Chemosphere 73 (2008) 1247–1252

Contents lists available at ScienceDirect

Chemosphere

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

Model approach for estimating potato pesticide bioconcentration factor

Lourival Costa Paraíba [a,*], Karen Kataguiri [b]

[a] *Embrapa Meio Ambiente, Embrapa Environment, CxP. 69, CEP 13820-000, Jaguariúna, São Paulo, Brazil*
[b] *Faculdade de Engenharia Ambiental, Universidade Estadual de São Paulo, UNESP. Av. Três de Março, n.511, 18087-180, Sorocaba, São Paulo, Brazil*

ARTICLE INFO

Article history:
Received 11 February 2008
Received in revised form 11 July 2008
Accepted 14 July 2008
Available online 26 August 2008

Keywords:
BCF
Daily ingestion
Bioaccumulation
Food diet
Insecticide
Fungicide

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. [Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in potato and carrot slices and application for a potato model. Environ. Sci. Technol. 41 (9), 3103–3108], 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. [Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in potato and carrot slices and application for a potato model. Environ. Sci. Technol. 41 (9), 3103–3108] the hypothesis that the pesticide degrades in the soil. The value of BCF suggests which pesticides should be monitored in potatoes.

1. Introduction

Potato plants 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. In Brazil, the potato is pointed out as the main root tuber, with a cultivated area larger than one hundred and forty thousand hectares. The production in 2005 was of two million tons IBGE (2008). 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 (Caldas et al., 2004; López-Pérez et al., 2006; Leistra and Van Den Berg, 2007). 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.

Potatoes are low in fat and are rich in several micronutrients. Sized potato of 150 g provides nearly half the daily adult requirement (100 mg). They are a moderate source of iron, and its high vitamin C content promotes iron absorption and a good source of vitamins B1, B3 and B6 and minerals such as potassium, phosphorus and magnesium, and contains folate, pantothenic acid and riboflavin. Potatoes also contain dietary antioxidants, which may play a part in preventing diseases related to ageing, and dietary fiber, which benefits health. 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% of the potato crop can be used for human consumption, significantly more than for cereals like corn and wheat.

The bioconcentration of a substance in an organism is a process that describes the increase of the concentration of the substance in the organism in relation to the concentration of the substance in the medium. The bioconcentration factor (BCF) of a substance in an organism is a numeric value that measures the bioconcentration

---

* Corresponding author. Tel.: +55 19 33 11 2667; fax: +55 19 33 11 2640.
E-mail address: lourival@cnpma.embrapa.br (L.C. Paraíba).

0045-6535/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2008.07.026

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. As in every partition coefficient, the BCF does not also depend on dose or on the concentration in medium**,** and should always be estimated by the limit in time of the quotient between the concentration of the substance in the organism and the concentration of the substance in medium (EPA, 1996; Paraíba, 2007). When the organisms are cultivated foods, BCF permits an approximation of the pesticide's daily ingestion through its food consumption and establishes safe limits for pesticide concentrations in medium and indicates which pesticides should be monitored in the food.

A classic experimental procedure used to estimate a pesticide BCF in fish consists of exposing a fish test group to a constant pesticide concentration in the water, until the quotient between the concentration of the pesticide in the fish and the concentration of the pesticide in the water reaches a steady state, this is the accumulation phase, that is followed by an elimination phase of the pesticide in which the previously contaminated fish are put in clean water and the pesticide concentrations are monitored. The experimental data concentrations obtained in both phases make it possible to calculate BCF by the quotient between the pesticide accumulation and elimination rates (OECD, 1996). However, this procedure presents two main difficulties: keeping a constant concentration in water during the accumulation phase, and previously determining the time required to reach the steady state. The difficulties are even greater when the organisms are potato plants. It is not easy to maintain a constant concentration in the soil and later transport the contaminated potato plants to an appropriate pesticide-free soil.

Most pesticides have a low or moderate persistence in the soil, when compared with persistent organic pollutants. For this reason, a model that takes into account that a constant concentration of pesticides in the soil is not, in itself, adequate to estimate BCF in potatoes of pesticides degrading in the soil. The experimental procedure, and respective mathematical model, must not only incorporate the degradation of the pesticide in the soil, it must also describe a hypothetical situation in which it's not necessary to accomplish the transplant of polluted potatoes to a pesticide free soil. The model should also simulate concentrations of pesticides in the soil solution and in the potato, so that these can be used to estimate the BCF, calculating the quotient's steady state between the concentrations in the potato and in the soil solution.

