

A PESTICIDE SURFACE WATER MOBILITY INDEX AND ITS RELATIONSHIP WITH CONCENTRATIONS IN AGRICULTURAL DRAINAGE WATERSHEDS

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Abstract—An index to benchmark pesticide mobility relevant to surface water runoff and soil erosion (surface water mobility index, or SWMI) was derived based on two key environmental fate parameters: degradation half-life and organic carbon–normalized soil/water sorption coefficient (K_{oc}). Values assigned with the index of each individual compound correlate well with the concentration trend of 13 pesticides monitored in six Lake Erie, USA, tributaries from 1983 to 1991. Regression using a power function of SWMI fits concentration data well at various percentiles in the database for each tributary and all six tributaries combined, with r^2 ranging from 0.71 to 0.94 for the concentrations at the 95th percentile. Good agreement was also obtained between SWMI and the time-weighted annual mean concentration immediately after application), SWMI explains the peak concentration data generally well ($r^2 = 0.53-0.86$). The SWMI–concentration relationship was further evaluated with two other pesticide monitoring databases: the Higginsville City Lake, Missouri, USA (1995–1997). The ability of the proposed SWMI to discriminate pesticide runoff mobility and its correlation with surface water monitoring data can be significant in the development of screening methodologies and data-based models for government agencies and/or practitioners in general facing increasing pressure to assess pesticide occurrence in aquatic environments.

Keywords-Pesticide Mobility index Surface water runoff Soil erosion Regression model

INTRODUCTION

Assessment of surface water exposure to pesticides in watersheds usually requires estimation of chemical concentrations over different time frames of concern (e.g., peak, annual, or long-term averages). However, a dilemma often encountered in these estimations is the lack of modeling tools that are data based and can reliably predict either high-percentile or longterm average pesticide concentrations in rivers and lakes/reservoirs receiving runoff water from agricultural fields. While physically based numerical models, such as the Pesticide Root Zone Model (PRZM), have been used for pesticide regulatory assessment [1], the validity of these mechanistic models has been established only under small-scale and edge-of-field conditions, where physical features, such as soil hydrological properties and slope, are relatively homogeneous [1,2].

Several recent studies have shown that field-scale runoff and erosion do not extrapolate well to larger, heterogeneous watershed scales because of spatial variability in land use and hydrological processes [3–7]. Merz and Plate [6] reported that the spatial variability in soil hydraulic properties affects runoff differently among different catchment sizes $(0.32–3.52 \text{ km}^2)$. In their study, deterministic modeling based on a mean parameter input did not result in a mean output for a heterogeneous field. Instead, the results could differ from -50% to 180% compared to the homogeneous cases, indicating complex propagation of input parameter variability to model outputs on watershed scales. That is, average values of input parameters do not necessarily produce model outputs that represent the mean of the simulated system such as a watershed. The variability in rainfall, topography, vegetative cover, and farming practices in a watershed further complicates the scale problem of accurately predicting water runoff, soil erosion, and ultimately pesticide off-field transport into surface water. Fieldscale models thus often fail to accurately predict pesticide concentrations in water bodies within a watershed, with predictions often orders of magnitude different from the monitoring data [8].

Many well-controlled small plot studies have investigated the edge-of-field processes of runoff and erosion [9]. However, watershed-scale information has been generally lacking to warrant a detailed, accurate, and mechanistic quantification of pesticide transport throughout regional drainage networks. Several recent watershed monitoring studies have documented some general patterns of pesticide occurrence in tributaries of Lake Erie and the Mississippi River, USA [10,11]. These studies generally indicated that the variation of riverine pesticide concentrations is dependent on the quantity of chemical used and the size of the watershed. Using statistical regression, Battaglin and Goolsby [12] were able to show that the chemical occurrence in U.S. midwestern rivers was in relation with a range of watershed factors, including soil properties, chemical use, stream flow, and basin topographic characteristics. Very few studies, however, have shown a quantitative relation between watershed monitoring data and individual pesticide physical/ chemical properties. Such empirical relations would allow a better evaluation of the relative runoff and erosion potential for different compounds and provide quick estimates of potential concentration levels in watersheds. Comparison of the empirical models based on watershed data to a more detailed and field-scale process-oriented model would also provide insight into the scale effect on pesticide transport behavior.

The objective of this paper was to evaluate the potential

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effect of two key environmental fate properties (soil half-life and soil/water sorption coefficient) on pesticide occurrence in surface water and to assess if a correlation could be established to allow predictions of surface water concentrations of different pesticides in agricultural drainage networks. Three working steps were involved. First, based on a standard exposure scenario and the basic equations of field runoff and erosion, the two environmental fate parameters were integrated into the surface water mobility index (SWMI) to benchmark individual pesticide mobility potential specifically relevant to surface water runoff and soil erosion. Second, historical surface water monitoring data sets (two from river systems and one with a reservoir) were selected and analyzed for timeweighted percentile concentrations. The two river data sets included the monitoring program for six tributaries of Lake Erie as reported by Richards and Baker [10] and the U.S. Geological Survey NAWQA White River Study Unit (1991-1996) at Hazelton (http://www-dinind.er.usgs.gov/nawqa/) [13]. The reservoir data set was from the Syngenta (previously Novartis) voluntary monitoring program (1995-1997) conducted on the Higginsville City Lake [14]. The third step involves regression and model calibration using the Lake Erie Basin monitoring data together with the corresponding pesticide usage and watershed sizes to establish a relationship with SWMI. The established relationship was then evaluated as a screening tool to predict surface water pesticide concentrations and compare them with the monitored concentrations noted in the other two data sets.

THEORY

Previous quantification of pesticide mobility based on chemical environmental fate properties has focused primarily on the pesticide propensity relevant to leaching in soil [15– 17]. Applicability of these approaches to pesticide transport by surface water runoff and soil erosion is limited because of the different transport mechanisms involved in surface water hydrology compared to leaching in the subsurface environment. In the remainder of this paper, we focus on addressing pesticide surface runoff and erosion potential.

