

Sorption and predicted mobility of herbicides in Baltic soils

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This study was undertaken to determine sorption coefficients of eight herbicides (alachlor, amitrole, atrazine, simazine, dicamba, imazamox, imazethapyr, and pendimethalin) to seven agricultural soils from sites throughout Lithuania. The measured sorption coefficients were used to predict the susceptibility of these herbicides to leach to groundwater. Soil-water partitioning coefficients were measured in batch equilibrium studies using radiolabeled herbicides. In most soils, sorption followed the general trend pendimethalin>alachlor>atrazine~amitrole~simazine>imazethapyr>imazamox>dicamba, consistent with the trends in hydrophobicity (log K_{ow}) except in the case of amitrole. For several herbicides, sorption coefficients and calculated retardation factors were lowest (predicted to be most susceptible to leaching) in a soil of intermediate organic carbon content and sand content. Calculated herbicide retardation factors were high for soils with high organic carbon contents. Estimated leaching times under saturated conditions, assuming no herbicide degradation and no preferential water flow, were more strongly affected by soil textural effects on predicted water flow than by herbicide sorption effects. All herbicides were predicted to be slowest to leach in soils with high clay and low sand contents, and fastest to leach in soils with high sand content and low organic matter content. Herbicide management is important to the continued increase in agricultural production and profitability in the Baltic region, and these results will be useful in identifying critical areas requiring improved management practices to reduce water contamination by pesticides.

Keywords: Alachlor; amitrole; atrazine; dicamba; imazamox; imazethapyr; pendimethalin; simazine; adsorption.

Introduction

Sorption of pesticides to soil controls the pest-control efficacy and environmental fate of pesticides, including the availability of pesticides for microbial degradation and offsite transport by leaching, runoff, and volatilization. Extensive use of pesticides in production agriculture has resulted in their widespread occurrence in surface and ground waters. In areas subject to extensive monitoring, such as the United States and Western Europe, surface and ground waters are found to be widely contaminated with low concentrations of a variety of pesticides.^[1,2] In both the United States and Europe, *s*-triazine herbicides and their degradation products are common contaminants of ground water resources.^[2,3]

Little information is available in the peer-reviewed literature regarding pesticide fate in soils of the Baltic region. A limited survey of Lithuanian water resources conducted in cooperation with the United States Environmental Protection Agency found the insecticide lindane and the herbi-

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cides atrazine, desmetryn, dichlorprop, lenacil, prometryn, propazine, and simazine in ground water; this survey also found the herbicide alachlor in surface water. [4] Herbicides, including atrazine and simazine, have been measured in surface water in Poland and in the southern Baltic Sea. [5]

Measurements of pesticide sorption are required to predict movement of pesticides following application. Transport models, including GLEAMS (Groundwater Loading Effects of Agricultural Management Systems), LEACHM (Leaching Estimation and Chemistry Model), and Hydrus, typically use equilibrium sorption estimates (K_d) or sorption coefficients normalized to the organic carbon content of the soil (Koc) to describe pesticide retention by soil.^[6] Accuracy of sorption estimates can be more important than the model choice in accurately simulating pesticide leaching, [6] which emphasizes the need for evaluating pesticide sorption under local conditions. This study was conducted to evaluate the sorption of eight herbicides including alachlor (2-chloro-2',6'-diethyl-Nmethoxymethylacetanilide), amitrole (1H-1,2,4-triazol-3-amine), atrazine (6-chloro-N-ethyl-N'-isopropyl-1,3,5triazine-2,4-diamine), simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine), dicamba (3,6-dichloro-2-methoxybenzoic acid), imazamox (2-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methoxymethylnicotinic

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Table 1. Selected properties of soils used in this study: seven Baltic soils collected from throughout Lithuania						
Location	Texture	pH	Organic carbon (weight %)	Sand (%)	Silt (%)	

Location	Texture	pH	Organic carbon (weight %)	Sand (%)	Silt (%)	Clay (%)
Dotnuva	Sandy loam	7.2	2.48	55.8	25.0	19.2
Joniskelis	Silty clay	6.9	1.36	9.5	48.4	42.1
Perloja	Sandy loam	5.8	0.95	59.8	30.4	9.8
Rumokai	Clav	6.5	2.24	27.3	27	45.6
Rumokai IX	Silt loam	6.2	1.4	30.6	50.2	19.2
Traku Voke	Sandy loam	6.1	1.1	53.4	35.5	11.1
Vezaiciai	Loam	5.7	1.37	40.7	38.1	21.2

acid), imazethapyr (5-ethyl-2-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]nicotinic acid), and pendimethalin (N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine). To seven agricultural soils of Lithuania. These herbicides are representative of six chemical classes and are in common use in Lithuania and throughout the Baltic region. The measured sorption coefficients were used to predict the potential mobility of each herbicide in these soils.

