Agrochemical modeling in rivers: the Sampaio irrigation project case study

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Abstract

This study evaluates the agrochemical impact present in irrigation effluents of the surrounding hydric environment. The case studied refers to the Sampaio Irrigation Project, located at the far north of Tocantins State, on the left margin of the Tocantins River, in which case this river is the receiving body of polder drainage intended for a rice culture using flood irrigation. By using mathematical modeling, three distinct hydrological scenarios were simulated, aiming to identify concentrations of the chemical compounds used in the Tocantins River, and the range of the impacted area, adopted as the area under direct influence of this impact. We concluded that only the compound Carbaryl had higher concentrations than the limitations allowed for the Tocantins River by CONAMA [National Environmental Council] Resolution No. 357/2005 for class 1 and class 2 rivers, and that the extension of the area affected by such concentrations is of about 6 km [3.73 miles]. Having obtained these results from our model, specific measures were recommended to prevent the identified impact, and added to the Environmental Impact Study and Environmental Impact Report (EIA/RIMA) for the project.

Keywords: environmental impact, agrochemical composts, toxic substances modeling in water.

1 Introduction

The drainage of agricultural areas often introduces strong environmental impacts in surrounding areas as it carries part of the agrochemical substances applied to crops to natural water resources. These impacts are an object of concern all over

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the world, and although efforts are being made to reduce the use of agrochemical substances by means of new and restrictive laws, they are widely used in modern agricultural practice.

Mathematical modeling is an important tool to assess environmental impact of these substances in the water column in order to evaluate their dispersion and to select the substances that cause the least problems.

2 The Sampaio irrigation project

2.1 General features

The Sampaio project is an irrigation perimeter of 1.071 ha area in the towns of Sampaio, Carrasco Bonito and Augustinópolis. Part of this area (142 ha) is used to grow fruits, the remaining area receives crops of rice, corn and soy beans (929 ha) and is situated in a polder near the left bank of the Tocantins river.

The Tocantins river is a tributary of the lower basin of the Amazon river and its mean annual flow is 8.136,8 m^3/s. It provides the source of water for irrigation and also receives the drainage of the rice crops.

The project is constituted of: a protection dam against Tocantins river floods, main channel, pumping station, distribution channels, pressurizing station, drainage channels, drainage pumping station, energy supply system, and road system.

2.2 Agrochemical compounds design

As the tropical environment is aggressive to crops, some agrochemicals compounds were recommended in the agronomic project, in particular for their use in rice crops, which will be flooded, and for this reason generate almost all of the drainage water. The proposed substances that could reach the Tocantins river were: Carbaryl, Carbofuran, Cyfluthrin, Diazinon, Dibrom, Esfenvalerate, Fenitrothion, Lambda(λ)cyhalothrin, Malathion and Permethrin.

3 Mathematical modeling of toxic substances

3.1 Agrochemicals: characteristics and environmental fate

Table 1 shows the maim characteristics of the agrochemicals that are employed in the rice crops. Table 2 presents the environmental fate of each agrochemical modeled and Table 3 shows the level of significance of each substance. From these tables it can be seen that the majority of the products associate to particles, and for some products that remain in the water column, such as Carbaryl, Carbofuran and Malathion, the mass transference and degradation processes are relevant features.

Table 5 presents the main physical and chemical rates and constants of modeled agrochemicals.

Table 1: Main characteristics of the agrochemicals employed.

Substance	Application rates	Limits (*)
Carbaryl	960 a 1.110 g/ha	0,02 μg/L
Carbofuran	450 a 500 g/ha	< 10 μg/L Paration
Cyfluthrin	7,5 a 10 g/ha	-
Diazinon	0,25 a 0,5 kg/ha	< 10 μg/L Paration
Dibrom	0,25 a 0,5 kg/ha	-
Esfenvalerate	-	-
Fenitrothion	-	-
λcyhalothrin	270 g/ha	< 10 μg/L Paration
Malathion	-	-
Permethrin	0,8 a 2,0 L/ha	< 10 μg/L Paration

(*) Brazilian law: Resolução do CONAMA 357/2005.

Table 2: Environmental fate of the agrochemicals employed.

