Using Lysimeters To Evaluate the Relative Mobility and Plant Uptake of Four Herbicides in a Rye Production System

ONA SAKALIENE,[†] SHARON K. PAPIERNIK,*[‡] WILLIAM C. KOSKINEN,[§]
IRENA KAVOLIŪNAITE,[†] AND JANINA BRAZENAITEI[||]

Lithuanian Institute of Agriculture, Vilnius, Lithuania, North Central Soil Conservation Research
Laboratory, U.S. Department of Agriculture Agricultural Research Service, Morris, Minnesota 56267,
U.S. Department of Agriculture Agricultural Research Service, St. Paul, Minnesota 55108, and
Department of Biochemistry and Biophysics, Vilnius University, Vilnius, Lithuania

Information regarding pesticide mobility is critical for the evaluation of pesticide management practices. Lysimeters have been used worldwide to assess the transport and plant uptake of solutes under relevant moisture regimes and crop production practices. We used repacked field lysimeters to evaluate the leaching and plant uptake of the herbicides pendimethalin, clopyralid, mecoprop (MCPP), and dicamba following fall and spring application to soil cropped to winter rye (*Secale cereale* L.). In most fall and spring trials, mass loss of herbicide through leaching was <3% of the amount applied. On the basis of this 6 year experiment, it appears that clopyralid is the most mobile of the tested herbicides in this soil, followed by dicamba, mecoprop, and pendimethalin. None of the herbicides was present in rye grain or straw at concentrations that exceed current E.U. or U.S. tolerances.

KEYWORDS: Clopyralid; dicamba; leaching; mecoprop; MCPP; pendimethalin

INTRODUCTION

Agricultural pesticides are common contaminants of water resources in Europe and the United States (*1, 2*). Pesticides enter water through runoff and leaching. Differences in herbicide leaching in soils have been attributed to differences in the chemical properties of the herbicides and differences in the physical and chemical properties of the soils that determine water movement (infiltration, leaching volumes and velocities, and the presence of macropores), pesticide retention and transformation, and other factors affecting pesticide fate. The influence of these variables on herbicide movement through the profile can be illustrated by the numerous studies that have been conducted using disturbed and undisturbed soil columns. While laboratory column studies can be useful for estimating the effects of varying soil properties on pesticide mobility, column studies cannot replicate field conditions.

In the field, pesticide transport and degradation vary with soil texture, the amount and timing of water application, properties of soil horizons, crop rooting characteristics, tillage, and other factors which typically are not considered in laboratory column

studies. Previously, large field lysimeters (>0.3 m diameter × 0.9−1.0 m depth) have been successfully used worldwide to provide information about the flux of water and solutes in soil (*3*). A typical lysimeter is designed to isolate a portion of a soil profile and provide a means of collecting the leachate from the isolated soil profile. Lysimeters installed in the field are subject to soil and climatic conditions similar to those of the surrounding field soil and provide information regarding the transport and plant uptake of solutes under relevant moisture regimes and crop production practices. All lysimeters disrupt the local hydrology. Lysimeter walls limit horizontal water flux, and the bottom boundary condition of free-draining lysimeters affects vertical water flux (*4*). Simulations have suggested that gravity-drained lysimeters may underestimate solute transport velocities and thus underestimate the concentrations of reactive solutes in leachate because drainage will not occur until saturated conditions exist at the bottom of the lysimeter (*4*). Despite their limitations, lysimeter experiments have been required for pesticide registration in Europe (*5*).

Lysimeters have been widely used to evaluate the mobility and persistence of individual pesticide compounds. Limited information is available concerning the use of lysimeters in comparing the leaching and plant uptake of multiple pesticide compounds. Field soils often exhibit high spatial variability, and replicate lysimeters in the same field operated under the same conditions have shown high variability in solute transport (*6*). Therefore, comparative evaluations of the transport of multiple

* To whom correspondence should be addressed: USDA-ARS, Morris, MN 56267. Phone: (320) 589-3411. Fax: (320) 589-3787. E-mail: Sharon.Papiernik@ars.usda.gov.
† Lithuanian Institute of Agriculture.
‡ North Central Soil Conservation Research Laboratory, U.S. Department of Agriculture Agricultural Research Service.
§ U.S. Department of Agriculture Agricultural Research Service.
|| Vilnius University.

1976 *J. Agric. Food Chem.,* Vol. 57, No. 5, 2009

Sakaliene et al.

Table 1. Characteristics of Soil in Lysimeters

horizon	depth (cm)	pH	CEC (mequiv kg^{-1})	organic carbon (%)	exchangeable acidity (mequiv kg^{-1})	phosphorus (mg of P$_2$O$_5$ kg^{-1})	potassium (mg of K$_2$O kg^{-1})
A	0−22	6.1	79	0.97	10	66	320
A$_1$A$_2$	22−32	5.0	35	0.46	14	28	126
A$_2$B	32−42	4.5	42	0.35	15	30	122
B$_1$	42−55	4.4	72	0.30	16	33	110

pesticides should be conducted simultaneously in the same lysimeters under the same climatic conditions.

Eastern Europe is an important rye-producing region, accounting for 63% of the global rye (*Secale cereale* L.) production (*7*). Lithuania produced 141000 Mg of rye in 2004, ranking 15th among the world's rye producers (*7*). In eastern Europe, rye is planted in the early fall, and fall and spring applications of herbicides are common. Lysimeter experiments are a low-cost approach to evaluating the total pesticide lost for a cropping system with multiple pesticide applications and may be a valuable tool in evaluating herbicide strategies for crop production. In a previous study evaluating the sorption of eight herbicides to representative soils of Lithuania, pendimethalin showed the highest sorption (average K_d of 104 L kg^{-1}) and dicamba the lowest sorption (average K_d of 0.06 L kg^{-1}) (*8*). These herbicides provided benchmarks expected to represent the extremes of herbicide behavior in this 6 year experiment, which used field lysimeters to evaluate the leaching and plant uptake of four herbicides used in rye production. The behavior of fall-applied pendimethalin and mecoprop (MCPP), clopyralid, and dicamba applied in the fall and spring was compared as part of three weed management strategies.

