SCREENING METHOD FOR ASSESSING PESTICIDE LEACHING POTENTIAL

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Screening methods are required in order to determine which pesticides should receive greatest attention with respect to environmental problems. Several authors have proposed screening methods for determining whether a pesticide is likely to leach to groundwater. The Groundwater Ubiquity Score (GUS) developed by GUSTAFSON (5) has been used, as the first step of a tiered approach for specifying which chemicals should deserve longer attention and expensive studies of leachability. However, GUS is empirically based and has a deficiency due to the prediction of anomalous negative values for pesticides with short half-life and/or large sorption coefficient. In the present work, it was developed a method for evaluating the leachability denominated index *LIX* as simple as index GUS however enabling faster and better visualization and interpretation of results.

KEYWORDS: LEACHABILITY; INDEX GUS; HALF-LIFE; PERSISTENCE; SORPTION COEFFICIENT; MOBILITY.

1 INTRODUCTION

Government agencies, at both state and federal levels, have faced increasing pressures to assess the likelihood of pesticide occurrence in groundwater. Screening methodologies are required in order to determine which pesticides in use should receive the greatest attention with respect to groundwater contamination, and in order to determine whether elaborate and expensive groundwater testing should be required. Thus, it is important to accelerate the development of simplified, yet acceptably accurate, pesticide leaching models that minimize input data requirements (9).

Screening methods are simple models that do not have extensive input data requirements and are relatively easy to use. The quality of output from such methods varies considerably depending upon the theory underlying their development. Anyway, screening methods will not only help the agricultural users and professionals but will also help regulatory agencies to understand the subtler issues related to pesticide usage and, it is hoped that it results in more equitable public policy decisions (6).

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Several authors have proposed screening methods for determining whether a pesticide is likely to leach. Some have attempted to set threshold values for a physical property or set of properties which, when exceeded, should indicate that the pesticide will leach (1, 16). Others have proposed very simple analytical or numerical models which are run using the measured or estimated properties of the pesticide and soil, in order to predict the likelihood of leaching (3, 6, 7, 11, 14). Clearly, any method of assessing leachability must account for both the persistence and the mobility of the chemical. A number of varying complexity models have been derived to assess leaching potential taking into consideration persistence and mobility.

GUSTAFSON (5) plotted together and examined graphically the properties of the chemicals representing soil mobility and soil persistence in order to define a region containing leaching compounds. Gustafson's methodology is suitable as the first part of a tiered approach for specifying which chemicals deserve the most attention during more intensive and expensive studies of leachability, such as small-scale prospective groundwater studies. Thus, Gustafson presented an index based on graphical examination of a plot formed by two pesticide properties: half-life in soil ($t_{½soil}$) and partition coefficient between soil organic carbon and water (K_{oc}): GUS = $\log_{10}(t_{½}\text{soil}) \times (4 - \log_{10}(K_{oc}))$. These properties have useful power in discriminating between "leachers" and "nonleachers" pesticides. However, the methodology proposed by GUSTAFSON (5) is empirically based and has an apparent problem due to the prediction of negative values of GUS for pesticides with short half-life and/or large sorption coefficient, what does not make sense when considering the physical properties.

This work purpose was to develop a simple leachability index limited to pesticide screening, showing which compounds require more attention in determining the leaching potential.

2 METHODS

Degradation

In the absence of quantitative information on the functional dependence of organic compound degradation on soil and environmental parameters, the degradation potential of a given chemical is described with a half-life ($t_{½}$) value, assuming first-order rate degradation. The half-life represents the combined influence of degradation in all phases, and the first-order degradation rate constant is usually measured by determining the fraction of a given initial quantity of applied pesticide remaining after a time (t) according to:

$$Mt = Mo \cdot \exp(-k \cdot t) \quad [1]$$

and the pesticide first-order rate constant (*k*) is given by;

$$k = \frac{ln\, 2}{t\frac{1}{2}} \quad [2]$$

where *Mo* is the initial pesticide mass in the soil, *Mt* is the remaining mass in the soil after a time *t*, and *ln* is the natural logarithm.

Mass Balance

In a one-dimensional, homogeneous porous medium, the mass conservation equation for a single non-reactive pesticide undergoing no decay may be written as:

$$\frac{\partial \theta C}{\partial t} = -\frac{\partial qs}{\partial z} \quad [3]$$

where *C* and *qs* are pesticide concentration and flow, respectively, θ represents the volumetric soil water content, *t* is time and *z* is soil depth.

