INTERACTION EFFECTS ON SORPTION AND DESORPTION OF HERBICIDES

by

Xiaolong Hu

Submitted in Partial Fulfillment of

the Requirements for the Degree of

Master of Science in Hydrology

August, 1992

New Mexico Institute of Mining and Technology

Socorro, New Mexico

ABSTRACT

The objective of this study was to investigate the behavior of sorption and desorption of herbicides and the effect of their competition on sorption and desorption. Three herbicides with a broad range of sorption characteristics were chosen. They were 5-bromo-6-methyl-2,4-(1H,3H) pyrimidinedione (bromacil), N,N-diethyl-2-(1-naphthalenyloxy)- propanamide (napropamide) and N,N′-bis(1-methylethyl)-6-(methylthio)-1,3,5-2,4,-diamine (prometryn). Batch methods were used in this study. The soil used in the study was a Casa Grande sandy loam (fine-loamy, mixed, hyperthermic Typic Natragrids), located at the Maricopa Agriculture Center (MAC), Arizona. High performance liquid chromatography was used to analyze the concentrations of the three herbicides in solution.

Napropamide and prometryn exhibited linear sorption, while bromacil showed non-linear sorption. The linear equation and Freundlich equation were used to analyze the data. The linear partition coefficient (K_d) and the Freundlich coefficients (K_f and n) of the three herbicides were 0.0975 (for initial concentrations less than 40 μg/ml), 0.13, and 0.9 for bromacil, 0.275, 0.281, and 0.98 for prometryn, and 0.975, 0.98, and 0.98 for napropamide, respectively.

All the three herbicides showed marked desorption hysteresis. The ratios of $K_{d(sorp)}/K_{d(des)}$ and n_{sorp}/n_{des} of the three herbicides ranged from 1.75, 2.31 (bromacil) to 1.52, 1.58 (napropamide) and 1.3, 1.39 (prometryn).

Sorption of bromacil and napropamide decreased slightly in the presence of other herbicides, while the effects on prometryn sorption by other herbicides was not significant. The desorption hysteresis of bromacil and napropamide decreased slightly in the presence of other herbicides. The prometryn desorption was not significantly affected by other herbicides.

TABLE OF CONTENTS

LIST OF TABLES

APPENDIX

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

With increasing concern over groundwater contamination, research in contaminant fate and transport, contamination-transport modeling, and groundwater remediation has grown rapidly. Knowledge of the various physical, chemical, and biological processes that affect groundwater contamination is essential for such research. Of the various processes, sorption is one of the most important; it can have profound effects on contaminant fate, transport, and removal.

In modeling contaminant transport in the subsurface, the sorption process is often simplified by assuming instantaneous equilibrium, isotherm linearity, and sorption and desorption singularity. These assumptions simplify transport analysis and may be adequate under certain conditions. Data exhibiting behavior that deviates from that predicted by this simple model have been reported, however, challenging the validity of this simple approach. This non-ideal sorption behavior has been attributed to several different factors, including kinetically limited sorption reactions, and diffusive mass-transfer resistances (Brusseau, 1989).

Investigation of sorption nonideality is relatively recent. Sorption behavior of organic compounds in soil is linked with chemical characteristics of the compounds (Kier and Hall, 1986) and the organic carbon content in the soil (Bailey and White, 1964, Mingelgrin and Gerstl, 1983). The influence of dissolved organic carbon on sorption and transport of organic chemicals has been studied (e.g., Chiou et al, 1983, Voice and Weber 1985). Chiou (1989) strictly defined the terms of sorption, adsorption and partition and characterized the mechanistic functions of soil organic matter and mineral matter in uptake of organic compounds under various system conditions. Much research has been done on the sorption nonequilibrium (e.g., Karickhoff, 1984, Jaffe and Ferrara, 1983; McCall and Agin, 1985; Oliver, 1985; and Curtis et al, 1984). There are many reports of nonsingularity in the literature, as exemplified by those compiled by Di Toro (1985).

Although much research has shown sorption-desorption nonsingularity of many organic compounds, little attention is paid on the relation between the behaviors of sorption and desorption. Furthermore, most of the research on non-ideal sorption and desorption is confined to a single compound interacting with water and the soil matrix; effects of interaction among different organic compounds have been rarely investigated. Under field conditions, several organic compounds often exist in the same soil-water system. Effects of the interaction of the compounds on sorption and desorption is little known.

In this research project, three herbicides (bromacil, napropamide and prometryn) with a broad range of sorption and degradation characteristics were chosen. The selection was same as that of Turin (1992), so that the data obtained in this study could be used to explain some phenomena shown in the field experiment in Turin's research. The main objectives of this study were to investigate sorption and desorption of each single herbicide and effects of interaction of different herbicides on sorption and desorption when multiple herbicides exist in the same soil-water system. This research project attempted to improve understanding of such systems.

CHAPTER 2

PREVIOUS WORK

2.1 GENERAL TREATMENT OF SORPTION DATA TO NATURAL SOILS

The most common method of analyzing sorption data is via the sorption isotherm. Data for sorption isotherms must be collected at equilibrium, and at constant temperature and pressure. It may be necessary to correct for secondary reactions such as precipitation, or other interferences, especially when the sorption of ionic compounds is evaluated. Although many isotherm shapes have been observed, the most commonly evaluated shapes for aqueous solution are the linear, Langmuir, and Freundlich types (Bohn, et al.,1985).

The linear isotherm is often seen with sorption of low-solubility organic compounds to soils. This isotherm is described by the equation:

$$S=K_dC \tag{2-1}$$

where:

S: Mass of solute sorbed to substrate, [mg/kg]

K_d: Distribution coefficient, [L/kg]

C: Equilibrium solution concentration, [mg/L]

A plot of S vs. C will yield a straight line of slope K_d if sorption can be described by the linear isotherm. The linear form of the isotherm implies the sorbent has infinite capacity to retain dissolved species. This is probably never the case, and this linear form is usually valid only at low solute concentrations.

The Langmuir isotherm can be described by an equation of the form:

$$S=\frac{K_1CM}{1+K_1C} \tag{2-2}$$

where, in addition to variables already defined:

K_1: Langmuir constant, [L/mg]

M: Maximum amount of solute that can be sorbed in a complete monolayer[mg/kg]

This equation was derived assuming energy of sorption is constant and independent of surface coverage, solute molecules do not interact, adsorption is on specific sites, and maximum sorption is reached when a complete monolayer is filled on the adsorbent. Note that when concentrations are low, especially relative to the maximum number of surface sorption sites, $K_1C<<1$, and the equation reduces to a linear form. This is most probably the case for most low-solubility organic compounds; the number of organic molecules in solution is so low that the number of available sorption sites is effectively infinite, resulting in a linear isotherm. The Langmuir isotherm is often linearized in the form:

$$\frac{C}{S}=\frac{1}{K_1M}+\frac{C}{M} \tag{2-3}$$

such that a plot of C/S vs. C will result in a straight line with slope 1/M and intercept $1/MK_1$.

The Freundlich isotherm is described by the equation:

$$S=K_fC^n \qquad (2-4)$$

or, in the linearized form:

$$\log S=n\log C+\log K_f \qquad (2-5)$$

where, in addition to previously defined variables,

n: Empirical constant, [-]

K_f: Freundlich constant, [L/kg]

The Freundlich equation is used primarily as an empirical equation, but with the proper set of assumptions, it can be theoretically derived. Similar to the Langmuir equation, the Freundlich equation implies that an infinite number of sorption sites are available, but in contract it implies that energy of sorption decreases logarithmically as surface coverage increases. It must be very careful to compare Freundlich constants K_f and n values from different studies, as the values of these constants are highly dependant upon the system of units used. Note that when n=1, the equation is reduced to a linear form.

2.2 CONCEPT OF 'SITES'

The most important purpose of investigating the sorption and desorption behavior of contaminants in soil and groundwater is to predict the transport of the contaminants. The concept of sorption 'sites' is often used to explain the sorption and desorption behavior of contaminants in soil.

The term 'sites' has been given several different meanings, explained by Brusseau (1989) as:

(1) specific, molecular-scale,reaction sites;
(2) sites of differing degrees of accessibility;
(3) sites of differing sorbent type, such as organic matter and mineral surfaces;
(4) sites of different sorption mechanisms

2.3 NONLINEAR SORPTION

According to Chiou (1989), the term sorption is used to denote uptake of a solute by soil (or by a constituent of the soil) without reference to a specific mechanism. The term adsorption refers to condensation of vapors or solutes (both being referred to as adsorbates) on surfaces or interior pores of a solid (adsorbent) by physical or chemical bonding forces. In contract to adsorption, the term partition or partitioning is used to denote an uptake in which the sorbed organic chemical permeates into the network of an organic medium by forces common to solution (e.g., by van der Waals forces). The partition uptake is analogous to the extraction of an organic compound from water into an organic phase. When the organic phase is a solid (e.g, soil organic matter), partition is distinguished from adsorption by the homogeneous distribution through the entire volume of the solid phase.

For organic solutes, particularly nonpolar hydrophobic contaminants, the linearity of sorption isotherm is predicated upon the partition coefficient being independent of the equilibrium solution concentration. The theoretical basis for the occurrence of linear isotherm was discussed by Karickhoff (1984). Nonlinear sorption can result from either of the following two conditions:

(1) solution concentrations are high enough that the activity coefficient is not constant.

(2) sorption mechanisms other than partitioning are operating.

2.4 SORPTION-DESORPTION SINGULARITY

Sorption and desorption isotherm singularity is another major assumption employed in the conventional solute-transport equation. Non-singularity has often been reported, as exemplified by the compilation of Di Toro (1985). The possible causes of sorption nonsingularity or hysteresis are summarized by Brusseau (1989) as:

(1). Apparent Hysteresis

  a. Organic compounds are failing to reach sorption equilibrium.

  b. Organic compounds are failing to reach desorption equilibrium. In some conditions, the rate of desorption is much slower than that of sorption.

  c. Experimental method and measurement errors.

(2). True Hysteresis

a. Chemical/biological interactions.
b. Other sorption mechanisms (non-partitioning sorption).
c. Physical binding: the sorbate may become physically bound within the sorbent, thereby producing a sorbed component resistant to sorption.

Discrimination between true and apparent hysteresis may be assisted by analyzing various types of experimental data (Rao and Davidson, 1980). For example, true hysteresis does not affect the breakthrough front of a solute. Therefore, if a breakthrough curve exhibits early breakthrough and/or breakthrough front tailing as well as elution tailing, it may be concluded that nonsingularity is not the primary nonideality factor involved.

CHAPTER 3

MATERIALS AND METHODS

3.1. Selection of herbicides

The herbicides chosen for this study were bromacil, napropamide and prometryn. The selection criteria included:

1). A broad range of sorption and degradation characteristics.
2). Relatively low toxicity.
3). Relatively low volatility.
4). Ease of analysis by high performance liquid chromatography (HPLC).

Some basic chemical information about the three herbicides is shown on Table 3-1 (Herbicide Handbook, 1989).

Relevant physical and chemical properties of the three herbicides are shown in Table 3-2.

3.2. Soil characterization

The soil used for this study was a Case Grande sandy loam(fine-loamy, mixed, hyperthermic Typic Natragrids) well drained and slowly permeable , located at the Maricopa Agriculture Center (MAC) of the University of Arizona. The soil for the batch experiments was from the top 30 cm. It is a brown to reddish brown sandy loam. The soil used for this study had been uncropped for the past 4 years.

MAC is located three miles east of Maricopa, Arizona, and three miles north of the Case Grande-Maricopa Highway. This location was picked to coincide with a concurrent field study,

Table 3-1 Basic chemical information of the three herbicides

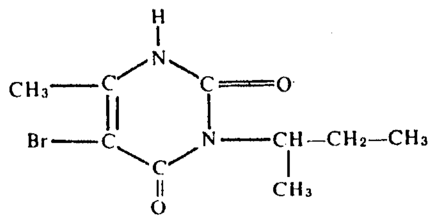
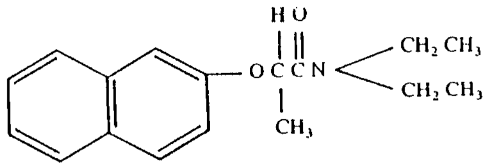
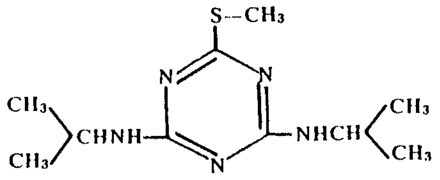
common name	chemical name	molecular formula	structural formula
bromacil	5-bromo-6-methyl-2,4-(1H,3H) pyrimidinedione	$C_9H_{13}BrN_2O_2$	
napropamide	N,N-diethyl-2-(1-naphthalenyloxy) - propanamide	$C_{17}H_{21}NO_2$	
prometryn	N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-2,4,-diamine	$C_{10}H_{19}N_5S$	

Table 3-2 Some Physical and Chemical Properties of The Three Herbicides (Jury et al, 1984).

Herbicide	Aqueous Solubility (mg/L)	Koc (m^3/kg)	Half-Life in soil (days)	Henry's constant
bromacil	820	0.072	350	$3.7*10^{-8}$
napropamide	73	0.3	70	$7.9*10^{-7}$
prometryn	48	0.61	61	$5.6*10^{-7}$

at the same location, on nonideal aspects of vadose-zone pesticide fate and transport (Turin, 1992). The site was also used by Bowman and Rice (1986) for a field experiment concerning preferential flow effects on a suite of conservative and retarded tracers. Information gained from each study can be used to give a clearer picture of the overall physical and chemical processes that affect pesticide transport at the site.

3.3 Soil Pretreatment

The soil collected from the field was air-dried, weighed, ground and passed through a 2-mm sieve. A number of subsamples of 10 grams each from the sieved soil were weighed, then put into 50 mL teflon tubes.

3.4 Preparation of solutions

0.005 M $CaCl_2$ solution was made. A 1:1 mL/g ratio of the solution to the soil was used to make a soil extract. Herbicide solutions were made in 0.005 M $CaCl_2$. Several sets of concentrations of bromacil, napropamide, prometryn, and mixtures of any two of the three compounds as well as all the three compounds were made. The details of the concentrations of the solutions of different compounds as well as their mixture will be discussed in the following chapters.

3.5 Procedure

Adsorption. A 10-mL aliquot of each solution was added to 10 g soil in a 50-mL teflon tube. All the samples were prepared in duplicate. The tubes were shaken mechanically for 24 hr. Time study results by Turin (1992) indicated thet 98% of the herbicides were adsorbed in the first 24 hr. Following equilibration, the suspentions were centrifuged for 25 minutes at $5.1*10^5$ g centrifugal force. A 3-mL aliquot of the supernatant was removed. The amount of herbicide in solution was determined by HPLC analysis.

The amount of herbicide adsorbed to the soil after equilibration was assumed to be the difference between herbicide concentration in soil-free blanks and herbicide concentration in solution after equilibration with soil. The data from the analysis of the samples were used to determine the sorption isotherm.

Desorption. Desorption studies were conducted by initially adsorbing herbicides to the soil from 0.005 M $CaCl_2$ solutions containing different concentrations of different herbicides as described previously. A 3-ml aliquot was removed after the 24 hr equilibration period. The concentration of herbicide in the aliquot was determined by HPLC.

Desorption of herbicides was accomplished by replacing a 3-mL aliquot previously removed for analysis with 3 mL of the herbicide-free soil extract. After solution replacement, tubes were vibrated to disperse the soil pellet, mechanically shaken for 24 hr, and recentrifuged. The 24-hr desorption process with the herbicide-free soil extract was repeated several times. The data was used to analyze the desorption process of the herbicides.

3.6 Measurement Method

3.6.1. Analysis Equipment

An HPLC system was used to analyze the concentrations of all the samples. The HPLC system consisted of four parts, which are listed in the table below:

Table 3-3 The Parts of HPLC

Pump	Sampler	Detector	Integrator
Waters 501 HPLC Pump made in Milford, MA	Perkin Elmer ISS-200 Advanced LC Sample Processor or Water U6K made in Norwalk, CT	Waters Lambda-Max Model 481 LC Spectra-photometer made in Milford, MA	Waters 745 Data Module made in Milford,MA

3.6.2. Analysis Method

a. mobile phase

The mobile phase for the analysis of the three organic compounds (bromacil, napropamide and prometryn) was prepared from 70 % methanol + 30 % water. Methanol was purchased from EM SCIENCE, Gibbstown, NJ. The water was demineralized using a Milli Q water purification system (Millipore, Bedford, MA). Since the three organic compounds are non-electrolytes, the change of pH of the mobile phase had a relatively insignificant effect the analysis result.

b. column

The column used in the HPLC was a 15cm * 4.6mm I.D. Rexchrom reversible HPLC column filled with 5 μm diameter ODS packing material, purchased from REGIS Inc., Morton Grove,IL.

c. Pumping rate

The pumping rate of the mobile phase was 1 cm^3/min, which resulted in a back pressure of 2500-3000 psi.

3.7 Analysis of Sorption and Desorption Data on Soil

Sorption. In this study, the linear and Freudlich equations were used to analyze the sorption data. The two methods are introduced in chapter 2.

Desorption. The calculation of desorption is based on the process where 3-mL aliquot of the supernatant is removed from the tube and the concentration of herbicide, C_1, is analyzed. The concentration of herbicide in soil, S, can also be calculated, where S=X/M; X is amount of herbicide adsorbed on soil (μg), and M is the mass of soil (g). Then, 3 mL herbicide-free soil solution is injected into the tube. The mixed solution is shaken and centrifuged. Another 3-mL aliquot of the supernatant is removed and the concentration of herbicide, C_2, is measured. If there is no desorption, the concentration of herbicide in the 'new' solution (C_2') can be calculated from the following equation:

$$C_2' = \frac{C_0 (V_W - V_0)}{V_W} \qquad (3\text{-}1)$$

C_2': calculated concentration of herbicide in the 'new' solution; (mg/L)

V_0: amount of supernatant removed; here, V_0 is 3 mL.

V_w: total amount of the solution; here, V_w is 10 mL.

V_w-V_0: residual volume of the original solution; here, V_w-V_0 is 7 mL.

The difference between C_2 and C_2' ($Cd=C_2-C_2'$) is attributed to the desorption of herbicide from soil. The amount of herbicide desorbed can be calculated by the following equation:

$$X_d=C_d*V_w=(C_2-C_2')V_w \qquad (3\text{-}2)$$

X_d: mass of the desorbed herbicide; (μg)

The linear equation and Freundlich equation were also used to analyze the desorption data. The Freundlich equation used in analysis of desorption data was the same form used in analysis of sorption data. Owing to desorption hysteresis of the three herbicides, the linear equation used in desorption is in a different form:

$$S=K_dC+b \tag{3-3}$$

where, in addition to previously defined varibles,

b: hysteresis parameter; (μg/g)

IV

RESULTS

4.1 Chromatographic Analysis

4.1.1. Wavelength

The detection of an organic compound is very sensitive to the wavelength. When choosing a wavelength for detection of a compound, not only the absorption maximum of the compound but also the absorption of other compounds and the mobile phase should be considered. According to Reupert et al. (1990), the absorption maximum for bromacil is 270 nm and for prometryn is 230 nm. The absorption maximum for napropamide was not known.

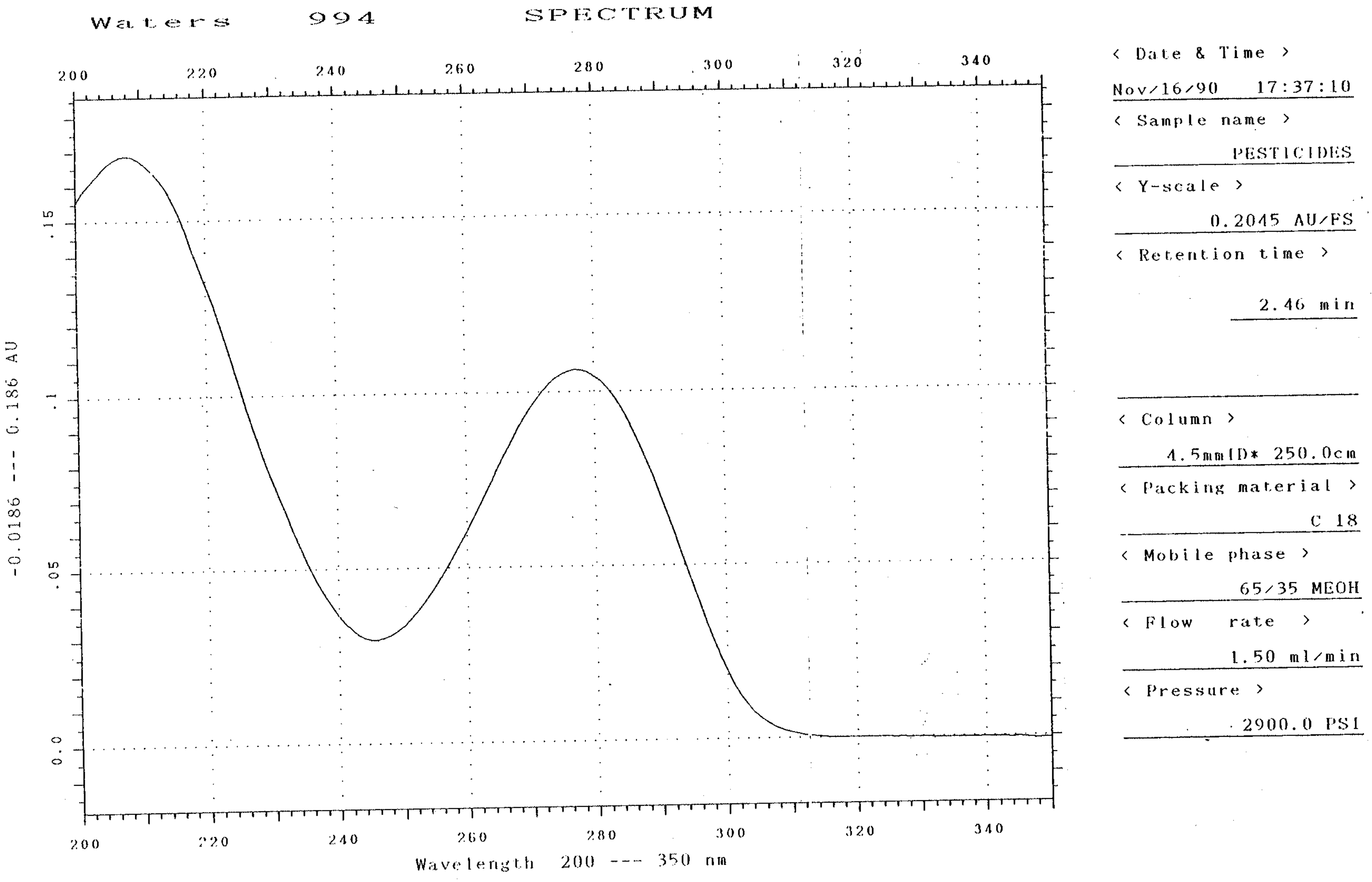
In this study, another HPLC system (Table 4-1) was used to determine the UV spectra of the three compounds in the range of 200 to 340 nm. The spectra are shown in Figures 4-1, 4-2, and 4-3. From the Figures, the absorption maxima of bromacil, prometryn, and naprpamide are 270 nm, 201 nm, and 203 nm, respectively.