MATERIALS AND METHODS

The experiment was conducted at the Voke Branch of the Lithuanian Institute of Agriculture under natural climatic conditions. Lysimeters (1 m deep, 1.75 m^2 area) were made of reinforced concrete, had a conical bottom, and had a water collection device in the bottom. Lysimeters had a gravel and quartz sand base and were filled to a depth of 0.55 m with a Haplic Luvisol sandy loam soil from a field at the Voke Branch Experiment Station. Soil was collected by horizon, and horizonation was preserved when the lysimeters were packed (**Table 1**). Surface (0−22 cm) soil properties were as follows: pH, 6.1; organic carbon (OC), 0.97%; total nitrogen (N), 0.13%; sand, 53%; silt, 36%; and clay, 11%. Additional selected properties of each soil horizon are given in **Table 1**. Soil properties were determined as follows: pH$_{KCl}$ by potentiometry (*9*), OC by spectrophotometry after sulfochromic oxidation (*10*), total N by Kjeldahl apparatus (*11*), soil texture by the hydrometer method (*12*), exchangeable bases by 0.1 M BaCl$_2$ (1:10) extraction (*13*), and mobile P and K by the Egner−Riem−Domingo method (AL method) (*14*).

Two years prior to the start of the experiment, the soil in the lysimeters was sown with red clover. Starting in 1996, three trials were conducted: trial 1, 1996−1997; trial 2, 1998−1999; and trial 3, 2000−2001. Each trial started with application of herbicide to winter rye in September and lasted 16 months. In each trial, triplicate lysimeters were treated with one of four herbicide combinations: (1) fall application of mecoprop and clopyralid, spring application of dicamba; (2) fall application of pendimethalin, spring application of mecoprop; (3) fall application of dicamba, spring application of clopyralid; and (4) untreated. Dicamba (Banvel, 0.15 kg ha^{-1}, a.i.), mecoprop (Mecoprop, 1.5 kg ha^{-1}, a.i.), and clopyralid (Lontrel, 0.3 kg ha^{-1}, a.i.) were applied at the three- to four-leaf stage (treatments 1−3) for control of annual and perennial broadleaf weeds. Pendimethalin (Stomp, 1.0 kg ha^{-1}, a.i.) was applied preemergent in the fall (treatment 2) for control of annual grasses. Selected properties of these herbicides, which represent four different chemical classes of herbicides, are listed in **Table 2**.

Table 2. Selected Properties of Herbicides Used in This Study

	pendimethalin	mecoprop	clopyralid	dicamba
chemical class	dinitroaniline	aryloxyalkanoic acid	pyridinecarboxylic acid	benzoic acid
log K_{ow}[a]	5.18	0.10 (pH 7)	−1.81 (pH 5)	0.60 (pH 5)
water solubility[a] (g L^{-1})	0.0003	0.73	118 (pH 5)	6.5
DT$_{50}$[a] (days)	90−120	7−13	14−56	<14
K_{oc}[a] (L kg^{-1})		12−25	0.4−12.9	2
K_d (L kg^{-1})	37,[a] 115[b]		0.009−0.094[a]	0.07[b]

[a] Data from ref *30*. [b] Data for this soil from ref *8*.

Herbicides were applied using a backpack sprayer, applying herbicides with 0.5 L of water for each lysimeter. The water application rate was ∼10 times greater than that normally used for large-scale pesticide application but was used to ensure a uniform distribution of herbicide on the soil surface of the lysimeter. The depth of water application was approximately 0.3 mm, which is not expected to significantly alter postapplication herbicide transport compared to the standard water application rate. In 1996, the preplant crop for winter rye was red clover, while in 1998 and 2000, it was a mix of oat and vetch. Preplant crops were physically removed; no herbicides were used on the preplant crops.

Water leached from each lysimeter was collected in 20 L glass bottles. Water collected during the month from the replicate lysimeters was combined and measured, and replicate 3 L samples were removed for herbicide analysis. In the case of insufficient percolated water, samples collected for 2 months were combined for residue determination. Samples were stored at 4 °C until extraction.

Rye was harvested at maturity for residue determination. The aboveground portion of plants in each lysimeter was clipped and separated into stems and grain. Plant material from triplicate lysimeters was combined into one sample for each treatment. Grain and straw were weighed, air-dried, ground in a mill, and stored at −20 °C until they were extracted.

Water Extraction. *Dicamba and 3,6-Dichlorosalicylic Acid (5-hydroxydicamba).* Replicate 3 L leachate samples were filtered, acidified to pH 2 with concentrated H$_2$SO$_4$, and extracted by liquid−liquid extraction, once with 300 mL and twice with 150 mL of diethyl ether. Combined ether extracts were dried by being passed through anhydrous Na$_2$SO$_4$ and then evaporated at 35 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream. A diazomethane/ether solution (5 mL) was added to derivatize dicamba to 3,6-dichloro-2-methoxybenzoic acid methyl ester. Derivatization of analytical standards and samples was performed at the same time.

Pendimethalin. Replicate 3 L leachate samples were filtered, acidified by adding 60 mL of 1.0 M HCl, and extracted three times by liquid−liquid extraction with 120 mL of *n*-hexane. The combined extracts were dried with anhydrous Na$_2$SO$_4$ and then evaporated at 45 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream and then dissolved in 2.0 mL of toluene.