For a single rain event, pesticide loss from an agricultural field, dissolved in runoff water and bound to soil particles, can be expressed as

$$M = M_w + M_s = 1000 \cdot Q_v \cdot C_w + r_{om} \cdot E_r \cdot C_s \quad \text{and}$$
$$\ln(r_{om}) = 2 - 0.2 \ln(E_r/A_{ha}) \tag{1}$$

where *M* is total pesticide mass loss in both runoff water and soil particles (mg), M_w is total pesticide mass in runoff water (mg/L), M_s is total pesticide mass bound to soil particles in erosion (mg/kg), Q_v is total runoff water (m³), C_w is concentration in runoff water (mg/L), A_{ha} is area of the runoff field (ha), E_r is total soil erosion (kg), C_s is concentration in eroded soil particles (mg/kg), 1,000 is a unit conversion factor (from m³ to L), and r_{om} is an empirical soil organic matter enrichment ratio based on Mullins et al. [1]. The enrichment ratio is used to account for the particle-selective effect during erosion and is an adjustment factor in eroded soil relative to field soil.

Assuming instantaneous sorption equilibrium and that the concentration of the chemical sorbed by the soil solid is directly proportional to the concentration in liquid phase, C_w and C_s can be calculated as [2,18]

$$C_w = \frac{C_a \epsilon}{1 + K_d \epsilon} \quad \text{and} \tag{2}$$

$$C_s = \frac{C_a K_d \epsilon}{1 + K_d \epsilon} \tag{3}$$

where ϵ is mass of soil on which pesticide can be extracted by runoff water, or runoff extraction coefficient (kg/L); C_a is total pesticide concentration available for transport due to runoff and soil erosion (mg/kg); and K_d is soil or sediment/water sorption coefficient (or sorption coefficient; L/kg). The K_d is often normalized by soil organic carbon content (OC, %), that is, $K_{oc} = K_d$ /OC. Thus, K_{oc} refers to an organic carbon–normalized soil/water sorption coefficient with a unit same as K_d .

The C_a is further calculated by the first-order degradation equation:

$$C_a = C_{a0} e^{-0.693t/T_h} \tag{4}$$

where C_{a0} is the initial total concentration (adsorbed and dissolved) at day 0 after application (mg/kg), T_h is pesticide soil half-life (d), and t is time when first runoff event occurs.

Substituting Equations 2 to 4 into Equation 1 gives

$$M = \frac{\epsilon C_{a0} e^{(-0.693t/T_h)}}{(1 + \epsilon K_d)} (10^5 Q_d A_{ha} + r_{om} E_r K_d)$$
(5)

where Q_d is runoff water depth (cm). All other variables are the same as defined previously.

The runoff water depth can be calculated by the U.S. Department of Agriculture–Soil Conservation Service curve number method [19]:

$$Q_d = \frac{[R - 0.2S]^2}{R + 0.8S}$$
 and $S = 25.4 \left(\frac{100}{\text{CN}} - 1\right)$ (6)

where R is precipitation (cm) and CN is the curve number, which can be estimated on the basis of the method of antecedent moisture condition II [20].

Soil erosion can be estimated by the modified universal soil loss equation [1]:

$$E_r = 11.8(q_p Q_v)^{0.56} K LS C P$$
(7)

where q_p is peak runoff rate (m³/s), *K* is soil erodability coefficient, *LS* is length–slope factor, *C* is crop cover factor, and *P* is management practice factor. The peak runoff rate is further approximated on the basis of a simple trapezoidal hydrograph [1]:

$$q_{p} = \frac{0.0278A_{ha}RQ_{d}}{T_{R}\left[R - 0.508\left(\frac{1000}{CN} - 10\right)\right]}$$
(8)

where T_R is peak storm duration (h).

The derivation in Equations 5 to 8 shows that pesticide offfield transport to surface water is not only a function of pesticide environmental fate properties but also dependent on the soil and hydrological conditions. To quantify pesticide mobility only by its environmental fate properties, a uniform exposure environment under identical runoff conditions must be specified to obtain a standardized basis for all pesticides. For this purpose, a Loring silt loam in Yazoo County, Mississippi, USA, was selected. The selection was based primarily on the readily available hydrological properties that have been used frequently by the U.S. Environmental Protection Agency as a standard surface water assessment scenario [21]. Assuming conventional till and cotton growth, this soil is highly vul-

Table 1. Soil and field hydrological parameters of a Loring silt loam soil, Yazoo (MS, USA), for the standard runoff scenario to define the pesticide surface water mobility index (SWMI)

Soil erodability coefficient $K = 0.49$	Bulk density = 1.6 kg/L
Length-slope factor $LS = 0.4$	Organic carbon = 1.16%
Management practice factor $p = 0.75$	Incorporation depth = 3 cm
Field area $A_{ha} = 10$ ha	Field capacity $(\theta_f) = 0.294$
Peak storm duration $T_R = 5.8$ h	Wilting point $(\theta_n) = 0.094$
Standard application rate $= 1.12$	Initial soil water content $(\theta_{in}) =$
kg/ha	$\theta_f = 0.294$
Curve number $(CN) = 97^{a}$	<i>9</i>

^a Based on the method of antecedent moisture condition II (Haith et al. [20]).

nerable to surface runoff as represented by its high CN value (Table 1).

Further parameterization includes the runoff extraction coefficient ϵ , which has been reported as K_{∞} dependent and within the range from 0.1 to 0.5 [18]. To retain simplicity, a medium value $\epsilon = 0.3$ was used. Additionally, a 5.08-cm precipitation event was assumed to occur 5 d after application. It should be noted that the hypothetical scenario characterized by somewhat arbitrary selection of environmental parameters may not realistically exist. However, the objective here was to benchmark pesticide runoff potential (mobility) solely by the compound environmental fate properties.