Substance	Air	Soil	Water
Carbaryl	Particulate phase and vapor	Moderate mobility	Remains is water column
Carbofuran	Particulate phase and vapor	High mobility	Remains is water column
Cyfluthrin	No volatilization, remains associated to particles	Adsorb to soil, shows some mobility	Adsorb to suspended particles
Diazinon	Particulate phase and vapor	Low to Moderate mobility	Adsorb to suspended particles
Dibrom	Associate to particles	Low mobility	Adsorb to suspended particles
Esfenvalerate	Particulate phase and vapor	Very low mobility. No lichiviation	Adsorb to suspended particles
Fenitrothion	Particulate phase and vapor	Low to Moderate mobility	Low adsorption to suspended particles
λcyhalothrin	No volatilization, remains associated to particles	Adsorb to soil, shows no mobility	Adsorb to suspended particles
Malathion	Vapor only	Very high mobility	Remains is water column
Permethrin	Particulate phase and vapor	Adsorb to soil, shows no mobility	Adsorb to suspended particles
Thriclorfon	Particulate phase and vapor	Very high to high mobility	Remains is water column

Table 3: Level of significance of the main degradation factors in water for the studied substances.

Substance	Biodegradation	Volatilization	Photolysis	Hydrolysis	Bio-accumulation
Carbaryl	V I	L	I	I*	L
Carbofuran	I	I	I	I	L
Cyfluthrin	I	VI	VI	VL	H
Diazinon	I	ND	VI	VL	M to H
Dibrom	CD	L	S	S (pH=7)	L
Esfenvalerate	ND	I	I	I *	H
Fenitrothion	I	L	VI	VI**	M to L
λcyhalothrin	I	VI	VI	VI ***	M ***
Malathion	VI	L	I	VL*	L
Permethrin	I	I	I	VL*	H
Thriclorfon	I	VL	L	Variable *	L

CD – Conflicting data, ND – No data available, L – Low, VL – Very low, M – medium, H – high, I – important, VI – Very important, S – sable.
*increases with pH.
** decreases with pH.
***decreases in presence of fulvic acids.

Table 4: Scenarios for modeling.

Flow (m^3/s)		Occurrence	Water height (m)	Time after application (d)
Drainage effluent	Tocantins river			
1,26	3.503	No rain. Drain by gravity	0,1	2
0,40	2.760	During medium rain	0,2	1
6,40	8.137	Heavy storms, maximum pumping	0,2	2

3.2 Scenarios

The scenarios modeled were based on the following assumptions:

1. The compounds must stay in contact with the culture for at least 48 hours;
2. The flooded areas act as fully mixed reactors;
3. The water column height in flooded rice is 10 cm, producing a total volume of $9.3\ 10^5\ m^3$;
4. In case of strong showers the maximum water column is 20 cm, in order to avoid drowning of the rice plants;
5. Agrochemicals are not applied simultaneously, it was assumed that 10% of the area is affected by the compounds studied.
6. Rice cultures grow from December to March when it is harvested.

Table 5: Physical and chemical rates and constants for the modeled compounds.

