SUGARCANE HERBICIDE LEACHING RISK EVALUATION IN GUARANY AQUIFER

Lourival Costa Paraíba[1]; Karen Kataguiri[2]; Antonio Luiz Cerdeira[1]; Sônia Cláudia Nascimento de Queiroz[1] & Vera Lúcia Ferracini[1]

Abstract – The region of Ribeirão Preto, São Paulo State, Brazil, is located over recharge area of the Guarany aquifer, the most important source of groundwater in the South Central region of the country. This region is also the most important sugarcane producing area of the country which produces a large amount of the ethanol. This study was conducted to determine the potential risk of herbicide groundwater contamination. The leaching risk potential of herbicides to groundwater was conducted using the weather simulator "Weather Generator" (WGEN) coupled with the model "Chemical Movement Trough Layered Soils" (CMLS94). The following herbicides were evaluated in clayey and sandy soils (Typic Haplorthox and Typic Quartzipsamment soils) found in the region: ametryn (N-ethyl-N'-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine), atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone), diuron (3,4-dichlorophenyl)-N,N-dimethylurea), halosulfuron (3-chloro-5-[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl], hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4 (1H,3H)-dione), imazapic ((±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid), imazapyr ((±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid), MCPA (4-chloro-2-methylphenoxy)acetic acid), metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), MSMA (Amonosodium salt of MAA), paraquat (1,1'-dimethyl-4,4'-bipyridinium ion), pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine), picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine), sulfentrazone [N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide], and tebuthiuron [N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea]. Results obtained by our simulation study have shown that the herbicides picloram, tebuthiuron, and metribuzin have the highest leaching potential, in either sandy or clayey soils, with picloram reaching the root zone of sugarcane at 0.6m in less than 150 days.

Keywords: CMLS94, groundwater; biofuel.

[1]Pesquisador(a) da Embrapa Meio Ambiente. CP. 69; CEP 13820-000, Tel. 19-3311-2600; Jaguariúna, São Paulo, Brasil. e-mails: lourival@cnpma.embrapa.br; cerdeira@cnpma.embrapa.br; sonia@cnpma.embrapa.br; veraf@cnpma.embrapa.br; [2]Bolsista do PIBIC/Embrapa. Faculdade de Engenharia Ambiental; UNESP - Campus Experimental Sorocaba; São Paulo; Brasil; e-mail: karen.kataguiri@terra.com.br

INTRODUCTION

The protection and conservation of the quality of groundwater resources are an essential part of sustainable 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 the groundwater is mainly used for human consumption. Virtually all the drinking water utilized by Ribeirão Preto's city population in São Paulo, Brazil, comes from Guarany aquifer groundwater, from either rural or urban wells. The aquifer 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^2. Consequently, the movement of agricultural chemicals through soils into groundwater represents a potential threat to water quality of the region. In general, the pesticides may be transported to groundwater due to their solubility, large amount applied, presence of seasonally high water tables, shallow and high permeability. Certain areas of the watershed are composed of highly permeable sandy soil which allows leaching of agrochemicals applied to crops (Miklós and Gomes, 1996).

Large-scale, industrial farming systems require high-input of pesticides, mainly herbicides, in sugarcane for ethanol and biofuel production (Sattin et al., 1995). The intensive use of herbicides in sugarcane crop, and the high persistence of many of them, has required a rigorous control of possible environmental contamination, especially of groundwater and other drinking water sources. Sugarcane cropping systems demands use of large amount of soil applied herbicides with potential leaching into groundwater. Herbicides represent 56 % of the total dollar value of the pesticide business in Brazil (Oliveira et al., 2001). 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.