Table 4-1 The HPLC System Used to Find Absorption Maximum of The Three Herbicides

injector	pump	detector	printer plotter
Waters U6K	Waters 501 HPLC pump	Waters 994	Waters 5200

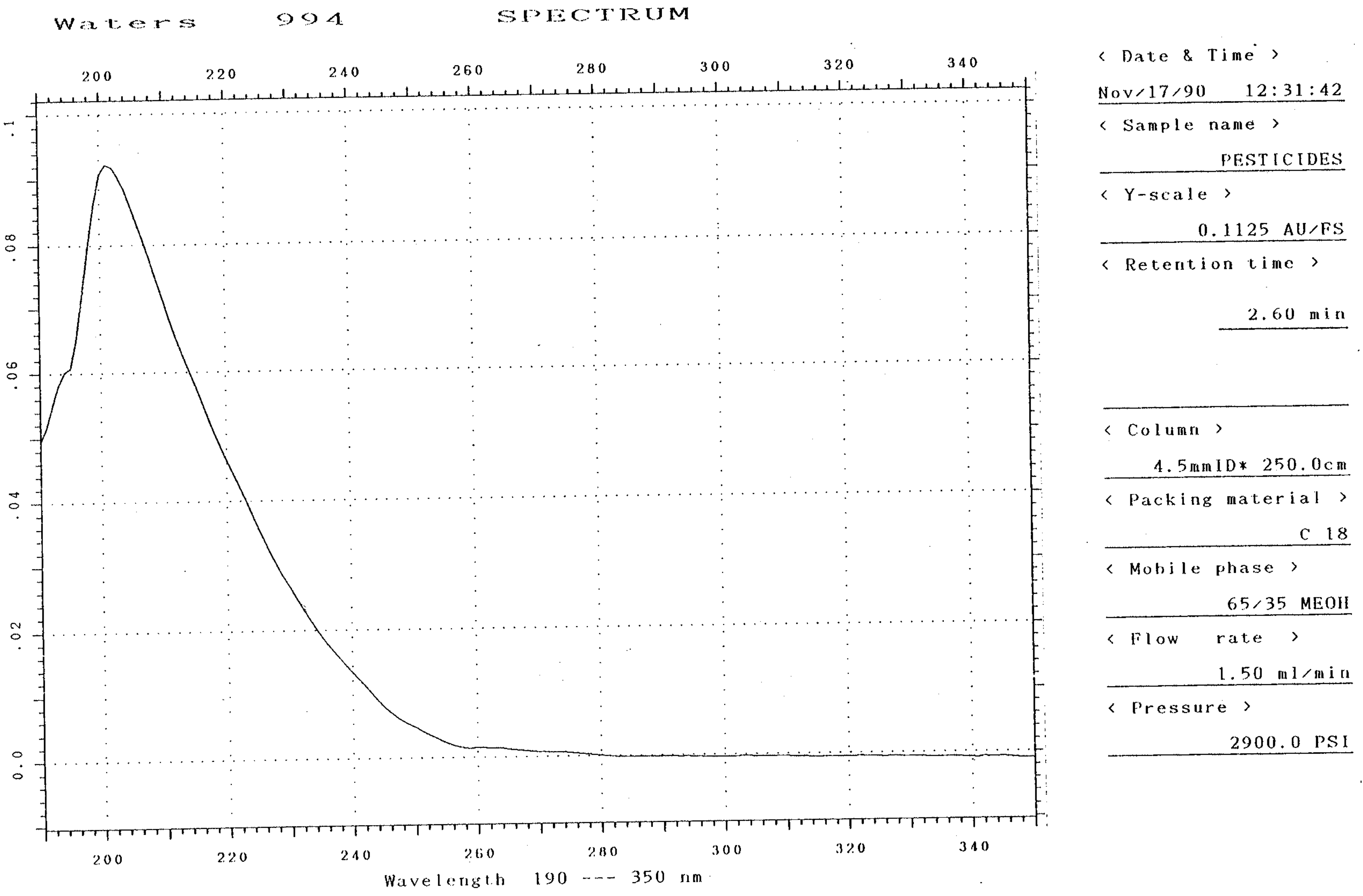
Note: All the three parts of the system are made in Milford, MA.

The difference between the absorption maxima of prometryn found in this study and in Reupert et al.'s (1990) research data is probably due to the different calibration of the detector or the mobile phase used in the analysis. In



< Date & Time >
Nov/16/90 17:37:10
< Sample name >
PESTICIDES
< Y-scale >
0.2045 AU/FS
< Retention time >
2.46 min
< Column >
4.5mmID* 250.0cm
< Packing material >
C 18
< Mobile phase >
65/35 MEOH
< Flow rate >
1.50 ml/min
< Pressure >
2900.0 PSI

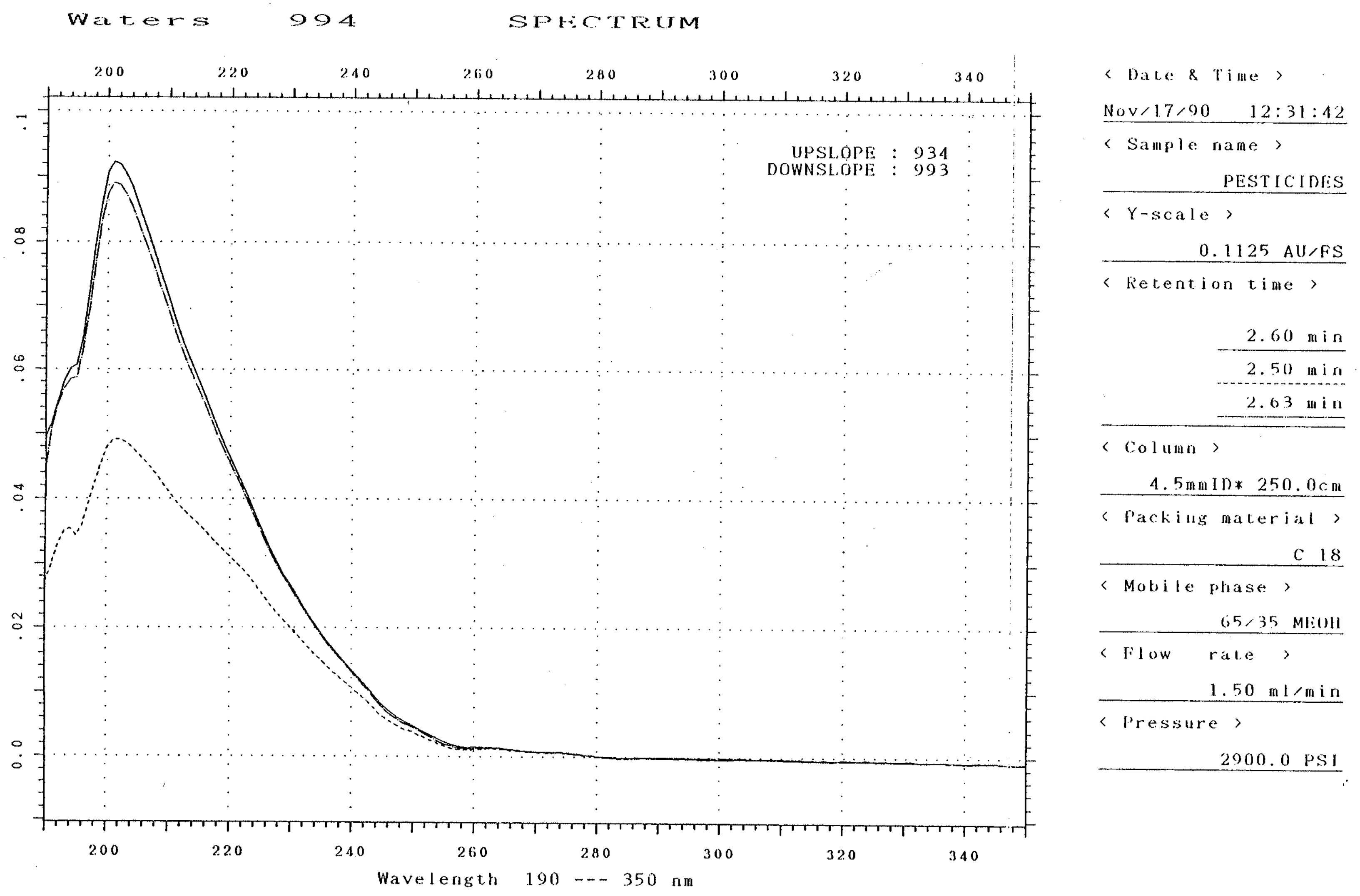
Fig. 4-1 Spectrum of Bromacil Absorption



< Date & Time >
Nov/17/90 12:31:42
< Sample name >
PESTICIDES
< Y-scale >
0.1125 AU/FS
< Retention time >
2.60 min

< Column >
4.5mmID* 250.0cm
< Packing material >
C 18
< Mobile phase >
65/35 MEOH
< Flow rate >
1.50 ml/min
< Pressure >
2900.0 PSI

Fig. 4-2 Spectrum of Prometryn Absorption



< Date & Time >
Nov/17/90 12:31:42
< Sample name >
PESTICIDES
< Y-scale >
0.1125 AU/FS
< Retention time >
2.60 min
2.50 min
2.63 min
< Column >
4.5mmID* 250.0cm
< Packing material >
C 18
< Mobile phase >
65/35 MEOH
< Flow rate >
1.50 ml/min
< Pressure >
2900.0 PSI

Fig. 4-3 Spectrum of Napropamide Absorption

R.Reupert's research, the mobile phase was 65% acetonitrile + 35% water.

Another factor which should be considered is the absorption characteristics of methanol. The spectral characteristics of methanol are listed in Table 4-2. From the table, when the wavelength is less than 230 nm, the absorbance of methanol is not negligible.

Table 4-2 Spectral Characteristics of Methanol⁺
(EM SCIENCE, Gibbstown, NJ, 1992)

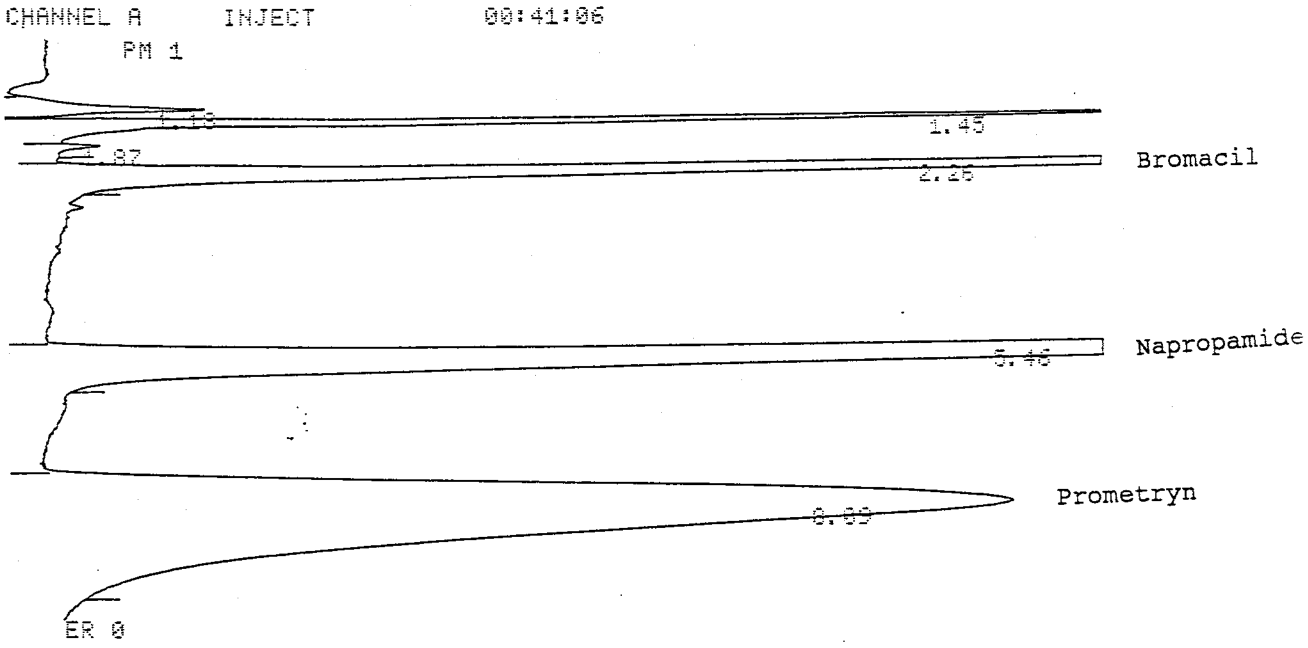
Wave length	300	260	250	230	220	210	205	203
absorbance	0.001	0.003	0.003	0.018	0.038	0.134	0.455	0.746

+ As listed on lable on bottle

When all the factors that affect the analysis results were considered, the wavelengths for analysis of bromacil, prometryn and napropamide were chosen to be 270 nm, 230 nm and 230 nm, respectively.

4.1.2 Retention time

The retention time of a herbicide determines the specific position of the herbicide in the HPLC chromatogram and the minimum analysis time for the herbicide. The HPLC chromatogram of a standard mixture solution of bromacil (133 μg/mL), prometryn (5 μg/mL) and napropamide (6.66 μg/mL) is shown in figure 4-4. From the figure, the retention times of bromacil, prometryn and napropamide are 2.26 min, 8.09 min and 5.46 min, respectively.



```
INPUT OVERRANGE AT RT=     1.37

                                 00:41:06     CH= "A"  PS=  1.

FILE  1.      METHOD  0.     RUN   2     INDEX   2

PEAK#        HT%         RT      PK HT BC

    1        5.017      1.18      6584 01
    2       13.008      1.45     17072 02
    3        1.78       1.87      2336 03
    4       39.364      2.26     51664 01
    5       35.213      5.46     46216 01
    6        5.618      8.09      7373 01

TOTAL      100.                 131245
```

Fig. 4-4 Retention Times of Bromacil, Prometryn and Napropamide

4.1.3 Integration Method

There are two peak integration methods in the integrator of the HPLC system. One method is peak height (PH=1), while the other is area. If there are many unknown compounds in supernatant, the curve shapes of the herbicides will be influenced by these compounds. In this study, it was found that the peak height method was less affected by the unknown compounds than area method. Therefore, the peak height was used in the analysis of all samples.

4.2 Sorption and Desorption of a single herbicide

4.2.1 Bromacil

A set of bromacil solutions with the following concentrations of 1, 4, 10, 40, 100, 200, and 400 μg/mL were made in 0.005 M $CaCl_2$. Since the solubility of bromacil in water at 25 ^{0}C is 815 μg/mL (Table 3-2), the maximum concentration of bromacil in this study was chosen 400 μg/ml, or about half of the solubility. The methods for the batch experiments were discussed in chapter 3. The sorption and desorption data are shown in Appendix-Tables 1 and 2. The data are plotted in Figures 4-5 and 4-6, using normal and logarithmic coordinates, respectively.

Sorption . For the sorption process, Figure 4-5 shows that the data points from initial concentrations less that 40 ppm fall on a straight line; the data points with higher initial concentrations deviate from the straight line; but all the

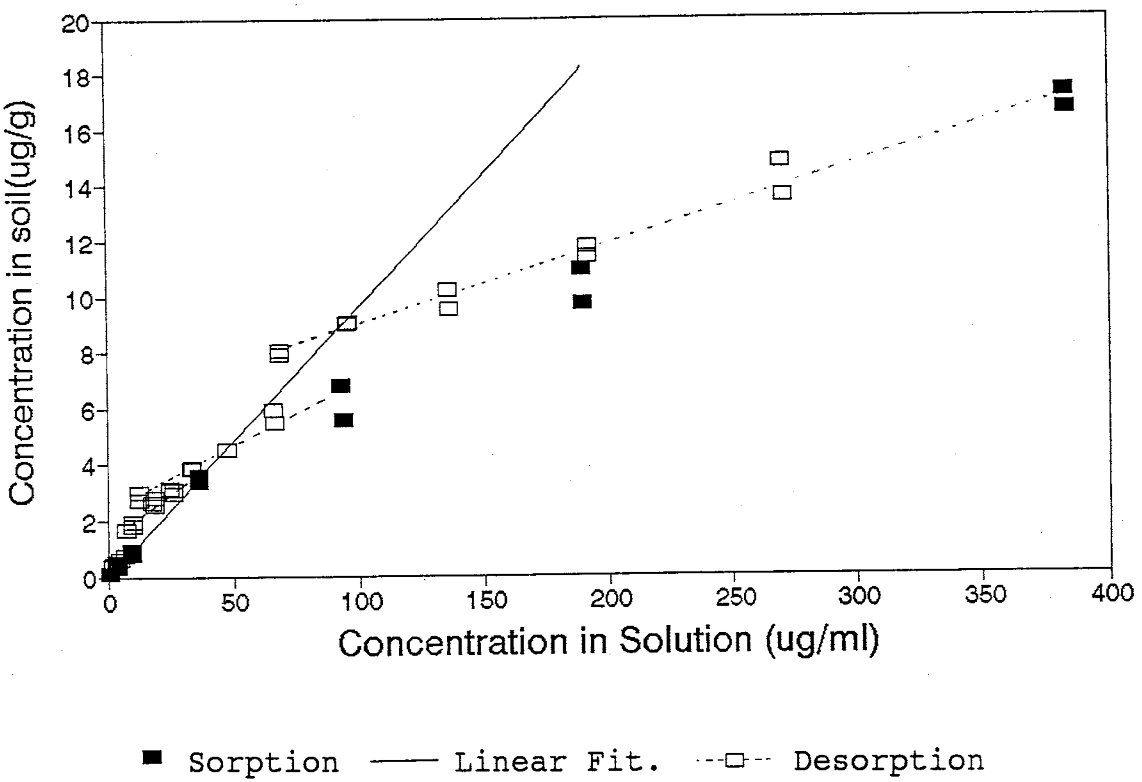


Fig. 4-5 Bromacil Sorption and Desorption Results

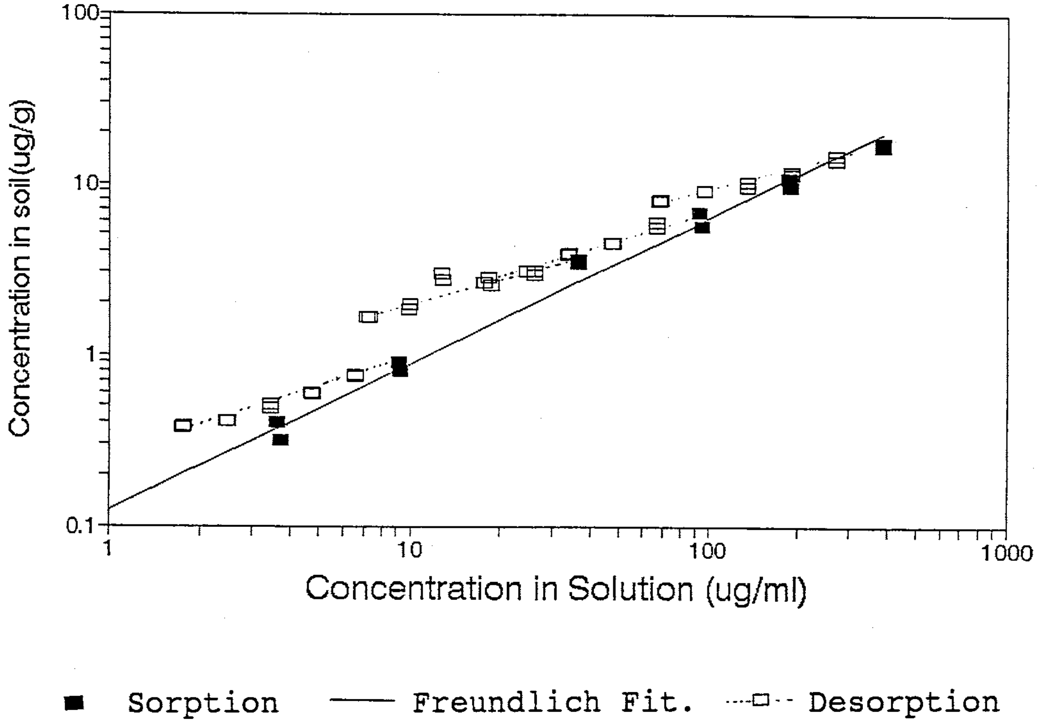


Fig. 4-6 Bromacil Sorption and Desorption Results

data points appear in a straight line in Figure 4-6. Therefore, in the data analysis, all the data were used to evaluate K_f and n in Freudlich Equation; but only the data corresponding to initial concentrations less than 40 mg/L were used to evaluate K_d in linear Equation. The Least squares and T-test (α=0.05) methods were used in data analysis (the two methods were used for all the data analysis in chapter 4). The linear equation was forced through zero. The calculated results are shown in Table 4-3.

Table 4-3. The Parameters for Bromacil Sorption

parameter	value	R^2	No. of data points	significant
K_d	0.0975	0.997	7	yes
K_f	0.125	0.99	13	yes
n	0.85	0.99	13	yes

Desorption. Both Figure 4-5 and 4-6 show that sorbed bromacil concentrations decrease with the decrease of bromacil concentration in solution; furthermore, the desorption isotherms are not coincident with the sorption isotherm. Hysteresis exists in desorption process.

The calculated results for different initial bromacil concentrations are shown in Table 4-4.

Since the values of b and K_f are affected by the initial bromacil concentrations, the values will not be used to

Table 4-4. Parameters for Bromacil Desorption

Initial conc(μg/ml)	4	10	40	100	400
K_d	0.058	0.067	0.056		
b	0.16	0.27	1.55		
R^2	0.79	0.96	0.79		
significant	yes	yes	yes		
Log K_f	-0.66	-0.57	-0.12	-0.25	0.80
n	0.4	0.52	0.44	0.54	0.44
R^2	0.85	0.98	0.84	0.97	0.97
significant	yes	yes	yes	yes	yes

analyze hysteresis of desorption process. Comparing the values of K_d and n in desorption with the values of K_d and n in sorption, the degree of hysteresis can be evaluated. The ratios of $K_{d(sorp)}/K_{d(des)}$ and n_{sorp}/n_{des} are shown in Table 4-5.

Table 4-5. Bromacil Desorption Hysteresis Ratios

initial cons.(μg/mL)	4	10	40	100	400
$K_{d(sorp)}/K_{d(des)}$	1.68	1.46	1.74		
n_{sorp}/n_{des}	2.13	1.63	1.89	1.57	1.93

4.2.2. Prometryn.

A series of prometryn solutions with concentrations of 1, 5, 10, and 20 μg/mL were made in 0.005 M $CaCl_2$. The solubility of prometryn in water at 20 $_0$C is 48 μg/mL. So, the maximum concentration chosen was 20 μg/mL, about half of the solubility. The sorption and desorption data are shown in Appendix-Tables 3 and 4. The data are plotted in Figures 4-7 and 4-8 in normal and logarithmic coordinates, respectively.

Sorption. All the data points in Figure 4-7 and 4-8 appear in

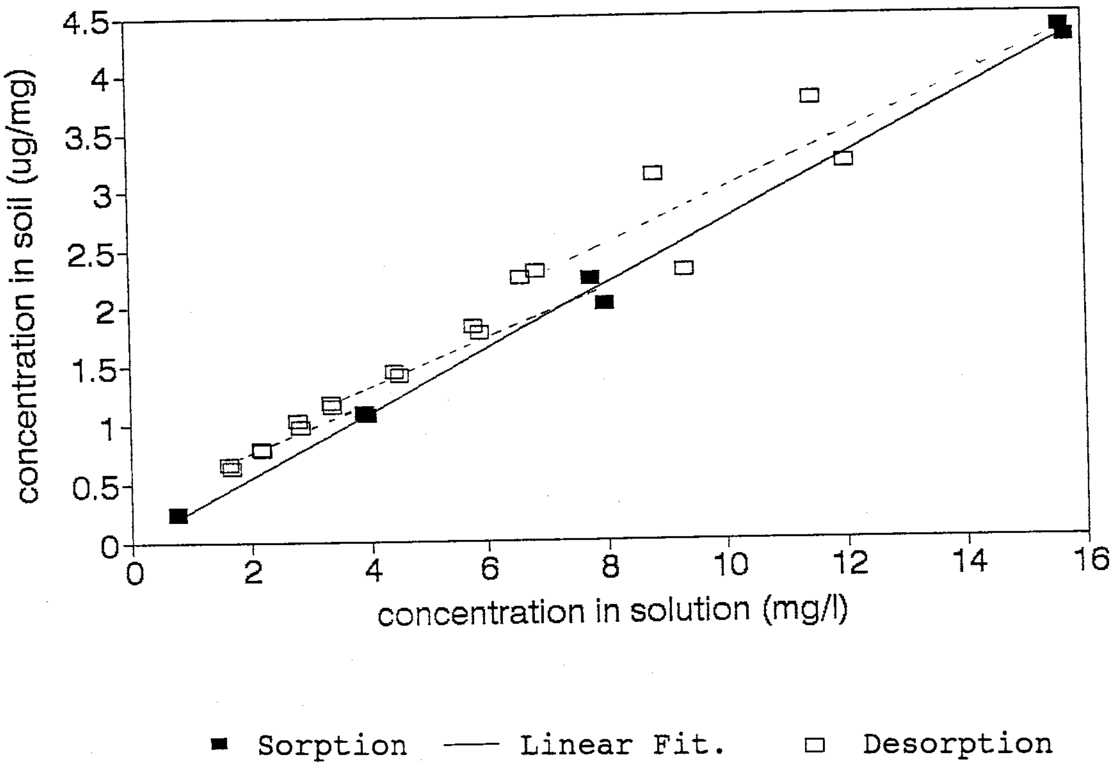


Fig. 4-7 Prometryn Sorption and Desorption Results

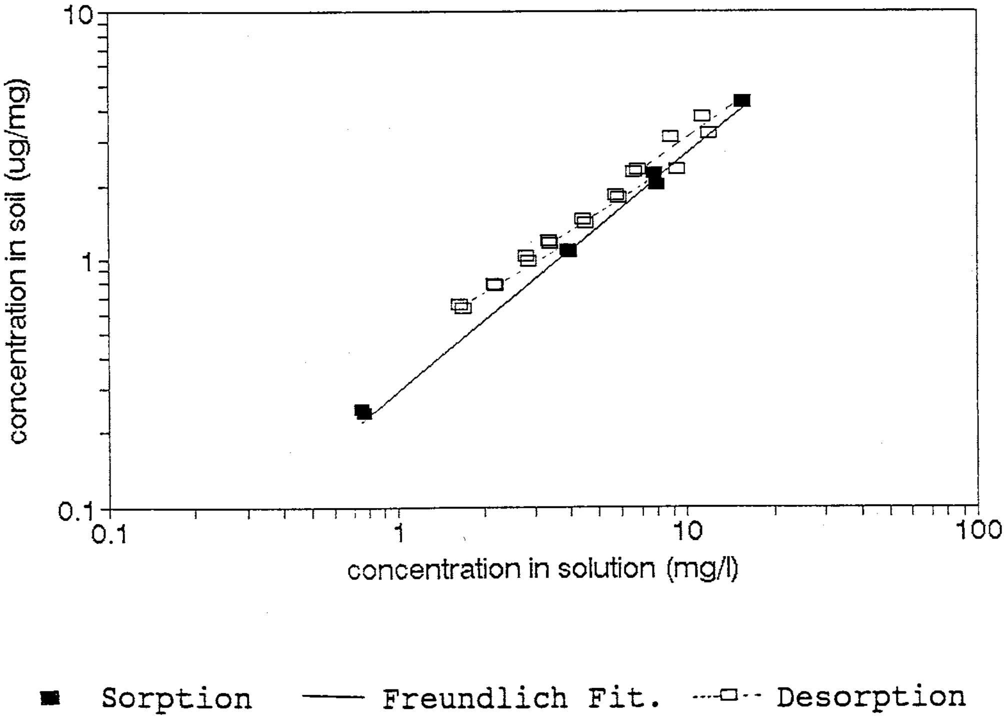


Fig. 4-8 Prometryn Sorption and Desorption Results

a straight line. All the data are used to evaluate K_d value in linear equation and K_f and n in Freudlich Equation. The calculated results are shown in Table 4-6.