Materials and methods

Soils

Soils were collected from agricultural fields throughout Lithuania at sampling sites indicated in Figure 1. Samples were collected from the surface 20 cm, air dried, and sieved to <2 mm. Selected soil properties of each soil are given in Table 1. Soil pH was measured in 1:1 (w:w) soil:0.01 M CaCl₂ solution. Organic carbon content was measured using a modified Walkley Black method. [7] Proportions of sand, silt, and clay were determined by the hydrometer method.[8]

Chemicals

Eight herbicides from six chemical classes were used in this study. Selected properties of these herbicides are listed



Fig. 1. Sampling sites in Lithuania.

in Table 2. Unlabeled analytical chemicals (>98% purity) were obtained from Chem Service, Inc. (West Chester, PA). Radiolabeled (UL-ring-14C) compounds were obtained from Pathfinder Laboratories (St. Louis, MO) (alachlor, atrazine, and dicamba), American Cyanamid (Princeton, NJ) (imazamox, imazethapyr, and pendimethalin), Geigy Research Laboratories (Yonkers, NY) (simazine), and Rhone Poulenc (Research Triangle Park, NC) (amitrole). Specific activities ranged from 100 to 999 kBq mmol⁻¹ and all radiopurities were > 97%. Herbicide solutions (1 mg L^{-1}) were prepared in 0.01 M CaCl₂. Final solution activities ranged from 1600 to 5980 dpm mL^{-1} .

Sorption

Solution (10 mL) containing 1 mg L^{-1} of a single herbicide was added to triplicate soil samples (5 g dry weight) in 50mL centrifuge tubes. Dicamba is weakly sorbed, and 10 g of soil was spiked with 10 mL of solution to increase the proportion of dicamba removed from solution in an attempt to improve the precision of the sorption estimate. Tubes were capped with a Teflon-lined cover. Vials with no soil served as controls to evaluate sorption to glassware. Samples were agitated using a vortex mixer and placed on a horizontal shaker for 24 h. Equilibrated samples were centrifuged for 30 min at 2000 rpm (478 × g). A 1-mL aliquot of the supernatant was transferred to a scintillation vial containing 5 mL of Ecolite scintillation cocktail (MP Biomedicals, Solon, OH). Vials were shaken for 20 s, and stored in the dark for 24 h before counting radioactivity using a Packard 1500 Tri-Carb liquid scintillation analyzer.

The difference between the solution activity prior to its addition to soil and the activity after equilibration with soil was attributed to sorption. A sorption coefficient (K_d, L kg⁻¹) was calculated for each herbicide-soil combination

$$K_{d} = \frac{C_{s}}{C_{w}} \tag{1}$$

where C_s is the concentration of herbicide sorbed to soil (mg kg^{-1}) and C_w (mg L^{-1}) is the concentration of herbicide in solution at equilibrium. Organic carbon normalized sorption coefficients $(K_{oc}, L kg^{-1})$ were calculated by

$$K_{oc} = \frac{100 \times K_d}{f_{oc}} \tag{2}$$

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Table 2. Selected physical-chemical properties of the herbicides included in these experiments (from Tomlin^[26])

Herbicide	Chemical class	Molecular weight	$Melting point(^{\circ}C)$	Water solubility $(mg\ L^{-1})$	Octanol-water partition coefficient (log K_{ow})	Acid pKa
Alachlor	Chloroacetanilide	269.8	40–42	242	3.09	None
Amitrole	Triazole	84.1	159	280,000	-0.97	4.2
Atrazine	Chlorotriazine	215.7	175–177	33	2.5	1.7
Dicamba	Benzoic acid	221.0	114–116	6500	-0.15	1.97
Imazamox	Imidazolinone	305.3	166–167	4100*	0.73	3.3*
Imazethapyr	Imidazolinone	289.3	169-173	1400	1.49	3.9
Pendimethalin	Dinitroaniline	281.3	47–57	0.3	5.18	None
Simazine	Chlorotriazine	201.7	225–227	6.2	2.1	1.62

^{*}Data from Cedergreen et al.[27]

where f_{oc} is the weight fraction of organic carbon in the soil. Relationships between soil properties and sorption coefficients were tested by Kendall correlation. Analysis of variance was used to detect differences in sorption coefficients within each soil (differences between eight herbicides) and within each herbicide (differences between seven soils). Significant differences in sorption coefficients were determined using a Tukey test with a probability of Type I error < 0.05.

