Journal of Cleaner Production 234 (2019) 925–932

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Review

Assessment of the gray water footprint of the pesticide mixture in a soil cultivated with sugarcane in the northern area of the State of Pernambuco, Brazil

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ARTICLE INFO

Article history:
Received 5 August 2018
Received in revised form
22 June 2019
Accepted 24 June 2019
Available online 25 June 2019

Handling editor. Prof. Jiri Jaromir Klemeš

Keywords:
Gray water footprint
Pesticide
Sugarcane
Water quality

ABSTRACT

In sugarcane crops, several agricultural pesticides are applied simultaneously, and a set of these can be detected in groundwater and surface waters, characterizing a contamination by pesticides mixtures with different concentrations in these bodies of water. Thus, the aim of this work is to estimate the gray water footprint of the pesticide mixture (herbicides) used in a dystrophic Yellow Ultisol in a sugarcane cultivation system, in Pernambuco, Brazil, based on the toxicity of each pesticide used in the mixture. For this objective, the model proposed by Paraiba et al. (2014) was used, where the gray water footprint is determined by physicochemical characteristics of the soil and pesticides, the pesticide application rates (dose), and the lowest value of the effective mean dose of these substances in a population of organisms (*EC50*). The gray water footprint of the pesticide mixture was 1.32×10^5 m^3 ha^{-1}. The highest volumes of gray water and higher ranks of the mixture were due to Amicarbazone and Hexazinone, with 1.05×10^5 m^3 ha^{-1} ($r = 5$) and 3.71×10^4 m^3 ha^{-1} ($r = 4.6$), respectively, and the lowest values were due to Paraquat and Glyphosate, with gray water footprint of 1.64 and 8.43 m^3 ha^{-1}, respectively. The gray water footprint for the yield of the sugarcane crop was estimated at 1731.1 m^3 t^{-1}, considered a high value for the gray water footprint of the sugarcane, demonstrating how much this crop can demands water resources to dilute its load of contaminants.

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https://doi.org/10.1016/j.jclepro.2019.06.282
0959-6526/

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Abbreviation

A_C	cultivated area
A_D	pesticide dose
ADFE	air-dried fine earth
A_F	attenuation factor
A_{SF}	assessment factor
CA	concentration addition
YUd	dystrophic Yellow Ultisol
EC50	median effective concentration
GDP	Gross Domestic Product
GUS	Groundwater Ubiquity Score
J_W	is the water daily net recharge of the soil area
PEC	predicted environmental concentration
PNEC	predicted no effect concentration
r	pesticide rank
R_F	retardation factor
GWF	gray water footprint of the pesticide
GWF_{PM}	gray water footprint of the pesticide mixture
Y	crop volume produced in one year
α	dose fraction that reaches the surface water due to runoff

1. Introduction

There is currently a strong and unavoidable commitment to protecting water and its natural characteristics, as well as the fulfillment of human needs, such as: obtaining food in quantity and quality, fibers, fossil fuels, biofuels and biomass, industry, among others. Moreover, the global production of biological energy resources is expanding and accelerating the growth of agricultural production. As a consequence of these demands, water scarcity represents a major commercial and environmental concern worldwide (Popp et al., 2014).

In the agricultural sector, the increased use of technology to produce food, fiber and fuel, for example, has contributed greatly to the productivity gains of agricultural crops (Brodt et al., 2011). However, the inappropriate use of these same technologies as, for example, pesticides, could jeopardize the developments observed in the Agricultural sector (Damalas and Eleftherohorinos, 2011).

About the sugarcane culture, Brazil is the world's largest sugarcane producer, being responsible together with India, for more than half of the production of this commodity on the world.

Despite the relevance of the sugarcane crop and its economic results for Brazil in terms of trade balance and also GDP, it is necessary to take into account the environmental aspects resulting from the cultivation of this crop. Studies have shown that the sugarcane crop has negatively impacted the environmental compartments, as well as its biotic and abiotic components (Liboni and Cezarino, 2012; Pignati et al., 2017).

In sugarcane crops, various pesticides are applied simultaneously as for example, pesticides Glyphosate and Hexazinone, applied in the same mixture in the modalities of scavenging and perennial spontaneous plants. As a result, a number of pesticides can be detected in the same body of water, featuring some water contamination by means of pesticide mixtures with different concentrations.

In many sustainable agricultural systems, for sustaining life in all its dimensions it is necessary to maintain the water quality and evaluate it through indicators of contamination risks arising from agricultural practices and techniques. One way to monitor and quantify the use of this important natural resource is by using "water footprint", whose concept was introduced by Hoekstra and Hung (2002) in order to have an indicator of the use of water in relation to consumption, i.e., a numerical indicator to express the volume of water used throughout the production chain of a particular agricultural product.

The total water footprint of an individual or a community is divided into three components: blue, green and gray water footprints. Blue water footprint is the amount of surface or groundwater that evaporates or is incorporated into products, returned to the sea or dumped into another basin. Green water footprint is rainwater that evaporates or is incorporated into a product during its production. Gray water footprint is the amount of water needed to obtain a concentration of pollutants below an acceptable level (Hoekstra et al., 2011). However, according to Jeswani and Azapagic (2011), the lack of a standard method for quantifying the volume of water needed to dilute the pollutants for assimilation renders the estimation of the water footprint subjective.

Several works have calculated the gray water footprint for several agricultural products, such as wheat (Zhai et al., 2019), apple (Gush et al., 2019) and saffron (Bazrafshan et al., 2019). However, these studies consider only the use of fertilizers, mainly nitrogen fertilizers, in the calculation of the gray water footprint, disregarding pesticides, which results in an underestimation of the gray water footprint. According to Paraíba et al. (2014), this is due to the fact that government agencies, pesticide sellers, manufacturers and farmers rarely report on the volume of pesticides applied to the field, making it difficult to estimate the pesticide fractions that actually reach surface and groundwater bodies.

The most usual model for determining the gray water footprint does not consider the volume of water required to dilute concentrations of pesticide mixtures in freshwater and depends on the acceptable maximum concentration limit in water. Thus, based on the model of Hoekstra and Hung (2002), Paraiba et al. (2014) proposed a model in which water footprint 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 methodology, gray water footprint can be determined by physicochemical characteristics of soil and pesticides, pesticide application rates (dose), and the lowest concentration value of the compound for which 50% of effect is observed (EC50) in the most susceptible aquatic organisms. 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.

