PESTICIDE LEACHING POTENTIAL ASSESSMENT IN MULTI-LAYERED SOILS

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The Attenuation Factor (*AF*) model generalized for multi-layered soils was used to estimate the leaching potentials of non-ionic and non-ionizable pesticides in Brazilian soils. The model applied takes into account pesticide and soil properties, as well as the net recharge rate. Advective transport of pesticides and piston water flow, instantaneous equilibrium between phases in soil, and first-order pesticide degradation were assumed. The highest overall leaching potential pesticides were Tebuthiuron and Hexazinone, which present half-life (*t½*) values exceeding 90 days and sorption coefficient (*Koc*) less than 80 mL/g. For all of the pesticides in the three soils, the percent of the pesticide entering at the top of each layer that exits, the bottom of that layer increased with depth because of the decrease in the pesticide travel time (*tr*), which is, in turn, due to the lower retardation factor (*RF*). In a Typic Quartzipsamment soil, the shortest water travel time values, due to the lowest field capacity (*FC*) values, resulted in the highest *AF* values and leaching potential. Results allow estimating that about 54% of Tebuthiuron and 13% of Hexazinone that reaches the soil surface would pass through the top 120 cm of the Typic Quartzipsamment.

KEY-WORDS: ATTENUATION FACTOR; NON-IONIZABLE PESTICIDE; LEACHING POTENTIAL; GROUNDWATER CONTAMINATION POTENTIAL; MULTI-LAYERED SOIL.

1 INTRODUCTION

Following entry of pesticides into the soil system, various physical, chemical, physico-chemical, and biological processes determine their behavior. The retention, transformation, and transport processes, and the interactions of these processes govern the dynamic of a pesticide in the

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soil. In addition to the variety of processes involved in determining pesticide behavior, many factors can affect the kinetics of the processes.

The highly aggregated Oxisols present very stable aggregates coated with oxides and organic matter, and the hydraulic conductivity of many clayey Oxisols is considerable. Oxisols have variable charge because of the presence of pH-dependent minerals such as kaolinite, and iron and aluminum oxides and hydroxides, as well due to organic matter. The Quartzipsamments are sandy soils with high hydraulic conductivity. Oxisols and Quartzipsaments, in spite of having relatively homogeneous properties in sub-surface, have different top layers, especially in agricultural areas.

As noted by DeCOURSEY (3), experience has shown that models of low order and few parameters that incorporate the dominant modes of behavior can often represent the response of complex natural systems. 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. 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.

A number of comprehensive computer simulation models are available for site-specific evaluations of the pesticide behavior in root zone. Models have also been developed to describe the various environmental processes that influence pesticide dynamics in soils. Such models are usually data intensive and require knowledge of a number of soil environment, crop, and pesticide parameters. In the majority of the cases, such parameters are neither available nor likely to be available in the near future due to the high cost associated with obtaining such data for a large number of soil-crop-pesticide combinations.

For many years, pesticide mobility has been identified as a key characteristic in assessing leaching potential, and has led to use of such factors as soil thin layer chromatography residence time, octanol-water partition coefficient, and pesticide distribution or organic carbon partition coefficient to rank the potential for chemical mobility in soil. However, mobility alone is not a good indicator of leaching and groundwater contamination potential, but rather the combination of mobility and persistence determine whether or not a compound will be degraded to an innocuous form, or a miniscule mass, during its residence time in the vadose zone. As an alternative to simplify mobility indices, JURY et al. (9) recommended use of a screening model that includes the influence of mobility and biochemical half-life in assessing the potential for leaching.

A similar approach was used by RAO et al. (11) in forming a simple index based on the vadose zone residence time in the soil and biochemical half-life.

Considering only advective transport of pesticides, assuming piston flow of water in soil, and instantaneous equilibrium between phases, JURY et al. (9) defined the convective time as a function of soil bulk density, fraction of organic carbon, organic carbon pesticide partitioning coefficient, volumetric water content, volumetric air content, Henry's law constant, distance over which flow occurs, and water flux.

