



## Evaluation of soil temperature effect on herbicide leaching potential into groundwater in the Brazilian Cerrado

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### Abstract

The effect of annual variations in the daily average soil temperatures, at different depths, on the calculation of pesticide leaching potential indices is presented. This index can be applied to assess the risk of groundwater contamination by a pesticide. It considers the effects of water table depth, daily recharge net rate, pesticide sorption coefficient, and degradation rate of the pesticide in the soil. The leaching potential index is frequently used as a screening indicator in pesticide groundwater contamination studies, and the temperature effect involved in its calculation is usually not considered. It is well known that soil temperature affects pesticide degradation rates, air–water partition coefficient, and water–soil partition coefficient. These three parameters are components of the attenuation and retardation factors, as well as the leaching potential index, and contribute to determine pesticide behavior in the environment. The Arrhenius, van't Hoff, and Clausius–Clapeyron equations were used in this work to estimate the soil temperature effect on pesticide degradation rate, air–water partition coefficient, and water–soil partition coefficient, respectively. The relationship between leaching potential index and soil temperature at different depths is presented and aids in the understanding of how potential pesticide groundwater contamination varies on different climatic conditions. Numerical results will be presented for 31 herbicides known to be used in corn and soybean crops grown on the municipality of São Gabriel do Oeste, Mato Grosso do Sul State, Brazil.

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### 1. Introduction

The protection and conservation of the quality of groundwater resources are an essential part of a sus-

tainable agricultural production systems. Thus, the impact of pesticides on groundwater quality has been the subject of scientific and public health concerns worldwide, especially in areas where groundwater is mainly used for human consumption. Only in the last decade has pesticide leaching to groundwater been considered an important nonpoint source of agricultural pollution. Over a decade ago, it was assumed that pesticides would not leach to underlying groundwater (Bouwer, 1990). However, groundwater quality surveys conducted during this decade have revealed contamination of some USA aquifers with both inorganic and organic compounds, several of them are pesticides (Williams et al., 1988).

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Large-scale high-input food production, based on mechanized monocultures in industrial farming systems, strongly depend on the use of pesticides, with herbicides representing about 50% of all pesticides used in many countries (Sattin et al., 1995). The intensive use of herbicides in agriculture, and the high persistence of many of them, have required a rigorous control of possible environmental contamination, especially of groundwater and other drinking water sources. Corn and soybean cropping systems represent about 30% of the total world market share of herbicides (Sattin et al., 1995), and have been intensified for the last 20 years in the Brazilian Cerrado region (Goedert, 1983), with more than 30 million hectares being used for cereal, corn, and soybean production (Resck, 1998). Herbicides represent 56% of the total dollar value of the pesticide business in Brazil (Oliveira et al., 2001).

The municipality of São Gabriel do Oeste, located in the Midwest of Brazil, Mato Grosso do Sul State, is an important corn and soybean producing region, with an intensive herbicide utilization. This region is also an important recharge area for groundwater supply of the Guarani aquifer, which spreads under the area of eight Brazilian states, as well as parts of Argentina, Uruguay, and Paraguay, with a total area of approximately 1 200 000 km<sup>2</sup>. The problem has worsened, given the high permeability of some soils occurring in the area, and the common usage of products with high mobility, which constitute factors that elevate the potential of risk of undesirable contamination of the aquifer. This risk of negative environmental impacts become even greater, considering that 100% of the water for urban provisioning in this region is coming from that aquifer. This region has been chosen, as a research site, because of its characteristics in order to study the movement of corn and soybean herbicides through the soil profile.

Intensive laboratory and field studies are required to identify and characterize the predominant physical and chemical processes that describe the transport, persistence and fate of a particular pesticide at a determined site of application. Risk analysis of groundwater pesticide contamination involves the assessment of the pesticide properties, soil characteristics, and weather conditions. Laabs et al. (2002), in a pilot study of leaching and degradation of corn and soybean pesticides in an Oxisol of the Brazilian Cerrados, have shown that the overall pesticide half-life in the studied soil conditions differs from temperate weather conditions, and leaching studies revealed low or moderate mobility. They reported a faster degradation rate of pesticides in comparison to the rate found in temperate climates, due to enheightened microbial populations and activities under the modified environmental conditions as a result of higher temperature in the soil. Thus, the objective of this study is to consider soil temperature effect, herbicide characteristics and soil properties to classify 31 herbi-

cides used in the corn and soybean cropping region of São Gabriel do Oeste into leachability classes of the potential groundwater contamination.

## 2. Methods

Pesticide leaching indices are frequently used by government agencies and private corporation to rank groundwater contamination risk because the transport and degradation of organic compounds is too complex involving physical, chemical, and biological processes (Gustafson, 1994; Boesten, 2000). The soil temperature decreases with depth during daytime in the summer; and sorption, physical, and microbial degradation processes are known to be affected by temperature (Walker and Barnes, 1981; Hulscher and Cornelissen, 1996). Walker (1974) considered the transformation and degradation within the soil as the only processes involved in pesticide loss. Assuming that they are controlled by soil temperature and moisture content, he used an Arrhenius type equation to describe the pesticide transformation rate. The half-life of the herbicide atrazine in soil is temperature dependent (Rattanagreetakul et al., 1991). Brücher and Bergström (1997), studying the herbicide linuron sorption to three different agricultural soils and having observed that the partition coefficient changed by a factor up to 1.5 at low linuron concentrations. They also observed that the isotherms increased with decreasing temperature in sandy soils, as opposed to clay soils, where the isotherms increased along with soil temperature. Hulscher and Cornelissen (1996) presented a review enhancing the importance of temperature on the sorption and sorption kinetics of organic compounds.

