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Environmental fate of pesticides applied on coffee crops in southeast of Brazil

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The aim of this paper was evaluate the environmental fate of pesticides applied in coffee crops in southeast of Brazil, using the level I fugacity model. Chemical and physical characteristics of the pesticides were considered in different environmental compartments and applied fugacity equations. The preliminary evaluation of contamination risk due the use of pesticides in coffee crops, using fugacity models, proved to be good tools to be used in the process of making decision to select pesticides with less impact on the environment, as well to prioritize the pesticides to be monitored. For most of the pesticides evaluated, the soil/sediment compartment was the most vulnerable.

Key words: Environmental fate, fugacity, organic micropollutants, pesticide.

INTRODUCTION

The benefits of pesticides are evident. However, the risk of adverse effects must be diminished. So, it is necessary to exert effective control of use and have available methods of calculating their environmental behavior.

The models employ calculations that use concepts of activity and fugacity to characterize the equilibrium that exists between environmental compartments. Most of the emphasis is on organic chemicals, which are more susceptible to generalization than inorganic chemical, when assessing environmental behavior (Mackay, 2001).

The best way to assess the pesticides impact potential in the environment consists of conducting field monitoring for a long period of time. However, this process requires high financial resources to produce consistent data.

The modeling is interesting to avoid unnecessary costs of residue analyses in vulnerable compartments. Nevertheless, none of these models consider the behavior of the compound in the soil and volatilization, leaching, superficial runoff and degradation process, simultaneously (Brooks and Roberts, 1999).

This study can contribute to predicting the environmental destination of pesticides and suggest the pollutants and compartments that must be investigated in monitoring programs. These models are interesting in the process of listing pesticides that present characteristics of environmental risks.

Mackay (2001) proposed a methodology to predict pesticides environmental destination, using fugacity

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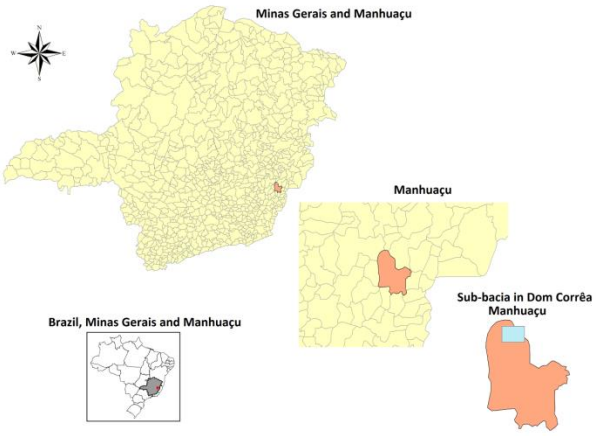

Figure 1. Localization of the study area.

concepts.

According to the author, fugacity can be the best way to quantify the transport, bioaccumulation and transference among different compartments (air, water, soil, sediment, biota, suspended solid and others). So, the model is proposed as a strategy to assess the environmental exposure to pesticides applied to crops. Based on fugacity, the model presents an estimate of concentration and partition in each compartment in the environment.

The application of fugacity concepts is convenient to chemical balance and partition calculations usually applied only in the last decades. Fugacity is also useful for describing mathematically the rates (pollutant quantities) in which chemical diffusion or transport occurs among phases. The transfer rate can be expressed as being proportional to the fugacity difference that exists between the source (origin) and the final phase (destiny). The mathematical procedures used in this methodology were developed from thermodynamic concepts, transport phenomena and kinetic reactions (Mackay, 2001; Mackay et al., 1997).

The model of fugacity has four complexity levels and is applied in environmental systems previously selected. The Level I calculates the pesticides distribution among compartments, considering thermodynamic balance of the partition coefficients in steady state.

This work use the model of fugacity Level I, due the available data to carry out the calculations. Thus, any degradations reactions and advance effects will not be taken into consideration.

The aim of the present work was to assess environmental destiny of pesticides, applied in coffee crops and marketed in Manhuaçu-MG, Brazil from 2007 to 2010, using fugacity models Level I. Some metabolites and pesticides detected in the surface water of sub-basin, situated in northern of Manhuaçu-MG, were also assessed to be checked with the results of the model.

MATERIALS AND METHODS

Study region

Manhuaçu is located in the Rio Doce hidrographic basin in Minas Gerais and highlights among other cities of the state, by its significant coffee production, more than 16,000 tons in 2014 (IBGE, 2016).

There are about 20 thousand coffee-producing properties in Manhuaçu region. This number represents 71% of the coffee-producing properties in the Zona da Mata, the second-largest coffee-producing region in the state. The local topography is mountainous, with altitudes ranging from 561 to 1,760 m. The average annual rainfall is 1,860 mm. Rainfall in the region, according to a field survey, occurs predominantly during the months of November through March (Soares et al., 2013). The rainy period is the same in the application of pesticides, increasing contamination of water and soil.

