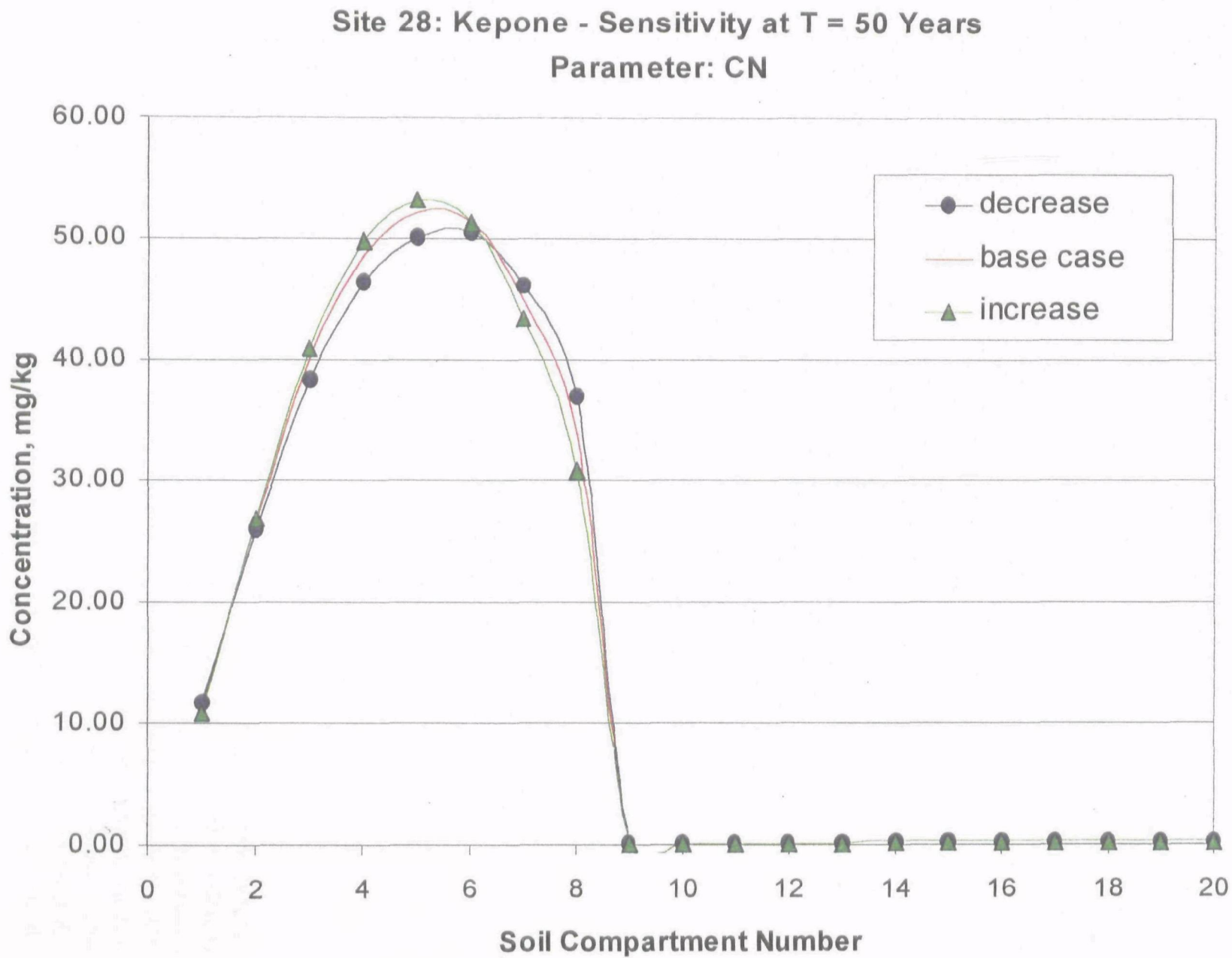


Figure 4.4 Sensitivity Analysis Results for CN: Concentration Profiles for Kepone at Site 28.

5.0 DEVELOPMENT OF PREDICTIVE METHODOLOGY

5.1 INITIAL STATISTICAL ANALYSIS OF PRZM-3 DATA

Output from the PRZM-3 model runs were assembled into a spreadsheet file. Simulation results for all of the POPs that exhibited steady state tendencies (DDD, DDT, dieldrin, kepone, methoxychlor, and toxaphene) were grouped into pages in the spreadsheet, one for each compound. Each spreadsheet page included data which described the input parameters and the results of a particular model run. The data included the following (PRZM-3 input parameters are shown in bold):

K_s ,
 K_d ,
 K_{oc} ,
 K_h ,
 D_a ,
percent organic carbon in the soil,
average annual loss due to decay,
average annual loss due to erosion,
average annual loss due to runoff,
average annual loss due to volatilization,
average annual remaining core storage,
average annual precipitation,
average annual evaporation,
average annual throughfall,
average annual snowfall,
average annual snow melt,
average annual runoff,
average annual infiltration,
average annual sediment loss,
average annual evapotranspiration,
average annual recharge,
 C_{ss} , and
 T_{ss} .

All of the parameters identified in the sensitivity analysis described in Section 4 were included with the exception of curve number CN. The CN is used to compute the amount of runoff (and hence infiltration) associated with a given increment of rainfall. It is known to vary seasonally, and 3 separate values for CN are required in the PRZM-3 input file. The effect of variation in CN was considered by including average annual values for precipitation, infiltration, runoff, evapotranspiration, and recharge. Separate consideration of each of these hydrologic water budget parameters allowed a more rigorous investigation of the effect of these parameters on computed values for C_{ss} and T_{ss} . The average annual values were computed from data parsed from the PRZM-3 output files.

A statistical analysis was performed, the objective of which was to determine a set of functions that would fit the existing model runs reasonably well. Two functions were desired: one to predict C_{ss} , and one to predict T_{ss} . This approach required balancing the two opposing goals of equation fit and equation simplicity. If allowed to use all the input parameters, an equation could be constructed which would match the model output very closely. This equation would be too complex and cumbersome to be practical, however. A simpler equation was therefore desirable.

The following discussion describes the search for an equation to fit C_{ss} data. The same approach was used in the search for an equation to fit T_{ss} data.

The analysis involved attempting to construct a function with the highest correlation coefficient (R^2) using the least number of terms and variables. The desired function would calculate C_{ss} in terms of one or more independent input variables. Some of the prospective input variables were rejected as possible candidates due to the difficulty in determining them without extensive modeling efforts. These included total evapotranspiration, and all of the average annual the loss terms. The list of potential predictor variables was then narrowed to these:

- K_s ,
- K_d ,
- K_{oc} ,
- K_h ,
- D_a ,
- percent organic carbon in the soil,
- average annual precipitation,
- average annual evaporation,
- average annual runoff,
- average annual infiltration, and
- total recharge.

Some of the variables on the above list were considered more likely candidates than others based on the results of the model sensitivity analysis.

The first steps taken in the search involved looking for a suitable function of a single variable using Microsoft Excel. In Excel, separate x-y plots were generated using each of the candidate variables as the independent variable with C_{ss} as the dependent variable. For each of the x-y relationships plotted, an R^2 value was computed for each of the following best fit curves: linear, logarithmic, polynomial (up to degree 6), power, and exponential. None were found to be useful. The highest reported R^2 value in this series was less than 0.5. Smaller data sets – one for each compound – were generated and, where appropriate, analyzed using the same methodology. (For instance, this would not be appropriate for K_s , since K_s is constant for a given compound.) A slightly higher R^2 value (0.7) was found in isolated cases, but in general this approach did not provide acceptable results.

In pursuit of a possible single-variable function, more analysis was performed using another piece of software. NCSS 2000, from Number Cruncher Statistical Systems, is a robust, elaborate statistical analysis package with a large number of available fit models. The existing spreadsheet data were imported into NCSS and all of the single-variable fit models were attempted. As in

Excel, none of these models had an acceptable R^2 value. At this point, the search for a single-variable function was abandoned.

Next, the NCSS software was employed in the search for a suitable multi-variable function. The number of possible *forms* of a multi-variable function is more limited, but the number of possible functions is staggering. Fortunately, NCSS provides a method for evaluating possible functions without having to construct each and every one. Using a process called "multivariate ratio search," NCSS will evaluate whole classes of possible functions in sequence, and report the results ranked by R^2 value. The basic approach is to construct a rational function (one in which there is a polynomial function in the numerator and another in the denominator) based on certain types of combinations of the independent variables. The user can specify the types of combinations to be considered, but in this case no limitations were placed on the search. In addition to the basic independent variables, this process can also utilize some transformations of the independent variables in the search. The allowable transformations are:

$$x' = \frac{1}{x^2}$$

$$x' = \frac{1}{x}$$

$$x' = \frac{1}{\sqrt{x}}$$

$$x' = \ln(x)$$

$$x' = \sqrt{x}$$

$$x' = x^2$$

In most cases, all of these transformations were tested. A special situation occurred, though, when K_s was used as one of the independent variables. Since K_s has a K_s of 0, some transformations (e.g., $\ln(x)$) would result in an overflow or underflow condition. Two approaches to this problem were taken. In one case, K_s was allowed to go to 0 and error-producing transformations were not considered. In the other, K_s was allowed to go only to 1×10^{-15} , and all transformations were considered.

Using the multivariate ratio search capabilities of NCSS, all possible combinations of two and three of the independent variables were explored. (Combinations of four variables were also considered briefly, but most of these tests produced functions with more than 50 terms. This was deemed too many terms for a useful application.) For each combination, all possible allowable functions were evaluated using all the available transformations. The best R^2 value for each combination was noted, along with the number of variables involved in the equation, the transformations applied, and the form of the equation itself. These were then ranked by R^2 , and the top echelon in each category (two- and three-variable functions) were chosen for closer inspection.

Closer inspection of each function consisted of generating several plots and exploring the overall behavior of the function. In each case, plots were generated showing the concentration predicted by PRZM-3 for each compound, with values predicted by the function overlaid for comparison.

These plots gave an indication of how well each function predicted the model output for specific compounds. Additional plots were generated for some of the two-variable cases. These were x-y plots which showed a curve generated by fixing one of the two variables and allowing the other to vary over the range found in the data set. The specific model output data points were graphed against these curves, providing further evidence of how well each function might predict the behavior of similar compounds.

Two tools were employed in exploring the overall behavior of each function. First, simple mathematical tests were applied to determine discontinuities, local maxima and minima, and other behavior patterns. Second, a small visualization program was written which graphed each function over the range of independent variables.

The three-variable functions generally had very high R^2 values (>0.96) when compared to the model data points, but had an exorbitant number of terms. Table 5.1 shows the best of the three variable predictive functions which were considered.

Table 5.1
Summary of Candidate Three-Variable Functions to Predict C_{ss}

Variables				
1	2	3	R^2	number of terms
K_h	K_d	Infiltration	0.975	26
D_{air}	K_d	Infiltration	0.969	26
K_h	K_d	Precipitation	0.696	26
Organic Carbon	K_h	Infiltration	0.968	26
K_h	K_d	Runoff	0.963	26
D_{air}	K_d	Precipitation	0.960	26
Organic Carbon	K_h	Precipitation	0.959	26
Organic Carbon	K_h	Runoff	0.959	26
K_h	K_d	Recharge	0.958	26
D_{air}	K_d	Recharge	0.953	26
Organic Carbon	K_{oc}	Infiltration	0.951	18

Ultimately all the three-variable functions were rejected due to behavior problems or computational complexities.

The highest R^2 values for the two-variable functions were all around 0.9. The two-variable functions were generally more well-behaved than the three-variable ones, and there were several from which to choose in the top echelon. Table 5.2 shows the best of the two variable predictive functions which were considered.