Taking the above, this work aims to apply the model developed by Paraiba et al. (2014) to assess the gray water footprint of the pesticide mixtures (herbicides) based on the toxicity of each

pesticide used in a smaller area cultivated with sugarcane, considering the local soil characteristics and the data obtained through field tests and physicochemical of the pesticides used in Pernambuco, Brazil.

2. Material and methods

2.1. Study area and soil characterization

Data of physical properties of the studied soil, as well as the application of pesticides and water data (precipitation and irrigation) are necessary to validate the model of Paraiba et al. (2014). The soil samples were collected in a dystrophic Yellow Ultisol - hillside (YUd) cultivated with sugarcane in an area of 11.86 ha (7°48′0,54″S and 35°0′18,45″W) in the northern area of the State of Pernambuco, Brazil.

Ten simple undisturbed samples were collected in the 0–20 cm layer to obtain dry bulk density and volumetric water content at field capacity. Ten deformed samples (0–20 cm) were also collected to form a composite sample used to obtain the other physicochemical parameters.

The samples were sent to the Soil Contamination Assessment Laboratory (SCAL) of the Federal University of Pernambuco (UFPE), where they were prepared for the analysis, by disintegration, air-dried and sieved in 2 mm mesh to obtain air-dried fine earth (ADFE).

Physical and chemical soil analyses were performed according to EMBRAPA (2011), as well as soil water infiltration tests conducted in the field by using the Beerkan method (Lassabatère et al., 2006; Di Prima et al., 2016).

2.2. Model for assessing the gray water footprint

Paraiba et al. (2014) 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 for the toxicity of the mixture in aquatic organisms. The model was developed assuming conventional growing systems that require the use of a set of pesticides applied in known doses (rate of applications), in which such applications have the potential to contaminate freshwater (surface or groundwater) with mixtures of the pesticides applied to the crop system. The CA model assumes that the toxicity of the mixture is the sum of toxicity of each component of the mixture. According to Backhaus and Faust (2012), CA model assumes that there are no interactions between the components in a mixture, that is, they do not influence the uptake, distribution or metabolization of one another.

Based on information obtained from a sugarcane mill, readily available in the literature, physicochemical characterization of dystrophic Yellow Ultisol and data of rainfall, evapotranspiration and daily recharge rate, the volume of gray water of the pesticide mixture, GWF_{PM}, was calculated by using the model developed by Paraiba et al. (2014), given by:

$$GWF_{PM} = \sum_{i=1}^{n} \left(\frac{\alpha^i A_C^i A_D^i + (1-\alpha^i) A_C^i A_D^i A_F^i}{PNEC^i} \right) \quad (1)$$

where α represents the fraction of herbicides that reach surface freshwater due to runoff, A_C (ha) is the cultivated area yearly, A_D (kg ha^{-1}) is the pesticide dose, A_F is the pesticide attenuation factor and $PNEC$ (kg m^{-3}) is the Predicted No Effect Concentration of pesticide in water.

The data of the application of pesticides were obtained from the sugarcane mill. Table 1 shows the application dates of the pesticides, the crop area where they were applied, A_C (ha), and the pesticide dose of each application, A_D (kg ha^{-1}).

The pesticides were applied at different stages of sugarcane production (pre and post-emergence), in different combinations, periods, areas and doses, which produced a different gray water footprint for each situation for the same herbicide.

The application of 12/07/2015 was in the pre-emergency mode when the herbicide Amicarbazone was applied throughout the area (1.86 ha). On 01/19/2016, the products Glyphosate and Hexazinone were applied in the manner of perennial herbage in 3.36 ha where there were weeds. On 03/30/2016, Paraquat, Hexazinone and 2,4-D + Picloram were applied in the post-emergency mode. On the same day, Glyphosate and Fluroxypir + Picloram were applied in treatment mode. Similarly to 05/17/2016 there as a post-emergency complement, Glyphosate, Hexazinone and Paraquat have been applied, the latter being applied in two different areas. In addition, on 8/26/2016, another post-emergency complement was performed, with the application of Paraquat and Triclopyr.

The evaluation concerning the attenuation factor (A_F) was based on the analytical solution of the convection-dispersion equation given by:

$$A_F = \exp\left(\frac{-kzR_F\theta_{fc}}{J_W} \right) \quad (2)$$

where k (d^{-1}) is the soil pesticide degradation rate estimated by $k = \ln(2)/t_{1/2}$, being $t_{1/2}$ (d) 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 d^{-1}) is the water daily net recharge of the soil area.

$$R_{F=}1 + \frac{\rho_d f_{OC} K_{OC}}{\theta_{fc}} \quad (3)$$

where ρ_d (kg L^{-1}) is the dry bulk density and f_{OC} (g g^{-1}) is the soil organic carbon content, both determined through the physical characterization of YUd, and K_{OC} (L kg^{-1}) is the pesticide soil organic carbon partition coefficient (pesticide soil sorption).

The values of the pesticide half-life in soil $t_{1/2}$ (d) and the pesticide soil organic carbon partition coefficient K_{OC} (L kg^{-1}) were obtained from USEPA and NPIC (National Pesticide Information Center) and by Eq. (4), respectively. The depth of the soil was defined as 2 m, the same applied by Rao et al. (1985) in the estimation of the attenuation factor. They used the approximate real distance to the groundwater underlying a given soil in the calculation of the relative leaching potential. The soil volumetric water content at field capacity θ_{fc} (cm^3 cm^{-3}) was determined from the soil water retention curve $h(\theta)$ estimated by the field infiltration test by using the Beerkan Method (Lassabatère et al., 2006; Di Prima et al., 2016).

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (4)$$

where K_d represents the partition coefficient (L kg^{-1}).

For the calculation of the water daily net recharge of the soil area in the YUd, the soil water balance method calculated by Equation (5) was used:

$$JW_{OC} = P + I + A - D - ET_R \pm RO \quad (5)$$

where P (mm d^{-1}) is the daily precipitation rate; I (mm d^{-1}) is the daily irrigation rate; A (mm d^{-1}) is the rate of capillary rise, which was taken as null because it is a site with groundwater depth of

Table 1
Data of the cultivation area A_C (ha) and the dose of pesticides A_D (kg ha^{-1}) applied in the dystrophic Yellow Ultisol under sugarcane cultivation.