Table 4-6. Parameters For Prometryn Sorption

parameter	K_d	K_f	n
value	0.275	0.29	0.96
R_2	0.997	0.998	0.998
significant	yes	yes	yes

Desorption. The desorption data points in Figure 4-7 and 4-8 show that sorbed prometryn concentrations decrease with the decrease of prometryn concentrations in solution, but compared with sorption data points, desorption processes exist hysteresis. The calculated values of parameters are listed on Table 4-7. The ratios of $K_{d(sorp)}/K_{d(des)}$ are shown in the table 4-8.

Table 4-7. Parameters For Prometryn Desorption

Initial conc(μg/mL)	20	10	5
K_d	0.23	0.21	0.20
b	0.73	0.5	0.36
R^2	0.87	0.95	0.89
significant	no	yes	no
log (K_f)	-0.51	-0.3	-0.082
n	0.76	0.71	0.71
R^2	0.84	0.97	0.97
significant	no	yes	yes

Table 4-8. Prometryn Desorption Hysteresis Ratios

Initial conc. (μg/g)	5	10	20
$K_{d(sorp)}/K_{d(des)}$	1.2	1.31	1.38
n_{sorp}/n_{des}	1.26	1.35	1.52

4.2.3. Napropamide.

A set of napropamide solutions with concentrations of 1, 5, 10, 15, and 30 μg/mL were made in 0.005 M $CaCl_2$. Since the solubility of napropamide in water at 25 ^{0}C is 73 μg/mL, the maximum concentration is 30 μg/mL, roughly half of the solubility. The method and procedures of the batch experiment were described in chapter 3.

The data of sorption and desorption are shown in Appendix-Tables 5 and 6, and plotted on Figure 4-9 and 4-10, respectively.

Sorption. For the sorption process, all the data points appear on a straight line in Figure 4-9 and 4-10. All the data are used to calculate K_d in linear equation and K_f and n in Freundlich Equation. The calculated results are listed on Table 4-9.

Table 4-9. Parameters For Napropamide Sorption

Parameter	K_d	K_f	n
value	0.97	0.974	0.98
R^2	0.999	0.999	0.999
significant	yes	yes	yes

Desorption. The desorption data points in Figures 4-9 and 4-10 show that the some of the sorbed napropamide will desorb when the napropamide concentration in solution decreases. Compared with sorption data points, the desorption processes show some degree hysteresis. The parameters for napropamide desorption

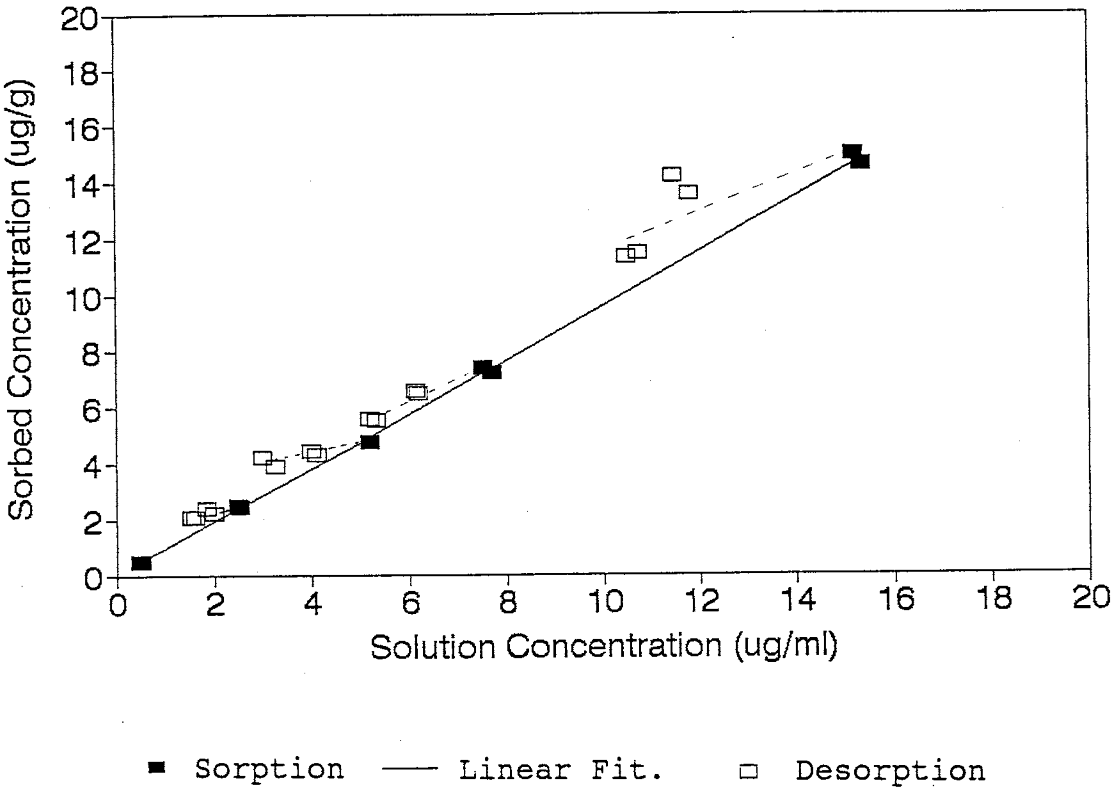


Fig. 4-9 Napropamide Sorption and Desorption Results

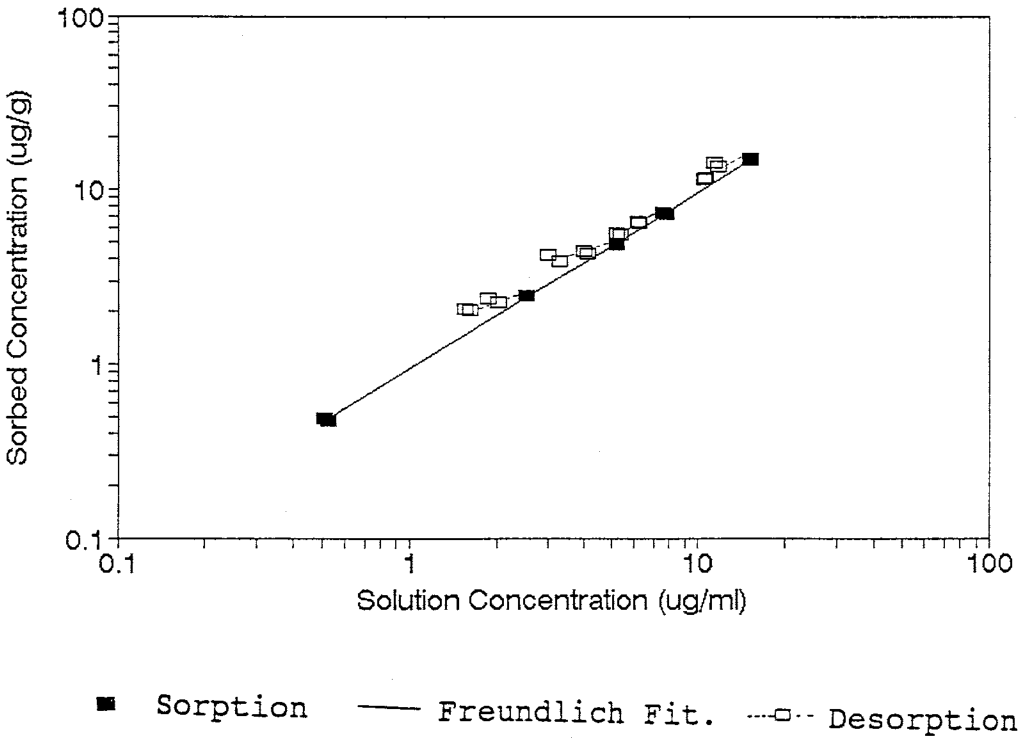


Fig. 4-10 Napropamide Sorption and Desorption Results

are calculated and listed on Table 4-10. The ratios of $K_{d(sorp)}/K_{d(des)}$ans n_{sorp}/n_{des} are shown in Table 4-11.

Table 4-10. Parameters For Napropamide Desorption

Initial cons(μg/mL)	30	15	10	5
K_d	0.6	0.72	0.35	0.37
b	5.88	1.9	2.97	1.51
R^2	0.69	0.95	0.83	0.8
significant	no	no	no	no
n	0.60	0.72	0.315	0.34
Log (K_f)	0.47	1.7	2.82	1.78
R^2	0.7	0.95	0.82	0.82
significant	no	no	no	no

Table 4-11. Napropamide Desorption Hysteresis Ratios

Initial conc (μg/g)	5	10	15	30
$K_{d(sorp)}/K_{d(des)}$	1.62	1.35	2.77	2.62
n_{sorp}/n_{des}	1.63	1.36	3.1	2.88

4.3. Effects of Interaction of Two Pesticide on Sorption and Desorption

4.3.1. Sorption and desorption of Bromacil affected by Prometryn or Napropamide

Two sets of bromacil solutions with concentrations of 10, 40, and 200 μg/mL were made, one in 10 μg/mL prometryn, another in 15 μg/mL napropamide. The two sets of mixed concentration were used to determine the sorption and desorption processes as affected by prometryn or napropamide. The sorption and desorption data are shown in Appendix-Tables 7 and 8 and plotted in Figures 4-11, 4-12, 4-13, and 4-14 in linear or logarithmic coordinates.

Sorption. For the sorption process of bromacil, the three different data points (bromacil only, bromacil with prometryn, and bromacil with napropamide) appear in slightly different positions. The three sets of calculated parameters are listed in Table 4-12. The difference between the parameters of bromacil only and the parameters of bromacil with prometryn or napropamide is considered significant if the relative difference is greater than 10%. The criterion is used in all the tests of difference in chapter 4.

Table 4-12. Bromacil Sorption Affected by Prometryn or Napropamide

parameter	bromacil only	bromacil with P^*	significant difference	bromacil with N^*	significant difference
K_d	0.098	0.084	yes	0.94	no
R^2	0.994	0.998		0.99	
significant	yes	yes		yes	
K_f	0.138	0.105	yes	0.121	yes
n	0.9	0.93	no	0.91	no
R_2	0.996	0.997		0.998	
significant	yes	yes		yes	

Note: P: prometryn; N: napropamide

Desorption. Only the samples with 40 μg/mL initial bromacil concentration were chosen for the desorption experiment. The three different sets of desorption data (bromacil only, bromacil with prometryn, and bromacil with napropamide) are

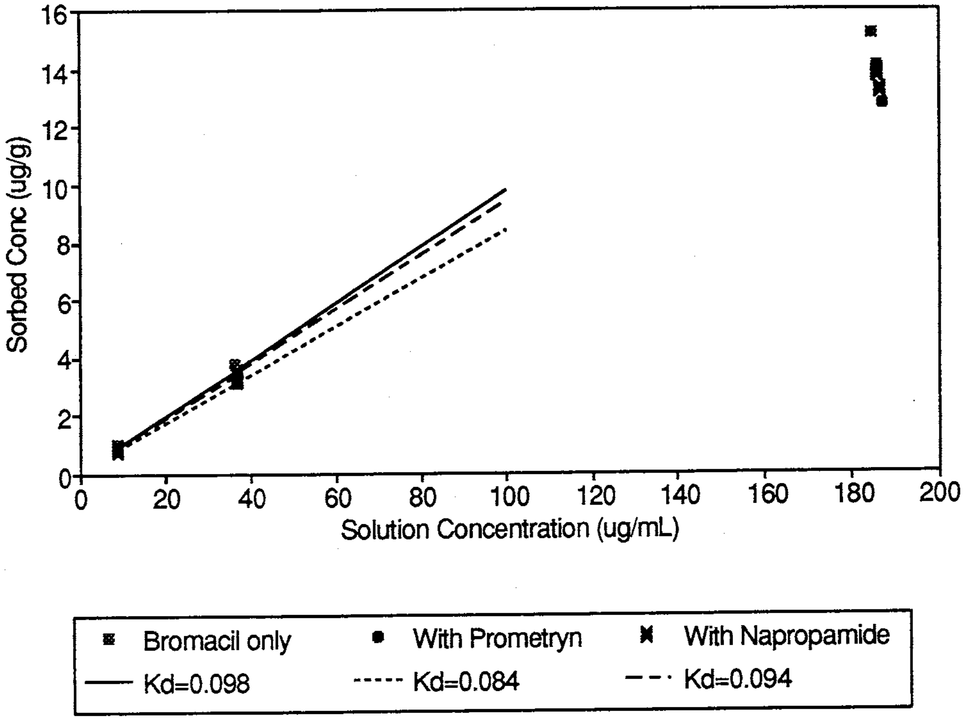


Fig. 4-11 Bromacil Sorption Affected by Prometryn or Napropamide

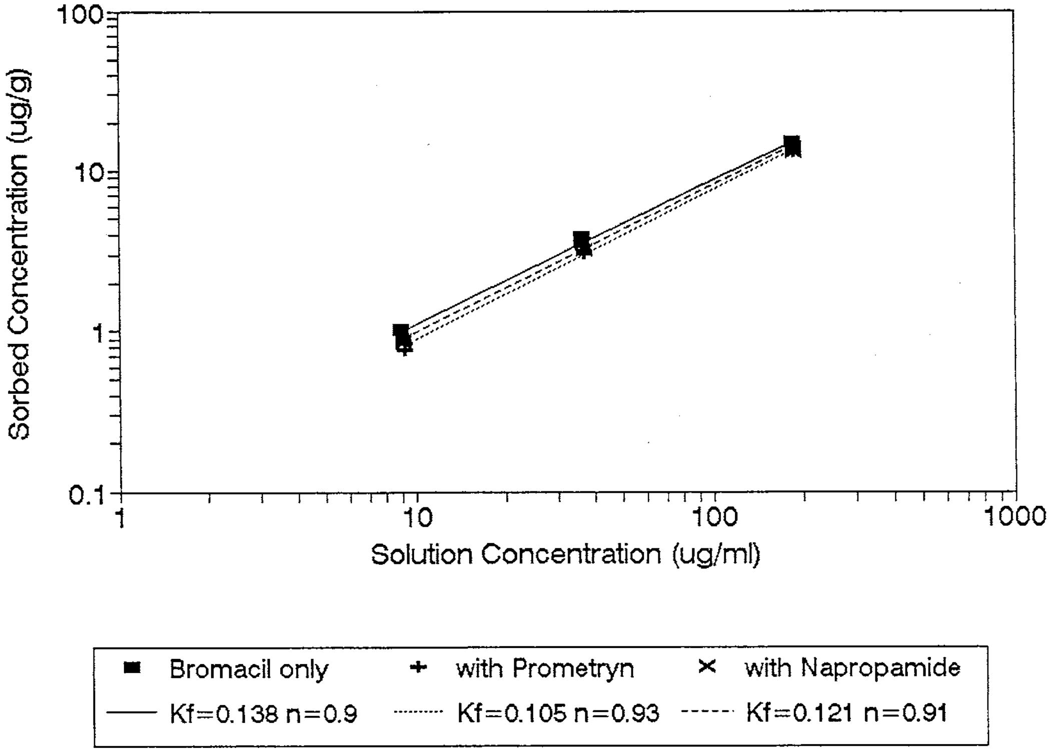


Fig. 4-12 Bromacil Sorption Affected by Prometryn or Napropamide

listed in appendix-Table 8. The data are plotted in Figures 4-13 and 4-14 in linear and logarithmic coordinates, respectively. The different points appear in slightly different positions. The calculated results are listed in Table 4-13 and Table 4-14.

Table 4-13. Bromacil Desorption Affected by Prometryn or Napropamide

parameter	bromacil only	bromacil with P*	significant difference	bromacil with N*	significant difference
K_d	0.0568	0.055	no	0.039	yes
b	1.7	1.08	yes	1.25	yes
R^2	0.84	0.81		0.56	
significant	no	no		no	
$Log(K^f)$	-0.2	-0.26	no	-0.42	yes
n	0.5	0.52	no	0.61	yes
R^2	0.86	0.84		0.64	
significant	no	no		no	

Note: P: Prometryn ; N: Napropamide

Table 4-14. Bromacil Desorption Hysteresis Ratios Affected by Prometryn and Napropamide

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
bromacil only	1.73	1.86
bromacil with prometryn significant difference	1.47 yes	1.48 yes
bromacil with napropamide significant difference	1.54 yes	1.49 yes

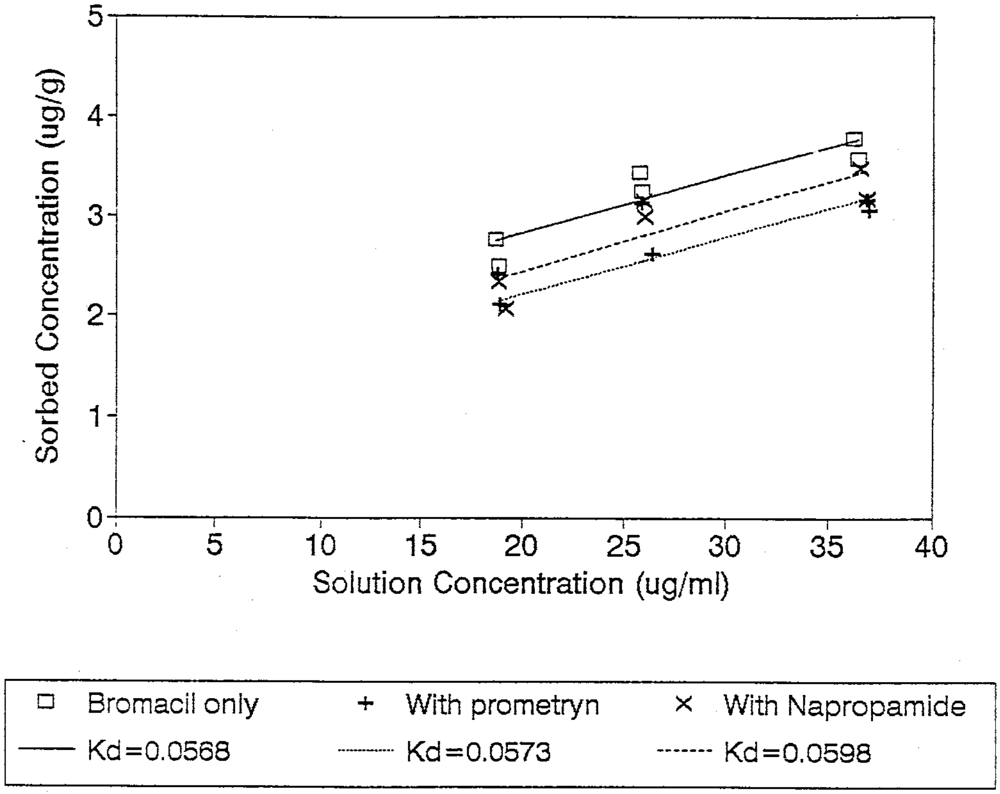


Fig. 4-13 Bromacil Desorption with Initial Conc: 40 μg/mL

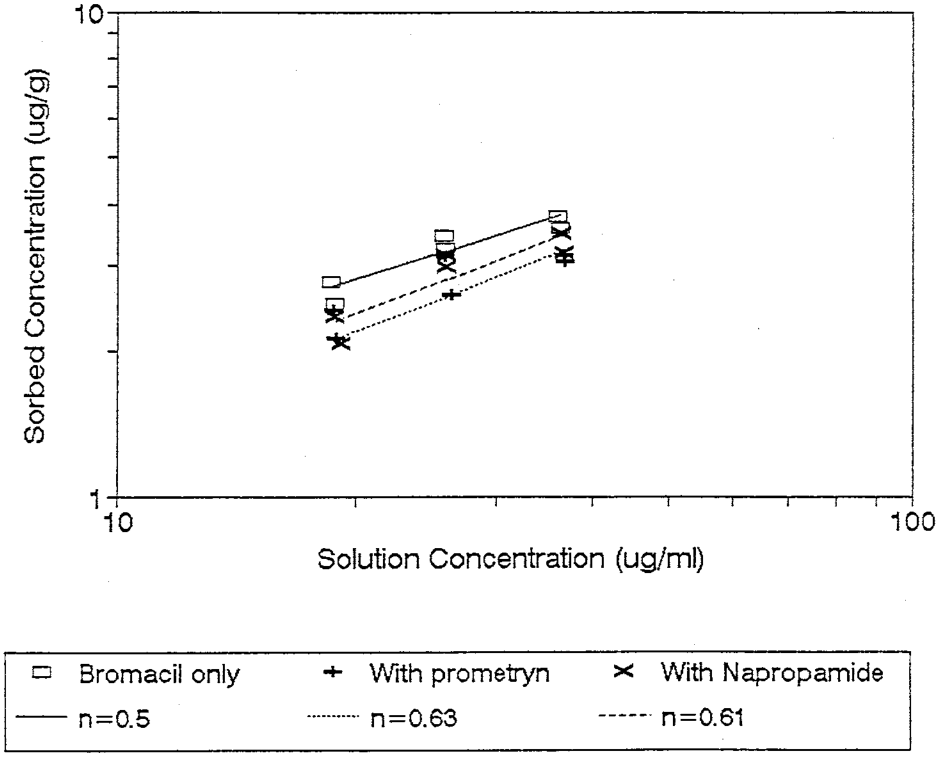


Fig. 4-14 Bromacil Desorption with Initial Conc: 40 μg/mL

4.3.2. Sorption and Desorption of prometryn affected by Bromacil or Napropamide

Two set of prometryn solutions were made, one in 200 μg/mL bromacil, another in 15 μg/mL napropamide. The prometryn concentrations with bromacil were 5, 10, and 20 μg/mL, and the concentration with napropamide were 6.66 and 10 μg/mL. The experimental results are shown in Appendix-Table 10 and 11, and plotted in Figures 4-15, 4-16, 4-17, 4-18, 4-19 and 4-20.

Sorption. For the prometryn sorption process, the three different types of data points (prometryn only, prometryn with bromacil, and prometryn with napropamide) in Figures 4-15 and 4-16 take almost the same positions. The three sets of calculated parameters for the linear equation and the Freundlich equation are listed in Table 4-15.

