

A theoretical underpinning of the pesticide Groundwater Ubiquity Score (GUS)

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Abstract: The Groundwater Ubiquity Score (GUS) is widely used to indicate the relative leachability of pesticides based on the soil half-life and the adsorption partition coefficient. In this manuscript, we derive mathematically the Theoretical Groundwater Ubiquity Score (TGUS) that, based on considerations of the preferential movement of pesticides to groundwater and a first-order pesticide degradation model, leads to a similar function as the GUS model. In the preferential flow model, movement to groundwater is fast, and the adsorption partition coefficient is thus not used for calculating the travel time to the groundwater (as it is in the advective-dispersive equation) but rather only determines the distribution of the pesticide between the water and soil phases. Both the GUS and TGUS models well predict the groundwater contamination of the originally studied pesticides for rainfall event(s) that caused pesticide leaching from 30 days after application. The theoretically derived Groundwater Ubiquity Score (TGUS) shows, in accordance with experimental evidence, that for leaching events shortly after spraying, the mass lost to (and resulting concentration in) groundwater is inversely related to the adsorption partition coefficient and not necessarily to the GUS index.

Keywords: Agriculture; Contamination; Groundwater; Groundwater Ubiquity Score; GUS; Half-life; Index; Leachability; Pesticides.

1 INTRODUCTION

Pesticides protect crops against insects and diseases and help prevent severe food shortages for the growing world population. At the same time, the leaching of pesticides may harm the environment, and long-term exposure may lead to severe adverse effects. Pesticide contamination of groundwater is especially concerning because it is often the only source of drinking water in the many agricultural areas where these substances are applied.

Experiments to test pesticide leaching risk are expensive and can only test a limited set of compounds and usage contexts. A prime example of the potential consequences of using a pesticide in contexts that differed markedly from initial experimental settings occurred in the 1980s in the potato-growing areas of Long Island, NY. In this case, the presence of preferential flow and a longer-than-expected half-life enabled the pesticide Aldicarb to rapidly leach to groundwater and contaminate many household wells (Fisher et al., 2021; Zaki et al., 1982). Consequently, screening models and indexes are important tools to help predict the tendency for pesticides to leach into groundwater under conditions beyond those specifically tested in experiments.

Although some progress has been made in predicting pesticide leaching in the last half century, an agreed model for predicting groundwater contamination does not exist (Kaiglová and Langhammer, 2014). Many of the models and indexes developed in the last part of the 20th century were based on convective transport by estimating the travel time of the pesticide to the groundwater calculated by dividing the downward water flux by a retardation factor (derived from the organic carbon partition coefficient K_{oc}) and subsequently using the travel time to calculate the decrease in pesticide concentration assuming a first-order degradation (e.g., Hamaker, 1975; Jury et al., 1983;

Meeks and Dean, 1990; Rao et al., 1985; Spadotto, 2002). Alternatively, other models considered preferential flow instead of convective flow, such as MACRO (Larson and Jarvis, 2000), the Root Zone Water Quality Model (RZQM) (Ahuja et al., 1996), and TAM-MO-DEL (Steenhuis et al., 1997). However, most of the models mentioned above were not validated with field data, or if field data was used, only the concentrations in the soil profile were compared (Di et al., 1995; Jury et al., 1984), making it difficult to tease out the relatively small yet significantly impactful amounts leached to groundwater (Kladivko et al., 1991; Steenhuis et al., 1997). In recognition of the problematic performance of models in predicting leaching losses to groundwater, indices based on observed pesticide leaching data and pesticide properties were developed by several researchers (e.g., Gramatica and Di Guardo, 2002; Gustafson, 1989; Papa et al., 2004).

As the costs of pesticide analysis decreased greatly, enabling broader testing, it became obvious that early models based on the convective dispersive equation could not account for the rapid movement of pesticides to groundwater (Jung et al., 2024; Kladivko et al., 1991); This was an incentive for many scientists to develop leaching indices in addition to the few that were available before 2000 (e.g., Demir et al., 2019; Jung et al., 2024). Despite the many new indices, the Groundwater Ubiquity Score (GUS) by Gustafson (1989) is still considered the most representative method for predicting the propensity for pesticide leaching into groundwater (Jung et al., 2024; Pawlowski et al., 2023). For example, the GUS was recently used to predict pesticide-leaching hazards for groundwater sources in Ireland (Harmon O'Driscoll et al., 2022).

The Groundwater Ubiquity Score, GUS, was derived by Gustafson (1989) by plotting the log of the adsorption partition coefficient of organic carbon, K_{oc} , versus the log of the half-life, $t_{1/2}$. The 29 pesticides that Gustafson (1989) used were classified

by Wilkerson and Kim (1986) of the California Department of Food and Agriculture (CDFA) as known contaminants of groundwater (leachers), known noncontaminants (non-leachers) and transition pesticides for which evidence was available of groundwater contamination. After plotting the log of the two pesticide properties, Gustafson (1989) devised a hyperbolic scoring equation expressing how both sorption and degradation affect occurrences in groundwater:

$$\text{GUS} = \log\left(\frac{t_1}{2}\right) (4 - \log(K_{oc})) \quad (1a)$$

where t_1 is half-life in days and K_{oc} the organic carbon partition coefficient in $\text{m}^3 \text{Mg}^{-1}$. Gustafson further stratified these GUS scores, finding that GUS scores greater than 2.8 for a pesticide represent leachers, scores between 1.8 and 2.8 are in the transition zone between leachers and non-leachers, and values less than 1.8 indicate that the pesticide has a low probability of leaching to groundwater and is called a non-leacher. Interestingly, Eq. (1a) can also be written as the product of two logs:

$$\text{GUS} = \log\left(\frac{t_1}{2}\right) \log\left(\frac{10^4}{K_{oc}}\right) \quad (1b)$$

The drawback of Eq. (1) is that this functional form does not have a theoretical background. Therefore, its applicability is empirical and limited to those pesticides that Gustafson originally studied and to past expert judgments about their leachability. The objective of this manuscript is to find a physically based justification for the original GUS approach. By deriving a GUS-like equation from first principles, it will be possible to obtain the physical meaning of a constant, such as the 4 in Eq. (1a) or 10^4 in Eq. (1b), and interpret expert judgment embedded in thresholds (1.8 and 2.8) in the GUS equation for different groundwater sampling strategies.

To find a physical-based explanation of the GUS equation, we first explain and present a bare-bone conceptual model of preferential pesticide movement in soils, followed by a section that translates the conceptual model into mathematical form. The mathematical form is then written in the form of the GUS Equation (Eq. 1a). We call this new model the Theoretical Groundwater Ubiquity Score (TGUS). The next section compares the TGUS and GUS equations and explains the physical dependence of the constant 4 in Eq. (1a). Then, using the original data from Gustafson (1989), we discuss whether GUS and TGUS are similar in predicting pesticide leachability. Finally, we show that the leachability of a pesticide depends not only on the pesticide properties, soil properties, and analytical detection limit but also on the time lag between the application and the rainfall event that transports the pesticide to shallow groundwater.

2 THEORY

2.1 Preferential pesticide movement in the vadose zone

Since the unexpected contamination of the Long Island aquifer with aldicarb in the 1980s and the research on preferential flow by Germann and Beven (1981) and others half a century ago, it has become clear that, in humid climates, preferential flow is the rule rather than the exception (Ritsema et al., 1998). Water and solutes (including pesticides) flowing through these channels bypass most of the soil matrix (Camobreco et al., 1996; Domagalski and Johnson, 2011; Starr et al., 1986; Tesoriero et al., 2009). Scotter (1978) found that for

continuous channels at least 0.2 mm nominal diameter, dissolved contaminants can theoretically move to 2 m depth in less than 10 minutes. In a later review by Jarvis (2007), 0.3 mm diameter pores are considered the cutoff for non-equilibrium transport of dissolved substances.

Based on the above findings, some agreement exists that preferential movement of pesticides in the critical vadose zone is responsible for groundwater contamination. Since there is no consensus on soil properties to describe preferential flow, most models for pesticide movement, especially those that originated in the 1980s, use the advective dispersive equation first employed by van der Molen (1956) to model pesticides. The advantage of using advective transport is that it allows for numerical modeling of the pesticide transport (Hutson and Wagenet, 1993; Sahoo et al., 2005). However, the capacity of these models to predict pesticide movement to groundwater is mixed at best.

2.2 Preferential pesticide transport model

2.2.1 Pesticide transport

Experiments in which blue dye is applied to the soil are used to formulate the model (Li et al., 2021; Richards et al., 2003). Figure 1a is an example of one of these blue dye experiments. Figure 1b is a conceptual representation of the flow with a distribution zone in the highly conductive root zone through which the water moves to the transmission zone below (Darnault et al., 2004).

The subsurface transmission zone below the distribution zone extends to the water table. The preferential flow paths in the transmission zone (as its name implies) transmit the water and the dissolved pesticides to the groundwater below. The transmission zone is conceptually divided into preferential continuous flow paths with diameters larger than 0.3 mm and the soil matrix, including any dead-end macropores (Larsson and Jarvis, 2020; Scotter, 1978).

Since this manuscript intends to develop a pesticide scoring index, the pesticide transport processes are greatly simplified. We will ignore dispersion, assume steady state precipitation, and assume pesticides in preferential flow paths move within one day to the groundwater without interaction with the pore walls.

