The bioconcentration factor of pesticides in potatoes

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Abstract

We presented a model that estimates the bioconcentration factor (BCF) of pesticides in potatoes supposing that the pesticide in the soil solution is absorbed by the potato by passive diffusion, following Fick's second law. The pesticides in the model are nonionic organic substances, traditionally used in potato crops that degrade in the soil according to a first order kinetic equation. This presents an expression that relates BCF with the pesticide elimination rate by the potato, with the pesticide accumulation rate within the potato, with the rate of growth of the potato and with the pesticide degradation rate in the soil. BCF was estimated supposing steady state equilibrium of the quotient between the pesticide concentration in the potato and the pesticide concentration in the soil solution. It is suggested that a negative correlation exists between the pesticide BCF and the soil sorption partition coefficient. The model was built based on the work of Trapp *et al.* (2007), [*Diffusion of PAH in Potato and Carrot Slices and Applications for a Potato Model*] in which an expression to calculate the diffusivity of persistent organic substances in potatoes is presented. The model consists in adding to the expression of Trapp *et al.* (2007) the hypothesis that the pesticide degrades in the soil. The value of BCF suggests which pesticides should be monitored in potatoes.

Keywords: BCF, diffusivity, daily ingestion, bioaccumulation, food diet, food.

Introduction

Potato plants (*Solanum tuberosum*) are cultivated in more than one hundred countries from different continents because of their extraordinary adapting capacity to different climatic and soil conditions, only being surpassed by wheat, rice and corn, and more than one billion people consume these tubers. The potato's agronomic efficiency guarantees the use of several types of soils destined to food production, which contributes to increase the potato cropping area in a global scenario of rapid population growth and economic development. All over the world, the main limiting factor to potato cropping is its susceptibility to a great number of pests and diseases, some of them capable of causing serious production damages, which impose the use of many and several types of pesticides, causing serious environmental and feeding problems (López-Pérez *et al.*, 2006).

Even by taking into account that the most recent agronomic management techniques, suggested by the integrated production systems reduce risks of environmental and feeding contamination, it is fundamental that managers, technicians and researchers know how to estimate the accumulative potential of pesticides in potatoes, enabling them to recommend new products and technologies in order to have economically and environmentally sustainable productions. The UN FAO (United Nations Food and Agriculture Organization) is currently promoting the tuber as a more efficient food crop that can improve food security in developing countries. About 80 per cent of the potato crop can be used for human consumption, significantly more than for cereals like corn and wheat.

The bioconcentration factor (BCF) of a substance in an organism is a numeric value that measures the bioconcentration and expresses the partition of the substance between the organism and the medium. In the chemical steady state equilibrium, this coefficient is the quotient between the pesticide concentration in the organism and the pesticide concentration in the medium. When the organisms are cultivated foods, BCF permits an approximation of the pesticide's daily

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ingestion through its food consumption and establishes safe limits for pesticide concentrations in medium and indicates which pesticides should be monitored in the food.

Several studies indicate the presence of pesticides and organic substances in potatoes (Samsoe-Petersen *et al.*, 2002; Fismes *et al*, 2002; Jensen *et al.*, 2003; Cesnik *et al.*, 2006; Zohair *et al.*, 2006) but none of them present a theoretically acceptable and experimentally model that one can use to estimate BCF in potatoes of pesticides degrading in the soil.

Thus, the objective of this work was to model the kinetics of pesticide uptake for potatoes, to use this model to estimate BCF in potato pesticides frequently used in this cultivation and to indicate which of them should be monitored in potato samples. For hypothesis, the studied pesticides are nonionic organic substances that degrade in the soil, following a first order kinetic equation. The model was built based on the work of Trapp *et al.* (2007) in which Fick's second law is used for modeling the diffusive flow of the pesticide through the potato tissues. The model developed by Trapp *et al.* (2007) makes it possible to estimate the diffusivity of organic substances in soil for potatoes, and helps significantly to elaborate useful mathematical models to determine the potato's bioconcentration factor of nonionic pesticides degrading in the soil.

