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A MATHEMATICAL MODEL TO ESTIMATE THE VOLUME OF GREY WATER OF PESTICIDE MIXTURES

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Abstract: We propose a model to estimate the grey water footprint of crops by calculating the volume of water necessary to dilute pesticide mixtures reaching freshwaters. The model requires short-term toxicity data from aquatic organisms based on EC50 values, soil pesticide half-life and soil sorption coefficient values, and does not require maximum concentration limit acceptable in water. The lixiviation rate and runoff rate of each pesticide was estimated by attenuation factor and by Soilfug model, respectively. The usefulness of the proposed model was illustrated by estimating the volume of grey water required to dilute the 17 most widely used herbicides in sugarcane crops of Brazil. The grey water footprint corresponding to the recommended agronomic dose for each herbicide varied between 4.20×10^{6} m^3 yr^{-1} and 1.20×10^{12} m^3 yr^{-1} and the grey water footprint of the mixture of herbicides was 2.36×10^{12} m^3 yr^{-1} in a cultivated area of 8.4×10^{6} ha. These results establish the ranking position of each herbicide in the composition of the grey water footprint of mixture of herbicides. The rank of each herbicide could be used to create a label to be placed on the package of the pesticide, thus informing farmers about the volume of grey water per hectare due to the use of this herbicide.

Keywords: water footprint, herbicide, sugarcane, toxicity.

1. Introduction

The water footprint is an indicator of freshwater use that considers the indirect as well as the direct water use of a consumer or producer (HOEKSTRA; CHAPAGAIN, 2008). The water volume from the water footprint is divided into green, blue and grey water footprint and is calculated according to procedures described by Hoekstra et al. (2011). Green water is any amount of water evapotranspirated by the agricultural crop (rainwater stored in the soil). Blue water is defined as any amount of water volume added to the crop production by irrigation. Grey water is defined as the volume of water required to assimilate the load of pollutants (pesticides and fertilizers) based on water quality standards (HOEKSTRA et al., 2011). Thus, the grey water footprint is the amount of water needed to get pollutants concentration down to an acceptable level. It is argued that environmental impacts of grey water are more suitably addressed in other impact categories such as eutrophication or toxicity. Several studies have calculated the water footprint of a wide variety of agricultural products such as rice (CHAPAGAIN; HOEKSTRA, 2011), wheat (MEKONNEN; HOEKSTRA, 2010), meat and derivates (RIDOUTT et al., 2012), olives and olive oil (SALMORAL et al., 2011) and fresh tomatoes (PAGE et al., 2011). The aim of this paper is to propose a model to estimate the volume of grey water for an agricultural product based on the toxicity of each pesticide used in a particular crop system.

2. Material and methods

The model uses the method by Finizio et al. (2005) in analyzing the impact of mixtures of contaminants on water quality and assumes the concept of concentration addition (CA) as a hypothesis of the toxicity of the mixture in aquatic organisms.

2.1. Model development

The volume of grey water by crop yield produced, VGW_Y (m^3 ton^{-1}), is given by:

$$VGW_Y = \frac{VGW_{PM}}{Y} \tag{1}$$

where VGW_{PM} (m^3 yr^{-1}) is the volume of grey water of the pesticide mixture of pesticides used in the crop production and Y (ton yr^{-1}) is the total annual crop production (MEKONNEN; HOEKSTRA, 2010). The volume of grey water of the pesticide mixture, VGW_{PM}, was calculated through the application of the Concentration Addition model given by:

$$\sum_{i=1}^{n} \frac{PEC_i}{PNEC_i} = 1 \tag{2}$$

where n is the number of pesticides used in the crop system, PEC (kg m^{-3}) is the Predicted Environmental Concentration in water of the pesticide and $PNEC$ (kg m^{-3}) is the Predicted No Effect Concentration of pesticide in water (FINIZIO et al., 2003). The $PNEC$ values were determined based on the observation of the pesticide acute toxicity effect, $EC50$ (mg L^{-1}) values on the organism population, indicator of water quality, and representative of reference trophic levels of the aquatic ecosystem (algae, daphnids and fish). A security factor nominated assessment factor, A_{SF} is applied to the lowest $EC50$ value derived from the more susceptible organism. The predicted environmental concentration of pesticide in freshwater, PEC (kg m^{-3}), was estimated by equation:

$$PEC = \frac{M}{VGW_{PM}} \tag{3}$$

where M (kg) is the pesticide mass. Assuming that each pesticide has a linear sorption and a first order kinetic degradation in soil, the pesticide mass in freshwater is given by:

$$M = \alpha A_C A_D + (1-\alpha) A_C A_D A_F \tag{4}$$

where A_C (ha) is the cultivated area by year, A_D (kg ha^{-1}) is the pesticide dose, $0 \le A_F \le 1$ (dimensionless) is the pesticide attenuation factor from soil surface to groundwater, and $0 \le \alpha \le 1$ (kg yr kg^{-1} yr^{-1}) is the pesticide dose fraction that reaches the freshwater due to runoff. Replacing Eq. (3) and (4) in Eq. (2) the volume of grey water of the pesticide mixture, VGW_{PM} (m^3), can be expressed as:

$$VGW_{PM} = \sum_{i=1}^{n} \left(\frac{\alpha^i A_C^i A_D^i + (1-\alpha^i) A_C^i A_D^i A_F^i}{PNEC_i} \right) \tag{5}$$

where $PNEC_i = \frac{10^{-3}}{A_{SF}} \min\left\{ EC50^i_{\{a\lg ae, daphnids, fish\}} \right\}$ (FINIZIO et al., 2003). From Eq. (5), the volume of grey water of each pesticide in the mixture, VGW_i (m^3), is given by:

$$VGW_i = \frac{\alpha^i A_C^i A_D^i + (1-\alpha^i) A_C^i A_D^i A_F^i}{PNEC_i} \tag{6}$$

In addition, we propose a new way to express the relative position of each individual pesticide in the mixture, referred to as pesticide rank. Considering only one hectare, the volume of grey water of each pesticide, VGW_i^{ha}, was estimate dividing the VGW_i by A_C^i, that is, $VGW_i^{ha} = VGW_i / A_C^i$. The pesticide rank, r_i, is calculated as the logarithm of VGW_i^{ha} given by:

$$r_i = \log\left(VGW_i^{ha}\right) \tag{7}$$

2.1.2. Numerical simulation: input data

The model given by Eq. (5) was used to estimate the water volume of herbicide used in Brazilian sugarcane crops in sugar and ethanol production. Some of the main herbicides registered in Brazil for sugarcane cropping are listed in Table 1, as well as the information on their recommended dose (kg ha^{-1}), area of application (ha), toxicity (mg L^{-1}) on algae, daphnids and fish data (EC50 values) were gathered from US-EPA Pesticide Ecotoxicity Database (www.ipmcenters.org/Ecotox/DataAccess.cfm), soil organic carbon partition coefficient (L kg^{-1}), and half-life (day) in soil (HORNSBY et al., 1996). The assessment factor, in the calculations of PNEC in this work we assume the value of 100. The Soilfug model, using daily rainfall data for the period of 2009/2011 of the Ribeirão dos Marins Watershed was used to determine the average values of the runoff rate a (kg yr kg^{-1} yr^{-1}), for each herbicide in Table 1. The Ribeirão dos Marins Watershed is located in a traditional region for sugarcane cropping to produce sugar and ethanol (MACHADO et al., 2003). To find an estimate of area for each herbicide we adopted the same percentage of area per herbicide found by Armas et al. (2005) and we extrapolated the data for all Brazilian area (Table 1).

3. Results and discussion

The Table 2 shows average values of the runoff rate $0 \le \alpha^i \le 1$ estimated by the Soilfug model, for each herbicide indicated in Table 1. It also shows the values of grey water of each one of the herbicides. The rank r_i of the herbicides in the mixture is given in Table 2. The herbicides in the hypothetical mixture were ranked according to the method summarized in Eq. (7), based in the relative contribution of each herbicide to the sugarcane grey water volume, related to their potential hazards to aquatic life. The total volume of grey water of herbicide mixtures, was estimated in VGW_{PM} = 2.36×10^{12} m^3 yr^{-1} (Eq. 5). The sugarcane Brazilian production, harvest 2011/2012, reached 5.96×10^8 tons on a cultivated area of 8.4×10^6 ha. From these production values and cultivated area, and from the grey water volume of herbicides of 2.36×10^{12} m^3 yr^{-1} it is possible to estimate the volume of grey water per volume of produced sugarcane in 3,966 m^3 ton^{-1}, (Eq. 1), in the Brazilian harvest of 2011/2012.

Table 1. Data on application (recommended dose and sprayed area), toxicity to aquatic organisms (algae, daphnids and fishes) and pesticide fate coefficients in soil (degradation and sorption) for the studied herbicides in a hypothetical Brazilian sugarcane production system.