The most used pesticides in the study region are fungicides, herbicides and insecticides and are classified as non-mobile (Koc> 4000 $mL.g^{-1}$) or low mobility in the environment (500 <Koc <4.000 $mL.g^{-1}$), and according these characteristics, they are more prone to contamination of surface waters in the rainy season. Furthermore, it is necessary to highlight the characteristics of soils in the region – latosol – with thick and clayey layers. These characteristics favor runoff and reduce the risk of groundwater contamination, but increase the risk of surface water contamination.

The water source evaluated in this study was selected using multi-criteria analysis, as shown by Soares (2012). The sub-basin of the study in Dom Corrêa district is located in the upper-left corner of the polygon: X1= -42.17; Y1= -20.03; and, the lower right corner: X2= -42.10; Y2= -20.08 (Coordinates Lat. Long., WGS84), to the north of the city of Manhuaçu, according to presented Figure 1.

Study model

In this study, the mathematical model used applies concepts of fugacity, which was introduced by Lewis in 1901 as a more convenient thermodynamic equilibrium criterion than chemical potential. Its convenience in environmental chemical equilibrium or partitioning calculation has become apparent in only last three decades. This model shows that fugacity is useful to quantify mathematically the rates that chemicals diffuse or are transported between phases: for example volatilization of pesticides from soil to air. The transfer rate can be expressed as being led by, or proportional to, the fugacity difference that exists between the source and destination phases. Thus, this model express the behavior of the pesticides in the environment by: transforming chemical reaction, advective flow and nondiffusive transport rate equations into fugacity expressions and build up sets of fugacity equations describing the complex behavior of chemicals in multiphase. The steps by calculation of the equilibrium Level I distribution of a chemical are (Mackay, 2001):

1. Definition of the environment (volumes and compositions)
2. Input of relevant physical chemical properties
3. Calculation of Z values for each medium (Table 1)
4. Input of chemical amount (in this study, it was considered 1 mol)
5. Calculation of fugacity, and hence concentration, amounts, and percent distribution

The calculations were performed for 54 pesticides and metabolites of the three active ingredients of pesticides most used in coffee crops in Brazil (ETU; 1,2,4-triazole and endosulfan sulfate), totaling 57 substances.

Table 1. Definitions of Z values and equations used in Level I calculations.

Definitions of "Z" values
$Z_A = 1/RT$
$Z_w = 1/H = C^S/P^S = Z_A/K_{AW}$
$Z_o = Z_W K_{ow}$ (octanol)
$Z_P = 1/v_P P^S$ (pure phase)
$Z_S = y_{oc} K_{oc} Z_w (\rho_S/1000)$ (soils, sediments)
$K_{oc} = 0,41 K_{ow}$ (there are variations in this equation, as presented)
Where:
R: Gas constant (8,314 Pa.m³/mol K)
T: Absolute temperature (K)
H: HENRY´s law constant (Pa.m³.mol^{-1})
C^s: Solubility in water (mol.m^{-3})
P^s: Vapor pressure (Pa)
K_{AW}: Air-water partition coefficient
K_{ow}: Octanol-water partition coefficient
K_{oc}: Organic carbon-water partition coefficient
v_P: Molar volume of pure chemical (m³.mol^{-1})
y_{oc}: Mass fraction organic carbon
Note that the Z value is expressed by $Z_T = \Sigma v_i Z_i$; where v_i is the volume fraction of phase i.
Fugacity equation
$f = M/\Sigma V_i Z_i$
Where: f: fugacity (Pa); M: total amount of chemical (mol); V: volume (m³)
$C_i = Z_i f$; $m_i = C_i V_i = V_i Z_i f \therefore m_i$ is amount in phase i (mol)

Fonte: Mackay (2001).

The methodology presented by MACKAY (2001) and Excel® 10.0 (Office XP) software was used for the application of algorithms to each substance, according to equations presented in the Table 1. The method of evaluation describes the physic-chemical properties of pesticides assessed. The fugacity model Level I was used in this research, due the availability of data to apply the mathematic model.

Pesticides chemical properties used to calculate the potential of distribution in the environmental compartments were: molecular mass (M), vapour pressure at 25°C (VP), solubility in water at 20°C (S), Henry's law constant at 25°C (K_H), octanol water partition coefficient (K_{ow}), organic carbon water partition coefficient (K_{oc}), air-water partition constant (K_{AW}), soil-water partition constant (K_{SoW}) and sediment-water partition constant (K_{SeW}). The partition constants (K_{SoW} and K_{SeW}) were estimate by means of K_{oc} values, according to Mackay (2001). All necessary data to calculate potential pesticides distribution in the environment came from IUPAC database (IUPAC, 2016).