In comparisons where soil bulk density, fraction of organic carbon, and relation between distance over which flow occurs and water flux, are relatively constant, organic carbon based pesticide partitioning coefficient (*Koc*) is a useful index of mobility or predictor of advective time. Compounds with low *Koc* have smaller advective time and, therefore, are more likely to move over greater distances or in a shorter time and to have higher potential to leach.

RAO et al. (11) incorporated pesticide degradation functions into expressions for travel time to yield Attenuation Factor (*AF*), which is the relation between pesticide mass entering groundwater at some distance below the soil surface, and pesticide mass applied to the surface. In computing relative mobility indices, JURY et al. (10) used an arbitrary depth of 10 cm, while RAO et al. (11) used the approximate actual distance to groundwater underlying a given soil in computing the relative leaching potential. Futhermore, soil properties were depth-weighted averaged for a 2-m depth soil profile, and the net annual recharge rate to groundwater was used in RAO et al. (11).

An important issue is related to the impacts of many layers in soils with different properties on the estimate of pesticide leaching potential. Thus, this work aim was to estimate the leaching potentials of non-ionic and non-ionizable pesticides by means of Attenuation Factor (*AF*) model generalized for multi-layered soils.

2 MATERIALS AND METHODS

Thirteen non-ionic and non-ionizable pesticides in use in the Espraiado watershed in Ribeirão Preto region, State of São Paulo, Brazil, were assessed regarding their leaching potentials. The mean values of pesticide properties came from various sources and are presented in Table 1, and cover a wide range of half-life (*t½*), sorption coefficient (*Koc*) and Henry' law constant (*KH*).

Soil samples were obtained from the Espraiado watershed, and their properties were determined based on methods presented by EMBRAPA (4), and CAMARGO et al. (2). A total soil depth of 120 cm was considered, and soil properties represent those of major soils in that region and are presented in Tables 2, 3, and 4. The annual net recharge rate (50 cm/yr.) in the watershed was estimated as the difference between rainfall (150 cm/yr.) and evapotranspiration (100 cm/yr.), which assumes steady flow in the soil zone considered. The Espraiado watershed is located in an area where the risk of contamination tends to be high for groundwater because of aquifer vulnerability (6). The watershed is on a recharge area of an important aquifer, which covers about 1,194,000 km^2 and is one of the world's largest aquifer (1,12).

TABLE 1 - PROPERTIES OF PESTICIDES USED IN AGRICULTURAL AREAS OF RIBEIRÃO PRETO REGION, SÃO PAULO, BRAZIL

Pesticide	$t_{1/2}$ (days)	K_{oc} (mL/g)	K_H*
Chlorothalonil	30	1380	2.4E-02
Cypermethrin	30	100000	8.0E-06
Diuron	90	480	2.1E-08
Endosulfan	50	12400	1.2E-05
Fenitrothion	4	2000	5.1E-07
Fluazifop-P-Butyl	15	5700	2.6E-06
Hexazinone	90	54	8.4E-11
Lambda-Cyhalothrin	30	180000	7.4E-06
Methamidophos	6	5	6.2E-09
Parathion-Methyl	5	5100	3.9E-06
Profenofos	8	2000	6.6E-07
Tebuthiuron	360	80	1.0E-08
Thiophanate-Methyl	10	1830	5.4E-07

Sources: Adapted from JURY et al (1984), RAO et al (1985), HORNSBY et al. (1996).