Materials and Methods

From the pesticide concentration in the soil the pesticide concentration in the soil solution was estimated by

$$C_w(t) = \frac{\rho_w C_s(0) e^{-k_s t}}{(\rho_s f_{oc} K_{oc} + f_w + f_a K_{aw})} \tag{1}$$

where $C_w(t)$ (mg kg^{-1}) is the pesticide concentration in the soil solution, $C_s(0)$ (mg kg^{-1}) is the initial pesticide concentration in soil matrix and k_s (day^{-1}) is the pesticide degradation rate in the soil matrix estimated by $k_s = 0.693/t_{1/2}$, in which $t_{1/2}$ (day) is the half-life pesticide in the soil; The ρ_w (kg l^{-1}) and ρ_s (kg l^{-1}) are the soil densities in a humid and dry basis, respectively; The f_{oc}, f_w and f_a coefficients are the volumetric fractions of organic carbon, water and air of the soil, respectively; The K_{oc} (l kg^{-1}) is the soil sorption partition coefficient of the pesticide and K_{aw} is air-water partition coefficient of the pesticide.

The uptake and elimination of pesticides from surrounding medium into a potato can be described by a compartment system given by $\frac{dC_p}{dt} = k_u C_w - (k_e + k_g) C_p$, where C_p (mg kg^{-1}) is the pesticide concentration in the potato, k_u (l kg^{-1} day^{-1}) is the pesticide uptake rate by potato, k_e (day^{-1}) is the pesticide elimination rate by potato and k_g (day^{-1}) is the potato growth rate. The pesticide uptake rate was estimated supposing a passive diffusion of the pesticide by potato from soil solution with diffusion coefficient given by (Fick's second law; Trapp *et al* 2007) $k_u = \frac{23 D_p}{r^2 \rho_p K_{sw}}$, where D_p (m^2 day^{-1}) is the effective diffusion coefficient of pesticide by potato tissue, r (m) is the radius of the potato, ρ_p (kg l^{-1}) is the density of the potato and K_{sw} (dimensionless) is the soil-water partition coefficient of the pesticide. The dimensionless soil-water partition coefficient of the pesticide was calculated by $K_{sw} = \rho_s f_{oc} K_{oc} + f_w + f_a K_{aw}$. The pesticide effective diffusion coefficient by potato tissue was estimated by $D_p = p_w T_w D_w$, where T_w is a tortuosity coefficient to account for the porosity of the soil, and p_w (dimensionless) is the volumetric fraction of pesticide dissolved in the water phase of potato tissue, calculated

cadusafos	767[b]	45[b]	5.28E-05	5.30E-05	2	7943	0.0440
profenofos	2000[a]	8[a]	6.46E-07	5.31E-05	3	47863	0.0430
parathion methyl	523[c]	75[c]	1.32E-06	6.36E-05	1	724	0.0406
iprodione	700[a]	14[a]	4.79E-09	5.68E-05	2	1000	0.0368
difenoconazole	1098[b]	120[b]	3.64E-10	4.91E-05	3	19953	0.0368
phenthoate	1000[a]	35[a]	4.08E-06	5.32E-05	2	4898	0.0307
tetradifon	1794[b]	90[b]	5.90E-08	5.67E-05	3	40738	0.0292
phorate	1000[a]	60[a]	1.79E-04	5.81E-05	2	3631	0.0290
fenthion	1500[a]	34[a]	2.10E-05	5.73E-05	3	12303	0.0274
chlorothalonil	1380[a]	30[a]	1.36E-05	7.11E-05	2	1122	0.0189
chlorpyrifos	6070[a]	30[a]	3.42E-04	5.51E-05	3	91201	0.0110
fipronil	3352[c]	360[c]	3.44E-08	5.55E-05	3	10000	0.0108
mancozeb	2000[a]	70[a]	6.20E-10	7.24E-05	0.5	21	0.0089
chlorfluazuron	7457[b]	50[b]	6.04E-11	4.50E-05	3	630957	0.0088
deltamethrin	12038[a]	40[a]	2.04E-04	4.63E-05	3	1584893	0.0060
chlorfenapyr	24160[c]	360[c]	1.44E-05	5.14E-05	3	67608	0.0022
famoxadone	37760[c]	120[c]	1.86E-06	4.96E-05	3	44668	0.0013
cypermethrin	100000[a]	30[a]	1.72E-05	4.66E-05	3	3981072	0.0008
alpha-cypermethrin	108000[c]	360[c]	3.88E-04	4.66E-05	3	8709636	0.0006
lambda-cyhalothrin	180000[a]	30[a]	4.26E-05	4.48E-05	3	10000000	0.0004
beta-cyfluthrin	178600[c]	360[c]	1.17E-06	4.62E-05	3	891251	0.0004

[1]Values from (a)Hornsby *et al.* (1996), (b)PETE (Nicholls, 1994) or (c)EPI-SUITE (EPA, 2007)

[2]Values from SRC (2007); [3]Estimated by Crank (1975); [4]Values from Chiou *et al.* (2001).