Mobility indices

To provide a first approximation of the tendency for these herbicides to leach in Lithuanian soils, a unitless retardation factor (RF) was estimated for each herbicide in each soil under saturated conditions using

$$RF = 1 + \frac{\rho_B K_d}{n} \tag{3}$$

where ρ_B is the bulk density (g cm⁻³) of the soil and n is the total porosity, estimated by

$$n = 1 - \frac{\rho_{\rm B}}{\rho_{\rm p}} \tag{4}$$

where ρ_p is the particle density estimated as 2.65 g cm⁻³. The time (h) required for the peak concentration of each herbicide to occur at 10 cm depth under saturated flow conditions was estimated assuming no degradation and no preferential flow using

time required to leach to
$$10 \text{ cm} = \frac{\text{RF} \times 100 \text{ mm}}{\text{K}_s}$$
 (5)

where K_s is the saturated hydraulic conductivity (mm h⁻¹) calculated using the pedotransfer functions (PTFs) presented in Saxton and Rawls.^[9] Bulk density was estimated by taking the average of four PTFs (Equations 6–9) based on soil texture and organic matter classifications:

$$\rho_{\rm B} = (1 - \theta_{\rm S}) *2.65 \text{ from Saxton and Rawls}^{[9]} \quad (6)$$

$$\rho_{\rm B} = 1.70398 - 0.00313(\text{Silt})$$

$$+ 0.00261(\text{Clay}) - 0.1855(\text{OM})$$
from Leonavičiūtė^[10] (7)

$$\begin{split} \ln(\rho_{\rm B}) &= -2.31 - 1.079 \ln({\rm OM}) \\ &- 0.113 [\ln({\rm OM})]^2 \ {\rm from \ Federer}^{[11]} \ {\rm and} \quad (8) \\ \ln(\rho_{\rm B}) &= 0.313 - 0.382 ({\rm OM}) + 0.02102 ({\rm Clay}) \\ &- 0.000476 ({\rm Clay})^2 - 0.00432 ({\rm Silt}) \\ {\rm from \ Kaur \ et \ al.}^{[12]} \end{split} \tag{9}$$

where Sand, Silt, Clay, and OM are the decimal percentages (0-1) of sand, clay, and organic matter, respectively. Θ_Sis the saturated volumetric moisture content that was estimated from soil texture and organic matter by the relationships in Saxton and Rawls.^[9] Organic matter contents were estimated from measured organic carbon contents assuming that the ratio of soil organic matter to soil organic carbon was 1.72.^[7]

Bernard et al.^[13] describe a mobility classification based on RF. They suggest that compounds with a RF=1 are very mobile, those with RF >1 but <2 are mobile, those with RF \geq 2 but <3 are moderately mobile, those with RF \geq 3 but <10 are moderately immobile, and those with RF \geq 10 are very immobile. We used these mobility classifications to indicate the soil-herbicide combinations that might be flagged as most likely to result in groundwater contamination based on the sorption information obtained in these experiments and the estimated total porosity of the soil (Equation 3). These estimated RF values are heavily influenced by equilibrium pesticide sorption results. Because water flow also strongly impacts pesticide transport, the time required to leach each herbicide to 10 cm depth under saturated flow conditions was also estimated (Equation 5) for each soil.