TABLE 2 - SOIL 1 (QUARTZIPSAMMENTIC HAPLORTHOX) PROPERTIES

Depth (cm)	Clay Content (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0 20	24	55.8	22.3	1.29	0.72
20 40	26	62.1	21.7	1.22	0.50
40 60	30	54.9	21.3	1.21	0.34
60 80	29	54.4	20.2	1.28	0.25
80 100	32	56.5	19.6	1.21	0.22
100 120	34	51.7	18.8	1.16	0.20

TABLE 3 - SOIL 2 (TYPIC HAPLORTHOX) PROPERTIES

Depth (cm)	Clay Content (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0 20	68	58.2	26.2	1.37	1.38
20 40	74	57.7	24.6	1.38	1.05
40 60	73	60.4	23.5	1.32	0.87
60 80	70	61.6	23.1	1.19	0.67
80 100	67	65.2	22.8	1.16	0.64
100 120	63	64.7	21.4	1.18	0.60

TABLE 4 - SOIL 3 (TYPIC QUARTZIPSAMMENT) PROPERTIES

Depth (cm)	Clay Content (%)	Porosity (%)	Field Capacity (%)	Bulk Density (g/cm^3)	Organic Carbon (%)
0 20	6	44.6	19.4	1.46	0.30
20 40	8	62.5	18.7	1.52	0.24
40 60	11	61.0	17.3	1.48	0.20
60 80	8	42.3	17.0	1.46	0.13
80 100	7	57.6	16.5	1.45	0.08
100 120	10	61.7	16.1	1.44	0.03

The leaching potentials of the pesticides were assessed for soils by means of the Attenuation Factor (7, 11). According RAO et al (11), Attenuation Factor is defined as the fraction of the amount of pesticide applied at the soil surface that leaches through a given soil depth, and can be expressed as:

$$AF = \exp(-t_r \times k) \qquad [1]$$

where, *tr* stands for travel time, and *k* for first-order rate constant for pesticide degradation. Pesticide half-life (*t½*) is related to by:

$$k = \frac{0.693}{t\,½} \qquad [2]$$

The travel time according to RAO et al. (1985) is:

$$tr = \frac{L \times FC}{q} \times RF \qquad [3]$$

where, *L* is the distance to groundwater, *FC* is the soil field capacity, and q is the net recharge rate. The retardation factor (*RF*) for pesticide flow is:

$$RF = 1 + \frac{(BD \times OC \times K_{oc})}{FC} + \frac{(AC \times K_H)}{FC} \qquad [4]$$

where, *BD* is the soil bulk density, *OC* is the fraction of organic carbon, *Koc* is the organic carbon pesticide partitioning coefficient, *AC* is the air-filled porosity, and *KH* is the Henry's Law constant.

In a post-publication addendum, HORNSBY and RAO (7) presented a generalized form of the Equation 1 for a multi-layered soil as follows:

$$AF^* = \Pi\, exp\ (-\ tr_i\ x\ k_i) \qquad [5]$$

where Π indicates the product of the exponential expression by layers, the subscript *i* designates the layers (*i* = 1,..., n), the counter n represents the number of layers, and the values for *tr* and *k* are unique to each layer. Thus, in this study, the Attenuation Factor was calculated for each pesticide using the multi-layer *AF* equation and taking into consideration soil properties for each layer.

3 RESULTS AND DISCUSSION

The pesticides *AF** values were calculated for each soil and the pesticides having the largest overall leaching potentials, especially Tebuthiuron and Hexazinone, are presented in Table 5, in which the numeric values represent the percent of the amount of pesticide applied at the soil surface that moves through the bottom of successive layers. The overall *AF** has, by definition, the same value as that of the bottom layer for each soil and pesticide combination shown in Table 5.

TABLE 5 - PESTICIDE ATTENUATION FACTOR IN DIFFERENT DEPTHS OF THREE SOILS, CALCULATED BY MEANS OF MULTI-LAYER ATTENUATION FACTOR (*AF)**