Substituting all the specified parameters into Equations 5 to 8 and redefining the mass loss as the fraction of total pesticide used (F_m) yields

$$F_m = \frac{0.3e^{-3.466/T_h}}{(1 + 0.00348K_{oc})}(0.9 + 0.000234K_{oc})$$
(9)

Given T_h and K_{oc} that can only be positively valued, Equation 9 is mathematically bounded within 0 and 0.27. That is, F_m asymptotically approaches 0 as T_h approaches 0 and K_{oc} approaches infinity, whereas F_m approaches 0.27 as T_h approaches infinity and K_{oc} approaches 0. For convenience, Equation 9 is rescaled to a mathematical bound between 0 and 1, and we define

$$SWMI = \frac{e^{-3.466/T_h}}{(1 + 0.00348K_{oc})}(1 + 0.00026K_{oc})$$
(10)

By definition, therefore, SWMI determines monotonically the relative pesticide mobility scale, with value of 0 being the asymptotically least mobile and 1 the asymptotically most mobile to be transported by the processes of surface water runoff and soil erosion.

A contour line plot of SWMI as a function of K_{oc} and T_h is illustrated in Figure 1, where the contour lines represent equal values of SWMI. Three regions may be differentiated in the figure. For compounds with a relatively short half-life (<10 d), the mobility index is sensitive predominantly to halflife variations rather than to changes in K_{oc} . Because of their short-lived nature, it is often the temporal and spatial coincidence of pesticide application and the occurrence of the runoff event that governs the mobility for this type of compounds. For compounds with a half-life between 10 and 40 d, the mobility index is sensitive to both parameters (region II in Fig. 1). For more persistent compounds, the index is determined primarily by K_{oc} (region III in Fig. 1). The 13 pesticides monitored in the Lake Erie Basin as described later fall gen-



Fig. 1. Contour plot of the pesticide surface water mobility index as a function of K_{oc} and T_{h} EPTC = s-ethyl dipropylthiocarbamate.

erally within the SWMI range of 0.1 to 0.7, with the contour line at about 0.3 as a divider between insecticides and herbicides.

Our further postulation is that SWMI, as defined in Equation 10, is correlated to pesticide concentrations observed in surface water resulting from agricultural field water runoff and soil erosion. With the pesticide concentrations being directly proportional to its use intensity in drainage basins as reported in the literature [10-12], we assume a power function as a plausible relationship to describe the correlation between SWMI and pesticide concentrations:

$$C_{P(x)} = \frac{M_{use}}{A_b} \alpha \cdot SWMI^{\beta} \quad \text{or} \tag{11}$$

$$Log(C_P(x)/R_b) = \beta \cdot Log(SWMI) + Log(\alpha)$$
(12)

where $C_{P(x)}$ is concentration at percentile *x* in a surface water monitoring database (µg/L), M_{use} is total annual use of a pesticide in a basin or watershed, A_b is total area of a drainage basin or watershed (ha), R_b is basin application rate (kg/ha), and α and β are regression constants. The power function model would predict a 0 concentration as SWMI approaches 0 (the most immobile compound).

The basin application rate R_b in a given drainage watershed characterized by the total area, A_b , may be obtained from the total area treated ($A_{treated}$, ha) and the label application rate (R_{labeb} , kg/ha):

$$R_b = \frac{R_{label}A_{treated}}{A_b} \tag{13}$$

The ratio $A_{treated}/A_b$ in Equation 13 is the fraction of treated cropland in the overall basin area. Denoting the ratio as f_c and substituting Equation 13 back to Equation 11 gives

$$C_{P(x)} = R_{label} f_c \; \alpha \cdot SWMI^{\beta} \tag{14}$$

Equation 14 assumes that the treated area received the label recommended use rate. The equation can be used when no basin use rate is available for direct use of Equation 11. Hence,



Fig. 2. Lake Erie tributary drainage basins and locations of pesticide sample stations in the Ohio, USA, agricultural runoff monitoring program. Listed along with the sampling stations are the U.S. Geological Survey (USGS) stream gauging station numbers (courtesy of Peter Richards).

either Equation 11, 12, or 14 is referred to as the SWMI model in this paper.

MONITORING DATA SETS AND ANALYSIS

Lake Erie Basin data

The primary data set selected to establish the relationship of SWMI with measured pesticide concentrations in surface water was collected by Richards and Baker for six tributaries of the Lake Erie Basin (Maumee River, Sandusky River, Honey Creek, Rock Creek, River Raisin, and Lost Creek, USA) [10]. The monitoring locations and each of the tributary drainage areas are illustrated in Figure 2. This monitoring program provided a complete database of pesticide riverine concentrations monitored for nine consecutive years (April 1983–December 1991). More than 4,000 samples were analyzed for 13 different pesticides (Table 2). The sampling frequency during the highrunoff period (April 15–August 15) was usually three samples per day and less frequently the rest of the calendar year (two samples/month). Agriculture was the predominant land use (67–83% row crop) in the six watersheds.