In this study, the evaluated pesticides were selected through personal interviews with traditional Brazilian potato producers and were consulted on the Brazilian legally registered pesticide list for potato crop use (ANVISA, 2007). Due to the nature of the model, only pesticides with nonionic physical-chemical characteristics were selected for the simulations.

Results and Discussion

The model given by Eq. (3) was developed to estimate potato pesticide BCF of soil degrading pesticides. For that, the potato pesticide uptake and elimination rates were supposed to be driven by passive diffusion processes in both soil solution and potatoes, intermediated by the soil, water or potato pesticides sorption coefficients. Moreover, the pesticide degradation in the soil and pesticide dilution in the potatoes was supposed to be described by first order kinetic equations, Eq. (1) and Eq. (2), respectively. Thus, the model assumes that the bioconcentration factor (BCF) of pesticides in potatoes is a result of the pesticide mass balance between pesticide concentration in the soil solution and pesticide concentration in the potato.

The BCF varied between 0.0004 l kg^{-1} (alpha-cyfluthrin) and 1.3161 l kg^{-1} (methamidophos), indicating that the pesticide potato concentration is, at most, within the same concentration range or, at least, several ten-thousand times lower than the pesticide concentration in soil solution ($C_p = C_w BCF$).

In general pesticides with high soil sorption partition coefficient can be found sorbed in soil matrix making them unavailable for lixiviation or plant uptake. On the other hand, pesticides with low water solubility are theoretically the most available ones to bioconcentrate into potatoes, due to their high water diffusivity and low soil sorption partition coefficient. Apart from that, pesticides with relatively high soil half-life and low soil sorption partition coefficient are classified as potential leaching pesticides because of their GUS index values (Tables 2) (Gustafson, 1989).

Considering soil sorption partition coefficient of the pesticide, K_{oc}, and BCF values together, methamidophos, cymoxanil, imidacloprid, dimethoate, carbofuran, aldicarb, ethoprophos, cartap, metalaxyl, captan, azoxystrobin, dimethomorph, folpet, carbaryl, methidathion, triazophos and tebuconazole are the priority pesticides to be monitored in potatoes. Although Rissato *et al.* (2005) have found 0.092 mg kg^{-1} of chlorothalonil, 0.013 mg kg^{-1} of tebuconazole and 0.022 mg kg^{-1} of cypermethrin in commercial potato samples

Fig. 1 shows the relationship between $\log K_{oc}$ (the logarithm of soil sorption partition coefficient) and $\log BCF$ (the logarithm of bioconcentration factor). The empirical regression model obtained was $\log BCF = 0.85(\pm 0.05) - 0.78(\pm 0.02) \log K_{oc}$ (n = 40) with R-squared = 0.98 percent, correlation coefficient = - 0.99 and $p < 0.001$, indicating a liner regression and a negative correlation between the dependent variable ($\log BCF$) and the independent variable ($\log K_{oc}$). The logK_{oc} had good correlation with logBCF. Zohair *et al.* (2006) also pointed out that the polyaromatic hydrocarbon (PAH) BCF's in potatoes may decrease when the K_{ow} value increases, which for PAH is equivalent to the soil sorption partition coefficient increase.

Furthermore, the BCF value permits an approximation of the pesticide's daily intake (DI) per body weight by consumption of potatoes cultivated in pesticide contaminated soils, and establishing environment pesticide acceptable limits for agricultural use. For example a soil solution supposed to contain 1.0 mg kg^{-1} of methamidophos result a potato pesticide concentration of 1.3161 mg kg^{-1} ($C_p = C_w BCF$) and a daily intake of 0.0094 mg kg^{-1} (mg of methamidophos per kg body weight, considering a 70 kg b.w. person with a daily potato consumption of 0.5 kg), calculated by $DI = 0.5 \times C_p / 70$. This DI value would be 188 times higher than the reference dose (RfD) of 5.0×10^{-5} mg kg^{-1} day^{-1}, defined by EPA for methamidophos (EPA, 2007). On the overall, RfD is an estimate of human daily exposition to chemical agents that would not present a health injury risk along a lifetime and it is expressed in milligrams of chemical agents per kg body weight per day (mg kg^{-1} dia^{-1}) (EPA, 2007).

by $p_w = w_p / K_{pw}$, in which w_p is the pore water fraction in the potato tissue, D_w (m^2 day^{-1}) is the pesticide diffusivity in water or soil solution.