Since the distribution zone behaves as a linear reservoir, the concentration of solutes leaching from the distribution zone can be expressed as (Asano and Uchida, 2012; Steenhuis et al., 1994)

$$C_{dist}^w = C_0^w \exp\left(-\frac{q t}{W_{dist}}\right) \quad (2)$$

where C_{dist}^w [M L^{-3}] is the dissolved pesticide concentration in the distribution zone, C_0^w [M L^{-3}] is the initial dissolved pesticide concentration in the distribution zone after application and mixing, q [$\text{L}^3 \text{L}^{-2} \text{T}^{-1}$] is the imposed flux or rain, t [T] is the time since the water was applied, and W_{dist} [$\text{L}^3 \text{L}^{-2}$] is the apparent water content of the pesticide distribution zone, defined as (Sinkevich et al., 2005; Steenhuis et al., 1994)

$$W_{dist} = d(\theta_s + \rho k_d) \quad (3a)$$

where d [L] is the thickness of the pesticide distribution zone, θ_s [$\text{L}^3 \text{L}^{-3}$] is the saturated volumetric moisture content, ρ [M L^{-3}] is the bulk density of the soil and k_d [$\text{L}^3 \text{M}^{-1}$] is the pesticide distribution coefficient. W_{dist} [L] is equal to the actual water in the distribution zone for non-sorbing solutes (i.e., $k_d = 0$). The apparent water content increases for pesticides due to adsorption effects on the soil. Thus, pesticide leaching is slower than

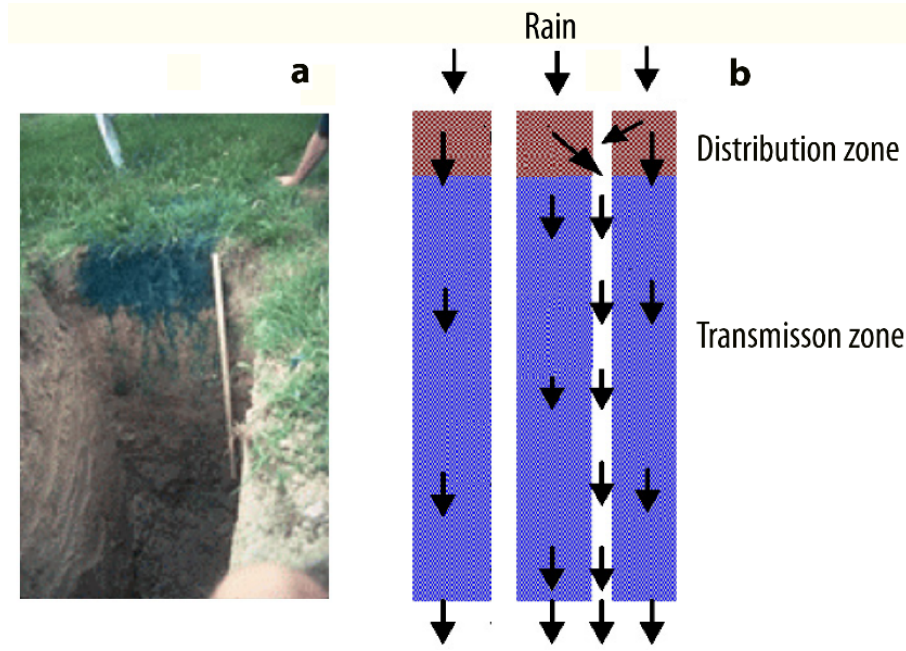


Fig. 1. (a) A blue dye #1 tracer distribution in a soil profile after infiltration in a field experiment. (b) A schematic representation of the transport model includes an upper distribution zone and a lower transmission zone containing preferential flow paths and the soil matrix.

non-sorbing solutes for the same water flux. The initial dissolved pesticide concentration in the distribution zone after pesticide application, C_0^w [M L⁻³] can be expressed as

$$C_0^w = \frac{M_0^{app}}{W_{dist}} \quad (3b)$$

where M_0^{app} [M L⁻²] is the amount of the pesticide applied per unit area. Eqs. (2) and (3a,b) have been shown to describe pesticide leaching in the critical zone well (Hassanpour et al., 2019; Steenhuis et al., 1994, 1997).

In the underlying transmission zone, flow through the preferential paths is fast, and pesticides neither degrade nor adsorb to the macropore walls (Scotter, 1978). Conversely, pesticide transport through the soil matrix is negligible because the pesticides are degraded by the time that they would have arrived at the groundwater.

2.2.2 Pesticide degradation

Pesticide degradation rates in field soils vary widely depending on factors such as previous history of applications, pH, moisture content, redox potential, temperature, etc. (Schwarz et al., 2022). Microbiologists also point out that first-order degradation is a generalization. Despite these valid arguments, most transport models and indices nevertheless use a first-order pesticide degradation rate with average rates from the literature. The first-order degradation can be expressed as (Beulke and Brown, 2001):

$$C^D(t) = C_0^D \exp(-at) \quad (4)$$

where $C^D(t)$ [M L⁻³] is the pesticide mass per unit volume of soil (including the water) in the distribution zone at time t , and the coefficient a [T⁻¹] is the reaction rate, which can also be expressed as a function of the half-life, $t_{1/2}$ [T] as

$$a = \frac{0.69}{t_{1/2}} \quad (5a)$$

and C_0^D [M L⁻³] is the distribution zone pesticide concentration at the time of application

$$C_0^D = \frac{M_0^{app}}{d} \quad (5b)$$

As noted above, we will assume that pesticide degradation occurs in the distribution zone and is subsequently minimal in the groundwater.

2.2.3 Simplifying the combined transport and degradation equation

Combining Eqs. (2) and (4), the concentration in the preferential flow is

$$C_{prfl}^w = C_0^w \exp\left(-\left(\frac{q}{W_{dist}} + a\right)t\right) \quad (6)$$

where C_{prfl}^w [M L⁻³] is the dissolved pesticide concentration in the preferential flow path. Due to the adsorption increasing the apparent water content of the distribution zone (Eq. (3a)), the loss from the distribution zone of pesticides is small compared with loss due to degradation (i.e., $a \gg q/W_{dist}$),

$$C_{prfl}^w = C_0^w \exp(-a t) \quad (7)$$

Thus, the pesticide degradation in Eq. (4) describes the pesticide concentration in preferential flow when it arrives at the groundwater, using the simplifying assumptions made above.

To calculate the resulting concentration in the groundwater $C_{gr,prfl}^w$ [M L⁻³], we should consider that the flux through the preferential flow paths is only a small portion of the total recharge because most recharge to the groundwater is via the matrix (Jarvis, 2007)

$$C_{gr}^w = \beta C_{prfl}^w \quad (8)$$

where β [dimensionless] is the fraction of recharge that reaches the aquifer by preferential flow. It is assumed that what flows through the matrix moves much slower, and the pesticides moving via the matrix are effectively degraded before reaching the groundwater. Thus, recharge reaching the groundwater via the soil matrix simply dilutes the concentration of the pesticides conveyed by the preferential flow paths.

2.3 Pesticide ubiquity score index

2.3.1 Theoretical index development

To develop the index, we need to understand the meaning of pesticide *detection* in the groundwater. Detection of a pesticide means its concentration is equal to or greater than an analytical detection limit. Thus, as implicitly assumed by Gustafson (1989), the Groundwater Pesticide index, I [dimensionless], is defined as

$$I = \frac{C_{gr}^w}{C_{lim}^w} \quad (9)$$

where C_{gr}^w [$M L^{-3}$] is the concentration in the groundwater due to the application of pesticides and C_{lim}^w [$M L^{-3}$] is the analytical detection limit of the instrument. The definition is equally valid if we use, for example, the drinking water standard, but the constants in the equation would differ. When the concentration in the groundwater is equal to or greater than the detection limit (i.e., $I < 1$), it is called a "detect" (or a leacher in Gustafson, 1989); otherwise, when $I > 1$, it is a "non-detect". When I is around 1 (i.e., $C_{gr} \cong C_{lim}$), the term "transition" is used in Gustafson's terminology.

Substituting Eqs. (8) and (9) into Eq. (7) yields

$$I = \frac{C_{lim}^w}{\beta C_0^w} \exp(at) \quad (10)$$

A reduction factor, Φ [dimensionless], is introduced, which indicates the fraction that the initial pesticide in the soil needs to be reduced to reach a concentration at the detection limit,

$$\Phi = \frac{M_0^{app}}{C_{lim}^w d} = \frac{C_0^w (\theta_s + \rho k_d)}{C_{lim}^w} \quad (11)$$

Rearranging Eq. (11) gives

$$C_{lim}^w = \frac{(\theta_s + \rho k_d) C_0^w}{\Phi} \quad (12)$$

Combining Eqs. (10) and (12), assuming $\theta_s \ll \rho k_d$, eliminating C_{lim}^w results in

$$I = \frac{\rho k_d \exp(at)}{\beta \Phi} \quad (13)$$

Taking the natural log on both sides of Eq. (13) and substituting Eq. (5)

$$\ln I = \frac{0.69}{t_1} t + \ln \left(\frac{\rho k_d}{\beta \Phi} \right) \quad (14)$$

In Eq. (14), by setting $I = 1$, and rearranging, the contour that separates the detects from non-detects is found:

$$0.69 \frac{t}{t_1} + (\ln(\rho k_d) - \ln(\beta \Phi)) = 0 \quad (15)$$

Separating the variables that describe the pesticide (t_1, Φ, k_d) and the soil properties (β, ρ) and those that do not (i.e., 0.69 t) yields

$$t_1 \left(\ln \frac{\beta \Phi}{\rho} - \ln k_d \right) = 0.69 t \quad (16)$$

Since Eq. (16) is obtained by setting $I = 1$ in Eq. (9) for other combinations of parameters when the left-hand side of Eq. (16) is greater than 0.69 t , the pesticides are leachers, and when less, the pesticides are non-leachers.