Clopyralid. Replicate 3 L leachate samples were filtered, acidified to 1−2 pH with concentrated H$_2$SO$_4$, and extracted by liquid−liquid extraction, once with 300 mL and twice with 50 mL of ethyl acetate. Combined extracts were dried with anhydrous Na$_2$SO$_4$, and the sample was then evaporated at 40 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream. We derivatized clopyralid to the ethyl ester of 3,6-
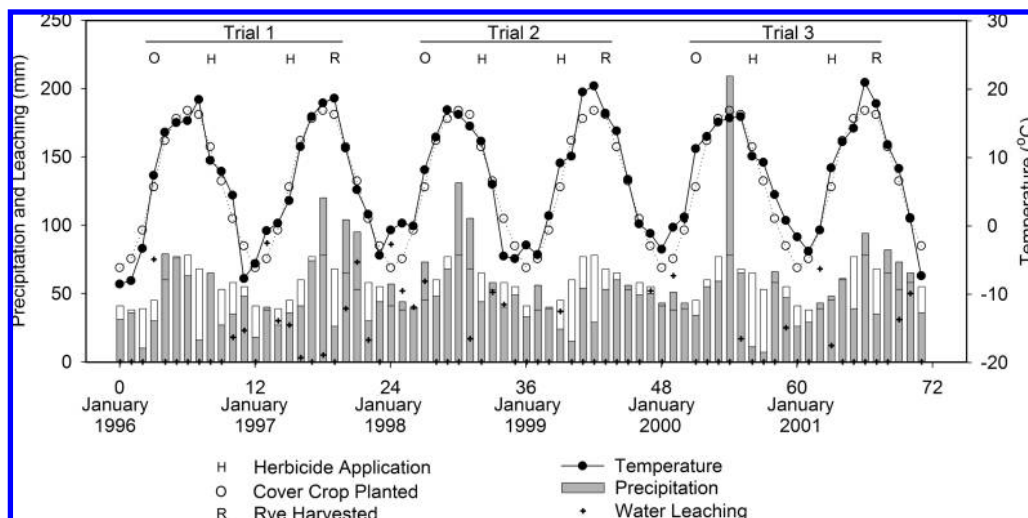
Figure 1. Precipitation (shaded bars) and air temperature (shaded symbols) during the experiment compared to the long-term average precipitation (white bars) and air temperature (white symbols). Approximate timing of field operations is indicated.

dichloropicolinic acid by adding 1.0 mL of concentrated H_2SO_4 and 5.0 mL of ethanol, slightly shaking the solution, and then heating the sample for 15 min at 70 °C in a water bath. The solution was then cooled to room temperature, and after the sample had been slightly shaken with 1.0 mL of *n*-hexane, the aqueous and organic phases were separated and the organic phase was retained for analysis. Derivatization of analytical standards and samples was performed at the same time.

Mecoprop. Replicate 3 L leachate samples were filtered, acidified to pH 1 with 5 mL of 24% H_2SO_4, and extracted by liquid−liquid extraction, once with 100 mL and twice with 50 mL of dichloromethane. Extracts were combined, and 100 mL of 1% NaOH was added. After the sample had been shaken, the organic phase was removed and saved. The alkaline water phase was acidified to pH 1−2 with 2 mL of 24% H_2SO_4 and then extracted twice with 40 mL of dichloromethane. Both organic phases were combined, dried using anhydrous Na_2SO_4, filtered, and evaporated at 30 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream. Then 2-(4-chloro-2-methylphenoxy)propionic acid was derivatized to the methyl ester with a diazomethane/ether solution. Derivatization of analytical standards and samples was performed at the same time.

Biomass Extraction. *Dicamba and 3,6-Dichlorosalicylic Acid (5-hydroxydicamba).* Straw or grain (10 g) was extracted by being shaken for 1 h with 40 mL of 80% methanol in water. After removal of the solvent, each sample was extracted again by being shaken for 20 min with 20 mL of 80% methanol in water. Methanol was evaporated from the combined extracts and the remaining water processed as described in Water Extraction.

Pendimethalin. Straw or grain (20 g) was extracted first by being shaken with 50 mL of acidic methanol (20 mL of HCl in 1 L of methanol) for 1 h. After removal of the supernatant, the plant material was extracted a second time with 30 mL of acidic methanol. The plant material was washed with 20 mL of acidic methanol; the combined extracts were partitioned three times with 30 mL of *n*-hexane, and the combined hexane extracts were dried with anhydrous Na_2SO_4. Two drops of 1% polyethylene glycol 600 in acetone was added to each sample. Samples were evaporated to ∼0.5−1.0 mL using a vacuum rotary evaporator at 45 °C and then evaporated just to dryness with an air stream. Each sample was dissolved in 5 mL of *n*-hexane and quantitatively transferred to a Florisil column. Pendimethalin was eluted with 50 mL of an *n*-hexane/toluene mixture (80:20, v:v). Polyethylene glycol PEG (3 drops) was added to the eluant. Each sample was evaporated to ∼1 mL using a vacuum rotary evaporator and then just to dryness with an air stream. The contents of the flask were then dissolved in 2 mL of toluene.

Clopyralid. To 20 g of homogenized plant material were added 100 mL of 1 N NaCl and 3 mL of 0.1 N NaOH. After being shaken for 1 h using a horizontal shaker, the samples were centrifuged at 3000 rpm for 30 min. The aqueous phase was removed, and plant material was

extracted a second time using the same procedure. Supernatants were combined and acidified to pH <2 with 50% H_2SO_4 and then extracted three times with 3.0 mL of ethyl acetate by liquid−liquid extraction. The combined extracts were dried with anhydrous Na_2SO_4, and the sample was evaporated at 40 °C to ∼0.5−1.0 mL using a vacuum rotary evaporator. The remaining solution was evaporated just to dryness with an air stream. Derviatization was performed as described above in Water Extraction.

Mecoprop. Grain or straw (20 g) was shaken with 150 mL of an aqueous 0.1 M KOH solution for 30 min. Alkaline extracts (100 mL) were acidified with 1 mL of concentrated H_2SO_4 and processed as described in Water Extraction.