The outputs of potential groundwater pesticide contamination simulation models can differ if the effects of soil temperature on the degradation rate, air–water partition, and water–soil sorption processes are not considered (Wu and Nofziger, 1999; Paraíba and Spadotto, 2002). Thus, we propose a modified version of a leaching potential index (LPI) that can estimate the potential pesticide leaching taking into consideration the periodical variation of the average daily soil temperatures on pesticide degradation rates, soil sorption coefficient, and dimensionless pesticide partition air–water coefficient.

### 2.1. Leaching potential index

In order to study the effect of the soil profile mean temperature on the leaching potential of any pesticide in a specified area, the methodology proposed by Meeks and Dean (1990) was adapted. Meeks and Dean (1990) have proposed a LPI to evaluate the risk of groundwater contamination by a pesticide or organic chemical adding

the effects of depth of water table, net rate of daily recharge, pesticide sorption coefficient, and degradation rate of the pesticide in the soil. By introducing minor modifications to the LPI, Schlosser et al. (2002) were successful in evaluating the vulnerability of the Weld County, Colorado, aquifer. Schlosser and McCray (2002) have analyzed the sensibility of the LPI to the physical and chemical parameters of the pesticides and the soil hydrologic characteristics. Bari and Anwar (1998) have used LPI to evaluate groundwater vulnerability to pesticide leaching, prioritizing monitoring sites in northwest Bangladesh. Pickus and Hewitt (1992) have developed the Pesticide User Management Planning System (PUMPS) to assist natural resource managers in understanding the effects of pesticides on groundwater. PUMPS uses geographical information system (GIS) and LPI to assess groundwater sensitivity to pesticides, and was first used in Delaware, USA. Soil temperature effect was not considered in these studies.

Dispersion–advection equations describe the mass movement of a pesticide leaching into the soil. If hydrodynamic dispersion is neglected, by assuming a steady state flow of the soil solution, the result produced by this simplified equation is a practical expression that estimates the pesticide mass remaining at a  $z$  depth of the soil and at  $t$  time. This simplified solution is known as attenuation factor, AF (Rao et al., 1985) and it can be expressed by the equation

$$AF(z) = \exp\left(\frac{-kzR_f\theta_{fc}}{J_w}\right) \quad (1)$$

where  $AF(z)$  (dimensionless) is the attenuation factor or the remaining pesticide is relative mass in the depth soil  $z$  (m),  $k$  ( $\text{day}^{-1}$ ) is the soil pesticide degradation rate estimated by  $k = \ln(2.0)/t_{1/2}$ , where  $t_{1/2}$  (day) is the pesticide half-life in the soil,  $R_f$  (dimensionless) is the retardation factor,  $\theta_{fc}$  is the soil volumetric water content at field capacity, and  $J_w$  ( $\text{m day}^{-1}$ ) is the water daily net recharge of the specific soil area. The retardation factor ( $R_f$ ) in Eq. (1) is given by

$$R_f = 1 + \frac{\rho f_{oc} K_{oc}}{\theta_{fc}} + \frac{\delta H}{\theta_{fc}} \quad (2)$$

where  $\rho$  ( $\text{kg m}^{-3}$ ) is the soil density,  $K_{oc}$  ( $\text{m}^3 \text{kg}^{-1}$ ) is the pesticide soil organic carbon partition coefficient,  $f_{oc}$  is the volumetric organic carbon content of the soil,  $\delta$  is the volumetric air content when at field capacity, and  $H$  (dimensionless Henry's constant) is the pesticide air–water partition coefficient. Meeks and Dean (1990) have used the inverse of the exponential argument of the Eq. (1) for a specific site and constant daily soil temperature to produce the LPI defined as

$$LPI = \frac{1000J_w}{kzR_f\theta_{fc}} \quad (3)$$

where the factor 1000 was used to convert the quotient given by Eq. (3) to numerical values of practical use. Meeks and Dean (1990) have suggested five leachability classes to classify the leaching potential of a pesticide, which are very low, low, moderate, high, and very high. The variations produced by Eq. (3) were associated to numerical intervals  $[0, 24]$ ,  $(24, 49]$ ,  $(49, 74]$ ,  $(74, 89]$ ,  $(89, +\infty)$ , respectively. Thus, LPI can be used as a groundwater vulnerability index to pesticide contamination according to the leaching potential of each compound.

## 2.2. Temperature leaching potential index

It is possible to use the effect of soil temperature as an attenuation factor, and calculate the remaining mass of a pesticide throughout a soil profile, by a pesticide degradation kinetics Arrhenius equation. It is also possible to calculate the retardation factor by adding the effect of soil temperature on the pesticide soil sorption coefficient, of Clausius–Clapeyron equation, and air–water pesticide partition coefficient, given by van't Hoff equation. The proposed adaptation is similar to the one suggested by Paraíba and Spadotto (2002) which calculates the attenuation and retardation factors, by adding the soil temperature effect. Since the pesticide degradation rate and retardation factor are included, in the LPI value the risk indicator of pesticide contamination of the groundwater can not neglect soil temperature, particularly in tropical areas. Soil temperature was included in the equation to calculate the LPI. It is necessary to adopt a function that describes daily average temperature at different depths. The following sinusoidal function expression describes the annual variation of daily average soil temperature at different depths

$$T(z, t) = T_a + A_0 \exp(-z/d) \sin(\omega t - z/d - \varphi_0) + 273 \quad (4)$$

