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Adsorption and Volatilization of 2,4-D, Dicamba and MCPP in Soils

Keon-Joong Hwang and Asmare Atalay*
Division of Analysis, Korea Ginseng & Tobacco Research Institute
**School of Civil Engineering and Environmental Science, University of Oklahoma*

토양중 2,4-D, Dicamba 및 MCPP의 흡착과 휘발에 관한 연구

황건중 · Asmare Atalay*
한국인삼연초연구원, 분석부
*오클라호마대학, 토목 · 환경과학과

초 록

본 실험은 제초제인 2,4-D, dicamba, 및 MCPP의 토양에서의 이동을 확인하고 평가하기 위하여 토양종류에 따른 이들 제초제의 흡착과 휘발을 일정시간 동안 조사하였다. 제초제의 토양중 흡착은 batch isotherm으로 조사하였는데, MCPP와 2,4-D는 Freundlich 식에서 직선으로 나타났으며, dicamba는 곡선으로 나타났다. Silty clay 토양에서 MCPP의 K_d 및 K_{tr} 값이 가장 높았으며, loamy sand 토양에서는 dicamba의 K_d, K_{tr} 값이 가장 낮았다. 전반적으로 silty clay 토양에서 K_d, K_{tr} 값이 높았고 N값은 낮았다. 토양에 살포된 제초제의 약 40%가 처리 25일 경과시 휘발되거나 분해되었으며, 이들 제초제중 2,4-D가 dicamba와 MCPP에 비하여 분해 및 휘발속도가 빨랐다. 모든 토양에서 이들 제초제의 분해 및 휘발속도는 공기에 노출된 초기에 현저하게 빠른 것으로 나타나고 있다. 본 연구의 결과는 자연환경중에서 이들 제초제의 이동 및 잔류 현황을 예견하는데 사용될 수 있을 것으로 사료된다.

Keyword : Adsorption, Volatilization, Herbicide, Soil remediation

I. Introduction

The last decade has been characterized by a growing concern over the pollution potential of pesticide chemicals applied to soils. The current widespread use of herbicides has resulted in problems to human health, adverse effects to non-target organisms, and contamination of air, soil and water. Many of these problems result from the improper use, handling, or storage of herbicides.[1] A thorough understanding of the factors affecting herbicide degradation is necessary to maximize agricultural benefits and minimize adverse environmental impacts. The adsorption of herbicides on soil colloids is a major factor determining the mobility, persistence, and activity of soil applied herbicides, because adsorption influences the amount of herbicide in the soil solution.[2] The sorption process plays an important role in assessing the behavior of herbicides in soil. As a result of sorption, the concentration in the liquid phase is lowered, which causes the transport rate in soil to slow down and reduces the amount of herbicide available to organisms. The Freundlich model is most widely used for describing the adsorption of chemicals on solid surfaces.[3]

The mechanisms of sorption for chlorophenoxy herbicides are proton association and, for the molecular form, van der Waals sorption. Hydrogen bonding and electrostatic interactions are other possible mechanisms for sorption. Sorption data showed an initial rapid rate followed by a slower rate of sorption. Both the Freundlich two-site kinetic equation, and the parabolic diffusion law fitted well to the data.[4] The rapid component of sorption varied from 0 to 25 percent of total sorption for various pesticides. Under batch conditions, the instantaneous component of sorption was very high. The physical properties of the soil also affected the rate of sorption of the pesticides. For instance, a well structured soil with high organic matter content showed a slower rate of sorption compared with a dispersed soil with low organic matter content.[4] Adsorption was only slightly correlated with the soil clay content but was highly correlated with soil organic matter content. Generally, the more clay-size particles contained within a soil, the more likely it will be to develop a heterogeneous pore system and consequently, the greater will be the asymmetry of the breakthrough curves.[5-7] Gerstl and Yaron(1983)[8] investigated that temperature and moisture content of soils affected degradation more than did soil type or initial concentration. The degree of sorption of herbicides on soils influenced their biological activity, persistence, and mobility.[9]