The Lake Erie Basin pesticide data set was selected to calibrate the SWMI model (Eqn. 12) for three reasons. First, the annual sample frequency was intentionally designed to collect more samples during storm-related river flow than during dry weather base flow. This time-weighted design optimized the likelihood of capturing transient pesticide individual peak concentrations subsequent to the springtime pesticide application period. Second, the number of pesticides monitored provided a wide range of soil degradation half-lives, sorption coefficients, and agricultural crop use patterns (Table 2). Third, the study duration was nine years (1983-1991). This extended time period of continuous monitoring helps provide a range of annual weather patterns that capture normal as well as above- and below-normal annual and seasonal precipitation. Thus, the annual and multiyear mean concentrations for each pesticide should be representative of long-term exposure, while seasonal short-term maximum exposure would be associated with the spring-period runoff events. A detailed de-

Table 2. Pesticide properties, values of the surface water mobility index (SWMI), and total annual use in Ohio Agricultural Statistics Service (OASS), USA, crop reporting Districts 1 and 2 in the Lake Erie Basin, USA, 1986 [22]

Pesticide	Туре	$K_{\rm oc}~({\rm L/kg})^{\rm a}$	T_h (d)	^b SWMI	Total use (kg)
Alachlor	Herbicide	170	15	0.5207	1,058,896
Metolachlor	Herbicide	200	90	0.5969	665,417
Atrazine	Herbicide	100	60	0.7184	581,750
Cyanazine	Herbicide	190	14	0.4932	206,463
Metribuzin	Herbicide	224°	40 ^c	0.5453	203,405
Linuron	Herbicide	370	60	0.4523	110,931
Terbufos	Insecticide	1,504 ^d	7 ^d	0.1388	59,265
Butylate	Herbicide	400	13	0.3536	50,558
Chlorpyrifos	Insecticide	6,070	30	0.1038	24,565
EPTC ^e	Herbicide	200	6	0.3482	30,757
Phorate	Insecticide	540 ^d	3 ^d	0.1248	25,358
Fonofos	Insecticide	870	40	0.2792	19,432
Simazine	Herbicide	130	60	0.6718	14,132

^a K_{oc} = organic carbon–normalized soil/water sorption coefficient.

^b T_h = degradation half-life in soil. Data from Richards and Baker [10] or as otherwise noted.

^c [28]. Average K_{oc} of 81, 65, and 526 calculated from multiple K_d values: 1.32 (2.8% organic matter), 1.90 (5.0% organic matter), 1.53 (0.5% organic matter).

^d Data from American Cyanamid (Wayne, NJ, USA).

^e EPTC = *s*-ethyldipropylthiocarbamate.

scription of the monitoring program can be found in Richards and Baker [10].

Four input parameters are required to calibrate the SWMI model. One parameter is the pesticide annual use data. Regional annual use data for the 13 pesticides monitored by Richards and Baker for 1986 in northwestern Ohio, USA, were obtained from Waldron (Table 2) [22]. The other three SMWI parameter inputs were the size of each individual watershed, the individual pesticide's soil degradation half-life (T_h), and organic carbon–normalized soil/water sorption coefficient (K_{oc}). These properties were obtained either from Richards and Baker [10] or from other sources as noted in Table 2.

Because crop-specific pesticide use information was not available for each of the six agricultural watersheds and the regional use data were available only for 1986, a uniform use rate for each pesticide was applied over each of the six agricultural watersheds for the nine-year period. For each pesticide, the basin use rate R_b was calculated on the basis of the 1986 annual use surveyed in the Ohio Agricultural Statistics Service crop reporting districts 1 and 2, which encompass five of the six Lake Erie tributaries in Ohio (except River Raisin in Michigan, USA) (Fig. 2) [22]. The total county land area is 2,341,468 ha in the two districts. The calculated average basin use rate was applied to River Raisin.

NAWQA Program

Monitoring data of 12 pesticides (Table 3) were obtained from the U.S. Geological Survey NAWQA Program for the sampling site on White River at Hazelton. These data were used to evaluate the SWMI model, which had been calibrated on the basis of the monitoring data from the six river systems in the Lake Erie Basin. The data set was downloadable from the U.S. Geological Survey Internet site (http://www.dinind. er.usgs.gov/nawqa/). The Hazelton location is approximately 19 miles upstream of the White River's confluence with the Ohio River. This location on the White River receives flow from essentially the entire watershed drainage area (2,938,382

Table 3. Pesticide annual use and concentration data from U.S. Geological Survey, National Water Quality Assessment Program White River Study Unit, at Hazelton (IN, USA) (May 1, 1991, to September 23, 1996)^a

Pesticide	Basin annual use (kg)	Basin annual use rate (kg/ha/year)	TWMC (ppb) ^b	95th (ppb)°	Peak (ppb) ^d	
Alachlor	562,500	0.1930	0.1052	0.5000	3.2000	
Metolachlor	931,500	0.3195	0.5164	2.2800	5.3000	
Atrazine	999,000	0.3427	1.3476	6.3800	13.4000	
Cyanazine	355,950	0.1221	0.3056	1.3800	5.1000	
Metribuzin	33,300	0.0114	0.0219	0.0990	0.3800	
Linuron	35,550	0.0122	<0.05°	<0.05 ^e	0.1230	
Terbufos	38,250	0.0131	<0.05°	<0.05 ^e	0.0500	
Butylate	399,150	0.1369	0.0055	0.0240	0.0830	
Chlorpyrifos	69,300	0.0238	< 0.056°	$< 0.056^{\circ}$	0.1300	
EPTC	37,350	0.0128	<0.008°	$< 0.008^{e}$	0.0270	
Fonofos	73,350	0.0252	<0.005°	<0.005°	0.3200	
Simazine	15,750	0.0054	0.1333	0.4700	1.2000	

^a For some compounds in the table, half the limit of detection (LOD) is applied when the measured values < LOD; otherwise, it is noted specifically.

^b TWMC = annual time-weighted mean concentration.

 $^{\circ}$ 95th = concentration at which 95% of time the value is below or equal to.

^d Peak = maximum concentration value.

e Less than LOD.

 f EPTC = s-ethyldipropylthiocarbamate.

ha) [13]. The monitoring period was about six years (May 1991–September 1996). The annual sample frequencies were twice weekly to twice monthly from May to August and approximately monthly during other times of the year [13]. Pesticide analysis was by gas chromatography/mass spectrometry. More detailed descriptions of the monitoring program are in Crawford [13] and Shelton [23]. Pesticide use data (annual average 1992–1994) for the White River Basin were obtained from Anderson and Gianessi [24].