Date	Application	Pesticide	Toxicological Class[a]	A_C (ha)	A_D (kg ha^{-1})
12/07/2015	I	Amicarbazone	II	11.86	1.500
01/19/16	II	Glyphosate	III	3.63	0.512
		Hexazinone	I	3.63	0.137
03/30/16	III	Paraquat	I	1.72	0.174
		Hexazinone	I	1.72	0.174
	IV	2,4 D	I	2.70	0.246
		Picloram	I	2.70	0.065
	V	Fluroxypyr methyl	I	2.20	0.193
		Picloram	I	2.20	0.217
	VI	Glyphosate	III	2.10	2.380
05/17/16	VII	Glyphosate	III	2.11	2.369
	VIII	Paraquat	I	2.60	0.192
		Hexazinone	I	2.60	0.192
	IX	Paraquat	I	5.75	0.198
08/26/16	X	Paraquat	I	4.00	0.150
	XI	Triclopyr	I	1.08	0.926
		Fluroxypyr methyl	I	1.08	0.320

[a] ANVISA (1990) - Class I: Extremely toxic, Class II: Highly toxic, Class III: Moderately toxic, Class IV: Slightly toxic; A_C: area of cultivation; A_D: dose of applied pesticide. Source: Agricultural Inputs/Mixture Application Report from sugarcane mill.

more than 1 m; D (mm d^{-1}) is the rate that represents deep drainage; ET_R (mm d^{-1}) is the actual evapotranspiration rate of the crop; and RO (mm d^{-1}) represents the water runoff rate, which was also considered null because it is a flat topography area.

For the calculation of the ET_R, the cultivation coefficient method was used, in which the ET_R is given by the product between the reference evapotranspiration (ET_0, obtained from the Class A pan evaporation) and the crop coefficient (K_C), as shown in Equation (6). Data from ET_0, precipitation (P) and irrigation (I) were furnished by the sugarcane mill by means of the Data Collection Platform of the plant itself.

$$ET_R = K_C ET_0 \tag{6}$$

The cultivation coefficients K_C adopted were those proposed by Silva et al. (2013) for sugarcane (Table 2), as they were more consistent for tropical regions than those proposed by FAO Bulletin 56 (Allen et al., 1998).

The α factor of the herbicides studied, that represents the fraction of the herbicides that reach the freshwater surface due to runoff was determined from the interpolation of the α data of other herbicides found in the literature with K_{OC} values of the applied herbicides. The curve used to fit the values of α with log(K_{OC}) was the logistic curve of four parameters:

$$\alpha = K_{OC\min} + \frac{K_{OC\max} - K_{OC\min}}{1 + \left(\frac{\log(K_{OC})}{PT50}\right)^{-Hillslope}} \tag{7}$$

where K_{OCmax} and K_{OCmin} are the maximum and minimum values; $PT50$ is the inflection point (that is, the point on the S-shaped curve midway between K_{OCmax} and K_{OCmin}) and $HillSlope$ is the parameter that is related to the slope of the curve at point $PT50$. The data were fitted by using the least squares curve fitted by the Levenberg-Marquardt algorithm (Madsen et al., 2004).

The predicted no effect of pesticides on water, $PNEC$ (kg m^{-3}), was determined on the basis of the acute toxicity effects of pesticides, by taking into account the $EC50$ (mg L^{-1}) of water quality (Table 3), and representative of the trophic reference levels of the aquatic ecosystem (algae, daphnids and fish) by the equation:

$$PNEC_i = \frac{10^{-3}}{A_{SF}} \min\left\{EC50^i(\text{algae, daphnids, fish})\right\} \tag{8}$$

The assessment factor (A_{SF}) is applied at the lowest $EC50$ value of the most susceptible organism and ranges from 1 to 1000, where 1 makes the model less conservative of the environment, and 1000 makes the model highly conservative. It is used to extrapolate undesirable effects from acute toxic effects on indicator species, and was chosen considering the uncertainties surrounding the pesticides studied, adopting an A_{SF} of 100 for pesticides thus making the conservation model intermediate.

To calculate the gray water footprint of the pesticide mixture (Equation (1)) the gray water footprint of each pesticide in the mixture was previously calculated. As some pesticides were applied more than once in different periods, with different areas and doses, and in different mixtures (Table 1), it was necessary to calculate the gray water footprint of this pesticide for each of its application. The volume of final gray water footprint of the pesticide being calculated by the weighted average of the volumes of each application, as can be seen in the example below for Glyphosate:

Table 2
Cultivation coefficients (K_C) of sugarcane as a function of the stages of development of the crop.

Developmental stage	Days	K_C
Initial	30	0.18
Development	50	0.74
Medium	180	1.06
Final	60	0.76

Source: Silva et al. (2013).

Table 3
Toxicity ($EC50$) of the pesticides studied in species representing the trophic reference levels of the aquatic ecosystem (algae, daphnids and fish).

Pesticide	Toxicity ($EC50$)		
	Algae (mg L^{-1})	Daphnids (mg L^{-1})	Fish (mg L^{-1})
2,4 D	0.695	25	24.5
Amicarbazone	0.252	0.084	13
Fluroxypyr	2.4	100	14.3
Glyphosate	2.2	3	1.3
Hexazinone	0.0068	33.1	100
Paraquat	0.32	1	1
Picloram	3.7	16.5	0.88
Triclopyr	0.353	0.35	0.048

Source: USEPA (2018).

$$GWF_{Glyphosate} = \frac{GWF_{AII}AC_{II} + GWF_{AVI}AC_{VI} + GWF_{AVII}AC_{VII}}{Total\ area\ of\ Glyphosate\ application} \quad (9)$$

where the final gray water footprint of Glyphosate to be taken into account in the gray water footprint of the pesticide mixture is the weighted average of its volume in applications II, VI and VII (Table 1).