Table 5.2
Summary of Candidate Two-Variable Functions to Predict C_{ss}

Variables			
1	2	R^2	number of terms
K_s	K_d	0.901	6
K_h	K_d	0.900	8
Organic Carbon	K_d	0.898	10
Organic Carbon	K_h	0.893	8
Organic Carbon	K_{oc}	0.893	10
D_{air}	K_d	0.893	8
K_d	K_{oc}	0.888	16
Organic Carbon	D_{air}	0.852	8

After considering the model sensitivity analysis, the function utilizing K_s and K_d was chosen as the primary candidate (this function was developed with the option of allowing K_s to go to 0; this option was adopted for all subsequent analyses). Further analysis of this function showed that it did a good job of fitting the data already produced by the model, but had problems elsewhere. The range of values for K_s for the existing compounds was wide but highly concentrated (see Table 3.2). This caused the function to fit well on opposite ends of the range, but allowed wide latitude in between. To overcome this problem, additional PRZM-3 simulations were designed and conducted using existing site and meteorological data, but with compound characteristics made up to fill the data gaps. These simulations are described in the next section.

5.2 ADDITIONAL PRZM-3 SIMULATIONS

PRZM-3 simulations were conducted using "made up" compound characteristics that were designed primarily to include solid phase decay rate values (K_s) that fell within the range between the value for methoxychlor ($K_s = 1.89E-03/\text{day}$) and toxaphene ($K_s = 1.92E-04/\text{day}$). A total of 5 different K_s values were used for these new compounds, which were designated A through E. The K_s values for these POPs are shown in Table 5.3.

Table 5.3
K_s Values for "New" POPs

POP	K _s , day ⁻¹
A	4.70E-04
B	8.20E-04
C	1.12E-03
D	1.36E-03
E	1.61E-03

A total of forty additional PRZM-3 simulations were conducted using the K_s data shown in Table 5.3; eight simulations were conducted for each of these values for solid phase decay rate. Simulations were conducted by using the PRZM-3 input data files from the base simulations, and modifying them to reflect a range of K_s and K_d values required to fill in the data gaps described in Section 5.1. For each K_s value shown in Table 5.3, a series of K_d values were assumed to reflect the effect of variation in the percent of organic carbon. Simulations were conducted using "default" input data files for both dieldrin and toxaphene, and using sites 5 and 27. Table 5.4 summarizes the distinguishing characteristics for the additional PRZM-3 simulations, and presents simulation results.

Table 5.4
Summary of Additional PRZM-3 Simulations Conducted to Support Development of Screening Level Methodology

Sim #	Site	Crop	Default Input File	POP	K _d	C _{ss} , mg/kg	T _{ss} , yrs
1	5	Corn	Toxaphene	A	7920	2.120	25.67
2	5	Corn	Toxaphene	A	22090	2.148	25.67
3	5	Corn	Toxaphene	A	32410	2.154	25.67
4	5	Corn	Toxaphene	A	51180	2.158	25.67
5	5	Corn	Toxaphene	B	9890	1.289	17.75
6	5	Corn	Toxaphene	B	16100	1.289	17.75
7	5	Corn	Toxaphene	B	31000	1.294	17.75
8	5	Corn	Toxaphene	B	45610	1.296	17.75
9	5	Corn	Toxaphene	C	2910	0.939	15.33
10	5	Corn	Toxaphene	C	11110	0.961	15.92
11	5	Corn	Toxaphene	C	45610	0.967	15.33
12	5	Corn	Toxaphene	C	71280	0.968	14.58

Table 5.4 (continued)
Summary of Additional PRZM-3 Simulations Conducted to Support Development of
Screening Level Methodology

Sim #	Site	Crop	Default Input File	POP	K _d	C _{ss} , mg/kg	T _{ss} , yrs
13	5	Corn	Toxaphene	D	4210	0.791	13.67
14	5	Corn	Toxaphene	D	21200	0.803	13.67
15	5	Corn	Toxaphene	D	31000	0.804	13.67
16	5	Corn	Toxaphene	D	49060	0.805	13.67
17	5	Corn	Toxaphene	E	710	0.632	12.17
18	5	Corn	Toxaphene	E	10020	0.681	12.17
19	5	Corn	Toxaphene	E	14810	0.682	12.17
20	5	Corn	Toxaphene	E	26300	0.684	12.17
21	27	Wheat	Dieldrin	A	7920	2.44	26.42
22	27	Wheat	Dieldrin	A	22090	2.54	26.42
23	27	Wheat	Dieldrin	A	32410	2.56	24.83
24	27	Wheat	Dieldrin	A	51180	2.58	24.83
25	27	Wheat	Dieldrin	B	9890	1.50	18.42
26	27	Wheat	Dieldrin	B	16100	1.52	18.42
27	27	Wheat	Dieldrin	B	31000	1.54	18.42
28	27	Wheat	Dieldrin	B	45610	1.54	18.42
29	27	Wheat	Dieldrin	C	2910	1.06	17.58
30	27	Wheat	Dieldrin	C	11110	1.13	17.58
31	27	Wheat	Dieldrin	C	45610	1.15	17.58
32	27	Wheat	Dieldrin	C	71280	1.16	17.58
33	27	Wheat	Dieldrin	D	4210	0.91	17.58
34	27	Wheat	Dieldrin	D	21200	0.95	17.58
35	27	Wheat	Dieldrin	D	31000	0.95	17.58
36	27	Wheat	Dieldrin	D	49060	0.96	17.58
37	27	Wheat	Dieldrin	E	710	0.66	15.75
38	27	Wheat	Dieldrin	E	10020	0.80	16.17
39	27	Wheat	Dieldrin	E	14810	0.80	16.17
40	27	Wheat	Dieldrin	E	26300	0.81	16.25

5.3 FINAL STATISTICAL ANALYSIS OF PRZM-3 DATA

The new model runs described in Section 5.2 were incorporated into the existing data set and a new function of K_s and K_d was generated. The revised function is shown in Equation 5.1, with coefficients rounded to two decimal places.

$$C_{ss} = \frac{-9.39 + 581.45\sqrt{k_s} + 2.44\sqrt{k_d} - 61.99\sqrt{k_s k_d}}{1 + 8.31\sqrt{k_s} - 2.76 \times 10^{-2}\sqrt{k_d} + 20.66\sqrt{k_s k_d}} \quad (5.1)$$

Equation 5.1 produced an overall R^2 value of 0.906 for the PRZM-3 simulations considered.

Using the same approach, an equation which estimates T_{ss} was also developed. The T_{ss} equation is also a function of K_s and K_d only. The best fit time prediction equation is presented in Equation 5.2.

$$\begin{aligned} T_{ss} = & -477.04 + 43638.61\sqrt{k_s} - 763761.24k_s + 175.35\ln(k_d) \\ & - 14257.37\sqrt{k_s}\ln(k_d) + 239032.10k_s\ln(k_d) \\ & - 11.16\ln(k_d)^2 + 896.57\sqrt{k_s}\ln(k_d)^2 - 14847.59k_s\ln(k_d)^2 \end{aligned} \quad (5.2)$$

Equation 5.2 produced an overall R^2 value of 0.811 for the PRZM-3 simulations considered.

Equations 5.1 and 5.2 are interesting in that both are functions of K_s and K_d only. In other words, the only site specific information that is required to apply these equations is the percent organic carbon in the top 15 cm of the soil (since %OC is used in the determination of K_d).

5.4 APPLICABILITY OF THE PREDICTIVE METHODOLOGY FOR C_{ss}

Some things are worth noting about Equation 5.1. First, like any rational function, it has a discontinuity when the denominator is 0. Setting the denominator equal to 0 will yield a function that can be solved to determine the location of the discontinuity for a given value of K_s . Second, the concentration function can predict negative values. Figure 5.1 shows the behavior of the function in the numerator in Equation 5.1. This figure shows the regions where the numerator function will predict positive, zero, and negative values.

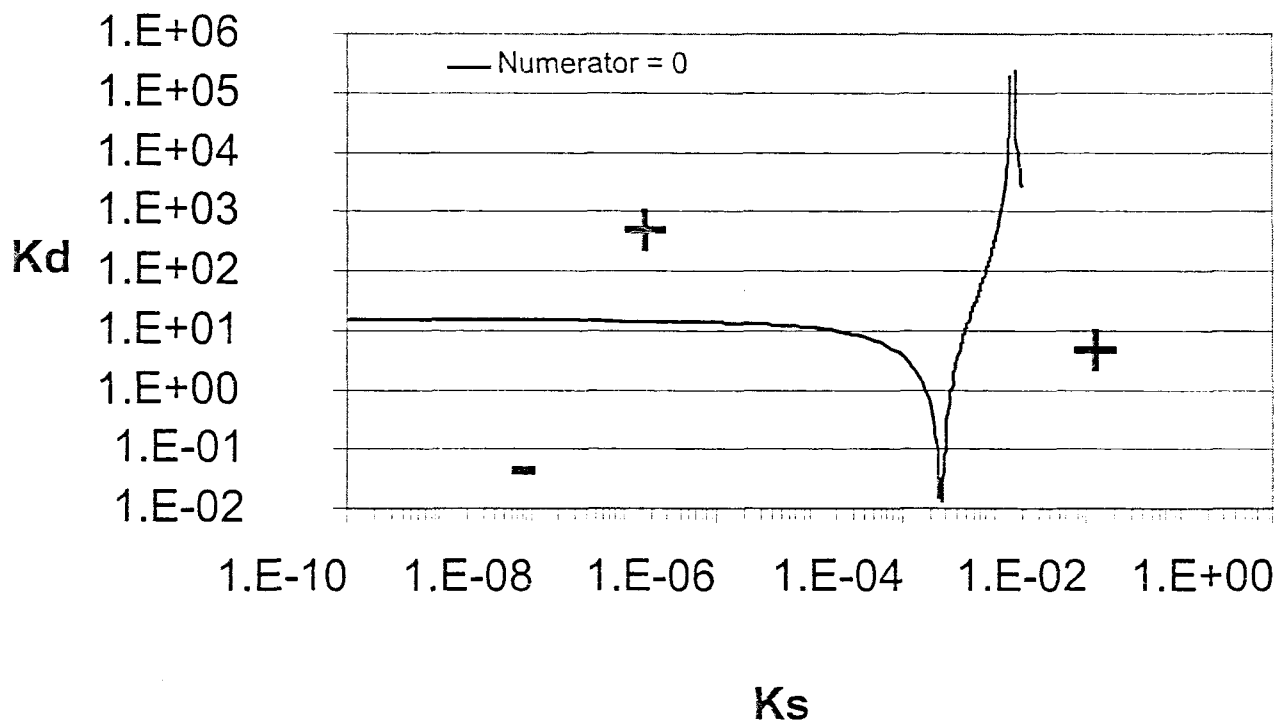


Figure 5.1 Behavior of Numerator Function in Equation 5.1.

Figure 5.2 shows the behavior of the function in the denominator in Equation 5.1. This figure shows the regions where the denominator function will predict positive, zero, and negative values.