Herbicides	Pesticide's dose (kg ha^{-1}) (A_D)	Crop area (ha) (A_C)	Toxicity* (*EC50*)[1]			Pesticide fate coefficients[2]	
			Algae	Daphnids (mg L^{-1})	Fish	Half-life (day) $(t_{1/2})$	Sorption (L kg^{-1}) (k_{oc})
Ametryn	2.23	1.88×10^6	0.0037	28.0	1.0	60	300
Amicarbazone	1.00	3.36×10^4	0.084	0.252	13.0	54	37
Carfentrazone	0.04	3.36×10^4	0.0127	9.8	0.0164	3	750
Clomazone	1.00	1.52×10^6	3.5	5.2	19.0	24	300
Diuron	1.83	1.00×10^6	0.0024	0.113	0.0618	90	480
Glyphosate	1.62	9.22×10^5	2.2	3.0	1.3	47	24000
Hexazinone	0.29	8.51×10^5	0.0068	33.1	100.0	90	54
Imazapic	0.22	6.69×10^5	0.0523	100.0	98.7	90	1
Imazapyr	0.33	5.02×10^5	12.2	100.0	100.0	90	100
Isoxaflutole	0.16	3.03×10^5	0.14	1.5	1.7	100	400
Metribuzin	1.58	2.78×10^5	0.0081	4.18	42.0	40	60
Oxyfluorfen	2.00	1.32×10^4	0.0003	0.08	0.17	35	5000
Pendimethalin	1.38	2.53×10^5	0.0054	0.28	138.0	90	5000
Sulfentrazone	0.70	7.08×10^4	0.031	60.4	93.8	540	887
Tebuthiuron	1.00	6.06×10^4	0.05	297.0	106.0	360	80
Trifloxysulfuron	0.04	5.31×10^4	0.0065	108.0	103.0	78	1
Trifluralina	0.80	3.32×10^4	0.339	0.56	0.0007	60	8000

Table 2. Pesticide-specific estimates compounding grey water for the herbicide mixture in a hypothetical sugarcane production system over 8.4×10^6 ha in 2011/2012.

Herbicides	α^i (kg yr kg^{-1} yr^{-1})	VGW_i (m^3)	VGW_i^{ha} (m^3 ha^{-1})	r_i
Ametryn	0.0110	1.29×10^{12}	6.87×10^5	5.8
Amicarbazone	0.0470	1.88×10^9	5.59×10^4	4.7
Carfentrazone	0.0001	4.20×10^6	1.25×10^2	2.1
Clomazone	0.0070	2.91×10^8	1.91×10^2	2.3
Diuron	0.0080	6.07×10^{11}	6.05×10^5	5.8
Glyphosate	0.0001	1.56×10^7	1.69×10	1.2
Hexazinone	0.0450	1.64×10^{11}	1.93×10^5	5.3
Imazapic	0.1130	9.58×10^{10}	1.43×10^5	5.2
Imazapyr	0.0300	4.07×10^7	8.11×10	1.9
Isoxaflutole	0.0100	3.29×10^8	1.09×10^3	3.0
Metribuzin	0.0310	1.69×10^{11}	6.09×10^5	5.8

Table 2. Continuation...

Herbicides	α^i (kg yr kg^{-1} yr^{-1})	VGW_i (m^3)	VGW_i^{ha} (m^3 ha^{-1})	r_i
Oxyfluorfen	0.0010	5.12×10^9	3.86×10^5	5.6
Pendimethalin	0.0010	5.29×10^9	2.09×10^4	4.3
Sulfentrazone	0.0060	9.33×10^8	1.32×10^4	4.1
Tebuthiuron	0.0440	1.21×10^{10}	2.00×10^5	5.3
Trifloxysulfuron	0.1100	9.47×10^9	1.78×10^5	5.3
Trifluralina	0.0001	1.71×10^9	5.15×10^4	4.7

We using “The Water Footprint Assessment Manual” method (HOEKSTRA et al., 2011), the grey water of ametryn was estimated as 8.03×10^{10} m^3 yr^{-1}, whereas the grey water of ametryn estimated by Eq. (6) (Table 2), was 1.29×10^{12} m^3 yr^{-1}, showing that the method of Hoekstra et al. (2011) is more conservative than the method proposed by Eq. (6).

4. Conclusion

The model allows the estimate of grey water footprint of pesticide mixtures considering the pesticide mixture toxicity effect in aquatic organisms. This water footprint component can be used as an indicator in formulation of governmental directives for the establishment of crop production sustainable systems that take into consideration appropriate patterns of water quality. The rank of each herbicide could be used to create a label to be placed on the package of the pesticide, thus informing farmers about the volume of grey water per hectare due to the use of this herbicide.

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