Paraiba et al. (2014) to relate the possible risks to aquatic life defined a new way to express the relative position of each individual pesticide in the mixture, referred to as pesticide rank (r_i) by calculating the decimal log of the ratio between the gray water footprint of each pesticide (GWF_i) by the sum of the application areas A_C (ha) of the pesticide or total area of application, as follows:

$$r_i = \log\left(GWF_i^{ha}\right) \quad (10)$$

3. Results and discussion

3.1. Physical and chemical properties of the soil

According to the particle size analysis (Table 4), Dystrophic Yellow Ultisol (YUd) was classified as loamy sand soil, presenting a high soil density (1.67 g cm^{-3}). The soil pH in water (Table 4) is 6.7. This property influences the degradation of some pesticides and in the case of triketone herbicides and their byproducts (mesotrione, sulcotrione and tembotrione), for example, the more alkaline the soil, the more stable these compounds will be (Barchanska et al., 2016). For organochlorine pesticides, the degradation increases in alkaline pH (Ali et al., 2014). Potential Cation Exchange Capacity (CEC) and organic carbon (OC) concentration are considered low values for good soil fertility. The low CEC is related to the low concentration of clay in the soil (less than 10%).

3.2. Gray water footprint (GWF)

3.2.1. Characteristics of herbicides

The gray water footprint for the studied area can be estimated from the volume of the gray water footprint of the pesticide mixture used in the cultivation of sugarcane. A wide variety of pesticides can be applied in the same area throughout the development stages of the crop, alone or in combination with other pesticides, and all they should be considered for the calculation of the volume of the gray water footprint of the pesticide mixture.

In sugarcane crops, the main pesticides used in cultivation are of the herbicide type, and in the area studied this only type of pesticide was applied, as informed by the sugarcane mill, that makes the gray water footprint of the sugarcane to be estimated by the volume of gray water footprint of the herbicide mixture.

Table 5 shows the values of the retardation factor (R_F) of pesticides applied in the study area and the values of the attenuation factor (A_F) calculated by the retardation factor (Eq. (3)). The R_F was calculated based on the dry bulk density (ρ_d) and considering the organic carbon content (f_{OC}), as 1.67 kg L^{-1}, 0.0082 cm^3 cm^{-3}, respectively. The volumetric water content at field capacity (θ_{fc}), 0.17 cm^3 cm^{-3}, was estimated from the water retention curve obtained by the soil infiltration assay by using Beerkan methodology, the parameters being the soil water retention curve and the hydraulic conductivity curve obtained with the BEST program (Lassabatère et al., 2006; Di Prima et al., 2016); K_{OC} was calculated for each pesticide under study (Eq. (4)). The A_F was calculated from the R_F and the half-life of the pesticide in the soil, considering a depth of 2 m. The GUS (Groundwater Ubiquity Score) index proposed by Gustafson (1989) is defined as:

$$GUS = \log\left(t_{1/2}\right)(4 - \log(K_{OC})) \quad (11)$$

This equation evaluates the contamination of groundwater by pesticides, taking into account the potential of leaching.

The herbicides Glyphosate and Paraquat presented very high values of K_{OC}, indicating a high potential of adsorption of the compound to soil organic matter, preventing it from being leached out and reach the groundwater (Sadegh-Zadeh et al., 2017). As a result of the high K_{OC} values, R_F of these compounds was also high, which nullifies the A_F from the surface of the soil to the groundwater.

The A_F index is a function of the following properties: the depth of the soil layer through which the pesticide is moving, the annual net groundwater recharge, the specific pesticide half-life considered and the soil moisture at field capacity. Thus, the high values of the attenuation factors represent conditions of low attenuation. For this reason, is of great importance to obtain the total mass of pesticide that reaches freshwater.

Fluroxypyr presented the lowest value of K_{OC}, and consequently the lowest R_F. It did not present a high A_F value since it has the lowest half-life of all the herbicides studied (only 1 day), which makes it a compound of low risk of contamination of the groundwater. Triclopyr, despite having a half-life of 45 days, also presented a very low A_F value, with an order of magnitude of 10^{-65}, since it has a high K_{OC}, thus being the third higher herbicide as compared to Glyphosate and Paraquat.

The herbicides with the highest A_F were Picloram, Hexazinone and Amicarbazone, respectively. This was due to the combination of low K_{OC} values and relatively high half-lives that make these pesticides potentially contaminating substances of groundwater.

Hexazinone obtained the second highest A_F with 2.05×10^{-3}. The same was observed by Spadotto et al. (2002) who had the same conclusion while estimating pesticide leaching potentials by using the generalized A_F model for multi-layer soils. Hexazinone was considered the second herbicide with the highest potential for leaching and contamination of groundwater among the 13 herbicides studied. These authors observed that about 13% of the Hexazinone that reaches the soil surface would pass through the upper layer of 120 cm of the soil and reach groundwater (Spadotto et al., 2002).

Table 5 shows that the calculated values of A_F corroborate with the leaching potential information of the herbicides used in the study area, obtained from the calculated values of the GUS index which evaluates the contamination of the groundwater by pesticides.

3.2.2. Calculation of mass of herbicides

Table 6 shows the pesticide application data (A_C and A_D), the attenuation factors for groundwater due to leaching (A_F) and the fraction of the pesticide in surface water due to the flow (α). Those data are used to calculate the pesticide mass load in the surface water due to runoff [$\alpha A_C A_D$ (kg)], the pesticide mass load in the groundwater due to leaching [$(1\text{-}\alpha)A_C A_D A_F$ (kg)], being M (kg) the

Table 4
Chemical and physical attributes of dystrophic Yellow Ultisol under sugarcane culture.

Layer	pH	CEC	OC	Sand	Silt	Clay	ρd
cm	H_2O	$cmol_c$ dm^{-3}		g kg^{-1}			g cm^{-3}
0–20	6.7	4.83	8.2	859.1	47	93.9	1.67

CEC: Cation exchange capacity; OC: Organic Carbon; ρ_d: dry bulk density.

Table 5
Chemical properties, retardation factor (R_F), attenuation factor (A_F) and GUS index of the herbicides applied in the dystrophic Yellow Ultisol.