The mechanism of volatilization, in which herbicide molecules leave the soil or plant surface in the vapor phase and move into atmospheric air, is a significant cause of dissipation. The magnitude of the loss is comparable to or greater than that of chemical degradation. Volatilization losses exceeded 50 percent of the application within 20 days or less when residues of herbicides are exposed on point soil.[5] The principal factors controlling the rate of volatilization are 1) the vapor pressure of the herbicide, 2) the distribution of the residues and 3) the moisture status of the soil or plant surface. The highest rates of volatilization are found where residues are exposed to the atmosphere after direct application to moist soil or plant surfaces.[5] The overall loss or dissipation of organic contaminants from soils is dependent on the physicochemical properties of the soil and the chemicals themselves, environmental factors including temperature, precipitation, and anthropogenic factors such as cultivation and drainage.[5] The herbicide molecules that are strongly adsorbed on dry soils are often readily dislodged under damp conditions. Soil type influences the persistence and effectiveness of a particular application rate of herbicide.[10]

II. Materials and Methods

1. Soil Collection and Analysis.

In choosing a soil for the laboratory tests, the applicability of the procedure to actual field situations is a primary consideration. Soil selection included identification of native soils at three sites near Norman, Oklahoma. Three different soils (a clay, loam, and sandy soil) were used in

Table 1. Physical and chemical characteristics of soils used in the study.

Parameter	Soil material[c]		
	A	B	C
% Soil moisture	6.2	12.7	18.0
pH	6.4	7.5	7.6
% Organic matter	0.78	2.80	3.80
CEC[a]	4.97	10.06	11.29
Inorganic separates (%)			
Sand	82.0	20.02	9.0
Silt	13.8	58.2	44.1
Clay	4.2	21.6	46.9
Texture[b]	Loamy sand	Silt loam	Silty clay

[a] CEC; Cation exchange capacity (in meq./100 g)
[b] Based on the soil texture classification system (U.S. Department of Agriculture)
[c] Location of soils:
A : Field near the west Main St. and 48th Ave NW in Norman, Oklahoma
B : Field near the east Lindsey St. and 36th Ave SE in Norman, Oklahoma
C : Field near the Robinson St. and 60th Ave NW in Norman, Oklahoma

all experiments. This allowed a comparison of the chemical behaviors of the selected herbicides in physically diverse soils. The soils were air-dried for one week, crushed and then passed through a 1 mm sieve. To obtain the small particles of clay or loam soils for test, a grinder was used to break up large clods. Soil properties such as moisture, pH, organic matter content, cation exchange capacity(CEC), and soil texture were determined by soil testing in the laboratory following the Method of Soil Analysis.[11]

The results of the soil analyses are shown in Table 1. These soils showed different moisture content, organic matter content, CEC value, and inorganic texture.

2. Soil Contamination

Herbicide concentrations used in the study were selected on the basis of the chemical and physical properties of each herbicide. The compounds selected were 2,4-D, Dicamba and MCPP. These compounds are widely used herbicides for broadleaf weed control. The 2,4-D, dicamba and MCPP utilized for standards and stock solutions were analytical grade (98 % pure) and obtained from Chem Service, Inc. (Westchester, PA). In order to reach field capacity moisture content, 0.62, 0.89 and 1.80 m*l* deionized water was added to 10 g loamy sand, silt loam and silty clay soil, respectively. Also, to get to 0.2 mg herbicide/ 10 g soil contamination, 0.3226, 0.2247 and 0.1111 ppm of each herbicide was added to each of the three soils. To make the mixing more homogeneous, the herbicide contaminated soil was used 20 hours after spiking. For soil applications of a commercial herbicides, Weed-B-Gone for Southern Lawns, Formula II (ORTHO, Chevron Chemical Company, San Ramon, CA) was used. The labeled active ingredients of Weed-B-Gone were 2.53 percent 2,4-D; 1.08 percent Dicamba; 8.76 percent MCPP, but the actual active ingredients of Weed-B-Gone, determined by GC analysis, were 2.48 percent 2,4-D; 1.11 percent dicamba; and 8.76 percent MCPP.