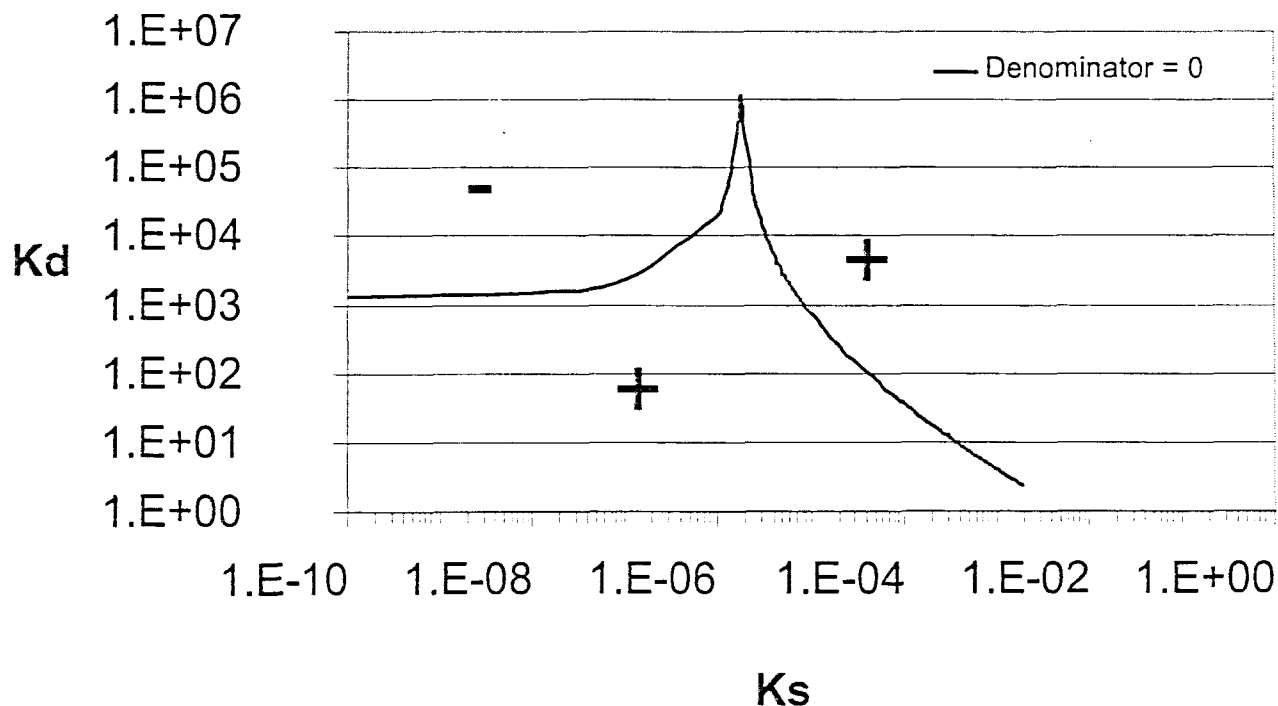


Figure 5.2 Behavior of Denominator Function in Equation 5.2.

Figure 5.3 shows the region where Equation 5.1 is applicable. This figure was generated by overlaying Figures 5.1 and 5.2, and investigating the behavior of the predictive equation for C_{ss} at each point. The figure also includes 4 discrete points labeled A, B, C, and D; these points will be discussed in Section 5.5.

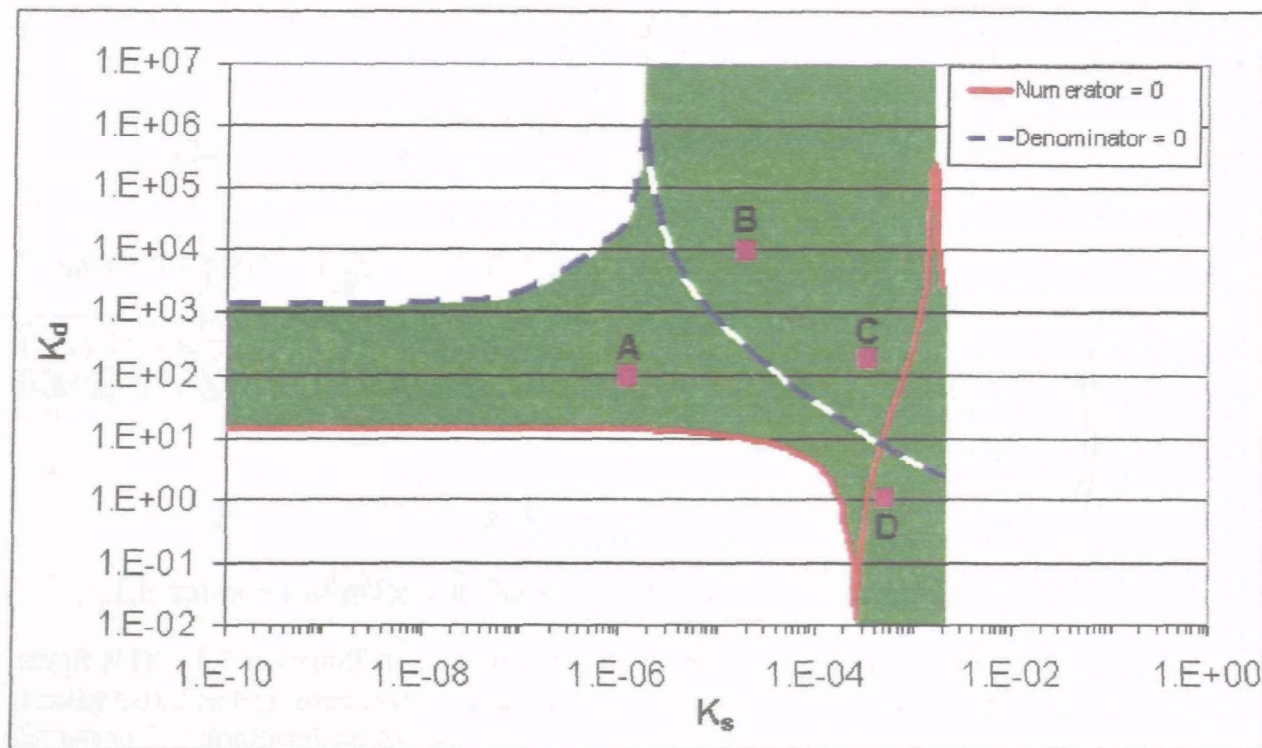


Figure 5.3 Region of Applicability of Predictive Methodology.

Figures 5.4 through 5.8 demonstrate how well the predictive equation for C_{ss} matches the simulation results from PRZM-3 for specific compounds. Figure 5.4 shows the computed (based on PRZM-3 simulations) vs. predicted (based on Equation 5.1) values for C_{ss} for a range of different POPs. The x axis on Figure 5.4 is simply an arithmetic scale utilized to allow plotting of C_{ss} data from individual (i.e. site specific) PRZM-3 simulations.

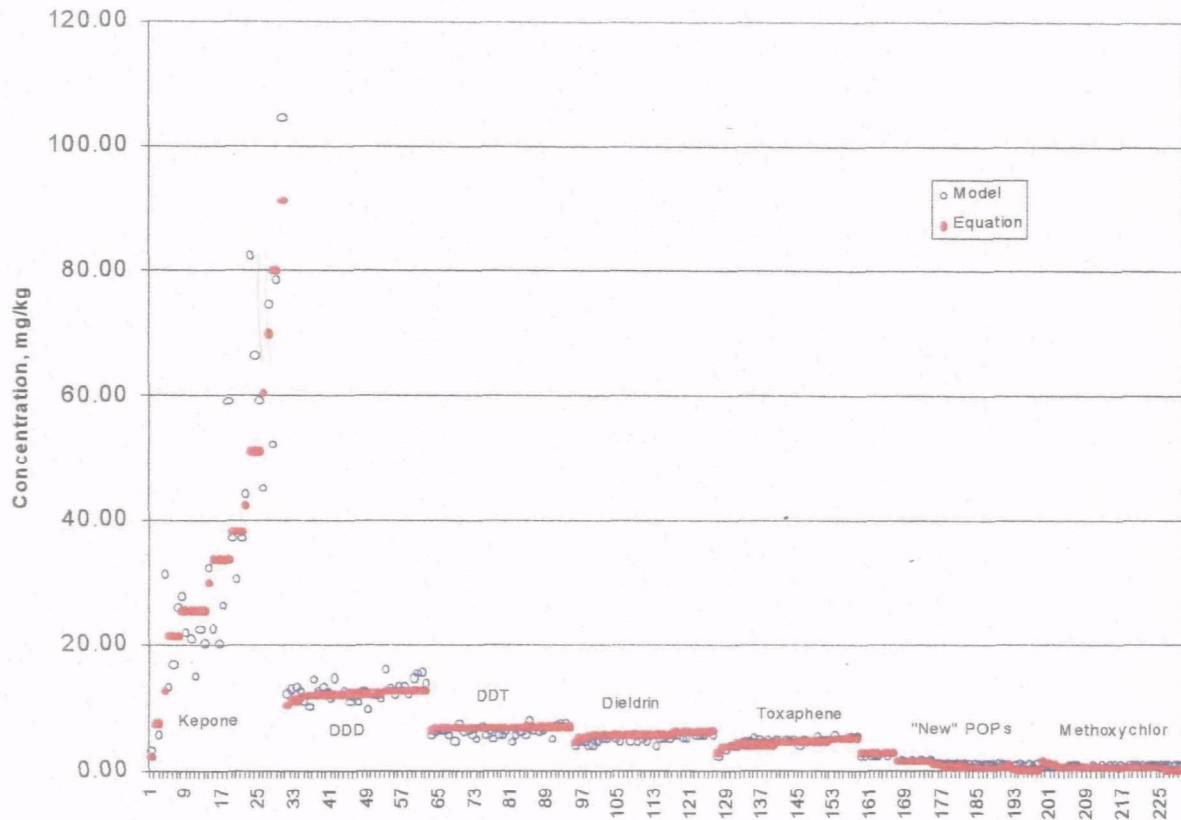


Figure 5.4 Computed vs. Predicted Values of C_{ss} for Selected POPs.

Figures 5.5 through 5.8 show the computed vs predicted values for C_{ss} for kepone, toxaphene, POP A, and methoxychlor, respectively. These figures each contain discrete points from the site specific PRZM-3 simulations and a curve generated by applying the respective K_s values for each compound to Equation 5.1.

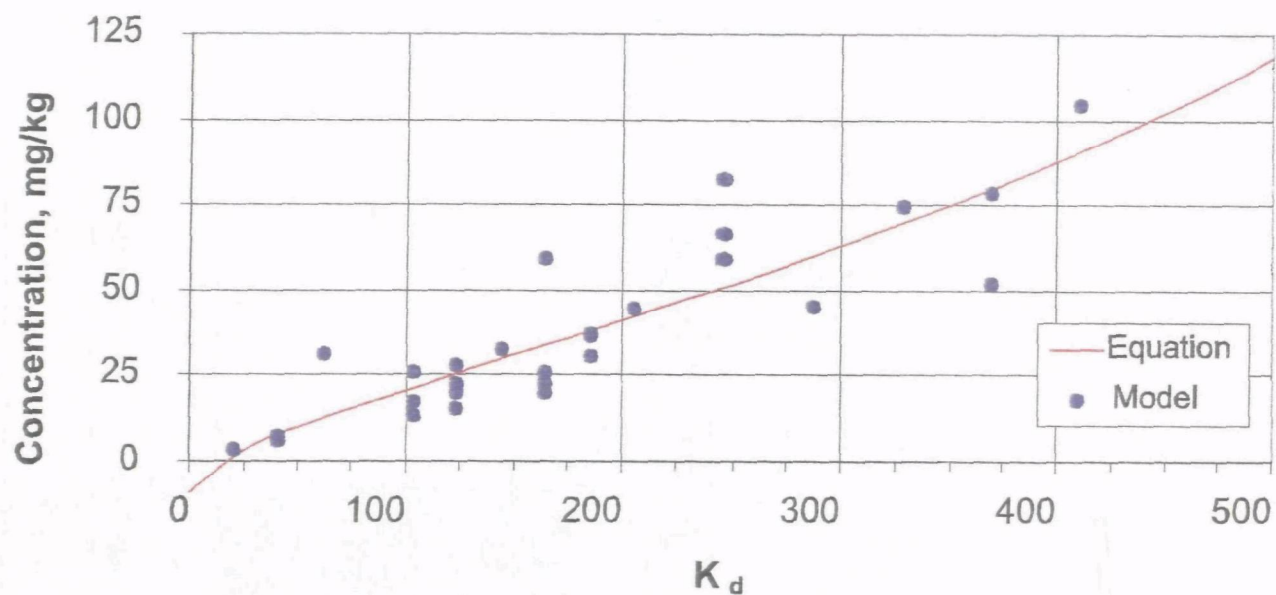


Figure 5.5 Computed vs. Predicted Values of C_{ss} for Kepone; $K_s = 0/\text{day}$.