Higginsville Community Water Systems monitoring data

Concentrations of the herbicide atrazine at the Higginsville City Lake were monitored through the Syngenta (previously Novartis) Voluntary Monitoring Program with Community Water Systems (CWS) during 1995–1997 [14]. The drainage area of the city lake is about 1,386 ha and had annual atrazine use in the range 107 to 116 kg during the three monitoring years [25] (Table 4). Water samples were taken both at the point of distribution (finished drinking water) and at the intake point (raw water). Two sampling frequencies were established for a 12-month period (January-December) to cover potential seasonal variations in concentrations, with weekly samples from May to July and two samples per month the other nine months. Sample analysis included both gas chromatography and immunoassay with limit of detection at 0.1 ppb (μ g/L). The parent atrazine in the immunoassay analysis was adjusted from a relationship between the gas chromatography-detected atrazine and the immunoassay results. Concentrations below the limit of detection (LOD) 0.1 ppb were reported as 0.05 ppb (half the LOD) in the calculations of annual means.

Data processing

The three monitoring programs were designed to sample rivers and reservoirs more frequently in high-runoff periods subsequent to the field application of the pesticides (usually late spring to early summer), with less frequent samples collected the rest of the year. The unequal sampling interval was selected to more accurately monitor the seasonal variation in pesticide concentrations prior to, during, and subsequent to the pesticide application period in the Great Lakes, upper Mississippi, and Ohio River systems. The uneven sample frequency within a calendar year requires the measured pesticide concentrations to be organized in a time-weighted fashion. Assuming that each sampling point represents half the time to the preceding sample and half to the following sample as described in Richards and Baker [10], a time weight for each sample was calculated as

$$w_i = \left[(t_{i+1} - t_{i-1})/2 \right] / \sum_{i=1}^n t_i$$
 (15)

where t_i is the sampling time point of sample *i* and *n* is number of samples during the total sampling period. The weights were then organized by their associated corresponding concentrations in an ascending order. The cumulative time-weighted

Table 4. Atrazine annual use and concentrations monitored at the Higginsville City Lake (MO, USA), 1995–1997

Total annual use			Measure	ed water (ppb),	finished	Measured water (ppb), raw			
Year	(kg)	rate (kg a.i./ha)	TWMC ^a	95th ^b	Peak ^c	TWMC	95th	Peak	
1995 1996 1997	113.5 106.8 116	0.0819 0.0771 0.0837	0.72 0.83 1.72	1.38 1.34 3.14	1.64 1.46 3.93	2.79 1.88 2.95	4.27 2.99 4.72	4.71 2.99 5.50	

^a TWMC = annual time-weighted mean concentration.

 b 95th = concentration at which 95% of time the value is below or equal to.

^c Peak = maximum concentration value.

Table 5. The 95th-percentile concentrations (µg/L) of 13 pesticides monitored in the six Lake Erie Basin tributaries, USA, 1986

Pesticides	Maumee River Sandusky River Honey C		Honey Creek	Rock Creek	River Raisin	Lost Creek
Alachlor	4.0890	8.9863	10.8784	6.1818	3.5783	3.9996
Metolachlor	4.3858	10.9704	11.8958	10.5550	6.1903	1.6824
Atrazine	7.9799	15.0301	15.0658	12.2378	15.2498	6.0666
Cyanazine	2.7404	4.5416	2.1908	1.8529	1.5562	1.1928
Metribuzin	2.3862	2.4816	2.1109	2.5859	1.2928	1.7664
Linuron	0.2369	1.1338	2.0831	1.7921	0.4499	0.4816
Terbufos	0.0073	0.0180	0.0113	0.0070	0.0060	0.0288
Butylate	0	0.1503	0.0503	0.0300	0	0.1808
Chlorpyrifos	NA ^a	NA	NA	NA	NA	NA
EPTC ^b	0	0.0508	0.0412	0.0000	0.0000	0.0998
Phorate	0.0080	0.0100	0.0030	0.0040	0.0048	0.0024
Fonofos	0.0335	0.0397	0.0303	0.0279	0.0093	0.0174
Simazine	0.7068	0.5532	0.4926	0.2299	0.1802	0.9204
No. of samples	75	75	125	124	17	135
Sampling period	Jan. 13-Sept. 15	Jan. 13-Sept. 8	Jan. 13-Sept. 29	Jan. 13-Sept. 29	Apr. 6-Sept. 27	Jan. 13-Sept. 22

 a NA = no data available.

^b EPTC = s-ethyl dipropylthiocarbamate.

percentile associated with each concentration thus was determined as

$$P_i = 100 \sum_{i=1}^n w_i$$
 (16)

where P_i corresponds to the time-weighted percentile at concentration C_i of sample *i*. An exact percentile, for example, the 95th, was estimated by linear interpolation between two adjacent samples. A time-weighted percentile, therefore, represents the percentage of the total time during the observation period over which a particular concentration is not exceeded. For example, a 95th percentile of 1 ppb indicates that a concentration <1 ppb occurred during 95% of the observation period.

Time-weighted mean concentration (TWMC) was calculated as

$$TWMC = \sum_{i=1}^{n} w_i C_i \tag{17}$$

where C_i is the concentration of sample *i*.

The 95th-percentile concentrations for the 13 pesticides over the nine-year period (1983–1991) in the six flowing water bodies in the Lake Erie Basin can be found in Richards and Baker [10], while the 95th percentile for the same rivers in 1986 are shown in Table 5. The atrazine time-weighted means and the 95th-percentile and peak individual concentrations for the CWS at the Higginsville City Lake during 1995–1997 are illustrated in Table 4. The monitoring data of time-weighted means and the 95th-percentile and peak individual concentrations for 12 pesticides from the U.S. Geological Survey–NAWQA site at Hazelton are shown in Table 3.