Pesticide	K_{oc} (L kg^{-1})	R_F	$t_{1/2}$ (d)[a]	k (d^{-1})	A_F	GUS	GUS result
2,4-D	39.3	4.14	10	0.069315	1.41×10^{-19}	2.41	I
Amicarbazone	37	3.95	54	0.012836	4.61×10^{-4}	4.21	L
Fluroxypyr	0.136	1.01	1	0.693147	8.83×10^{-47}	0	NL
Glyphosate	24,000	1917.13	47	0.014748	0	–	NL
Hexazinone	54	5.31	90	0.007702	2.05×10^{-3}	4.43	L
Paraquat	1,000,000	79,840.44	3000	0.000231	0	–	NL
Picloram	13	2.04	82.8	0.008371	7.56×10^{-2}	5.54	L
Triclopyr	780	63.27	45	0.015403	8.69×10^{-65}	1.83	I

I, Intermediate; L, Leachable; NL, Non-Leachable. Source: [a]Hornsby et al. (1996).

Table 6
Attenuation factor (A_F) and application data of herbicides (A_C and A_D), herbicide fraction in surface water by runoff (α), herbicide mass in surface water ($\alpha A_C A_D$) and groundwater ($(1\text{-}\alpha)A_C A_D A_F$), and mass of the herbicides that reach freshwater (M), calculated for the dystrophic Yellow Ultisol.

Date	Application	Pesticide	A_F	A_C^a	A_D^a	α	$\alpha A_C A_D$	$(1\text{-}\alpha)A_C A_D A_F$	M
				ha	kg ha^{-1}	kg yr kg^{-1} yr^{-1}	––kg––	––––––kg––––––	––kg––
12/07/2015	I	Amicarbazone	4.61×10^{-4}	11.86	1.500	5.86×10^{-2}	1.04×10^{0}	7.73×10^{-3}	1.05×10^{0}
01/19/2016	II	Glyphosate	0	3.63	0.512	2.42×10^{-4}	4.50×10^{-4}	0	4.50×10^{-4}
		Hexazinone	2.05×10^{-3}	3.63	0.137	4.21×10^{-2}	2.09×10^{-2}	9.76×10^{-4}	2.19×10^{-2}
03/30/2016	III	Paraquat	0	1.72	0.174	9.68×10^{-5}	2.90×10^{-5}	0	2.90×10^{-5}
		Hexazinone	2.05×10^{-3}	1.72	0.174	4.21×10^{-2}	1.26×10^{-2}	5.87×10^{-4}	1.32×10^{-2}
	IV	2,4 D	1.41×10^{-19}	2.70	0.246	5.09×10^{-2}	3.38×10^{-2}	8.88×10^{-20}	3.38×10^{-2}
		Picloram	7.56×10^{-2}	2.70	0.065	8.10×10^{-2}	1.42×10^{-2}	1.22×10^{-2}	2.64×10^{-2}
	V	Fluroxypyr methyl	8.83×10^{-47}	2.20	0.193	7.00×10^{-2}	2.97×10^{-2}	3.49×10^{-47}	2.97×10^{-2}
		Picloram	7.56×10^{-2}	2.20	0.217	8.10×10^{-2}	3.87×10^{-2}	3.32×10^{-2}	7.19×10^{-2}
	VI	Glyphosate	0	2.10	2.380	2.42×10^{-4}	1.21×10^{-3}	0	1.21×10^{-3}
05/17/2016	VII	Glyphosate	0	2.11	2.369	2.42×10^{-4}	1.21×10^{-3}	0	1.21×10^{-3}
	VIII	Paraquat	0	2.60	0.192	9.68×10^{-5}	4.83×10^{-5}	0	4.83×10^{-5}
		Hexazinone	2.05×10^{-3}	2.60	0.192	4.21×10^{-2}	2.10×10^{-2}	9.79×10^{-4}	2.20×10^{-2}
	IX	Paraquat	0	5.75	0.198	9.68×10^{-5}	1.10×10^{-4}	0	1.10×10^{-4}
08/26/2016	X	Paraquat	0	4.00	0.150	9.68×10^{-5}	5.81×10^{-5}	0	5.81×10^{-5}
	XI	Triclopyr	8.69×10^{-65}	1.08	0.926	4.51×10^{-3}	4.51×10^{-3}	8.65×10^{-65}	4.51×10^{-3}
		Fluroxypyr methyl	8.83×10^{-47}	1.08	0.320	7.00×10^{-2}	2.42×10^{-2}	2.84×10^{-47}	2.42×10^{-2}

Source: aSugarcane mill Input / Mix Application Technical Report obtained in December 2016.

total pesticide mass (groundwater + surface water) in the freshwater of the studied pesticides.

The herbicide with the highest risk to the surface water due to runoff is Amicarbazone (Table 6), in which 1.04 kg of 1.5 kg applied to each hectare may reach surface water, and the total mass of that herbicide in freshwater [$M = \alpha A_C A_D + (1\text{-}\alpha)A_C A_D A_F$] may reach 1.05 kg. This risk is associated with the high dose of this herbicide that is applied per hectare of soil and its physicochemical properties have relatively low K_{OC} but a high half-life.

Due to the null attenuation factor (A_F), Glyphosate and Paraquat had no pesticide load in groundwater through leaching, which influenced the total mass of these herbicides in freshwater (M) with small values, in the order of magnitude 10^{-3} to 10^{-5}. The other herbicides had larger freshwater mass with an order of magnitude ranging from 100 to 10^{-3}, for Amicarbazone and Triclopyr, respectively. Thus, it is possible to observe that A_F has great importance in the calculation of the mass of herbicides in freshwater (surface and groundwater), and consequently in the gray water footprint of the pesticides.

The herbicide mass was found to be higher in the process involving the surface runoff ($\alpha A_C A_D$), except for Picloram, where values for both runoff and leaching approached to one another (Table 6), that is, the risk of contamination is greater for the runoff condition in the case of application on undulating terrain.

3.2.3. Predicted No-Effect concentration (PNEC)

Table 7 shows the values of the predicted no effect concentration of pesticide in water, *PNEC* (kg m^{-3}). This factor, determined on the basis of observations of the effect of acute pesticide toxicity on the populations of water quality indicator organisms, is of great importance in the calculation of the gray water footprint of the pesticide mixture, once it is inversely proportional to that, since a high *PNEC* means that a smaller volume of water will be needed to dilute the pollutant load before reaching freshwater. Therefore, it is essential that the most vulnerable organism for each pesticide be chosen so that all organisms that make up the ecosystem are within a safe range of the concentration of these pollutants.