where  $T = T(z, t)$  (K) is the daily average soil temperature,  $t$  is the time (day),  $T_a = (T_{\max} + T_{\min})/2$  is the annual average surface temperature of the soil ( $^{\circ}\text{C}$ ),  $A_0 = (T_{\max} - T_{\min})$  is the annual amplitude between maximum ( $T_{\max}$ ) and minimum ( $T_{\min}$ ) annual surface soil temperature in  $^{\circ}\text{C}$ , respectively. The parameter  $d$ , in Eq. (4), designates the thermal damping depth, which characterizes attenuation of the diurnal temperature wave along with soil depth. This value can be calculated by the formula  $d = \sqrt{2\tau/(C_h\omega)}$ , where  $\tau$  ( $\text{kJ mol}^{-1} \text{K}^{-1} \text{m}^2 \text{day}^{-1}$ ) is the soil thermal conductivity,  $C_h$  ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ) is the heat soil volumetric capacity, and  $\omega = 2\pi/365$  ( $\text{day}^{-1}$ ) is the radial frequency.  $\varphi_0 = \pi/2 + \omega t_0$  (dimensionless) is the phase constant, and  $t_0$  (day) is the time lag from the arbitrary starting date to the occurrence of the minimum annual temperature

(Hillel, 1982; Campbell, 1985; Jury et al., 1992; Wu and Nofziger, 1999).

The relationship between the soil pesticide degradation rate and the soil temperature can be described by the Arrhenius equation given by

$$k(z, t) = \left( \frac{\ln(2.0)}{t_{1/2}} \right) \exp \left( \frac{E_a}{R} \left( \frac{1}{T_r + 273} - \frac{1}{T(z, t)} \right) \right) \quad (5)$$

where  $T_r$  (= 20 or 25 °C) is the reference temperature,  $E_a$  (kJ mol<sup>-1</sup>) is the pesticide degradation activation energy and  $R = 8.314 \times 10^{-3}$  kJ mol<sup>-1</sup> K<sup>-1</sup> is the gas constant (Keen and Spain, 1992; Rocha and Walker, 1995).

Based on fundamental thermodynamic concepts, the Clausius–Clapeyron equation can be used to determine soil temperature and air–water pesticide partition coefficient (Sagebiel et al., 1992; Bacci, 1994; Rice et al., 1997), using the following equation

$$H(z, t) = \left( \frac{P_m P_v^{T_r}}{SR(T_r + 273)} \right) \times \exp \left( \frac{\Delta H_v}{R} \left( \frac{1}{T_r + 273} - \frac{1}{T(z, t)} \right) \right) \quad (6)$$

where  $P_m$  (g mol<sup>-1</sup>) is the pesticide molecular weight,  $P_v^{T_r}$  (Pa) is the pesticide vapor pressure at the reference temperature,  $S$  (g m<sup>-3</sup>) is the pesticide aqueous solubility, and  $\Delta H_v$  (kJ mol<sup>-1</sup>) is the enthalpy of volatilization. The coefficient  $P_m P_v^{T_r} / (SR(T_r + 273))$  in Eq. (6) is the dimensionless Henry's constant or pesticide air–water partition coefficient.

Thus, pesticide air–water partition coefficient can be determined using depth  $z$  at time  $t$  in the function (6). For each depth  $z$  and each time  $t$  the function  $H = H(z, t)$  is a thermodynamic balance between soil air and soil water. It is expected that this balance exhibits dependence with soil temperature. According to Kavanaugh and Trussel (1980), Schwarzenbach et al. (1993), and Rice et al. (1997), the pesticide air–water partition coefficient increases a range factor of 1.2–1.8 for each Celsius degree of temperature increase, in a range of 10–20 °C.

The calculation of the pesticide water–soil partition coefficient, or pesticide sorption coefficient,  $K_D = K_D(z, t)$  can be estimated for different soil temperatures using the van't Hoff equation given by

$$K_D(z, t) = (f_{oc} K_{oc}) \exp \left( \frac{\Delta H_a}{R} \left( \frac{1}{T_r + 273} - \frac{1}{T(z, t)} \right) \right) \quad (7)$$

where  $\Delta H_a$  (kJ mol<sup>-1</sup>) is the sorption enthalpy. The coefficient  $f_{oc} K_{oc}$  in Eq. (7) is the pesticide sorption coefficient or pesticide water–soil partition coefficient, at the reference temperature  $T_r$ .

When  $\Delta H_v$  and  $\Delta H_a$  are not known, or when they are not available in the literature, one can use the Goss and Schwarzenbach (1999) relationship to estimate those values. Such empirical relations are given, respectively, by

$$\Delta H_v = -3.8 \ln(P_v^{20}) + 70.0 \quad (8)$$

$$\Delta H_a = -4.17 \ln \left( \frac{f_{oc} K_{oc}}{1.0 \times 10^3 \text{ SSA}} \right) - 88.1 \quad (9)$$

where  $P_v^{20}$  (Pa) is the pesticide vapor pressure at the reference temperature  $T_r = 20$  °C, and SSA (m<sup>2</sup> g<sup>-1</sup>) is the soil specific surface area. The specific surface is estimated as follows (Pionke and De Angelis, 1972)

$$\text{SSA} = 100.0(100.0f_{oc} + 2.0f_{cl} + 0.4f_{st} + 0.005f_{sd}) \quad (10)$$

where  $f_{cl}$  is the soil clay volumetric fraction,  $f_{st}$  is the soil silt volumetric fraction and  $f_{sd}$  is the soil sand volumetric fraction. In this simulation, the Goss and Schwarzenbach (1999) equation was used to estimate  $\Delta H_v$  and  $\Delta H_a$ .