Several studies indicate the presence of pesticides and organic substances in potatoes (Dogheim et al., 2002; Fismes et al., 2002; Samsoe-Petersen et al., 2002; Jensen et al., 2003; Poulsen and Andersen, 2003; Rissato et al., 2005; 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 work of Trapp et al. (2007) suggests that the mass transfer through the potato tissue occurs predominantly by the soil solution. 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.

2. Materials and methods

Pesticide concentration in the soil surrounding the potato was taken into account describing the equation below

$$C_s(t) = C_s(0)e^{-k_s t} \tag{1}$$

where C_s (mg kg^{-1}) is the pesticide concentration in soil, $C_s(0)$ (mg kg^{-1}) is the initial pesticide concentration in soil and k_s (day^{-1}) is the pesticide degradation rate in the soil estimated by, $k_s = 0.693/t_{1/2}$, in which $t_{1/2}$ (day) is the half-life pesticide in the soil.

From the pesticide concentration in the soil, Eq. (1), the pesticide concentration in the soil solution was estimated by

$$C_w(t) = \frac{\rho_w C_s(0)e^{-k_s t}}{(\rho_s f_{oc} K_{oc} + f_w + f_a K_{aw})} \tag{2}$$

where 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. 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 estimated by

$$K_{aw} = \frac{P_v \times P_m}{S \times R \times (273 + T)} \tag{3}$$

where (T = 25 °C) is the air temperature (R = 8.314 Pa m^3 mol^{-1} T^{-1}) is the gas constant, P_v (Pa) is the pesticide vapor pressure, P_m (g mol^{-1}) is the pesticide molar mass and S (g m^{-3}) is the pesticide water solubility.

The uptake and elimination of pesticides from surrounding medium into a potato can be described by a compartment system given by

$$\frac{dC_p}{dt} = k_u C_w - (k_e + k_g)C_p \tag{4}$$

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)

$$k_u = \frac{23 D_p}{r^2 \rho_p K_{sw}} \tag{5}$$

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 potato density is necessary to correctly define the pesticide uptake rate with unity of L kg^{-1} day^{-1} and to produce the bioconcentration factor with units of L kg^{-1}, and also, the pesticide uptake rate is inversely proportional to the potato's density (Crank, 1975). The dimensionless soil–water partition coefficient of the pesticide was calculated by

$$K_{sw} = \rho_s f_{oc} K_{oc} + f_w + f_a K_{aw} \tag{6}$$

The pesticide effective diffusion coefficient by potato tissue was estimated by

$$D_p = p_w T_w D_w \tag{7}$$

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 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 estimated by

$$D_{\mathrm{w}} = \frac{4.93 \times 10^{-6} T \sqrt{\phi_{\mathrm{w}} w_{\mathrm{m}}}}{\mu_{\mathrm{w}} (v_{\mathrm{m}})^{0.6}} \tag{8}$$

where $\varphi_w = 2.6$ is an association term for the solvent (water), $w_m = 18\ \mathrm{g\ mol^{-1}}$ is the molar mass of the water, $\mu_w = 8.9 \times 10^{-1}$ cp is the water viscosity, and v_m ($\mathrm{cm^3\ mol^{-1}}$) is the molar volume of the pesticide (Clark, 1996).

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)

$$k_{\mathrm{e}} = \frac{23 D_{\mathrm{p}}}{r^2 K_{\mathrm{pw}}} \tag{9}$$

where K_{pw} (dimensionless) is the potato–water partition coefficient of the pesticide estimated by equation given by (Trapp et al., 2007)

$$K_{\mathrm{pw}} = w_{\mathrm{p}} + \mathrm{CH_p} \times K_{\mathrm{ch}} + 0.8197 \times l \times (K_{\mathrm{ow}})^{0.77} \tag{10}$$

where $\mathrm{CH_p}$ 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 can be given by the equations