Results and discussion

Sorption Coefficients

A wide range in soil textures were represented by these soils; all had $\geq 1\%$ organic carbon and tended to be slightly acidic (Table 1). Except for sand and clay content, soil properties were not correlated with one another at p < 0.05. Sorption coefficients for pendimethalin were significantly higher ($\alpha = 0.05$) than those for all other herbicides on each

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Table 3. Sorption coefficients (mean± standard error) for herbicides on seven Baltic soils*

	Soil							
	Dotnuva	Joniskelis	Perloja	Rumokai	Rumokai IX	Traku Voke	Vezaiciai	
Herbicide				$K_d (L kg^{-1})$				
Alachlor	3.36 ± 0.003 a	$2.24 \pm 0.07 \text{ c}$	$1.5 \pm 0.1 \text{ e}$	$2.59 \pm 0.04 \text{ b}$	$1.70 \pm 0.04 \mathrm{de}$	$1.74 \pm 0.03 \text{ de}$	$1.91 \pm 0.08 d$	
Amitrole	$0.83 \pm 0.03 \text{ a}$	$0.95 \pm 0.02 \text{ a}$	$0.68 \pm 0.007 \text{ b}$	0.92 ± 0.007 a	$0.40 \pm 0.02 c$	$0.87 \pm 0.04 a$	$0.93 \pm 0.05 a$	
Atrazine	$0.9 \pm 0.3 \text{ b}$	$1.09 \pm 0.02 \text{ ab}$	$1.04 \pm 0.02 \text{ ab}$	1.50 ± 0.06 a	$0.86 \pm 0.02 \text{ b}$	$0.18 \pm 0.02 c$	$1.35 \pm 0.09 \text{ ab}$	
Dicamba	0.07 ± 0.009 a	$0.05 \pm 0.01 \text{ ab}$	0.08 ± 0.004 a	$0.03 \pm 0.001 \text{ b}$	$0.05 \pm 0.002 \text{ ab}$	0.07 ± 0.008 a	0.05 ± 0.008 ab	
Imazamox	$0.26 \pm 0.009 \text{ bc}$	0.42 ± 0.02 a	$0.33 \pm 0.03 \text{ b}$	$0.30 \pm 0.02 \text{ b}$	$0.19 \pm 0.006 c$	$0.28 \pm 0.008 \text{ b}$	$0.26 \pm 0.02 \text{ bc}$	
Imazethapyr	$0.60 \pm 0.01 \text{ ab}$	$0.67 \pm 0.009 \text{ ab}$	$0.59 \pm 0.02 \text{ ab}$	$0.7 \pm 0.1 a$	$0.32 \pm 0.01 c$	$0.50 \pm 0.008 \text{ bc}$	$0.59 \pm 0.01 \text{ ab}$	
Pendimethalin	$153 \pm 11a$	$83 \pm 4 d$	$75 \pm 2 d$	$91 \pm 1 \text{ cd}$	$83 \pm 4 d$	115 ± 5 bc	131 ± 5 ab	
Simazine	1.35 ± 0.03 a	$0.71 \pm 0.02 \text{ de}$	$0.66 \pm 0.01 \text{ e}$	$1.05 \pm 0.06 \text{ b}$	$0.35\pm0.01~\mathrm{f}$	$0.88\pm0.01~\mathrm{c}$	$0.83 \pm 0.02 \text{ cd}$	

^{*}For each herbicide, values followed by different lowercase letters are significantly different ($\alpha = 0.05$).

soil; K_d values for pendimethalin were at least one order of magnitude greater than those for the other herbicides (Table 3). Except for the Traku Voke soil, sorption coefficients followed the trend pendimethalin>alachlor>atrazine ~amitrole~simazine>imazethapyr>imazamox>dicamba (Table 3). The Traku Voke soil followed the same general trends, except that atrazine K_d values were low in this soil (Table 3). This trend generally agrees with the trends in log K_{ow} values (Table 2), except in the case of amitrole, which has a low K_{ow} (Table 2), but sorption similar to the triazine herbicides in these soils (Table 3).

Sorption coefficients for alachlor, pendimethalin and simazine were significantly correlated (p<0.05) with organic carbon contents, but K_d values for the remaining five herbicides were not correlated with the weight fraction of organic carbon in soil. Because organic carbon is widely identified as the primary sorbent of hydrophobic organic compounds, [14] K_{oc} values are often observed to be less variable than K_d values. In this study, organic-carbon normalized sorption coefficients (K_{oc}) were less variable than K_d values across the seven soils only for the triazine (atrazine and simazine) and chloroacetanilide (alachlor) herbicides.