Ignoring sorbed-phase transport, hydrodynamic dispersion, and diffusion, the solute mass flux may be written as:

$$qs = q \cdot C \quad [4]$$

where *q* is soil water flow. Therefore,

$$\frac{\partial \theta C}{\partial t} = -\frac{\partial qC}{\partial z} \quad [5]$$

or

$$\frac{\partial C}{\partial t} = -\frac{\partial \upsilon C}{\partial z} \quad [6]$$

where *u* is the effective solute convection velocity for a non-reactive pesticide and it is given by:

$$\upsilon = \frac{q}{\theta} \quad [7]$$

Other than mass flow in the soil-water phase, the two dominant transport processes for pesticides in soil are vapor and liquid diffusion. When mass flow by convection is small or negligible, the pesticide is able to move through the soil only by liquid or vapor diffusion. Many models of chemical transport in soil include a dispersion term in the flux equation to account for solute spreading due to water velocity variations, however at low average water fluxes in uniform soil, this term is relatively unimportant.

When conducting leaching screening tests, the convective mobility may be classified by the concept of convection time (*tc*), which is defined as:

$$tc = \frac{L}{\upsilon} = \frac{L.\theta}{q} \quad [8]$$

where, *L* stands for the distance to groundwater. For a reactive pesticide the convection time (*tc*') is given by:

$$tc' = \frac{L.\theta}{q} \cdot RF \quad [9]$$

where *RF* is the pesticide retardation factor and, in turn, taking no volatilization into consideration, is given by:

$$RF = 1 + \frac{BD \cdot Kd}{\theta} = 1 + \frac{BD \cdot OC \cdot Koc}{\theta} \quad [10]$$

where *BD* stands for the soil bulk density, *Kd* is the pesticide sorption coefficient, *OC* represents the soil organic carbon content, and *Koc* is the pesticide sorption coefficient normalized for organic carbon content.

The pesticide sorption is treated as an instantaneous, reversible, and linear process, thus the sorbed phase concentration (*S*) in soils can be related to the dissolved phase concentration (*C*) by the following:

$$S = Kd \cdot C \quad [11]$$

From the Equation 1, the pesticide degradation can be estimate considering the convection time:

$$\frac{Mt}{Mo} = \exp(-k \cdot tc) \quad [12]$$

The pesticide property taken into account in the retardation factor calculation is *Koc*, and according to JURY et al. (12), it appears to be a useful benchmark property for characterizing susceptibility to leaching for compounds that move primarily in the liquid phase. Thus, it can be used when constructing a relative leaching index. Therefore, a screening leachability (*LIX*) index is proposed as:

$$LIX = \exp(-k \cdot Koc) \qquad [13]$$

where *k* is the pesticide first-order rate constant (day^{-1}), and *Koc* is the pesticide organic carbon sorption coefficient (mL/g O.C.). The *LIX* index varies between 0 (zero) and 1 (one), representing, respectively, minimum and maximum leaching potential.

Data on soil half-life and sorption coefficient normalized for organic matter content for some pesticides as examples, were collected from the literature. The values of GUS and *LIX* were calculated to each pesticide, and the pesticide ranking was compared with information from groundwater monitoring programs. The screening index introduced here is based on a number of simplifying assumptions. The purpose in using this index is not to simulate pesticide transport in a given field situation, but rather to assess the potential of a compound to leach, comparing the leachability of one chemical relative to another in an identical environmental setting.

3 RESULTS AND DISCUSSION

Data on pesticide first-order rate constant in soil (*k*) and sorption coefficient normalized for soil organic matter content (*Koc*) is presented in Table 1. In Table 2 the values of GUS and *LIX* calculated to each pesticide are shown, allowing comparing to each other. Either GUS or *LIX* presents approximately the same ranking of pesticides regarding the leaching potential, however it is clear that *LIX* provides a prompt-to-understand view and better interpretation of the results. The index proposed here shows higher consistence of results with physical basis because it does not present negative values. The *LIX* values are between 0 and 1 what facilitate a comparison between a given pesticide value and values for other pesticides. Pesticide leachability increases progressively (though not necessarily proportionally) as the *LIX* index increases from 0 (nonleachable) to 1 (maximally leachable).