3. Adsorption of Herbicides

Adsorption of 2,4-D, dicamba and MCPP on soils is commonly investigated in the laboratory by using batch studies. The batch study consists of placing a known quantity of the soil and a known mass of the herbicide into a reactor and shaking until equilibrium adsorption is reached. Sorption of the herbicides from aqueous solution and methanol was determined at ambient laboratory temperature (22±2℃) in a batch suspension with a solution/soil ratio of 2:1 and a 24 hour equilibration time. Using the same solution/soil ratio, a sorption isotherm experiment was conducted in duplicate using three different soils and five solution concentrations (10, 20, 30, 40, and 50 ppm). The linear portion of the isotherms has been described with the Linear sorption coefficient (K_d) and Freundlich sorption coefficient (K_f) values.

4. Volatilization and Decomposition of Herbicides

For defining decomposition and volatilization characteristics of the selected herbicides, comparisons of sealed and open soil samples were made. The vials containing contaminated soil were sealed with Teflon-lined screw caps and shaken for 2 min to mix the herbicides with soil. The vials were then allowed to equilibrate for 20 hours, and then the caps were left opened. Samples used in this experiment were kept in a glove box which was continuously vented with nitrogen gas in the presence of UV light for preventing recolonization by microbes. After a certain period of time (from 1 to 25 days), the contaminated

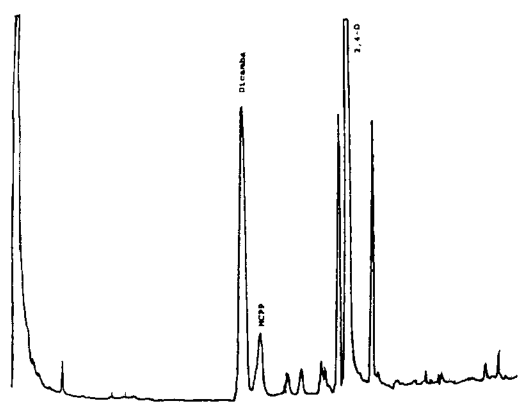

Fig. 1. Gas chromatogram of 2,4-D, dicamba and MCPP from methanol extracted sample.

soils in the sealed and open vials were analyzed for herbicides by methanol extraction after 24 hours shaking. The extracts were converted to their methyl esters by using Boron trichloride-methanol solution as the derivatization reagent.

The herbicide extracts from derivatized samples were quantified by injecting a 0.1 μl aliquot into the GC. Typical chromatograms of 2,4-D, dicamba and MCPP from contaminated soil samples are presented in Fig. 1.

III. Results and Discussion

In order to assess the movement and fate of 2,4-D, dicamba and MCPP in the soil environment, soil adsorption, degradation and volatilization of herbicide were evaluated.

1. Soil Adsorption

The adsorption of herbicides on soils is an important interphase mass-transfer process for many common conditions. Sorption of many contaminants by soils and sediments has been shown to be an effective means of reducing their mobility. Sorption can also affect the bioactivity, persistence, biodegradability, leachability, and volatility of herbicides.[12] The treatment of adsorption equilibrium data generall single value linear relationship between the adsorbed concentration, S (μg/g), and the dissolved solution concentration, C (μg/ml), $S=K_dC$, where K_d (ml/g) is called the distribution coefficient. This model has the advantage of describing a given set of adsorption data in terms of a single parameter K_d, and it is simple for modeling purposes because it can be solved implicitly for any of the other terms.[13] Sorption coefficient (K_d) is related to organic carbon content, soil pH, and cation exchange capacity. Soil which exhibited higher sorption also exhibited lower desorption. The sorptive behaviors of 2,4-D, dicamba and MCPP in different soils using the linear isotherms are shown in Fig. 2. The plot of S vs Ce using the linear isotherm did not show linear relationships.