$$C_{\mathrm{p}}(t) = \begin{cases} \frac{C_{\mathrm{w}}(0) k_{\mathrm{u}} (\mathrm{e}^{-k_{\mathrm{s}} t} - \mathrm{e}^{-(k_{\mathrm{e}} + k_{\mathrm{g}}) t})}{(k_{\mathrm{e}} + k_{\mathrm{g}} - k_{\mathrm{s}})} & \text{if} \quad k_{\mathrm{e}} + k_{\mathrm{g}} \neq k_{\mathrm{s}} \ \text{case 1a} \\ C_{\mathrm{w}}(0) k_{\mathrm{u}} t \mathrm{e}^{-k_{\mathrm{s}} t} & \text{if} \quad k_{\mathrm{e}} + k_{\mathrm{g}} = k_{\mathrm{s}} \ \text{case 2a} \end{cases} \tag{11}$$

The BCF ($\mathrm{L\ kg^{-1}}$) in the steady state equilibrium can be determined using Eqs. (2) and (11) by

$$\mathrm{BCF} = \lim_{t \to \infty} \left[\frac{C_{\mathrm{p}}(t)}{C_{\mathrm{w}}(t)} \right] = \begin{cases} \frac{k_{\mathrm{u}}}{k_{\mathrm{e}} + k_{\mathrm{g}} - k_{\mathrm{s}}} & \text{if} \quad k_{\mathrm{e}} + k_{\mathrm{g}} > k_{\mathrm{s}} \ \text{case 1b} \\ +\infty & \text{if} \quad k_{\mathrm{e}} + k_{\mathrm{g}} \leqslant k_{\mathrm{s}} \ \text{case 2b} \end{cases} \tag{12}$$

that is, $\mathrm{BCF}(t) = C_p(t)/C_w(t)$ converges to a steady state as time tends to infinity if, and only if $k_e + k_g > k_s$, Eq. (12 – case 1b). Eq. (12 – case 1b) demonstrates that finite BCF values depend 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. In this paper we are assuming that $k_e + k_g > k_s$, Eq. (11 – case 1a) and Eq. (12 – case 1b).

It is important to observe that the condition $\mathrm{d}C_p/\mathrm{d}t = 0$ frequently used to estimate the steady state of equation Eq. (4) is true if, and only if the pesticide concentration in the medium is constant, in this case, $\mathrm{BCF} = \frac{k_u}{k_e + k_g}$. When the soil pesticide concentration is not constant the $\mathrm{d}C_p/\mathrm{d}t = 0$ determines an unstable equilibrium point of the $C_p = C_p(t)$.

Eq. (11 – case 1a) was used to estimate the required time to obtain the maximum pesticide concentration in the potato by $t_{\max} = \frac{\ln(k_e + k_g) - \ln(k_s)}{k_e + k_g - k_s}$. The maximum pesticide concentration in potato was estimated by $C_p^{\max} = C_p(t_{\max})$ ($\mathrm{mg\ L^{-1}}$).

2.1. 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, water solubility, vapor pressure and molecular mass were obtained in the Syracuse Research Corporation (SRC, 2007). The 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). The EPI (Estimation Programs Interface) EPI Suite™ is a Windows® based suite of physical–chemical property and environmental fate estimation models developed by the United States Environmental Protection Agency's Office of Pollution Prevention Toxics and Syracuse Research Corporation (http://www.epa.gov/opptintr/exposure/docs/episuite.htm).

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[a]	w_p	0.778	$\mathrm{g\ g^{-1}}$
Potato lipid volumetric content[a]	l	0.001	$\mathrm{g\ g^{-1}}$
Potato carbohydrate volumetric content[a]	$\mathrm{CH_p}$	0.154	$\mathrm{g\ g^{-1}}$
Potato growth rate[a]	k_g	0.139	$\mathrm{day^{-1}}$
Potato density[b]	ρ_p	1.10	$\mathrm{kg\ L^{-1}}$
Average potato sphere-ray[a]	r	0.04	m
Soil-organic carbon volumetric fraction[a]	f_{oc}	0.018	$\mathrm{g\ g^{-1}}$
Soil–water volumetric fraction[a]	f_w	0.28	$\mathrm{g\ g^{-1}}$
Soil–air volumetric fraction[a]	f_a	0.12	$\mathrm{g\ g^{-1}}$
Soil density on humid base[a]	ρ_w	1.95	$\mathrm{kg\ L^{-1}}$
Soil density on dry base[a]	ρ_s	1.60	$\mathrm{kg\ L^{-1}}$

[a] Trapp et al. (2007).

