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A mathematical model to estimate the volume of grey water of pesticide mixtures

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Abstract

The usual method to calculate grey water footprint does not take into account the volume of water required to dilute concentrations of pesticide mixtures in freshwater and it also depends on maximum concentration limit acceptable in water. 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 $4.20 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ and $1.20 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ and the grey water footprint of the mixture of herbicides was $2.36 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ in a cultivated area of $8.4 \times 10^6 \text{ ha}$. 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.

Additional key words: water footprint; pesticide management; sugarcane; herbicide; water quality objective (WQO).

Introduction

The contamination of natural freshwater sources is resulting in a high environmental liability that endangers terrestrial ecosystems and weakens their life-sustaining capability. There is a strong and inevitable commitment between water protection and the actions for accomplishment of human's needs, such as obtaining foods, feeds, fibers, bio-fuels and biomass. Furthermore, global production of biological energy resources is expanding and accelerates growth of agricultural production. As a consequence of these pressures, water scarcity represents one of the major environmental concerns worldwide (Pfister *et al.*, 2011). In any

sustainable agricultural system, for the maintenance of life in all its dimensions, it is necessary to maintain the freshwater quality and evaluate it using indicators of contamination risks originated from farming practices and techniques.

The water footprint (WF) 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 concept of water footprint was first introduced and refined by Hoekstra & Hung (2002), based on the virtual water concept of Allan (1993; 1994), who proposed a numerical indicator to express the water volume used in the entire production chain of a certain agricultural product.

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Abbreviations used: A_C (cultivated area); A_D (pesticide dose); A_F (attenuation factor); A_{SF} (assessment factor); CA (concentration addition); EC50 (median effective concentration); IA (independent action); PEC (predicted environmental concentration); PNEC (predicted no effect concentration); r (pesticide rank); R_F (retardation factor); V_{GW} (volume of grey water of the pesticide); $V_{GW_{PM}}$ (volume of grey water of the pesticide mixture); V_{GW_Y} (volume of grey water by cropping volume produced); WF (water footprint); WQO (water quality objective); Y (crop volume produced in one year); α (dose fraction that reaches the surface water due to runoff).

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 evapotranspired by the agricultural crop (rain-water 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. Moreover, in the absence of an agreed method for the quantification of dilution volumes for assimilation, the usual estimation of grey water footprint is subjective (Milà i Canals *et al.*, 2009; Jeswani & Azapagic, 2011).

The term “grey water footprint” was for the first time introduced by Hoekstra & Chapagain (2008) and defined as the pollutant load divided by the maximum acceptable concentration in the receiving water body. A bit later, it was recognized that the grey water footprint is better calculated as the pollutant load divided by the difference between the maximum acceptable and the natural background concentration (Hoekstra *et al.*, 2011; Liu *et al.*, 2012).

Several studies have calculated the water footprint of a wide variety of agricultural products such as cotton (Chapagain *et al.*, 2006), rice (Chapagain & Hoekstra, 2011), wheat (Mekonnen & Hoekstra, 2010), mango fruit (Ridoutt *et al.*, 2010), tea and coffee (Chapagain & Hoekstra, 2007), meat and derivatives (Ridoutt *et al.*, 2012), olives and olive oil (Salmoral *et al.*, 2011) and fresh tomatoes (Page *et al.*, 2011). Most of these studies have estimated the volume of grey water for fertilizers, especially nitrogen and phosphorus, ignoring the potential contamination by applied pesticides, resulting in an underestimation of the volume of grey water. This is probably due to the fact that governmental agencies, pesticide sellers, manufacturers, enterprise or industry and rural producers rarely publish reports about pesticide volumes applied to the crop fields, making difficult to estimate the fractions of pesticides actually reach the surface and groundwater bodies by runoff or leaching.

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(CSTE/EEC, 1994), a water quality objective (WQO), in order to protect water quality and aquatic life, is defined such as to permit all stages in the life of aquatic organisms to be successfully completed; WQO should not produce conditions that cause these organisms to avoid parts of the habitat where they would normally be present; should not give rise to the accumulation of substances that can be harmful to the biota (including man) whether via the food chain or otherwise; and should not produce conditions that alter the functioning of the ecosystem.