Level I model of fugacity was described in such a way that fugacity "f" is related to concentration "C" in mol.m^{-3}, by means of fugacity capacity "Z", given, in mol.m^{-3}.Pa^{-1} (MACKAY, 2001). Thus, one can calculate the concentration of a compound in a compartment by Equation 1.

$C = Z.f$ [Equation 1]

Where "f" is fugacity, given in Pascal units (Pa).

In this study, it is necessary to calculate the volumes the compartments considered in the environment, where the aim is to know pesticides dispersion. In this case, the compartments studied were: air, water, soil and sediment of a sub-basin located in northern Manhuaçu (called Dom Corrêa district sub-basin).

From the results of geoprocessing obtained by Soares et al. (2011), an approximate volume of 20 km^3 was selected, according to scheme presented in Figure 2. These volumes were calculated as follows:

1. Air volume: it was considered the topographical area of sub-basin Dom Corrêa district (16,933,086.48 m²) and the air located at an altitude of 1000 m, above the soil surface, according to Mackay (2001). This altitude is justified by the fact that the author reported that it is unlike that most of the pollutants can disperse in altitudes above the range of 500 to 2000 m. Thus, the air volume obtained was 1.69 x 10^{10} m³.
2. Water volume: the extension of watercourses located in the sub-basin is 37,015 m (Extension obtained from the vector measurement of the hydrographic network (two dimensions), with adjustment of 10%, to consider the terrain relief (three dimensions) the average width considered to waterways was 3.0 m and the maximum average depth of 1.0 m. Considering the transversal section of the streams as parabolic, these measures result in a volume of surface water in the sub-basin of 74,030 m³.
3. Sediment volume: the extent of watercourses located in the sub-basin is 37,015 m, considering the average width of the gutter of the streams equal 3.0 m, maximum average depth 1.0 m, sediment layer 3 cm, as suggested by Mackay (2001). From this data, a volume of sediment equal 3,331.35 m³ was obtained along the entire section of watercourses. For this calculation, the sediment being delimited between the two parables with vertices distant 3 cm

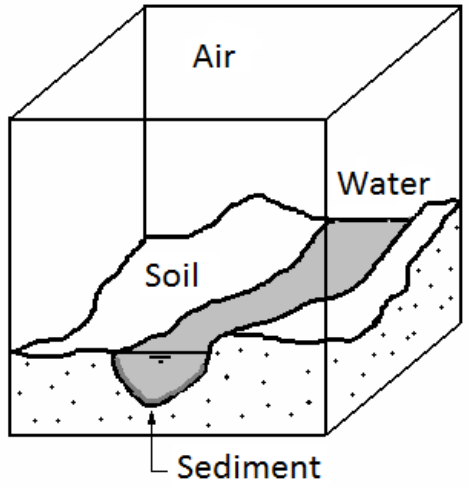

Figure 2. Schemetic representation of environmental compartments considered in this study.

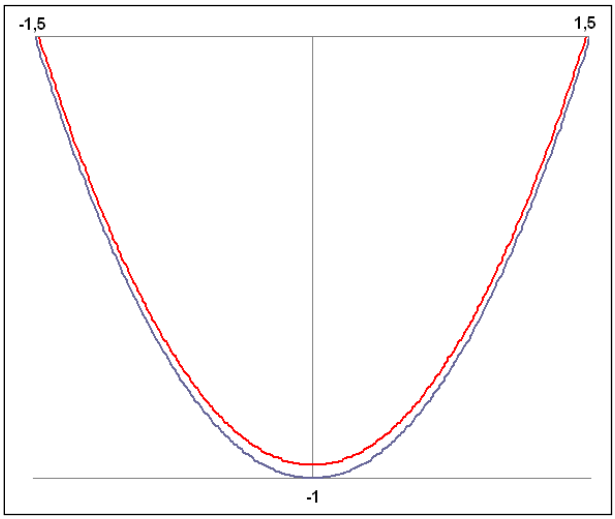

Figure 3. Parabolic section simulating streams gutter pipe (lower parable) and sediment layer (upper parable).

was considered, according to Figure 3. Thus, the volume of sediment in the sub-basin is 3331.35 m³.
4. Soil volume: taking into consideration the topographic area of the sub-basin (16.933.086,48 m²) and the soil situated 10 cm of depth, according to Mackay (2001), the soil volume considered in sub-basin is 1.693.308,65 m³.

The arithmetic average of the concentrations of organic carbon obtained for three different profiles of soil and seven sediment sampling sites, distributed along the sub-basin were calculated, as shown in Table 2. Thus, the values used in the calculations were the averages presented in Table 3.

In equifugacity state, Plese et al. (2009) explained that the compartments that have high fugacity capacity will have high concentrations of the compound. Thus, the authors reported that the fugacity capacity consists of a measure of the "solubility" of the compound in the compartment studied. Therefore, each compartment requires that its fugacity capacity be defined and that depends on physic-chemical properties of the compound and of the compartment nature studied. The fugacity capacities were calculated to each compartment by means of Equation 2.

$$C_i = Z_{ij}.f_i \quad (4) \qquad 2$$

Where: i = air (1); water (2); soil (3) and sediment (4). So, i = 1; 4 compartments; j = 1; 57 pesticides/metabolites.