Since this function of the left-hand side of Eq. (16) is similar to the GUS (Eq. (1a)), where a comparable combination of variables indicates the pesticide is leachable, the left-hand side of Eq. (14) is defined as TGUS_e. TGUS_e stands for the Theoretical Groundwater Ubiquity Score because the soil physics theory is used to derive it:

$$TGUS_e = t_1 \left(\ln \frac{\beta \Phi}{\rho} - \ln k_d \right) \quad (17a)$$

$$\text{leachers: } TGUS_e > 0.69 t \quad (17b)$$

$$\text{non-leachers: } TGUS_e < 0.69 t \quad (17c)$$

Subscript e was added because the natural log is used on the right-hand side. The k_d value is not widely available in the literature but can be derived from the adsorption partition coefficient of organic carbon, K_{oc} [$L^3 M^{-1}$] as (Gustafson, 1989)

$$k_d = f_{oc} K_{oc} \quad (18)$$

where f_{oc} [$M M^{-1}$] is the organic carbon fraction in the soil. Combining Eqs. (17a) and (18):

$$TGUS_e = t_1 (\ln \xi - \ln K_{oc}) \quad (19a)$$

$$\xi = \frac{\beta \Phi}{f_{oc} \rho} \quad (19b)$$

where ξ [$L^3 M^{-1}$] is a constant that is a function of the soil characteristics (organic matter, bulk density, and the amount of preferential flow) and a regulatory parameter that indicates the factor by which the concentration at the surface should be reduced to meet the imposed analytical detection limit (or groundwater standard).

To comply with the log to the base 10 values in GUS, we can easily convert the natural log in Eq. (17) by multiplying the numerator and denominator by $\log_{10} e = 0.43$, viz

$$TGUS = t_1 (\log \xi - \log K_{oc}) \quad (20a)$$

$$\text{leachers: } TGUS > 0.30 t \quad (20b)$$

$$\text{nonleachers: } TGUS < 0.30 t \quad (20c)$$

where TGUS is now $\log_{10}$ based.

3 RESULTS

3.1 Reconciling TGUS and GUS

This section will reconcile the theoretically derived TGUS (Eq. (20)) with the GUS (Eq. (1)). To do this, we employ the same 44 pesticides that Gustafson (1989) used to derive the functional form of GUS, as shown in Table 1. Wilkerson and Kim (1986) of the California Department of Food and Agriculture (CDFA) compiled a list that designated known

contaminants of groundwater (leachers), known noncontaminants (non-leachers), and so-called transition pesticides that were sometimes detected in groundwater (Table 1). Wilkerson and Kim (1986) also collected pesticide properties related to leachability but could not find some of the K_{OC} and $t_{1/2}$ values. At the time of analysis in the late nineteen eighties, Gustafson (1989) only had the K_{OC} and $t_{1/2}$ values for pesticides #1 through #26 and # 42 through #44 (Table 1) for his calculation of the GUS. We obtained the values for the remaining pesticides (#27–41, Table 1) from Vogue et al. (1994) and the University of Hertfordshire (2024), except for a few that were not in the database.

3.1.1 Linear regression of TGUS with GUS

The first step in reconciling the TGUS and GUS equation is to determine the value of the constant, $\log \xi$ value in Eq. (20). To do this, we systematically changed the $\log \xi$, finding the best fit with the highest R^2 in the linear regression of TGUS and GUS values for the original Gustafson data (pesticides # 1–26 in Table 1). The chlorinated hydrocarbon insecticides (#42–44, Table 1) were not included in the regression because their extremely high K_{OC} values would have an undue impact on the regression. We found that the linear regression of GUS and TGUS with a value of $\log \xi = 3.4$ (ξ is in cm^3g^{-1}), had the greatest R^2 of 0.72, (Figure 2).

Table 1. List of pesticides Gustafson (1989) considered in calculating the Groundwater Ubiquity Score (GUS). The properties and GUS values for pesticides 1–26 and 42–44 are taken from Table 1 in Gustafson. Properties for pesticides 27–31 were from other sources. GUS was calculated with Eq. (1); the Theoretical Groundwater Ubiquity Score (TGUS) was computed with Eq. (20a) and TGUS* with Eq. (26a). The list was originally published by Wilkerson and Kim (1986) and copied by Gustafson (1989). Outliers are pesticides that are not considered in the regression.

			K_{OC} [m^3/Mg]	Soil half-life [day]	GUS	TGUS	TGUS*
Leacher	1	Aldicarb	17	7	2.3	15	0.4
Leacher	2	Atrazine	107	74	3.7	98	2.4
Leacher	3	Diuron	389	188	3.2	143	3.5
Leacher	4	Metolachlor	99	44	3.3	60	1.5
Leacher	5	Oxamyl	26	8	2.3	15	0.4
Leacher	6	Picloram	26	206	6.0	399	9.9
Leacher	7	Prometryn	614	94	2.4	53	1.3
Leacher	8	Simazine	138	56	3.3	68	1.7
Non-leacher	9	Chlordane	19269	37	-0.4	-35	-0.9
Non-leacher	10	Chlorothalonil	1380	68	1.6	14	0.4
Non-leacher	11	Chlorpyrifos	6085	54	0.4	-23	-0.6
Non-leacher	12	2,4-D	53	7	1.9	11	0.3
Non-leacher	13	Dicamba	511	25	1.8	16	0.4
Non-leacher	14	Endosulfan	2040	120	1.4	5	0.1
Non-leacher	15	Heptachlor	13330	109	-0.3	-84	-2.1
Non-leacher	16	Lindane	1727	569	2.1	64	1.6
Non-leacher	17	Phorate	1660	38	1.2	5	0.1
Non-leacher	18	Propachlor	794	4	0.7	2	0.0
Non-leacher	19	Toxaphene	95816	9	-0.9	-15	-0.4
Non-leacher	20	Trifluralin	7950	83	0.2	-46	-1.1
Transition	21	Alachlor	161	14	2.1	16	0.4
Transition	22	Carbaryl	423	19	1.8	14	0.3
Transition	23	Carbofuran	55	37	3.5	60	1.5
Transition	24	Dinoseb	5900	30	0.3	-13	-0.3
Transition	25	Ethoprop	26	63	4.7	122	3.0
Transition	26	Fonofos	5105	25	0.4	-9	-0.2
Leacher	27	Chlorthal dimethyl	25119	34	-0.6	-36	-0.9
Leacher	28	Cyanazine	190	14	2.0	15	0.4
Leacher	29	DBCP	70	180	4.9	271	6.7
Leacher	30	EDB	34	100	4.9	182	4.5
Leacher	31	Metribuzin	60	40	3.6	63	1.6
Leacher	32	Naled	180	1	0.0	1	0.0
Leacher	33	Prometon	150	500	4.9	587	15
Leacher	34	Propylene dichloride	0	52	13.7	382	9.5
Non-leacher	35	Aldrin	5000	365	0.8	-127	-3.2
Non-leacher	36	Chloramben	15	14	3.2	30	0.8
Non-leacher	37	1,3-D	32	10	2.5	18	0.5
Non-leacher	38	DDD	100000	1000	-3.0	-1650	-41
Non-leacher	39	Endosulfan sulfate	12400	50	-0.2	-37	-0.9
Non-leacher	40	Pendimethalin	5000	90	0.6	-31	-0.8
Non-leacher	41	Silvex	80	10	2.1	14	0.4
Outlier	42	DDT	213600	38200	-6.1	-75621	-1871
Outlier	43	Endrin	11188	2240	-0.2	-1565	-39
Outlier	44	Dieldrin	12100	934	-0.2	-684	-17

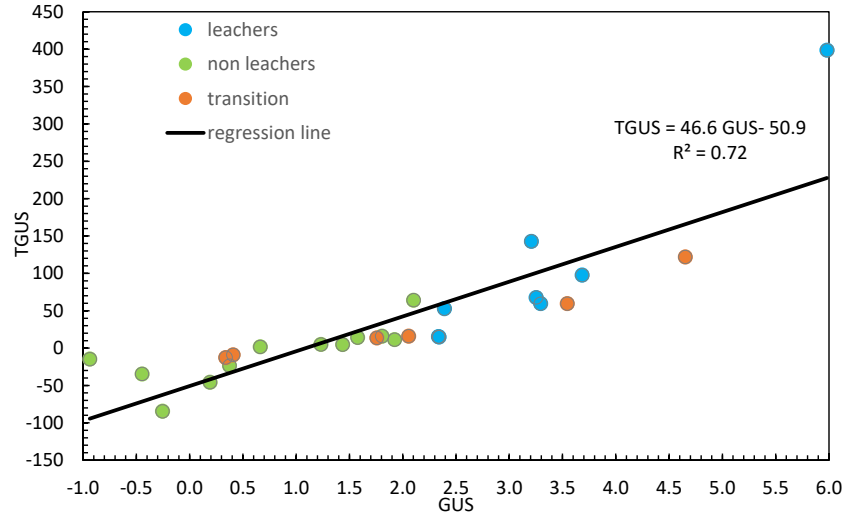


Fig. 2. The Theoretical Groundwater Ubiquity Score (TGUS, Eq. (20a) with $\log \xi = 3.4$) vs. Groundwater Ubiquity Score (GUS) for pesticide #1–26 in Table 1, which Gustafson (1989) used in developing the GUS.