Depth (cm)	Soil 1 Quartzipsammentic Haplorthox	Soil 2 Typic Haplorthox	Soil 3 Typic Quartzipsamment
Tebuthiuron *AF (%)**			
0 20	76.2	60.7	85.8
20 40	65.5	40.9	74.9
40 60	53.7	29.6	66.7
60 80	47.2	23.2	61.0
80 100	42.0	18.4	56.7
100 120	37.9	14.8	53.8
Overall *AF**	**37.9**	**14.8**	**53.8**
Hexazinone *AF (%)**			
0 20	44.3	23.6	61.6
20 40	24.0	7.4	40.0
40 60	14.7	2.8	27.5
60 80	9.6	1.3	20.2
80 100	6.6	0.7	15.7
100 120	4.6	0.3	12.8
Overall *AF**	**4.6**	**0.3**	**12.8**
Diuron *AF (%)**			
0 20	0.5	<0.1	7.6
20 40	<0.1	<0.1	0.9
40 60	<0.1	<0.1	0.1
60 80	<0.1	<0.1	<0.1
80 100	<0.1	<0.1	<0.1
100 120	<0.1	<0.1	<0.1
Overall *AF**	**<0.1**	**<0.1**	**<0.1**
Methamidophos *AF (%)**			
0 20	1.1	0.2	2.6
20 40	<0.1	<0.1	<0.1
40 60	<0.1	<0.1	<0.1
60 80	<0.1	<0.1	<0.1
80 100	<0.1	<0.1	<0.1
100 120	<0.1	<0.1	<0.1
Overall *AF**	**<0.1**	**<0.1**	**<0.1**

* Used to distinguish between original *AF* and multi-layer *AF*. Numeric values are the percent of surface applied pesticide that exits each layer into the next lower layer or exits the bottom layer.

All other pesticides presented very low overall leaching potential levels for the three soils studied. Results of the multi-layer *AF* allow estimating that 37.9, 14.8, and 53.8% of Tebuthiuron and 4.6, 0.3, and 12.8% of Hexazinone that reaches the soil surface would pass through the top 120 cm of the Quartzipsammentic Haplorthox, Typic Haplorthox, and Typic Quartzipsamment soil profiles, respectively. In soil 3, Typic Quartzipsamment, the shortest water travel time values, due to the lowest field capacity (*FC*) values, resulted in the highest *AF* values and leaching potential.

It is noteworthy that, in a monitoring study performed 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, and in concentrations up to 0.08 µg/L for Tebuthiuron and 0.06 µg/L for Hexazinone (5). Tebuthiuron has moderate to low acute toxicity in experimental animals when ingested (acute oral LD_{50} for rats = 644 mg/kg), however damage to the pancreas has been observed in animals studies as a result of exposure to Tebuthiuron (13). The USEPA lifetime drinking water health advisory (HA) for Tebuthiuron is 0.5 mg/L (13). Hexazinone is less (acute oral LD_{50} for rats = 1690 mg/kg) toxic than Tebuthuiron. The USEPA lifetime drinking water health advisory (HA) for Hexazinone is 0.2 mg/L (2.5 times more toxic in drinking water than is Tebuthiuron). The USEPA HA is defined as the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects over a lifetime of exposure (70 yrs), with a margin of safety.

For all of the pesticides studied, the retardation due to the volatilization was very low when compared with the retardation due to sorption. The highest overall values for retardation factor (*RF*) were calculated for Lambda-cyhalothrin and Cypermethrin, and the lowest *RF* values were for Tebuthiuron, Hexazinone and Methamidophos. The pesticides having the highest leaching potential ranking, Tebuthiuron and Hexazinone, have half-life ($t_{½}$) values exceeding 90 days and sorption coefficient (*Koc*) less than 80 mL/g. Tebuthiuron have the longest half-life ($t_{½}$ = 360 days) among the pesticides studied. Hexazinone and Diuron have the same half-life ($t_{½}$ = 90 days), but Hexazinone *Koc* value (54 mL/g) is much lower than Diuron *Koc* (480 mL/g). Methamidophos presents a combination of short half-life ($t_{½}$= 6 days) and very low sorption coefficient (*Koc* = 5 mL/g).

For all of the pesticides in the three soils, the percent of the pesticide entering at the top of each layer that exits the bottom of that layer (not presented in Table 5) increased with depth because of the decrease in the compound travel time (*tr*), which is, in turn, due to the shorter water travel time and lower retardation factor (*RF*). The percent of

Diuron entering at the top of each layer that in exits, the bottom of that layer increased markedly with depth in soils 1 and 3 as a result of the large decline in organic carbon content, especially in soil 3.