In air, the fugacity of a compound (f_{ar}) is equal to its vapor pressure, expressed in terms of concentration, and is obtained by Equation 3:

$$F_{air} = C_{air}RT \qquad 3$$

Where: C_{air}, in mol.m^{-3}, is the concentration of the compound in the air; R = 8,314 Pa.m³.mol^{-1} and T is the absolute temperature in Kelvin degrees (*K*). Thus, the capacity of fugacity from the air (Z_{ar}) is given by Equation 4.

$$Z_{air} = \frac{1}{RT} \qquad 4$$

In water, the fugacity of a pesticide dissolved is roughly equivalent to its partial vapor pressure, described by Henry's Law, according to Equation 5.

$$f_{water} = HC_{water} \qquad 5$$

Where: f_{water} is the fugacity of the pesticide in water, expressed in Pa; H is the Henry's law constant (Pa.m³.mol^{-1}) and C_{water}, in mol m^{-3} is the concentration in the water. Thus, the capacity of the water fugacity (Z_{water}) is given by Equation 6:

$$Z_{water} = \frac{1}{H} \qquad 6$$

For soil and sediment compartments, the fugacity has no direct relation with the physico-chemical parameters of the compounds. This way, the capacity of fugacity "Z" to these compartments is obtained using the expression presented by Mackay (2001), according to Equation 7.

$$Z_{soil\ and\ sediment} = y_{oc}K_{oc}Z_{water}\frac{\rho_s}{1000} \qquad 7$$

Where: y_{oc} is the fraction of organic carbon (% OC); ρ_s is the density of soil or sediment (kg.m^{-3}). And the value "Z" of a phase was obtained by Equation 8:

$$Z_T = \Sigma\ V_iZ_i \qquad 8$$

V_i: is the volume fraction in phase "i" expressed in m³, the fugacity "f" in Pa, is given by Equation 9.

$$f = \frac{M}{\Sigma ViZi} \qquad 9$$

Table 2. Collection points for soil and sediment samples in Dom Corrêa sub-basin district of Manhuaçu

	Collection point	Coordinates geographical[1]	Description
Soil	Profile 1	0798228; 7780534	Under coffee crops. Altitude: 920m
	Profile 2	0799646; 7780426	
	Profile 3	0799839;7778527	Under coffee crops. Altitude: 950 m
Sediment	Sed 1	796811;7780716	Stream João Bento
	Sed 2	797127;7780925	
	Sed 3	798312;7780730	
	Sed 4	798966;7780626	
	Sed 5	799121;7780858	Tributary stream João Bento
	Sed 6	799399;7779540	Stream Bom Jardim
	Sed 7	799269;7778794	

[1]Datum SAD69.

Table 3. Contents of organic carbon (OC) and densities (Ds) obtained for samples of soil and sediment collected in the Dom Corrêa sub-basin.

	Point	OM[1] (dag.kg^{-1})	OC (dag kg^{-1})	Ds (g.cm^{-3})
Soil	Profile 1	3.45	2.00	1.36
	Profile 2	1.97	1.14	1.33
	Profile 3	2.34	1.36	1.11
	Average	**2.59**	**1.50**	**1.27**
Sediment	Sed 1	2.84	1.65	1.40
	Sed 2	1.47	0.85	1.60
	Sed 3	2.19	1.27	1.70
	Sed 4	2.31	1.34	1.50
	Sed 5	4.33	2.51	-
	Sed 6	3.67	2.13	1.45
	Sed 7	4.76	2.76	-
	Average	**3.08**	**1.79**	**1.53**

[1]Organic matter (OM) = Organic carbon (OC) x 1,724 – Walkley-Black. Source: Cunha (2011).

Where M is the total amount of pesticides (mol). The concentration in each phase (Ci) is calculated by Equation 10:

$$C_i = Z_i f \quad (10)$$

And the amount in each compartment (m_i) was obtained using Equation 11:

$$m_i = C_i V_i = V_i Z_i f \quad (11)$$

RESULTS AND DISCUSSION

Environmental fate of pesticides applied in coffee crops

The assessment of the environmental destination of pesticides, was performed in a relatively simple way through physic-chemical properties of the compounds, characteristics of the environmental compartments (content organic carbon and density), using the fugacity model Level I.

Considering the hydrographic sub-basin of study, the soil was the environmental compartment that showed the greatest vulnerability and disposition in the distribution of pesticides and some metabolites. Only acephate and methamidophos were predominant in water compartment, according to Table 4.