Substance	CAS Number	Molecular Weight	Density	log K_{ow}	K_{oc}	Henry's Constant	Vapor Pressure (mm Hg)	Solubility (mg/L)	Hydrolysis ($t_{1/2}$) (d)	Photolysis ($t_{1/2}$) (d)		Volatility
										water	soil	
Carbaryl	63-25-2	201.22	1.232	2.36	251	8.80E-08	3.97 E-05	120	10.5	45	ND	ND
Carbofuran	1563-66-2	221.26	1.180	2.32	160	6.84E-08	3.40 E-06	700	57.4	5.6	45	ND
Cyfluthrin	68359-37-5	434.29	0.830	5.62	1.00 E+4	5.80E-10	1.62 E-08	2	231	0.67	ND	L
Diazinon	333-41-5	304.35	1.116	3.81	191 to 1.840	1.17E-07	9.01 E-05	40	185	1,4	1	2.4 (mg/m^3)
Dibrom	300-76-5	344.05	1.220	-4.60	2.00 E+3	1.40E-13	1.00 E-07	7.08 E+5	ND	ND	ND	L
Esfenvalerate	66230-04-4	419.90	1.175	6.77	3.98 E+5	1.19E-07	5.00 E-07	2.00 E-4	16.3	30	100	L
Fenitrothion	122-14-5	277.24	1.323	3.38	254 to 1,531	9.30E-07	5.40 E-05	38	4.30	1,1	ND	0.09 (mg/m^3)
λcyhalothrin	68085-85-8	449.86	1.250	6.80	1.20 E+5	1.50E-05	7.50 E-09	5.00 E-3	S	ND	ND	$t_{1/2}$ =1,46 d
Malathion	121-75-5	330.36	1.230	2.36	30,0	4.90E-09	1.78 E-04	145	11.0	16	ND	L
Permethrin	52645-53-1	391.29	1.190	2.88	1.05 E+4 to 8.60 E+4	1.90E-06	2.18 E-08	0,006	S	33	30	ND
Thriclorfon	52-68-6	257.45	1.730	0.51	6.00 to 79.0	1.70E-11	7.80 E-06	1.54 E+5	0.27	L	ND	L

The rates and constants needed for modeling were obtained in public databanks: Cornell University, National Library of Medicine (Hazardous Substances Data Bank) and California Department of Pesticide Regulation.

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3.3 Equations

For steady state CHAPRA [1] presents the following mass balance for solids:
(a) aquatic phase

$$-U\frac{dm_1}{dx}-\frac{v_s}{H_1}m_1+\frac{v_r}{H_1}m_2=0 \tag{1}$$

(b) solid phase

$$v_s m_1 - v_r m_2 - v_b m_2 = 0 \tag{2}$$

where U is the river velocity; m_1 is solid concentration in water; m_2 is solid concentration in sediment layer, which can be written as porosity times density; v_s is sedimentation velocity; v_b is burial velocity; and v_r is ressuspension velocity.

Equations (1) and (2) are solved for:

$$m_1 = m_1(0)e^{-\frac{v_s}{H_1 U}x}+\frac{v_r(1-\phi)\rho}{v_s}\left(1-e^{-\frac{v_s}{H_1 U}x}\right) \tag{3}$$

where ϕ is porosity and ρ is sediments specific weight.

If the initial concentration of solids $m_1(0)$ is low, the downstream concentration will approach steady state and will be given by:

$$m_1(\infty)=\frac{v_r(1-\phi)\rho}{v_s} \tag{4}$$

Using the previous results it is possible to make the constituent mass balance:
(a) aquatic phase

$$-U\frac{dc_1}{dx}-k_1c_1-\frac{v_v}{H_1}F_{d1}\cdot c_1-\frac{v_s}{H_1}F_{p1}\cdot c_1+\frac{v_d}{H_1}\left(F_{d2}\cdot c_2-F_{d1}\cdot c_1\right)+\frac{v_r}{H_1}c_2=0 \tag{5}$$

(b) solid phase

$$v_s\cdot F_{p1}\cdot c_1+v_d\left(F_{d1}\cdot c_1-F_{d2}\cdot c2\right)-k_2\cdot H_2\cdot c_2-v_r\cdot c_2-v_b\cdot c_2=0 \tag{6}$$

where c_1 is the concentration of constituent in water (μg/L), c_2 is the concentration of constituent in the sediment layer (μg/L), k_1 is the first order decomposition rate in water and k_2 is the first order decomposition rate in sediment, the F factors are the ratios of constituent in d- dissolved form, p- particulate form and 1- aquatic phase and 2- solid phase.