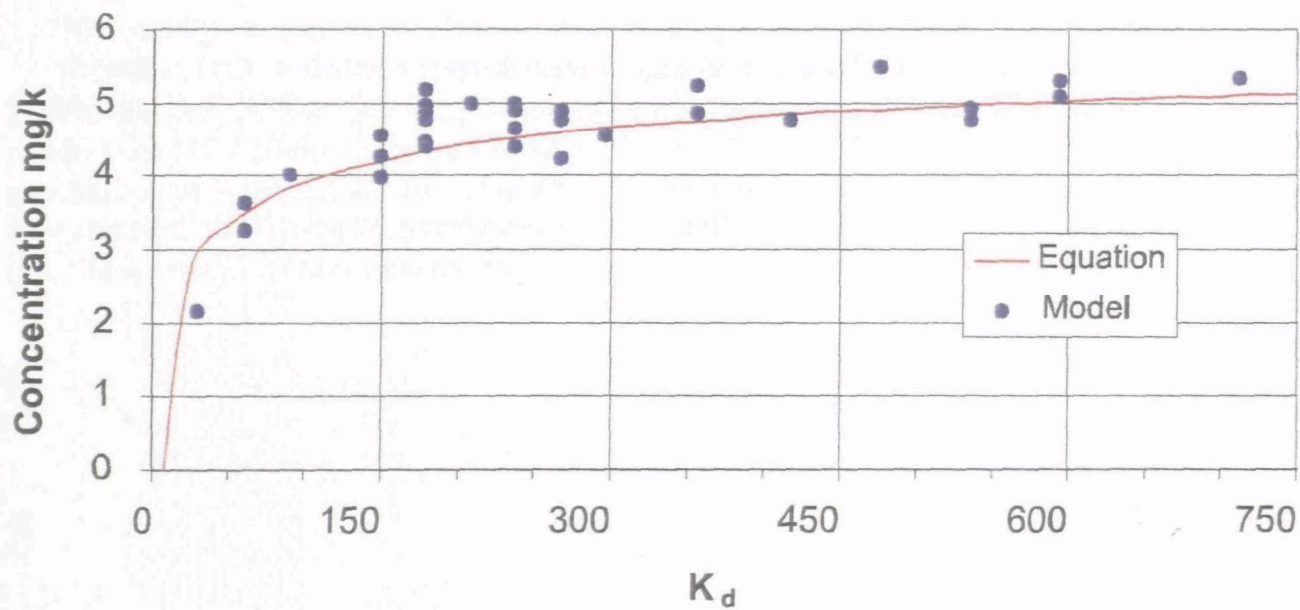


Figure 5.6 Computed vs. Predicted Values of C_{ss} for Toxaphene; $K_s = 1.92\text{E-}04/\text{day}$.

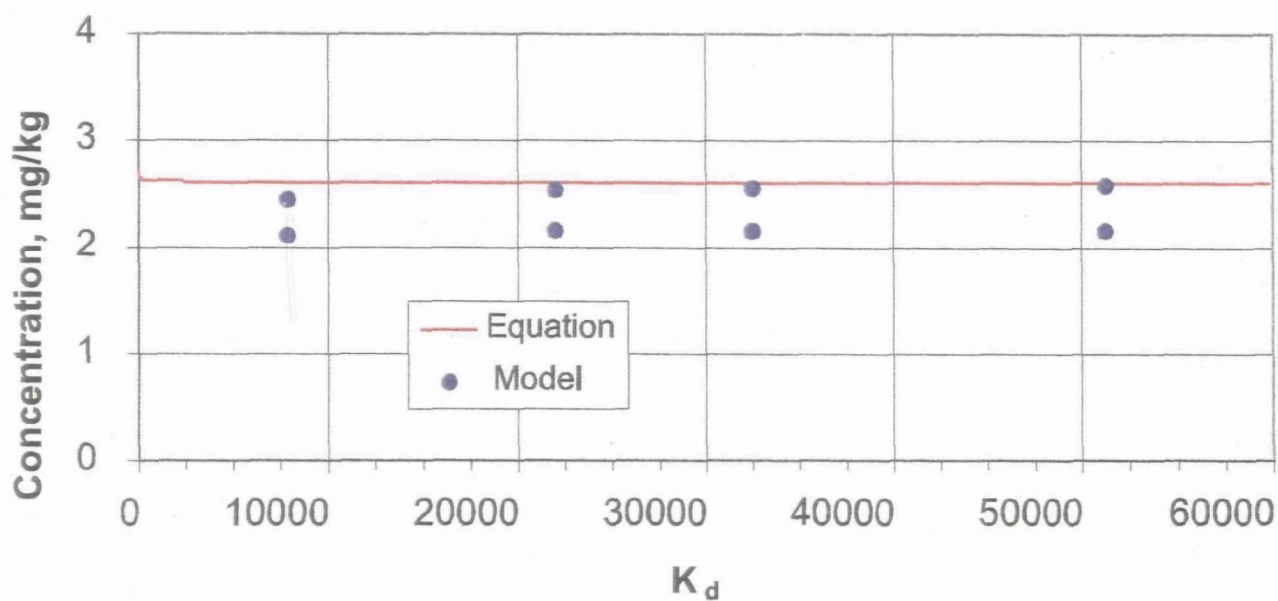


Figure 5.7 Computed vs. Predicted Values of C_{ss} for POP A; $K_s = 4.70\text{E-}04/\text{day}$.

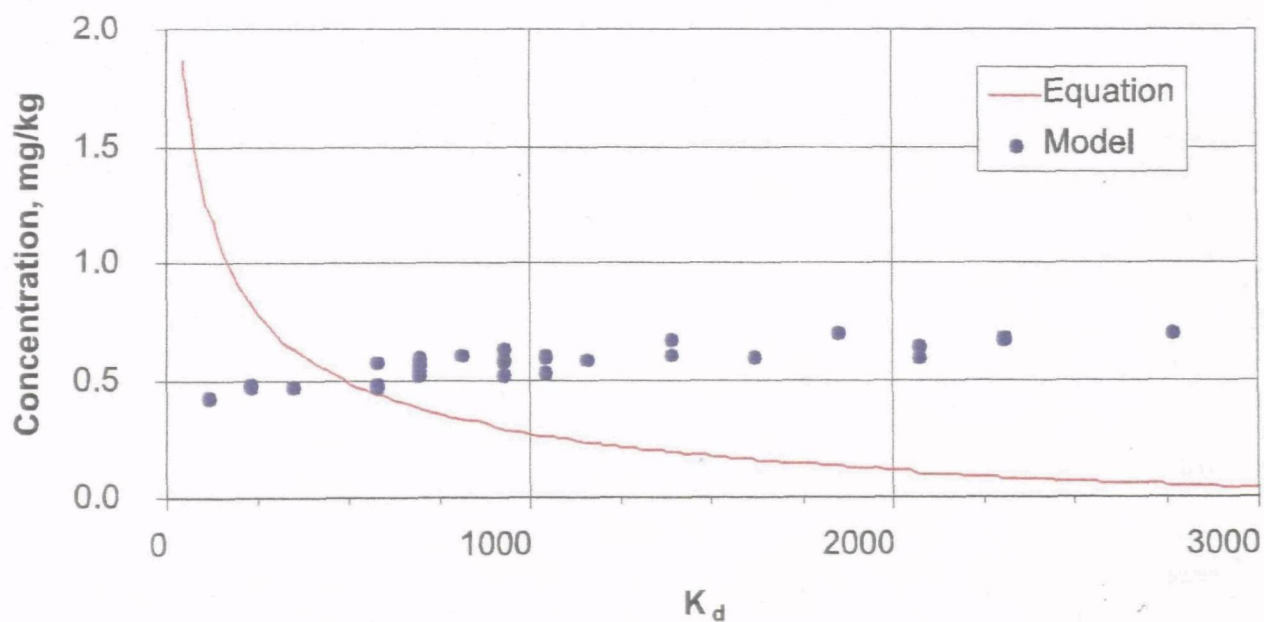


Figure 5.8 Computed vs. Predicted Values of C_{ss} for Methoxychlor; $K_s = 1.89\text{E-}03/\text{day}$.

Since Equation 5.1 was developed by applying statistical methods to empirical data, one would be ill-advised to apply it beyond the bounds of the data used to construct the equation. In this regard, the K_d values do not appear to be a limiting factor. However, the bounds of K_s do provide some guidance. In the current study, K_s varied from 0 to 1.89×10^{-3} for the POPs exhibiting steady state behavior. The function should therefore not be applied when values of K_s are greater than about 1.9×10^{-3} . Additionally, care should be taken when applying the methodology to very small values of K_s . In particular, small values of K_s (lower than approximately 1×10^{-6}) should only be combined with small values of K_d as shown in Figure 5.3. (Compounds with low values of K_s and high values of K_d , such as chlordane and DDE, did not reach steady state conditions in the PRZM-3 simulations described in this report.)

5.5 APPLICABILITY OF THE PREDICTIVE METHODOLOGY FOR T_{ss}

The equation to predict T_{ss} (Equation 5.2) is a simple polynomial (and not a rational function); it has no discontinuity. It is therefore possible to apply this equation to any set of parameters for which the concentration equation can be applied. The only limitation to the time equation is that K_d can never be 0, since $\ln(0)$ is not defined. Since this condition is not likely to be satisfied, particularly for agriculturally managed soils, this limitation is not judged to be significant.

Figures 5.9 through 5.13 demonstrate the applicability of Equation 5.2, and are a repeat of Figures 5.4 through 5.8 for T_{ss} instead of C_{ss} .