The objective of this study was to evaluate the behavior of the herbicides based on their chemical characteristics and properties of Typic Haplorthox and Typic Quartzipsamment soils and classify the herbicides used in the sugarcane cropping system in the region of Ribeirão Preto based on leaching risk the potential to groundwater contamination. The study was conducted to determine the potential risk of groundwater contamination after hundred and fifty days of applications using the weather simulator "Weather Generator" (WGEN) (Richardson and Wright, 1994) coupled with the model "Chemical Movement Trough Layered Soils" (CMLS94) (Nofzier and Hornsby, 1994). The following herbicides were evaluated in sandy and clay soil conditions typical of the region: ametryn (N-ethyl-N'-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine), atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine), clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone), diuron (3,4-dichlorophenyl)-N,N-dimethylurea), halosulfuron (3-chloro-5-[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl], hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4 (1H,3H)-dione), imazapic ((±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-methyl-3-pyridinecarboxylic acid), imazapyr ((±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-pyridinecarboxylic acid), MCPA (4-chloro-2-methylphenoxy)acetic acid), metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one), MSMA (Amonosodium salt of MAA), paraquat (1,1'-dimethyl-4,4'-bipyridinium ion), pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine), picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), simazine (6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine), sulfentrazone [N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide], and tebuthiuron [N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea].

The CMLS94 is a one-dimensional solute transport model that uses a piston flow approach to simulate the vertical movement of selected chemicals through the agricultural root zone on a layer by layer basis. Although this model was written primarily as a management and educational tool, it has been tested favorably and used with several different types of input data in many parts of the word (Inskeep et al., 1996; Wilson et al., 1996; Pessoa et al., 2003). The weather simulator WGEN generates data that allows the simulation of daily precipitation, maximum and minimum temperatures and daily solar radiation for a chosen period and location. The WGEN PAR is an added feature to the model the utilizes the statistical parameters of the WGEN incorporated to the CMLS94 allowing the construction of weather data independent and equally probable.

MATERIAL AND METHODS

CMLS94 model was used to evaluate the risk of groundwater contamination of sugarcane applied herbicides adding the weather simulator model WGEN allowing the study of series sinteticas of independent weather parameters with same probability. It was assumed that there is a risk when the herbicide reached the depth of 0.60 m from soil surface at the root zone after 150 days of spraying. With the WGEM added, the CML94 can be used to study the probability of a compound to reach a specific depth after chosen days of application to the soil surface. Daily data of precipitation and air temperature of fourteen consecutive years (1993-2007) were obtained from the Experimental Station of the Campinas Agronomic Institute at the city of Ribeirão Preto. The CML94 models was then used to simulate the sequence of 1000 years independent and equally probable to estimate the probability of a herbicide reach 0.60 m 150 days after the application at the area.

Soil samples from the sugarcane watershed were characterized by the content of sand, clay and granulometry. The sampled of soils were classified as clayey and sandy soils (Typic Haplorthox and Typic Quartzipsamment soils). The properties of two soils were measured and are shown on tables 1 and 2 and each layer properties were used to simulate the herbicides leaching with the CML94.

Those values of tables 1 and 2 were added to the CML94 model with sugarcane crop coefficient values (CC) for several stages of growth (Table 3) to estimate evapotranspiration and hydric balance of the soils layers simulated with the CMLS94. It was assumed that the risk for groundwater contamination was high when the herbicides leached deeper than the root zone at depth of 0.60 m from soil surface 150 days after the application. The CMLS94 models was added with the WGEN model data allowing the risk evaluation of groundwater contamination using synthetic and equally probable series of independent weather data .

The herbicide properties were then added to the model to estimate the leaching risk using the CMLS94 and WGEN (Table 4). It is shown the percentage from a thousand simulations that an herbicide reached the depth of 0.60 m after 150 days of application. Picloram has shown the highest risk regardless the type of soil. Typic Quartzipsamment soil was most vulnerable to leaching and has lower organic matter content (Table 4). Those herbicides were chosen by their importance is sugarcane.

Soil sorption, K_{OC} (l kg^{-1}), half-life in soil, $t_{1/2}$ (days), concentration applied, mg kg^{-1} were added to the model. It was assumed 1.0 mg kg^{-1} applied and that the herbicides were applied on December 13 (normal for the region) and that sugarcane was planted on December 18, 2007. The rainy season is on the following 150 days.