[b] http://www.starch.dk/isi/starch/tm5www-potato.htm.

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.

3. Results and discussion

The model given by Eq. (12 – case 1b)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, Eqs. (1) and (4), 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 pesticide lixiviation potential can be estimated through the empirical GUS index calculus, given by, $\mathrm{GUS} = (4 - \log K_{oc}) \times \log t_{1/2}$. Depending on the GUS index numerical value, the pesticide is classified as a leaching potential ($\mathrm{GUS} \geqslant 2.8$), a non-leaching potential ($\mathrm{GUS} \leqslant 1.8$) or an undetermined leaching potential pesticide (transient) ($1.8 \leqslant \mathrm{GUS} \leqslant 2.8$) (Gustafson, 1989).

Six of the fifty studied pesticides (12%) are potentially leaching pesticides. Thirty four (68%) are potential non-leaching pesticides. And 10 (20%) are transient or of undetermined leaching potential which means they might or might not be leaching pesticides (Table 3). The BCF varied between $0.0004\ \mathrm{L\ kg^{-1}}$ (α-cyfluthrin) and $1.3161\ \mathrm{L\ kg^{-1}}$ (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 ($C_p = C_w\mathrm{BCF}$).

Eq. (12 – case 1b) does not describe a first-order kinetics uptake and elimination process of pesticide for potato, but allows estimating the time in which the potato pesticide concentration is maximum, $t_{\max}$ (days), and the maximum potato pesticide concentration $C_p(t_{\max})$. An initial soil solution pesticide concentration of $1.0\ \mathrm{mg\ L^{-1}}$ ($C_w(0) = 1.0\ \mathrm{mg\ L^{-1}}$) would result in a potato concentration in $t_{\max}$ those are given in Table 3. Such values ($t_{\max}$ and $C_p(t_{\max})$) will provide information for planning potato