Soil temperature effect was introduced in the retardation factor and LPI, supposing that soil profile is layered. Depth  $L$  meters is layered in  $n$  layers of thickness  $\Delta L$ , that is,  $\Delta L = L/n$ . The value of  $l_{n+1} = l_i + \Delta L$  (m) represents the soil depth  $i \in \{0, 1, 2, \dots, n-1\}$ , with  $l_0 = 0$  representing the soil surface and  $l_n = L$ . In each layer of soil of thickness  $[l_i, l_{i+1}]$  the pesticide is degraded according to Arrhenius equation. For each soil layer  $[l_i, l_{i+1}]$ , where  $i \in \{0, 1, 2, \dots, n-1\}$ ,  $z \in [l_i, l_{i+1}]$ ,  $0 \leq t \leq t_h$ , and  $t_h$  (day) is the maximum number of days of the leaching simulation, several values of retardation factor is given by

$$R_f(z, t) = 1 + \frac{\rho K_D(z, t)}{\theta_{fc}^z} + \frac{\delta H(z, t)}{\theta_{fc}^z} \quad (11)$$

where  $\theta_{fc}^z$  is the volumetric water content at field capacity in the soil depth  $z$ . Minor modifications in LPI, considering soil temperature effects, were made as follows:

$$\text{TLPI} = \frac{1000J_w}{k(L, t_h)LR_f(L, t_h)\theta_{fc}^L} \quad (12)$$

where TLPI is the temperature leaching potential for soil depth  $L$  and after  $t_h$  days of pesticide application,  $\theta_{fc}^L$  is the volumetric water content at field capacity in soil depth  $L$ . The values  $k(L, t_h)$  and  $R_f(L, t_h)$  in expression (12) are, respectively, the pesticide degradation rate and the retardation factor calculated by Eqs. (5) and (11) at depth  $z = L$  and time ( $t = t_h$ ). Thus, defining a simulation time horizon  $t_h$  in days, and soil depth  $L$  in meters, it is possible to estimate the risk of groundwater pesticide contamination at a specific site by the proposed equation (12). Thus keeping the same risk classification parameters and numerical intervals of LPI, suggested by Meeks and Dean (1990), it is possible to determine levels

of potential contamination or leachability classes of different pesticides groups using TLPI equation. This novel approach takes into consideration the influence of soil temperature on the pesticide half-life, pesticide sorption coefficient, and pesticide air–water partition coefficient. Therefore, the TLPI index corresponds to the LPI index when the soil temperature effect is also considered factor in this equation.

### 2.3. Classification in leachability class

The 31 main herbicides used in corn and soybean crops in the Cerrado region of São Gabriel do Oeste were selected to classify these compounds by their potential to contaminate the groundwater, after temperature effect was included into the potential index (TLPI). According to the pesticide database compiled by Hornsby et al. (1996), the necessary physical and chemical data used to calculate the risk by TLPI are presented in Table 1. Since these physical and chemical characteristics were obtained in laboratory experiments

at 20 or 25 °C average temperature of, for the numerical calculations of the TLPI index the value  $T_r = 20$  °C, as the reference temperature.

For all herbicides, the Arrhenius activation energy constant  $E_a$  used in the expression (5) was the  $E_a = 56$  kJ mol<sup>-1</sup>. This value is in agreement with the Arrhenius activation energy obtained by Veeh et al. (1996) for herbicide 2,4-D, with the average values obtained by Baer and Calvet (1999) for herbicides atrazine, sulcotrione, simazine, and diuron; and the average values obtained for Gómez de Barreda (1999) for herbicides molinate, terbuthylazine, terbacil, and thiobencarb; in eight different soil types of the Valencia Community, Spain. For each pesticide, the enthalpy of volatilization  $\Delta H_v$  was estimated by Eq. (8), and used separately to calculate the TLPI values. Those values were used to calculate the average value of the  $\Delta H_v = 106$  kJ mol<sup>-1</sup>. This value is in agreement with enthalpy of volatilization predicted by Nirmalakhandan et al. (1997) for several organic compounds. We have taken two representative soil sample from studied site, each having contrasting

Table 1  
Properties of the main herbicides used in the area (Hornsby et al., 1996; Tomlin, 2000)