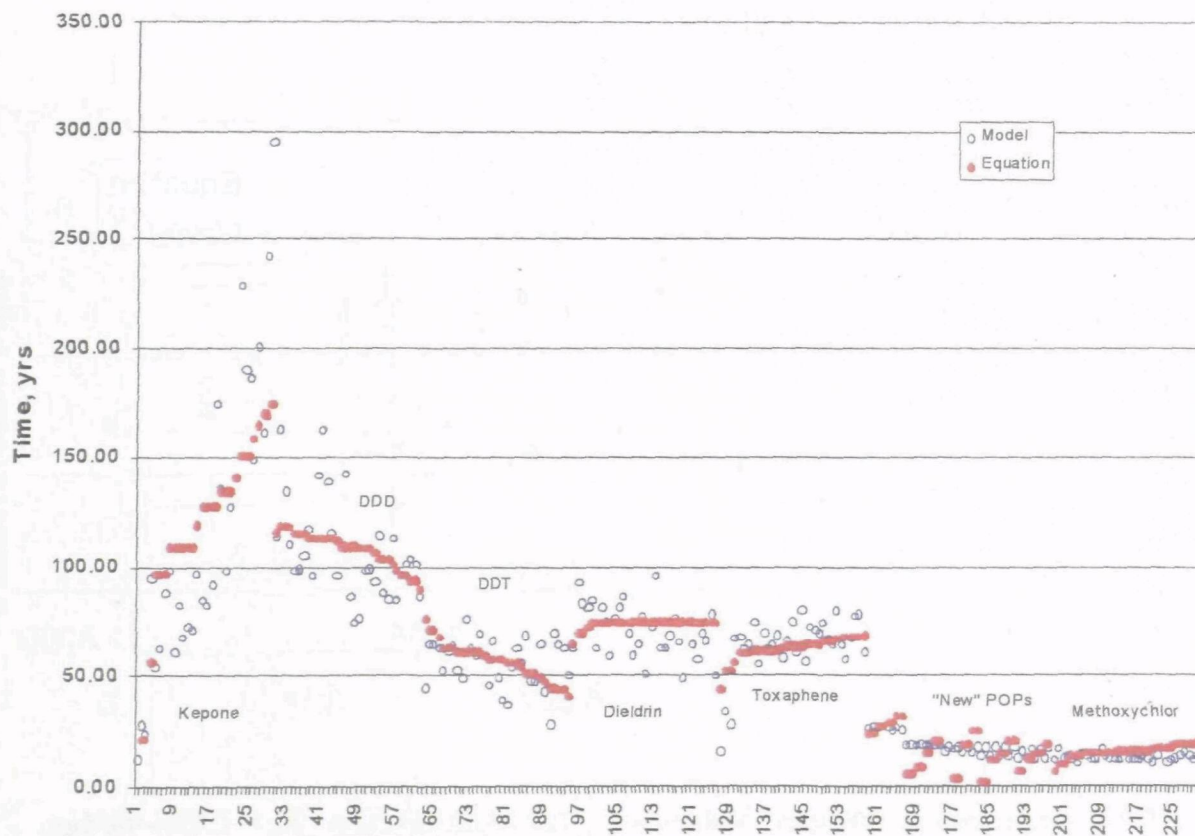


Figure 5.9 Computed vs. Predicted Values of T_{ss} for Selected POPs.

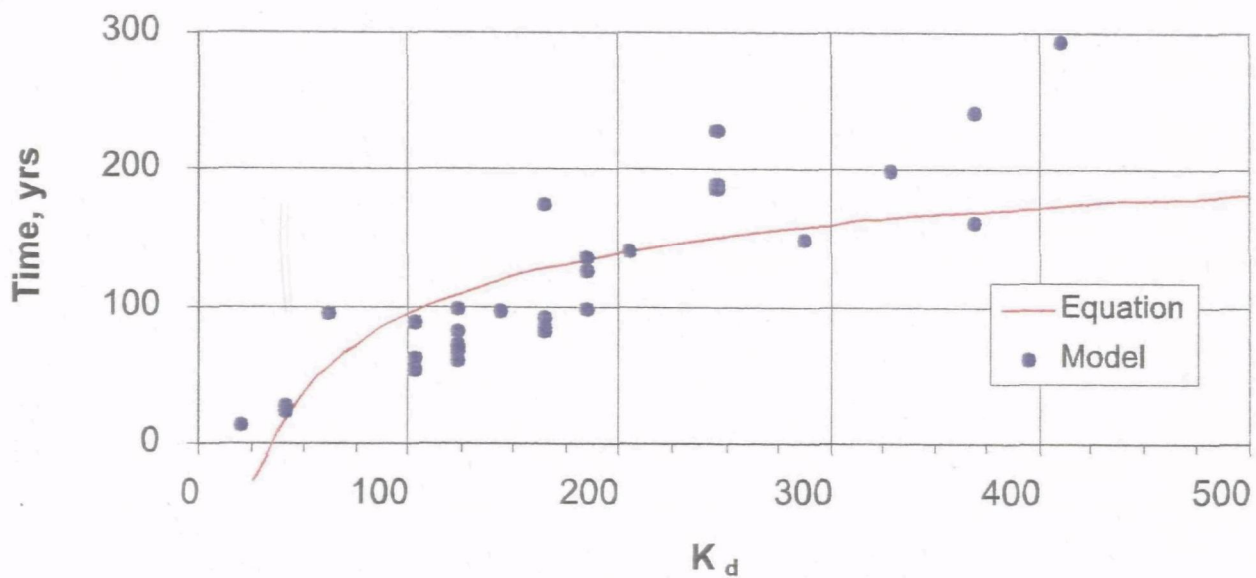


Figure 5.10 Computed vs. Predicted Values of T_{ss} for Kepone; $K_s = 0/\text{day}$.

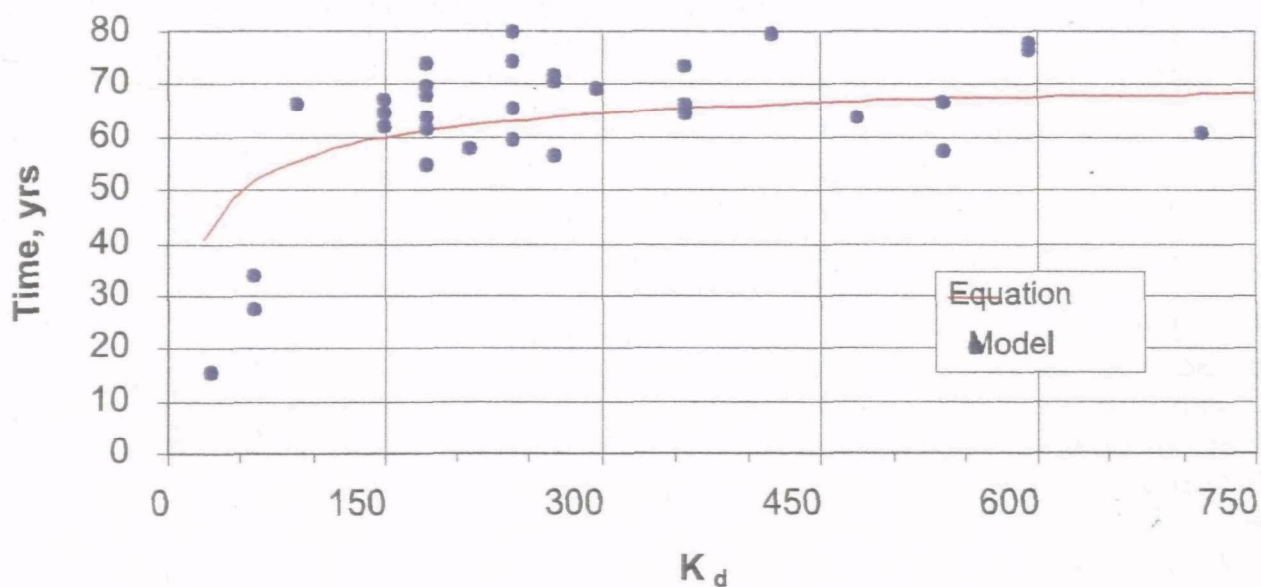


Figure 5.11 Computed vs. Predicted Values of T_{ss} for Toxaphene; $K_s = 1.92\text{E-}04/\text{day}$.

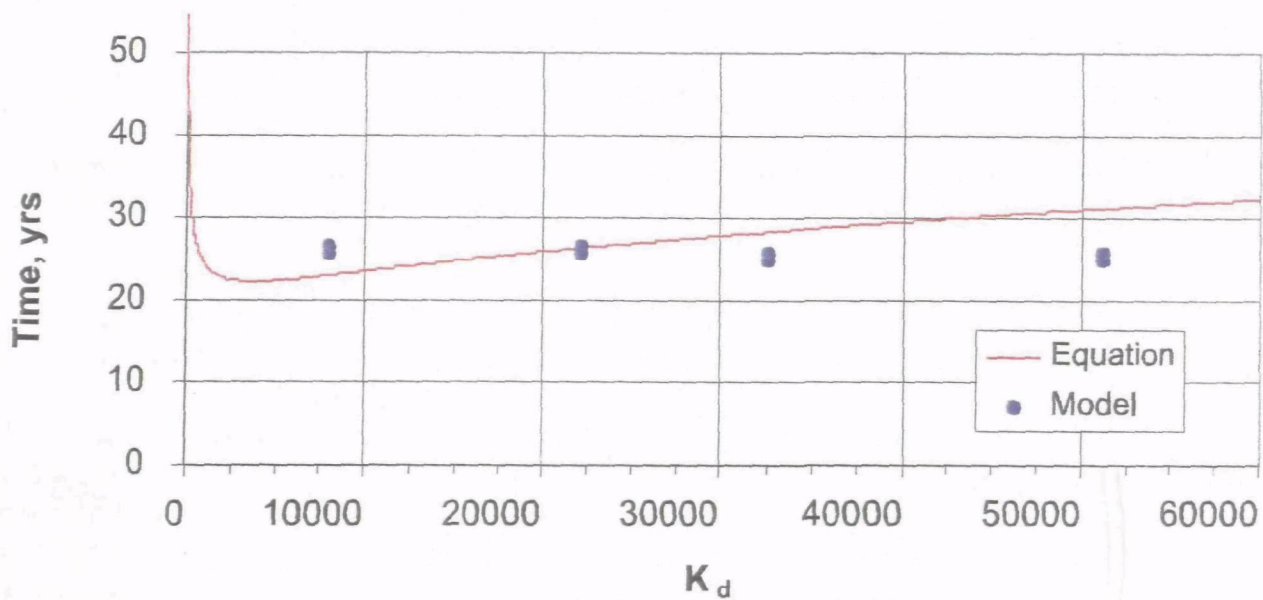


Figure 5.12 Computed vs. Predicted Values of T_{ss} for POP A; $K_s = 4.70\text{E-}04/\text{day}$.

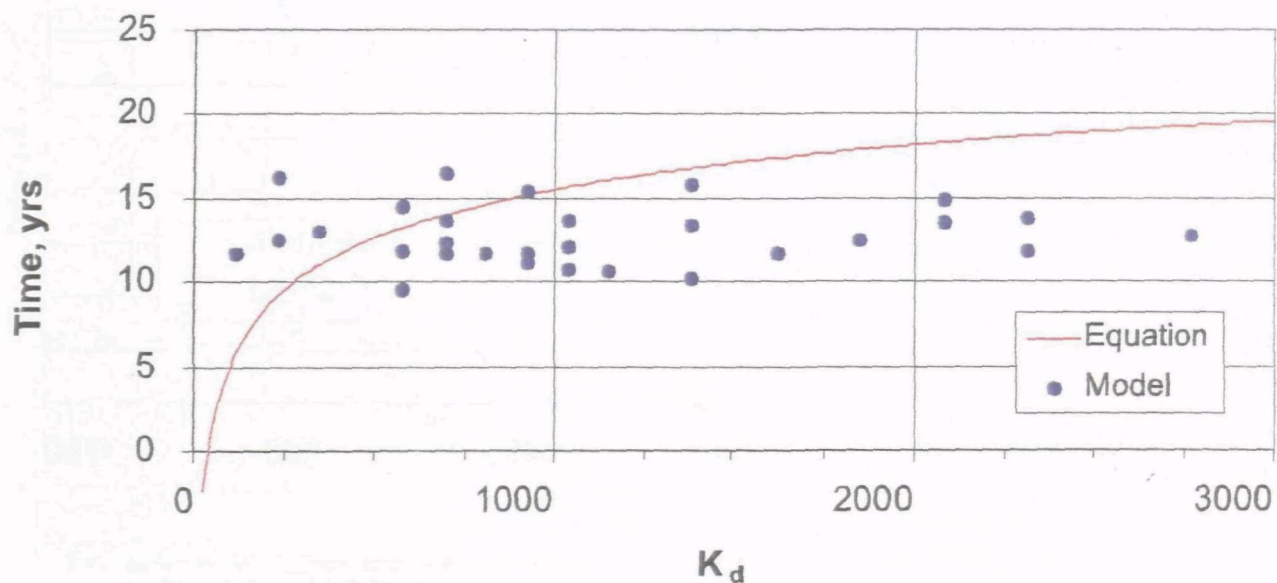


Figure 5.13 Computed vs. Predicted Values of T_{ss} for Methoxychlor; $K_s = 1.89\text{E-}03/\text{day}$.