RESULTS AND DISCUSSION

Regression

The first regression analysis was conducted on the entire database obtained over the period of 1983 to 1991 from the six Lake Erie Basin tributaries. The time-weighted 95th-percentile concentrations of 13 pesticides were obtained directly from Richards and Baker [10]. The time-weighted mean and peak concentrations were also available from the same source. The reported TWMC values, however, were limited only to the six herbicides of highest usage in the region (Table 2). The other compounds with smaller uses were not reported in the publication of Richards and Baker [10] because the small TWMC values calculated using uncensored analytical results were far below their corresponding LODs.

Regression results of the proposed SWMI relationship (Eqn. 12) to the concentrations normalized for each pesticide basin scale use rate, including the 95th percentile, peak, and TWMC data, are shown in Figure 3A to C and Table 6 (Yr 83-91 models). Data for all the six tributaries were plotted and used in the regression. Thus, the spread of data points at a given SWMI value represents the variations among the six rivers. A few zero values in the original uncensored data were excluded because of uncertainty in the true value. As shown in Figure 3A and Table 6, a significant relationship exists between the proposed SWMI and the 95th-percentile concentrations obtained from the six agricultural drainage basins throughout the entire monitoring period (1983–1991) ($r^2 =$ 0.71). In comparison, the TWMC and the peak data are rather scattered with much variability exhibited among different tributary drainage basins (more discussions follow).

The regressions of multiyear monitoring data (1983–1991) were based on the single-year survey of pesticide use information conducted in 1986 by Waldron [22]. To further explore the SWMI relationship when more accurate pesticide use information is available, the original database of the Lake Erie Basin was reanalyzed specifically for 1986 (personal communication, P. Richards, Heidelberg College, OH, USA). The sampling period in 1986 covered generally from January to September across the six Lake Erie tributaries (Table 5). Data of insecticide chlorpyrifos data were not available during that monitoring year.

Regressions of the 1986 single-year monitoring and product use data were conducted for each of the six tributaries individually as well as all rivers combined (Table 6). Results of the combined regression are illustrated in Figure 4A to C (Yr 86 models in Table 6). An example for one of the six individual river regressions (Honey Creek) is shown in Figure 5A to C. Compared to the results based on the multiyear data, all the new regressions were improved significantly (Table 6). With the data for all rivers combined, the r^2 value of the 95thpercentile regression increased from 0.71 (n = 64) (Fig. 3A) to 0.87 (n = 67, Fig. 4A), while the TWMC regression increased from 0.33 (n = 36, Fig. 3B) to 0.67 (n = 72, Fig.



Fig. 3. Regressions between the proposed pesticide surface water mobility index (SWMI) and the basin use–normalized concentrations. Data are derived from the multiyear database of the six agricultural tributaries in the Lake Erie Basin, USA, sampled from April 1983 to December 1991. TWMC = time-weighted mean concentration.

4B), and the regression of peak data increased from 0.24 (n = 78, Fig. 3C) to 0.53 (n = 72, Fig. 4C). All results were significant at the 95% level of *Z* statistics [26]. Individual river regressions were generally better than all rivers combined because of reduced variability among different tributary watersheds. The overall improvement of the SWMI relationship as more relevant pesticide use information was incorporated thus supports the concept of SWMI as a generic chemical mobility index. It also underlines the importance of obtaining accurate annual pesticide use data in order to allow quantitative analysis of regional scale monitoring programs.

Although a general improvement in the SWMI regression on the monitoring data was achieved with more accurate annual pesticide use information, it remains true that SWMI correlates best with the 95th-percentile concentrations, particularly when data for all rivers were combined (Table 6). Percentiles either above or below the 95th, including the TWMC and the peak data, appear more scattered, with a few cases of weak correlation, particularly to the peak concentrations (Table 6). The variable ability of SWMI to explain different percentile data can be attributed to a number of reasons. First, the overall wide range of peak concentrations among different pesticides and watersheds (0.09-97 ppb in the multiyear database and 0.004-96 ppb in the single year, 1986), on one hand, appears to provide a sensitive basis responding to the variations of the compound properties (SWMI). The occurrence of individual peak concentrations, on the other hand, is strongly dependent on the nature of the rainfall-generated runoff events (the magnitude as well as the temporal and spatial concurrence with pesticide applications). It can be seen from Figures 3B and 4B that the peak variations among different compounds are about the same in significance as the relative variations of a single compound within the six different watersheds. This would weaken the response of the compound properties to the overall variation of the peak data across different pesticides. The typically heavy soil with high clay content and low infiltration in the Lake Erie drainage basin is of particular relevance to the production of rapid and strong overland flow that directly washes into the tributaries [10]. Peak concentrations usually occur at the time of a pesticide's maximum availability to runoff, often shortly after application. This means that the dependency of peak concentrations on individual chemical properties is reduced regardless of a soil short or long halflife compound even though the trend of correlation (increases as SWMI increases) still remains valid as demonstrated by the overall improved agreement with the 1986 as well as the individual river data.

Second, similar to the peak concentrations, SWMI explained the variation of TMWC data relatively well except for the 1983–1991 data of the six herbicides (Table 6). Compared to the 95th-percentile data, the relatively low r^2 values (even though not statistically different) were probably partly due to the fact that the overall variation in the observed TWMC values were low across the pesticides monitored (range 0.05–2.33 ppb during 1981–1991 and 0.0004–2.99 ppb in 1986). It is expected that the precision of the lower TWMC values could also be adversely affected by the lower precision of the uncensored analytical results near the method LODs. This effect can propagate to the TWMC calculations since the low and relatively less accurate concentrations often have higher time weights representing a wider time period because of the sparser off-season sampling events.