For all other herbicides, K_{oc} values were more variable than K_d values, but for both K_d (Table 3) and K_{oc} , values varied by less than an order of magnitude. The ratio of maximum to minimum K_{oc} values ranged from 1.4 for alachlor to 6.6 for atrazine, a variability that is commonly observed in surface soils.^[14] These results suggest that organic carbon may not be the sole sorbent in these soils and/or the organic matter in these soils may have differing sorptivities to these herbicides. The processes influencing differential herbicide sorption in these soils were not investigated, and a number of factors can affect the variation in sorption coefficients.^[14]

Sorption coefficients for alachlor, amitrole, atrazine, and imazethapyr were positively correlated with clay content, whereas dicamba sorption was negatively correlated with clay content (Table 4). Experimental evidence has shown that sorption of neutral organics (such as these herbicides) to natural sediments is generally not significantly affected by mineral contributions until the ratio of clay minerals to organic carbon is ~ 30 or greater. [15] In this study, only one soil (Joniskelis) had a relatively high ratio of claysized particles to organic carbon content (Table 1), and only for imazamox did this soil have significantly higher

Table 4. Kendall correlation coefficients between herbicide sorption coefficients (K_d) and soil properties*

	Soil property							
	Organic carbon (%)	pH	Sand (%)	Silt (%)	Clay (%)			
Alachlor K _d	0.59 (0.0003)	0.50 (0.002)	-0.23 (0.1)	-0.30 (0.06)	0.56 (0.0007)			
Amitrole K _d	0.02 (0.9)	0.09 (0.5)	-0.40(0.01)	-0.01(0.9)	0.45 (0.006)			
Atrazine K _d	0.24(0.1)	-0.02(0.9)	-0.20(0.2)	-0.17(0.3)	0.49 (0.003)			
Dicamba K _d	-0.31(0.05)	-0.14(0.4)	0.59 (0.003)	-0.23(0.1)	-0.57(0.0005)			
Imazamox K _d	-0.25(0.1)	0.13(0.4)	-0.06(0.7)	-0.11(0.5)	0.10(0.5)			
Imazethapyr K _d	0.04(0.8)	0.17 (0.3)	-0.16(0.3)	-0.23(0.1)	0.37(0.02)			
Pendimethalin K _d	0.38 (0.02)	0.05(0.7)	0.19(0.2)	-0.27(0.1)	0.10(0.5)			
Simazine K _d	0.41 (0.01)	0.30 (0.06)	0.12 (0.4)	-0.66(0.0001)	0.19 (0.2)			

^{*}Values in parentheses are p values.

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K_d values than other soils (Table 3). No significant correlation between K_d and clay content was observed for alachlor, atrazine, imazethapyr, or dicamba sorption to tropical soils.[16] Numerous studies have demonstrated specific herbicide-clay mineral interactions.^[15] Clay mineralogy and the availability of mineral surfaces in the soil were not determined in this study, so the mechanistic significance of a statistical correlation between sorption coefficients and clay content is not known. Alachlor was the only herbicide for which sorption was significantly correlated with pH (Table 4). Alachlor is not ionizable (Table 2). The soils included in this study tended to be slightly acidic and varied over a relatively small range in pH (pH 5.7 to 7.2, Table 1). The correlation of alachlor K_d and soil pH is expected to be due to the relationship between organic carbon and pH (correlated with p < 0.1) and the strong influence of organic carbon in alachlor sorption.

Atrazine and alachlor have been heavily-used in many agricultural areas; they are frequently detected in ground and surface waters [1,2] and these herbicides are well-studied. In these experiments, the alachlor K_d was 1.4 to 10 times higher than the atrazine K_d in each soil (Table 3). Other studies evaluating atrazine and alachlor sorption in the same soils have indicated that alachlor is often more highly sorbed than atrazine in a variety of soils from temperate [17–19] and tropical regions. [13,16,20] Many studies evaluating the sorption of multiple pesticides to a soil include atrazine, providing a basis for comparative sorption estimates. In the present study, dicamba had K_d values 3 to 50 times lower than those for atrazine in all soils (Table 3), in agreement with previous studies that reported dicamba K_d values that were 4 to 16 times lower than those for atrazine in surface soils. [21] Pendimethalin sorption co-

efficients were >60 times higher than those for atrazine (Table 3), in agreement with previous observations. [22] In these studies, simazine K_d values were generally similar to atrazine K_d values, as has been observed in other soils. [22,23] All other herbicides (imazamox, imazethapyr, and amitrole) were sorbed to a greater extent than atrazine in the Traku Voke soil and to a lesser extent in all other soils (Table 3). Other studies of comparative sorption have shown results similar to those presented here, including greater sorption of imazethapyr than of imazamox $^{[24]}$ and greater sorption of pendimethalin than of simazine. $^{[22]}$