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

Pesticide	Molar mass^{A} (g mol^{-1})	Vapor pressure^{A} (Pa)	Water solubility^{A} (g m^{-3})	log K_{ow}^{A}	K_{oc}^{B} (L kg^{-1})	Half-life^{B} (days)	K_{ch}^{C}
Aldicarb	190.27	4.63E−03	6030	1.13	30^{a}	30^{a}	0.50
α-Cypermethrin	416.31	2.31E−05	0.01	6.94	108000^{c}	360^{c}	3.00
Azoxystrobin	403.40	1.10E−10	6	2.50	143^{b}	14^{b}	1.00
β-Cyfluthrin	434.30	2.00E−08	0.003	5.95	178600^{c}	360^{c}	3.00
Cadusafos	270.40	1.20E−01	248	3.90	767^{b}	45^{b}	2.00
Captan	300.59	1.20E−05	5.10	2.80	200^{a}	3^{a}	1.00
Carbaryl	201.23	1.81E−04	110	2.36	300^{a}	10^{a}	1.00
Carbofuran	221.26	6.47E−04	320	2.32	22^{a}	50^{a}	1.00
Cartap	273.81	9.40E−07	89100	−0.95	42^{c}	75^{c}	0.10
Chlorfenapyr	407.62	9.81E−06	0.11	4.83	24160^{c}	360^{c}	3.00
chlorfluazuron	540.66	1.21E−12	0.0044	5.80	7457^{b}	50^{b}	3.00
Chlorothalonil	265.91	7.60E−05	0.60	3.05	1380^{a}	30^{a}	2.00
Chlorpyrifos	350.59	2.71E−03	1.12	4.96	6070^{a}	30^{a}	3.00
Cymoxanil	198.18	1.51E−04	890	0.59	14^{b}	5^{b}	0.20
Cypermethrin	416.31	4.09E−07	0.004	6.60	100000^{a}	30^{a}	3.00
Deltamethrin	505.21	2.00E−06	0.002	6.20	12038^{a}	40^{a}	3.00
Difenoconazole	406.27	3.33E−08	15	4.30	1098^{b}	120^{b}	3.00
Dimethoate	229.26	1.10E−03	25000	0.78	20^{a}	7^{a}	0.20
Dimethomorph	387.87	9.84E−07	18.70	2.68	182^{b}	10^{b}	1.00
Ethion	384.48	2.00E−04	2	5.07	10000^{a}	150^{a}	3.00
Ethoprophos	242.34	5.07E−02	750	3.59	70^{a}	25^{a}	2.00
Famoxadone	374.40	6.40E−07	0.05	4.65	37760^{c}	120^{c}	3.00
Fenamiphos	277.24	7.20E−03	38	3.30	2000^{a}	4^{a}	2.00
Fenthion	278.33	1.40E−03	7.50	4.09	1500^{a}	34^{a}	3.00
Fipronil	437.15	3.71E−07	1.90	4.00	3352^{c}	360^{c}	3.00
Fludioxonil	248.19	3.91E−07	1.80	4.12	998^{b}	150^{b}	3.00
Folpet	296.56	2.09E−05	0.80	2.85	294^{a}	5^{a}	1.00
Imidacloprid	255.67	4.00E−10	610	0.57	11^{b}	120^{b}	0.20
Iprodione	330.17	5.00E−07	13.90	3.00	700^{a}	14^{a}	2.00
λ-Cyhalothrin	449.86	2.00E−07	0.0009	7.00	180000^{a}	30^{a}	3.00
Lufenuron	511.16	1.11E−08	0.06	5.12	3303^{b}	15^{b}	3.00
Mancozeb	541.03	1.76E−08	6.20	1.33	2000^{a}	70^{a}	0.50
Metalaxyl	279.34	3.31E−03	26000	1.71	50^{a}	70^{a}	0.50
Methamidophos	141.13	4.71E−03	1000000	−0.80	5^{a}	6^{a}	0.10
Methidathion	302.33	4.49E−04	187	2.20	400^{a}	7^{a}	1.00
Parathion methyl	263.21	4.67E−04	37.70	2.86	523^{c}	75^{c}	1.00
Pencycuron	328.85	5.00E−10	0.30	4.82	8791^{c}	75^{c}	3.00
Phenthoate	320.37	3.47E−04	11	3.69	1000^{a}	35^{a}	2.00
Phorate	260.38	8.51E−02	50	3.56	1000^{a}	60^{a}	2.00
Procymidone	284.14	1.87E−02	4.50	3.08	1500^{a}	7^{a}	2.00
Profenofos	373.64	1.20E−04	28	4.68	2000^{a}	8^{a}	3.00
Propiconazole	342.23	1.33E−04	110	3.72	650^{a}	110^{a}	2.00
Prothiofos	345.25	1.25E−03	0.07	5.67	6382^{b}	35^{b}	3.00
Quintozene	295.34	6.67E−03	0.44	4.64	2252^{b}	200^{b}	3.00
Tebuconazole	307.83	1.71E−06	36	3.70	603^{b}	120^{b}	2.00
Teflubenzuron	381.12	8.00E−10	0.02	4.56	1237^{b}	20^{b}	3.00
Tetradifon	356.06	3.20E−08	0.08	4.61	1794^{b}	90^{b}	3.00
Tolylfluanid	347.26	2.00E−04	0.90	3.90	1728^{c}	120^{c}	2.00
Triazophos	313.32	3.87E−04	39	3.34	504^{b}	18^{b}	2.00
Triflumuron	358.71	4.00E−08	0.03	4.91	2569^{b}	40^{b}	3.00

[A] Values from SRC (2007).
[B] Values from [a]Hornsby et al. (1996) or [b]PETE (Nicholls, 1994) or estimated by [c]EPI-Suite (http://www.epa.gov/opptintr/exposure/docs/episuite.htm).
[C] Chiou et al. (2001).

pesticide monitoring programs regarding maximum allowed concentrations of pesticide would also be helpful for establishing safe strategies for potato crop management in a contaminated soil with pesticides.

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 high 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 (Table 3).