The pesticides in Table 2 classified as leachable according to GUS (> 2.8) were: Sulfentrazone, Picloram, Tebuthiuron, Prometon, Imazaquin, Carbofuran, Bromacil, Fomesafen, Hexazinone, Flumetsulam, Dicamba, Chlorsulfuron, Aldicarb, Metsulfuron-methyl, Atrazine, Metribuzin, Fenamiphos, Nicosulfuron, Metolachlor, Bentazon, and Chlorimuron-ethyl. The *LIX* index, as well as GUS, is simple and, thus, limited to the screening pesticide purpose showing which compounds require more attention in determining the leaching potential. According to *LIX* values presented in Table 2, Bromoxynil, Captan, Diclofop-methyl, Dicofol, Disulfoton, Glyphosate, Lactofen, Lambda-cyhalothrin, Methiocarb, Oxyfluorfen, Paraquat, Parathion-ethyl, Phorate, and Thiobencarb have minimum leaching potential. All of the other pesticides considered in this paper have some degree of potential for leaching.

TABLE 1 - PROPERTIES OF SOME PESTICIDES USED TO CALCULATE *LIX* AND GUS INDEXES

Pesticide	Degradation Constant *k* (day^{-1})	Sorption Coefficient *Koc* (mL/g)
2,4-D	0.069	20
Aldicarb	0.023	30
Ametryn	0.012	300
Atrazine	0.012	100
Bentazon	0.035	34
Bromacil	0.012	32
Bromoxynil	0.099	1079
Captan	0.28	200
Carbofuran	0.014	22
Chlorimuron-ethyl	0.017	110
Dicamba	0.05	2
Diclofop-methyl	0.023	16000
Dicofol	0.015	5000
Dimethoate	0.099	20
Disulfoton	0.023	600
Diuron	0.0077	480
Fenamiphos	0.014	100
Flumetsulam	0.012	35
Fomesafen	0.0069	60
Glyphosate	0.015	24000
Hexazinone	0.0077	54
Imazaquin	0.0077	100
Lactofen	0.23	10000
Lambda-cyhalothrin	0.023	180000
Methamidophos	0.12	5
Methiocarb	0.023	300
Metolachlor	0.0077	200
Metribuzin	0.017	60
Metsulfuron-methyl	0.023	35
Nicosulfuron	0.033	30
Oxyfluorfen	0.02	100000
Paraquat	0.00069	1000000
Parathion-ethyl	0.049	5000
Phorate	0.011	1000
Picloram	0.0077	16
Prometon	0.0014	150
Simazine	0.012	130
Sulfentrazone	0.0035	10
Tebuthiuron	0.0019	80
Thiobencarb	0.033	900

Data source: HORNSBY et al. (8).

TABLE 2 - CALCULATED *LIX* AND GUS VALUES

Pesticide	*LIX**	GUS**
Sulfentrazone	**0,97**	6,90
Dicamba	**0,91**	4,24
Picloram	**0,88**	5,46
Tebuthiuron	**0,86**	5,36
Prometon	**0,81**	4.92
Imazaquin	**0,79**	4,80
Carbofuran	**0,74**	4,52
Bromacil	**0,69**	4,44
Flumetsulam	**0,67**	4,37
Fomesafen	**0,66**	4,44
Hexazinone	**0,66**	4,43
Methamidophos	**0,56**	2,57
Aldicarb	**0,50**	3,73
Metsulfuron-methyl	**0,45**	3,63
Nicosulfuron	**0,37**	3,34
Metribuzin	**0,35**	3,56
Atrazine	**0,31**	3,56
Bentazon	**0,31**	3,21
Fenamiphos	**0,25**	3,40
2,4-D	**0,25**	2,70
Simazine	**0,22**	3.35
Metolachlor	**0,21**	3,32
Chlorimuron-ethyl	**0,15**	3,14
Dimethoate	**0,14**	2,28
Ametryn	**0,03**	2,71
Diuron	**0,02**	2,58
Bromoxynil	**0,00**	0.82
Captan	**0,00**	0,68
Diclofop-methyl	**0,00**	- 0,30
Dicofol	**0,00**	0,50
Disulfoton	**0,00**	1.80
Glyphosate	**0,00**	- 0,64
Lactofen	**0,00**	0,00
Lambda-cyhalothrin	**0,00**	- 1,85
Methiocarb	**0,00**	2.25
Oxyfluorfen	**0,00**	- 1,54
Paraquat	**0,00**	- 6,00
Parathion (ethyl)	**0,00**	0.35
Phorate	**0,00**	1.78
Thiobencarb	**0,00**	1.38

* Calculated using Equation 13. ** According to GUSTAFSON (5).