Mobility Indices

Estimated retardation factors provide a preliminary indication of the potential for these herbicides to leach in these soils. The mean precipitation (1960-1990) was obtained from Rawlins and Willmott^[25] for each site from which soil was collected. These records indicate that rainfall in spring and early summer, when herbicides are most likely to be applied, is relatively consistent among these sites. The mean total precipitation occurring at each site is 26 to 31 mm in March, 37 to 39 mm in April, 55 to 64 mm in May, 55 to 70 mm in June, and 75 to 81 mm in July. Since rainfall is relatively consistent among these sites, water transport and herbicide sorption and degradation may be the primary drivers of differential herbicide leaching at these sites. Estimated RFs were calculated for saturated soils to give a preliminary estimate of herbicide retention by these soils (Table 5). Due to the large influence of K_d on calculated RF, all herbicides were predicted to be susceptible to leaching (low RF, Table 5) in the Rumokai IX soil, which has intermediate organic carbon content and sand content (Table 1)

Table 5. Estimated retardation factor and time required to leach 10 cm under saturated conditions.

			Soil							
Herbicide		Dotnuva	Joniskelis	Perloja	Rumokai	Rumokai IX	Traku Voke	Vezaiciai		
Alachlor	Retardation factor	12	8.2	5.6	9.8	6.4	6.4	7.1		
	Time to leach 10 cm (h)	89	620	12	1100	68	23	59		
Amitrole	Retardation factor	3.7	4.0	3.1	4.1	2.3	3.7	4.0		
	Time to leach 10 cm (h)	28	310	6.8	470	24	13	33		
Atrazine	Retardation factor	4.1	4.5	4.3	6.1	3.7	1.5	5.3		
	Time to leach 10 cm (h)	31	340	9.2	700	40	5.6	44		
Dicamba	Retardation factor	1.2	1.2	1.3	1.1	1.2	1.2	1.2		
	Time to leach 10 cm (h)	9.2	88	2.7	130	12	4.3	9.5		
Imazamox	Retardation factor	1.8	2.3	2.0	2.0	1.6	1.9	1.8		
	Time to leach 10 cm (h)	14	180	4.4	230	17	6.7	15		
Imazethapyr	Retardation factor	3.0	3.1	2.9	3.4	2.0	2.5	2.9		
	Time to leach 10 cm (h)	22	240	6.2	390	22	9.1	24		
Pendimethalin	Retardation factor	500	270	240	310	260	360	420		
	Time to leach 10 cm (h)	3700	20,000	510	36,000	2800	1300	3500		
Simazine	Retardation factor	5.4	3.3	3.1	4.6	2.1	3.7	3.7		
	Time to leach 10 cm (h)	40	250	6.7	520	23	13	30		

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and low herbicide K_d (Table 3). High RF values were calculated for soils with high organic carbon contents (Table 1) and high herbicide K_d , the Dotnuva and Rumokai soils (Tables 3 and 5).

The RF as calculated here is a function of sorption and soil properties (primarily soil texture as it affects bulk density and volumetric water content at saturation). Retardation factors for all herbicides were strongly positively correlated with K_d , so that the estimated RF increased with increasing sorption for these herbicides. Soil organic carbon content and sand content are often cited as important factors influencing pesticide mobility. In this study, estimated RFs were not correlated with organic carbon contents for any herbicide (p > 0.05) and were only significantly correlated with sand content for dicamba (with a positive correlation, indicating that dicamba was predicted to be less mobile in soils with higher sand contents).

Using a mobility classification based on retardation factors^[13] for saturated conditions, pendimethalin was predicted to be very immobile in all soils. Dicamba was classified as mobile in all soils. Alachlor, amitrole, atrazine, and simazine were predicted to be moderately immobile in all soils except Dotnuva (alachlor very immobile), Traku Voke (atrazine mobile) and Rumoaki IX (amitrole and simazine moderately mobile). The predicted mobility of imazamox ranged from moderately mobile (3 soils) to mobile (4 soils), whereas imazethapyr's classification ranged from moderately immobile (3 soils) to moderately mobile (4 soils).