$$F_{d1}=\frac{1}{1+K_{d1}m} \tag{7}$$

$$F_{p1}=\frac{K_{d1}m}{1+K_{d1}m} \tag{8}$$

$$F_{d2} = \frac{1}{\phi + K_{d2}(1-\phi)\rho} \tag{9}$$

If the initial concentration is $c_1(0)$, differential equation (7) is solved for:

$$c_1 = R_{21} \cdot c_1(0) \cdot e^{-\frac{v_T}{H_1 U} \cdot x} \quad (10) \qquad \text{and } c_2 = R_{2,1} \cdot c_1 \tag{10}$$

where:

$$v_T = k_1 \cdot H_1 + v_v \cdot F_{d1} + (v_s \cdot F_{p1} + v_d \cdot F_{d1})(1 - F_r') \tag{11}$$

$$R_{2,1} = \frac{v_s F_{p1} + v_d F_{d1}}{v_d F_{d2} + k_2 H_2 + v_r + v_b} \tag{12}$$

$$F_r' = \frac{v_r + v_d F_{d2}}{v_d F_{d2} + k_2 H_2 + v_r + v_b} \tag{13}$$

3.4 Mass transference mechanisms

3.4.1 Sorption

In this process part of dissolved mass is transferred to solid phase. The ratio of transference K_d can be evaluated from the carbon content in particulate (f_{oc}) matter and from the partition coefficient for organic carbon (K_{oc}), which is related to the water octanol partition coefficient (K_{ow}), characteristic for each substance.

3.4.2 Volatilization

Volatilization is the mass transference from water or soil to air, leaving the system. It is accounted by the volatilization velocity v_v.

$$v_v = K_l \frac{H_e}{H_e + R \cdot T_a \cdot \left(\frac{K_l}{K_g}\right)} \tag{14}$$

with

H_e is the Henry's Constant,

T_a is temperature (K)

R is gas constant (8,206 x10^{-5} atm. m^3/K/mol)

$K_l = K_{l,O_2}\left(\frac{32}{M}\right)^{0,25}$, is the mass transference coefficient to liquid

$K_g = 168 \cdot U_v \cdot \left(\frac{18}{M}\right)^{0,25}$, is the mass transference coefficient to air

M is the molecular weight and K_{l,O_2} is the mass transference coefficient of oxygen (0.864/d).

3.5 Degradation mechanisms

3.5.1 Photolysis
Photolysis can be direct whereby the compound is directly degraded by light or indirect when intermediate compounds react with light.

3.5.2 Hydrolysis
Hydrolysis is the reaction in which the molecule bounds are broken to form new bounds with hydrogen and hydroxyl. These reactions are catalyzed by acids and bases, and to a lesser extent, by water.

3.5.3 Biodegrading
The compounds are transformed by microorganisms. The term refers to several mechanisms, such as mineralization, activation, cometabolism, detoxification and defusing.

All of these three mechanisms are accounted in the model by it's half life ($t_{1/2}$), which is related to the degradation coefficient by: $t_{1/2} = \frac{0{,}6931}{k}$, k being the degradation coefficient: photolysis (K_f), hydrolysis (K_h) or microorganisms (K_b).

4 Application and results

Table 6 shows the values calculated using the data in Table 5, and equations (1)–(14).

Table 7 shows the initial value for concentrations in each scenario modeled. It can be seen that only Carbaryl exceeds the limits stated by Brazilian law for initial dilution in the Tocantins river.

Table 6: Calculated parameters.

Substance	K_{ow}	K_d	m = 120 (mg/L)		Volatilization		
			F_d	F_p	k_l	k_g	v_v
Carbaryl	2.29E+02	1.41E-04	0.983	0.017	1.637	275.6	9.91E-04
Carbofuran	2.09E+02	1.29E-04	0.985	0.015	1.598	269.2	7.53E-04
Cyfluthrin	4.17E+05	2.57E-01	0.031	0.969	1.350	227.4	5.39E-06
Diazinon	6.46E+03	3.98E-03	0.677	0.323	1.476	248.5	1.19E-03
Dibrom	2.51E-05	1.55E-11	1.000	0.000	1.431	241.0	1.38E-09
Esfenvalerate	5.89E+06	3.63E+00	0.002	0.998	1.362	229.3	1.12E-03
Fenitrothion	2.38E+03	1.47E-03	0.850	0.150	1.511	254.4	9.61E-03
λcyhalothrin	6.31E+06	3.89E+00	0.002	0.998	1.339	225.4	1.25E-01
Malathion	2.29E+02	1.41E-04	0.983	0.017	1.446	243.5	4.88E-05
Permethrin	7.59E+02	4.68E-04	0.947	0.053	1.386	233.4	1.79E-02
Thriclorfon	3.24E+00	2.00E-06	1.000	0.000	1.539	259.2	1.80E-07

Table 7: Initial concentrations for the three scenarios modeled.