The pesticide elimination rate by potato was estimated supposing a passive diffusion of the pesticide by soil solution from potato with diffusion coefficient given by (Fick's second law; Trapp *et al.* 2007) $k_e = \frac{23D_p}{r^2 K_{pw}}$, where K_{pw} (dimensionless) is the potato-water partition coefficient of the pesticide estimated by equation given by (Trapp *et al* 2007) $K_{pw} = w_p + CH_p \times K_{ch} + 0.8197 \times l \times (K_{ow})^{0.77}$, where CH_p and l are the volumetric fractions of carbohydrate and lipid of the potato tissue, respectively. K_{ch} is the partition coefficient of carbohydrate-water (Chiou *et al.*, 2001).

Thus, the potato pesticide concentrations is given by equation

$$C_p(t) = \frac{k_u C_w(0)(e^{-k_s t} - e^{-(k_e+k_g)t})}{(k_e + k_g - k_s)} \tag{2}$$

The BCF (l kg^{-1}) in the steady state equilibrium was determined using equations Eq. (1) and Eq. (2) by

$$\mathrm{BCF} = \lim_{t \to \infty} \left[\frac{C_p(t)}{C_w(t)} \right] = \frac{k_u}{k_e + k_g - k_s} \tag{3}$$

The Eq. (3) demonstrates that BCF depends on the pesticide uptake rate by potato, the pesticide elimination rate by potato, potato growth rate, and pesticide degradation rate in soil. Thus, BCF depends on the potato, pesticide and soil physical-chemical characteristics.

Input date of the model

Table 1 shows the potato and soil characteristics and Table 2 shows the pesticide parameters used in the model to estimate the BCF values. The octanol-water partition coefficient were obtained in the Syracuse Research Corporation (SRC, 2007). The pesticide diffusivity in water or soil solution molar volume was estimated using the ChemSketch 5.0 computer program (Advanced Chemistry Development/ACD, Inc 2006). The soil sorption partition coefficient of the pesticide and the pesticide half-life in the soil values were obtained from Hornsby *et al.* (1996) or PETE model data base (Nicholls, 1994), or else, estimated by the EPI-SUITE system (Table 2).

Table 1. Potato plants and soil physical-chemical parameters applied to the model to estimate the bioconcentration factor of pesticides in potatoes (BCF).

Parameter	symbol	value	unit
potato water volumetric content^1	w_p	0.778	g g^{-1}
potato lipid volumetric content^1	l	0.001	g g^{-1}
potato carbohydrate volumetric content^1	CH_p	0.154	g g^{-1}
potato growth rate^1	k_g	0.139	dia^{-1}

potato density[2]	ρ_p	1.10	kg l^{-1}
average potato sphere-ray[1]	r	0.04	m
soil-organic carbon volumetric fraction[1]	f_{oc}	0.018	g g^{-1}
soil-water volumetric fraction[1]	f_w	0.28	g g^{-1}
soil-air volumetric fraction[1]	f_a	0.12	g g^{-1}
soil density on humid base[1]	ρ_w	1.95	kg l^{-1}
soil density on dry base[1]	ρ_s	1.60	kg l^{-1}

[1]Trapp *et al* (2007); [2]http://www.starch.dk/isi/starch/tm5www-potato.htm

Table 2. Pesticides and physical-chemical properties applied to the model to estimate the bioconcentration factor of pesticides in potatoes (BCF).