Figures 5.9 through 5.13 show that Equation 5.2 can be used with reasonable confidence to predict T_{ss} . While the R^2 value for this equation is not as high as the R^2 value for the equation to predict C_{ss} , it is judged to be within acceptable tolerance for its intended application. Our approach was based on the assumption that the critical feature of the predictive methodology described herein was to provide the ability to estimate C_{ss} . Section 5.5 describes the analyses conducted to investigate the uncertainty associated with the C_{ss} predictive methodology.

5.6 UNCERTAINTY ANALYSIS

In order to quantify the uncertainty in the predictive analysis and provide confidence levels for the results, the concentration equation (Equation 5.1) was encoded in an Excel spreadsheet and the software package @Risk was applied. @Risk is a spreadsheet add-in that performs Monte Carlo or Latin Hypercube uncertainty analysis, and provides summary statistics and graphs of the result. Four representative points were chosen from different regions of the domain in which the Equation 5.1 is applicable (see Figure 5.3). The K_s and K_d values from these points were entered into a spreadsheet that was linked to @Risk. Input variables in @Risk can be defined by specifying an underlying distribution and some descriptive information about the distribution.

Previous research (Baes and Sharp, 1983) in the development of a model to predict leaching constants for solutes in agricultural soils was conducted assuming a lognormal distribution for K_d . The assumption of a lognormal distribution for both K_s and K_d appears to be appropriate for this study (personal communication, S. Karickhoff @ EPA Athens).

Therefore, K_s and K_d were defined as input variables by applying a lognormal distribution. The pertinent lognormal distribution parameters in @Risk are the mean and standard deviation. In each of the test point cases, the mean values for K_s and K_d were identified from the points for which the analysis was to be performed. It was then necessary to estimate a standard deviation for K_s and K_d .

Estimates of the coefficient of variation (CV) for degradation rate coefficients for various "persistent" pesticides (in this case, those pesticides with a half-life exceeding 100 days) have been previously published (Rao and Davidson, 1980). Published values include those for DDT (CV = 82.9% for anaerobic conditions and CV = 130.8% for aerobic conditions) and chlordane (CV = 104.2%). Published estimates of CV for the degradation rate coefficients for other "persistent" pesticides (including trifluralin, bromacil, and picloram) range from 49.4% to 116.2%.

Table 5.31 in the PRZM-3 User's Manual presents descriptive statistics for % organic matter, based on previously published research (Carsel et al., 1988). The published estimates for coefficient of variation range from 66% to 114%. Percent organic matter is generally considered to be linearly related to % organic carbon, and for the purposes of this study the value of both K_s and K_d at a given site can be considered to be primarily functions of % organic carbon (personal communication, S. Karickhoff @ EPA Athens). We assumed these estimates for CV for % organic matter could also be used for % organic carbon.

Therefore, a CV of 100% was estimated for both K_s and K_d for the purposes of conducting uncertainty analysis using the @Risk software. (It should be noted that while the PRZM-3 model has Monte Carlo simulation capabilities, it is not currently capable of performing the calculations

as described herein. The model could easily be modified to provide this capability, but the effort required to do so was beyond the scope of the current study.) Additional research is required before CV estimates for K_s and K_d can be refined further. However, a CV of 100% was judged to be suitable for the purposes of assessing the uncertainty associated with usage of the predictive methodology described in this report. Since the coefficient of variation is equal to the standard deviation divided by the mean, a value of standard deviation was easily calculated for each of the four test points. (The standard deviation in each case was set to the same value as the mean.)

The Monte Carlo analysis spreadsheet consisted of four pairs of test values of K_s and K_d , the lognormal distribution functions defined around these values, and four output variables. The output variables were the concentrations predicted by Equation 5.1. @Risk was then directed to perform the Monte Carlo analysis using 2000 simulations for each test point. Results of these simulations were stored in the @Risk output file, and summary statistics were generated. From the output tables, cumulative distribution functions were generated for each of the test points.

Table 5.5 presents summary information for the Monte Carlo analyses performed using the @Risk software.

Table 5.5
Summary Statistics from Monte Carlo Analyses

Point	K_s (mean)	K_d (mean)	C_{ss} in mg/kg	
			from Eqn 5.1	from @Risk
A	1.00E-06	1.00E+02	15.9	15.2
B	2.00E-05	1.00E+04	27.9	42.8
C	3.00E-04	3.00E+02	3.6	4.5
D	4.00E-04	1.00E+00	2.2	2.5

Figures 5.14 through 5.17 show the cumulative distribution functions for points A through D.

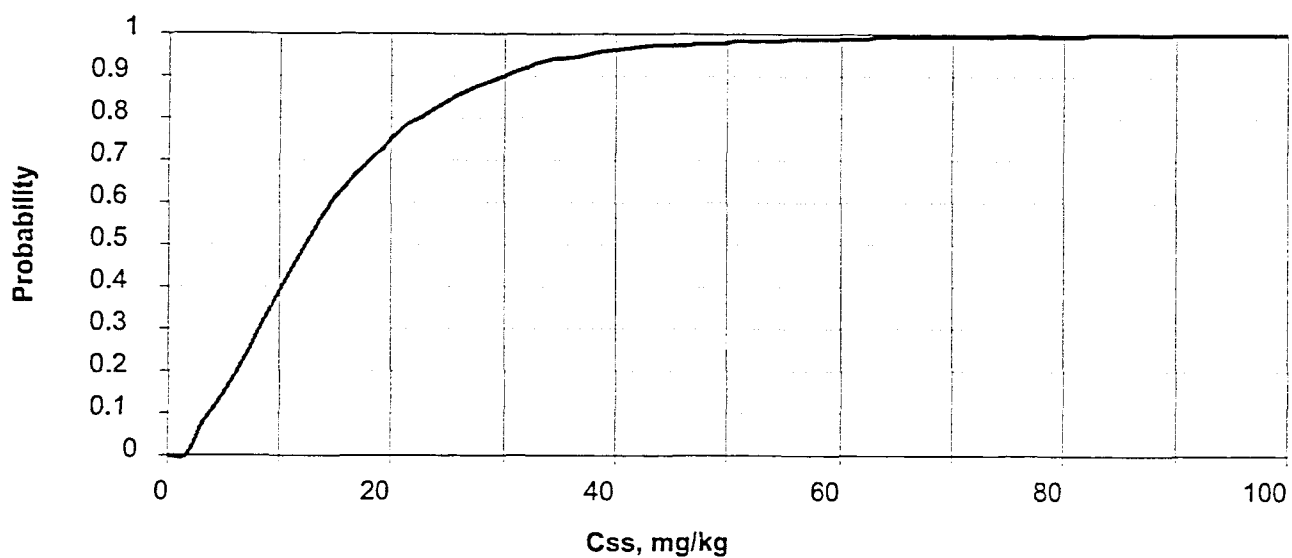


Figure 5.14 Cumulative Distribution Function for C_{ss} at Point A.

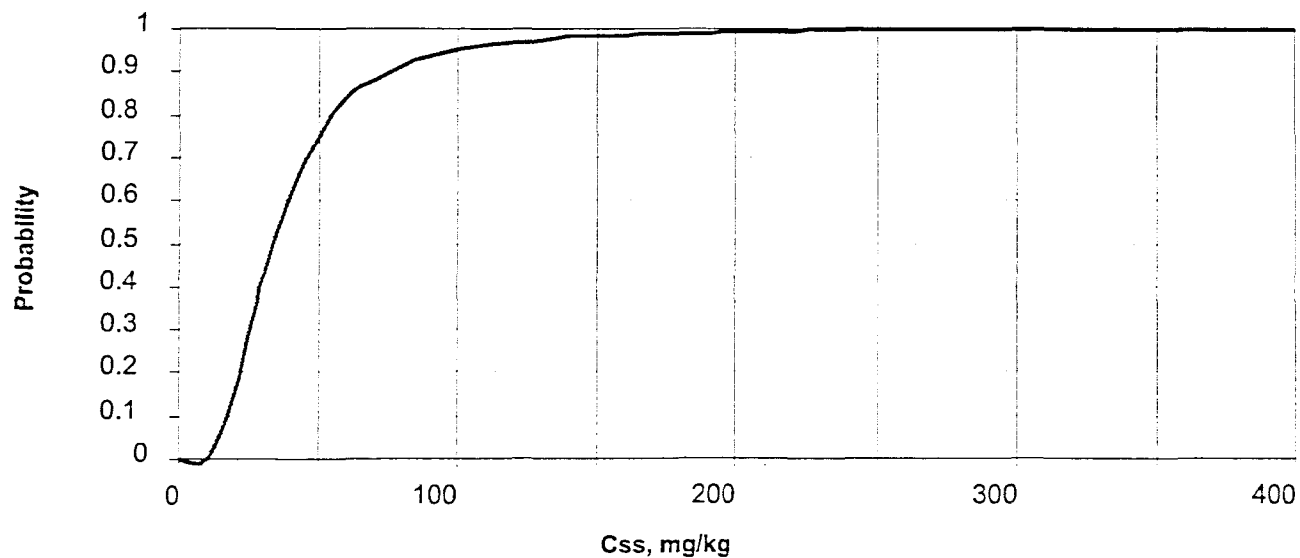


Figure 5.15 Cumulative Distribution Function for C_{ss} at Point B.

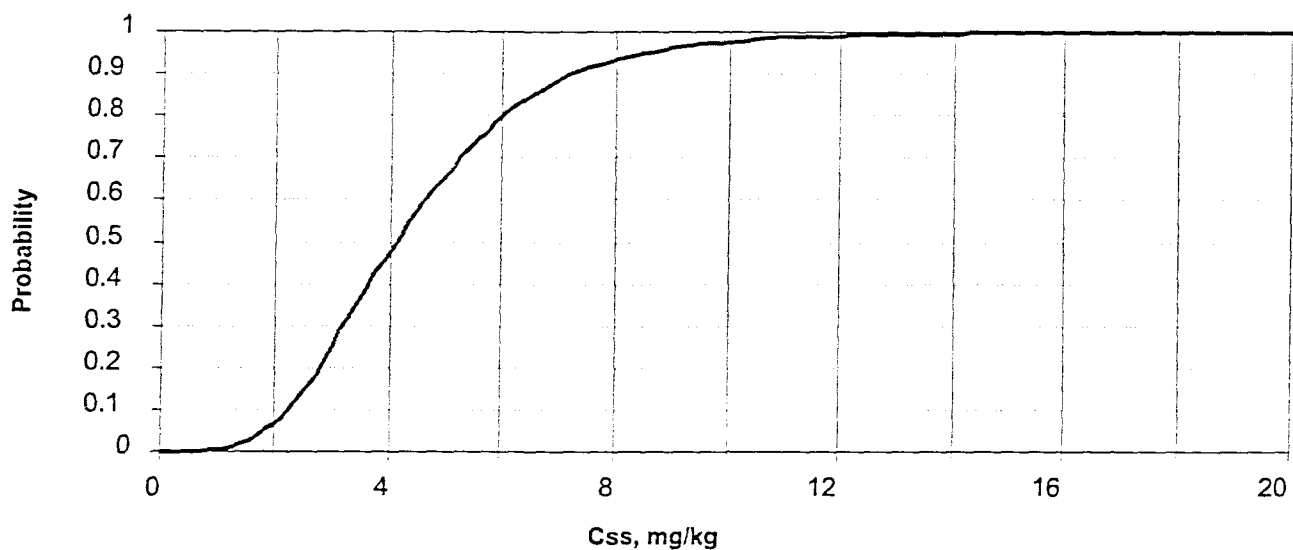


Figure 5.16 Cumulative Distribution Function for C_{ss} at Point C.