Analysis. Derivatization of analytical standards and samples was performed at the same time. Gas liquid chromatographic analyses of herbicide residues were performed using a Hewlett-Packard model 5890 instrument, equipped with an electron capture detector and a 30 m long × 0.32 mm diameter × 0.25 μm film thickness 5% phenylmethyl silicone (HP-5) column. The carrier gas (N_2) flow rate was 35 mL min^{-1}. Mecoprop analysis used an injection port temperature of 230 °C, a detector temperature of 250 °C, and an oven temperature of 200 °C. The retention time of 2-(4-chloro-2-methylphenoxy)propionic acid methyl ester was 7.6−7.9 min. Clopyralid analysis used an injection port temperature of 220 °C, a detector temperature of 240 °C, and an oven temperature starting at 70 °C, followed by an increase of 30 °C min^{-1} to 180 °C, held for 10 min. The retention time of the ester of 3,6-dichloropicolinic acid was 6.5−7.8 min. Pendimethalin analysis used an injection port temperature of 225 °C, a detector temperature of 250 °C, and an oven temperature beginning at 120 °C, followed by an increase of 30 °C min^{-1} to 195 °C, held for 22 min. The retention time of pendimethalin was 19.1−20.2 min. Analyses of dicamba and 3,6-dichlorosalicylic acid used an injection port temperature of 250 °C, a detector temperature of 300 °C, and an initial oven temperature of 120 °C, followed by an increase of 30 °C min^{-1} to 200 °C, held for 10 min. Retention times were 5.5−5.7 min for 3,6-dichloro-2-methoxybenzoic acid methyl ester and 8.8−8.9 min for 5-hydroxy-3,6-dichloro-2-methoxybenzoic acid methyl ester. Quantitation used external standards. The limit of quantitation (LOQ) in plant material was 0.005 mg kg^{-1} for each herbicide; the LOQ values in water were 0.05 μg L^{-1} for clopyralid, 0.03 μg L^{-1} for pendimethalin, 0.03 μg L^{-1} for mecoprop, 0.01 μg L^{-1} for dicamba, and 0.05 μg L^{-1} for 3,6-dichlorosalicylic acid. Recoveries of all compounds ranged from 85 to 102%.

RESULTS AND DISCUSSION

Weather Conditions. Annual and monthly precipitation was extremely variable during the 6 years of the experiment (**Figure 1**). Precipitation was greatest in 1998 (757 mm) and was 80

mm greater than the long-term annual average. Precipitation was lowest in 1996 (516 mm) and in 1999 (519 mm), approximately 160 mm less than the long-term average. July was particularly wet in 1997, 1998, and 2000. Spring and summer precipitation was high in 1998 and low in 1999; fall precipitation was high in 1997 and low in 2000. Temperatures were less variable from year to year and were generally similar to the long-term average (**Figure 1**).

Leaching. *Water.* During the 6 years of the experiment, the amount of leachate varied by a factor of 3, with the greatest amount of leachate in 1998 (347 mm, 46% of the precipitation for the year) and the smallest amount of leachate in 1999 (89 mm, 17% of the yearly rainfall) (**Figure 1**). Water leached during the height of the growing season (May to September) was not measurable in three of the six years of the experiment and was <50 mm in all years, amounting to <15% of the precipitation occurring during this time. Most of the water leaching occurred between harvest and planting, which is common under nothern European conditions (*15*). In each calendar year, the amount of leachate in the first collection exceeded the amount of precipitation occurring that month.

Fall-Applied Herbicides. Detectable concentrations of herbicides occurred in leachate in the fall and winter, but concentrations of fall-applied herbicides in leachate were usually greatest the following spring (**Figure 2**). In trial 1, the first leachate (collected in November and December 1996) accounted for approximately one-fourth of the total amount of mecoprop and dicamba leached on a mass basis, but very little of the total clopyralid mass leached (**Figure 3A**). The largest leaching loss on a mass basis occurred in February for clopyralid and pendimethalin and in March or April for mecoprop, dicamba, and dicamba's 3,6-dichlorosalicylic acid metabolite. Throughout the growing season, leaching of the parent compound accounted for <0.1% of the applied mecoprop and pendimethalin and ~1−3% of the applied dicamba and clopyralid. Some leaching of 3,6-dichlorosalicylic acid was observed, but its contribution was smaller than that of the parent compound (**Figures 2A** and **3A**). Similar clopyralid concentrations in leachate and cumulative mass loss (1.5% of applied) have been observed following fall application of clopyralid with frequent irrigation (*16*).

In trial 2, leachate was collected in the first 2 months after application, and not again until the following April (**Figure 2B**). Fall leaching accounted for most of the total leaching loss of pendimethalin and dicamba in trial 2; leaching losses were <0.1% of the applied mass for these herbicides (**Figure 3B**). Leaching of mecoprop and clopyralid was greatest in April on both a concentration basis and a mass basis, and leaching totaled ~0.4% of the amount applied (**Figures 2B** and **3B**). Studies in Denmark also showed little leaching of fall-applied mecoprop, with low concentrations reported in December leachate and maximum concentrations in February of the following year (*17*).

Water leaching in trial 3 followed the same general pattern as in trial 2: leachate was collected in December, and not again until March and April of the following year (**Figure 2C**). The highest concentrations of mecoprop, clopyralid, and dicamba observed during the 6 year study were recorded in the March/ April 2001 leachate (**Figure 3C**). These high concentrations resulted in the greatest herbicide leaching losses observed during the 6 year study: mass losses exceeded 20% of the applied clopyralid but were <2% for the other herbicide parent compounds and degradation product (**Figure 3C**).