In the case where the adsorption isotherm is nonlinear, it is necessary to utilize a nonlinear equilibrium adsorption expression. The Freundlich equilibrium adsorption equation is the most commonly utilized nonlinear equilibrium adsorption expression for pesticides and soils.[3] $S=K_nC^N$, where K_n is the Freundlich partition coefficient $[(L^3/M)^N]$ and N is called the Freundlich exponent. Even though nonlinearity is observed at higher concentration, the isotherm is often observed to be linear at lower concentrations.[14] The sorptive behaviors of 2,4-D, dicamba and

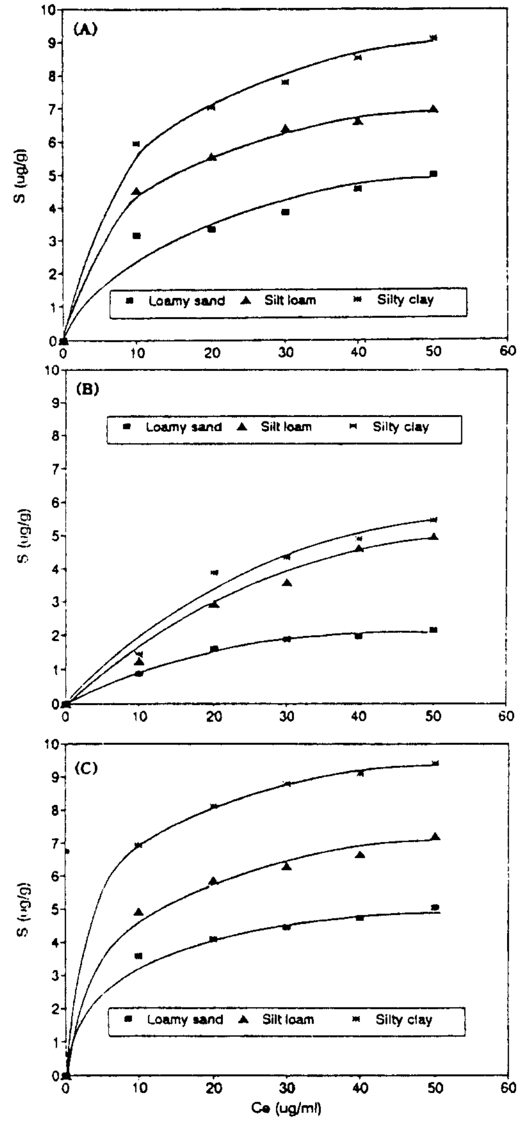

Fig. 2. Linear adsorption isotherms of (a) 2,4-D, (b) Dicamba, and (c) MCPP in three soils.

MCPP in different soils were compared using water as solvent via the Freundlich isotherm shown in Fig. 3. The freundlich isotherm was able to describe the nonlinear nature of the selected herbicide isotherm. The adsorbed concentration log (S) increased linearly as the herbicide concentration log (C_e) increased. The data shows that the overall sorptive behavior of the three herbicides was different. The MCPP and 2,4-D in the Freundlich isotherm showed straight line relationships between log S and log C_e, while the same relationship was non-linear for dicamba for the three soil types.