Generally, several pesticides are applied to a crop. As a consequence, a set of pesticides may be detected in a same water body, characterizing a water contamination by pesticide mixtures with different concentrations, occurring simultaneously in a particular water body (Finizio *et al.*, 2005; Verro *et al.*, 2009). According to United States Environmental Protection Agency (<http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=29260>), a mixture of toxicological relevance can be defined as any combination of two or more chemical substances, regardless of the source of spatial or of temporal proximity that can influence a target population. Several studies have demonstrated that pesticide mixtures can contaminate fresh water (surface or groundwater) bodies (Squillace *et al.*, 2002; Fava *et al.*, 2010; Battaglin *et al.*, 2011). Water contamination by a mixture of substances can be defined as the mixture occurrence at concentration levels that cause loss of water quality, which is established by governmental directives (CSTE/EEC, 1994).

The quantification of grey water of an agricultural product, based on produced grey water from a pesticide mixture and an approach based on WQO is the volume of freshwater required to dilute the concentration of the mixture in freshwater at a level which would lead to the protection of aquatic organisms against the toxic effects of each pesticide in the mixture. In this consists the difference in calculating the grey water between our proposed model and the model proposed by Hoekstra *et al.* (2011), which does not consider in their calculations the volume of water required to dilute concentrations of pesticide mixtures in freshwater.

The grey water volume can be determined through the pesticide physical-chemical characteristics, pesticide rates applied (dose), and the lowest EC50 value from the more susceptible aquatic organism. Median effective concentration (EC50) is the statistically derived concentration of a substance in an environmen-

tal medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions. Thus, grey water volume based on pesticide mixture approach does not depend upon threshold concentrations for contaminants established by governmental agencies, but upon effective concentrations for key aquatic organisms, ecotoxicological data most often available.

The aim of this paper is to propose a model to estimate the volume of grey water (grey water footprint) for an agricultural product based on the toxicity of each pesticide used in a particular crop system. The model assumes that the adopted pesticides are organic compounds with well defined functions and well known toxic effects on water quality indicator organisms, and that their degradation in soil follows a first order kinetics and linear sorption process. The model was developed assuming conventional growing systems that require the use of a set of pesticides applied at known doses (rate of applications), in that such applications have the potential to contaminate freshwater (surface or groundwater) by mixtures of the pesticides applied to the crop system.

Although it is evident that pesticides present in a mixture cannot share the same mode of action and that, probably, the Bliss model of independent action (IA) (Bliss, 1939) would be more appropriate, we used Concentration Addition model (CA) (Loewe, 1953) for several reasons: the calculated mixture potency using CA is higher than the IA concept, thus the additive model can be considered as a conservative worst case. Besides, one of the results reached by the EU BEAM project (BEAM: Bridging Effect Assessment of Mixtures to Ecosystem Situations and Regulations) demonstrated that the ratio between CA/IA generally does not exceed the value of 4 (Backhaus *et al.*, 2003). This means that the overestimation of CA could be acceptable in a frame of worst-case analysis (Finizio *et al.*, 2005).

The application of the Bliss model (IA) would require knowledge on the dose-response curve of each pesticide. In contrast, in literature it is generally possible to find only data on EC50. The implementation of the CA model, using as toxicological endpoints Predicted Environmental Concentration (PEC) and Predicted No Effect Concentration (PNEC), for non-target representative organisms of aquatic ecosystems (algae, daphnids and fish), made it possible to estimate the volume of grey water of pesticides mixtures. In this regard, Liess *et al.* (2008) concluded that, relating

pesticide exposure to species traits in communities enables the identification and prediction of ecotoxicological effects of pesticides on the ecosystem level.

In order to demonstrate the utility of our model, using ecotoxicology of pesticide mixtures and WQO approaches for grey water footprint estimation, we present a study for a sugarcane cropping system in Brazil destined to sugar and ethanol production, using a set of herbicides. Brazil is the world largest sugarcane producer and the largest exporter of sugar and ethanol extracted from sugarcane. According to Carneiro *et al.* (2012), Brazil has also been ranked as the largest world consumer of pesticides since 2008 and pesticide sales reached more than US\$ 8.488 billion in 2011. The Brazilian edaphic and climatic conditions in regions of sugarcane production associated with the agronomic crop management procedures, adopted by agricultural conventional systems, have imposed the use of several types of herbicide to an efficient production and weed control. It is known that the competitive growth between weeds and sugarcane might significantly reduce sugarcane productivity, causing more than 30% increase in production costs (Lorenzi, 2000).