Table 4-15. Prometryn Sorption Affected by Bromacil or Napropamide

parameter	Prometryn only	Prometryn with B*	significant difference	P* with N*	significant difference
Kd	0.281	0.272	no	0.272	no
R^2	0.98	0.999		0.995	
significant	yes	yes		yes	
K_f	0.282	0.27	no	0.273	no
n	0.99	1.003	no	0.997	no
R^2	0.988	0.999		0.997	
significant	yes	yes		yes	

Note: P: prometryn ; B: bromacil; N: napropamide

Desorption. The samples with initial bromacil concentrations of 6.66 μg/mL and 10 μg/mL in sorption process were chosen for desorption experiments. The three different prometryn

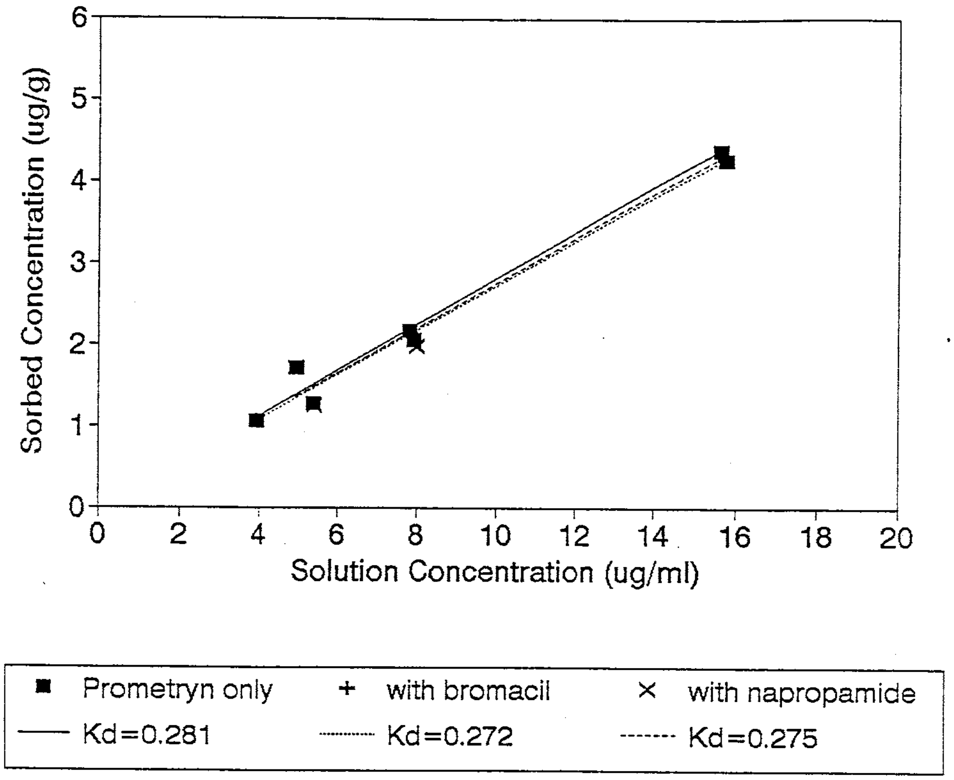


Fig. 4-15 Prometryn Sorption Affected by Bromacil or Napropamide

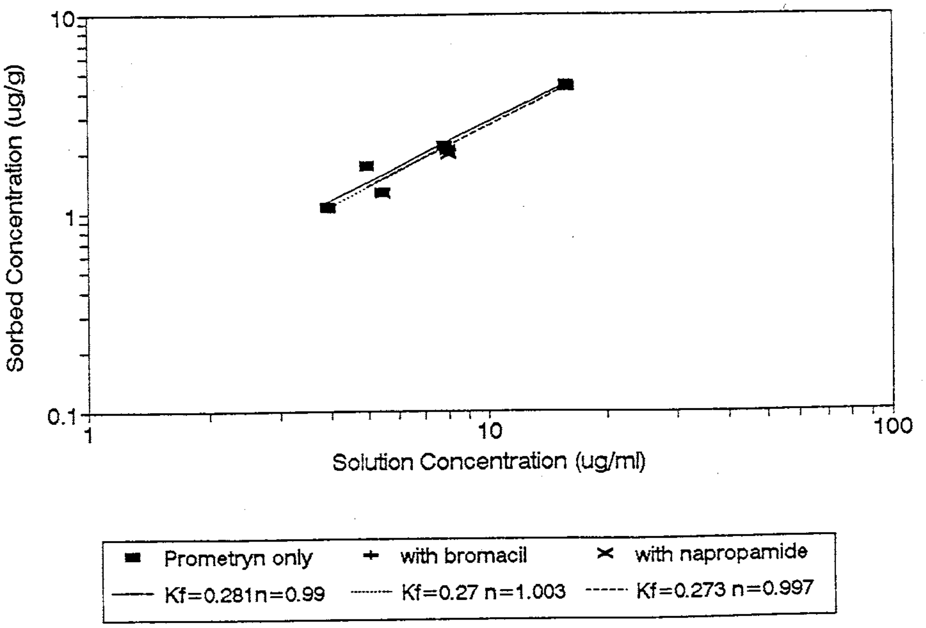


Fig. 4-16 Prometryn Sorption Affected by Bromacil or Napropamide

desorption data (prometryn only, prometryn with bromacil, and prometryn with napropamide) are plotted in Figures 4-17, 4-18, 4-19 and 4-20. The desorption parameters are calculated and listed in Table 4-16, and the ratios of desorption hysteresis degree are shown in Table 4-17.

Table 4-16. Prometryn Desorption Affected by Bromacil or Napropamide

parameter	prometryn only	prometryn with B	significant difference	P* with N	significant difference
6.66 µg/mL					
K_d	0.226	0.24	no	0.25	no
b	0.3	0.11	yes	0.05	yes
R^2	0.6	0.73		0.42	
significance	no	no		no	
K_f	0.41	0.36	no	0.28	yes
n	0.78	0.84	no	0.94	yes
R_2	0.67	0.64		0.38	
significance	no	no		no	
10 µg/mL					
K_d	0.235	0.21	no	0.18	yes
b	0.32	0.44	yes	0.65	yes
R^2	0.91	0.37		0.82	
significance	yes	no		no	
K_f	0.37	0.44	yes	0.52	yes
n	0.86	0.74	yes	0.82	no
R^2	0.92	0.35		0.83	
significance	yes	no		no	

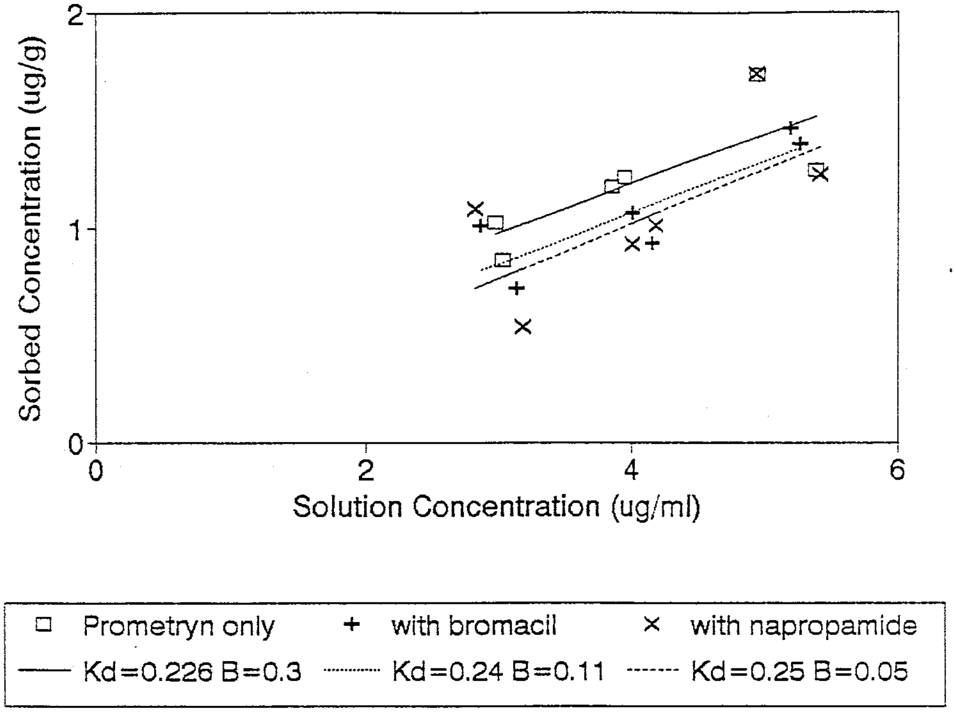


Fig. 4-17 Prometryn Desorption with Initial Conc: 6.66 $\mu g/mL$

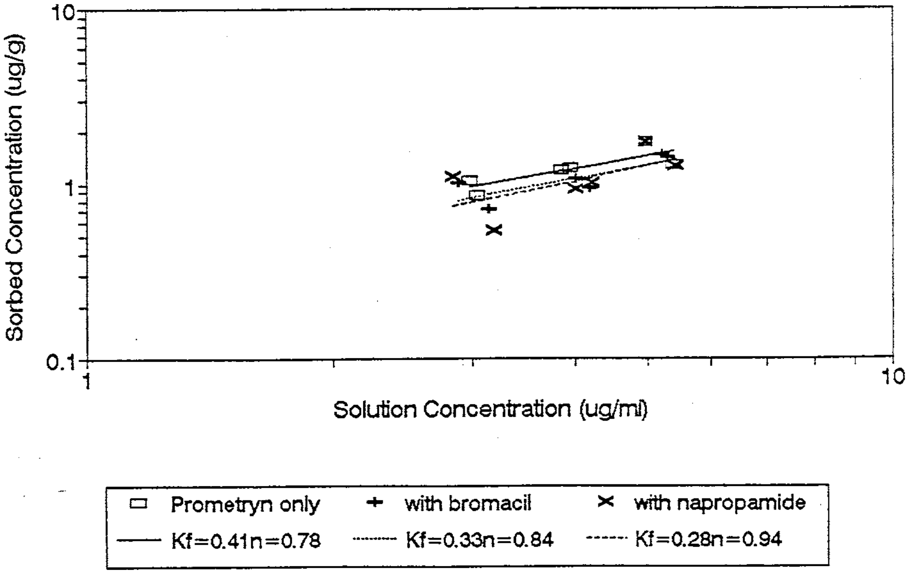


Fig. 4-18 Prometryn Desorption with Initial Conc: 6.66 $\mu g/mL$

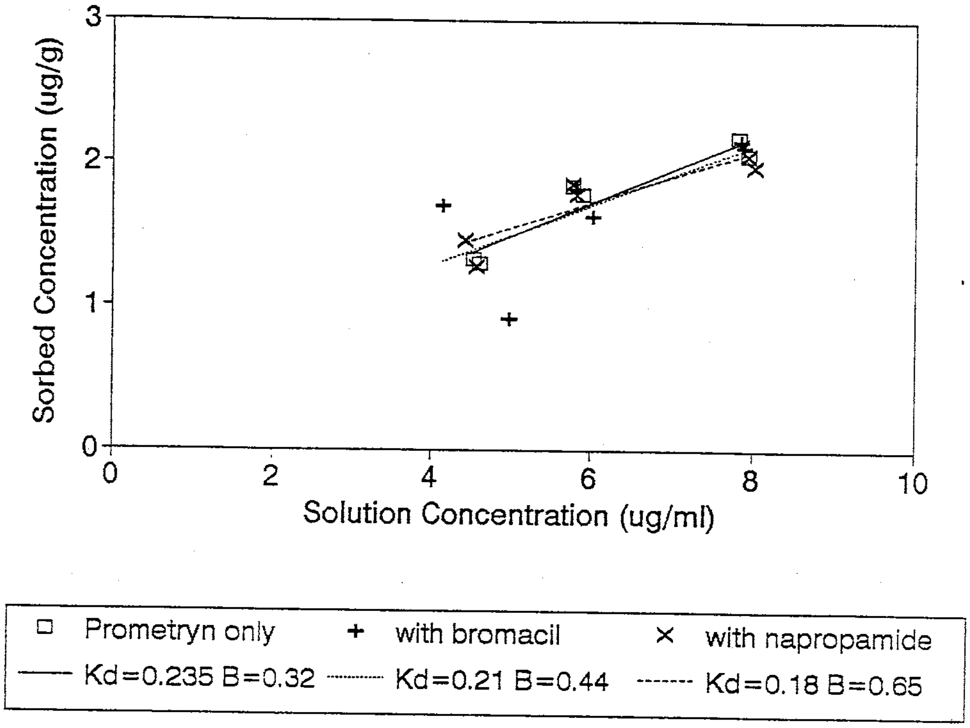


Fig. 4-19 Prometryn Desorption with Initial Conc: 10 μg/mL

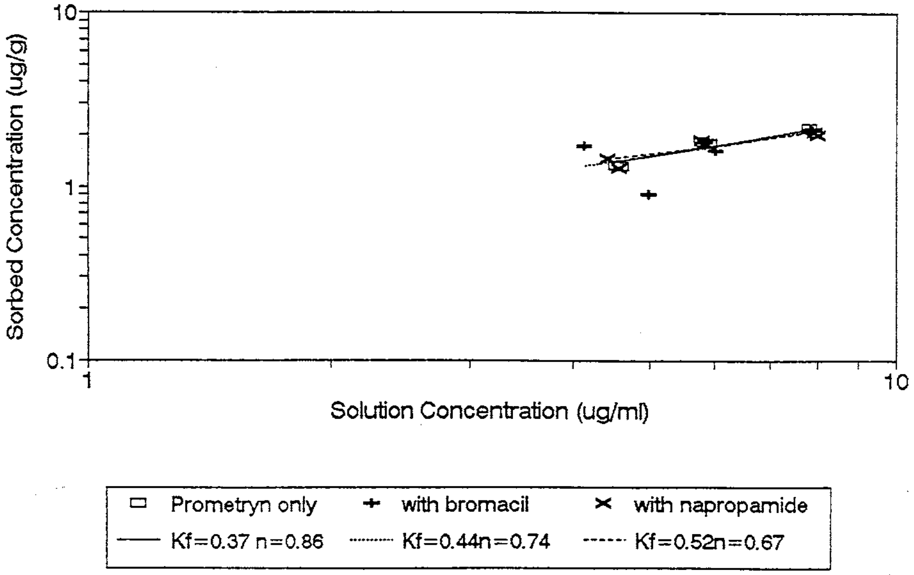


Fig. 4-20 Prometryn Desorption with Initial Conc: 10 μg/mL

Table 4-17. Prometryn Desorption Hysteresis Ratios Affected by Bromacil or Napropamide

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
prometryn conc: 6.66 μg/mL		
prometryn only	1.24	1.27
prometryn with bromacil	1.13	1.19
prometryn with napropamide	1.1	1.16
significant difference	no	no
prometryn conc: 10 μg/mL		
prometryn only	1.27	1.15
prometryn with bromacil	1.3	1.25
prometryn with napropamide	1.53	1.22
significant difference	no	no

4.3.3. Sorption and Desorption of Napropamide Affected by Bromacil or Prometryn

Two sets of napropamide solutions with various concentrations were made, one in 200 μg/mL bromacil solution, another in 10 μg/mL prometryn solution. The napropamide concentrations in both bromacil and prometryn solution were 1, 5, 10, and 15 μg/mL. The experimental results are shown in Appendix-Tables 12, 13 and Figures 4-21, 4-22, 4-23, 4-24, 4-25, 4-26, 4-27 and 4-28.

Sorption. The three different kinds of napropamide sorption data points in Figures 4-21 and 4-22 appear in slightly different positions. The three sets of parameters for the linear equation and the Freundlich equation are calculated and listed on Table 4-18.

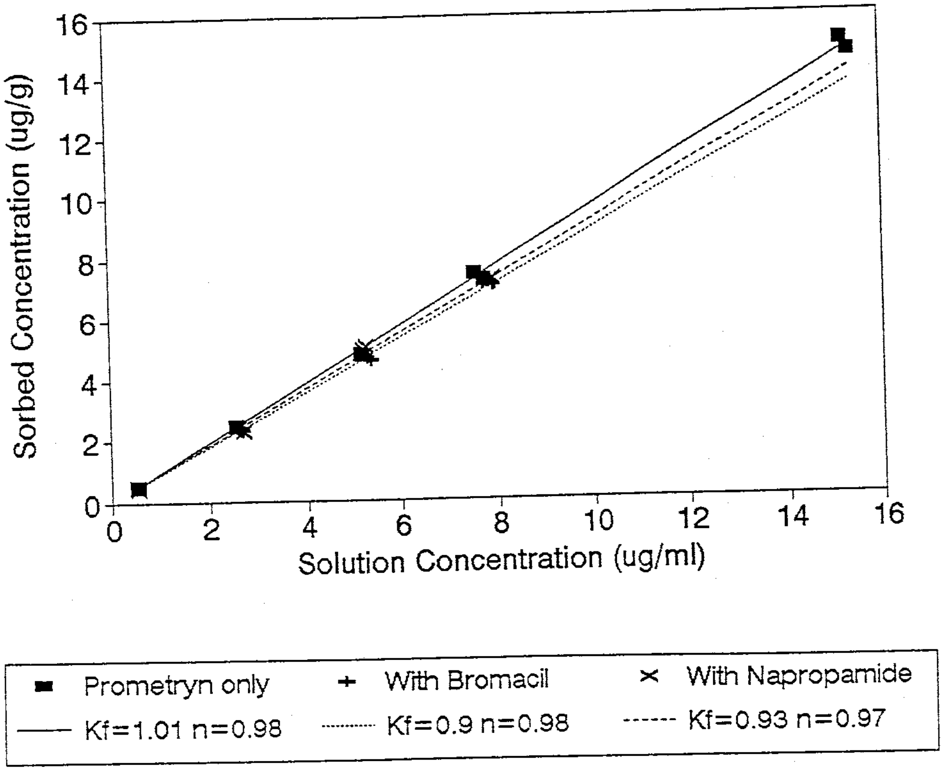


Fig. 4-21 Napropamide Sorption Affected by Bromacil or Prometryn

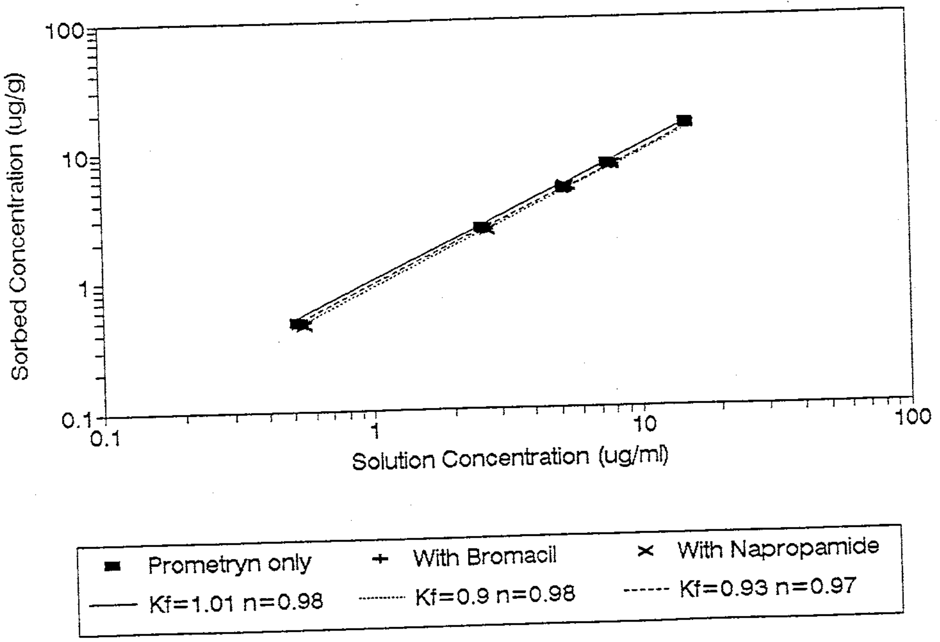


Fig. 4-22 Napropamide Sorption Affected by Bromacil or Prometryn

Table 4-18. Napropamide Sorption Parameters Affected by Bromacil or Prometryn

Parameter	Napropamide only	Napropamide with B	N^* with P	significant difference
K_d	0.97	0.89	0.92	no
R^2	0.999	0.998	0.998	
significant	yes	yes	yes	
K_f	1.01	0.9	0.93	yes
n	0.98	0.98	0.97	no
R^2	0.999	0.999	0.999	
significant	yes	yes	yes	

Desorption. The samples with initial napropamide concentrations of 5, 10, and 15 μg/mL were chosen for the desorption experiments. The three different types of napropamide desorption data (napropamide only, napropamide with bromacil, and napropamide with prometryn) are plotted in Figures 4-23, 4-24, 4-25, 4-26, 4-27 and 4-28. The desorption parameters are calculated and shown in Table 4-19, and the ratios of $K_{d(sorp)}/K_{d(des)}$ and n_{sorp}/n_{des} are shown in Table 4-20.

4.4. Effects of Competition among Three Herbicides on Sorption and Desorption

A set of bromacil, prometryn and napropamide mixed solutions were made in 0.005 M $CaCl_2$ (Table 4-21). The concentrations of the three herbicides in solution were analyzed in HPLC simultaneously. The experimental methods and procedures were discussed in chapter 3.