Comparison of the two regression constants α or Log(α) and β in Table 6 reveals that Log(α) increases as the concentration data used for regression changed from TWMC to peak, whereas the general trend for constant β is decreasing. Constant α in Equation 11, or Log(α) in Equation 12, is a scaling parameter that determines the elevation of the model predictions. That is, it adds a linear multiplicity α to the overall regression. Constant β is the exponent of SWMI that defines the shape of the regression model. Generally, as β decreases, the regression model in the form of a power function (Eqn. 11) becomes less concave and thus less sensitive to SWMI.

To illustrate variations among different-size watersheds, the six individual tributary models for the peak and TWMC were plotted in Figure 6A and B. As compared in Figure 6A, the peak models of the three relatively smaller tributaries (Lost,

Table 6. Regression results of the multiyear (1981–1991) and single-year (1986) data for the six Lake Erie, USA, agricultural tributary drainage basins

D		TWMC (µg/L) ^a			95th percentile $(\mu g/L)^b$			Peak (µg/L) ^c					
(regression group)	Drainage area (ha)	$Log(\alpha)$	β	r^2	n^{d}	$Log(\alpha)$	β	r^2	n^{d}	$Log(\alpha)$	β	r^2	n^{d}
All river (1983–1991 models)	2,233,400	1.128	2.720	0.33	36 ^e	1.725	2.408	0.71	64	2.522	1.157	0.24	78
All rivers (1986 models)	2,233,400	1.253	2.854	0.67	72	2.093	2.825	0.87	67	2.492	2.267	0.53	72
Lost Creek	1,130	1.057	3.049	0.72	12	1.963	2.865	0.94	10	2.680	1.960	0.76	12
Rock Creek	8,800	1.411	3.359	0.87	12	2.165	3.049	0.90	11	2.782	2.950	0.85	12
Honey Creek	38,600	1.577	3.478	0.86	12	2.301	3.207	0.92	12	2.952	2.983	0.86	12
River Raisin	269,900	1.063	2.490	0.76	12	1.896	2.507	0.79	12	2.097	2.486	0.83	12
Sandusky River	324,000	1.224	1.712	0.73	12	2.205	2.683	0.93	12	2.346	0.799	0.21	12
Maumee River	1,639,500	1.186	3.037	0.58	12	2.012	2.661	0.86	10	2.095	2.425	0.74	12

^a TWMC = annual time-weighted mean concentration.

^b 95th percentile = concentration at which 95% of time the value is below or equal to.

^c Peak = maximum concentration value.

^d Number of data points. The different number of data points is due to no samples or values excluded when below limit of detection.

^e Only six herbicides were included for the TWMC 1983 to 1991 regression.

Rock, and Honey) deviate clearly from the larger rivers, particularly River Raisin and Maumee River, projecting much higher peak concentrations. The noticeably flatter predictions by the Sandusky peak model were probably due to its low r^2 (=0.21, Table 6). Compared to the peak models, the TWMC models did not exhibit a similar trend of consistent high predictions for the small rivers than for the large ones (Fig. 6B). Predictions of TWMCs were relatively close among differentsize rivers. For example, Lost Creek had TWMC predictions only slightly lower than Maumee River even though it is a much smaller tributary of the latter.

Larger watersheds tend to have lower observed peak concentrations while longer duration of moderate concentrations because of mixing of storm runoff at different stages from their various tributaries [10]. As discussed previously, higherpercentile concentrations (>95th percentile) are primarily storm driven and relatively less dependent on specific pesticides properties. Similarly, low concentrations (<95th percentile) and TWMC may be less associated with basin-scale hydrology in the sense that low concentrations often occur in the postapplication season (winter) and that the pesticide transport, if any, is controlled more by the aged residues in soil and thereby by the pesticide properties. For a given use, the relative importance of the basin-scale characteristics, such as watershed sizes, in determining pesticide occurrence varies with time, equivalently in determining different percentile concentrations. This observation agrees with the results of Richards and Baker [10], who compared concentration exceedency curves of different-size tributaries and found that smaller tributaries deviate from larger ones significantly only at concentrations exceeding the 99th percentile.

Preliminary model evaluation

The transportability of the SWMI regressions to watersheds other than the Lake Erie tributaries was evaluated by comparing the SWMI model predictions to monitored pesticide concentrations from two other monitoring data sets in midwestern corn states: one from a river system (White River at Hazelton, IN, USA) and the other from a reservoir system (Higginsville City Lake, MO, USA). The evaluation was to test the robustness/sensitivity of the regression models to variations in geohydrological/meteorological conditions, watershed size, and agricultural practices that are potentially different from the reference tributaries of the Lake Erie Basin.

The TWMC and 95th-percentile and peak concentrations of the White River Basin monitoring data obtained from Hazelton, Indiana, are compared to the SWMI model predictions in Figure 7A to C. Since no calculable TWMC and 95thpercentile data were available for chlorpyrifos, s-ethyl dipropylthiocarbamate (EPTC), fonofos, terbufos, and linuron, only peak concentrations were presented in Figure 7C for these compounds. Three groups of the SWMI regressions in Table 6 were used: the multiyear databased Yr 1983-91 model, the 1986 databased Yr 86 model, and the 1986 Maumee River model. The Maumee model was selected primarily because it was the largest Lake Erie tributary with drainage area about half of the White River watershed. As shown in Figure 7A to C, all three models, in the majority of the cases, had ratios of predicted percentiles of monitored concentrations in the range of 0.5 to 5 even though the Yr 86 and Maumee models were noticeably better than Yr 83-91 for the peak predictions. The Yr 83-91 model predicted considerably higher peaks than the other two models (1-13 times for most of the compounds, 46 and 165 times for EPTC and butylate, respectively). As discussed previously, the data on which the Yr 83-91 regression is based were obtained over the nine-year period (1983–1991) from the Lake Erie tributaries. The regression, and consequently its predictions, are likely to be biased toward the extreme runoff event values.