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. The concentration addition (CA) assumes that the toxicity of the mixture is the sum of the toxicity of each component of the mixture (Loewe, 1953). This assumption is always valid if each component in the mixture presents the same mode of action (route of toxicological action) in the organism (Backhaus *et al.*, 2003; Finizio *et al.*, 2005). So this gives us a maximum allowable concentration which is the corner stone in the calculation of grey water. The concentration reaching the freshwater (surface and groundwater) has to be diluted down to this level and the amount of water needed is the total grey water amount.

Model development

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

$$VGW_Y = \frac{VGW_{PM}}{Y} \quad [1]$$

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

$$\sum_{i=1}^n \frac{PEC_i}{PNEC_i} = 1 \quad [2]$$

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 $PMEC$ 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). The $PNEC$ is derived by selecting the most sensitive biotest (representing the most sensitive trophic level) which accounts for intra- and inter-laboratory variation of the data, biological variance, short-term to long-term extrapolation and laboratory to field extrapolation (Backhaus & Faust, 2012). A security factor nominated assessment factor, A_{SF} is applied to the lowest $EC50$ value derived from the more susceptible organism. The assessment factor (security or uncertainty) is an adjustment number ranging from 1 to 1,000, normally used to extrapolate undesirable toxic effects from acute toxic effects experimentally determined on indicator species. The values of the assessment factors (A_{SF}) depend on the extent and nature of the toxicity data.

Thus, the predicted environmental concentration of pesticide in freshwater, PEC ($kg m^{-3}$), was estimated by equation

$$PEC = \frac{M}{VGW_{PM}} \quad [3]$$

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 (groundwater + surface water) is given by

$$M = \alpha A_C A_D + (1 - \alpha) A_C A_D A_F \quad [4]$$

where A_C (ha) is the cultivated area by year, A_D ($kg ha^{-1}$) is the pesticide dose, $0 \leq A_F \leq 1$ (dimensionless) is the pesticide attenuation factor from soil surface to groundwater, and $0 \leq \alpha \leq 1$ ($kg yr kg^{-1} yr^{-1}$) is the pesticide dose fraction that reaches the freshwater due to runoff. In Eq. [4], the expression $\alpha A_C A_D$ (kg) estimates the pesticide mass load in the surface water due to runoff and the expression $(1 - \alpha) A_C A_D A_F$ (kg) estimates the pesticide mass load in the groundwater due to leaching.

In Eq. [4], the pesticide attenuation factor (A_F) is a measure related to pesticide mass emission to groundwater which was first developed as a screening index to order pesticides according to its pollutant potential. The A_F expression is obtained from the analytic solution of a simplified convection-dispersion equation of pesticide in soil solution. Under field capacity, this solution assumes the pesticide first-order degradation rate, omitting soil water flow, hydrodynamic dispersion and molecular diffusion (Jury *et al.*, 1992).

The pesticide attenuation factor is calculated by

$$A_F = \exp\left(\frac{-k z R_F \theta_{fc}}{J_w}\right) \quad [5]$$

where k (day^{-1}) is the soil pesticide degradation rate estimated by $k = \ln(2)/t_{1/2}$, being $t_{1/2}$ (day) the pesticide half-life in soil; z (m) is the soil depth; R_F (dimensionless) is the pesticide retardation factor; θ_{fc} ($L L^{-1}$) is the soil volumetric water content at field capacity, and J_w ($m day^{-1}$) is the water daily net recharge of the soil area.

The retardation factor is a number that represents the delay of the pesticide leaching with regard to the water flow in soil. This leaching delay is due to both pesticide sorption and pesticide aqueous diffusion in soil. The effect of the retardation factor on pesticide leaching can be noticed graphically in the breakthrough curve when solving the convection-dispersion equation of pesticide in soil solution. The graph of breakthrough curve represents the relationship between the relative concentration and time evolution concentration (Jury *et al.*, 1992). The retardation term refers to a relative travel time of pesticide displacement related to the time of water displacement in soil (Paraíba & Spadotto, 2002). In Eq. [5], the retardation factor is given by

$$R_F = 1 + \frac{\rho_s f_{oc} k_{oc}}{\theta_{fc}} \quad [6]$$

where ρ_s (kg L^{-1}) is the total soil density, k_{oc} (L kg^{-1}) is the pesticide soil organic carbon partition coefficient (pesticide soil sorption) and f_{oc} (L L^{-1}) is the soil volumetric organic carbon content (Rao *et al.*, 1985; Paraíba & Spadotto, 2002).