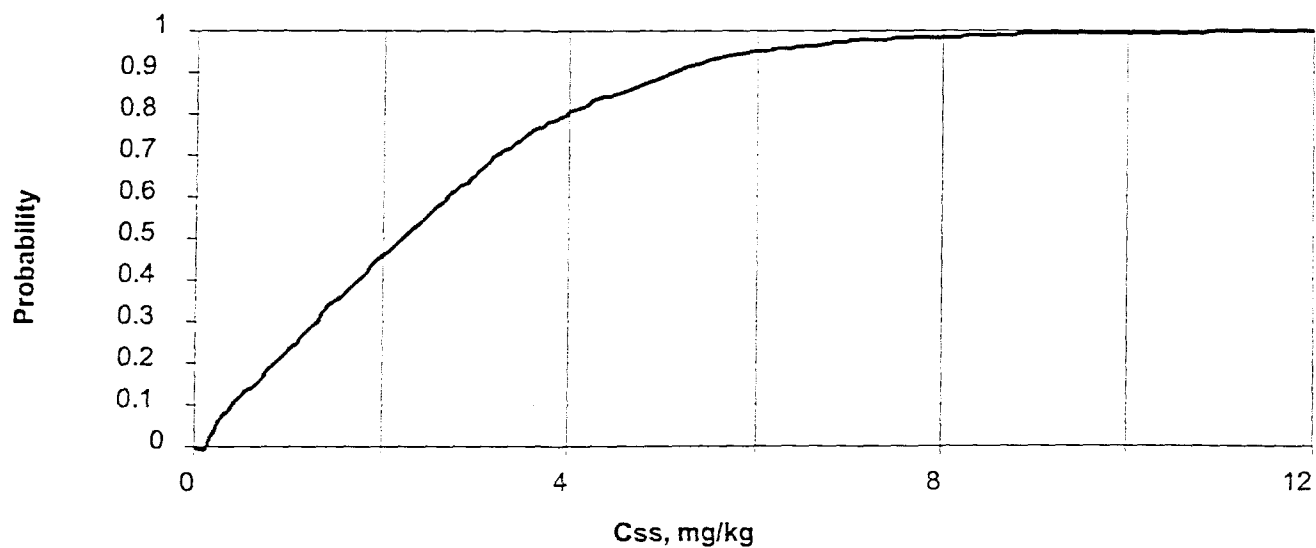


Figure 5.17 Cumulative Distribution Function for C_{ss} at Point D.

Figures 5.14 through 5.17 indicate that the uncertainty associated with application of Equation 5.1 can be quite large. For instance, at point A in Figure 5.3 (where $K_s = 1.00\text{E-}06/\text{day}$ and $K_d = 100$, Equation 5.1 predicts a value for C_{ss} of 15.9 mg/kg. The cumulative distribution function shown in Figure 5.14 indicates that the expected value of C_{ss} would be less than or equal to about 35 mg/kg with 95% confidence. Similar results are evident at the other 3 points investigated. The wide range in predicted values for C_{ss} is associated with the relatively large coefficient of variation adopted for this analysis.

6.0 SUMMARY AND CONCLUSIONS

The predictive methodology described in Section 5 can be used to quickly determine whether a particular chemical compound is likely to be persistent, that is, to degrade so slowly that repeated applications of that compound will cause increasing concentrations in the upper soil layer. All that is needed is knowledge of the solid phase decay rate, K_s , and the soil partition coefficient K_d at the site for which the analysis is required.

The methodology was developed assuming annual unit applications of 1 kg/ha. However, the methodology can be applied for other constant annual application rates. The C_{ss} value predicted by Equation 5.1 should then be multiplied by the ratio of (actual application rate/unit rate). Figures 6.1 through 6.3 show the effect of doubling and tripling the unit application rate at Site 1 for chlordane, dieldrin, and kepone, respectively. In each case, application of two and three times the unit rate produces concentrations two and three times as high as those for the unit rate, respectively. (Even though chlordane is not one of the steady state compounds, the concentration curves are included here to lend credence to the assumption of linearity.)

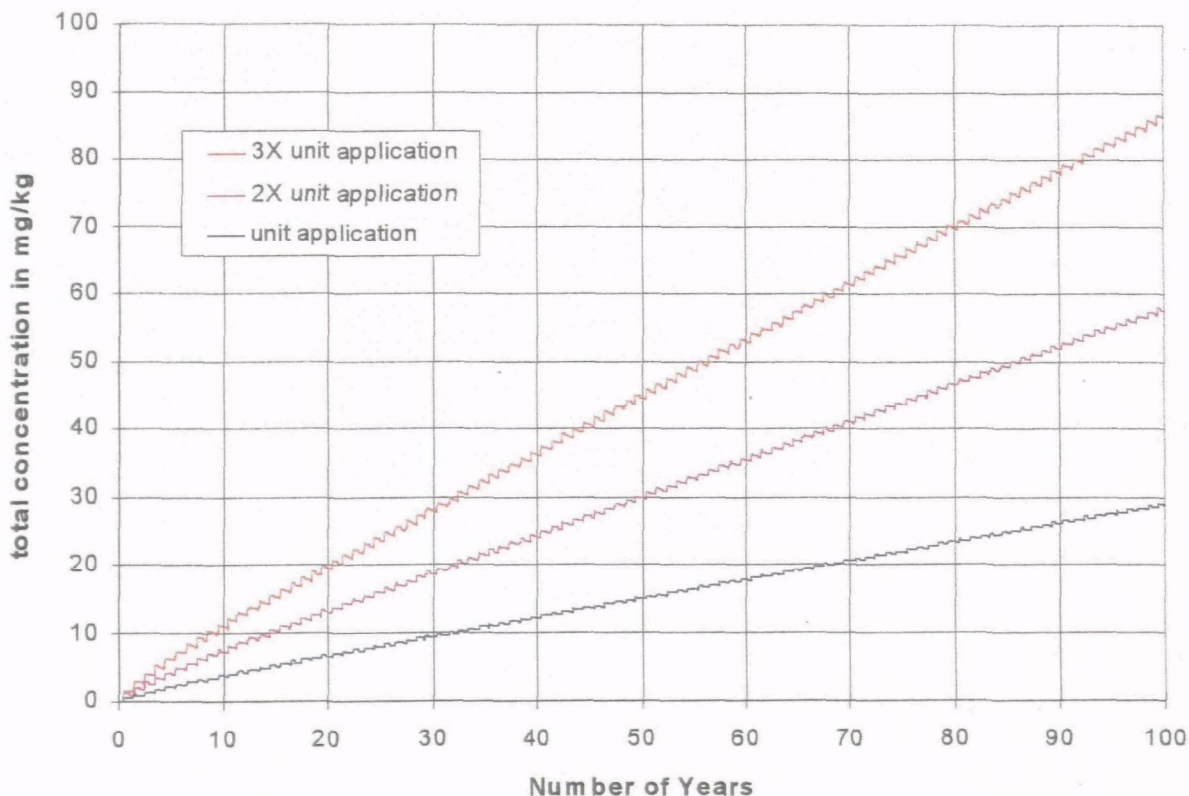


Figure 6.1 Effect of Various Application Rates on Predicted Concentrations; Chlordane.

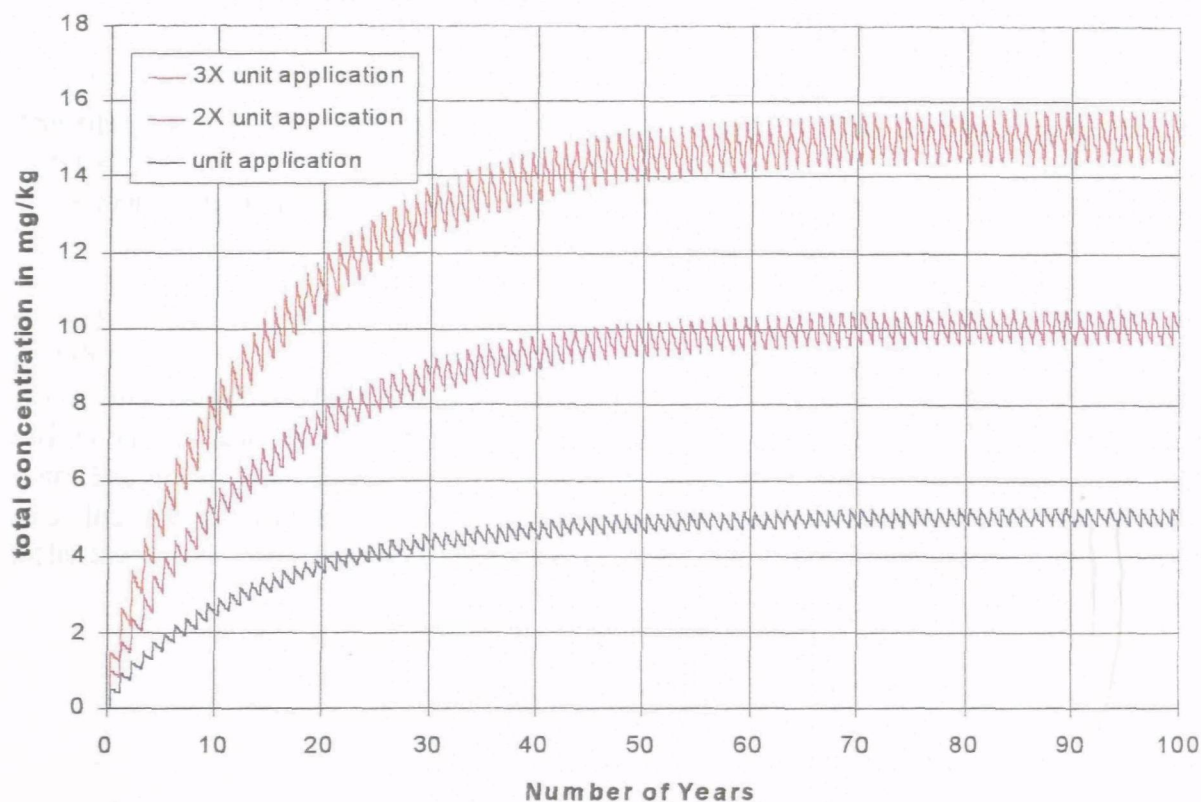


Figure 6.2 Effect of Various Application Rates on Predicted Concentrations; Dieldrin.