Pendimethalin is classified as very immobile in this soil (*8*), but low concentrations of pendimethalin were detected in leachate (**Figure 2**). Previous research has found low concentra-
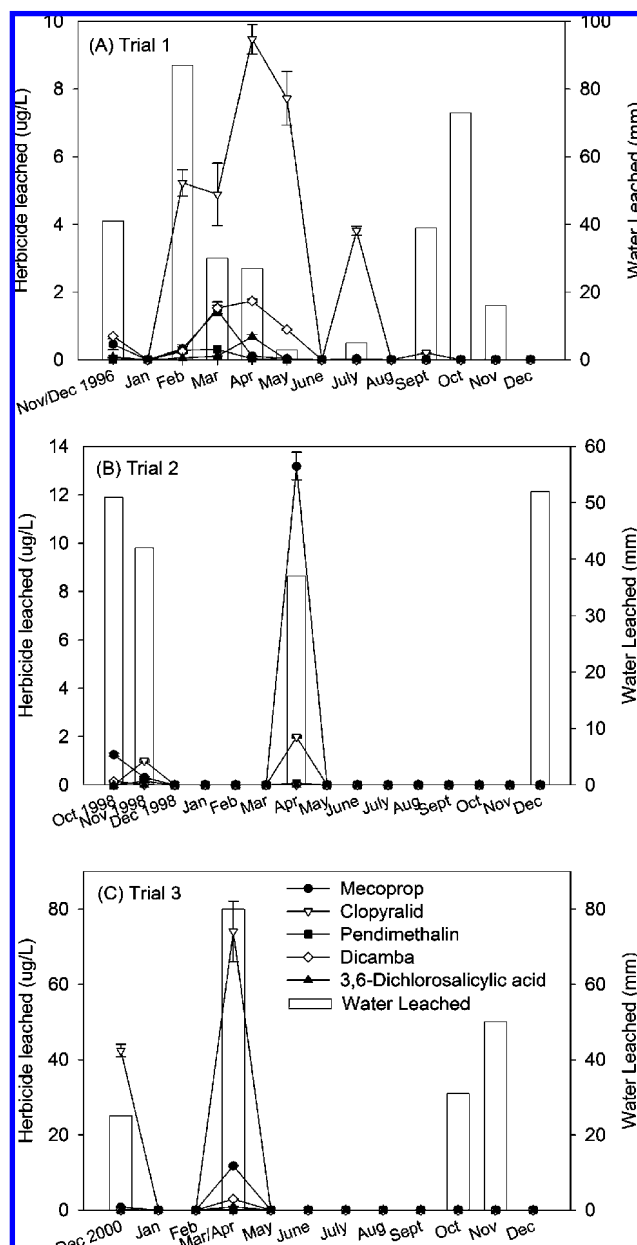

Figure 2. Leaching of water and fall-applied herbicides as a function of time: (**A**) trial 1, 1996−1997; (**B**) trial 2, 1998−1999; and (**C**) trial 3, 2000−2001.

tions of pendimethalin in leachate from soil columns (*18*) and tile drainage (*19*), with leaching accounting for <0.2% of the applied pendimethalin, consistent with our results.

Spring-Applied Herbicides. Herbicides were applied at the same rate in the fall and spring; however, no mecoprop was detected in leachate following spring application, and concentrations of clopyralid were much lower than those observed for fall application (**Figure 4**). An increased level of evapotranspiration is expected to be the primary reason for the markedly lower leaching losses of spring-applied compared to fall-applied herbicides.

Trial 1 was the only spring application trial with a significant amount of water leached during the summer months. As we observed for fall application (trial 1, **Figure 2A**), the maximum concentration of clopyralid in leachate occurred earlier than the maximum concentrations of dicamba and 3,6-dichlorosalicylic acid (**Figure 4A**). Leaching accounted for <0.1% of the applied mass of clopyralid and dicamba (**Figure 5A**). In another
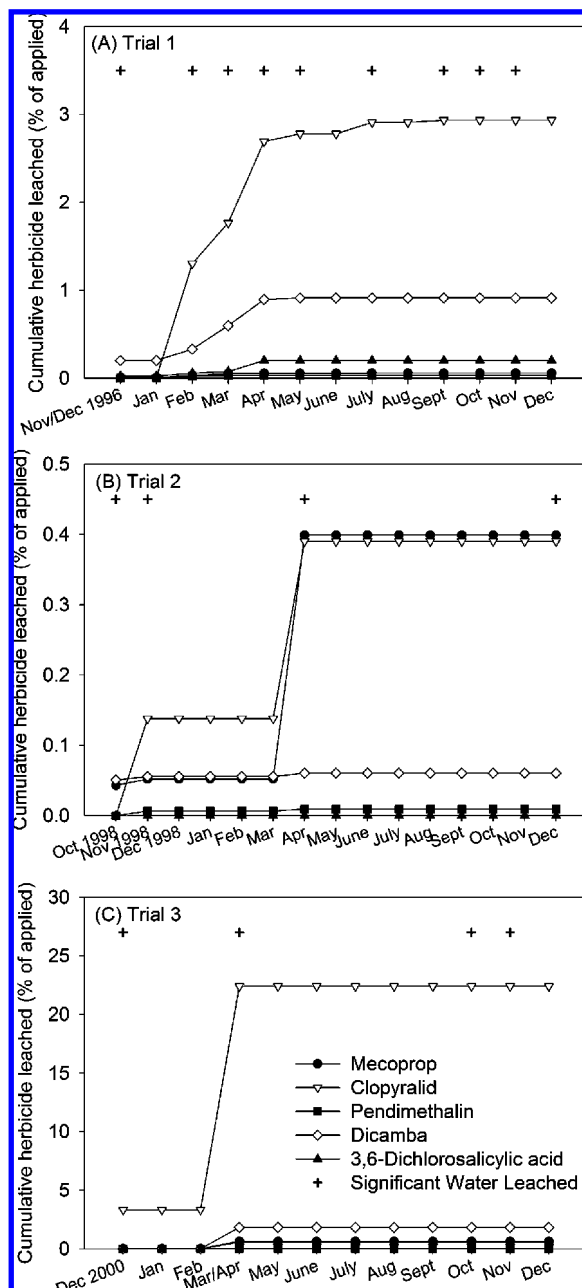
Relative Mobility of Four Herbicides

J. Agric. Food Chem., Vol. 57, No. 5, 2009 **1979**

Figure 3. Cumulative leaching of fall-applied herbicides: (**A**) trial 1, 1996–1997; (**B**) trial 2, 1998–1999; and (**C**) trial 3, 2000–2001.

Figure 4. Leaching of water and spring-applied herbicides as a function of time: (**A**) trial 1, 1997; (**B**) trial 2, 1999; and (**C**) trial 3, 2001.

lysimeter study with overall precipitation and leachate amounts similar to those from our trial 1, no clopyralid was detected in leachate during the 11 month period following spring application (*20*).