In Eq. [4], the factor α stands for the pesticide runoff fraction, defined as the fraction of applied pesticide reaching surface water by runoff. The SoilFug model was utilized to estimate the dimensionless factor α . The Soilfug model was specifically developed for the prediction of pesticide in surface water (Di Guardo *et al.*, 1994). It is a very simple model requiring a few input data both for physical-chemical properties and for environmental scenarios. Soilfug was successfully validated in comparison with experimental monitoring at different spatial scales, from experimental fields up to small river basins (Barra *et al.*, 1995; Calamari & Zhang, 2002; Peruzzo *et al.*, 2008).

Replacing Eq. [3] and [4] in Eq. [2] we obtain the following equalities

$$\sum_{i=1}^n \left(\frac{\alpha^i A_C^i A_D^i + (1 - \alpha^i) A_C^i A_D^i A_F^i}{\frac{VGW_{PM}}{PNEC_i}} \right) = 1 \Rightarrow \quad [7]$$

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

Consequently, the volume of grey water of the pesticide mixture, VGW_{PM} (m^3), can be expressed as

$$VGW_{PM} = \sum_{i=1}^n \left(\frac{\alpha^i A_C^i A_D^i + (1 - \alpha^i) A_C^i A_D^i A_F^i}{PNEC_i} \right) \quad [8]$$

where $PNEC_i = \frac{10^{-3}}{A_{SF}} \min \left\{ EC50_{\{algae, daphnids, fish\}}^i \right\}$ (Finizio *et al.*, 2003).

From Eq. [8], the volume of grey water of each pesticide in the mixture, (m^3), is given by

$$VGW_i = \frac{\alpha^i A_C^i A_D^i + (1 - \alpha^i) A_C^i A_D^i A_F^i}{PNEC_i} \quad [9]$$

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} ($\text{m}^3 \text{ ha}^{-1}$), was estimate dividing the VGW_i (m^3 , Eq. [9]) by A_C (ha), that is, $VGW_i^{ha} = VGW_i / A_C$.

The pesticide rank, r_i , is calculated as the logarithm of VGW_i^{ha} given by

$$r_i = \log(VGW_i^{ha}) \quad [10]$$

Observing Eq [8], it is important to highlight that the volume of grey water of the pesticide mixture, VGW_{PM} , depends directly on the dosage of pesticide applied as also of the attenuation and retardation factors and it depends indirectly on the predicted no effect concentration of pesticide (PNEC). So, the volume of grey water of pesticide mixture does not depend on the maximum allowable concentration of contaminants in water, which forms the basis of calculating of the Hoekstra's grey water footprint model. Moreover, the inverse relationship between the volume of grey water and the PNEC value also reflects the concern for protecting water quality for the preservation of aquatic life, as suggested by WQO.

Numerical simulation: input data

The model given by Eq. [8] was used to estimate the water volume of herbicide used in Brazilian sugarcane crops in sugar and ethanol production. Generally, in Brazil, sugarcane cropping uses two types of herbicides: dry weather (fall/winter) herbicides, with physical-chemical characteristics appropriate to withstand edaphic and climatic conditions with low soil humidity, and herbicides classified as wet weather (spring/summer), with physical-chemical characteristics appropriate to withstand edaphic and climatic conditions with medium or high soil humidity.

In weed infested areas, to be prepared for sugarcane cropping the application of (pre-emergence) herbicides is recommended, adequate to dry weather and low moisture soil, such as glyphosate + imazapyr, glyphosate + imazapic, glyphosate + isoxaflutole or glyphosate + carfentrazone. During wet weather and high moisture soil periods, in weed infested areas with sugarcane plants in grand growth stage, the use of tebutiuron, clomazone, sulfentrazone, hexazinone + diuron, trifloxysulfuron + ametryne, clomazone + ametryne, metribuzin, ametryne, trifluraline, pendimethalin and their combinations is suggested (Christoffoleti *et al.*, 2005). Furthermore, the trifluraline herbicide can be applied in moist soils of weed infested forage areas destined to sugarcane crop expansion. Therefore, due to the high number of possible herbicide combinations for sugarcane cropping, we decided, in this

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 (A_D) (kg ha ⁻¹)	Crop area (A_C) (a)	Toxicity*(EC_{50}) ¹			Pesticide fate coefficients ²	
			Algae (mg L ⁻¹)	Daphnids (mg L ⁻¹)	Fish (mg L ⁻¹)	Half-life ($t_{1/2}$) (day)	Sorption (k_{oc}) (L kg ⁻¹)
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	24,000
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	5,000
Pendimethalin	1.38	2.53×10^5	0.0054	0.28	138.0	90	5,000
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	8,000

Sources: ¹ <http://www.ipmcenters.org/ECotox/index.cfm>; ² Hornsby *et al.* (1996).

study, to estimate the sugarcane grey water by calculating the volume of grey water of herbicide mixture from the main herbicides recommended in sugarcane crops in Brazil.