Herbicide	$P_m$ (g mol <sup>-1</sup> )	$P_v$ (Pa)	$S$ (g m <sup>-3</sup> )	$K_{oc}$ (m <sup>3</sup> kg <sup>-1</sup> )	$t_{1/2}$ (day)
2,4-D	221.0	1.86E-02	20031.00	2.00E-02	10
Acifluorfen-sodium	383.6	1.00E-05	62.07	1.13E-01	14
Alachlor	269.8	2.00E-03	170.31	1.50E-01	15
Atrazine	215.7	3.85E-05	33.00	1.00E-01	77
Bentazone	240.3	1.70E-04	570.00	3.40E-02	20
Butoxydim	399.5	1.00E-05	6.90	4.30E-02	9
Chlorimuron-ethyl	414.8	4.90E-07	1200.00	1.10E-01	40
Clomazone	239.0	1.92E-03	1100.00	3.00E-01	30
Cyanazine	240.0	2.13E-07	171.00	1.90E-01	14
Diclosulam	406.2	6.70E-13	6.32	1.10E-02	65
Dimethenamid	275.8	3.67E-02	1.20	9.40E-02	43
Diquat	344.0	1.00E-05	700.00	1.00E+03	1000
Fenoxaprop	361.8	5.30E-07	0.70	3.00E-01	21
Fluazifop- <i>p</i> -butyl	383.4	3.33E-05	1.10	5.70E+00	15
Flumetsulam	325.3	3.70E-10	100.00	2.00E-03	60
Flumiclorac-pentyl	423.9	1.00E-05	0.19	2.83E+00	5
Fomesafen	438.8	4.00E-06	10.00	6.00E-02	100
Haloxypop	361.7	1.33E-06	1590.00	7.50E-02	55
Imazaquin	311.3	1.30E-05	120.00	2.00E-02	60
Imazethapyr	289.3	1.30E-05	1400.00	1.00E-02	90
Lactofen	461.8	9.30E-06	1.00	1.00E+02	7
Linuron	249.1	5.10E-05	63.80	4.00E-01	60
Metolachlor	283.8	4.20E-03	488.00	2.00E-01	90
Metribuzin	214.3	5.80E-05	1050.00	6.00E-02	40
Paraquat	257.2	1.00E-05	620000.00	1.00E+04	1000
Pendimethalin	281.3	4.00E-03	0.30	5.00E+00	90
Picloram	241.5	8.40E-05	430.00	5.00E+00	30
Sethoxydim	327.5	1.30E-05	25.00	1.00E-01	5
Sulfentrazone <sup>a</sup>	387.2	1.30E-07	0.11	4.20E-02	540
Simazine	201.7	2.94E-06	6.20	9.50E-02	60
Trifluralin	335.3	6.10E-03	0.18	8.00E+00	60

<sup>a</sup> Tomlin (2000).

physical properties: a *Typic Orthic Neosol Quartzarenic Brazilian* (TONQ) (USDA, 1999), and a *Typic Distrophic Red Latosol* (TDRL) (USDA, 1999), Tables 2 and 3, respectively. The soil specific surface area (SSA) in Tables 2 and 3 were estimated by Eq. (10). Using the herbicide numerical values of Table 1 and the soil numerical values of Tables 2 and 3, the heat of sorption  $\Delta H_a$  was estimated by Eq. (9). The estimated values, and their respective average values  $-12.32 \text{ kJ mol}^{-1}$  and  $-12.75 \text{ kJ mol}^{-1}$ , are of the same order of magnitude of the heat of sorption, as well as of the respective average value ( $-8 \text{ kJ mol}^{-1}$ ) of the organic micropollutants compiled by Hulscher and Cornelissen (1996).

Computations of the temperature leaching potential index (TLPI) depends on the water recharge  $J_w$  for specific site and hydrologic soil properties. We have estimated this values by the water balance approach using daily precipitation and evapotranspiration data, water irrigation data and the hydrologic group of the respective soil sample. Thus, for the soil properties given by Tables 2 and 3, the estimated value  $J_w$  was  $0.0018$  and  $0.0021 \text{ m day}^{-1}$ , respectively. Eq. (4), and the calculation procedures described by Hillel (1980) and Wu and Nofziger (1999), were used to determine the annual varia-

tion of daily average soil temperature at different soil depths, as described in Tables 2 and 3. The minimal and maximal annual surface soil temperatures observed at a soil depth of 5 cm were  $T_{\min} = 15.3 \text{ }^\circ\text{C}$  and  $T_{\max} = 45.5 \text{ }^\circ\text{C}$ , respectively. The annual agronomic period of the herbicide applications and soil depth simulated was  $t_h = 180$  days and  $L = 2$  m (average depth of the vadose zone), respectively. This range of time horizon corresponds to the total of the 1600 mm annual precipitation in the São Gabriel do Oeste region. The numerical values of the TLPIs computed by Eq. (12) for all herbicides in the respective soil types (TONQ and TDRL) allows for classification into very low, low, moderate, high, and very high leachability classes. These results are summarized in Table 4 and suggest that a reasonable ranking of the groundwater potential herbicide contamination can be done considering the soil temperature effect. All the numeric results were accomplished by the mathematical scientific package MATLAB (1992).

Using TLPI equation a specific leachability class assigned to a particular herbicide varies with soil and herbicide properties. Monitoring data of herbicides atrazine, alachlor, metolachlor, simazine, and trifluraline in tropical soils of Brazil under field conditions,

Table 2  
TONQ properties used for calculating the TLPI

$\Delta L$ (m)	$\rho$ ( $\text{kg m}^{-3}$ )	$\delta$ (%)	$\theta_{fc}$ (%)	$f_{st}$ (%)	$f_{el}$ (%)	$f_{sd}$ (%)	$f_{oc}$ (%)	SSA ( $\text{m}^2 \text{g}^{-1}$ )
0.00–0.20	1661.98	0.1702	0.1670	0.0336	0.1083	0.8581	0.0048	71.90
0.20–0.40	1633.41	0.1944	0.1560	0.0195	0.1231	0.8574	0.0040	65.88
0.40–0.60	1603.28	0.2125	0.1501	0.0108	0.1341	0.8551	0.0033	60.70
0.60–0.80	1570.93	0.2241	0.1501	0.0083	0.1409	0.8508	0.0027	56.33
0.80–1.00	1535.13	0.2282	0.1574	0.0135	0.1420	0.8445	0.0023	52.76
1.00–1.20	1498.36	0.2267	0.1692	0.0234	0.1401	0.8366	0.0021	50.03
1.20–1.40	1466.74	0.2244	0.1793	0.0304	0.1411	0.8284	0.0018	48.22
1.40–1.60	1442.73	0.2232	0.1849	0.0317	0.1477	0.8206	0.0016	47.39
1.60–1.80	1425.11	0.2221	0.1874	0.0287	0.1585	0.8128	0.0014	47.50
1.80–2.00	1413.22	0.2208	0.1874	0.0221	0.1729	0.8050	0.0013	48.56