Predicting mobility based on RF (heavily influenced by sorption estimates) is only a partial consideration of pesticide transport. Water flow through soil is also an important factor affecting pesticide leaching. Matrix flow of water through each soil under saturated conditions was estimated using a saturated hydraulic conductivity (K_s) calculated using PTFs relating soil texture and organic matter to hydraulic conductivity.^[9] The time required for each pesticide to leach 10 cm was estimated using Equation 5, which assumes no preferential flow, no herbicide degradation, and saturated flow conditions, giving a conservative estimate of the risk of pesticide leaching. In these soils, K_s increased with increasing sand content and with decreasing clay content (p<0.05). The time required to leach 10 cm was strongly affected by soil bulk density and clay content (positive correlations, p<0.05) for all herbicides, but only for amitrole did the leaching time significantly increase with increasing RF. These estimated leaching times are more strongly affected by soil textural effects on predicted water flow than by herbicide sorption effects. All herbicides were predicted to be slowest to leach in soils with high clay content, low sand content, and low K_s (Rumokai and Joniskelis) and fastest to leach in soils with high sand content and low organic matter content (Perloja and Traku Voke) (Table 5).

Mobility classifications based on pesticide sorption did not always agree with the time required to leach the herbicide 10 cm under saturated conditions. For example, dicamba was predicted to be mobile in all soils, with calculated RF values ranging from 1.1 to 1.3 (Table 5). However, because of predicted differences in water flow, the time required for dicamba to leach 10 cm under saturated conditions ranged from about 3 h to more than 5 d (Table 5). In contrast, a herbicide-soil combination that was predicted to be very immobile (alachlor in Dotnuva soil) was predicted to leach 10 cm in approximately 90 h, less than the time required for alachlor leaching in high-clay soils with lower predicted RF (Table 5), and less than a herbicide with very low sorption (dicamba in Rumokai soil, Table 5). These results indicate that the sorption and mobility of these eight herbicides in these Lithuanian soils may not easily be discerned a priori based on soil properties. Additional experimentation is needed to more completely evaluate pesticide fate in these soils and other soils under conditions typical of the Baltic region.

Conclusion

This study, which evaluated the sorption of eight herbicides to soils representative of Lithuanian agricultural soils, provides preliminary information concerning areas prone to pesticide non-point contamination of water resources. Herbicide sorption coefficients generally followed the trend pendimethalin>alachlor>atrazine~amitrole~simazine> imazethapyr>imazamox>dicamba. Sorption coefficients were variable among soils, and were correlated with the weight fraction of organic carbon in soil only for alachlor, pendimethalin and simazine. Estimated mobility under saturated conditions indicated that most herbicides were predicted to be most mobile in a soil of intermediate organic carbon content and sand content. Soil textural effects on water flow may have a large impact on pesticide transport. Under saturated conditions, all herbicides were predicted to be slowest to leach in soils with high clay and low sand contents, and fastest to leach in soils with high sand content and low organic matter content. Agricultural production in the Baltic region is rapidly developing, and herbicide management will be important to the continued increase in agricultural production and profitability in this region. These results will be useful in developing improved pesticide management practices to reduce water contamination by pesticides.

References

- Gilliom, R.J.; Barbash, J.E.; Kolpin, D.W.; Larson, S.J. Testing water quality for pesticide pollution. Environ. Sci. Technol. 1999, 33(7), 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. In Groundwater quality and quantity in Europe, Environmental Assessment Report 3; European Environment Agency: Copenhagen, Denmark, 1999; 18–38.

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[3] Barbash, J.E.; Thelin, G.P.; Kolpin, D.W.; Gilliom, R.J. Major herbicides in ground water: Results from the National Water-Quality Assessment. J. Environ. Qual. 2001, 30(3), 831–845.