Considering the GUS index, soil sorption partition coefficient of the pesticide, K_{oc} and BCF values all together, methamidophos, cymoxanil, imidacloprid, dimethoate, carbofuran, aldicarb, ethoprophos, cartap, metalaxyl, fenamiphos, azoxystrobin, tebuconazole, propiconazole, cadusafos, fludioxonil, parathion methyl and difenoconazole 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, such pesticide concentrations probably occurred because of the high pesticide concentrations in soil solution estimated by ($C_w = C_p/\mathrm{BCF}$) ($C_{\mathrm{tebuconazole}} = 0.27$ mg L^{-1}; $C_{\mathrm{chlorothalonil}} = 4.87$ mg L^{-1}; $C_{\mathrm{cypermethrin}} = 27.5$ mg L^{-1}), which was not experimentally verified by Rissato et al. (2005).

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 $\log \mathrm{BCF} = 0.85(\pm 0.06) - 0.78(\pm 0.02)\ \log K_{oc}$ ($n = 50$) with *R*-squared = 0.97%, correlation coefficient = −0.98 and $p < 0.001$, indi-

Table 3
Bioconcentration factor (BCF), time of the maximum potato pesticide concentration t_{max}, maximum potato pesticide concentration $C_p(t_{max})$, GUS index and lixiviation classes

Pesticide	BCF ($L\ kg^{-1}$)	t_{max} (days)	$C_p(t_{max})$ $C_w(0) = 1.0\ mg\ L^{-1}$	GUS	Lixiviation class
Methamidophos	1.3161	2	0.8837	2.57	Transient
Cymoxanil	0.8530	3	0.4982	1.99	Transient
Imidacloprid	0.8192	6	0.7855	6.15	Leaching
Dimethoate	0.6415	3	0.4162	2.28	Transient
Carbofuran	0.6294	6	0.5650	4.52	Leaching
Aldicarb	0.4543	5	0.3942	3.73	Leaching
Ethoprophos	0.3894	7	0.2965	3.01	Leaching
Cartap	0.3193	6	0.2994	4.46	Leaching
Metalaxyl	0.2886	7	0.2657	4.25	Leaching
Fenamiphos	0.2283	8	0.1966	3.40	Leaching
Captan	0.1629	3	0.0553	0.81	Non-leaching
Azoxystrobin	0.1349	5	0.0947	2.11	Transient
Dimethomorph	0.1152	5	0.0714	1.74	Non-leaching
Folpet	0.0913	3	0.0460	1.07	Non-leaching
Carbaryl	0.0714	4	0.0493	1.52	Non-leaching
Methidathion	0.0555	3	0.0335	1.18	Non-leaching
Triazophos	0.0549	6	0.0393	1.63	Non-leaching
Tebuconazole	0.0481	12	0.0441	2.54	Transient
Teflubenzuron	0.0465	10	0.0280	1.18	Non-leaching
Propiconazole	0.0461	12	0.0421	2.42	Transient
Cadusafos	0.0440	10	0.0359	1.84	Transient
Fludioxonil	0.0432	13	0.0400	2.18	Transient
Profenofos	0.0430	7	0.0134	0.63	Non-leaching
Parathion methyl	0.0406	7	0.0374	2.40	Transient
Iprodione	0.0368	5	0.0254	1.32	Non-leaching
Difenoconazole	0.0368	16	0.0328	1.99	Transient
Phenthoate	0.0307	9	0.0245	1.54	Non-leaching
Tetradifon	0.0292	16	0.0250	1.46	Non-leaching
Phorate	0.0290	9	0.0254	1.78	Non-leaching
Fenthion	0.0274	10	0.0209	1.26	Non-leaching
Quintozene	0.0262	18	0.0243	1.49	Non-leaching
Triflumuron	0.0242	14	0.0173	0.95	Non-leaching
Lufenuron	0.0224	11	0.0100	0.57	Non-leaching
Procymidone	0.0203	4	0.0110	0.70	Non-leaching
Tolylfluanid	0.0195	12	0.0178	1.59	Non-leaching
Chlorothalonil	0.0189	6	0.0158	1.27	Non-leaching
Prothiofos	0.0124	15	0.0080	0.30	Non-leaching
Chlorpyrifos	0.0110	13	0.0072	0.32	Non-leaching
Fipronil	0.0108	17	0.0104	1.21	Non-leaching
Mancozeb	0.0089	6	0.0084	1.29	Non-leaching
Chlorfluazuron	0.0088	18	0.0063	0.22	Non-leaching
Pencycuron	0.0062	17	0.0051	0.10	Non-leaching
Deltamethrin	0.0060	17	0.0039	−0.13	Non-leaching
Ethion	0.0056	21	0.0050	0.00	Non-leaching
Chlorfenapyr	0.0022	24	0.0021	−0.98	Non-leaching
Famoxadone	0.0013	18	0.0011	−1.20	Non-leaching
Cypermethrin	0.0008	15	0.0005	−1.48	Non-leaching
α-Cypermethrin	0.0006	31	0.0006	−2.64	Non-leaching
λ-Cyhalothrin	0.0004	15	0.0002	−1.85	Non-leaching
β-Cyfluthrin	0.0004	30	0.0003	−3.20	Non-leaching