Taking the pesticides applied in the area, almost all of them, except Amicarbazone and Glyphosate, belong to toxicological class I (ANVISA, 1990), that is, they are extremely toxic to living beings, and that increases the risks involved in the use of these herbicides.

3.2.4. Calculation of GWF and pesticide rank

With the mass data of pesticides reaching freshwater, M (kg), and the *PNEC* (kg m^{-3}), the gray water footprint of each pesticide,

Table 7
Non-target organisms of water quality indicator species most susceptible to each pesticide and the *PNEC*.

Pesticide	Non-target organism	*PNEC*
		kg m^{-3}
2,4 D	*Selenastrum capricomutum* (Algae)	6.95×10^{-6}
Amicarbazone	*Daphnia magna* (Daphnia)	8.40×10^{-7}
Fluroxypyr	*Selenastrum capricomutum* (Algae)	2.40×10^{-5}
Glyphosate	*Oncorhynchus mykiss* (Fish)	1.30×10^{-5}
Hexazinone	*Selenastrum capricomutum* (Algae)	6.80×10^{-8}
Paraquat	*Selenastrum capricomutum* (Algae)	3.20×10^{-6}
Picloram	*Oncorhynchus mykiss* (Fish)	8.80×10^{-6}
Triclopyr	*Oncorhynchus mykiss* (Fish)	4.80×10^{-7}

Source: USEPA (2018).

GWF_i (m^3), and the gray water footprint of the pesticide per hectare, GWF_i^{ha} (m^3), as well as the relative position of each individual pesticide in the mixture or pesticide rank, r_i, were estimated (Table 8).

Amicarbazone had the highest *GWF* of the pesticide mixture and an order of magnitude of 10^6, and the highest GWF^{ha} in the order of 10^5 (Table 8). This value was influenced mainly by the mass of the herbicide in freshwater that was of 1.05 kg, where almost all the mass (1.04 kg) reaches the superficial water bodies by surface runoff. Hexazinone had the second largest volume of *GWF* with 2.95×10^5 m^3, and like Amicarbazone, was also influenced by the high mass of this pesticide in freshwater. However, Hexazinone had the lowest *PNEC* among the other herbicides, due to the high toxicity of this herbicide to the algae *Selenastrum capricornutum*, and this influenced to a higher *GWF*.

The lowest *GWF* of the calculated pesticide mixture was from Paraquat, with 23.1 m^3 and GWF^{ha} of 1.64 $m^3\,ha^{-1}$ (Table 8) is explained by the null attenuation factor (A_F) that produced a small mass of the pesticide in freshwater. The same applies to Glyphosate, which had the second lowest *GWF* in the pesticide mixture and per hectare influenced by the absence of A_F. As can be observed, the A_F has great weight in the calculation of the GWF_{PM}.

The attenuation factor (A_F), together with the fraction of the pesticide volume that reaches freshwater due to the runoff (α) applied by Paraiba et al. (2014) provide a better insight into the effects of pesticide loading in different watercourses (groundwater and surface water). The same does not occur with the model of Hoekstra et al. (2011), which does not take into account A_F, and considers α as the fraction of pesticides that contaminates both surface water and groundwater, thus underestimating contamination by a particular pesticide.

Another important factor in the calculation of the GWF_{PM} is *PNEC*, being inversely proportional to the *GWF*. This factor may vary with the adoption of distinct assessment factors (A_{SF}) that should be chosen according to the risks involved in the use of a particular pesticide, either by studies that show these risks or by their absence and the uncertainties that appear in the absence of such studies.

Regarding ranking r_i, of the relative composition in the *GWF* of each pesticide applied to the dystrophic Yellow Ultisol, the final classification showed that the pesticide risk levels in the mixture vary from 0.2 for Paraquat to 5 for Amicarbazone. Hexazinone was second in the rank, with an r_i of 4.6. According to Paraiba et al. (2014), by knowing the position of herbicides in the relative composition of the GWF^{ha} of all pesticides it is possible to choose among all possible combinations of pesticides for weed control. This allows to minimize the *GWF* and would suggest that r_i could be used on herbicide labels, informing farmers about the amount of GWF^{ha} about the use of that herbicide.

The *GWF* calculated for each pesticide made it possible to calculate the GWF_{PM} used in the cultivation of sugarcane in an area of 11.86 ha of a dystrophic Yellow Ultisol, which was 1.57×10^6 m^3, equivalent to 1.32×10^5 $m^3\,ha^{-1}$. In terms of precipitation, an annual precipitation of 13,237.8 mm would be required, about eight times greater than the average precipitation for that area which is 1687 mm per year. Even if the volumes of water stored in the soil, surface water and irrigation levels are added, it is unlikely that the area reaches the volume of water needed to dilute these herbicides load.

Table 8
GWF of each pesticide in the mixture, GWF^{ha} and pesticide rank.

Pesticide	GWF_i (m^3)	A_C (ha)	GWF_i^{ha} (m^3)	r_i
2,4 D	4.86×10^3	2.70	1.80×10^3	3.2
Amicarbazone	1.25×10^6	11.86	1.05×10^5	5.0
Fluroxypyr	1.16×10^3	3.28	3.54×10^2	2.5
Glyphosate	6.61×10^1	7.84	8.43	0.9
Hexazinone	2.95×10^5	7.95	3.71×10^4	4.6
Paraquat	2.31×10^1	14.07	1.64	0.2
Picloram	5.32×10^3	4.90	1.09×10^3	3.0
Triclopyr	9.40×10^3	1.08	8.70×10^3	3.9
TOTAL	1.57×10^6			

According to Gerbens-Leenes and Hoekstra (2009), the water footprint of a given product can be increased by several orders of magnitude while considering the volume of gray water and the demanded water quality standards. On evaluating the water footprint of kiwifruit in New Zealand by using the method of Hoekstra et al. (2011), Deurer et al. (2011) observed how the results of this method are affected by the different natural concentrations used and the water quality standards.

Liu et al. (2017) studied some deficiencies in *GWF* accounting by using the method of Hoekstra et al. (2011) and noted that their calculation is highly sensitive to applied water standards and appointed the need to standardize water quality standards for a more consistent estimate of the *GWF*. They took into account the various aquatic ecosystems and water quality requirements, the water distribution in all regions, as well as the presence of multiple pollutants in some water bodies.