Thus, the surface water source contamination of the region of study is related to contamination by the carriage of contaminated soil with pesticides in rainy seasons. Concerning the concentration of pesticides in

Table 4. Percentage of pesticide in each compartment.

Pesticide/metabolites	Percentage (%) in compartments				Predominance
	Air	Water	Soil	Sediment	
Endosulfan sulfate*	6.30E-01	2.27E-01	9.89E+01	2.80E-01	Soil
ETU*	5.77E-06	4.40E-02	9.97E+01	2.82E-01	Soil
1,2,4-triazole*	2.64E+01	1.85E+00	7.16E+01	2.02E-01	Soil
2,4-D	4.71E-03	3.93E+00	9.58E+01	2.71E-01	Soil
Abamectin	1.01E-02	4.06E-02	9.97E+01	2.82E-01	Soil
Acephate	2.61E-04	5.34E+01	4.65E+01	1.32E-01	Water
Acetamiprid	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Ametryn**	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Atrazine**	3.10E-02	2.24E+00	9.75E+01	2.76E-01	Soil
Azoxystrobin	3.63E-07	5.38E-01	9.92E+01	2.81E-01	Soil
Benalaxyl	2.75E-02	4.58E-02	9.96E+01	2.82E-01	Soil
Cyhexatin	9.67E-02	5.24E-02	9.96E+01	2.82E-01	Soil
Cypermethrin	4.94E-03	2.67E-03	9.97E+01	2.82E-01	Soil
Cyproconazole	2.69E-03	5.83E-01	9.91E+01	2.80E-01	Soil
Cyromazine	2.98E-07	5.56E-01	9.92E+01	2.80E-01	Soil
Clethodim	1.75E-03	5.41E+00	9.43E+01	2.67E-01	Soil
Chlorfenapyr	1.02E-03	1.91E-02	9.97E+01	2.82E-01	Soil
Chlorpyrifos**	1.22E+00	2.77E-02	9.85E+01	2.79E-01	Soil
Deltametrin**	6.40E-05	2.24E-05	9.97E+01	2.82E-01	Soil
Difenoconazole	8.42E-06	6.08E-02	9.97E+01	2.82E-01	Soil
Diuron	3.95E-05	2.14E-01	9.95E+01	2.81E-01	Soil
Endosulfan Total	2.65E+00	1.94E-02	9.71E+01	2.75E-01	Soil
Enxofre	5.38E-01	1.17E-01	9.91E+01	2.80E-01	Soil
Epoxiconazole**	9.25E-03	2.13E-01	9.95E+01	2.81E-01	Soil
Esfenvalerate	1.95E-03	4.32E-02	9.97E+01	2.82E-01	Soil
Famoxadone	2.60E-02	6.11E-02	9.96E+01	2.82E-01	Soil
Fenoxaprop-p-ethyl	5.10E-04	2.02E-02	9.97E+01	2.82E-01	Soil
Fenpropathrin**	4.35E+01	2.59E-02	5.64E+01	1.59E-01	Soil
Fipronil	8.42E-03	3.95E-01	9.93E+01	2.81E-01	Soil
Fludioxonil	1.52E-05	3.05E-03	9.97E+01	2.82E-01	Soil
Flutriafol**	1.04E-04	8.89E-01	9.88E+01	2.80E-01	Soil
Fomesafen	8.08E-05	4.38E+00	9.54E+01	2.70E-01	Soil
Indoxacarb	1.97E-04	3.55E-02	9.97E+01	2.82E-01	Soil
Malathion	9.63E-02	1.04E+00	9.86E+01	2.79E-01	Soil
Mancozeb	1.25E-02	2.29E-01	9.95E+01	2.81E-01	Soil
Metalaxyl-M	1.12E-03	3.46E-01	9.94E+01	2.81E-01	Soil
Methamidophos	1.03E-02	6.96E+01	3.03E+01	8.58E-02	Water
Methomyl	1.64E-03	8.33E+00	9.14E+01	2.59E-01	Soil
Metolachlor	2.03E-01	1.00E+00	9.85E+01	2.79E-01	Soil
Metribuzin	1.05E-02	5.68E+00	9.40E+01	2.66E-01	Soil
Novaluron	4.22E+00	2.28E-02	9.55E+01	2.70E-01	Soil
Oxytetracycline	3.54E-21	2.23E-03	9.97E+01	2.82E-01	Soil
Pencycuron	1.86E-06	4.04E-02	9.97E+01	2.82E-01	Soil
Permethrin	3.99E-02	2.29E-03	9.97E+01	2.82E-01	Soil
Picloram	1.70E-04	6.14E+00	9.36E+01	2.65E-01	Soil
Pyraclostrobin	1.02E-05	2.08E-02	9.97E+01	2.82E-01	Soil
Pyriproxyfen	1.16E-02	1.08E-02	9.97E+01	2.82E-01	Soil
Profenofos	1.73E-02	1.13E-01	9.96E+01	2.82E-01	Soil

Table 4. Contd.