Summer rainfall was below normal in 1999, during trial 2 (**Figure 1**), and no leachate was recorded until December. No herbicides were detected in that leachate (**Figure 4B**). The highest concentrations and the greatest leaching losses of spring-applied herbicides were observed in trial 3, when leaching occurred in only October and November (**Figure 4C**), but leaching losses still accounted for <1% of the applied clopyralid and dicamba (**Figure 5C**). October/November leaching in trial 3 followed a summer with below-normal rainfall and no leaching events from May to September. Lysimeter studies conducted in Sweden demonstrated similar trends: clopyralid was detected in only one leachate sample following spring application, when significant rainfall occurred after a dry period (*21*). Leaching
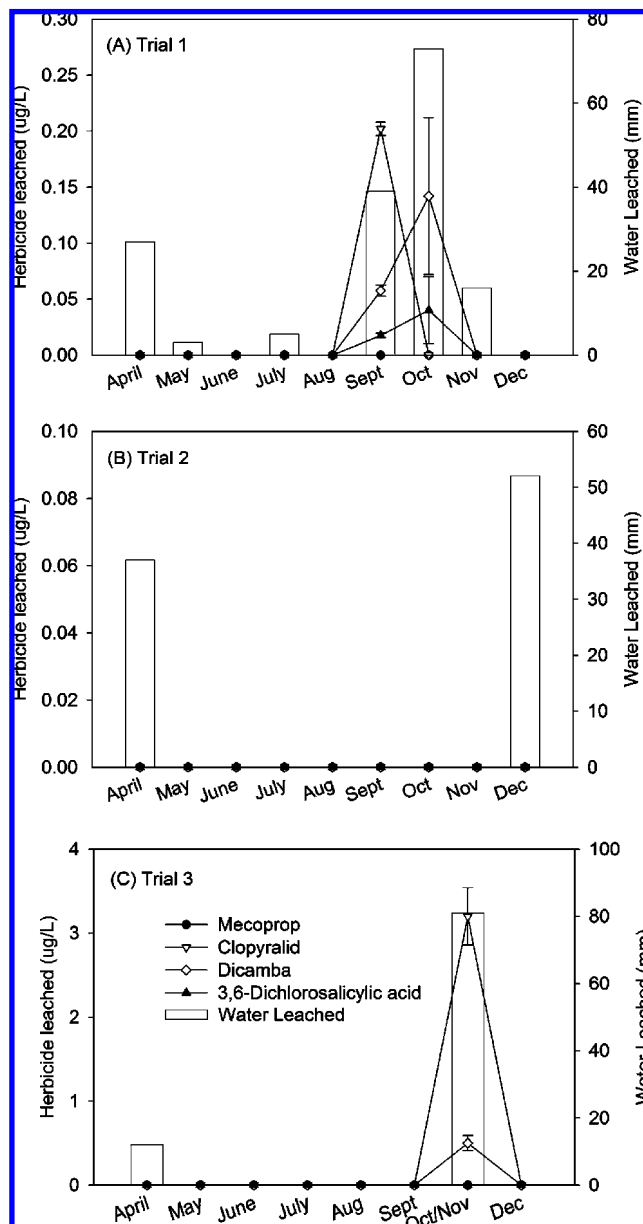
of dicamba >6 months after spring application has also been observed previously (*22, 23*).

Whereas we observed no detectable mecoprop in leachate following spring application, others have reported low concentrations of mecoprop in leachate following spring application (*17*). Other reports of clopyralid (*24, 25*) and dicamba (*22, 23, 26*) concentrations in leachate at depths of ≥50 cm following spring herbicide application are also consistent with our observations. In addition, previous studies showed that leaching to depths of >50 cm accounted for <1% of the mass of dicamba applied in spring to conventionally tilled soil (*23, 27*). Our results indicated that <1% of the applied mass of spring-applied mecoprop, clopyralid, and dicamba leached during each of three seasons in soil cropped to rye.

Comparative Mobility. Sorption studies showed that pendimethalin has a high sorption coefficient in this soil, and dicamba a low sorption coefficient (**Table 2**). Pendimethalin showed an expected low mobility in soil in these lysimeter experiments, with leaching losses accounting for <0.05% of the fall-applied pendimethalin in each of the three trials (**Figure**
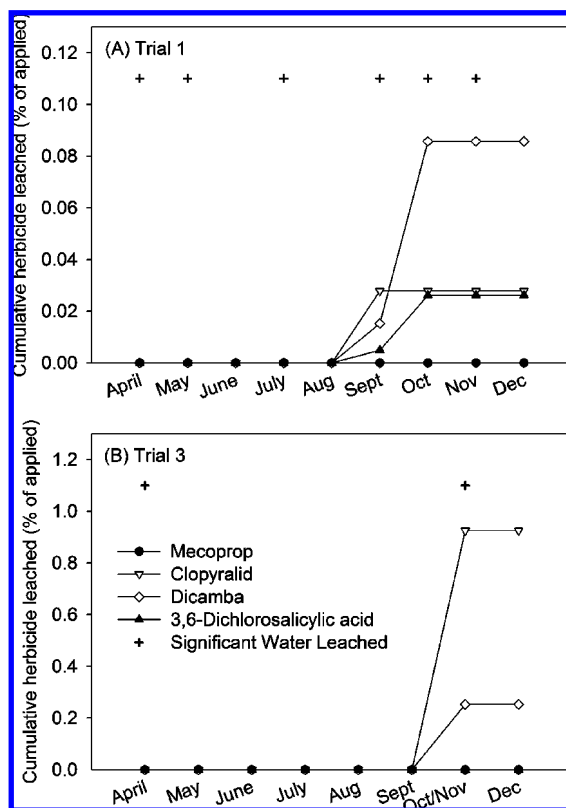
Figure 5. Cumulative leaching of spring-applied herbicides: (**A**) trial 1, 1997; and (**B**) trial 3, 2001. No herbicide leaching was observed for spring-applied herbicides in trial 2 (1999).