- [4] Ellington, J.J.; Thurston, R.V.; Sukyte, J.; Kvietkus, K. Hazardous chemicals in waters of Lithuania. Trends Anal. Chem. 1996, 15(6), 215–224.
- [5] Pempkowiak, J.; Tronczynski, J.; Pazdro, K. Spatial and temporal gradients of triazines in the Baltic Sea off Poland. Mar. Pollut. Bull. 2000, 40(12), 1082–1089.
- [6] Dann, R.L.; Close, M.E.; Lee, R.; Pang, L. Impact of data quality and model complexity on prediction of pesticide leaching. J. Environ. Qual. 2006, 35(2), 628–640.
- [7] Nelson, D.W.; Sommers, L.E. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis, Part 2*; Page, A.L., Ed.; American Society of Agronomy and Soil Science Society of America: Madison, WI, 1982; 539–577.
- [8] Gee, G.W.; Bauder, J.W. Particle-size analysis. In *Methods of Soil Analysis, Part 1*; Klute, A., Ed.; American Society of Agronomy and Soil Science Society of America: Madison, WI, 1988; 383–441.
- [9] Saxton, K.E.; Rawls, W.J. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Sci. Soc. Am. J. 2006, 70(5), 1569–1578.
- [10] Leonavičiūte, N. Predicting soil bulk and particle densities by pedotransfer functions from existing soil data in Lithuania. Geografijos metraštis (The Geographical Yearbook) 2000, 33, 317–330.
- [11] Federer, C.A. Nitrogen mineralization and nitrification: Depth variation in four New England forest soils. Soil Sci. Soc. Am. J. 1983, 47(5), 1008–1014.
- [12] Kaur, R.; Kumar, S.; Gurung, H.P. A pedo-transfer function (PTF) for estimating bulk density from basic soil data and its comparison with existing PTFs. Austr. J. Soil Res. 2002, 40(5), 847–858.
- [13] Bernard, H.; Chabalier, P.F.; Chopart, J.L.; Legube, B.; Vauclin, M. Assessment of herbicide leaching risk in two tropical soils of Reunion Island (France). J. Environ. Qual. 2005, 34(2), 534–543.
- [14] Wauchope, R.D.; Yeh, S.; Linders, J.B.H.J.; Kloskowski, R.; Tanaka, K.; Rubin, B.; Katayama, A.; Kördel, W.; Gerstl, Z.; Lane, M.; Unsworth, J.B. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. Pest Manag. Sci. 2002, 58(5), 419–445.

[15] Karickhoff, S.W. Organic pollutant sorption in aquatic systems. J. Hydraul. Eng. 1984 110(6), 707–735.

- [16] Oliveira, R.S., Jr.; Koskinen, W.C.; Ferreira, F.A. Sorption and leaching potential of herbicides on Brazilian soils. Weed Res. 2001, 41(2), 97–110.
- [17] Grundl, T.; Small, G. Mineral contributions to atrazine and alachlor sorption in soil mixtures of variable organic carbon and clay content. J. Contam. Hydrol. 1993, 14(2), 117–128.
- [18] Sonon, L.S.; Schwab, A.P. Adsorption characteristics of atrazine and alachlor in Kansas soils. Weed Sci. 1995, 43(3), 461–466.
- [19] Walker, A.; Welch, S.J.; Melacini, A.; Moon, Y.H. Evaluation of three pesticide leaching models with experimental data for alachlor, atrazine, and metribuzin. Weed Res. 1996, 36(1), 37–47.
- [20] Laabs, V.; Amelung, W. Sorption and aging of corn and soybean pesticides in tropical soils of Brazil. J. Agric. Food Chem. 2005, 53(18), 7184–7192.
- [21] Johnson, R.M.; Sims, J.T. Influence of surface and subsoil properties on herbicide sorption by Atlantic Coastal Plain soils. Soil Sci. 1993, 155(5), 339–348.
- [22] Barriuso, E.; Houot, S.; Serra-Wittling, C. Influence of compost addition to soil on the behaviour of herbicides. Pestic. Sci. 1997, 49(1), 65–75.
- [23] Gerritse, R.G.; Beltran, J.; Hernandez, F. Adsorption of atrazine, simazine, and glyphosate in soils of the Gnangara Mound, Western Australia. Austr. J. Soil. Res. 1996, 34(4), 599–607.
- [24] Aichele, T.M.; Penner, D. Adsorption, desorption, and degradation of imidazolinones in soil. Weed Technol. 2005, 19(1), 154– 159.
- [25] Rawlins, M.A.; Willmott, C.J. Arctic land-surface precipitation: 1960–1990 gridded monthly time series, version 1.01. University of Delaware Center for Climatic Research. http://climate.geog.udel.edu/~climate/index.shtml (accessed March 2007).
- [26] Tomlin, C.D.S., Ed. The Pesticide Manual: A World Compendium; British Crop Protection Council: Farnham, Surrey, UK, 1997; 1606 pp.
- [27] Cedergreen, N.; Andersen, L.; Olesen, C.F.; Spliid, H.H.; Streibig, J.C. Does the effect of herbicide pulse exposure on aquatic plants depend on K_{ow} or mode of action? Aquat. Toxicol. 2005, 71(3), 261–271.