Propanil	9.14E-03	5.69E-01	9.91E+01	2.80E-01	Soil
Simazine	8.94E-03	1.73E+00	9.80E+01	2.77E-01	Soil
Spinosad	1.15E-07	6.61E-03	9.97E+01	2.82E-01	Soil
Tebuconazole	2.74E-04	2.97E-01	9.94E+01	2.81E-01	Soil
Teflubenzuron	5.66E-03	8.78E-03	9.97E+01	2.82E-01	Soil
Thiobencarb	7.25E-01	2.13E-01	9.88E+01	2.79E-01	Soil
Triadimenol	2.69E-04	8.31E-01	9.89E+01	2.80E-01	Soil
Triazophos	2.87E-01	6.33E-01	9.88E+01	2.79E-01	Soil
Trifloxystrobin	2.04E-02	9.62E-02	9.96E+01	2.82E-01	Soil

(*) Metabolites; (**) these pesticides were also detected in chromatographic semi-quantitative assays of surface water in the study region (Streams João Bento and Bom Jardim).

Table 5. Concentration of pesticides in the compartments.

Pesticides/metabolites	Concentration (µg.L^{-1}) in the compartments				Predominance
	Air	Water	Soil	Sediment	
Endosulfan sulfate*	8.79E-10	7.26E-05	1.38E-03	1.98E-03	Sediment
ETU*	3.33E-14	5.82E-05	5.76E-03	8.28E-03	Sediment
1,2,4-triazole*	2.26E-07	3.61E-03	6.12E-03	8.80E-03	Sediment
2,4-D	1.26E-11	2.40E-03	2.56E-03	3.68E-03	Sediment
Abamectin	6.89E-12	6.32E-06	6.79E-04	9.76E-04	Sediment
Acephate	8.42E-13	3.94E-02	1.50E-03	2.16E-03	Water
Acetamiprid	7.07E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Ametryn**	7.08E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Atrazine**	8.48E-11	1.40E-03	2.67E-03	3.84E-03	Sediment
Azoxystrobin	5.31E-16	1.80E-04	1.45E-03	2.09E-03	Sediment
Benalaxyl	4.98E-11	1.90E-05	1.81E-03	2.60E-03	Sediment
Cyhexatin	1.48E-10	1.84E-05	1.53E-03	2.19E-03	Sediment
Cypermethrin	7.00E-12	8.68E-07	1.41E-03	2.03E-03	Sediment
Cyproconazole	5.45E-12	2.70E-04	2.01E-03	2.88E-03	Sediment
Cyromazine	1.06E-15	4.52E-04	3.52E-03	5.07E-03	Sediment
Clethodim	2.87E-12	2.03E-03	1.55E-03	2.22E-03	Sediment
Chlorfenapyr	1.48E-12	6.32E-06	1.44E-03	2.08E-03	Sediment
Chlorpyrifos**	2.06E-09	1.07E-05	1.66E-03	2.38E-03	Sediment
Deltametrin**	7.48E-14	5.98E-09	1.17E-03	1.68E-03	Sediment
Difenoconazole	1.22E-14	2.02E-05	1.45E-03	2.08E-03	Sediment
Diuron	1.00E-13	1.24E-04	2.52E-03	3.62E-03	Sediment
Endosulfan Total	3.84E-09	6.43E-06	1.41E-03	2.03E-03	Sediment
Enxofre	9.91E-09	4.91E-04	1.82E-02	2.62E-02	Sediment
Epoxiconazole**	1.66E-11	8.72E-05	1.78E-03	2.56E-03	Sediment
Esfenvalerate	2.75E-12	1.39E-05	1.40E-03	2.02E-03	Sediment
Famoxadone	4.10E-11	2.21E-05	1.57E-03	2.26E-03	Sediment
Fenoxaprop-p-ethyl	8.32E-13	7.52E-06	1.63E-03	2.34E-03	Sediment
Fenpropathrin**	7.35E-08	1.00E-05	9.52E-04	1.37E-03	Sediment
Fipronil	1.14E-11	1.22E-04	1.34E-03	1.93E-03	Sediment
Fludioxonil	3.62E-14	1.66E-06	2.37E-03	3.41E-03	Sediment
Flutriafol**	2.04E-13	3.99E-04	1.94E-03	2.78E-03	Sediment
Fomesafen	1.09E-13	1.35E-03	1.28E-03	1.85E-03	Sediment
Indoxacarb	2.20E-13	9.08E-06	1.12E-03	1.60E-03	Sediment

Table 5. Contd.