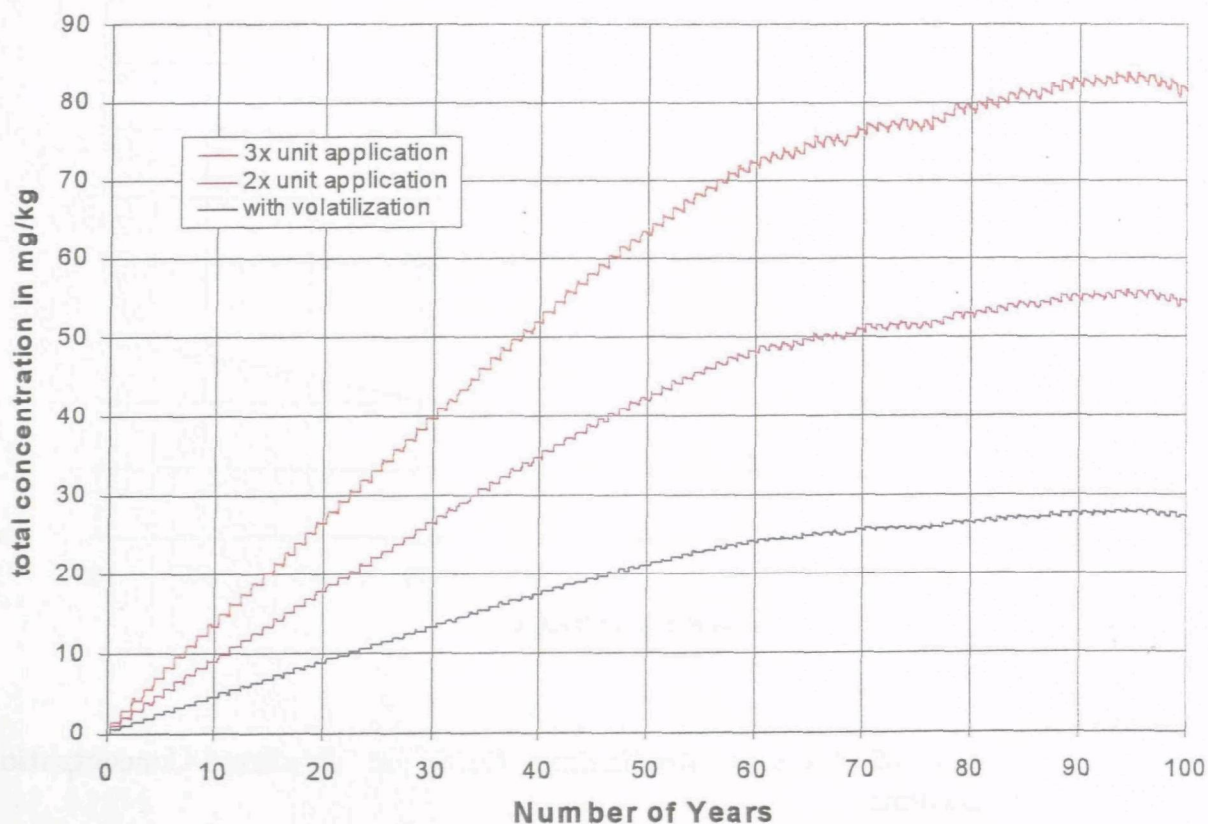


Figure 6.3 Effect of Various Application Rates on Predicted Concentrations; Kepone.

The methodology is appropriate for compounds falling within the shaded region of Figure 5.3. Application of the methodology outside that region is not recommended, and may lead to unreliable estimates of steady state concentration and the time required to reach steady state.

It is difficult to quantify the uncertainty associated with application of the predictive methodology because too little is known about the descriptive statistics for K_s and K_d . However, the cumulative distribution functions presented in Section 5.5 can be used as a guide to understanding the valid ranges of concentrations possible for a particular chemical at a specific site.

7.0 REFERENCES

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APPENDIX A

DOCUMENTATION OF SOURCES OF DATA USED FOR CREATION OF PRZM-3 INPUT FILES

RECORD 3

- PFAC: pan factor used to estimate daily evapotranspiration; obtained from Figure 5.1 of the PRZM-3 User's Manual.
- SFAC: snowmelt factor; taken from Table 5-1 of the PRZM-3 User's Manual. Range for open areas reported to be 0.20 - 0.80 (cm per degree C per day); constant value of 0.50 used for all sites.
- ANETD: minimum depth from which evaporation is extracted in the dormant season. Values obtained from Figure 5.2 of the PRZM-3 User's Manual.

When the simulation start date occurs before the crop emergence date, we assumed an initial crop (INICRP = 1) with a surface condition of "fallow" (ISCOND = 1).

RECORD 6

- ERFLAG: erosion flag; set to 2 for all simulations to invoke Modified Universal Soil Loss Equation.

RECORD 7

- USLEK: USLE soil erodability factor; obtained from the SOILS5 database. The mode of all of the values for individual samples within a county.
- USLELS: USLE topographic factor LS; computed in SOILS5 spreadsheet as a function of hydraulic length and slope.
- USLEP: USLE practice factor P; obtained from the SOILS5 database. The mode of all of the values for individual samples within a county.
- AFIELD: area of the field in hectares; assumed to be the square of the hydraulic length.
- IREG: SCS rainfall distribution region; obtained from Figure 5.12 of the PRZM-3 User's Manual.
- SLP: land slope in percent; obtained from the SOILS5 database. The average of all of the values for individual samples within a county.
- HL: hydraulic length in meters; obtained from the SOILS5 database. The average of all of the values for individual samples within a county.

RECORD 8

All PRZM-3 simulations were performed for a single crop (NDC = 1).

RECORD 9

- CINTP: max crop interception storage (cm); values from Table 5-4 of the PRZM-3 User's Manual. Corn = 0.28, cotton = 0.23, soybeans = 0.23, wheat = 0.08 (midpoint of respective ranges).
- AMXDR: max crop rooting depth (cm). Based on Table 5-9 of the PRZM-3 User's Manual and conversations with Dr. Paul Denton of the UT Agriculture Extension Service, the following values were adopted: corn (100 cm); cotton (90 cm); soybeans (60 cm); wheat (50 cm). The only value outside of the ranges published in Table 5-9 is wheat (range is 15-30 cm). Dr. Denton felt strongly that this was too low for wheat.
- COVMAX: max areal crop coverage in percent; assumed to be 95 for all crops. The PRZM-3 User's Manual says this number should be between 80 and 100; Dr. Denton told me the number "should approach 100%".
- ICNAH: crop surface condition after harvest. we assumed all crops were in residue condition after harvest (ICNAH = 3).
- CN: SCS curve numbers for fallow, cropping, and residue conditions. Values from PATRIOT database.
- HTMAX: max crop canopy height. Table 5-16 of the PRZM-3 User's Manual reports a range of 80 - 300 cm for corn; values for our other crops not reported. Based on conversations with Dr. Denton, the following values were adopted: corn (210 cm); all others (90 cm).

RECORD 9A

- CROPNO: crop number; 1 for all simulations.
- NUSLEC: number of USLE cover management factors; 3 for all simulations.

RECORD 9B

- GDUSLEC: starting days for 3 cover management factors, from PATRIOT
- GMUSLEC: starting months for 3 cover management factors, from PATRIOT

RECORD 9C

- USLEC: USLE cover management factors for fallow, cropping, and residue conditions. This factor reflects the tillage and erosion control practices most widely utilized for a given site. We assumed the cropping period begins with plant emergence and ends with plant harvesting, that fallow conditions (corresponding to tilling under the old crop residue to prepare the ground for planting of the new crop) begin one month prior to crop emergence, and that residue conditions begin at harvest and end with tilling. Values of C for cropping conditions were based on the SOILS5 database (the mode of all of the values for individual samples within a county), with most weight given to the 1992 values (1982, 1987, and 1992 values of C are included in the database). Values of C for fallow conditions varied from 0.4 to 0.6, and were based on the USDA map "Tillage Practices by NRCS Region, 1995". Where the predominant tillage practice in a region is conventional, a C value of 0.6 for fallow conditions was assigned.

Where the predominant tillage practice is NOT conventional (i.e. the combination of conservation tillage and reduced tillage practice), a C value of 0.4 for fallow conditions was assigned. If the area was about 50% conventional and 50% other, a value of 0.5 was assigned. C values for residue conditions were chosen to be about half way between cropping and fallow conditions.

RECORD 9D

MNGN: Manning n roughness coefficient. PRZM-3 User's Manual recommended default value of 0.17 used for all seasons at all sites.

RECORD 10

One cropping period assumed per year: NCPDS = 1.

RECORD 11

Crop emergence, maturation, and harvest dates per PATRIOT.

RECORD 13

A typical simulation is for 100 years, with 1 pesticide application per year; NAPS = 100. For most simulations, the number of pesticides (NCHEM) is 1; for DDT/DDD/DDE simulations, NCHEM = 3. The (FRMFLG = 1) flag was used to test for ideal soil moisture conditions, and bi-phase half lives were not used (DKFLG2 = 0).

RECORD 15

APD: target application day; assumed to be 5 days after crop emergence.
APM: target application month.
IAPYR: target application year.
WINDAY: number of days to check for ideal soil moisture; 10 days at most sites.
CAM: chemical application method, set equal to 1 (soil applied, default incorporation depth, linearly decreasing with depth).
DEPI: depth of pesticide application (cm); set to 4 cm for all simulations.
TAPP: target application rate; set to 1 kg/ha for all simulations.
APPEFF: application efficiency; set to 1 for all simulations to preserve unit load.
DRFT: not used.

RECORD 17

FILTRA: not used, set to 0.
UPTKF: plant uptake factor, set to 0 to indicate no plant uptake.

RECORD 19

Soil type identified from PATRIOT; most common agricultural soil for the specified crop in a given county used.

RECORD 20

CORED: soil core depth in cm; from PATRIOT.
BDFLAG: bulk density flag; set to 0 to allow input by user.
THFLAG: field capacity and wilting point flag; set to 0 to allow input by user.
KDFLAG: adsorption coefficient flag; set to 0 to allow input by user.
HSWZT: drainage flag; set to 0 to allow free drainage.
MOC: method of characteristics flag; set to 0 (not used).
IRFLAG: irrigation flag, set to 1 if irrigation simulated, 0 otherwise.
ITFLAG: soil temperature simulation flag; set to 0 (not used).
IDFLAG: thermal conductivity and heat capacity flag; set to 0.
BIOFLG: biodegradation flag; set to 0 (not used).

RECORD 26

DAIR: diffusion coefficient, see Table 3.2 of this report.
HENRYK: Henry's law constant, see Table 3.2 of this report.
ENPY: enthalpy of vaporization, see Table 3.2 of this report.

RECORD 27 (for irrigated sites only)

IRTP: type of irrigation; set to 4 (under canopy sprinkler);
FLEACH: leaching factor as a fraction of irrigation water depth; set to 0.0.
PCDEPL: fraction of water capacity at which irrigation is applied; set to 0.5.
RATEAP: maximum rate at which irrigation is applied; set to 1.3 cm/hr.

RECORD 34

HORIZN: horizon number, obtained from PATRIOT.
THKNS: horizon thickness, obtained from PATRIOT.
BD: bulk density, obtained from PATRIOT.
THETO: initial soil water content in the horizon, obtained from PATRIOT.
AD: soil drainage parameter, set to 0.
DISP: pesticide hydrodynamic solute dispersion coefficient, set to 0.
ADL: lateral soil drainage parameter, not used.

RECORD 36

DWRATE: dissolved phase decay rate, see Table 3.2 of this report.
DSRATE: adsorbed phase decay rate, see Table 3.2 of this report.
DGRATE: vapor phase decay rate, set to 0.0.

RECORD 37

DPN: thickness of compartments in the horizon, obtained from PATRIOT.
THEFC: field capacity in the horizon, obtained from PATRIOT.
THEWP: wilting point in the horizon, obtained from PATRIOT.
OC: percent organic carbon in the horizon, obtained from PATRIOT.
KD: pesticide partition coefficient, computed as $K_d = (\%OC) * (K_{oc})$; values of K_{oc} from Table 3.2 of this report.

RECORD 39 (used only for DDT/DDE/DDD parent-daughter simulations)

DKRW12: dissolved phase transformation rate for DDT to DDE, set to 4.04E-04.
DKRW13: dissolved phase transformation rate for DDT to DDD, set to 4.04E-04.
DKRW23: dissolved phase transformation rate for DDE to DDD, set to 0.0.
DKRS12: adsorbed phase transformation rate for DDT to DDE, set to 6.56E-05.
DKRS13: adsorbed phase transformation rate for DDT to DDD, set to 6.56E-05.
DKRS23: adsorbed phase transformation rate for DDE to DDD, set to 0.0.