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 (EC_{50} 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 (data were gathered from Hornsby *et al.*, 1996). For the calculus of the retardation and attenuation factors (Eqs. [5] and [6]) we assumed the following: a homogeneous soil with 2.0 m depth; total density of 1.5 kg L⁻¹; soil organic carbon volumetric fraction, f_{oc} of 0.003; water volumetric fraction at field capacity, θ_{fc} , of 0.25; and a net recharge rate, J_W , of 9.18×10^{-4} m day⁻¹ for soils cultivated with sugarcane (Wendland *et al.*, 2007). The assessment factor, in the calculations of PNEC, is arbitrarily chosen between 10 and 1000; in this work we assume the value of 100 (EEC, 2003).

The Soilfug model, using daily rainfall data for the period of 2009/2011 of the Ribeirão dos Marins Wa-

tershed, São Paulo State, registered by the Agrometeorology Integrated Information Center of the Agronomic Institute of Campinas, was used to determine the average values of the runoff rate (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).

There is no official data of pesticides use in Brazil per year and crop type, nor is there information about total area of application or total volume used. Only as an example to permit using the proposed method in Brazilian sugarcane crop we assumed that the total area cultivated in 2011/2012 received some herbicide. 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).

Results and discussion

Table 2 shows average values of the runoff rate $0 \leq \alpha' \leq 1$ estimated by the Soilfug model, for each herbicide indicated in Table 1. It also shows the values of

Table 2. Pesticide-specific estimates compounding grey water for the herbicide mixture in a hypothetical sugarcane production system over 8.4×10^6 ha: runoff rate α^i ; volume of grey water (VGW_i); volume of grey water per hectare (VGW_i^{ha}); and rank (r_i), as $\log(VGW_i^{ha})$

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
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
Trifluralin	0.0001	1.71×10^9	5.15×10^4	4.7

grey water of each one of the herbicides (VGW_i , Eq. [9]). The rank r_i of the herbicides in the mixture, Eq. [10], is given in Table 2. The herbicides in the hypothetical mixture were ranked according to the method summarized in Eq. [10], 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 $VGW_{PM} = 2.36 \times 10^{12}$ m³ yr⁻¹ (Eq. [8]).

The knowledge of the pesticide ranks in the relative composition of the volume of grey water per hectare of all pesticides used in an agricultural crop, allows choosing among all possible pesticide combinations in order to minimize the volume of grey water. It is worth noting that the lower the rank of applied pesticide, the lower the total volume of grey water of the mixture of pesticides. Thus, the model presented in this study can be used as a useful resource management tool to minimize the risk of freshwater contamination by pesticides used on agricultural crops. The resulting ranks (r) show hazard levels of herbicides in the mixtures, varying from glyphosate ($r = 1.2$) to ametryn, diuron or metribuzin ($r = 5.8$). These results suggest the possibility to apply different combinations of herbicides for weed control, reducing the total volume of grey water of mixture. As an example, if the chosen herbicides were glyphosate ($r = 1.2$) and ima-

zapyr ($r = 1.9$) for the dry season application, and carfentrazone ($r = 2.1$), for the wet season, the volume of grey water of herbicide mixture would be 2.23×10^2 m³ ha⁻¹. On the other hand, if the decision was to use glyphosate ($r = 1.2$) and hexazinone ($r = 5.3$), in dry season, and ametryn ($r = 5.8$), in wet season, the volume of grey water would be 8.08×10^5 m³ ha⁻¹, three thousand fold superior to the one generated in the previous option (Table 2). 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.

According to CONAB (2012), 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} m³ yr⁻¹ (Eq. [8]) it is possible to estimate the volume of grey water per volume of produced sugarcane in 3,966 m³ ton⁻¹ (cubic meters of grey water per ton of sugarcane) in the Brazilian harvest of 2011/2012.