Table 3  
TDRL properties used for calculating the TLPI

$\Delta L$ (m)	$\rho$ ( $\text{kg m}^{-3}$ )	$\delta$ (%)	$\theta_{fc}$ (%)	$f_{st}$ (%)	$f_{el}$ (%)	$f_{sd}$ (%)	$f_{oc}$ (%)	SSA ( $\text{m}^2 \text{g}^{-1}$ )
0.00–0.20	1316.1480	0.1638	0.3147	0.1017	0.6400	0.2619	0.0167	298.08
0.20–0.40	1315.8738	0.1795	0.3207	0.0825	0.6673	0.2502	0.0150	286.90
0.40–0.60	1294.1792	0.1928	0.3278	0.0678	0.6922	0.2400	0.0134	275.28
0.60–0.80	1246.6078	0.2038	0.3361	0.0577	0.7112	0.2311	0.0118	263.03
0.80–1.00	1164.6649	0.2128	0.3463	0.0522	0.7239	0.2238	0.0103	249.83
1.00–1.20	1065.3400	0.2193	0.3572	0.0513	0.7309	0.2178	0.0088	236.33
1.20–1.40	990.6894	0.2227	0.3654	0.0540	0.7334	0.2127	0.0075	224.19
1.40–1.60	957.7025	0.2226	0.3695	0.0601	0.7300	0.2082	0.0065	214.06
1.60–1.80	957.8846	0.2191	0.3703	0.0697	0.7260	0.2044	0.0058	205.61
1.80–2.00	986.7794	0.2125	0.3681	0.0829	0.7160	0.2015	0.0052	198.68

Table 4  
Herbicide-soil leachability class by TLPI results

Herbicide	TLPI in TONQ <sup>a</sup>	Leachability class in TONQ	TLPI in TDRL <sup>b</sup>	Leachability class in TDRL
2,4-D	19	Very low	11	Very low
Acifluorfen-sodium	15	Very low	8	Very low
Alachlor	34	Low	7	Very low
Atrazine	89	High	47	Low
Bentazone	33	Low	19	Low
Butoxydim	14	Very low	8	Very low
Chlorimuron-ethyl	44	Low	23	Very low
Clomazone	18	Very low	9	Very low
Cyanazine	11	Very low	6	Very low
Diclosulam	129	Very high	80	High
Dimethenamid	51	Moderate	27	Low
Diquat	0	Very low	0	Very low
Fenoxaprop	13	Very low	6	Very low
Fluazifop- <i>p</i> -butyl	1	Very low	0	Very low
Flumetsulam	129	Very high	83	High
Flumiclorac-pentyl	0	Very low	0	Very low
Fomesafen	142	Very high	79	High
Haloxypop	72	Moderate	39	Low
Imazaquin	111	Very high	67	Moderate
Imazethapyr	181	Very high	112	Very high
Lactofen	0	Very low	0	Very low
Linuron	30	Low	14	Very low
Metolachlor	72	Moderate	36	Low
Metribuzin	57	Moderate	31	Low
Paraquat	0	Very low	0	Very low
Pendimethalin	5	Very low	2	Very low
Picloram	2	Very low	1	Very low
Sethoxydim	6	Very low	3	Very low
Simazine	71	Moderate	38	Low
Sulfentrazone	856	Very high	488	Very high
Trifluralin	2	Very low	1	Very low

<sup>a</sup>Typic Orthic Neosol Quartzarenic.

<sup>b</sup>Typic Distrophic Red Latossol.

published by Laabs et al. (2002), Laabs et al. (2000), and of the herbicide atrazine by Cerdeira et al. (1998), corroborate the temperature leaching potential indexes presented in Table 4. The dependency of TLPI on the soil temperature and the lower half-life at high temperatures can be explained by the fact that most herbicides are associated with very high groundwater contamination potentials, but show low to moderate leaching potentials in tropical regions, despite the fact that pesticide degradation rates are positively related to soil temperature. It is universally accepted that the three most important characteristics of a pesticide, that influence their leaching potential to the groundwater, are: high aqueous solubility, low soil sorption, and high persistence in the soil matrix. Observing the herbicide characteristics in Table 1, and the results presented in Table 4, there are no contradictions to this general statement. The TLPI index is a numerical value that indicates the susceptibility of groundwater to herbicide

contamination. For example, the TLPI scoring for atrazine are 89 and 47, in the TONQ and TDRL soils, respectively. Based on these scores, the respective relative atrazine mass at a depth of 2 m to groundwater is estimated 1.3E–03 percent and 5.75E–08 percent of the applied mass after 180 days. In other words, the TLPI estimates that there will be 2.29E+4 times more atrazine in the TONQ soil than in the TDRL soil, with potential leaching into the groundwater. Thus, the results of Table 4 indicate the herbicides that should have priority in a monitoring program of groundwater herbicide contamination.