Substance	Load (g)	Scenario					
		1		2		3	
		C_d(mg/L) After 2 days	C_{w0} (µg/L)	C_d(mg/L) After 1 day	C_{w0} (µg/L)	C_d(mg/L) After 2 days	C_{w0} (µg/L)
Carbaryl	142,848	1.09E-01	3.91E-02	1.28E-01	1.86E-02	5.43E-02	4.27E-02
Carbofuran	74,400	4.56E-02	1.64E-02	5.99E-02	8.69E-03	2.28E-02	1.79E-02
Cyfluthrin	1,488	7.75E-07	2.79E-07	6.24E-06	9.04E-07	3.88E-07	3.05E-07
Diazinon	89,280	6.50E-02	2.34E-02	6.50E-02	9.41E-03	3.25E-02	2.55E-02
Dibrom	55,800	6.00E-02	2.16E-02	6.00E-02	8.69E-03	3.00E-02	2.36E-02
Esfenvalerate	74,400	1.40E-04	5.04E-05	1.60E-04	2.32E-05	7.01E-05	5.51E-05
Fenitrothion	1,488	5.52E-05	1.99E-05	2.74E-04	3.97E-05	2.76E-05	2.17E-05
λcyhalothrin	2,325	5.34E-06	1.92E-06	5.34E-06	7.74E-07	2.67E-06	2.10E-06
Malathion	74	5.14E-05	1.85E-05	6.36E-05	9.21E-06	2.57E-05	2.02E-05
Permethrin	3,720	3.24E-03	1.17E-03	3.50E-03	5.08E-04	1.62E-03	1.27E-03
Thriclorfon	148,800	4.88E-06	1.76E-06	8.84E-04	1.28E-04	2.44E-06	1.92E-06

C_d – concentration in drainage effluent Cw0 – initial concentration in Tocantins river.
For allowed concentrations see Table 1.

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Considering equation (10) the initial concentration of 4.27 10^{-2} μg/L for Carbaryl, and the limit of 2 10^{-2} μg/L stated by Brazilian legislation, the affected length of the Tocantins river can be calculated as:

$$C = 0{,}02 = C_o \cdot e^{-\left(\frac{v_T}{H_1}+k_h+k_b+k_f\right)\cdot\frac{x}{U}} \tag{15}$$

where

$$v_T = k_1 \cdot H_1 + v_v \cdot F_{d1} + \left(v_s \cdot F_{p1} + v_d \cdot F_{d1}\right)\left(1 - F_r'\right) =$$

$$0{,}052 * 10 + 9{,}1 \cdot 10^{-4} * 1 + (0{,}25 * 0 + 0 * 1)(1-1) = 0{,}521 \frac{m}{d}$$

$$k_h + k_b + k_f = 0{,}066 + 2{,}039 + 0{,}0154 = 2{,}641\ \mathrm{d}^{-1}$$

and

$$F_{d1} = \frac{1}{1 + K_{d1} m} = \frac{1}{1 + 7{,}07^{-7{,}100}} \approx 1$$

$$F_{p1} = \frac{K_{d1} m}{1 + K_{d1} m} = \frac{7{,}07^{-7{,}100}}{1 + 7{,}07^{-7{,}100}} \approx 0$$

k_h is the hydrolysis rate ($t_{1/2}$ =10,5 d -> k_h = 0,066)
k_b is the biodegrading rate ($t_{1/2}$ =0,34 d -> k_b = 2,039)
k_f is the photolysis rate ($t_{1/2}$ =45 d -> k_f = 0,0154)

Considering the river velocity (U) of 0.2 m/s and the depth (H_1) of 10 m, the length x affected will be 6.030 m.

5 Conclusions

The environmental study concluded that if Carbaryl is applied to crops, the area must stay without drainage for at least 7 days in order to reach the Tocantins river within concentration limits. As a recommendation of the study it is proposed that this compound should be replaced by another type of pesticide or, if it is unavoidable, heavy storm periods must be avoided in order to prevent maximum pumping flow.

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