Table 3. Residues (milligrams per kilogram) of Spring-Applied Herbicides in Rye Grain and Straw

herbicide		grain	straw	leaching
	1997			
mecoprop	concentration (mg kg^{-1})	ND^a	ND^a	ND^a
clopyralid	concentration (mg kg^{-1})	0.007	0.047	—
	% of applied	0.006	0.09	0.03
dicamba	concentration (mg kg^{-1})	0.006	0.027	—
	% of applied	0.006	0.07	0.09
3,6-dichlorosalicylic acid	concentration (mg kg^{-1})	ND^a	ND^a	—
	% of applied^b			0.03
	1999			
mecoprop	concentration (mg kg^{-1})	ND^a	ND^a	ND^a
clopyralid	concentration (mg kg^{-1})	0.008	0.053	ND^a
	% of applied	0.009	0.09	
dicamba	concentration (mg kg^{-1})	0.016	0.010	ND^a
	% of applied	0.02	0.12	
3,6-dichlorosalicylic acid	concentration (mg kg^{-1})	0.010	ND^a	ND^a
	% of applied^b	0.02		

^{a} Not detected; the limit of quantitation was 0.005 mg kg^{-1}. ^{b} % of applied dicamba.

3). Leaching losses of dicamba were also quite low following both fall and spring application (**Figures 3** and **5**) despite its predicted high mobility, perhaps due to its relatively short half-life in soil. The greatest loss through leaching on a mass basis was observed for fall-applied clopyralid (**Figure 3**), which has a water solubility greater than that of dicamba but a longer persistence (**Table 2**). In these studies, leaching losses of mecoprop were smaller than losses of dicamba for both fall and spring applications (**Figures 3** and **5**), except following fall application in trial 2, when high mecoprop concentrations were observed in April (**Figure 2B**).

Mass loss through leaching of pendimethalin, mecoprop, and dicamba was <3% of the amount applied for both fall and spring trials. Mass loss through leaching of clopyralid was <3% of the amount applied except for one season, in which sporadic leaching resulted in a >20% loss of the fall-applied clopyralid. On the basis of this 6 year experiment, it appears that clopyralid is the most mobile of the tested herbicides in this soil, followed by dicamba, mecoprop, and pendimethalin.

Herbicide Residues in Rye Straw and Grain. In addition to being used to compare leaching behavior of herbicides under different weed management strategies, field lysimeters can be used to evaluate plant uptake of herbicides. The herbicide treatments used in these lysimeter studies did not significantly affect the yields of rye straw and grain (data not shown). No residues of the four fall-applied herbicides were detected (LOQ = 0.005 mg kg^{-1}) in the grain or straw of winter rye 10 months after fall herbicide application in both trials 1 and 2.

No residues of spring-applied mecoprop were detected in the rye grain or straw 4 months after application in both trials 1 and 2 (**Table 3**). In contrast, clopyralid and dicamba were detected in small amounts in straw (≤0.05 mg kg^{-1}) and grain (<0.02 mg kg^{-1}) following spring application in both trials 1

and 2. 3,6-Dichlorosalicylic acid was detected in grain (0.01 mg kg^{-1}) after spring application of dicamba in trial 2 (**Table 3**).

The levels of herbicide residues detected in rye in these studies were well below tolerances established by the European Union and the United States. In the European Union, maximum concentrations of 0.5 mg kg^{-1} of dicamba and 5 mg kg^{-1} of clopyralid are allowed in rye for human consumption (*28*). No specific guidelines are available for rye in the United States, but food and feed tolerances in the grain and straw of other cereal grains are at least 0.5 mg kg^{-1} for dicamba plus 3,6-dichlorosalicylic acid and 1 mg kg^{-1} for clopyralid (*29*). These results suggest that under typical conditions, fall application of pendimethalin (1.0 kg ha^{-1}) and fall or spring application of mecoprop (1.5 kg ha^{-1}), clopyralid (0.3 kg ha^{-1}), and dicamba (0.15 kg ha^{-1}) is not expected to result in unacceptably high concentrations of these herbicides in rye grain or straw.

In these experiments, concentrations exceeding the EU drinking water limit of 0.1 μg L^{-1} were measured in at least one sampling event for each of the four fall-applied herbicides (**Figure 2**) and two of the three spring-applied herbicides (**Figure 4**). On the basis of these data, it appears that further investigation of the fate of these herbicides in rye production systems is required. Other factors should also be considered for a complete assessment of herbicide management strategies. For instance, herbicide management should be responsive to risk assessments that evaluate nontarget toxicity, food tolerances for vulnerable populations, development of herbicide-resistant weeds, herbicide transport under conditions favoring preferential flow (for example, cracking soils), the effect of severe storms on herbicide transport, and other factors. The use of field lysimeters can be an important tool in evaluating many of these factors under realistic soil, cropping, and climatic conditions.

LITERATURE CITED

(1) Gilliom, R. J.; Barbash, J. E.; Kolpin, D. W.; Larson, S. J. Testing water quality for pesticide pollution. *Environ. Sci. Technol.* **1999**, *33*, 164A–169A.

(2) Scheidleder, A.; Grath, J.; Winkler, G.; Stärk, U.; Koreimann, C.; Gmeiner, C.; Nixon, S.; Casillas, J.; Gravesen, P.; Leonard, J.; Elvira, M. Pressures on Groundwater Quality. Groundwater quality and quantity in Europe, Environmental Assessment Report 3; European Environment Agency: Copenhagen, 1999; pp 18–38.

Relative Mobility of Four Herbicides

J. Agric. Food Chem., Vol. 57, No. 5, 2009 **1981**

(3) Führ, F.; Burauel, P.; Dust, M.; Mittelstaedt, W.; Pütz, T.; Reinken, G.; Stork, A. Comprehensive tracer studies on the environmental behavior of pesticides: The lysimeter concept. In *The Lysimeter Concept: Environmental Behavior of Pesticides*; Führ, F., Hance, R. J., Plimmer, J. R., Nelson, J. O., Eds.; ACS Symposium Series 699; American Chemical Society: Washington, DC, 1998; pp 1−20.

(4) Boesten, J. J. T. I. Simulation of pesticide leaching in the field and in zero-tension lysimeters. *Vadose Zone J.* **2007**, *6*, 793–804.