### 3. Conclusions

The problems associated with the assessment of nonpoint source groundwater contamination by herbicides in tropical soils were addressed. The results

presented in Table 4 can be useful in other areas and the method to calculate the TLPI index can be used to refine pesticide leaching potential assessments in temperate climatic conditions, as demanded by Brücher and Bergström (1997). Application of the TLPI associated with spatial analysis and GIS can be useful in evaluating groundwater contamination potential of a large number of pesticides applied to a large area quickly and economically, and to inform decision makers in a more effective manner. Results of sensitivity analysis of the TLPI can be used to show that groundwater pesticide contamination depends on hydrological, pesticides and soil properties, and climatic conditions. However, soil characteristics, pesticides properties and climatic conditions appeared to be key factors in evaluating vulnerability in a hypothetical hydrological setting. Efforts have been made to evaluate herbicides leaching potential under field soil and climatic conditions, where abundant groundwater supplies occur in shallow, unconfined aquifers, and crop fields are intensively managed with herbicide applications.

Results have shown that the TLPI is a useful tool in classifying susceptible areas to groundwater degradation by herbicides and to indicate the priority herbicides to be assessed by monitoring programs. The thermodynamic parameters necessary to calculate the TLPI, activation energy, volatilization, and sorption enthalpy, depend not only on the pesticide–water–soil system, but also on the conditions under which the analyses are made. The temperature effect on sorption depends on the energy transfer during the sorption process, and an inverse relationship dependence has been found for a large number of nonionic organic chemical compounds (Chiou et al., 1979). The van't Hoff equation can be applied to estimate the pesticide partition coefficient in order to determine the retardation factor as a function of soil temperature. The choice of herbicide is most critical for farmers on vulnerable soil and water resources. This is a complex task that must take into account the crop, the tillage system, target species, and other important environmental factors. Physical and chemical properties of the herbicides must be considered when evaluating their leaching potential to the groundwater.

The inclusion of soil temperature in the LPI proved to be important and essential to estimate the leaching potential of the herbicides studied in tropical conditions. Van Duin (1956) has shown that the magnitude of temperature variation at the soil surface is greater in tilled than in untilled soils, and that this amplitude decreases with depth more steeply in tilled than untilled soil. It was also found that tilled soil could be warmer at surface but cooler below a certain depth, what enhance, the addition of temperature effect in our proposed temperature leaching potential index.

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## References

- Bacci, E., 1994. *Ecotoxicology of Organic Contaminants*. CRC Press, Inc., Boca Raton, FL.
- Baer, U., Calvet, R., 1999. Fate of soil applied herbicides: experimental data and prediction of dissipation kinetics. *J. Environ. Qual.* 28, 1765–1777.
- Bari, M.F., Anwar, A.H.M.F., 1998. Groundwater vulnerability to pesticide leaching and prioritizing monitoring sites in north-west Bangladesh. In: Wheeler, H., Kirby, C. (Eds.), *Hydrology in a Changing Environment*. Vol. II. Bangladesh University of Engineering and Technology, Dhaka, Bangladesh. Proceedings of the British Hydrological Society International Conference, Exeter, UK, July 1998. John Wiley & Sons Ltd., Chichester, UK, pp. 77–88.
- Boesten, J.J.T.I., 2000. From laboratory to field: uses and limitations of pesticide behaviour models for the soil/plant system. *Weed Res.* 40, 123–138.
- Bouwer, H., 1990. Agricultural chemicals and ground water quality. *J. Soil Water Conserv.* 42, 184–189.
- Brücher, J., Bergström, L., 1997. Temperature dependence of linuron sorption to three different agricultural soils. *J. Environ. Qual.* 26, 1327–1335.
- Campbell, G.S., 1985. *Soil Physics with Basic: Transport Models for Soil–Plant Systems*. Elsevier, New York.
- Cerdeira, A.L., Lanchote, V.L., Queiroz, R.C., Bonato, P.S., Gomes, M.A., Shuhama, I., Ueta, J., 1998. Herbicides residues in soil and water from sugarcane area in Brazil. In: *World Congress of Soil Science, 1998, Montpellier, France*. Proceedings, ISSS, International Soil Science Society, CIRAD, Paris.
- Chiou, C.T., Peters, L.J., Freed, V.H., 1979. A physical concept of soil–water equilibria for nonionic organic compounds. *Science* 206, 831–832.
- Goedert, W.J., 1983. Management of Cerrado soils of Brazil: a review. *J. Soil Sci.* 34, 405–428.
- Goss, K.U., Schwarzenbach, R.P., 1999. Empirical prediction of heats of vaporization and heats of adsorption of organic compounds. *Environ. Sci. Technol.* 33, 3390–3393.
- Gustafson, D.I., 1994. New advances in predicting pesticide fate and transport. In: Copin, A., Houins, G., Pussemier, L., Salembier, J.F. (Eds.), *Environmental Behaviour of Pesticides and Regulatory Aspects*. European Study Service, Rixensart, Belgique, pp. 453–458.
- Gómez de Barreda, D., 1999. *Comportamiento de herbicidas residuales en suelo: posible contaminación de acuíferos*. Tesis Doctoral. Universidad Politécnica de Valencia, Spain.