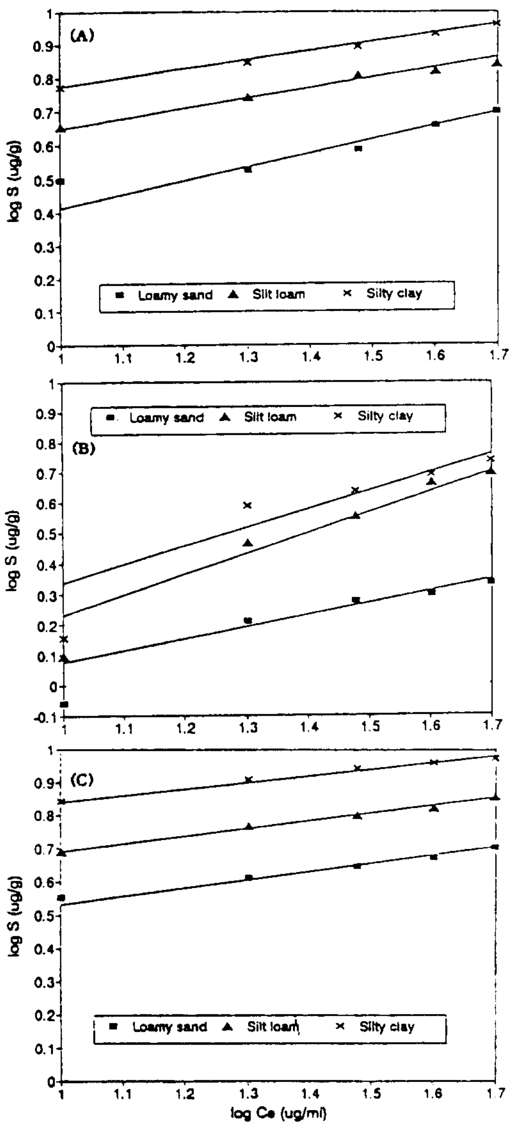

Fig. 3. Freundlich adsorption isotherms of (a) 2,4-D, (b) Dicamba, and (c) MCPP in three soils.

Soils with higher clay content resulted in steeper isotherm for dicamba, but the steepness of MCPP and 2,4-D in the Freundlich isotherm were similar in the three soil types. The sorption coefficients, K_d, K_{fr} and N values for the sorption of herbicides on the three soils are given in Table 2. The silty clay soil showed the highest K_d and K_{fr} value compared with the other two soils. One previous study indicated that other soil properties, such as the type and amount of clay, soil pH, hydrous oxide content, etc., have little effect on the sorption process except in low organic matter systems.[15] The value of K_d or K_{fr} can be taken as a relative indicator of adsorption capacity, while N is indicative of the energy or intensity of the reaction.[16] The K_d and K_{fr} values of individual herbicides in the three soils varied from 0.05 to 0.24 and from 0.17 to 4.56, respectively. MCPP in the silty clay soil had the higest K_d and K_{fr} values, and dicamba in loamy sand soil had the lowest K_d and K_{fr} value, and lower N value were most apparent in the silty clay soils. Calculated values of f_{oc}, r^2, K_{oc}, and estimated vlaues of K_{oc} from the Linear or Freundlich isotherm equation for 2,4-D, dicamba, and MCPP are shown in Table 3. The average K_{oc} values for dicamba, MCPP and 2,4-D were 4.6, 9.1 and 9.2, respectively. Comparing the observed K_{oc} with Ahrens's[17] estimated Koc, the observed K_{oc} for dicamba was twice higher than the estimated K_{oc}, but the observed K_{oc} for 2,4-D and MCPP was half of the estimated K_{oc}.

This study has demonstrated that batch isotherm data can be used to describe the combined sorptive behaviors of 2,4-D, dicamba and MCPP in soil systems. This is vital in order to predict the transport phenomenon of herbicides under field conditions. Predictive laboratory data is needed to simulate a naturally occurring environment. The sorption process is an important process that determines, along with the aqueous-vapor equilibrium described by Henry's Law, the relative fraction of the organic chemical that is in each phase.