The primary soil properties affecting sorptivity are variable, depending on the specific compound. One generalization in the literature is that the single most important soil property affecting pesticide sorption is the soil organic carbon content. While soil organic matter appears to dominate the sorption of most non-ionized pesticides, this cannot be assumed for ionic or highly polar compounds. It is important to remember that in this study only non-ionic and non-ionizable pesticides were considered. For ionic and ionizable compounds, the concept of constant *Koc* may not be directly applicable, particularly for variable-charge soils such as Brazilian Oxisols.

Pesticide half-life (*t½*) and, consequently, degradation constant (*k*) were taken as constant with depth and among soils in this study. In reality, flow through the root zone is highly transient, and the degradation rates are probably different in two soil zones. This may be important in situations where a chemical is rapidly flushed to the vadose zone by rainfall shortly after chemical application. Once in the vadose zone, the degradation rate may be lower than in the root zone so that potential transport to groundwater may be significantly underestimated. These assumptions may not present a serious problem when developing a relative ranking of compounds if it is realized that the relative position or rank may change somewhat under different assumptions about soils and climatic patterns.

4 CONCLUSION

The highest overall leaching potential pesticides were Tebuthiuron and Hexazinone, which have half-life (*t½*) values exceeding 90 days and sorption coefficient (*Koc*) less than 80 mL/g. Retardation due to the volatilization was very low when compared with the retardation due to sorption. For all of the pesticides in the three soils, the percent of the pesticide entering at the top of each layer that exits the bottom of that layer increased with depth because of the decrease in the travel time (*tr*), which is due to the lower retardation factor (*RF*). In the Typic Quartzipsamment soil, the shortest water travel time values, due to the lowest field capacity (*FC*) values, resulted in the highest *AF* values and leaching potential. Results allow estimating that about 54% of Tebuthiuron and 13% of Hexazinone that reaches the soil surface would pass through the top 120 cm of the Typic Quartzipsamment.

Resumo

AVALIAÇÃO DO POTENCIAL DE LIXIVIAÇÃO DE PESTICIDAS EM SOLOS COM VÁRIAS CAMADAS

O modelo **"**Attenuation Factor" (*AF*) generalizado para solos com multi-camadas foi utilizado para estimar os potenciais de lixiviação de pesticidas não-iônicos e não-ionizáveis em solos brasileiros. O modelo aplicado considera as propriedades dos pesticidas e dos solos, assim como a taxa de recarga líquida. O transporte advectivo dos pesticidas e o fluxo de água sem dispersão, o equilíbrio instantâneo entre fases no solo e a degradação de primeira ordem dos pesticidas foram assumidos como premissas. Os pesticidas com os maiores potenciais de lixiviação foram Tebutiuron e Hexazinone, os quais apresentaram valores de tempo de meia-vida (*t½*) maiores que 90 dias e coeficiente de sorção (*Koc*) menores que 80 mL/g. Para todos os pesticidas, nos três solos, os valores de AF aumentaram com a profundidade pelo decréscimo no tempo de percurso (*tr*) do pesticida. Tal fato se deve ao menor tempo de percurso da água e ao menor fator de retardo (*RF*). Em Neossolo Quartzarênico (Areia Quartzosa), o tempo de percurso mais curto, devido ao menor valor de capacidade de campo (*FC*) resultou em *AF* mais alto e maior potencial de lixiviação. Os resultados permitem estimar que cerca de 54% de Tebutiuron e 13% de Hexazinone aplicados na superfície do solo passariam através dos primeiros 120 cm do Neossolo Quartzarênico.

PALAVRAS-CHAVE: FATOR DE ATENUAÇÃO; PESTICIDA NÃO-IONIZÁVEL; SOLOS; POTENCIAL DE LIXIVIAÇÃO; ÁGUA SUBTERRÂNEA-CONTAMINAÇÃO.

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