For the TGUS equation to have a theoretical basis, we should verify that the values of the variables making up the ξ in Eq. (19b) and $\log \xi$ in Eq. (20a) have physical meaning. We can do this by setting $\log \xi = 3.4$ obtained from the regression. Thus, taking the antilog, we find

$$\frac{\beta\Phi}{f_{oc}\rho} = 10^{3.4} = 2240 \quad (21)$$

In the following section, we chose a set of variables in Eq. (21) and confirmed that a value of 2240 can be obtained. It should be noted that many other realistic combinations of parameters are valid. Based on recent New York state pesticide labels (the legal documents governing use), most pesticides in Table 1 have an application rate of 1 to 2 kg/ha of active ingredients. Steenhuis and Walter (1980) and Baker et al. (1978) found that the distribution layer depth was around 1 cm. Converting a mean application mass of 1.5 kg/ha (active ingredient) in the top 1 cm results in a concentration of 1.5×10^{-5} Mg m⁻³. Moreover, if we assume that a detection limit of 10^{-9} Mg m⁻³ (i.e., 1 ppb) was possible in 1988, it will result in $\Phi = 1.5 \times 10^4$. Furthermore, assuming that the bulk density of $\rho = 1.3$ Mg m⁻³, and the organic matter content is 3.3% (i.e., $f_{oc} = 0.02$ g g⁻¹) because the organic matter consists of 60% carbon, the preferential portion of the flow would be 0.4% to obtain a value of 2240 in Eq. (21). Since 1.4% or less of the annual recharge is preferential flow (Jarvis, 2007; Klavivko et al., 1991; Shipitalo et al., 1994), the above analysis shows that with a reasonable choice of physical parameters, the constant $\log \xi = 3.4$, in Eq. (20a) can be justified. A more refined analysis should be carried out on pesticide leaching and the effect of ignored parameters in the derivation. For example, the impact of dilution by groundwater flow from nearby fields is not considered. The calculated portion of the preferential flow would consequently be greater with lateral flow.

3.1.2 Mathematical gymnastics

Since the TGUS and GUS are very similar in functional form, despite their different origins, we should be able to show that TGUS and GUS are mathematically similar. The GUS and TGUS functions (Eqs. (1a) and (20)) that separate the non-

detects from the detects (transition) are repeated here to show this similarity.

$$\text{GUS} : \log\left(\frac{t_1}{2}\right) * (4 - \log(K_{oc})) = 1.8 \quad (22)$$

$$\text{TGUS} : \frac{t_1}{2} * (3.4 - \log(K_{oc})) = 0.30 * t \quad (23)$$

Nevertheless, while the GUS-based Equation (Eq. (22)) and the TGUS equation (Eq. (23)) look similar, there are three main differences. The first and greatest difference is that the first term in GUS (Eq. (21)) is $\log \frac{t_1}{2}$ while it is $\frac{t_1}{2}$ in the TGUS formulation (Eq. (23)). The second difference is that the TGUS depends on the occurrence of mobilizing rainfalls following the pesticide application, while the GUS is independent of t . The third difference is between the constants 4 and 3.4, which are only of the same order of magnitude.

The average half-life of the pesticide (# 1–26 in Table 1) on which the GUS was based was 76 days. To introduce the missing $\log$ in Eq. (23), we define an approximate $\log \frac{t_1}{2}$ in Eq. (22) as

$$\log\left(\frac{t_1}{2}\right) = \frac{\log\left(\frac{t_1}{2}\right)}{\frac{t_1}{2}} \frac{t_1}{2} \quad (24)$$

where for an average half-life of $\frac{t_1}{2} = 76$ days

$$\frac{\log\left(\frac{t_1}{2}\right)}{\frac{t_1}{2}} = \frac{\log 76}{76} = \frac{1.88}{76} = 0.025 \quad (25)$$

multiplying the left-hand side of Eq. (23) by the first term in Eq. (25) and the right side by the last term, an expression is obtained for the modified Theoretical Groundwater Ubiquity score, TGUS*

$$\text{TGUS}^* = \log\left(\frac{t_1}{2}\right) * (3.4 - \log(K_{oc})) - 0.0075 t \quad (26a)$$

$$\text{leachers: } \text{TGUS}^* > 0 \quad (26b)$$

$$\text{nonleachers: } \text{TGUS}^* < 0 \quad (26c)$$

Finally, setting the time equal to $t = 240$ days in Eq. (26a) for

the line that separates the detects from the non-detects becomes similar, i.e.,

$$\text{TGUS}^* = \log\left(\frac{t_1}{2}\right) * (3.4 - \log(K_{oc})) - 1.8 \quad (27)$$

where $\log\left(\frac{t_1}{2}\right) = 0.025t_{\frac{1}{2}}$. The TGUS* in Eq. (27) is nearly equal to the GUS expression in Eq. (22), except the constant of 3.4 in the TGUS* (Eqs. (26a), (27)) is less than the 4 in the GUS equation. One reason is that taking the average of the logs puts more weight on the large values than on the arithmetic average. The value of 3.4 in TGUS* (Eq. (26a)) compensates for the higher value log in Eq. (22). In Figure 3, the TGUS* vs. GUS are compared for pesticides # 1–26 on which the GUS equation was based. The slope of the regression line is nearly 1, confirming the resemblance of the two indices.

If we had chosen GUS = 2.8 to separate detects and non-detects in Eq. (22) and set it equal to 0.0075 t in Eq. (26), the time would have been 375 days. These time points are only mentioned here to render the GUS and TGUS* equations similar, but they might not have physical meaning since the GUS and TGUS* equations, while similar, are not identical. The significance of time in the equations will be elaborated upon in the discussion. Despite these differences, the GUS and the TGUS* equations predict leachability in the same way, as shown in Figure 3.

3.2 Evaluating the accuracy of GUS and TGUS* with observed data

Figure 4 plots the GUS versus TGUS* values for pesticides (# 1–41 except DDD, # 38 in Table 1) with the boundaries separating the non-leachers, transition, and leachers. The vertical

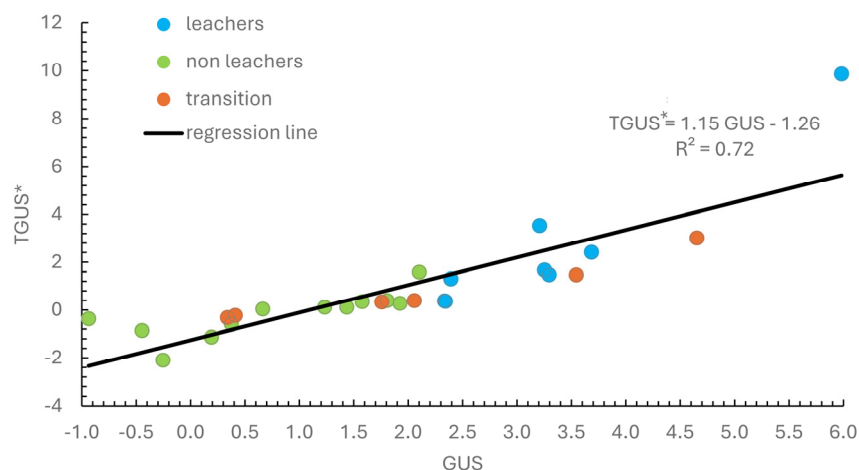


Fig. 3. The Theoretical Groundwater Ubiquity Score (TGUS*, Eq. (26a) with $\log \xi = 3.4$) vs. Groundwater Ubiquity Score (GUS* for the pesticide #1–26 Table 1) that were used by Gustafson (1989) in the development of the Groundwater Ubiquity Score. Transition pesticides are those that were occasionally found in California's groundwater in the nineteen eighties, while leachers appeared more regularly in groundwater samples.

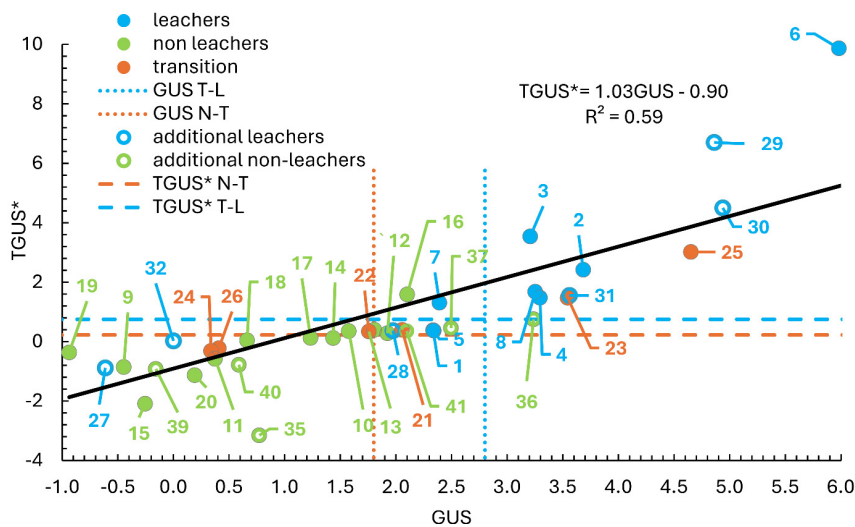


Fig. 4. The Theoretical Groundwater Ubiquity Score (TGUS*, Eq. (27)) vs. Groundwater Ubiquity Score (GUS, Eq. (1)) for the pesticides #1–41 except #38 in Table 1) that were listed by Gustafson (1989) in the development of the Groundwater Ubiquity Score. The additional pesticides are those that did not have all required for calculating the GUS value in Gustafson (1989) (#27–41 in Table 2). The vertical lines divide the GUS leachable categories. GUS N-T is the boundary between non-detect and transient pesticides at GUS = 1.8, and GUS T-L between the transient from the detects at GUS = 2.8. The horizontal lines are the boundaries for the TGUS* index. TGUS* values below 0.225 are non-leachers; between 0.225 and 0.75 transient and above TGUS* = 0.75 are the leachers. Transient pesticides are those that were occasionally found in California's groundwater in the nineteen eighties, while leachers appeared more regularly in groundwater samples.

lines divide the GUS leachable categories. $GUS = 1.8$ is the boundary between non-detect and transition pesticides, and $GUS = 2.8$ separates the transition pesticides from those detected in groundwater. The horizontal lines - obtained by inspection - are the boundaries for the $TGUS^*$ index. $TGUS^*$ values below 0.225 are non-leachers; between 0.225 and 0.75 are the transition pesticides, and above $TGUS^* = 0.75$ are the leachers. Equivalent $TGUS$ values for these boundaries can be obtained by dividing the $TGUS^*$ values by 0.025 (Eq. (27)). The boundaries are then $TGUS = 9$ and $TGUS = 30$. Solving Eq. (27) for t for $TGUS^*$ boundary values between non-leachers, transition pesticides, and leachers of 0.225 and 0.75 or Eq. (23) for boundary values 9 and 30, we find that the boundary between non-leachers and transition pesticides is equivalent to a leaching event of 30 days after the pesticide application and between transition pesticides

and leacher is 100 days. Further detail is given in the Discussion Section.