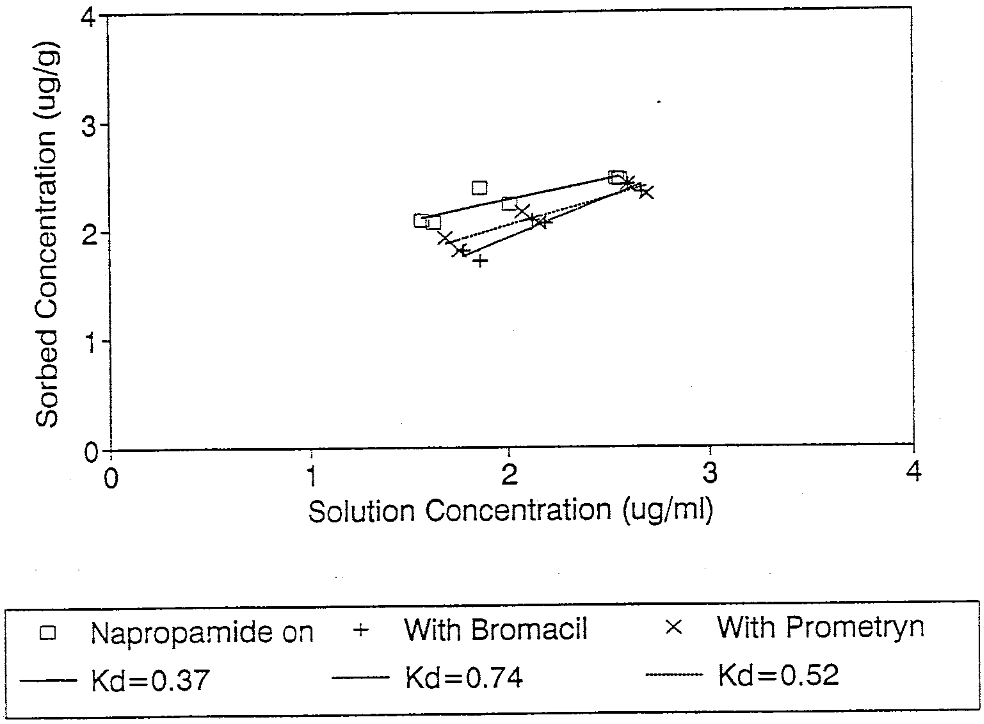


Fig. 4-23 Napropamide Desorption with Initial Conc: 5 $\mu g/mL$

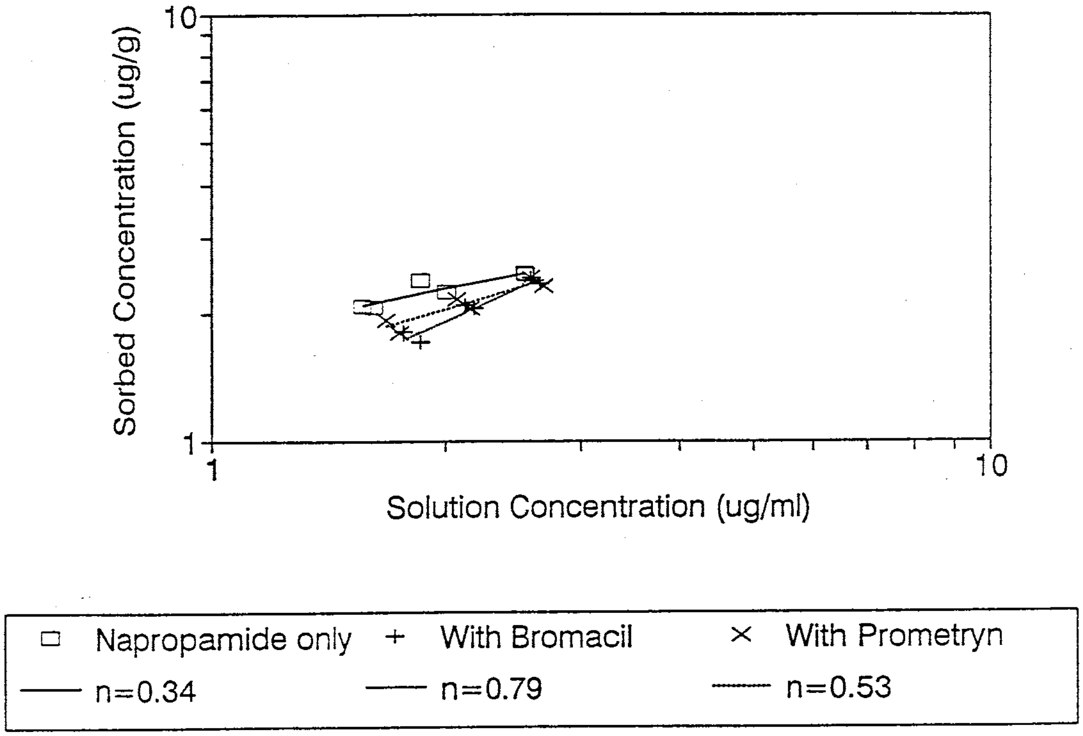


Fig. 4-24 Napropamide Desorption with Initial Conc: 5 $\mu g/mL$

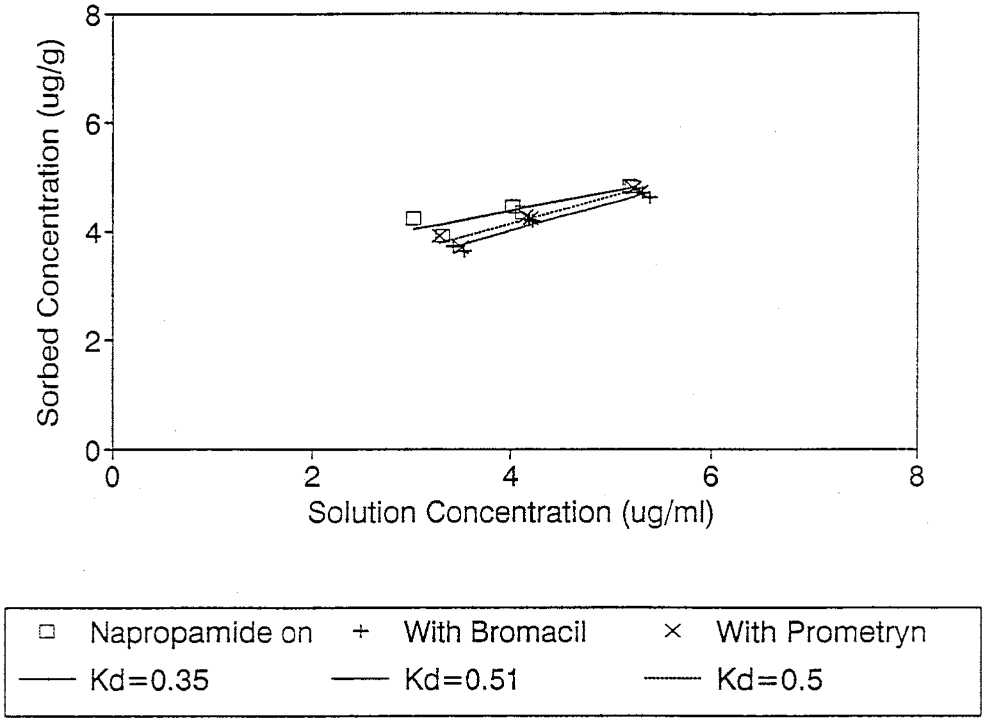


Fig. 4-25 Napropamide Desorption with Initial Conc: 10 $\mu g/mL$

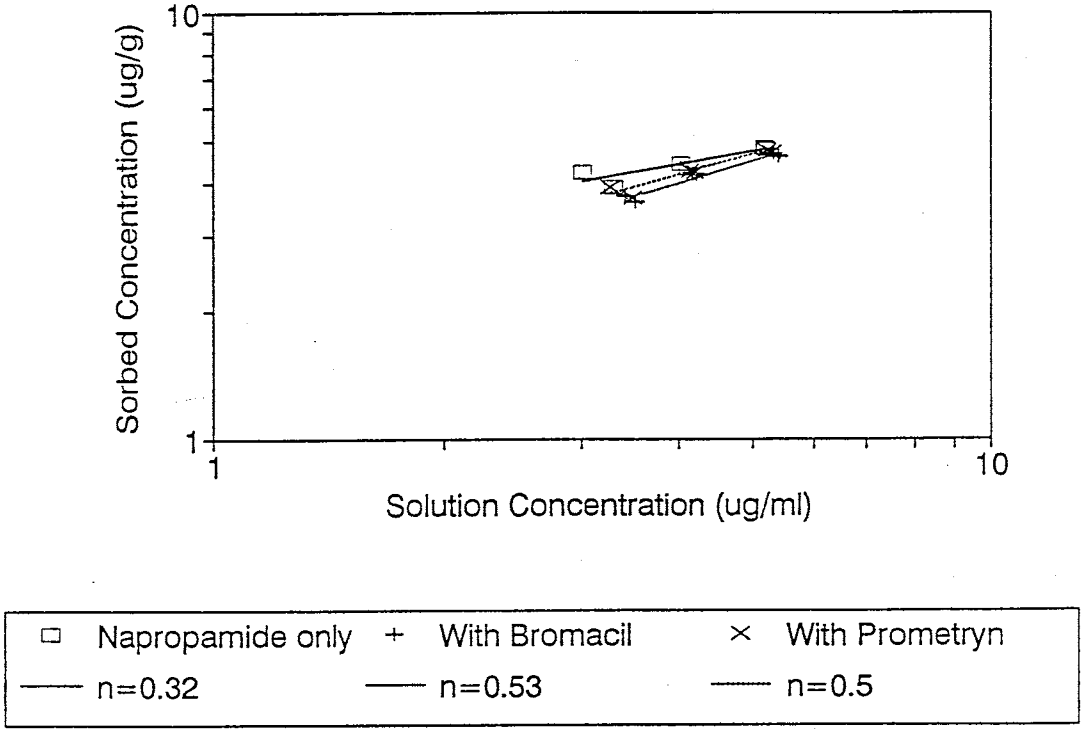


Fig. 4-26 Napropamide Desorption with Initial Conc: 10 $\mu g/mL$

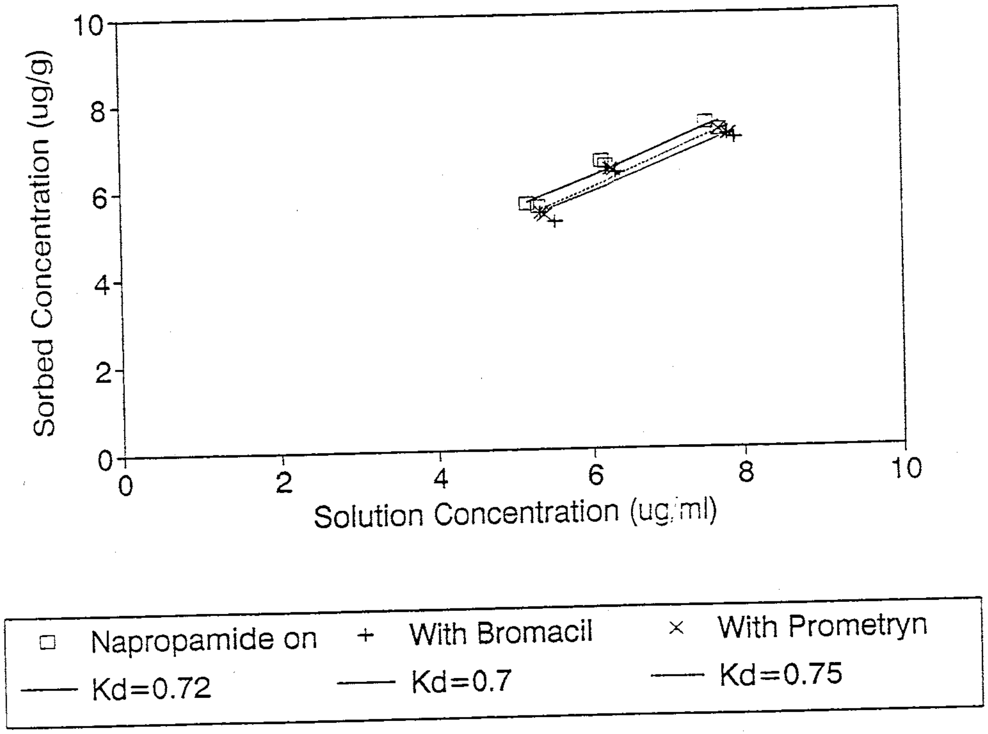


Fig. 4-27 Napropamide Desorption with Initial Conc: 15 μg/mL

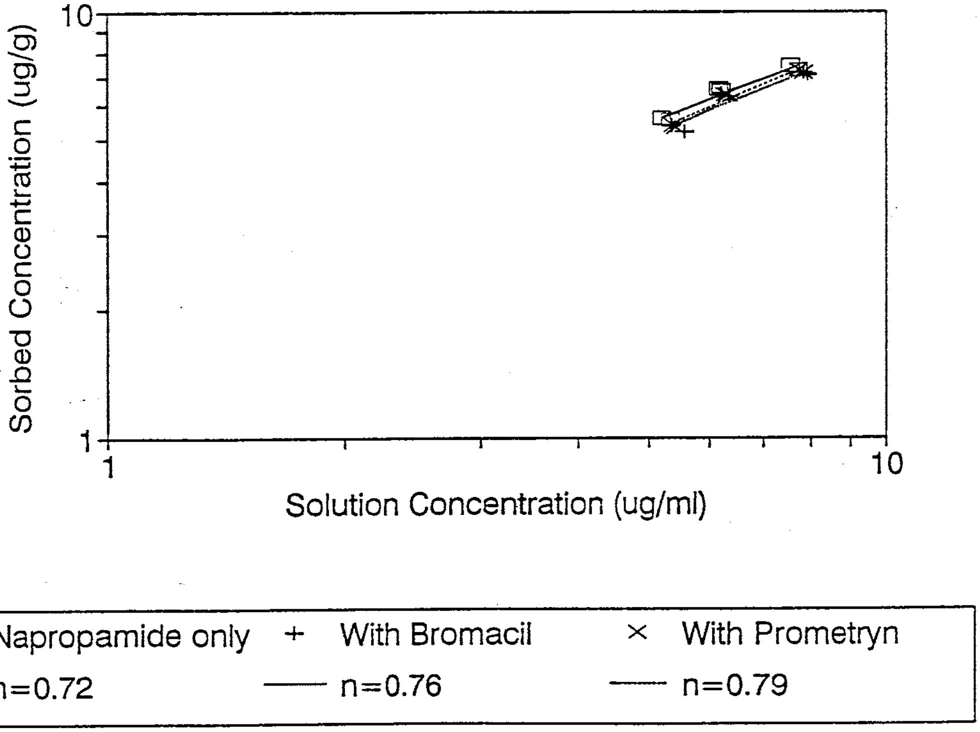


Fig. 4-28 Napropamide Desorption with Initial Conc: 15 μg/mL

Table 4-19. Parameters for Napropamide Desorption Affected by Bromacil or Prometryn

parameter	Kd	b	R^2	significance	logKf	n	R2	significance
5 μg/mL								
N* only	0.37	1.7	0.80	no	0.31	0.34	0.81	no
N with B	0.74	0.76	0.93	yes	0.08	0.79	0.92	yes
N with P	0.52	1.38	0.86	no	0.21	0.53	0.86	no
significant difference	yes	yes			yes	yes		
10 μg/mL								
N only	0.35	2.97	0.83	no	0.45	0.32	0.79	no
N with B	0.51	1.98	0.95	yes	0.28	0.53	0.96	yes
N with P	0.5	3.1	0.93	yes	0.32	0.49	0.92	yes
significant difference	yes	yes			yes	yes		
15 μg/mL								
N only	0.72	1.9	0.95	yes	0.23	0.72	0.95	yes
N with B	0.77	1.58	0.96	yes	0.21	0.76	0.95	yes
N with P	0.75	1.47	0.95	yes	0.16	0.79	0.96	yes
significant difference	no	yes			no	no		

Table 4-20. Napropamide Desorption Hysteresis Ratios Affected by Bromacil or Prometryn

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
napropamide conc: 5 μg/mL		
napropamide only	2.62	2.88
napropamide with bromacil	1.2	1.24
napropamide with prometryn	1.77	1.83
significant difference	yes	yes
napropamide conc: 10 μg/mL		
napropamide only	2.77	3.06
napropamide with bromacil	1.75	1.85
napropamide with prometryn	1.8	1.94
significant difference	yes	yes
napropamide conc: 15 μg/mL		
napropamide only	1.35	1.36
napropamide with bromacil	1.27	1.29
napropamide with prometryn	1.23	1.23
significant difference	no	no

Table 4-21. Concentrations of Different Herbicides in Mixed Solutions

Solution	Bromacil Conc. in Solution (μg/mL)	Prometryn Conc. in solution (μg/mL)	Napropamide Conc. in solution (μg/mL)
A	400	20	30
B	133	6.66	10
C	66.6	3.33	5

4.4.1. Sorption and Desorption of Bromacil Affected by Prometryn and Napropamide

The data of sorption and desorption of bromacil with or without prometryn and napropamide are shown in Appendix-Tables 13, 14 and Figures 4-29, 4-30, 4-31, 4-32, 4-33, 4-34, 4-35 and 4-36. Since all the bromacil concentrations in mixed solutions were greater than 40 μg/mL (compare with Figures 4-5 and 4-6), the sorption data points in figures 4-29 and 4-30 are only the those deviate from the straight line. The linear equation is not suitable for data analysis. Therefore, the equation 3-3 and the Freundlich equation (2-4) were used to analyze the data. The calculated parameters for sorption and desorption are presented in Tables 4-22 and 4-23, respectively. The ratios describing bromacil desorption hysteresis are shown in Table 4-24.

Table 4-22. Bromacil Sorption Parameters Affected by Prometryn and Napropamide

parameter	bromacil only	bromacil with P+N	significant difference
Kd	0.038	0.032	yes
b	2.51	2.18	yes
R^2	0.997	0.996	
significant	yes	yes	
Kf	0.125	0.095	yes
n	0.9	0.91	no
R^2	0.998	0.996	
significant	yes	yes	

(Note: P+N: Prometryn and Napropamide)