Table 2. Calculated values of K_d, K_{fr} and N from the linear or freundlich isotherm equations for the adsorption of three herbicides in three soils

Herbicide	Loamy sand			Silt loam			Silty clay		
	K_d	K_{fr}	N	K_d	K_{fr}	N	K_d	K_{fr}	N
	[ml/g]	[(g/g)/(g/L)^N]		[ml/g]	[(g/g)/(g/L)^N]		[ml/g]	[(g/g)/(g/L)^N]	
Dicamba	0.05	0.17	0.55	0.11	0.19	0.86	0.13	0.27	0.80
2,4-D	0.12	1.51	0.29	0.18	2.44	0.27	0.22	3.21	0.26
MCPP	0.13	2.17	0.21	0.18	2.91	0.23	0.24	4.56	0.19

Table 3. Calculated values of f_{oc}, r^2, K_{oc} and estimated value of K_{oc} for 2,4-D, Dicamba and MCPP in three soils

Herbicide	Soil	f_{oc}	r^2	K_{oc}	K_{oc}*
2,4-D	Loamy sand	0.0078	0.89	15.38	193.59
	Silt loam	0.0280	0.98	6.43	87.14
	Silty clay	0.0380	0.99	5.79	84.47
Dicamba	Loamy sand	0.0078	0.92	6.41	21.79
	Silt loam	0.0280	0.96	3.93	6.79
	Silty clay	0.0380	0.89	3.42	7.11
MCPP	Loamy sand	0.0078	0.99	16.67	278.20
	Silt loam	0.0280	0.99	4.43	103.92
	Silty clay	0.0380	0.99	6.32	120.00

*Values estimated from equation by Miller and Weber(1986)[20]

2. Volatilization and Decomposition

Volatilization and decomposition are also significant processes causing mass loss from the soil. Experiments have been conducted under non-sterile conditions to obtain the total amount of evaporative loss of the herbicides in soils. The results of these experiments are shown in Fig. 4, which plots of evaporative exposure time vs. percent removal of herbicides. There was a difference between the sealed samples and the opened samples in their degradation rate. As shown in these figures, about 40 percent of the three herbicides were lost after 25 days exposure to open atmosphere. The evaporation and decomposition of 2,4-D was much higher than dicamba and MCPP at the latter half period. The evaporation and decomposition processes were highest at earlier exposure periods, and became less significant as time progressed. From literature of Ahrens[17], the order of vapor pressure for the three herbicides are MCPP>dicamba>2,4-D. One possible explanation for the highest loss of 2,4-D during a 25 days experiment could be that the decomposition of 2,4-D by chemical reaction such as oxidation, hydroxylation and conjugation may be dominant. Evaporation may modify the physical, chemical and toxicological properties of a liquid, notably density, viscosity, and the fraction of lower molecular weight substances.[18] The actual quantity of herbicide lost to the atmosphere also depends upon the concentration in the soil, the soil water content, air flow over the soil surface, humidity, temperature, diffusion rates within the soil air and at the surface, adsorption to soil particles, and water solubility.[19]

The volatilization and decomposition rates of 2,4-D were higher than those for dicamba and MCPP for the three soil types, especially in the loamy sand soil. Volatilization from soil is complicated due to the numerous mechanisms that govern it in soil. To be volatilized from soil, the herbicide may be lost by sublimation directly from its solid form to its gaseous form, or it may be released from being adsorbed to soil particles into the soil solution, diffuse into the soil air, and move to the surface to be dispersed into the turbulent air flow above the soil.[19] The movement and fate of herbicides was first studied by measuring rates of adsorption, de-