3.2.1 Updating pesticide properties

Generally, both indexes predict the leachability of the pesticides well (Figure 4), with a few exceptions in which both indices were incorrect (Figure 4). Since the GUS index was developed 35 years ago, more information has been collected on the pesticides in Table 1. We will use the additional information to determine whether the original data were correct for the misclassified indices in Figure 4. The updated list of pesticides and their properties are shown in Table 2. The detailed discussion is given in Appendix A. A summary is provided below.

Table 2. List of pesticides Gustafson (1989) from table 1 with updated properties for half-life ($t_{1/2}$) and organic carbon partition coefficient (K_{oc}) leaching characteristics, Groundwater Ubiquity Score (GUS), Theoretical Groundwater Ubiquity Score ($TGUS$ and $TGUS^*$) and the Leaching Risk Period (T_{LRP}) for pesticides in bold font.

Leachability	Pesticides	K_{oc} [m ³ /Mg]	Soil half life [day]	GUS	$TGUS$	$TGUS^*$	Leaching risk period [day]
Leacher	1 Aldicarb	17	30	4.1	64	1.6	217
Leacher	2 Atrazine	107	74	3.7	98	2.4	338
Leacher	3 Diuron	389	188	3.2	143	3.5	508
Leacher	4 Metolachlor	99	44	3.3	60	1.5	206
Leacher	5 Oxamyl	26	20	3.4	39	1.0	132
Leacher	6 Picloram	26	206	6.0	399	9.9	1363
Leacher	7 Prometryn	614	94	2.4	53	1.3	192
Leacher	8 Simazine	138	56	3.3	68	1.7	235
Non-leacher	9 Chlordane	19269	37	-0.4	-35	-0.9	-109
Non-leacher	10 Chlorothalonil	1380	68	1.6	14	0.4	59
Non-leacher	11 Chlorpyrifos	6085	54	0.4	-23	-0.6	-69
Non-leacher	12 2,4-D	53	7	1.9	11	0.3	39
Non-leacher	13 Dicamba	511	25	1.8	16	0.4	58
Non-leacher	14 Endosulfan	2040	120	1.4	5	0.1	36
Non-leacher	15 Heptachlor	13330	109	-0.3	-84	-2.1	-263
Non-leacher	16 Lindane	1727	400	2.0	45	1.1	217
Non-leacher	17 Phorate	1660	38	1.2	5	0.1	23
Non-leacher	18 Propachlor	794	4	0.7	2	0.0	7
Non-leacher	19 Toxaphene	95816	9	-0.9	-15	-0.4	-47
Non-leacher	20 Trifluralin	7950	83	0.2	-46	-1.1	-138
Transition	21 Alachlor	161	14	2.1	16	0.4	56
Leacher	22 Carbaryl	120	30	2.8	38	0.9	132
Leacher	23 Carbofuran	55	120	4.7	193	4.8	664
Leacher	24 Dinoseb	30	30	3.7	56	1.4	192
Transition	25 Ethoprop	26	63	4.7	122	3.0	417
Transition	26 Fonofos	870	40	1.7	16	0.4	61
Non-leacher	27 Chlorthal dimethyl	25119	34	-0.6	-36	-0.9	-113
Leacher	28 Cyanazine	190	14	2.0	15	0.4	52
Leacher	29 DBCP	70	180	4.9	271	6.7	933
Leacher	30 EDB	34	100	4.9	182	4.5	623
Leacher	31 Metribuzin	60	40	3.6	63	1.6	216
Non-leacher	32 Naled	180	1	0.0	1	0.0	4
Leacher	33 Prometon	150	500	4.9	587	14.5	2040
Leacher	34 Propylene dichloride	0	52	13.7	382	9.5	1283
Non-leacher	35 Aldrin	5000	365	0.8	-127	-3.2	-364
Transition	36 Chloramben	15	14	3.2	30	0.8	104
Non-leacher	37 1,3-D	32	10	2.5	18	0.5	63
Non-leacher	38 DDD	100000	1000	-3.0	-1650	-40.8	-5333
Non-leacher	39 Endosulfan sulfate	12400	50	-0.2	-37	-0.9	-116
Non-leacher	40 Pendimethalin	5000	90	0.6	-31	-0.8	-90
Non-leacher	41 Silvex	80	10	2.1	14	0.4	50
Non-leacher	42 DDT	213600	38200	-6.1	-75621	-1871.4	-245700
Non-leacher	43 Endrin	11188	2240	-0.2	-1565	-38.7	-4844
Non-leacher	44 Dieldrin	12100	934	-0.2	-684	-16.9	-2126

The misclassified pesticides are considered from the left to the right for both the GUS and TGUS* in Figure 4. Chlorthal dimethyl (#27) was misclassified as a leacher in Table 1. According to the National Center for Biotechnology Information (2024), chlorthal dimethyl is a non-leacher (Table 2 and Figure 5). AERU (2024) reported that Naled has a half-life of 1-day in the environment with rapid soil degradation rates. When leached, it will be degraded if the rainfall does not occur shortly after application. The K_{oc} for Dinoseb (# 24) is 30 m³/Mg (Table 2; Vogue et al., 1994) and is classified correctly as a leacher (Figure 5). Vogue et al. (1994) reported that for Fonofos (# 26), a smaller K_{oc} = 870 m³/Mg and a greater half-life of 40 days than in Table 1, thus its revised classification is on the transition /non-leacher line for TGUS* and as a non-leacher for GUS (Figure 5). Lindane (# 16) is a non-leacher, whereas indices misclassify it as a leacher. Aldicarb (#1), Oxamyl (#5), Carbofuran (#23), and Carbaryl (#22) are carbamates that are known to leach into the groundwater under acidic soil conditions. Reported half-lives for the updated pesticides in Table 2 are generally greater than those reported in Table 1 (Vogue et al., 1994; Wauchope et al., 1992; Song, 2005; INCHEM (2024)). Three of the four carbamates in Figure 5 are classified as leachers for the maximum reported half-lives (Table 2). Carbaryl (#22) is at the high end of the transition pesticides. Chloramben (# 36) has a short half-life and tends to leach into groundwater AERU 2024) (Table 2). As discussed below, the two indices do not represent these pesticides.

Most pesticides are classified well in Figure 5 after the pesticide properties were updated (Table 2). The majority of the non-leachers are below TGUS* = 0.225 and left of GUS = 1.8. All non-leachers are below TGUS* = 0.75 and right of GUS = 2.8. Also, all leachers are above or at the line of TGUS* = 0.225 and left of GUS = 2.8, except dicamba (#13), which is right of GUS = 2.8 but just in the leachable range of TGUS*. The transition and non-leacher pesticides are intermixed between the boundaries of the two pesticide-leaching indices. Part of the reason for

this diffuse boundary between transition pesticides and non-leachers is the vague definition of transition pesticides as those that are found only occasionally in groundwater.

4 DISCUSSION

The theoretically-derived TGUS index provides important insights into interpreting the GUS index beyond those given in Appendix A and B in Gustafson et al. (1989). The GUS is a function of two parameters, K_{oc} and half-life, and a constant four, as shown in Eq. (1a). The derivation of the TGUS* shows that this constant depends on the mass applied, the chemical detection limit, the amount of preferential flow, the organic carbon content, and the bulk density of the soil. The disadvantage of both methods is that the division of leachers, transition pesticides, and non-leachers was done by inspection, which is not very satisfactory (Figures 4 and 5).

The time dependence in TGUS in Eq. (20) aids in a more adequate way of determining the leachability of the pesticides. To do this, we can rewrite TGUS (Eq. 20) in a more convenient form as

$$TGUS = \frac{t_1}{2} (\log \xi - \log K_{oc}) - 0.3t \quad (28a)$$

$$\text{leachers} \quad TGUS > 0 \quad (28b)$$

$$\text{non-leachers: } TGUS < 0 \quad (28c)$$

An alternative form to Eq. (28) can be obtained by setting TGUS = 0, as suggested by Eqs. (28b,c) and determining the Leaching Risk Period, T_{LRP} [T]. It is defined as the time window following pesticide application in which a sufficiently large irrigation or rainfall event can cause pesticide leaching from the distribution zone, resulting in a groundwater concentration above the detection limit. After the Leaching Risk Period ends, leaching may somewhat increase the groundwater concentration