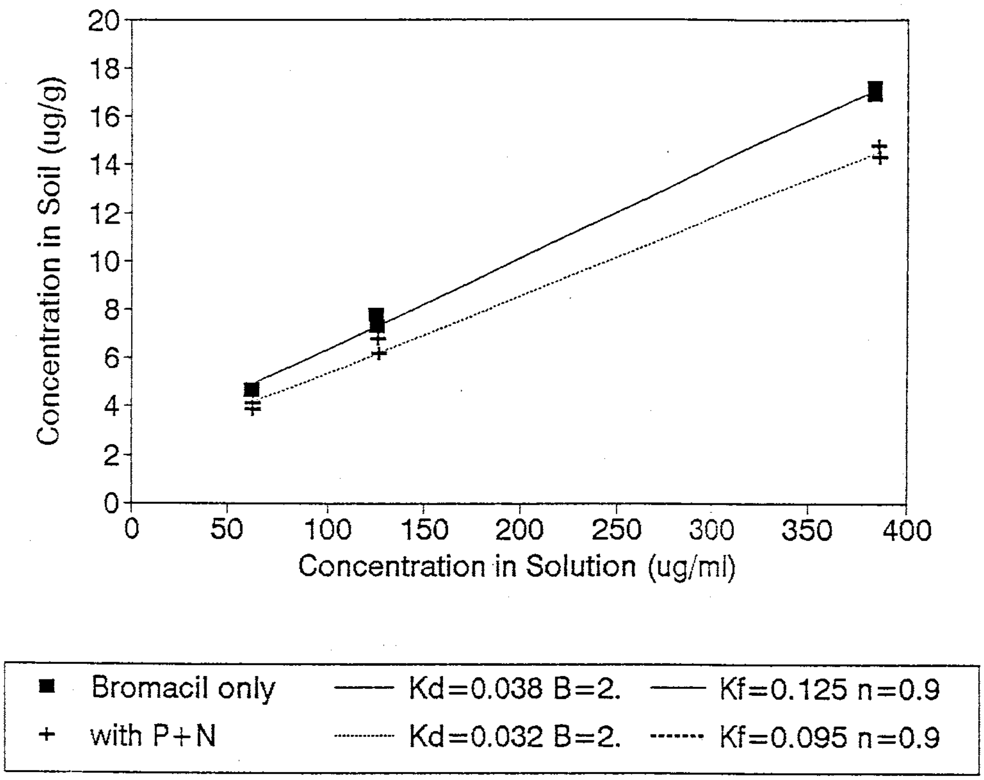


Fig. 4-29 Bromacil Sorption Affected by Prometryn and Napropamide

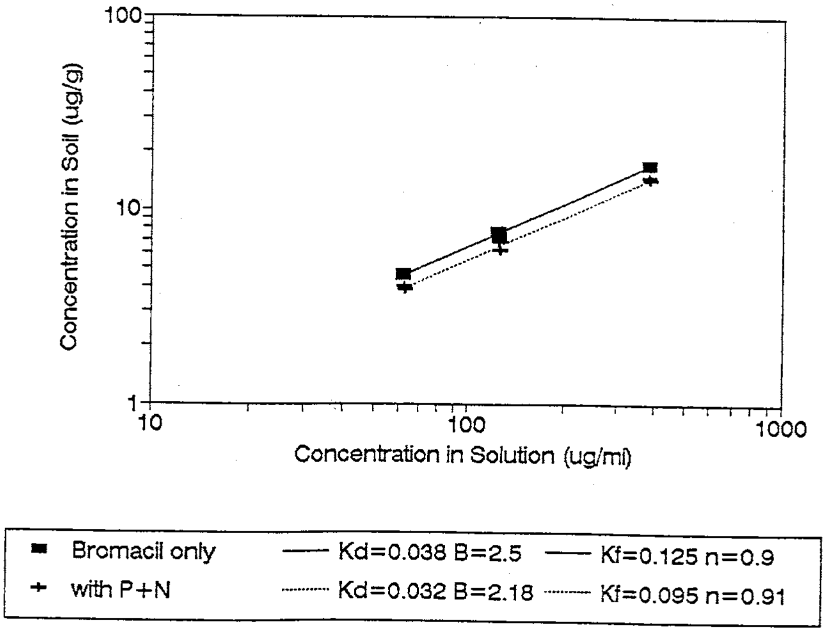


Fig. 4-30 Bromacil Sorption Affected by Prometryn and Napropamide

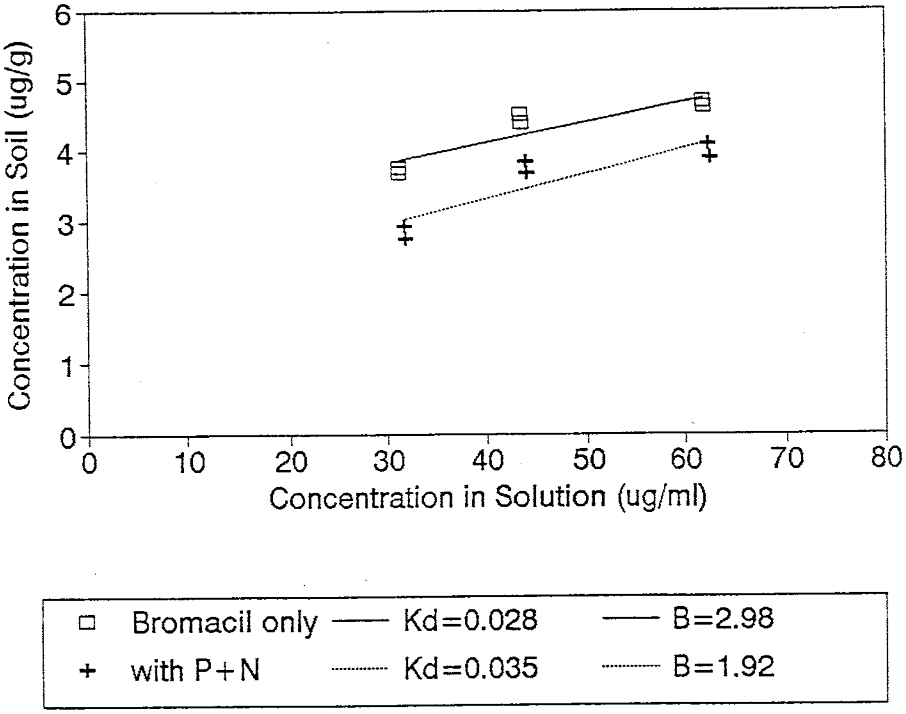


Fig. 4-31 Bromacil Desorption with Initial Conc: 66.6 μg/mL

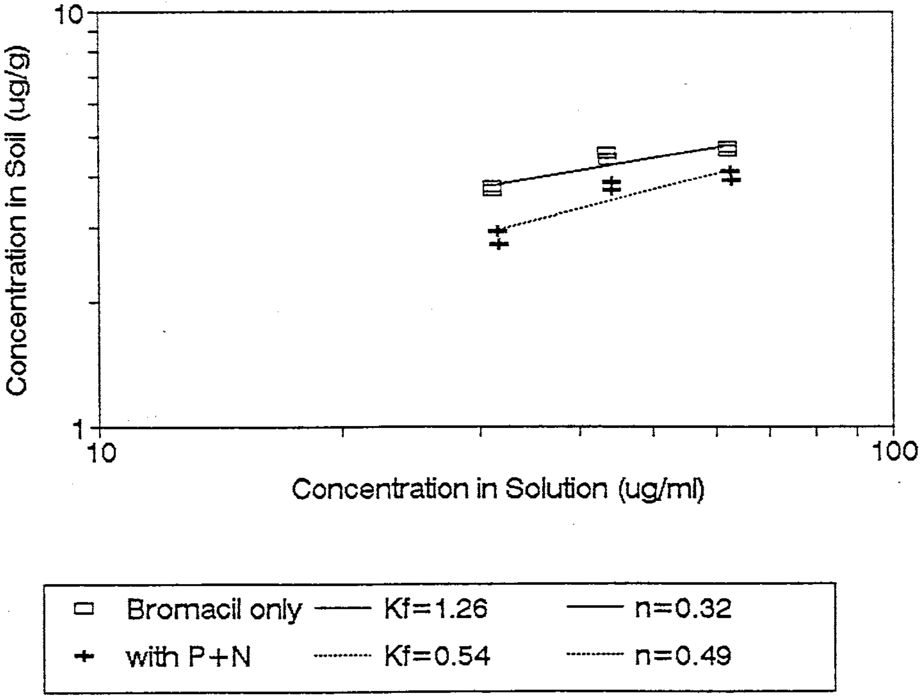


Fig. 4-32 Bromacil Desorption with Initial Conc: 66.6 μg/mL

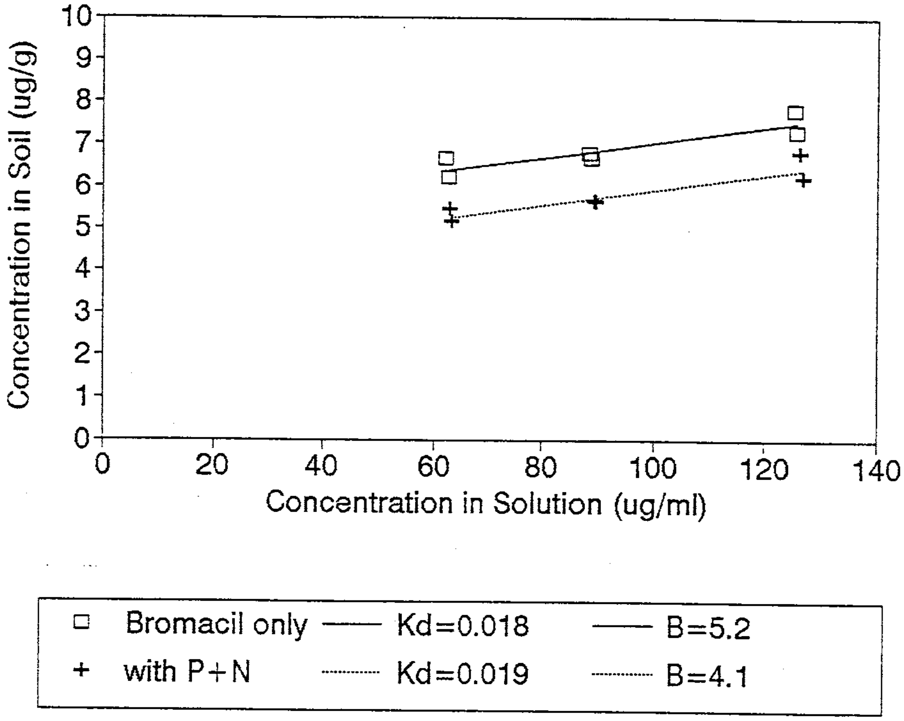


Fig. 4-33 Bromacil Desorption with Initial Conc: 133 μg/mL

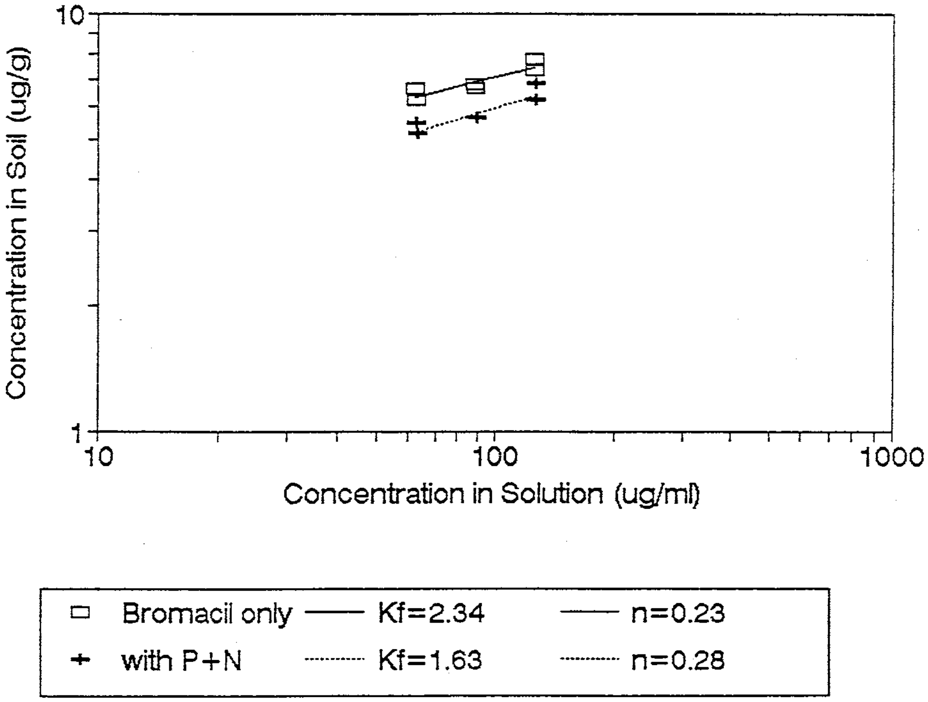


Fig. 4-34 Bromacil Desorption with Initial Conc: 133 μg/mL

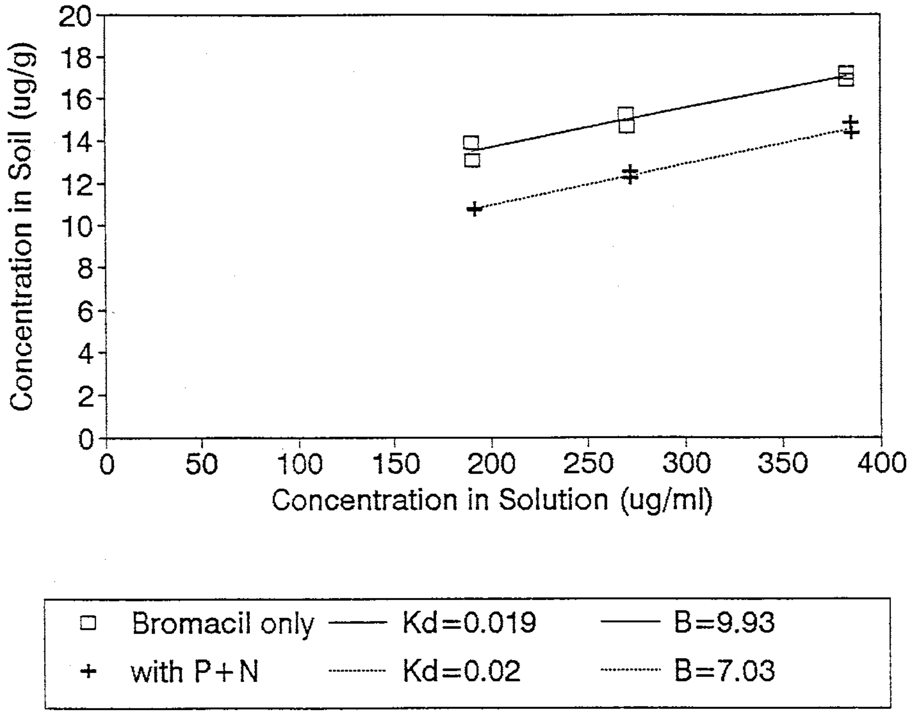


Fig. 4-35 Bromacil Desorption with Initial Conc: 400 μg/mL

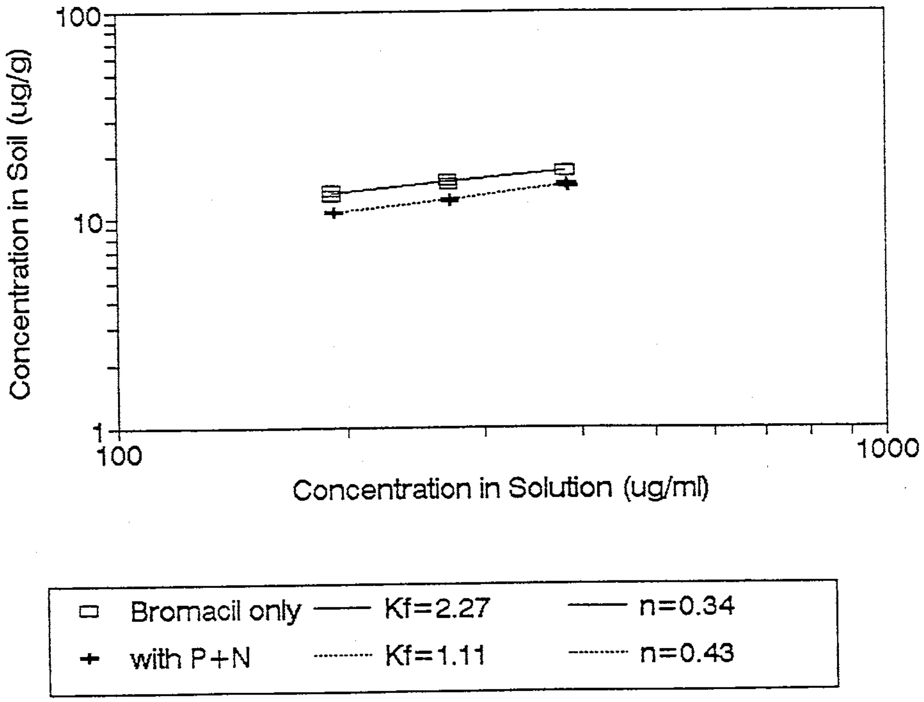


Fig. 4-36 Bromacil Desorption with Initial Conc: 400 μg/mL

Table 4-23. Bromacil Desorption Affected by Prometryn and Napropamide

parameter	bromacil only	bromacil with N+P	significant difference
66.6 μg/mL			
K_d	0.028	0.035	yes
b	2.98	1.92	yes
R^2	0.81	0.78	
significance	no	no	
Log K_f	0.1	-0.27	yes
n	0.32	0.49	yes
R^2	0.86	0.83	
significance	no	no	
133 μg/mL			
K_d	0.018	0.019	no
b	5.22	4.09	yes
R^2	0.82	0.84	
significance	no	no	
Log K_f	0.39	0.21	yes
n	0.23	0.28	yes
R^2	0.79	0.83	
significance	no	no	
400 μg/mL			
K_d	0.019	0.02	no
b	9.93	7.03	yes
R^2	0.95	0.98	
significance	yes	yes	
Log K_f	0.36	0.043	yes
n	0.34	0.43	yes
R^2	0.95	0.99	
significance	yes	yes	

Note: P+N: prometryn and napropamide.

Table 4-24. Ratios for Bromacil Desorption Hysteresis Affected by Prometryn and Napropamide

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
bromacil conc: 66.6 μg/mL		
bromacil only	1.36	2.84
bromacil with P+N	0.92	1.84
significant difference	yes	yes
bromacil conc: 133 μg/mL		
bromacil only	2.11	3.9
bromacil with P+N	1.68	3.25
significant difference	yes	yes
bromacil conc: 400 μg/mL		
bromacil only	2	2.65
bromacil with P+N	1.6	2.17
significant difference	yes	yes

4.4.2. Sorption and Desorption of Prometryn Affected by Bromacil and Napropamide

The prometryn sorption and desorption data with bromacil and napropamide are shown in Appendix-Tables 15 and 16 and plotted in Figures 4-37, 4-38, 4-39, 4-40, 4-41, 4-42, 4-43 and 4-44. The sorption and desorption parameters were calculated and shown in Tables 4-25 and 4-26, respectively. The ratios describing prometryn desorption hysteresis are shown in Table 4-27.

Table 4-25. Prometryn Sorption Parameters Affected by Bromacil and Napropamide

parameter	prometryn only	prometryn with (B+N)	significant difference
K_d	0.276	0.281	no
R^2	0.99	0.97	
significance	yes	yes	
Log K_f	-0.57	-0.56	no
n	1.009	1.007	no
R^2	0.98	0.96	
significance	yes	yes	

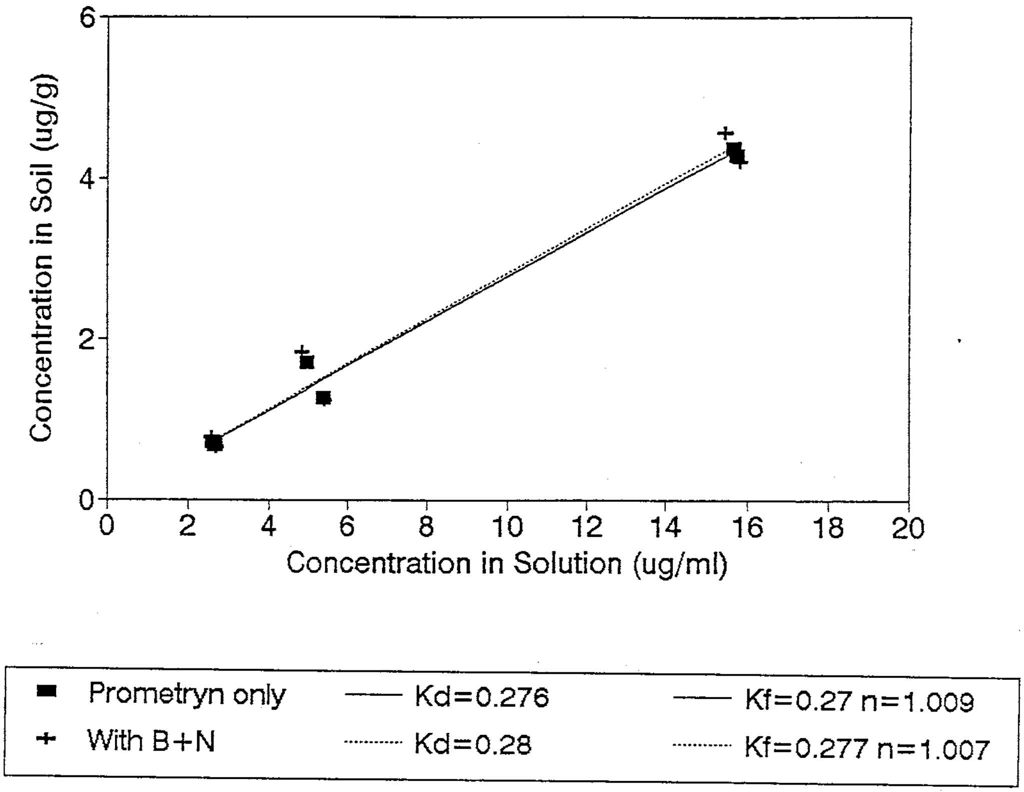


Fig. 4-37 Prometryn Sorption Affected by Bromacil and Napropamide

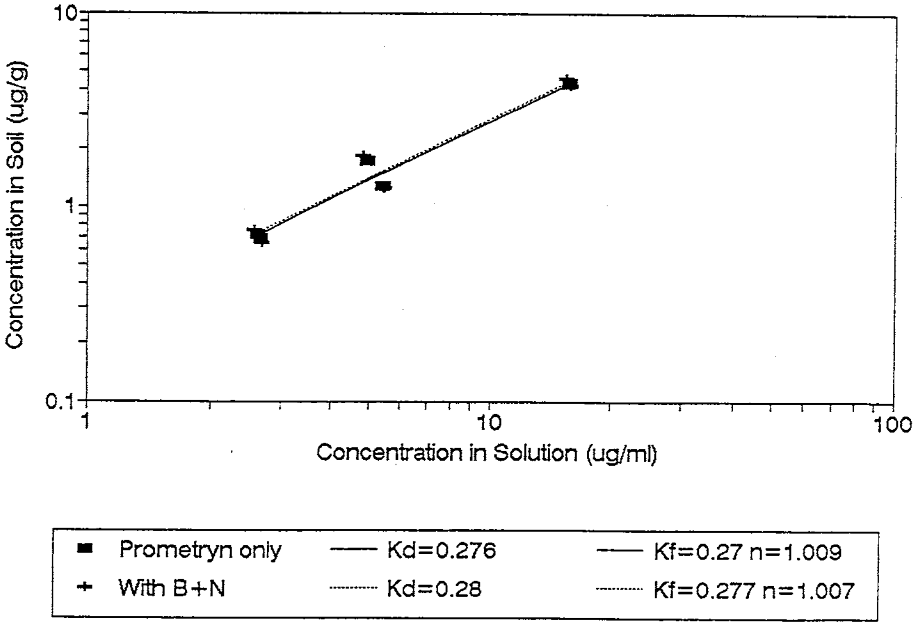


Fig. 4-38 Prometryn Sorption Affected by Bromacil and Napropamide

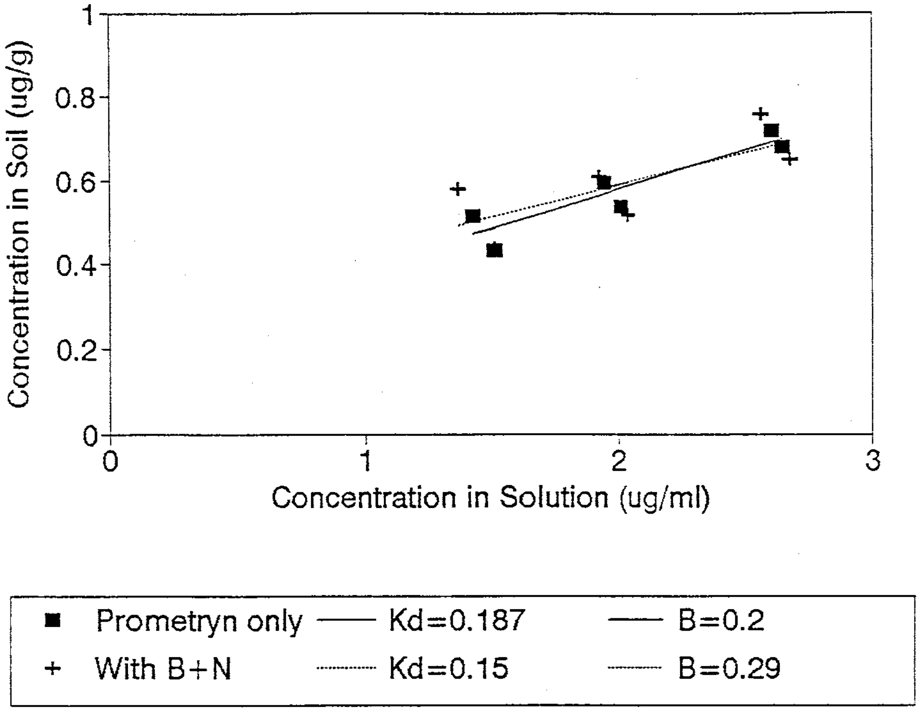


Fig. 4-39 Prometryn Desorption with Initial Conc: 3.33 μg/mL

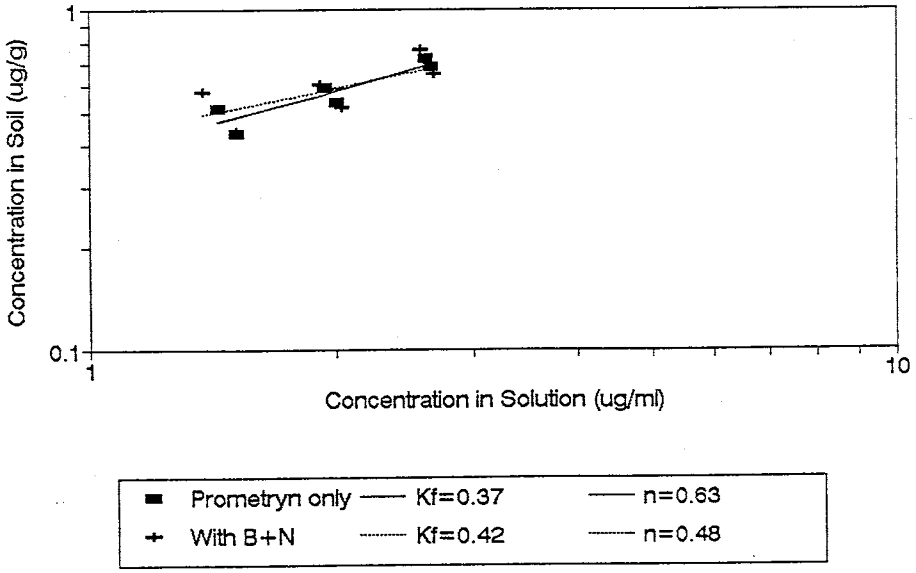


Fig. 4-40 Prometryn Desorption with Initial Conc: 3.33 μg/mL

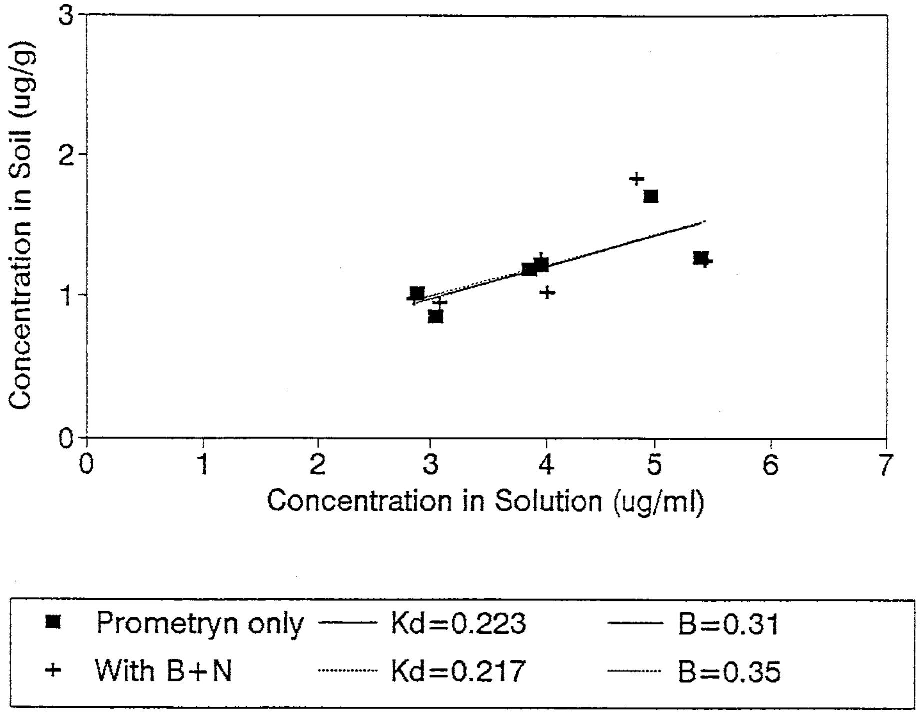


Fig. 4-41 Prometryn Desorption with Initial Conc: 6.66 μg/mL

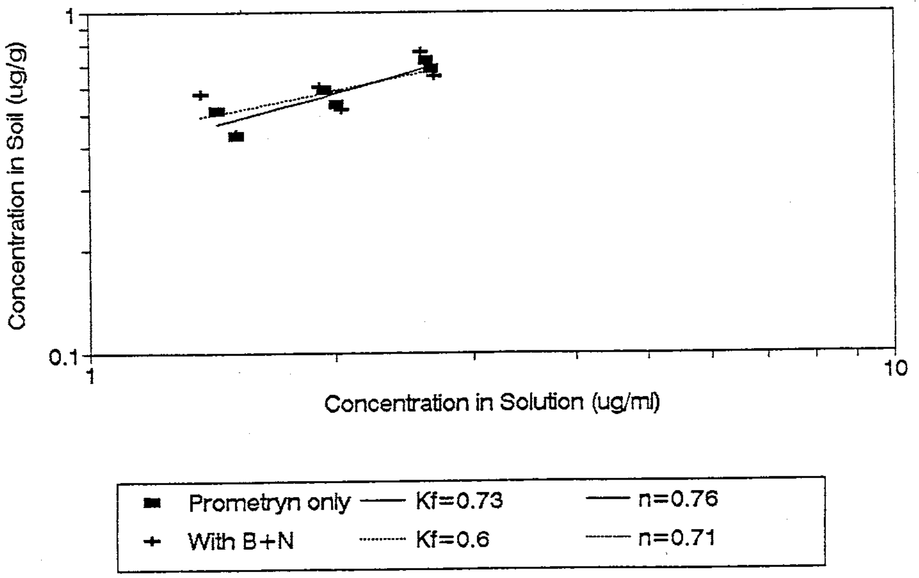


Fig. 4-42 Prometryn Desorption with Initial Conc: 6.66 μg/mL

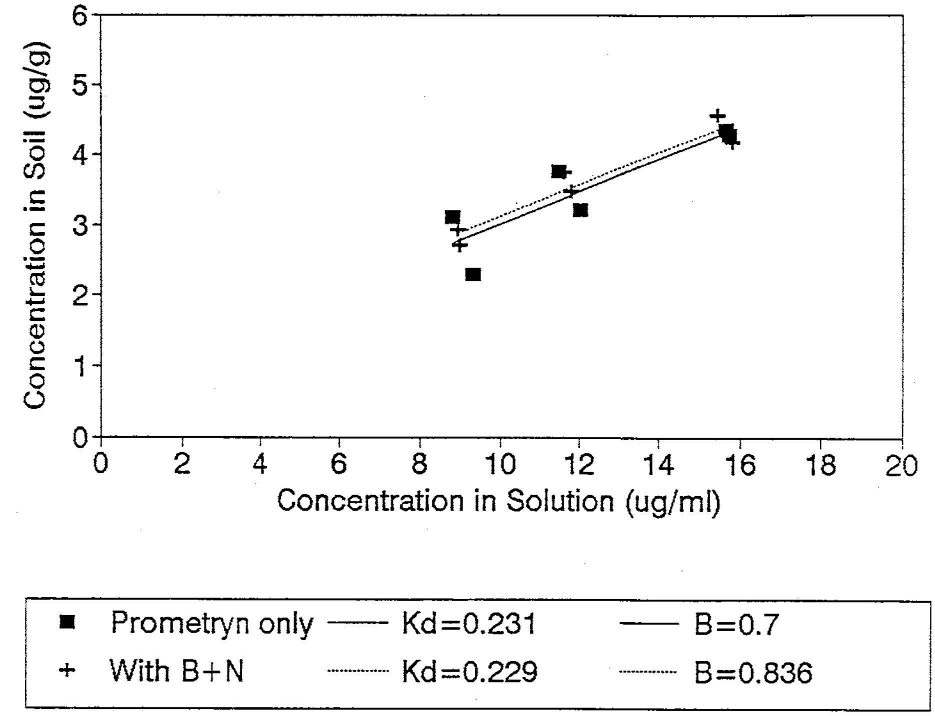


Fig. 4-43 Bromacil Desorption with Initial Conc: 20 μg/mL

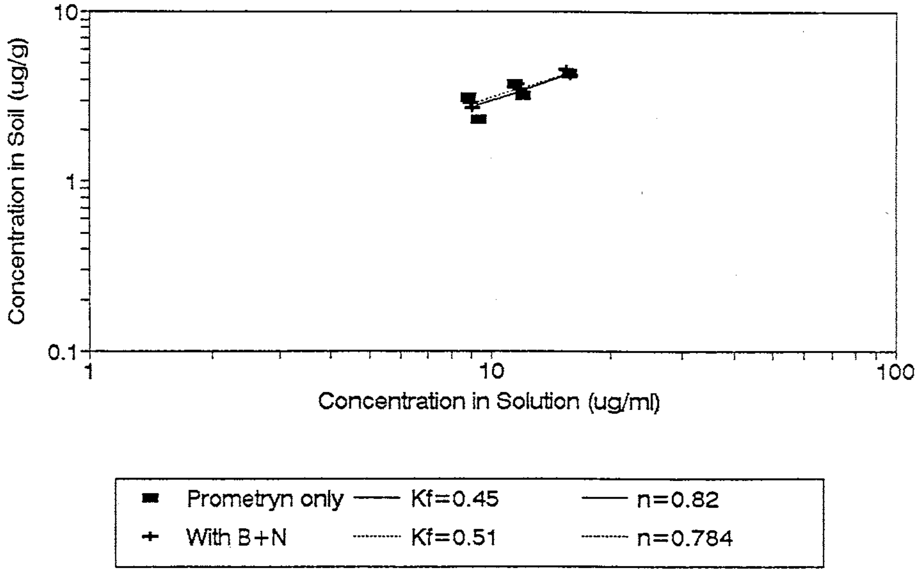


Fig. 4-44 Bromacil Desorption with Initial Conc: 20 μg/mL

Table 4-26. Prometryn Desorption Affected by Bromacil and Napropamide

parameter	prometryn only	prometryn with B+N	significant difference
3.33 $\mu g/mL$			
Kd	0.187	0.15	yes
b	0.2	0.29	yes
R^2	0.86	0.48	
significance	no	no	
Log K_f	-0.42	-0.37	no
n	0.63	0.48	yes
R^2	0.83	0.48	
significance	no	no	
6.66 $\mu g/mL$			
K_d	0.233	0.217	no
b	0.31	0.35	no
R^2	0.6	0.42	
significance	no	no	
Log K_f	-0.37	-0.34	no
n	0.76	0.71	no
R^2	0.66	0.5	
significance	no	no	
20 $\mu g/mL$			
K_d	0.231	0.229	no
b	0.7	0.836	yes
R^2	0.77	0.92	
significance	no	yes	
Log K_f	-0.35	-0.29	yes
n	0.82	0.78	no
R^2	0.71	0.93	
significance	no	yes	

Note: B+N: bromacil and napropamide

Table 4-27. The Ratios Describing Prometryn Desorption Hysteresis

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
prometryn conc: 3.33 μg/mL		
prometryn only	1.48	1.6
prometryn with B+N	1.8	2.1
significant difference	yes	yes
prometryn conc: 6.66 μg/mL		
prometryn only	1.24	1.33
prometryn with B+N	1.29	1.42
significant difference	no	no
prometryn conc: 20 μg/mL		
prometryn only	1.2	1.23
prometryn with B+N	1.22	1.28
significant difference	no	no

4.4.3. Sorption and Desorption of Napropamide Affected by Bromacil and Prometryn

The two sets of napropamide sorption and desorption data (one is napropamide alone, another is with bromacil and prometryn) are shown in Appendix-Tables 17 and 18, respectively. The data were plotted in Figures 4-45, 4-46, 4-47, 4-48, 4-49, 4-50, 4-51 and 4-52. The sorption and desorption parameters are calculated and shown in Tables 4-28 and 4-29. The ratios describing napropamide desorption hysteresis are shown in Table 4-30.