cating a liner regression and a negative correlation between the dependent variable (log BCF) and the independent variable (log K_{oc}). log K_{oc} had good correlation with log BCF. 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 body weight person with a daily potato consumption of 0.5 kg), calculated by DI = 0.5 × 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, http://www.epa.gov/iris/subst/0250.htm). 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} day^{-1}) (EPA, 2007).

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 3 (log $K_{ow} \geqslant 4.0$) are in the same BCF value range of the polyaromatic hydrocarbons (PAH)

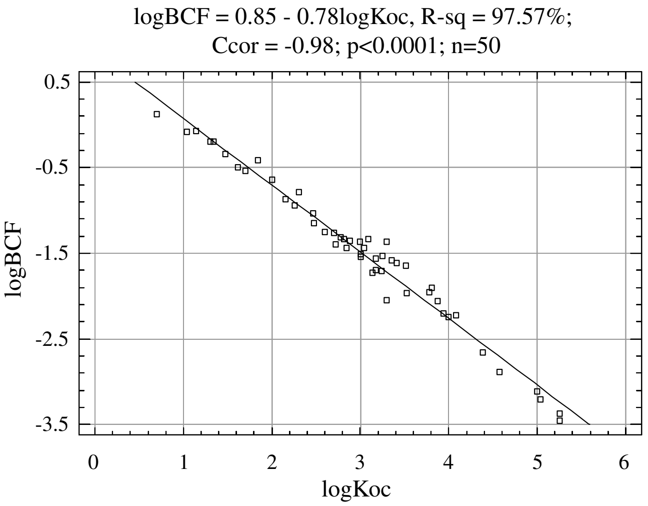

Fig. 1. Linear regression equation for the relationship between the logarithm of soil pesticide sorption coefficient ($\log K_{oc}$) and the logarithm of bioconcentration factor of pesticides in potatoes (log BCF) estimated by the potato pesticide bioconcentration model.

($\log K_{ow} \geqslant 4.0$) experimentally observed in potatoes by Fismes et al. (2002) and Samsoe-Petersen et al. (2002). No other experimental potato pesticide BCF values have been reported.

4. 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 soil sorption partition coefficient, it is possible to point out the existence of a negative linear correlation between the logarithms of the soil sorption partition coefficient and the logarithms of BCF. The potato BCF were estimated for about 50 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.

Acknowledgements

Financial support for this research was provided by Embrapa (*Empresa Brasileira de Pesquisa Agropecuária*) Grant Number MP3/03065100001, Fapesp (*Fundação de Amparo á Pesquisa do Estado de São Paulo*) Grant Number 2007/44280-8, and CNPq for the researcher formation of scientific initiation scholarship PIBIC (119791/2007-2) and EMBRAPA (800002/1996-2).

References

ACD/ChemSketch Freeware, version 5.0, Advanced Chemistry Development, Inc., Toronto, ON, Released in: 2006. <http://www.acdlabs.com> (accessed 30.09.07).

ANVISA (Agência Nacional de Vigilância Sanitária), 2007. Agrotóxicos e Toxicologia: monografias de produtos agrotóxicos. <http://www.anvisa.gov.br/toxicologia/monografias/index.htm> (accessed 20.08.07).

Caldas, E.D., Miranda, M.C.C., Conceição, M.H., Souza, L.C.K.R., 2004. Dithiocarbamates residues in Brazilian food and the potential risk for consumers. Food Chem. Toxicol. 42 (11), 1877–1883.