Pesticide	K_{oc}[1] l kg^{-1}	$t_{1/2}$[1] day	K_{aw}[2]	D_w[3] m^2 day^{-1}	K_{ch}[4]	K_{ow}[2]	BCF l kg^{-1}
methamidophos	5[a]	6[a]	2.68E-10	8.74E-05	0.1	0.16	1.3161
cymoxanil	14[b]	5[b]	1.35E-08	7.09E-05	0.2	4	0.8530
imidacloprid	11[b]	120[b]	6.77E-14	6.97E-05	0.2	4	0.8192
dimethoate	20[a]	7[a]	4.07E-09	6.59E-05	0.2	6	0.6415
carbofuran	22[a]	50[a]	1.80E-07	6.20E-05	1	209	0.6294
aldicarb	30[a]	30[a]	5.89E-08	6.61E-05	0.5	13	0.4543
ethoprophos	70[a]	25[a]	6.61E-06	5.77E-05	2	3890	0.3894
cartap	42[c]	75[c]	1.17E-12	6.47E-05	0.1	0.11	0.3193
metalaxyl	50[a]	70[a]	1.43E-08	5.34E-05	0.5	51	0.2886
captan	200[a]	3[a]	2.85E-07	6.40E-05	1	631	0.1629
azoxystrobin	143[b]	14[b]	2.99E-12	4.78E-05	1	316	0.1349
dimethomorph	182[b]	10[b]	8.24E-09	4.64E-05	1	479	0.1152
folpet	294[a]	5[a]	3.13E-06	6.72E-05	1	708	0.0913
carbaryl	300[a]	10[a]	1.34E-07	6.72E-05	1	229	0.0714
methidathion	400[a]	7[a]	2.93E-07	6.32E-05	1	158	0.0555
triazophos	504[b]	18[b]	1.25E-06	5.52E-05	2	2188	0.0549
tebuconazole	603[b]	120[b]	5.89E-09	5.11E-05	2	5012	0.0481
teflubenzuron	1237[b]	20[b]	6.48E-09	5.59E-05	3	36308	0.0465
propiconazole	650[a]	110[a]	1.67E-07	5.40E-05	2	5248	0.0461

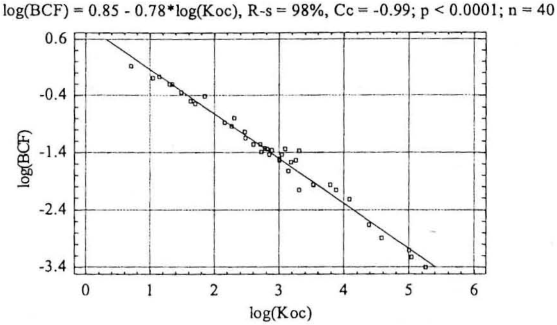

Figure 1. Linear regression for the relationship between the logarithm of soil pesticide sorption coefficient (log K_{oc}) and the logarithm of bioconcentration factor of pesticides in potatoes (log *BCF*) estimated by the potato pesticide bioconcentration model.

Therefore, potatoes treated with pesticides must be monitored for pesticide concentration and, in theory, when consumed they should not present pesticide concentrations above the RfD value. Or, for instance, soil methamidophos concentrations higher than 5.3×10^{-3} mg kg^{-1} ($C_{w-estimated} = 70\times \mathrm{RfD}/(0.5\times \mathrm{BCF})$) should be avoided, because such values might result in potato pesticide concentrations which are higher than the methamidophos RfD value. Wu *et al.* (2001) reported three clinical cases of human poisoning caused by consumption of methamidophos-contaminated vegetables, including sweet-potatoes. It is important to point out that the pesticide BCF values from Table 2 ($\log K_{ow} \geq 4.0$) are in the same BCF value range of the polyaromatic hydrocarbons (PAH) ($\log K_{ow} \geq 4.0$) experimentally observed in potatoes by Fismes *et al.* (2002) and Samsoe-Petersen *et al.* (2002).

Conclusions

A potato pesticide bioconcentration model is presented to estimate the BCF values of soil degrading nonionic pesticides. The BCF model expression depends directly on the potato pesticide uptake rate, and inversely, on the potato pesticide elimination rate, potato growth rate, and soil pesticide degrading rate. By means of the potato pesticide bioconcentration factor and the pesticide water solubility, it is possible to point out the existence of a negative linear correlation between the logarithms of the pesticide water solubility and BCF. The potato BCF were estimated for about 40 pesticides and a priority pesticide group was suggested to be monitored in potatoes. The pesticide daily intake by potato consumption estimate, the establishment of soil pesticide safe limits for potato cropping and the selection of pesticides for potato sample monitoring can be accomplished using the bioconcentration factor values. Mathematical models can contribute to forecasting pesticide concentrations and suggesting which pesticides should have priority and which should be systematically monitored in potato samples. Field and laboratory experiments must be conducted in order to test and validate the present model.

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