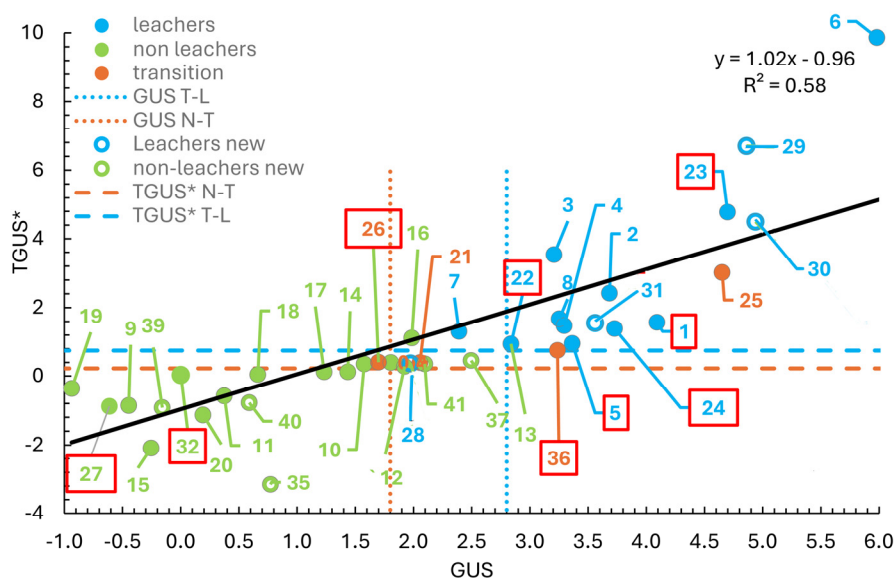


Fig. 5. The Theoretical Groundwater Ubiquity Score (TGUS*, Eq. (26)) vs. Groundwater Ubiquity Score (GUS, Eq. (1)) in Table 2 that were listed by Gustafson (1989) in the development of the Groundwater Ubiquity Score. The properties of the pesticide number with red square boxes were updated and are listed in Table 2. As a result, most of these pesticides are now assigned to the right category of leachability for both GIS and TGUS*. The vertical lines divide the GUS leachable categories. GUS N-T is the boundary between non-detect and transition pesticides at GUS = 1.8, and GUS T-L between the transition pesticides from the detects at GUS = 2.8. The horizontal lines are the boundaries for the TGUS* index. TGUS* values below 0.225 are non-leachers; between 0.225 and 0.75, transition pesticides and above, 0.75 are the leachers. Transient pesticides are those that were occasionally found in California's groundwater in the nineteen eighties, while leachers appeared more regularly in groundwater samples.

but will not exceed the detection limit. The Leaching Risk Period, T_{LRP} , can be derived from Eq. (28) as

$$T_{LRP} = 3.33 \frac{t_1}{2} (\log \xi - \log K_{OC}) \quad \text{for } K_{OC} < \xi \quad (29a)$$

$$T_{LRP} = 0 \quad \text{for } K_{OC} \geq \xi \quad (29b)$$

Combining Eqs. (24)–(26) for TGUS* will also result in Eq. (29). It is important to note that in our analysis, we have assumed that the breakdown of pesticides in groundwater is significantly slower than in surface soil. Therefore, even if a groundwater sample is taken a few months after the pesticides have leached into the groundwater, we would still expect to detect the presence of the pesticide in that sample.

By using $\log \xi = 3.4$ in Eq. (29), the Leaching Risk Period, T_{LRP} is plotted as a function of half-life and organic C partition coefficient, K_{OC} , in Figure 6 for the pesticides investigated by Gustafson (1989). Figure 6 presents the same pesticides as in Figure 5. Instead of two lines separating leachers, transition pesticides and non-leachers, the continuum of the Leaching Risk Periods from –500 to 3000 days is shown. The boundary between non-detect and transition pesticides Figures 4 and 5 for TGUS* = 0.225 (TGUS = 9) is at, $T_{LRP} = 30$ days, and between transitions pesticides and leachers for TGUS* = 0.75 (TGUS = 30) is at $T_{LRP} = 100$ days and are shown as solid lines in Figure 6.

In Figure 6, pesticides, including the chlorinated hydrocarbons, to the left of the vertical $T_{LRP} = 0$ line, have negative Leaching Risk Periods due to high K_{OC} . The model thus predicts that these pesticides will never cause groundwater concentrations over the detection limit, even if the leaching occurs on the same day they are applied. Other pesticides, to the right of the $T_{LRP} = 0$ line, have positive Leaching Risk Periods. According to the theoretical TGUS derivation, they can potentially bring groundwater above the detection limit when leaching occurs within the Leaching Risk Period time window. This finding is contrary to some of the pesticides (i.e., #10, 12, 13, 18, 37 and 41) in the Gustafson (1989) classification, which

were classified as non-leachers and are right of the $T_{LRP} = 0$ line. They have Leaching Risk Periods between 0 and 60 days. However, experimental data supports our argument that the pesticide can leach to groundwater at concentrations above detection limits within the Leaching Risk Period. For example, 2,4-D (#12, $T_{LRP} = 39$ days, Table 2) has been shown to leach to groundwater after application (Steenhuis et al., 1997; Miller et al., 1995; Elliot et al., 2000). Also, dicamba (#13, $T_{LRP} = 57$ days, Table 2) was detected in concentrations ranging from 2.0 to 37.0 $\mu\text{g/L}$ by Ritter et al. (1996) 12 days after it was applied, where 54 mm of rainfall occurred in the 12 days. These examples illustrate that the Leaching Risk Period concept might be more versatile and robust than a strict division of leachers and non-leachers.

Most of the transition pesticides fall within the $30 < T_{LRP} < 133$. If available, it would be of great interest to re-examine the original database to determine whether the detections of the transition pesticides had a mobilizing rainfall or irrigation events that could have leached the pesticide within the Leaching Risk Period.

Finally, the pesticide mass loss ranking (and the concentration in the groundwater) differs from the GUS or TGUS index ranking. The ranking between mass and index would be the same in cases where the advective-dispersive equation would have been valid for describing the pesticide movement in the vadose zone, as Gustafson (1989) suggested. Conversely, TGUS is based on preferential flow, where the travel time is fast and independent of the pesticide adsorption strength; hence, the resulting concentrations in water arriving at the groundwater are independent of the travel time, depending only on the adsorption partition coefficient and pesticide half-life in the distribution zone. Thus, for equal amounts of recharge, the lower the adsorption coefficient, the greater the concentration and the mass transported to the groundwater. This is in agreement with the preferential flow theory. Klavivko et al. (1991) found that pesticide losses were inversely correlated with the adsorption partition coefficient. Also, in the Jung et al. (2024) column experiments where water was added shortly after spraying in

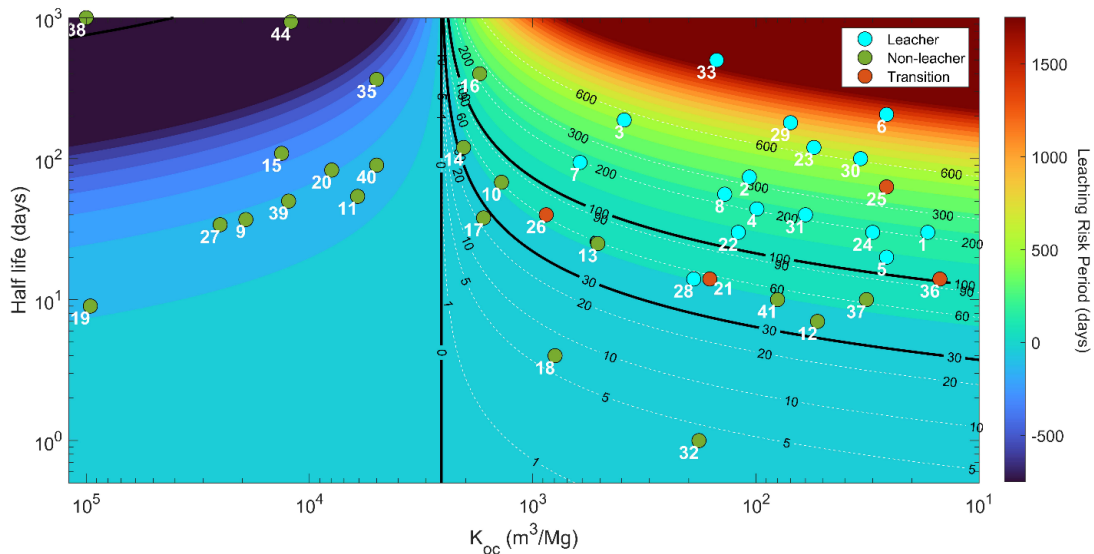


Fig. 6. Leaching Risk Period, T_{LRP} , contours (as indicated by a slight color change with black numbers) as a function of organic carbon partition coefficient and half-life. The leaching risk period is defined as the time after application that pesticide leaching by a rainfall event will result in a groundwater concentration above the detection limit. The white numbers are the pesticide identifiers in Table 2. Black solid contour lines at $T_{LRP} = 30$ separate non-leachers from transition pesticides and at $T_{LRP} = 100$, transition pesticides from leachers. The T_{LRP} of the individual pesticides are calculated with Eq. 29 with the properties in Table 2. Table 2 also indicates the classification of the pesticides in leachers, transition and non-leachers.

undisturbed columns, the pesticide with the lowest adsorption partition coefficient had the greatest losses, and the authors showed that the GUS could not predict the observed ranking of the mass losses. Finally, Steenhuis et al. (1994, 1997) found greater leachate concentrations for pesticides with smaller adsorption partition coefficients.

The limitation of both the GUS and the TGUS* leachability index remains that pesticide properties depend on local conditions, and leachability might thus differ from predictions based on mean values. However, the equation derivation clearly shows that the conditions at the soil surface determine the groundwater concentration, making it simpler to study a priori their potential impact on shallow groundwater.

5 CONCLUSION

Starting with a preferential flow model, we derived a nearly identical expression to the widely-used Groundwater Ubiquity Score (GUS) index, originally developed by Gustafson (1989) some 35 years ago. The preferential model consists of a distribution zone near the surface that funnels a small portion of water to a transmission zone where dissolved pesticides are transported in preferential flow paths that contaminate the groundwater when these paths are connected. The remaining water and pesticides move slowly through the soil matrix, where pesticides are assumed to be degraded before reaching the groundwater. In the distribution zone, the adsorption partition coefficient determines the equilibrium concentration between the pesticide adsorbed on the soil and dissolved in the water. Once the water and dissolved pesticides are in a surface-groundwater-connected preferential flow path, the movement is fast, and adsorption is minimal. Despite its bare-bone approach, we showed that the Theoretical Groundwater Ubiquity Score (TGUS) index was closely correlated with the GUS for the pesticides originally considered by Gustafson in 1989. However, the theoretical approach can provide significantly greater insight into how various pesticide characteristics, analytical detection limits, and soil properties of older and more recent pesticides will affect their leachability.