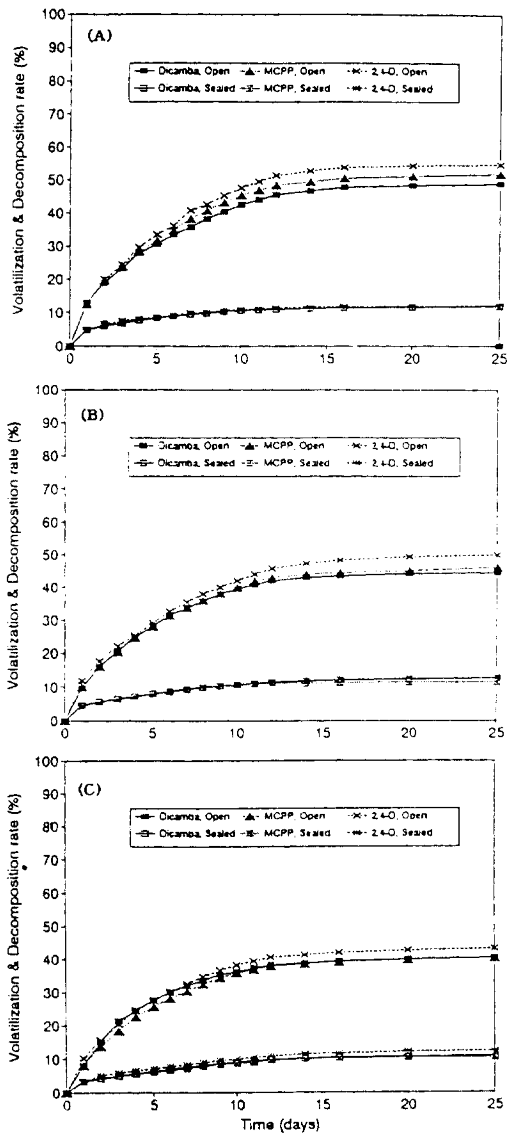

Fig. 4. Volatilization and decomposition rates of 2,4-D, Dicamba and MCPP in (a) Loamy sand, (b) Silt loam, and (c) Silty clay soil.

gradation, and volatilization of the compound after a certain period of time. The estimated mass balance of 2,4-D, dicamba and MCPP in the soil environment after 25 days are listed in Table 4. Volatilization and decomposition were the major contributing factors in soil applied herbicides based on mass balance. The identified methods contributing to the fate and transport of herbicides were volatilization or decomposition, and adsorption. Approximately 50 percent of the original soil applied herbicide remained as residue in the soil after 25 days. These results also indicate that each herbicide applied to soil showed a different fate and transport behavior. 2,4-D was the dominant herbicide that was lost from the soil at a given period. These results agree with the shortest half-life for 2,4-D.

Table 4. Estimated mass balance up to 25 days for 2,4-D, dicamba and MCPP in the soil environment

Environmental Compartment	2,4-D (%)	Dicamba (%)	MCPP (%)
Adsorption	10-20	5-10	15-25
Volatilization and decomposition	30-50	30-40	30-40
Residue	25-55	45-60	30-50

IV. Summary

This study was conducted to identify, evaluate, and optimize the movement of 2,4-D, dicamba and MCPP from soils. The movement and fate of herbicides was first studied by measuring rates of soil adsorption, and volatilization after a certain equilibration period. Batch isotherm data can be used to accurately describe competitive sorptive behavior of 2,4-D, dicamba and MCPP in soil systems. Using the Freundlich equation for the three soil types, the MCPP and 2,4-D isotherms were linear whereas the isotherm for dicamba were slightly curved. The K_d and K_F values of individual herbicides in the three soils varied from 0.05 to 0.24 and 0.17 to 4.56, respectively. MCPP in the silty clay soil had the highest K_d and K_F values; and dicamba in the loamy sand soil had the lowest K_d and K_F values. Higher K_d and K_F values and lower N values were most apparent in the silty clay soil. About 40 percent of the herbicides evaporated or decomposed after 25 days of exposure to an open atmosphere. Evaporation and decomposition losses of 2,4-D were higher than losses of dicamba and MCPP. The evaporation losses became less significant with time. In the clay soil, the evaporation rates of 2,4-D, Dicamba and MCPP were lower than those of the other soils during the initial exposure periods. Volatilization and decomposition were the major contributing factors in the soil applied herbicides based on mass balance. This data is very useful for the prediction of the persistency of these compounds in the environment.

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