Some pesticides, as the herbicide Paraquat, in spite of their comparably very long soil half-life (very low *k* values), present very high

Koc values, what cause *LIX* to be very low. On the other hand, Sulfentrazone and Picloram present long half-life and have low *Koc* values, what results in high leaching potential according to *LIX*, as well as Methamidophos and Dicamba which have very low *Koc* values, despite their short half-life.

The IOWA DEPARTMENT OF NATURAL RESOURCES (10) found 2,4-D, Atrazine, Carbofuran, and Metolachlor in public groundwater supply systems, while 2,4-D, Aldicarb, Atrazine, Carbofuran, Dicamba, Metolachlor, and Simazine were found in the Wisconsin Department of Natural Resources' monitoring program of wells in areas with known contamination problems (17). As reported by KLASEUS (13), 2,4-D, Aldicarb, Atrazine, Dicamba, Metolachlor, Picloram, and Simazine were found in the Minnesota Department of Natural Resources' monitoring program of wells in areas with vulnerable groundwater.

As results of a monitoring work made between 1995 and 1998, Tebuthiuron and Hexazinone were found, respectively, in 79.1% and 47.1% of water samples from wells in the Espraiado watershed, São Paulo State, Brazil, and in concentrations up to 0.08 μg/L of Tebuthiuron and 0.06 μg/L of Hexazinone (2, 4). According to data reported by U.S. GEOLOGICAL SURVEY (15), as a result of a national wide monitoring program, Disulfoton, Parathion, Phorate, Thiobencarb, Bromoxynil, and Methiocarb, which have *LIX* of or close to 0 (zero), were not found in groundwater, while Atrazine (*LIX* = 0.31), Metolachlor (*LIX* = 0.21), Prometon (*LIX* = 0.81), and Simazine (*LIX* = 0.22) were found in groundwater with high detection frequency (32.9%, 15.5%, 10.8%, and 15.9% of all groundwater sites sampled, respectively).

It is needed to keep in mind that a given pesticide occurrence in groundwater depends on site natural vulnerability, used pesticide amount and leaching potential. The *LIX* index is only intended to assess the pesticide leaching potential. It seems that *LIX* is a powerful tool to identify nonleachable (*LIX* = 0) and leachable pesticides (*LIX* ≥ 0.1), while the range between 0 and 0.1 on the *LIX* scale is characterized as a transition zone.

4 CONCLUSION

The leachability index (*LIX*) presented here is useful in order to determine which pesticide in use should receive the greatest attention with respect to groundwater, and in order to determine whether elaborate an expensive groundwater testing should be required in order to register a new pesticide. The *LIX* index offers a more easily interpretable range of values than the GUS index, and results in a scale bounding the minimum and maximum leaching potential, while GUS results in a less definable range, including negative values.

Resumo

MÉTODO PARA AVALIAÇÃO DO POTENCIAL DE LIXIVIAÇÃO DE PESTICIDAS
Métodos de seleção são necessários para determinar quais pesticidas deveriam receber maior atenção com respeito aos problemas ambientais. Vários autores têm proposto métodos de seleção para verificar se determinado pesticida é potencialmente lixiviável para águas subterrâneas. O índice "Groundwater Ubiquity Score" (GUS) desenvolvido por GUSTAFSON (5) tem sido usado como a primeira etapa em abordagem de aproximações sucessivas para especificar quais produtos deveriam merecer estudos mais demorados e caros de lixiviabilidade. Entretanto, o índice GUS é empiricamente baseado e apresenta o problema da previsão de valores negativos para pesticidas com meia-vida curta e/ou grande coeficiente de sorção. No presente trabalho desenvolveu-se método para avaliação da lixiviabilidade denominado índice *LIX*, tão simples como o índice GUS porém possibilitando mais rápida e melhor visualização e interpretação dos resultados.
PALAVRAS-CHAVE: LIXIVIABILIDADE; ÍNDICE GUS; MEIA-VIDA; PERSISTÊNCIA; COEFICIENTE DE SORÇÃO; MOBILIDADE.

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