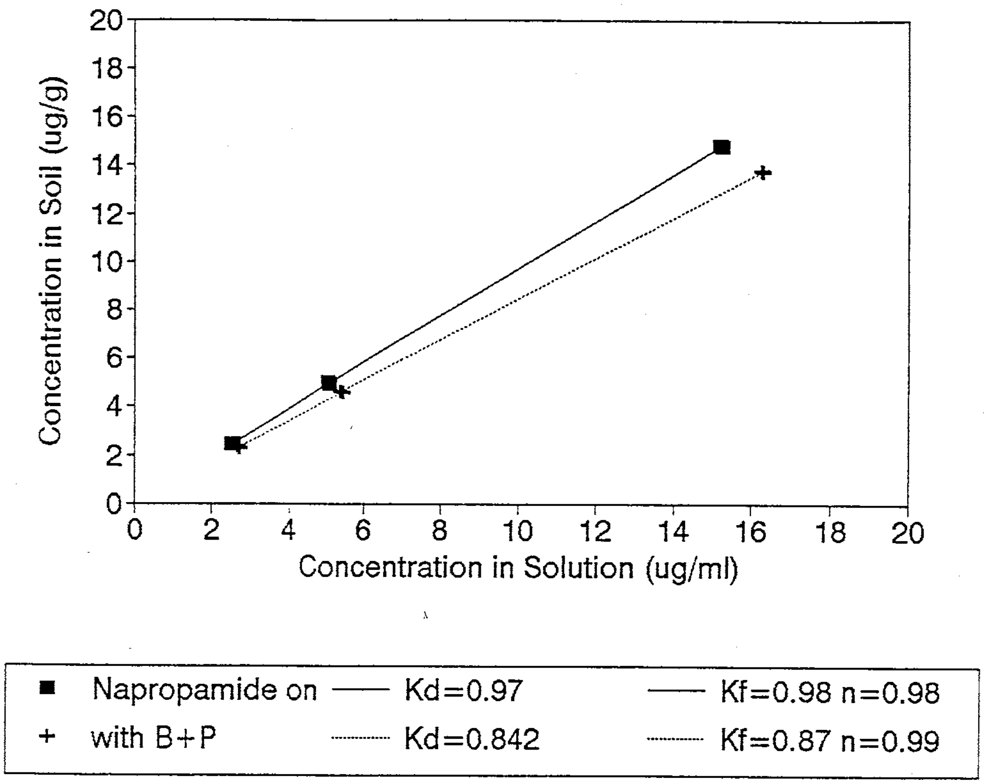


Fig. 4-45 Napropamide Sorption Affected by Bromacil and Prometryn

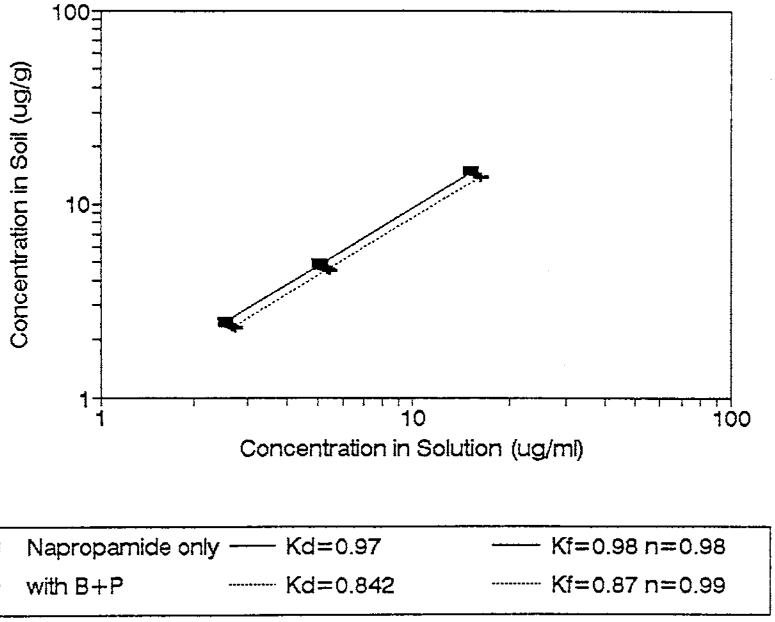


Fig. 4-46 Napropamide Sorption Affected by Bromacil and Napropamide

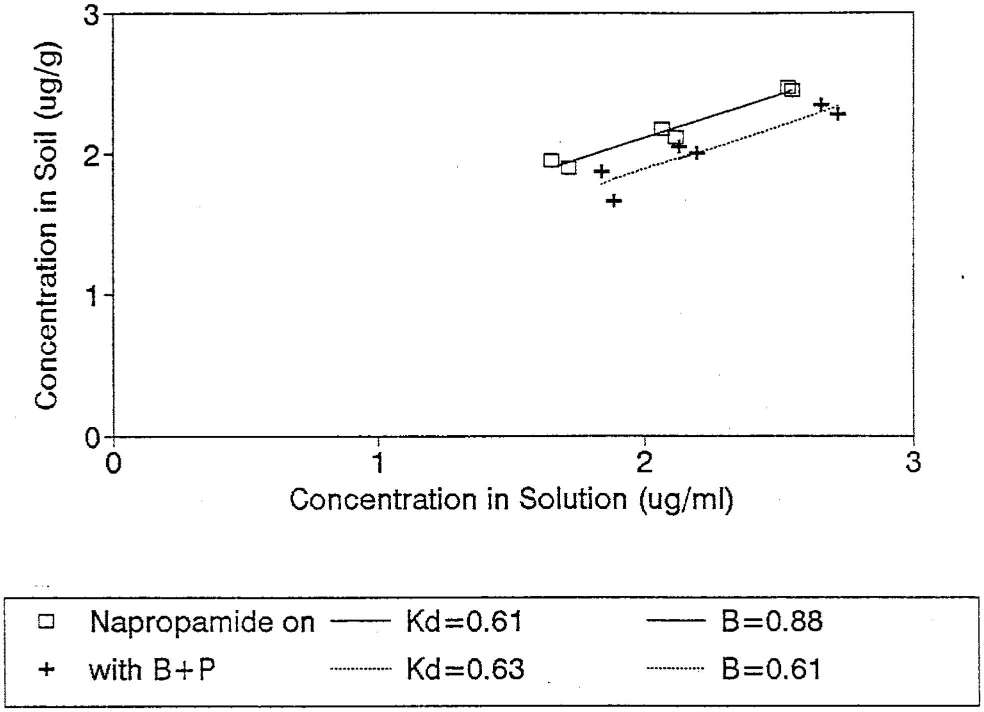


Fig. 4-47 Napropamide Desorption with Initial Conc: 5 μg/mL

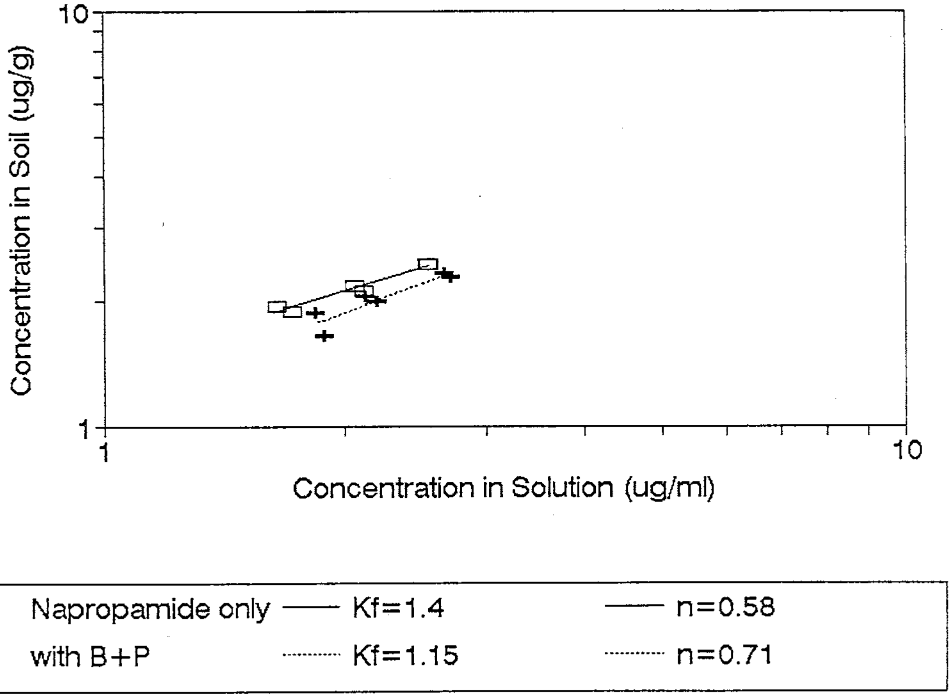


Fig. 4-48 Napropamide Desorption with Initial Conc: 5 μg/mL

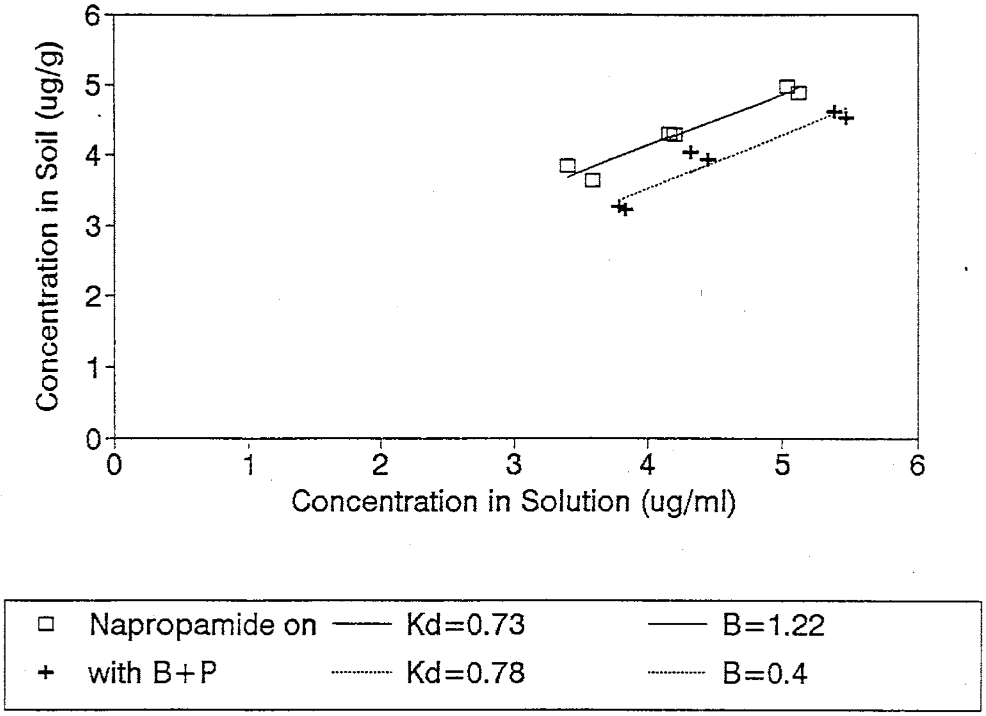


Fig. 4-49 Napropamide Desorption with Initial Conc: 10 μg/mL

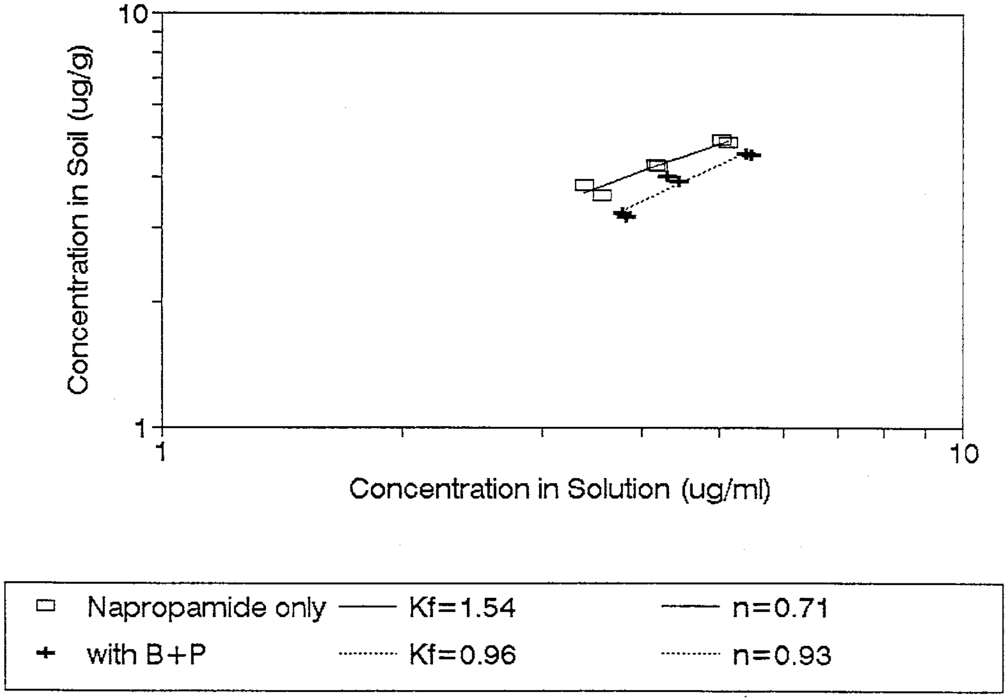


Fig. 4-50 Napropamide Desorption with Initial Conc: 10 μg/mL

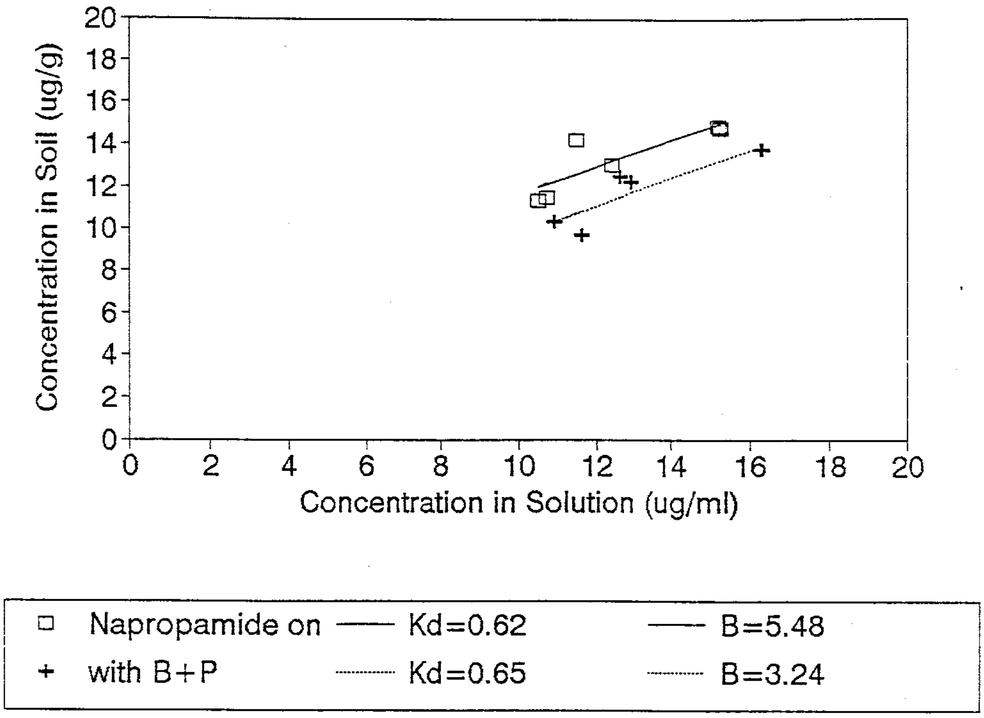


Fig. 4-51 Napropamide Desorption with Initial Conc: 30 μg/mL

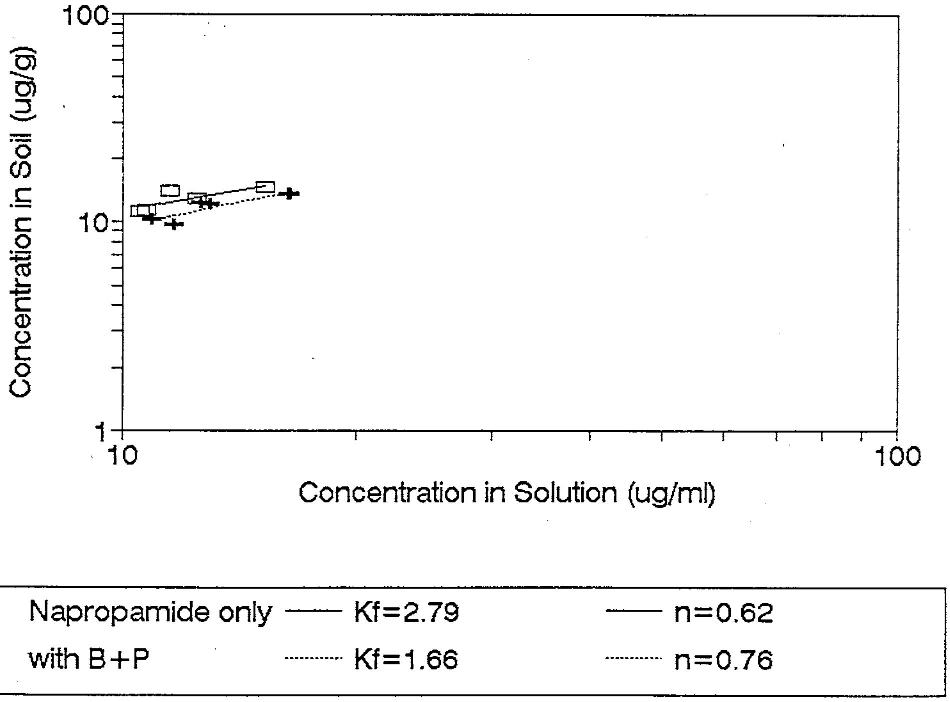


Fig. 4-52 Bromacil Desorption with Initial Conc: 30 μg/mL

Table 4-28. Napropamide Sorption Affected by Bromacil and Prometryn

parameter	napropamide only	napropamide with B+P	significant difference
K_d	0.97	0.842	yes
R^2	0.9999	0.9998	
significance	yes	yes	
K_f	-0.015	-0.06	yes
n	1.003	0.99	no
R^2	0.9998	0.9994	
significance	yes	yes	

Table 4-29. Napropamide Desorption Affected by Bromacil and Prometryn

parameter	napropamide only	napropamide with B+N	significant difference
5 μg/mL			
K_d	0.53	0.73	yes
b	1.13	0.38	yes
R^2	0.7	0.92	
significance	no	yes	
Log K_f	0.19	0.009	yes
n	0.51	0.84	yes
R^2	0.71	0.92	
significance	no	yes	
10 μg/mL			
K_d	0.73	0.78	no
b	1.23	0.4	yes
R^2	0.93	0.93	
significance	yes	yes	
Log K_f	0.19	-0.02	yes
n	0.71	0.93	yes
R^2	0.94	0.92	
significance	yes	yes	
30 μg/mL			
K_d	0.62	0.65	no
b	5.48	3.24	yes
R^2	0.72	0.65	
significance	no	no	
Log K_f	0.45	0.22	yes
n	0.62	0.76	
R^2	0.72	0.81	
significance	yes	yes	

Note: B+P: bromacil and prometryn

Table 4-30. Ratios Describing Napropamide Desorption Hysteresis

ratio	$K_{d(sorp)}/K_{d(des)}$	n_{sorp}/n_{des}
napropamide conc: 5 μg/mL		
napropamide only	1.59	1.69
napropamide with B+P	1.34	1.39
significant difference	yes	yes
napropamide conc: 10 μg/mL		
napropamide only	1.33	1.38
napropamide with B+P	1.24	1.06
significant difference	no	yes
napropamide conc: 20 μg/mL		
napropamide only	1.56	1.58
napropamide with B+P	1.3	1.3
significant difference	yes	yes

Note: B+P: bromacil and prometryn

CHAPTER 5

DISCUSSION

The major objectives of the study were to determine the sorption linearity and singularity of the three pesticides, and to check for competition effects between and among them.

5.1 Linearity

As the results showed in chapter 4 (Fig. 4-7 and Fig. 4-9) napropamide and prometryn exhibited linear sorption. The linear equation and the Freundlich equation both fit the data (Table 4-6 and Table 4-9). Bromacil showed non-linear sorption (Fig. 4-5), and the Freundlich equation fit the experimental data very well (Table 4-3).

5.1.1. Reasons for linear and nonlinear sorption

According to Worthing (1991), bromacil is the most polar of the three herbicides. The different sorption behavior of bromacil, prometryn and napropamide can be explained by the partition theory of nonpolar solute sorption (Chiou, 1989). Since prometryn and napropamide are less polar than bromacil, their sorption mechanism is more likely partitioning and independent of the equilibrium solution concentration. In the bromacil sorption process, sorption mechanisms other than partitioning are operating, and are dependent on the equilibrium solution concentration. Therefore, the sorption isotherms of prometryn and napropamide are expected to be linear compared to the bromacil sorption isotherm.

5.1.2. Effects of nonlinear sorption on solute transport

The conventional equation used to describe the advective-dispersive one-dimensional transport of a sorbing solute is given by

$$\frac{\partial C}{\partial t}+\frac{\rho}{\theta}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial X^2}-V\frac{\partial C}{\partial X} \qquad (5\text{-}1)$$

where, in addition to previously defined variables,

D: hydrodynamic dispersion coefficient (cm^2/hr)

t: time (hr)

X: distance (cm)

ρ: soil bulk density (g/cm^3)

Θ: volumetric water content (cm^3/cm^3)

Determining the parameters is often the critical step in model application. The typical approach has been to assume that conditions of local equilibrium, isotherm singularity, and isotherm linearity exist. This assumption greatly simplifies the resultant expression for dS/dt.

Sorption-isotherm linearity is a major assumption often employed in the advective-dispersive solute transport model. The linear equation of sorption is given in chapter 2 (equation 2-1). Differentiating the equation with respect to time yields

$$\frac{\partial S}{\partial t}=K_d\frac{\partial C}{\partial t} \qquad (5\text{-}2)$$

which can be substituted into Equation 5-1 to yield

$$R\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial X^2}-V\frac{\partial C}{\partial X} \qquad (5-3)$$

where, in addition to previously defined variables,

$$R=(1+\rho\frac{K_p}{\theta}) \qquad (5-4)$$

R: retardation factor (-)

(5-3) is the 1-D ADE model for linear, reversible sorption.

Nonlinear sorption isotherms are typically represented with the Freudlich equation (equation 2-4). The time-differentiated equation is

$$\frac{\partial S}{\partial t}=K_f n C^{n-1} \qquad (5-5)$$

The transport equation is then equivalent to Equation 5-2 except for the definition of R, which is now

$$R=1+\frac{\rho}{\theta}K_f n C^{n-1} \qquad (5-6)$$

The value of n can have a significant impact on solute transport. For the linear case (i.e., n=1), K_d is independent of C, and R, therefore, remains constant. For the nonlinear-isotherm cases, however, K_d is dependent upon C and R, and therefore no longer has a constant value. Generally, for sorption of organic compounds where n is less than 1, K_d decreases as C increases and R, therefore, decreases. The non-constant R could effect contaminant transport. At higher contaminant concentrations, retardation will be lower, and the potential for contaminant spreading will be greater than expected.

5.2. Sorption Hysteresis

All three herbicides exhibited marked hysteresis. The partition coefficients and hysteresis ratios of the three herbicides are shown in Table 5-1.