Malathion	1.72E-10	4.26E-04	1.76E-03	2.53E-03	Sediment
Mancozeb	2.71E-11	1.14E-04	2.17E-03	3.11E-03	Sediment
Metalaxyl-M	2.36E-12	1.67E-04	2.10E-03	3.02E-03	Sediment
Methamidophos	4.30E-11	6.66E-02	1.27E-03	1.82E-03	Water
Methomyl	5.96E-12	6.93E-03	3.33E-03	4.78E-03	Water
Metolachlor	4.23E-10	4.76E-04	2.05E-03	2.95E-03	Sediment
Metribuzin	2.89E-11	3.58E-03	2.59E-03	3.73E-03	Sediment
Novaluron	5.05E-09	6.26E-06	1.14E-03	1.65E-03	Sediment
Oxytetracycline	4.54E-30	6.54E-07	1.28E-03	1.84E-03	Sediment
Pencycuron	3.35E-15	1.66E-05	1.79E-03	2.57E-03	Sediment
Permethrin	6.02E-11	7.90E-07	1.50E-03	2.16E-03	Sediment
Picloram	4.16E-13	3.43E-03	2.29E-03	3.29E-03	Water
Pyraclostrobin	1.55E-14	7.25E-06	1.52E-03	2.18E-03	Sediment
Pyriproxyfen	2.13E-11	4.54E-06	1.83E-03	2.63E-03	Sediment
Profenofos	2.73E-11	4.10E-05	1.57E-03	2.26E-03	Sediment
Propanil	2.47E-11	3.52E-04	2.68E-03	3.86E-03	Sediment
Simazine	2.62E-11	1.16E-03	2.87E-03	4.13E-03	Sediment
Spinosad	9.22E-17	1.21E-06	7.97E-04	1.15E-03	Sediment
Tebuconazole	5.26E-13	1.30E-04	1.91E-03	2.74E-03	Sediment
Teflubenzuron	8.77E-12	3.11E-06	1.55E-03	2.22E-03	Sediment
Thiobencarb	1.66E-09	1.12E-04	2.26E-03	3.25E-03	Sediment
Triadimenol	5.36E-13	3.80E-04	1.97E-03	2.84E-03	Sediment
Triazophos	5.40E-10	2.73E-04	1.86E-03	2.68E-03	Sediment
Trifloxystrobin	2.95E-11	3.18E-05	1.44E-03	2.07E-03	Sediment

(*) Metabolites; (**) these pesticides were also detected in semi-quantitative chromatographic assays surface water of the study area (Streams João Bento and Bom Jardim).

compartments, that is, without considering the volume of each of these compartments, it can be noted in Table 5 that the sediment is the predominant compartment, except acephate, methamidophos, methomyl and picloram that were predominat in water.

Environmental fate of pesticides found in the surface waters of the hydrographic sub-basin study

Considering the pesticides found in the waters of the sub-basin study by GC/MS-MS and LC/MS-MS, according to Soares et al. (2013), the soil was the environmental compartment that presented the greatest vulnerability and disposition in the distribution of pesticides according Table 6.

This Table 6 presents the percentage amount of pesticide in compartments. One notes that only heptachlor, mirex and terbufos presented predominance in the air. The results indicate that the contamination of the waters may be attributed to the carriage of contaminated soil during the rainy season and favored by mountainous relief, predominant in the area of study, as well as the illegal occupation by crops in the banks of watercourses that should be destined to permanent preservation, according to Brazilian Forest Code.

The results indicated predominance of pesticides in the air, their occurrence in surface waters which may be due to rainfall. These results agree with those presented by estimating the risk of contamination of surface and ground water, using Goss and GUS criteria, respectively and presented by Soares et al. (2012).

Regarding the concentration of pesticides in compartments, the predominance of these substances occurred in the sediment (Table 7). However, after pluvial precipitation, suspended solids with pesticides absorbed, as well as the revolving of sediments of watercourses provide the highest concentration of pesticides in these periods in the water.

Thus, terbufos was found in the waterways of Manhuaçu (Soares, 2013). European Union classification reports that terbufos is “very toxic to aquatic life with long

Table 6. Percentage quantity of pesticides in the compartments.