REFERENCES

- AERU, 2024. PPDB: Pesticide properties database. Accessed on April 7, 2024 at <https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>
- Ahuja, L.R., Ma, Q.L., Rojas, K.W., Boesten, J.J.T.I., Farahani, H.J., 1996. A field test of root zone water quality model–pesticide and bromide behavior. *Pestic. Sci.*, 48, 101–108. [https://doi.org/10.1002/\(SICI\)1096-9063\(199610\)48:2<101::AID-PS431>3.0.CO;2-Y](https://doi.org/10.1002/(SICI)1096-9063(199610)48:2<101::AID-PS431>3.0.CO;2-Y)
- Asano, Y., and Uchida, T., 2012. Flow path depth is the main controller of mean base flow transit times in a mountainous catchment, *Water Resour. Res.*, 48, W03512, <https://doi.org/10.1029/2011WR010906>
- Baker, J.L., Lallen, J.M., Johnson, H.P., 1978. Effect of tillage systems on runoff losses of pesticides. A rainfall simulation study. *Transactions of the ASAE* 21, 886–892.
- Beulke, S., Brown, C.D., 2001. Evaluation of methods to derive pesticide degradation parameters for regulatory modelling. *Biol. Fertil. Soils*, 33, 558–564. <https://doi.org/10.1007/s003740100364>
- Camobreco, V.J., Richards, B.K., Steenhuis, T.S., Peverly, J.H., McBride, M.B., 1996. Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Science*, 161, 11, 740–750. <https://doi.org/10.1097/00010694-199611000-00003>
- Darnault, C.J.G., Steenhuis, T.S., Garnier, P., Kim, Y.J., Jenkins, M.B., Ghiorse, W.C., Parlange, J.Y., 2004. Preferential flow and transport of *Cryptosporidium parvum* oocysts through the vadose zone: Experiments and modeling. *Vadose Zone Journal*, 3, 262–270. <https://doi.org/10.2136/vzj2004.2620>
- Demir, A.E.A., Dilek, F.B., Yetis U., 2019. A new screening index for pesticides leachability to groundwater. *J. Environ. Manag.*, 231, 1193–1202. <https://doi.org/10.1016/j.jenvman.2018.11.007>
- Di, H.J., Kookana, R.S., Aylmore, L.A.G., 1995. Application of a simple-model to assess the ground-water contamination potential of pesticides. *Soil Research*, 33, 1031–1040. <https://doi.org/10.1071/SR9951031>
- Domagalski, J.L., Johnson, H.M., 2011. Subsurface transport of orthophosphate in five agricultural watersheds, USA. *Journal of Hydrology*, 409, 1–2, 157–171. <https://doi.org/10.1016/j.jhydrol.2011.08.014>
- Donald, D.B., Block, H., Wood, J., 1997. Role of ground water on hexachlorocyclohexane (Lindane) detections in surface water in western Canada. *Environmental Toxicology and Chemistry*, 16, 1867–1872. <https://doi.org/10.1002/etc.5620160915>
- Fisher, I.J., Phillips, P.J., Bayraktar, B.N., Chan, S., McCarthy, B.A., Sandstrom, M.W., 2021. Pesticides and their degradates in groundwater reflect past use and current management strategies, Long Island, New York, USA. *Sci. Total Environ.*, 15, 752, 141895. <https://doi.org/10.1016/j.scitotenv.2020.141895>
- Germann, P., Beven, K., 1981. Water flow in soil macropores I. An experimental approach. *Journal of Soil Science*, 32, 1, 1–13. <https://doi.org/10.1111/j.1365-2389.1981.tb01681.x>
- Gramatica, P., di Guardo, A., 2002. Screening of pesticides for environmental partitioning tendency. *Chemosphere*, 47, 9, 947–956. [https://doi.org/10.1016/S0045-6535\(02\)00007-3](https://doi.org/10.1016/S0045-6535(02)00007-3)
- Guan, Y., Wei, J., Zhang, D., Zu, M., Zhang, L., 2013. To identify the important soil properties affecting dinoseb adsorption with statistical analysis. *The Scientific World Journal*, 362854. <https://doi.org/10.1155/2013/362854>
- Gustafson, D.I., 1989. Groundwater ubiquity score: A simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry*, 8, 4, 339–357. <https://doi.org/10.1002/etc.5620080411>
- Hamaker, J.W., 1975. The interpretation of soil leaching experiments. In: Haque, R., Freed, V.H. (Eds): *Environmental Dynamics of Pesticides*. Springer US, pp. 115–133. https://doi.org/10.1007/978-1-4684-2862-9_8
- Harmon O'Driscoll, J., Siggins, A., Healy, M.G., McGinley, J., Mellander, P.E., Morrison, L., Ryan, P.C., 2022. A risk ranking of pesticides in Irish drinking water considering chronic health effects *Sci. Total Environ.*, 829, 154532.
- Hassanpour, B., Richards, B.K., Goehring, L.D., Parlange, J.-Y., Steenhuis, T.S., 2019. Predicting the fate of preferentially moving herbicides. *Vadose Zone Journal*, 18, 1, 1–11. <https://doi.org/10.2136/vzj2018.10.0193>
- Hutson, J.L., Wagenet, R.J., 1993. A pragmatic field-scale approach for modeling pesticides. *Journal of Environmental Quality*, 22, 494–499. <https://doi.org/10.2134/jeq1993.00472425002200030014x>
- INCHEM, 2024. Carbaryl. International Programme on Chemical Safety (IPCS) accessed on April 6, 2024, at <https://www.inchem.org/documents/ehc/ehc/ehc153.htm#Sub-SectionNumber:5.1.3>
- Jarvis, N.J., 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. *European Journal of Soil*