However, the *GWF* in the water footprint becomes much larger when one considers not only the water quality standards but also the toxic effects of these pollutants on water quality indicator organisms. That was observed by the low values of the *PNEC*, it led to the highest values of *GWF* in the mixture.

In Brazil, Souza and Cohim (2015) estimated the *GWF* of herbicides used in coffee crop by using the models of Paraiba et al. (2014) and Hoekstra et al. (2002). They was reported that the GWF_{PM} found in the model of Paraiba et al. (2014) is much larger than the volume found in using the model of Hoekstra et al. (2011) because the first one uses the concept of concentration addition (*CA*) that considers the toxicity of each component of the mixture instead of using only the toxicity of the most toxic component as in the model of Hoekstra et al. (2011).

This aspect makes the model developed by Paraiba et al. (2014) more protective of the environment, allowing a *GWF* closer to the actual volume required to dilute pesticide loads than that developed by Hoekstra et al. (2011). But that is not only due to the adoption of the concept of addition of concentration by Finizio et al. (2005), but for the adoption of the groundwater attenuation factor (A_F) defined by Rao et al. (1985). This factor takes into account soil physicochemical properties.

Souza and Cohim (2015), however, did not consider significant differences in values between the models, since both volumes of freshwater needed to dilute the herbicides are exorbitant. They just consider that both models can be used for determining the *GWF* of pesticides.

Paraiba et al. (2014) estimated the GWF_i^{ha} of the herbicides Amicarbazone, Glyphosate and Hexazinone to be 5.59×10^4, 1.69 and 1.93×10^5 m^3, respectively. The results found in this work varied in the order of magnitude of 10^1 or slightly varied for the same herbicides as those found by Paraiba et al. (2014), with GWF_i^{ha} of 1.05×10^5, 8.43 and 3.71×10^4 m^3, respectively. The volumes for Amicarbazone and Glyphosate were slightly higher, while Hexazinone volume was lower when compared to that obtained by Paraiba et al. (2014). These differences are because Paraiba et al. (2014) estimated the volume of gray water for sugarcane cultivation throughout the country, thus extrapolating crop data, and using average data for the physicochemical characteristics of all soils cultivated with sugarcane in the country. While in this study, real soil and cultivation data were obtained through field tests and physicochemical characterization that makes the GWF^{ha} for these

pesticides found in the present study closer to reality. Sausse (2011) states that the water footprint can vary widely from one place to another due to the variability of the conditions of production of a particular crop.

According to the data got from the sugarcane mill, an average of 1.3 million t yr^{-1} of sugarcane is produced in 17,000 ha destined to the production of the crop, which produces around 76.5 t ha^{-1}. As the thematic area of this study covers 11.86 ha, 907.29 t of cane are produced in this area per year. Considering the GWF^{ha} of the pesticide mixture (1.32×10^5 m^3 ha^{-1}), it was possible to estimate the *GWF* per sugarcane volume produced at about 1731.1 m^3 t^{-1}. This value is lower than that found by Paraiba et al. (2014), that was 3996 m^3 t^{-1}, but more reliable, since it was generated from an experimental evaluation with information obtained on rates, applied doses, leaching of pesticides in water bodies, rates of recharge of the aquifer and of the hydrological characteristics of the soil.

4. Conclusions

The gray water footprint of the pesticide mixture (GWF_{PM}) used in sugarcane cultivation in a dystrophic Yellow Ultisol in Pernambuco sugarcane zone was 1.57×10^6 m^3, or 1.32×10^5 m^3 ha^{-1}.

The herbicides with the highest gray water footprint per hectare (GWF^{ha}) and the greatest impact in the volume of gray water of the pesticide mixture, taking the pesticide ranking, were Amicarbazone and Hexazinone. On the contrary, the lower GWF^{ha} was found for Paraquat and Glyphosate.

The *GWF* of Hexazinone demonstrates how important it is to consider the most susceptible organism for each pesticide in the mixture for *PNEC* calculation, thus making the resulting *GWF* safe for the entire ecosystem.

In the dystrophic Yellow Ultisol the *GWF*for the sugarcane crop yield was estimated in 1731.1 m^3 t^{-1}. It is a high value for the *GWF*for sugarcane and demonstrates how much this crop can require water resources to dilute the load of contaminants.

With the data obtained from field experiments and the physicochemical characterization of the soil, it was possible to validate the model presented in this work to assess the GWF_{PM}. This model was more accurate and conservative of the environment among the existing models to obtain this component of the water footprint.

In this work, it was possible to observe how high the volume of freshwater needed to dilute the contaminant load of the sugarcane crop and the importance of the proper handling of pesticides. Therefore, by looking at the relative positions of the pesticides by ranking them in the mixture, and by choosing those that have a lower rating, it is possible to make adequate combinations of herbicides to produce the same productivity and quality results, generating a smaller GWF_{PM}.

The *GWF* of these herbicides can be used as an indicator of the best quality of water resources. It can also be used in the formulation of governmental guidelines for the sustainable use of these pesticides without causing less damage to the environment, and always considering water quality standards and avoiding the adverse effects on non-target organisms so that they can survive at the ecosystem in which they would naturally choose to be.

References

Ali, M., Kazmi, A.A., Ahmed, N., 2014. Study on effects of temperature, moisture and pH in degradation and degradation kinetics of aldrin, endosulfan, lindane pesticides during full-scale continuous rotary drum composting. Chemosphere 102, 68–75.

Allen, R.G., Pereira, l.S., Raes, D., Smith, M., 1998. In: Crop Evapotranspiration: Guidelines for Computing Crop Water Requirements, vol. 56. FAO Irrigation and Drainage Paper, Rome, p. 300.

ANVISA - National Health Surveillance Agency, 1990. Decree Nº 98.816, January 11, p. 1990 (in Portuguese), Available at: http://bvsms.saude.gov.br/bvs/saudelegis/svs1/1992/prt0003_16_01_1992.html. Online access: 03-12-2019.

Backhaus, T., Faust, M., 2012. Predictive environmental risk assessment of chemical mixtures: a conceptual framework. Environ. Sci. Technol. 46, 2564–2573.

Barchanska, H., Kluza, A., Krajczewska, K., Maj, J., 2016. Degradation study of mesotrione and other triketone herbicides on soils and sediments. J. Soils Sediments 16, 125–133.