Although overpredictions of the peak concentrations by the Yr 86 and Maumee models were not as severe as by the Yr 83-91 model, the bias to higher predicted concentrations was quite consistent for most compounds (Fig. 7C). Specific reasons for consistent over- or underprediction are not readily apparent even though potential influence by factors such as watershed characteristics and agricultural practices between the two basins may be expected. The entire White River Basin has a much larger drainage area than any of the SWMI model calibration tributaries and covers a mix of diverse hydrogeomorphic regions from the relatively impervious northern till plain to the better-drained southern glacial lowland [27]. Tile drain contribution to pesticide concentrations in surface water is also common in the region. As discussed previously, larger drainage basins with diverse hydrogeological properties tend to have lower peak concentrations. Additionally, some highly nonuniform pesticide use patterns in the watershed may have made it difficult to compare monitoring data from a given site to the SMWI models that are based on homogeneous use rates



Fig. 4. Regressions between the proposed pesticide surface water mobility index (SWMI) and the basin use-normalized concentrations. Data are derived from the single-year (1986) database of the six agricultural tributaries in the Lake Erie Basin, sampled from January to September 1986. TWMC = time-weighted mean concentration.

throughout a drainage basin. For example, the percentage of acres treated with the corn herbicide butylate in 1993 was eight times (four times in total amount) greater in southern Indiana than in the central, resulting in observed peak concentrations 27- to 59-fold different among different subdrainage basins in the White River watershed [27]. Other potential factors may also include the nonagricultural uses of several pesticides within the watershed as well as the sampling regimen for the White River that might not capture concentration peaks as in the Lake Erie Basin monitoring program.

The atrazine monitoring data from a much smaller watershed, the Higginsville City Lake, are presented in Figure 8 with annual TWMC and 95th-percentile and peak concentrations in both raw and finished water systems during 1995-1997. The corresponding SWMI model predictions are also



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Fig. 5. Regressions between the proposed pesticide surface water mobility index (SWMI) and the basin use-normalized concentrations. Data are derived from the single-year (1986) database of Honey Creek, USA, sampled from January to September 1986. TWMC = timeweighted mean concentration.

shown in Figure 8. The Yr 86 model predicted the 95th-percentile and peak concentrations very well, particularly for the raw water, with the prediction-to-measurement ratio ranging 0.9 to 1.2 for the 95th-percentile data and less than fourfold for the peak concentrations. The overall performance of the Yr 86 model was noticeably better than the Yr 83-91 model even though both underestimated the annual TWMCs by a factor of 2 to 5. The raw water annual TWMC was below 3 µg/L and the finished water below 2.0 µg/L during the threeyear monitoring period.

The relatively high runoff potential in the Higginsville City Lake drainage basin is generally attributed to the dominant soil types that had clay content in the range of 21 to 23% and the common presence of silty loess in the soils [25]. These relatively heavy soil types and gently to strongly sloping geo-



Fig. 6. The effect of river size on the pesticide surface water mobility index (SWMI) model predictions for the peak and annual time-weighted mean concentrations (TWMC). Refer to Figure 2 for creek and river locations.

morphology appear to resemble the general characteristics of the Lake Erie tributary drainage basins, which may have led to the closer model agreement with the 95th-percentile and peak concentrations. Compared to the river systems, however, water in the Higginsville City Lake is expected to be relatively static, resulting in longer residence time for pesticide residues in the lake than in a river system. Since TWMC is a longterm parameter while peak concentrations are temporary, underestimation of TWMC in reservoirs/lakes by the flow stream–based SWMI models may reflect the effect of water flow on the annual averages of potential pesticide residues (dilution factor).

CONCLUSIONS

This paper describes a pesticide surface water mobility index to quantify the movement of pesticides to surface water via overland runoff and erosion on various watershed scales. The proposed SWMI was found to statistically correlate with the various percentiles of pesticide concentrations in rivers obtained from a nine-year monitoring database for the Lake Erie Basin tributaries. The regression improved significantly with more accurate annual pesticide use information. This observation underlines the importance of collecting relevant pesticide use data within the watersheds in order to obtain a more realistic quantitative analysis of regional scale pesticide surface water monitoring programs. Watershed hydrology ap-



Fig. 7. Comparison of model-predicted concentrations to the observed data of 12 pesticides in White River at Hazelton (IN, USA) 1991–1996. TWMC = time-weighted mean concentration; EPTC = s-ethyl dipropylthiocarbamate.

peared to play an important role in determining pesticide occurrence in surface water, especially for the pesticide peak and higher-percentile (e.g., >95th percentile) concentrations. However, specific pesticide properties become more important at low concentration ranges. A preliminary model evaluation was conducted with two independent pesticide surface water



Fig. 8. Comparison of model-predicted concentrations to the observed data of atrazine in raw and finish waters at the Higginsville City Lake (MO, USA) 1995–1997. TWMC = time-weighted mean concentration.

monitoring data sets, one obtained from a much larger scale river system (drainage area 2,938,382 ha, White River at Hazelton) and the other from a small reservoir (1,386 ha, Higginsville City Lake). The SWMI models, based on the 1986 monitoring data and the 95th-percentile model based on multiyear data (1983-1991) from the six Lake Erie tributaries, demonstrated predictions of TWMC and peak and 95th-percentile concentrations mostly within fivefold of the observed data. It is suggested that these regression models may be used as simple screening tools to provide quick and reasonably conservative estimates of pesticide concentrations in surface water. For example, when monitoring data are not available, the TWMC and the 95th-percentile estimates by the SWMI models for a surface water system can be used for chronic and acute exposure assessments for ecological or human health purposes if the water system is used as a public drinking water supply.

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