Table 5-1. Sorption & Desorption Parameters of The Three Herbicides

parameter	bromacil	prometryn	napropamide
K_d (L/kg)	0.0975	0.275	0.97
$K_{d(sorp)}/K_{d(des)}$	1.75 ± 0.39	1.3 ± 0.18	1.52 ± 0.17
n_{sorp}/n_{des}	2.31 ± 1.58	1.22 ± 0.3	1.58 ± 0.22

It is found from Table 5-1 that for the three herbicides, as the K_d increases, the $K_{d(sorp)}/K_{d(des)}$ and n_{sorp}/n_{des} will decrease. The hysteresis ratios of bromacil are larger than those of prometryn and napropamide. Since bromacil is more polar than prometryn and napropamide, these results suggest that polarity of an organic compound will affect not only the sorption linearity of the compound, but also desorption hysteresis. Furthermore, sorption linearity of a organic compound seems to be related to the desorption hysteresis of the compound.

Another very interesting phenomenon is that the K_d value of prometryn is less than that of napropamide, which contracts to their expected values from their published Koc and aqueous solubility values (Jury et al., 1984).

5.3. Competition

5.3.1. Sorption Competition.

The calculated sorption parameters of the three herbicides with or without competition are summarized and shown in Table 5-2.

Table 5-2 Sorption Parameters of The Three Herbicides With or Without Competition

herbicide	K_d	n	K_f	R^2	Significance
bromacil only	0.098	0.90	0.138	0.997	yes
bromacil with P	0.084	0.93	0.105	0.997	yes
bromacil with N	0.090	0.91	0.121	0.998	yes
bromacil with P+N		0.91	0.095	0.996	yes
prometryn only	0.281	0.99	0.282	0.98	yes
prometryn with B	0.272	1.003	0.27	0.9	yes
prometryn with N	0.272	0.997	0.273	0.995	yes
prometryn with B+N	0.281	1.009	0.27	0.97	yes
napropamide only	0.97	0.98	1.01	0.999	yes
napropamide with B	0.89	0.98	0.9	0.998	yes
napropamide with P	0.92	0.97	0.93	0.998	yes
napropamide with P+N	0.842	0.99	0.87	0.9998	yes

Note: B: bromacil; P: prometryn; N: napropamide

It can be found from Table 5-2 that both napropamide and bromacil sorption decreased slightly in the presence of any other one or two herbicides, while prometryn sorption was not significantly affected. The details of bromacil and napropamide sorption in the presence of other herbicides is discussed below.

a. Interaction. The decrease of bromacil sorption is affected more seriously by napropamide than by prometryn, which is shown in Table 4-12. Similarly, the decrease of napropamide sorption is effected more seriously by bromacil than by prometryn, which is shown in Table 4-18. This phenomenon seems to show that the sorption interaction are mutually dependent. The relation between the sorption interaction of the two herbicides and their chemical characteristics is not clear.

b. Non-additive effect. It can be found From Table 5-2 that when the three herbicides exist in same solution, the decrease of bromacil sorption is affected more seriously by napropamide + prometryn than by only napropamide or only prometryn in the same concentration. Furthermore, the effect of bromacil by prometryn and napropamide is not equal to the sum of the effect of bromacil by only prometryn and the effect of bromacil by only napropamide. Napropamide competition sorption shows the same phenomenon.

5.3.2. Desorption Competition

The calculated desorption parameters of the three herbicides with or without competition are summarized and shown in Table 5-3. It is found from Table 5-3 that both the linear equation and the Freundlich equation do not fit the desorption data of the three herbicides well. This phenomenon seems to show that the desorption process is more complicated than sorption process.

The desorption of the three herbicides with and without competition shows marked hysteresis. The hysteresis ratios

Table 5-3. The Desorption Parameters of The Three Herbicides With or Without Competition.

parameter	bromacil only	bromacil with P	bromacil with N
K_d	0.0552 (± 0.0052)	0.0573	0.059
n	0.475 (± 0.075)	0.63	0.61
R^2	0.93(± 0.13)	0.81	0.56
significance	yes	no	no
$K_{d(sorp)}/K_{d(des)}$	1.75 (± 0.39)	1.47	1.54
n_{sorp}/n_{des}	2.31 (± 1.58)	1.48	1.49

parameter	prometryn only	prometryn with B	prometryn with N
K_d	0.22 (± 0.015)	0.225 ± 0.015)	0.215 (± 0.065)
n	0.764 (± 0.054)	0.79 (± 0.05)	0.88 (± 0.04)
R^2	0.64 ± 0.3	0.78 ± 0.06	0.67 ± 0.27
significant	no	no	no
$K_{d(sorp)}/K_{d(des)}$	1.3 ± 0.18	1.26 ± 0.02	1.32 ± 0.21
n_{sorp}/n_{des}	1.22 ± 0.3	1.22 ± 0.03	1.19 ± 0.03

parameter	napropamide only	napropamide with B	napropamide with P
K_d	0.61 (± 0.37)	0.68 (± 0.14)	0.59 (± 0.2)
n	0.47 (± 0.26)	0.69 (± 0.16)	0.61 (± 0.18)
R^2	0.84 ± 0.6	0.95 ± 0.2	0.91 ± 0.4
significant	no	yes	yes
$K_{d(sorp)}/K_{d(des)}$	1.52 ± 0.17	1.41 ± 0.34	1.46 ± 0.3
n_{sorp}/n_{des}	1.58 ± 0.22	1.46 ± 0.39	1.51 ± 0.4

Note: B: bromacil; P: prometryn; N: napropamide

$K_{d(sorp)}/K_{d(des)}$ and n_{sorp}/n_{des} of bromacil and napropamide decrease slightly in the presence of other herbicides. This means that desorption hysteresis of bromacil and napropamide will decrease in the presence of other herbicides. However, the hysteresis ratios of prometryn are not significantly affected by bromacil and napropamide.

Both sorption and desorption of bromacil and napropamide will be affected by other herbicides, while prometryn sorption and desorption will not be affected by the other herbicides. It seems to show that an organic compound affected by other compounds in the sorption process will also be affected in the desorption process; conversely, an organic compound not affected by other compounds in the sorption process will not be affected in the desorption process.

CHAPTER 6

SUMMARY AND CONCLUSIONS

6.1 SUMMARY

This study has produced a set of data describing the behavior of sorption and desorption of three herbicides on soil in laboratory batch experiments. It is hoped that the data can be used to explain some phenomena of herbicide transport and distribution in field studies, and verify the results of field experiments obtained by other researchers.

Analysis of this data set points out that all the sorption data fit the Freundlich equation very well, and the linear equation fit all the prometryn and napropamide sorption data and the part of the bromacil sorption data with initial concentrations less than 40 μg/mL. However, desorption data do not fit the Freundlich equation and the linear equation well.

The most noteworthy result is that the sorption and desorption of bromacil and napropamide will slightly decrease in the presence of other two herbicides, while the effect on prometryn sorption and desorption by other herbicides is not significant. The relation between different herbicide competition for sorption sites and their chemical and physical properties is not clear.

6.2 CONCLUSIONS

1). Prometryn and napropamide exhibit sorption linearity, while bromacil sorption is non-linear. The sorption parameters for the three herbicide are shown in the Table 5-2.

2). The desorption of the three herbicides show marked hysteresis. The ratios of $K_{d(sorp)}/ k_{d(des)}$ and n_{sorp}/n_{des} are shown in table 5-1.

3). Sorption of bromacil and napropamide is slightly affected by the presence of other herbicides, while the effect on prometryn sorption by other herbicides is not significant.

4. Bromacil and napropamide desorption hysteresis decreases slightly in the presence of other herbicides, while the effect of other herbicides on prometryn desorption is not significant.

REFERENCES

Bailey, C.W. and White J.L., Factors influencing the adsorption, desorption and movement of pesticides in soils. *Residue Rev.* 32:29-92, 1964.

Bowman, R.S. and Rice, R.C., Accelerated herbicide leaching resulting form preferential flow phenomena and its implication for groundwater contamination. *In. Proc. Conf. on Southwest Groundwater Issues.* Phoenix, AZ. October 20-22 1986. National Water Well Association, Dublin, OH.

Brusseau, M.L., Sorption Nonideality During Organic Contaminatant Transport in Porous Media. *CRC Crit. Rev. in Env. Control*, 19:33-99, 1989.

Chiou, C.T., Theoretical Considerations of the Partition Uptake of Nonionic Organic compounds by Soil Organic Matter. In B.L. Sawhney and K. Brown (eds), Reactions and Movement of Organic Chemicals in Soils, SSSA Spacial Publication 22, *Soil Sci. Soc. Am.*, Madison, WI, pp. 1-29, 1989.

Chiou, C.T., Poter, P.E., and Schmedding, D.W., Partition equilibria of nonionic organic compounds between soil organic matter and water, *Environ. Sci. Technol.*, 17, 227, 1983.

Curtis, G.P., Roberts, P.V., and Reinhard, M., A natural gradient experiment on natural sorbents, *Environ. Sci. Technol.*, 18, 910, 1984.

Di Toro, D.M., A particle interaction model of reversible organic chemical sorption, *chemosphere*, 14, 1503, 1985.

Herbicide Handbook. 6th ed. *Weed Science Sociaty of American*, Champaign, IL. 301 pp, 1989.

Jaffe, P.R. and Ferrara, R.A., Desorption kinetics in modelling of toxic chemicals, *J.Environ. Eng. Div. ASCE*, 109, 859, 1983.

Jury, W.A., Spencer, W.F, and Farmer, W.J., Behavior Assessment Model for Trace Organics in Soil: III. Application of Screening Model. *J. Env. Qual.*, 13:573-579, 1984.

Karickhoff, S.W., Organic pollutant sorption in aquatic systems, *J.Hydraul. Eng.*, 110, 707, 1984.

Kier, L.B. and Hall, L.H., Molecular connectivity in structure-activity analysis. Res. Studies Press, Letch Worth, England, 1986.

McCall, P,J. and Agin, G, L., Desorption kinetics of picloram as affected by residence time in the soil, *Environ. Tox.Chem.*, 4, 37, 1985.

Mingelgrin, U. and Gerstl, Z., Competitive adsorption of two dissolved organics onto activated carbon, *Chem. Eng. Sci.*, 36, 731, 1983.

Oliver, B.G., Desorption of chlorinated hydrocarbons from spiked and anthropogenically contaminated sediments, *Chemosphere*, 14, 1087, 1985.

Rao, P.S.C. and Davidson, J.M., Estimation of pesticide retention and transformation required in non-point source pollution models, in Environmental Impact of Nonpoint Source Pollution, Overcash, M.R., and Davidson, J.M., Eds., *Ann Arbor Science,* Ann Arbor, MI, 1980.

Reupert, R., Ploger, E, and Brausen, G., HPLC Determination of 29 Controlled Herbicides in Water Supplies, *Environ. Sci. Technol.*,19, 789, 1990.

Turin H.J., Nonideal transport of pesticides through the vadose zone. *Ph.D. diss*. New Mexico Tech., Socorro, 1992.

Voice, T.C. and Weber, W.J., Sorbent concentration effects in liquid/solid partitioning, *Environ. Sci. Technol.*, 19, 789, 1985.

Worthing, C.R., The pesticide Manual - A world Compendium. 9th ed. The British Crop Protection, Farnham, Surrey. 1141 pp, 1991.

APPENDIX

1. Bromacil Sorption data

Initial concentration (ug/mL)	Sorption Data			
	C(ug/mL)	S(ug/g)	log(C)	log(S)
1	0.905	0.095	-0.04335	-1.02228
4	3.6	0.4	0.556303	-0.39794
4	3.68	0.32	0.565848	-0.49485
10	9.2	0.8	0.963788	-0.09691
10	9.1	0.9	0.959041	-0.04576
40	36.4	3.6	1.561101	0.556303
40	36.6	3.4	1.563481	0.531479
100	94.4	5.6	1.974972	0.748188
100	93.2	6.8	1.969416	0.832509
200	189.1	10.9	2.276692	1.037426
200	190.3	9.7	2.279439	0.986772
400	382.7	17.3	2.582858	1.238046
400	383.4	16.6	2.583652	1.220108

2. Bromacil Desorption Data (different dilutions)

Initial concentra-tion(ug/mL)	1	1	2	2	3	3	4	4	5	5
	C	S	C	S	C	S	C	S	C	S
4	2.56	0.36	1.85	0.302	1.33	0.267	0.95	0.248	0.72	0.193
4	2.59	0.306	1.86	0.259	1.34	0.221	0.956	0.203	0.698	0.1742
10	6.5	0.74	4.7	0.59	3.39	0.49	2.45	0.413	1.75	0.378
10	6.51	0.76	4.73	0.587	3.39	0.508	2.47	0.411	1.76	0.38
40	26	3.08	18.46	2.82	12.78	2.962	9.95	1.958	7.26	1.663
40	26.1	2.92	18.66	2.53	12.9	2.692	9.9	1.822	7.09	1.662
100	66.2	5.48	47.33	4.49	33.8	3.821	24.4	3.081	17.56	2.601
100	66.1	5.94	47.7	4.51	34	3.9	24.6	3.1	17.71	2.61
400	270.4	14.79	192.3	11.77	136.2	10.18	96.5	9.02	68.52	8.05
400	271.4	13.58	192.15	11.41	136.4	9.515	96	8.995	68.3	7.895

3. Prometryn Sorption Data

Initial Concentration (ug/mL)	Sorption Data			
	C(ug/mL	S(ug/g)	log(C)	log(S)
20	15.72	4.28	1.196453	0.631444
20	15.64	4.36	1.194237	0.639486
10	7.98	2.02	0.902003	0.305351
10	7.77	2.23	0.890421	0.348305
5	3.93	1.07	0.594393	0.029384
5	3.9	1.1	0.591065	0.041393
1	0.76	0.24	-0.11919	-0.61979
1	0.75	0.25	-0.12494	-0.60206

4. Prometryn Desorption Data

Initial Concentration (ug/mL)	1	1	2	2	3	3
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
20	12.01	3.22	9.33	2.3	6.58	2.25
20	11.48	3.77	8.83	3.13	6.86	2.3
10	5.77	1.83	4.42	1.45	3.39	1.16
10	5.89	1.78	4.49	1.41	3.36	1.2
5	2.842	0.979	2.17	0.8	1.66	0.659
5	2.8	1.03	2.2	0.79	1.7	0.63

5. Napropamide Sorption Data

tial ncentration g/mL)	Sorption Data			
	C(ug/mL)	S(ug/g)	log(C)	log(S)
30	15.34	14.66	1.185825	1.166134
30	15.2	14.8	1.181844	1.176959
15	7.73	7.27	0.888179	0.861534
15	7.56	7.44	0.878522	0.871573
10	5.2	4.8	0.716003	0.681241
10	5.18	4.82	0.71433	0.683047
5	2.535	2.465	0.403978	0.391817
5	2.55	2.45	0.40654	0.389166
1	0.512	0.488	-0.29073	-0.31158
1	0.524	0.476	-0.28067	-0.32239

6. Napropamide Desorption Data

tial ncentration g/mL)	1	1	2	2
	C(ug/mL)	S(ug/g)	C(ug/mL)	S(ug/g)
30	11.8	13.598	10.5	11.358
30	11.47	14.2	10.72	11.509
15	6.2	6.481	5.2	5.621
15	6.15	6.582	5.34	5.547
10	4.12	4.32	3.3	3.904
10	4.02	4.426	3.01	4.23
5	2.01	2.2295	1.56	2.0765
5	1.86	2.375	1.62	2.057

7. Bromacil Sorption Data Affected by Prometryn and Napropamide

Initial concentration (ug/mL)	Bromacil only		With Promatryn		With Napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
10	9.1	0.9	9.24	0.76	9.1	0.9
10	8.97	1.03	9.16	0.84	9.15	0.85
40	36.21	3.79	36.84	3.16	36.51	3.49
40	36.42	3.58	36.94	3.06	36.82	3.18
200	185.93	14.07	187.2	12.8	186.8	13.2
200	184.8	15.2			186.2	13.8

8. Bromacil Desorption Data Affected by Prometryn or Napropamide

	bromacil only		with prometryn		with napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
Sorption	36.21	3.79	36.48	3.52	36.78	3.22
	36.42	3.58	36.56	3.44	36.34	3.66
Desorption (1)	25.69	3.447	25.72	3.336	25.89	3.076
	25.82	3.254	25.93	3.102	25.53	3.568
Desorption (2)	18.65	2.78	18.78	2.56	18.54	2.659
	18.82	2.508	18.91	2.343	18.73	2.709

9. Prometryn Sorption Data Affected by Bromacil (200 ug/mL) or Napropamide (15 ug/mL)

Initial Concentration (ug/mL)	Prometryn only		With Bromacil		With Napropamide	
	C	S	C	S	C	S
5(a)	3.93	1.07	3.94	1.06		
5(b)	3.94	1.06	3.92	1.08		
6.66(a)	4.95	1.71	5.2	1.46	4.945	1.715
6.66(b)	5.39	1.27	5.27	1.39	5.42	1.25
10(b)	7.94	2.06	7.89	2.11	7.94	2.06
10(a)	7.82	2.18	7.85	2.15	8.02	1.98
20(a)	15.74	4.26	15.68	4.32		
20(b)	15.63	4.37	15.73	4.27		

10. Prometryn Desorption Data Affected by Bromacil (200 ug/mL) or napropamide (15 ug/mL)

Dilution Time (1)

Initial Concentration (ug/mL)	Prometryn only		With Bromacil		With Napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
6.66(a)	3.95	1.23	4.17	1.01	4.01	0.92
6.66(b)	3.85	1.19	4.39	0.65	4.2	1.01
10(b)	5.77	1.83	5.82	1.79	5.77	1.848
10(a)	5.89	1.78	6.02	1.51	5.82	1.774

Dilution Time (2)

Initial Concentration (ppm)	Prometryn only		With Bromacil		With Napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
6.66(a)	2.97	1.025	2.68	1.249	2.83	1.09
6.66(b)	3.03	0.85	2.71	1.013	3.18	0.54
10(b)	4.07	1.799	3.98	1.884	4.13	1.74
10(a)	4.1	1.803	4.14	1.584	4.01	1.7

11. Napropamide sorption data affected by bromacil (200 ug/mL) and prometryn (10 ug/mL)

Initial Concentration (ug/mL)	napropamide only		with bromacil		with prometryn	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
30	15.34	14.66				
30	15.2	14.8				
15	7.73	7.27	7.52	7.48	7.72	7.28
15	7.56	7.44	7.61	7.39	7.84	7.16
10	5.2	4.8	5.45	4.55	5.04	4.96
10	5.18	4.82	5.12	4.88	4.97	5.03
5	2.535	2.465	2.51	2.49	2.53	2.47
5	2.55	2.45	2.66	2.34	2.16	2.84
1	0.512	0.488	0.53	0.47	0.527	0.473
1	0.524	0.476	0.48	0.52	0.52	0.48

12. Napropamide desorption data affected by bromacil (200 ug/mL) and prometryn (10 ug/mL)

Dilution Time (1)

Initial Concentration (ug/mL)	bromacil only		With Bromacil		With Napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
15	6.2	6.481	6.24	6.504	5.83	6.854
15	6.15	6.582	6.28	6.437	6.26	6.388
10	4.12	4.32	4.07	4.295	4.11	4.378
10	4.02	4.426	4.04	4.424	4.15	4.359
5	2.01	2.2295	2.18	2.067	2.07	2.171
5	1.86	2.375	1.92	2.282	1.96	2.392

Dilution Time (2)

Initial Concentration (ug/mL)	bromacil only		With Bromacil		With Napropamide	
	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
15	5.2	5.621	5.13	5.742	5.07	5.865
15	5.34	5.547	5.36	5.473	5.22	5.55
10	3.3	3.904	3.52	3.624	3.15	4.105
10	3.01	4.23	2.96	4.292	3.27	3.994
5	1.56	2.0765	1.48	2.113	1.61	2.01
5	1.62	2.057	1.64	1.986	1.55	2.214

13. Bromacil Sorption Data Affected by Napropamide & Prometryn

Initial Napropamide Concentration (ug/mL)	Initial Prometryn Concentration (ug/mL)	Initial Bromacil Concentration (ug/mL)	Bromacil	
			C (ug/mL)	S (ug/g)
0	0	66.6	61.9	4.7
0	0	66.6	61.98	4.62
0	0	133	125.7	7.3
0	0	133	125.2	7.8
0	0	400	383.1	16.9
0	0	400	382.8	17.2
5	3.33	66.6	62.5	4.1
5	3.33	66.6	62.7	3.9
10	6.66	133	126.8	6.2
10	6.66	133	126.2	6.8
30	20	400	385.7	14.3
30	20	400	385.2	14.8

14. Bromacil Desorption Data Affected by Prometryn & Napropamide

Initial Napropamide Cons (ug/mL)	Initial Prometryn Cons (ug/mL)	Initial Bromacil Concentration (ug/mL)	Dilution(1)		Dilution(2)	
			C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
0	0	66.6	43.5	4.53	31.2	3.78
0	0	66.6	43.6	4.406	31.24	3.686
0	0	133	88.5	6.79	62.1	6.64
0	0	133	88.8	6.64	62.6	6.2
0	0	400	270.4	14.67	190.9	13.05
0	0	400	269.9	15.26	190.3	13.89
5	3.33	66.6	44	3.85	31.7	2.95
5	3.33	66.6	44.1	3.69	31.8	2.76
10	6.66	133	89.3	5.66	62.7	5.47
10	6.66	133	89.5	5.64	63.1	5.19
30	20	400	272.1	12.19	191.9	10.76
30	20	400	271.9	12.54	192.1	10.77

15. Prometryn Sorption Data affected by Bromacil & Napropamide

Initial Bromacil Concentration (ug/mL)	Initial Napropamide Concentration (ug/mL)	Initial Prometryn Concentration (ug/mL)	Prometryn	
			C (ug/mL)	S (ug/g)
0	0	3.33(A)	2.61	0.72
0	0	3.33(B)	2.65	0.68
0	0	6.66(A)	4.95	1.71
0	0	6.66(B)	5.39	1.27
0	0	20(A)	15.72	4.28
0	0	20(B)	15.64	4.36
66.7	5	3.33(A)	2.68	0.65
66.7	5	3.33(B)	2.57	0.76
133	10	6.66(A)	5.42	1.24
133	10	6.66(B)	4.83	1.83
400	30	20(A)	15.81	4.19
400	30	20(B)	15.43	4.57

16. Prometryn Desorption Data effected by Bromacil & Napropamide

Initial Bromacil Concentration (ug/ml)	Initial Napropamide Concentration (ug/ml)	Initial Prometryn Concentration (ug/ml)	Dilution(1)		Dilution(2)	
			C (ug/ml)	S (ug/g)	C (ug/ml)	S (ug/g)
0	0	3.33(A)	2.01	0.537	1.43	0.514
0	0	3.33(B)	1.94	0.595	1.33	0.623
0	0	6.66(A)	3.95	1.22	3.04	0.85
0	0	6.66(B)	3.85	1.19	2.57	1.315
0	0	20(A)	12.01	3.22	9.33	2.3
0	0	20(B)	11.48	3.77	8.83	3.13
66.7	5	3.33(A)	1.92	0.606	1.51	0.44
66.7	5	3.33(B)	2.04	0.519	1.37	0.577
133	10	6.66(A)	4.01	1.024	2.93	0.901
133	10	6.66(B)	4.2	1.011	3.01	0.941
400	30	20(A)	11.78	3.477	9.01	2.713
400	30	20(B)	11.62	3.751	8.95	2.935

17. Napropamide Sorption Data Affected by Bromacil and Prometryn

Initial Bromacil Cons (ppm)	Initial Prometryn Concentration (ug/mL)	Initial Napropamide Concentration (ug/mL)	Sorption Data	
			C (ug/mL)	S (ug/g)
0	0	5(A)	2.535	2.465
0	0	5(B)	2.55	2.45
0	0	10(A)	5.12	4.88
0	0	10(B)	5.04	4.96
0	0	30(A)	15.24	14.76
0	0	30(B)	15.2	14.8
66.6	3.33	5(A)	2.72	2.28
66.6	3.33	5(B)	2.66	2.34
133	6.66	10(A)	5.47	4.53
133	6.66	10(B)	5.39	4.61
400	20	30(A)	16.28	13.72
400	20	30(B)	16.3	13.7

18. Napropamide Desorption Data affected by Bromacil & Prometryn

Initial Bromacil Concentration (ug/mL)	Initial Prometryn Concentration (ug/mL)	Initial Napropamide Concentration (ug/mL)	Dilution (1)		Dilution (2)	
			C (ug/mL)	S (ug/g)	C (ug/mL)	S (ug/g)
0	0	5(A)	2.07	2.17	1.72	1.9
0	0	5(B)	1.86	2.375	1.65	1.95
0	0	10(A)	4.17	4.29	3.58	3.63
0	0	10(B)	4.21	4.28	3.39	3.84
0	0	30(A)	12.4	13.03	10.5	11.358
0	0	30(B)	11.47	14.2	10.72	11.509
66.6	3.33	5(A)	2.13	2.054	1.89	1.655
66.6	3.33	5(B)	2.2	2.002	1.84	1.702
133	6.66	10(A)	4.32	4.039	3.79	3.273
133	6.66	10(B)	4.45	3.933	3.83	3.218
400	20	30(A)	12.93	12.186	10.9	10.34
400	20	30(B)	12.62	12.49	11.6	9.724