Pesticide	Quantity (%) in the compartments				
	Air	Water	Soil	Sediment	Predominance
Ametryn	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Atrazine	3.10E-02	2.24E+00	9.75E+01	2.76E-01	Soil
Bifenthrin	6.91E-06	9.67E-04	9.97E+01	2.82E-01	Soil
Cyfluthrin	9.03E-03	1.85E-03	9.97E+01	2.82E-01	Soil
Clorpirifos	1.22E+00	2.77E-02	9.85E+01	2.79E-01	Soil
DDT	1.18E-01	1.51E-03	9.96E+01	2.82E-01	Soil
Deltamethrin	6.40E-05	2.23E-05	9.97E+01	2.82E-01	Soil
Ethion	8.13E-02	2.29E-02	9.96E+01	2.82E-01	Soil
Epoxiconazole	9.25E-03	2.13E-01	9.95E+01	2.81E-01	Soil
Fenvalerate	1.68E-01	4.33E-02	9.95E+01	2.81E-01	Soil
Fenpropathrin	4.35E+01	2.59E-02	5.64E+01	1.59E-01	Soil
Flutriafol	1.04E-04	8.89E-01	9.88E+01	2.80E-01	Soil
Heptachlor	7.57E+01	2.32E-03	2.43E+01	6.87E-02	Air
L-cyhalotrin	2.35E-03	1.27E-03	9.97E+01	2.82E-01	Soil
Metolachlor	2.50E-01	1.13E+00	9.83E+01	2.78E-01	Soil
Metoxychlor	5.28E-03	2.86E-03	9.97E+01	2.82E-01	Soil
Mirex	9.68E+01	1.25E-03	3.15E+00	8.92E-03	Air
Permethrin	3.99E-02	2.29E-03	9.97E+01	2.82E-01	Soil
Pirimicarb	1.12E-02	3.67E+00	9.60E+01	2.72E-01	Soil
Pirimiphos ethyl	2.40E+01	5.75E-01	7.52E+01	2.13E-01	Soil
Pirimiphos methyl	1.17E-03	2.08E-01	9.95E+01	2.81E-01	Soil
Propargite	3.37E-01	5.70E-02	9.93E+01	2.81E-01	Soil
Temephos	4.20E-05	2.29E-03	9.97E+01	2.82E-01	Soil
Terbufos	5.32E+01	2.13E-01	4.65E+01	1.31E-01	Air

Table 7. Concentration of pesticides in compartments.

Pesticides	Concentration ($\mu g.m^{-3}$) in compartments				
	Air	Water	Soil	Sediment	Predominance
Ametryn	7.08E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Atrazine	8.48E-11	1.40E-03	2.67E-03	3.84E-03	Sediment
Bifenthrin	9.65E-15	3.09E-07	1.39E-03	2.00E-03	Sediment
Cyfluthrin	1.23E-11	5.74E-07	1.36E-03	1.95E-03	Sediment
Clorpyrifos	2.06E-09	1.07E-05	1.66E-03	2.38E-03	Sediment
DDT	1.96E-10	5.77E-07	1.66E-03	2.39E-03	Sediment
Deltamethrin	7.48E-14	5.98E-09	1.17E-03	1.68E-03	Sediment
Ethion	1.25E-10	8.03E-06	1.53E-03	2.20E-03	Sediment
Epoxiconazole	1.66E-11	8.72E-05	1.78E-03	2.56E-03	Sediment
Fenvalerate	2.36E-10	1.39E-05	1.40E-03	2.01E-03	Sediment
Fenpropathrin	7.35E-08	1.00E-05	9.52E-04	1.37E-03	Sediment
Flutriafol	2.04E-13	3.99E-04	1.94E-03	2.78E-03	Sediment
Heptachlor	1.20E-07	8.40E-07	3.84E-04	5.52E-04	Sediment
L-cyhalothrin	3.08E-12	3.82E-07	1.31E-03	1.88E-03	Sediment
Metolachlor	5.20E-10	5.37E-04	2.05E-03	2.94E-03	Sediment
Metoxychlor	9.02E-12	1.12E-06	1.70E-03	2.45E-03	Sediment
Mirex	1.05E-07	3.09E-07	3.42E-05	4.91E-05	Sediment
Permethrin	6.02E-11	7.90E-07	1.50E-03	2.16E-03	Sediment

Table 7. Contd.

Pirimicarb	2.77E-11	2.08E-03	2.38E-03	3.42E-03	Sediment
Pirimiphos ethyl	4.64E-08	2.55E-04	1.45E-03	2.09E-03	Sediment
Pirimiphos methyl	2.25E-12	9.18E-05	1.92E-03	2.77E-03	Sediment
Propargite	5.67E-10	2.20E-05	1.67E-03	2.41E-03	Sediment
Temephos	5.32E-14	6.63E-07	1.26E-03	1.81E-03	Sediment
Terbufos	1.09E-07	9.99E-05	9.52E-04	1.37E-03	Sediment

lasting effects".

Conclusions

In terms of concentration of the pesticides in the environment and without considering the volume of the compartments, the modeling studies (Fugacity Level I) indicated the predominance of the pesticides in the sediment. Already in terms of percentage and considering the volume of the compartments, the predominance of the pesticides was in the soil. Thus, for most of the pesticides evaluated, the sediment and soil compartment was the most vulnerable.

The model using concepts of fugacity, applied in this work, showed good tool for use in the process of decision to select pesticides that have less environmental impact, as well as prioritization process of the compounds to be monitored. It is emphasized, however, the importance of applying other levels of modeling (fugacity), considering environmental conditions, where there are: advection, degradation, emission and transfer of substance between compartments.

This modeling was proper when compared with results of chromatographic assays of surface water collected in hydrographic sub-basin of study.

Conflict of interests

The author has not declared any conflict of interests.

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