Bazrafshan, O., Etedali, H.R., Moshizi, Z.G.N., Shamili, M., 2019. Virtual water trade and water footprint accounting of Saffron production in Iran. Agric. Water Manag. 213, 368–374.

Brodt, S., Six, J., Feenstra, G., Ingels, C., Campbell, D., 2011. Sustainable agriculture. Nat. Educ. Knowl. 3, 1.

Damalas, C.A., Eleftherohorinos, I.G., 2011. Pesticide exposure, safety issues, and risk assessment indicators. Int. J. Environ. Res. Public Health 8, 1402–1419.

Deurer, M., Green, S.R., Clothier, B.E., Mowat, A., 2011. Can product water footprints indicate the hydrological impact of primary production? A case study of New Zealand kiwifruit. J. Hydrol. 408, 246–256.

Di Prima, S., Lassabatère, L., Bagarello, V., Lovino, M., Angulo-Jaramillo, R., 2016. Testing a new automated single ring infiltrometer for Beerkan infiltration experiments. Geoderma 262, 20–34.

EMBRAPA – Brazilian Agricultural Research Corporation, 2011. National Soil Research Center. Manual of Methods of Soil Analysis (In Portuguese). Embrapa Solos, Rio de Janeiro.

Finizio, A., Villa, S., Vighi, M., 2005. Predicting pesticide mixtures load in surface waters from a given crop. Agric. Ecosyst. Environ. 111, 111–118.

Gerbens-Leenes, P.W., Hoekstra, A.Y., 2009. The water footprint of sweeteners and bioethanol from sugar cane, sugar beet and maize. In: Value of Water Research Report Series, vol. 38. UNESCO-IHE. Available at: http://www.ayhoekstra.nl/pubs/Report38.pdf. Online access: 02-20-2018.

Gush, M., Dzikiti, S., Laan, M., Steyn, M., Manamathela, S., Pienaar, H., 2019. Field quantification of the water footprint of an apple orchard, and extrapolation to watershed scale within a winter rainfall Mediterranean climate zone. Agric. For. Meteorol. 271, 135–147.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environ. Toxicol. Chem. 8, 339–357.

Hoekstra, A.Y., Chapagain, A.K., Aldaya, M.M., Mekonnen, M.M., 2011. The Water Footprint Assessment Manual: Setting the Global Standard. Water Footprint Network, p. 224.

Hoekstra, A.Y., Hung, P.Q., 2002. Virtual water trade: a quantification of virtual water flows between nations in relation to international crop trade. In: Value of Water Research Report Series. Institute for Water Education. UNESCO-IHE, p. 66.

Hornsby, A.G., Wauchope, R., Herner, A.E., 1996. Pesticide Properties in the Environment. Springer, New York.

Jeswani, H.K., Azapagic, A., 2011. Water footprint: methodologies and a case study for assessing the impacts of water use. J. Clean. Prod. 19, 1288–1299.

Lassabatère, L., Angulo-Jaramillo, R., Soria Ugalde, J.M., Cuenca, R., Braud, I., Haverkamp, R., 2006. Beerkan estimation of soil transfer parameters through infiltration experiments-BEST. Soil Sci. Soc. Am. J. 70, 521–532.

Liboni, L.B., Cezarino, L.O., 2012. Social and environmental impacts of the sugarcane industry. Future Stud. Res. J. 4, 196–227.

Liu, W., Antonelli, M., Liu, X., Yang, H., 2017. Towards improvement of grey water footprint assessment: with an illustration for global maize cultivation. J. Clean. Prod. 147, 1–9.

Madsen, K., Nielsen, N.B., Tingleff, O., 2004. Methods for Nonlinear Least Squares Problems. Technical Report. Informatics and Mathematical Modeling. Technical University of Denmark.

Paraiba, L.C., Pazianotto, R.A.A., Luiz, A.J.B., Maia, A.D.H.N., Jonsson, C.M., 2014. A mathematical model to estimate the volume of grey water of pesticide mixtures. Span. J. Agric. Res. 2, 509–518.

Pignati, W.A., Souza e Lima, F.A.N., Lara, S.S., Correa, M.L.M., Barbosa, J.R., Costa Leão, R.H., Pignatti, M.G., 2017. Spatial distribution of pesticide use in Brazil: a strategy for Health Surveillance. Ciência Saúde Coletiva 22, 3281–3293.

Popp, J., Lakner, Z., Harangi-Rákos, M., Fári, M., 2014. The effect of bioenergy expansion: food, energy, and environment. Renew. Sustain. Energy Rev. 32, 559–578.

Rao, P.S.C., Hornsby, A.G., Jessup, R.E., 1985. Indices for ranking the potential for pesticide contamination of groundwater. Soil Crop Sci. Soc. Fl. 44, 1–8.

Sadegh-Zadeh, F., Wahid, S.A., Jalili, B., 2017. Sorption, degradation and leaching of pesticides in soils amended with organic matter: a review. Adv. Environ. Technol. 2, 119–132.

Sausse, C., 2011. On the water footprint of energy from bio-mass: a comment. Ecol. Econ. 71, 1–3.

Silva, V.P.R., Da Silva, B.B., Albuquerque, W.G., Borges, C.J., De Sousa, I.F., Neto, J.D., 2013. Crop coefficient, water requirements, yield and water use efficiency of sugarcane growth in Brazil. Agric. Water Manag. 128, 102–109.

Souza, T.A., Cohim, E.H.B., 2015. Gray water volume of the herbicide mixture used in coffee growing in Brazil. In: XIII Symposium on Water Resources of the Northeast (In Portuguese), Aracajú-SE.

Spadotto, C.A., Gomes, M.A.F., Hornsby, A.G., 2002. Pesticide leaching potential assessment in multi-layered soils. Pesticides: R. Ecotoxicol. e Meio Ambiente 12, 1–12.

USEPA - United States Environmental Protection Agency, 2018. OPP Pesticide Ecotoxicity Database. Available at: http://www.ipmcenters.org/Ecotox/index.cfm. Online access: 03-13-2019.

Zhai, Y., Tan, X., Ma, X., An, M., Zhao, Q., Shen, X., Hong, J., 2019. Water footprint analysis of wheat production. Ecol. Indicat. 102, 95–102.