- Science, 71, 3, 279–302. <https://doi.org/10.1111/ejss.12973>
- Jung, G.H., Lee, H.S., Lim, S.J., Choi, H., 2024. Evaluation of soil pesticide leaching to groundwater using undisturbed lysimeter: development of the pesticide groundwater leaching scoring system (PLS). *Environ Sci. Pollut. Res.*, 31, 21973–21985. <https://doi.org/10.1007/s11356-024-32595-5>
- Jury, W.A., Spencer, W.F., Farmer, W.J., 1983. Behavior assessment model for trace organics in soil: I. Model description. *Journal of Environmental Quality*, 12, 4, 558–564. <https://doi.org/10.2134/jeq1983.00472425001200040025x>
- Jury, W.A., Spencer, W.F., Farmer, W.J., 1984. Behavior assessment model for trace organics in soil: iv. Review of experimental evidence. *Journal of Environmental Quality*, 13, 580–586. <https://doi.org/10.2134/jeq1984.00472425001300040014x>
- Kaiglová, J., Langhammer, J., 2014. Analysis of efficiency of pollution reduction measures in rural basin using MIKE Basin model. Case study: Olšava River Basin. *Journal of Hydrology and Hydromechanics*, 62, 43–54. <https://doi.org/10.2478/johh-2014-0007>
- Kladivko, E.J., Van Scoyoc, G.E., Monke, E.J., Oates, K.M., Pask, W., 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. *Journal of Environmental Quality*, 20, 264–270. <https://doi.org/10.2134/jeq1991.00472425002000010043x>
- Larsson, M.H., Jarvis, N.J., 2000. Quantifying interactions between compound properties and macropore flow effects on pesticide leaching. *Pest Management Science*, 56, 2, 133–141. [https://doi.org/10.1002/\(SICI\)1526-4998\(200002\)56:2<133::AID-PS103>3.0.CO;2-N](https://doi.org/10.1002/(SICI)1526-4998(200002)56:2<133::AID-PS103>3.0.CO;2-N)
- Li, Y., Lv, G., Shao, H., Dai, Q., Du, X., Liang, D., Kuang, S., Wang, D., 2021. Determining the influencing factors of preferential flow in ground fissures for coal mine dump eco-engineering. *PeerJ*, 9, e10547. <https://doi.org/10.7717/peerj.10547>
- Meeks, Y.J., Dean, J.D., 1990. Evaluating groundwater vulnerability to pesticides. *Journal of Water Resources Planning and Management*, 116, 5, 693–707. [https://doi.org/10.1061/\(ASCE\)0733-9496\(1990\)116:5\(693\)](https://doi.org/10.1061/(ASCE)0733-9496(1990)116:5(693))
- Miller, J.J., Foroud, N., Hill, B.D., Lindwall, C.W., 1995. Short communication: Herbicides in surface runoff and groundwater under surface irrigation in southern Alberta. *Canadian Journal of Soil Science*, 75, 1, 145–148. <https://doi.org.proxy.library.cornell.edu/10.4141/cjss95-018>
- National Center for Biotechnology Information, 2024. PubChem Compound Summary for CID 2943, Chlorthal-dimethyl. Retrieved on April 4, 2024 from <https://pubchem.ncbi.nlm.nih.gov/compound/Chlorthal-dimethyl>
- NSCEP, 2014. Technical factsheet on Dinoseb. Retrieved on April 5 from <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockkey=P1012HTC.txt>
- Papa, E., Castiglioni, S., Gramatica, P., Nikolayenko, V., Kayumov, O., Calamari, D., 2004. Screening the leaching tendency of pesticides applied in the Amu Darya Basin (Uzbekistan). *Water Research*, 38, 16, 3485–3494. <https://doi.org/10.1016/j.watres.2004.04.053>
- Pawlowski, S., Aicher, L., Berends, A., Curtis-Jackson, P., Häner, A., Hollender, J., Jene, B., Jenner, K., Redman, A., Sanders, G., Vallotton, N., Wang, N., Wheeler, J.R., 2023. Mobility in the context of exposure-based assessment of chemicals for drinking water resource protection. *Integr. Environ. Assess. Manag.*, 19, 775–791. <https://doi.org/10.1002/ieam.4705>
- Rao, P.S.C., Hornsby, A.G., Jessup, R.E., 1985. Indices for ranking the potential for pesticide contamination of groundwater. *Proceedings Soil and Crop Science Society of Florida*, 44, 1–8.
- Richards, B.K., Peraginangin, N., Steenhuis, T.S., Geohring, L.D., 2003. The unintentional secret. *Journal of Soil and Water Conservation*, 58, 5, 104A–105A. <https://www.jswnonline.org/content/58/5/104A>
- Ritsema, C.J., Dekker, L.W., Nieber, J. L., Steenhuis, T.S., 1998. Modeling and field evidence of finger formation and finger recurrence in a water-repellent sandy soil. *Water Resources Research*, 34, 4, 555–567. <https://doi.org/10.1029/97WR02407>
- Ritter, W.F., Chirnside, A.E.M., Scarborough, R.W., 1996. Leaching of dicamba in a coastal plain soil. *Journal of Environmental Science and Health. Part A: Environmental Science and Engineering and Toxicology*, 31, 3, 505–517. <https://doi.org/10.1080/10934529609376371>
- Sahoo, B. Ray, C., Wade, H.F., 2005. Pesticide prediction in groundwater in North Carolina domestic wells using artificial neural networks. *Ecological Modelling*, 183, 29–46. <https://doi.org/10.1016/j.ecolmodel.2004.07.021>
- Scotter, D., 1978. Preferential solute movement through larger soil voids. I. Some computations using simple theory. *Soil Research*, 16, 3, 257. <https://doi.org/10.1071/SR9780257>
- Shipitalo, M.J., Edwards, W.M., Redmond, C.E., 1994. Comparison of water movement and quality in earthworm burrows and pan lysimeters. *Journal of Environmental Quality*, 23, 1345–1351. <https://doi.org/10.2134/jeq1994.00472425002300060031x>
- Sinkevich, M.G., Jr, Walter, M.T., Lembo, A.J., Jr, Richards, B.K., Peraginangin, N., Aburime, S.A., Steenhuis, T.S., 2005. A GIS-based ground water contamination risk assessment tool for pesticides. *Groundwater Monitoring & Remediation*, 25, 82–91. <https://doi.org/10.1111/j.1745-6592.2005.00055.x>
- Song, X., 2005. Carbofuran. In: Wexler, P. (Ed.): *Encyclopedia of Toxicology*, 2nd Ed. Elsevier, pp 417–418.
- Spadotto, C.A., 2002. Screening method for assessing pesticide leaching potential. In: *Revista de Ecotoxicologia e meio Ambiente*, pp. 69–78.
- Starr, J.L., Parlange, J.-Y., Frink, C.R., 1986. Water and chloride movement through a layered field soil. *Soil Sci. Soc. Am. J.*, 50, 1384–1390.
- Steenhuis, T.S. Walter, M.F., 1980. Closed form solution for pesticide loss in runoff water. *ASAE Trans.*, 23, 615–620, 628.
- Steenhuis, T.S., Boll, J., Shalit, G., Selker, J.S., Merwin, I.A., 1994. A simple equation for predicting preferential flow solute concentrations. *Journal of Environmental Quality*, 23, 5, 1058–1064. <https://doi.org/10.2134/jeq1994.00472425002300050030x>
- Steenhuis, T.S., Bodnar, M., Geohring, L.D., Aburime, S.-A., Wallach, R., 1997. A simple model for predicting solute concentration in agricultural tile lines shortly after application. *Hydrol. Earth Syst. Sci.*, 1, 823–833. <https://doi.org/10.5194/hess-1-823-1997>
- Schwarz, E., Khurana, S., Chakrawal, A., Chavez Rodriguez, L., Wirsching, J., Streck, T., Wirsching, J., Manzoni, S., Thullner, M., Pagel, H., 2022. Spatial control of microbial pesticide degradation in soil: a model-based scenario analysis. *Environ. Sci. Technol.*, 56, 144, 27–38. <https://doi.org/10.1021/acs.est.2c03397>
- Tesoriero, A.J., Duff, J.H., Wolock, D.M., Spahr, N.E., Almendinger, J. E., 2009. Identifying pathways and processes affecting nitrate and orthophosphate inputs to streams in agricultural watersheds. *Journal of Environmental Quality*, 38, 5, 1892–1900. <https://doi.org/10.2134/jeq2008.0484>
- University of Hertfordshire, 2024. PPDB: Pesticide Properties DataBase. <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm> last accessed June 14, 2024.
- van der Molen, W.H., 1956. Desalinization of saline soils as a column process. *Soil Sci.*, 81, 19–27.

- Vogue, P.A., Kerle, E.A., Jenkins, J.J., 1994. OSU Extension pesticide properties database. <http://npic.orst.edu/ingred/ppd-move.htm> (accessed April 1, 2024)
- Wauchope, R.D., Buttler, T.M., Hornsby, A.G., Augustijn-Beckers, P.W.M., Burt, J.P., 1992. SCS/ARS/CES pesticides properties database for environmental decision making. *Rev. Environ. Contam. Toxicol.*, 123, 1–157.
- Wilkerson, M.R., Kim, K.D., 1986. cited by Gustafson (1989). The pesticide contamination prevention act: setting specific numerical values. California Department of Food and Agriculture, Environmental Monitoring and Pest Management, Sacramento, CA.
- Zaki, M.H., Moran, D., Harris D., 1982. Pesticides in groundwater: the Aldicarb story in Suffolk County, NY. *Am. J. Public Health*, 72, 1982, 1391–1395.

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APPENDIX A

Reconsidering properties of selected pesticides

The misclassified pesticides are considered from left to right in Figure 4. The Chlorthal dimethyl (#27) was identified in Table 1 as a leacher. Our calculations show that the $GUS = -0.6$ and the $TGUS^* = -0.9$ (Table 1), putting it in the non-leacher category (Figure 4). The original Gustafson classification of a leacher was likely a mistake because, according to the National Center for Biotechnology Information (2024), Chlorthal dimethyl moved minimally in the soil profile due to its strong adsorption to clay and organic matter; sorption to clay is not reflected in K_{oc} . We could not find any reported losses to groundwater in the literature either. The change is reflected in Table 2 and Figure 5.

Very little is published on the fate of Naled (# 32) in soils. AERU (2024) reports that Naled is practically nonpersistent in the environment with rapid soil degradation rates. Due to its short half-life of one day, it will certainly not be found in groundwater when sampled a few months after application. So, our classification as non-detect is correct because the index assumes, as we will discuss later, that rainfall occurs and leaches the pesticides to the groundwater within 135 days after spraying.

Dinoseb (# 24) and Fonofos (# 26) were classified in Table 1 as "transition," while our calculated GUS and $TGUS^*$ values (Table 1) indicate that they are non-leachers. Table 1 lists $K_{oc} = 5,900 \text{ cm}^3/\text{g}$ for Dinoseb, while a value of $K_{oc} = 30 \text{ cm}^3/\text{g}$ can be found in Vogue et al. (1994), which is in agreement with K_{oc} values used in Guan et al. (2013). Taking $K_{oc} = 30 \text{ cm}^3/\text{g}$, Dinoseb becomes a leacher (Table 2, Figure 5). NSCEP 2014 reported that Dinoseb (# 24) was found extensively in groundwater; thus, the classification as a leacher is correct.

Vogue et al. (1994) reported for Fonofos (# 26) a smaller $K_{oc} = 870 \text{ m}^3/\text{Mg}$ and a greater half-life of 40 days than the values listed in Table 1. Using these values, we find that $GUS = 1.7$ and $TGUS^* = 0.4$ (Table 2, Figure 5), putting it in the transition/non-leacher line for $TGUS^*$ and just at the non-leacher site of the line for GUS (Figure 5).

Lindane (# 16) is listed in Table 1 as a non-leacher. However, GUS classified it as transition and $TGUS^*$ as a leacher. Donald et al. (1997) report that Lindane is primarily found in western Canada in surface runoff. According to Vogue et al. (1994), the half-life is 400 days, shorter than the 569 days in Table 1. Even using this lower half-life, it does not end up in the non-leacher category. Lindane is an organochlorine chemical compound that might not fit very well the classification.

Aldicarb (#1), Oxamyl (#5), Carbofuran (#23), and Carbaryl (#22) are carbamates that leach to the groundwater under acid soil conditions such as on Long Island. Half-lives reported in the literature are generally greater than those reported in Table 1; Vogue et al. (1994) reported 30 days for Aldicarb; Wauchope et al. (1992) mentioned 2–20 days for Oxamyl; Song (2005) reports for Carbofuran 30–120 days and INCHEM (2024) states half-lives for Carbaryl of 8–30 days. Using the maximum half-lives reported, all three of the four carbamates have become leachers (Table 2, Figure 5). Carbaryl is at the high end of the transition s in Figures 5 and 6.

Chloramben (# 36) is classified in Table 1 as a non-leacher. According to our calculation, it is a leacher with $GUS = 3.3$ or transition with a $TGUS^* = 0.8$. According to AERU (2024), Chloramben is highly soluble in water, volatile, and mobile, and tends to leach into groundwater. It is not normally persistent in soil or water systems.