Cesnik, H.B., Gregorcic, A., Bolta, S.V., Kmecl, V., 2006. Monitoring of pesticide residues in apples, lettuce and potato of the Slovegne origin, 2001–04. Food Addit. Contam. 23 (2), 164–173.

Chiou, C.T., Sheng, G., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environ. Sci. Technol. 35 (7), 1437–1444.

Clark, M.M., 1996. Transport Modeling for Environmental Engineers and Scientists. Wiley-Interscience Publication, New York.

Crank, J., 1975. The mathematics of diffusion, second ed. Clarendon Press, Oxford. p. 414.

Dogheim, S.M., El-Marsafy, A.M., Salama, E.Y., Gadalla, A.S., Nabil, Y.M., 2002. Monitoring of pesticide residues in Egyptian fruits and vegetables during 1997. Food Addit. Contam. 19 (11), 1015–1027.

EPA, 1996. Ecological Effects Test Guidelines: OPTS 850.730 Fish BCF. EPA, Washington, DC.

Fismes, J., Perrin-Ganier, C., Empereur-Bissonnet, P., Morel, J.L., 2002. Soil-to-root transfer and translocation of polycyclic aromatic hydrocarbons by vegetables grown on industrial contaminated soils. J. Environ. Qual. 31, 1649–1656.

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

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

IBGE (Fundação Instituto Brasileiro de Geografia e Estatística), 2008. Produção Vegetal. Anu Estat Brasil. <http://www.ibge.gov.br/home/>.

Jensen, A.F., Petersen, A., Granby, K., 2003. Cumulative risk assessment of the intake of organophosphorus and carbamate pesticides in the Danish diet. Food Addit. Contam. 20 (8), 776–785.

Leistra, M., Van Den Berg, F., 2007. Volatilization of parathion and chlorothalonil from a potato crop simulated by the PEARL model. Environ. Sci. Technol. 41 (7), 2243–2248.

López-Pérez, G.C., Arias-Estévez, M., López-Periago, E., Soto-González, B., Cancho-Grande, B., Simal-Gándara, J., 2006. Dynamics of pesticides in potato crops. J. Agric. Food Chem. 54, 1797–1803.

Nicholls, P.H., 1994. Physicochemical evaluation: the environment, and expert system for pesticide preregistration assessment. In: Proc. meet Brighton Crop Protection Conference: Pests and Diseases. (Organised by) British Crop Protection Council, Brighton, England, vol. 3, pp. 1337–1342.

OECD (Organization for Economic Cooperation and Development), 1996. Bioconcentration: flow-through fish test. OECD guidelines for the testing chemicals n 305, Paris, France.

Paraíba, L.C., 2007. Pesticide bioconcentration modelling for fruit trees. Chemosphere 66 (8), 1468–1475.

Poulsen, M.E., Andersen, J.H., 2003. Results from the monitoring of pesticide residues in fruit and vegetables on the Danish market, 2000–01. Food Addit. Contam. 20 (8), 742–757.

Rissato, S.R., Galhiane, M.S., Apon, B.M., 2005. Development of a supercritical fluid extraction method for simultaneous determination of organophosphorus, organohalogen, organonitrogen and pyretroids pesticides in fruit and vegetables and its comparison with a conventional method by GC–ECD and GC–MS. J. Braz. Chem. Soc. 16 (5), 1038–1047.

Samsoe-Petersen, L., Larsen, E.H., Larsen, P.B., Bruun, P., 2002. Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils. Environ. Sci. Technol. 36 (14), 3057–3063.

SRC (Syracuse Research Corporation), 2007. <http://www.syrres.com/esc/physdemo.htm> (accessed 20.08.07).

Trapp, S., Cammarano, A., Capri, E., Reichenberg, F., Mayer, P., 2007. Diffusion of PAH in Potato and carrot slices and application for a potato model. Environ. Sci. Technol. 41 (9), 3103–3108.

Wu, M.L., Deng, J.F., Tsai, W.J., Ger, J., Wong, S.S., Li, H.P., 2001. Food poisoning due to methamidophos-contaminated vegetables. J. Toxicol. Clin. Toxicol. 39 (4), 333–336.

Zohair, A., Salim, A.B., Soyibo, A.A., Beek, A.J., 2006. Residues of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides in organically-farmed vegetables. Chemosphere 63 (4), 541–553.