Table 1. Typic Haplorthox soil properties.

depth (cm)	organic carbon (g/g)	bulk density (kg/dm^3)	field capacity (m^3/m^3)	wilting point (kg/kg)	saturation (m^3/m^3)
0-10	0.0181	1.19	24.8	17.4	52.9
10-20	0.0170	1.26	28.7	17.7	50
20-30	0.0163	1.25	24.4	17.9	50.6
30-40	0.0116	1.34	27.8	18.5	46.8
40-50	0.0098	1.29	28.4	18.9	48.8
50-60	0.0075	1.23	28.8	19.2	51.1
60-70	0.0078	1.22	27.6	19.2	51.5
70-80	0.0070	1.13	24.3	19.2	55.3

Table 2. Typic Quartzipsamment soil properties

depth (cm)	organic carbon (g/g)	bulk density (kg/dm^3)	field capacity (m^3/m^3)	wilting point (kg/kg)	saturation (m^3/m^3)
0-10	0.0028	1.42	19.8	5.7	46.9
10-20	0.0021	1.55	17.4	5.7	42.1
20-30	0.0021	1.58	18.4	2.7	40.8
30-40	0.0013	1.61	18.9	2.7	39.7
40-50	0.0010	1.57	20	2.9	41.3
50-60	0.0010	1.57	16.9	2.9	41.3
60-70	0.0017	1.62	20	1.8	39.4
70-80	0.0019	1.56	18.4	1.8	41.6

Table 3. Sugarcane crop coefficients (CC).

Crop age(days)	development stages (meters)	CC values
1	seeding to 0.25	0.50
60	0.25 a 0.5	0.65
90	0.5 a 0.75	0.75
120	0.75 until maximum development	0.90
270	maximum development	1.10
300	begining of maturation phase	0.70
360	maturation	0.60

Source: Paranhos (1987).

RESULTS AND DISCUSSION

From those data is possible to select the worst case in terms of herbicide probability of groundwater contamination and they need to be studied in more details in the recharge area. The leaching risk potential could be linked to the low sorption capacity of those soils due to the low organic carbon content. Herbicides with low sorption coefficients in soil with low organic carbon and height half-life in soil layers have shown the highest risk potential of groundwater contamination.

According to Pessoa et al. (2003), the results obtained with the CML94 model are similar to those with more features such as PRZM, LEACHMP, GLEAMS or MOUSE. Cohen et al. (1995) suggested the use of the CMLS94 model as a decision tool to manage pesticides safety to the environment because it is an easier model to study leaching processes.

Table 4. Properties of herbicide and leaching percent risk[1] result by CMLS94 simulation in each soil type.

Herbicide	soil sorption Koc (ml/g)	soil half-life (days)	Typic Haplorthox (% risk)	Typic Quartzipsamment (% risk)
ametryn	300	60	0.0	0.5
atrazine	100	60	0.0	26.0
clomazone	300	24	0.0	0.0
diuron	480	90	0.0	0.0
halosulfuron	124	51	0.0	16.3
hexazinone	54	90	0.2	38.5
imazapic	206	140	0.0	5.3
imazapyr	100	90	0.0	22.0
MCPA	2000	25	0.0	0.0
metribuzin	60	40	0.0	40.9
MSMA	7000	180	0.0	0.0
paraquat	10000	1000	0.0	0.0
pendimethalin	5000	90	0.0	0.0
picloram	16	90	32.9	58.6
simazine	130	60	0.0	13.3
sulfentrazone	80	360	0.0	30.0
tebuthiuron	80	360	0.0	34.0

[1]Percentage number of the 1000 years of weather data independent and equally probable that the herbicide reached 0.6 m

In conclusion, the risk analysis suggested that the herbicides picloran and hexazinone must be evaluated and analyzed in groundwater regardless the type of soil where it is applied. The herbicides atrazine, halosulfuron, imazapyr, simazine e tebuthiuron must be followed in water from sandy soil regions. The fitness of these models has shown that the simulation is an useful tool to determine worst case scenarios of groundwater contamination under field conditions.

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