(5) Nolting, H.-G.; Schinkel, K. Lysimeter data in pesticide authorization. In *The Lysimeter Concept: Environmental Behavior of Pesticides*; Führ, F., Hance, R. J., Plimmer, J. R., Nelson, J. O., Eds.; ACS Symposium Series 699; American Chemical Society: Washington, DC, 1998; pp 238−245.

(6) Flury, M.; Yates, M. V.; Jury, W. A.; Anderson, D. L. Variability of solute transport in field lysimeters. In *The Lysimeter Concept: Environmental Behavior of Pesticides*; Führ, F., Hance, R. J., Plimmer, J. R., Nelson, J. O., Eds.; ACS Symposium Series 699; American Chemical Society: Washington, DC, 1998; pp 65−75.

(7) *FAO Statistical Yearbook 2004*; Food and Agriculture Organization of the United Nations: Rome, 2006; Vol. 1/1.

(8) Sakaliene, O.; Papiernik, S. K.; Koskinen, W. C.; Spokas, K. A. Sorption and predicted mobility of herbicides in Baltic soils. *J. Environ. Sci. Health, Part B* **2007**, *42*, 641–647.

(9) International Organization for Standardization (ISO) 10390. Soil Quality−Determination of pH; International Organization for Standardization: Geneva, 1994.

(10) International Organization for Standardization (ISO) 14235. Soil Quality−Determination of organic carbon by sulfochromic oxidation; International Organization for Standardization: Geneva, 1998.

(11) International Organization for Standardization (ISO) 11261. Soil Quality−Determination of total nitrogen: Modified Kjeldahl method; International Organization for Standardization: Geneva, 1995.

(12) Gee, G. W.; Bauder, J. W. Particle-size analysis. In *Methods of soil analysis. Part 1. Physical and mineralogical methods*, 2nd ed.; Klute, A., Ed.; American Society of Agronomy: Madison, WI, 1986; pp 383−409.

(13) International Organization for Standardization (ISO) 11260. Soil Quality−Determination of effective cation exchange capacity and base satuation level using barium chloride solution; International Organization for Standardization: Geneva, 1994.

(14) State Standards of the Russian Federation (GOST) 26208-91: Soils. Determination of mobile compounds of phoshorus and potassium by Wegner-Riem-Domingo method (AL-method); Standards Publishing House: Moscow, 1993.

(15) Thornthwaite, C. W.; Mather, J. R. The role of evapotranspiration in climate. *Theor. Appl. Climatol.* **1951**, *3*, 16–39.

(16) Elliott, J. A.; Cessna, A. J.; Best, K. B.; Nicholaichuk, W.; Tollefson, L. C. Leaching and preferential flow of clopyralid under irrigation: Field observations and simulation modeling. *J. Environ. Qual.* **1998**, *27*, 124–131.

(17) Felding, G. Leaching of phenoxyalkanoic acid herbicides from farmland. *Sci. Total Environ.* **1995**, *168*, 11–18.

(18) Starrett, S. K.; Christians, N. E.; Al Austin, T. Movement of pesticides under two irrigation regimes applied to turfgrass. *J. Environ. Qual.* **1996**, *25*, 566–571.

(19) Petersen, C. T.; Holm, J.; Koch, C. B.; Jensen, H. E.; Hansen, S. Movement of pendimethalin, ioxynil and soil particles to field drainage tiles. *Pest Manage. Sci.* **2002**, *59*, 85–96.

(20) Bergström, L.; Shirmohammadi, A. A review of herbicide leaching studies in Sweden: Field, lysimeter, and laboratory measurements. In *The Lysimeter Concept: Environmental Behavior of Pesticides*; Führ, F., Hance, R. J., Plimmer, J. R., Nelson, J. O., Eds.; ACS Symposium Series 699; American Chemical Society: Washington, DC, 1998; pp 76−87.

(21) Bergström, L.; McGibbon, A.; Day, S.; Snel, M. Leaching potential and decomposition of clopyralid in Swedish soils under field conditions. *Environ. Toxicol. Chem.* **1991**, *10*, 563–571.

(22) Glass, R. L.; Edwards, W. M. Dicamba in lysimeter runoff and percolation water. *J. Agric. Food Chem.* **1979**, *27*, 908–909.

(23) Hall, J. K.; Mumma, R. O. Dicamba mobility in conventionally tilled and non-tilled soil. *Soil Tillage Res.* **1994**, *30*, 3–17.

(24) Bovey, R. W.; Richardson, C. W. Dissipation of clopyralid and picloram in soil and seep flow in the Blacklands of Texas. *J. Environ. Qual.* **1991**, *20*, 528–531.

(25) Berisford, Y. C.; Bush, P. B.; Taylor, J. W., Jr. Leaching and persistence of herbicides for kudzu (Pueraria Montana) control on pine regeneration sites. *Weed Sci.* **2006**, *54*, 391–400.

(26) Zhang, R.; Krzyszowska-Waitkus, A. J.; Vance, G. F.; Qi, J. Pesticide transport in field soils. *Adv. Environ. Res.* **2000**, *4*, 59–68.

(27) Koskinen, W. C.; Sorenson, B. A.; Buhler, D. D.; Wyse, D. L.; Strand, E. A.; Leuschen, W. E.; Jorgenson, M. D.; Cheng, H. H. Use of field lysimeters to determine ^{14}C-dicamba persistence and movement in soil. In *The Lysimeter Concept: Environmental Behavior of Pesticides*; Führ, F., Hance, R. J., Plimmer, J. R., Nelson, J. O., Eds.; ACS Symposium Series 699; American Chemical Society: Washington, DC, 1998; pp 115−121.

(28) Maximum residue levels of pesticides in or on food and feed of plant and animal origin. Regulation (EC) No. 396/2005 of the European Parliament and of the Council, 2005.

(29) Tolerances and exemptions from tolerances for pesticide chemicals in food. *Code of Federal Regulations*; Title 40, Chapter 1, Part 180, 2007.

(30) *The Pesticide Manual*, 10th ed.; Tomlin, C., Ed.; BCPC: Farham, U.K., 1994.