Gerbens-Leenes & Hoekstra (2009) estimated the sugarcane water footprint volume of 209 m³ of water per ton of sugarcane, but they did not calculate the pesticide grey water volume used in sugarcane cropping. According to these authors, a water footprint volume may increase several orders of magnitude when the cal-

cultivation takes into consideration the grey water volume and severe water quality patterns because when grey water is based on nitrate, phosphorus, heavy metals or pesticide, each one gives a different amount of grey water. The grey water related to the use of atrazine in corn cultivation for ethanol production, in the United States, was estimated at $4.84 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$ (Aldaya & Hoekstra, 2009).

The procedures described in Hoekstra *et al.* (2011) estimate the volume of grey water by equation $VGW = (\alpha \times A_C \times A_D) / C_{\max}$, where $0 \leq \alpha \leq 1$ ($\text{kg yr kg}^{-1} \text{ yr}^{-1}$) is the pesticide dose fraction that reaches the freshwater due to runoff and leaching, VGW ($\text{m}^3 \text{ yr}^{-1}$) is the pesticide grey water, A_C (ha) is the crop area, A_D (kg ha^{-1}) is the applied dose, and C_{\max} (mg L^{-1}) is the maximum pesticide concentration acceptable in water (maximum acceptable concentration), respectively. According to US-EPA (http://www.epa.gov/oppsrrd1/REDs/ametryn_red.pdf), in Reregistration Eligibility Decision for Ametryn, the acceptable concentration limit of ametryne in groundwater is set to 0.0014 mg L^{-1} . Taking $\alpha = 0.05$ ($\approx 5\%$ of runoff and leaching) and using “The Water Footprint Assessment Manual” method (Hoekstra *et al.*, 2011), the grey water of ametryne was estimated as $8.03 \times 10^{10} \text{ m}^3 \text{ yr}^{-1}$, whereas the grey water of ametryn estimated by Eq. [9] (Table 2), was $1.29 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$, showing that the method of Hoekstra *et al.* (2011) is more conservative than the method proposed by Eq. [9], because the grey water depends on concentrations of indicator organisms with effects on water quality objective (WQO) and does not depend on values of maximum acceptable concentrations in water defined by water quality standards (Hamilton *et al.*, 2004).

As stated by Centofanti *et al.* (2008), although the use of numerical models has become increasingly common as tools to assess the magnitude of pesticide exposure in water resources simulating the environmental fate of pesticides, such models are usually only applied to local situations or to a limited number of representative scenarios; as in this paper, where we treat the production of sugarcane in Brazil as if it were done evenly. Therefore, in the future, this model could be applied by regions, allowing comparisons among different agricultural systems or profiles of pesticide use. In the same line, Sausse (2011) states that water footprint values can change a lot from one site to another due to the variability of production conditions and, due to this, it would be questionable to work at country level. We agree that this is especially true for Brazil,

which has a huge diversity of agro-ecological conditions.

As conclusions, the mathematical model presented in this paper is not based on experimental measures of pesticide contamination of surface or groundwater bodies, but on pesticide physico-chemical and ecotoxicological characteristics and water quality objective. The experimental assessment to information about pesticide leaching rates, doses applied, residues in water bodies, persistence in soil, toxicity effects in aquatic organisms, aquifer recharge rates and soil hydrological characteristics, will improve and refine the calculus of grey water volume of pesticides used in agriculture crops.

Using a set of herbicides we estimated the grey water volume corresponding to each herbicide considered in this study and the results varied between $4.02 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ and $1.29 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ and the total grey water volume for a mixture of 17 most used herbicides in Brazilian sugarcane was $2.36 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$. The pesticide rank expresses the relative position of the pesticide to the total volume of grey water of the pesticide mixture and can be used to select pesticides to minimize the volume of grey water in agricultural crops, because the lower the rank of pesticides in the mixture the less volume of grey water of pesticide mixtures. The grey water volume can be determined through the pesticide physico-chemical characteristics, pesticide rates applied (dose), and the lowest EC50 value from the more susceptible aquatic organism.

The model allows the estimate of grey water footprint of pesticide mixtures, a key component of the crop water footprint, considering the pesticide mixture toxicity effect in aquatic organisms and water quality. This water footprint component can be used as an indicator in agricultural sustainability or in formulation of governmental directives for the establishment of crop production sustainable systems that take into consideration appropriate patterns of water quality. We hope that this new method will contribute positively to the development of the water footprint and consequently to more sustainable use of freshwater resources.

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