- Hillel, D., 1980. *Fundamentals of Soil Physics*. Academic Press, Inc., London, UK.
- Hillel, D., 1982. *Introduction to Soil Physics*. Academic Press, Inc., San Diego, CA.
- Hornsby, A.G., Don Wauchope, R., Herner, A.E., 1996. *Pesticide Properties in the Environment*. Springer-Verlag, Inc., New York, NY.
- Hulscher, ten, Th.E.M., Cornelissen, G., 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants—a review. *Chemosphere* 32 (4), 609–629.
- Jury, W.A., Gardner, W.R., Gardner, W.H., 1992. *Soil Physics*. John Wiley & Sons, Inc., New York.
- Kavanaugh, M.C., Trussel, R.R., 1980. Design of aeration towers to strip volatile contaminants from drink water. *J. Am. Water Works Assoc.* 72 (12), 684–692.
- Keen, R.E., Spain, J.D., 1992. *Computer Simulation in Biology: A Basic Introduction*. Wiley-Liss, Inc., New York.
- Laabs, V., Amelung, W., Pinto, A., Altstaedt, A., Zech, W., 2002. Fate of pesticides in tropical soils of Brazil under field conditions. *J. Environ. Qual.* 31, 256–268.
- Laabs, V., Amelung, W., Pinto, A., Altstaedt, A., Zech, W., 2000. Leaching and degradation of soybean pesticides in an Oxisol of the Brazilian Cerrados. *Chemosphere* 41, 1441–1449.
- MATLAB, 1992. *The Student Edition of MATLAB*. MathWorks, Inc., Prentice Hall, Englewood Cliffs, NJ.
- Meeks, Y.J., Dean, J.D., 1990. Evaluating groundwater vulnerability to pesticides. *J. Water Resour. Plng. Mgmt.* 116, 693–707.
- Nirmalakhandan, N., Brennan, R.A., Speece, R.E., 1997. Predicting Henry's law constant and effect of temperature on Henry's law constant. *Water Res.* 31 (6), 1471–1481.
- Oliveira Jr., R.S., Koskinen, W.C., Ferreira, F.A., 2001. Sorption and leaching potential of herbicides on Brazilian soils. *Weed Res.* 41, 97–110.
- Paraíba, L.C., Spadotto, C.A., 2002. Soil temperature effect in calculating attenuation and retardation factors. *Chemosphere* 48, 905–912.
- Pickus, J., Hewitt, M., 1992. Resource at risk: analyzing sensitivity of groundwater to pesticides. *Geo. Info. Syst.* 2 (10), 50–55.
- Pionke, H.B., De Angelis, R.J., 1972. Method for distributing pesticide loss in field runoff between the solution and adsorbed phase. In: *CREAMS, a Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems*, USDA Conservation Res. Rep. 26, USDA, SEA, Washington, DC, pp. 607–645.
- Rao, P.S.C., Hornsby, A.G., Jessup, R.E., 1985. Indices for ranking the potential for pesticide contamination of groundwater. *Proc. Soil Crop Sci. Soc. Fla.* 44, 1–8.
- Rattanagreetakul, C., Korpraditskul, R., Korpraditskul, V., 1991. Effect of temperature and soil moisture on atrazine degradation. *Kasetsart J. (Nat. Sci. Suppl.)* 25, 75–79.
- Resck, D.V., 1998. Agricultural intensification systems and their impact on soil and water quality in the Cerrados of Brazil. In: Lal, R. (Ed.), *Soil Quality and Agricultural Sustainability*. Ann Arbor Press, Chelsea, pp. 288–300.
- Rice, C.P., Chernyak, S.M., McConnell, L.L., 1997. Henry's law constants for pesticides measured as a function of temperature and salinity. *J. Agric. Food Chem.* 45, 2291–2298.
- Rocha, F., Walker, A., 1995. Simulation of the persistence of atrazine in soil at different sites in Portugal. *Weed Res.* 35, 179–186.
- Sagebiel, J.C., Seiber, J.N., Woodrow, J.E., 1992. Comparison of headspace and gas-stripping methods for determining the Henry's law constant (*H*) for organic compounds of low to intermediate *H*. *Chemosphere* 25 (12), 1763–1768.
- Sattin, M., Berti, A., Zanin, G., 1995. Agronomic aspects of herbicide use. In: Vigh, M., Funari, E. (Eds.), *Pesticide Risk in Groundwater*. CRC Press, Inc., Lewis Publishers, Boca Raton, FL, pp. 45–70.
- USDA, 1999. Soil survey staff. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, second ed. Washington, US Govt. Printing Office, 869 p. (US Department of Agriculture Handbook, p. 436).
- Schlosser, S.A., McCray, J.E., 2002. Sensitivity of a pesticide leaching-potential index model to variations in hydrologic and pesticide-transport properties. *Environ. Geosci.* 9 (2), 66–73.
- Schlosser, S.A., McCray, J.E., Murray, K.E., Brad, A., 2002. A subregional-scale method to assess aquifer vulnerability to pesticides. *Ground Water* 40 (4), 361–367.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 1993. *Environmental Organic Chemistry*. John Wiley & Sons, Inc., New York.
- Tomlin, C.D.S., 2000. *The Pesticide Manual*. British Crop Protection Council, Farnham, UK.
- Van Duin, R.H.A., 1956. On the Influence of Tillage on Conduction of Heat Diffusion of Air, and Infiltration of Water in Soil. *Versl. Landbouwk. Onderz.* p. 62.
- Veeh, R.H., Inskeep, W.P., Camper, A.K., 1996. Soil depth and temperature effects on microbial degradation of 2,4-D. *J. Environ. Qual.* 25, 5–12.
- Walker, A., 1974. A simulation model for prediction of herbicide persistence. *J. Environ. Qual.* 4, 396–401.
- Walker, A., Barnes, A., 1981. Simulation of herbicides persistence in soil: a revised computer model. *Pest. Sci.* 12, 123–132.
- Williams, W.M., Holden, P.W., Parsons, D.W., Lorber, M.N., (1988). *Pesticides in Ground Water Database*, Interim Report. US Environmental Protection Agency, Washington, DC.
- Wu, J., Nofziger, D.L., 1999. Incorporating temperature effects on pesticide degradation into a management model. *J. Environ. Qual.* 28, 92–100.