PESTICIDE BIOCONCENTRATION FACTOR ESTIMATE IN APPLES

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Abstract

This work objective was to estimate the bioconcentration factor (BCF) of thirty six pesticides used in the Brazilian integrated apple production systems (IAP), in order to select priority pesticides to be monitored in apples. A hypothetical apple orchard was assumed and the model applied was according to Paraíba (2007) [Pesticide bioconcentration modeling for fruit trees. Chemosphere (66:1468-1475)]. The model relates BCF with plant and pesticide characteristics. The octanol-water partition coefficients of pesticides and their degradation rates in the soil were used. The following plant variables were considered: growth rate, total dry biomass, daily water transpiration rate, and total volume of water necessary to produce one kg of fresh fruit per plant. The pesticide stem-water partition coefficient and the transpiration stream concentration factor were calculated using equations that relate each coefficient with the octanol-water partition coefficient. The pesticide BCF in fruits is an important indicator of the pesticide affinity to fruits, and helps to improve the integrated production systems.

Key words: *Malus domestica*, fungicides, insecticides, IAP, integrated production systems, fruits.

Introduction

Fruits are worldwide enjoyed by people for their flavor, aroma, color, form and nutritional values and consumed in natura or as processed food. The temperate climate regions provide adequate conditions to cultivate several fruit species, but also favor the proliferation of many organisms that negatively affect orchards and their economical production. For instance, a certain combination of air temperature and humidity induces several pathogenic fungi species to appear, causing fruit production decrease. For this reason, all over the world's temperate regions, marketable orchards are cultivated with the aid of pesticides.

Brazil is among the world nation's greater consumers and exporters of fresh fruits and fruit juices, but it is also ranked among the ten greatest pesticide users (Armas *et al.*, 2005). The Brazilian government is concerned about the fruit quality offered to the internal and external market. Therefore, the Brazilian government actions are within the expectations of Brazilian and foreign consumers of fresh fruits and derivates. As for instance, the 91/414/EEC directive of the European Economic Community (EEC) establishes which pesticides are authorized for the EEC use to produce plants and the pesticide residue limit values for agricultural vegetal products. Therefore, the EEC imposes sanitary constraints for vegetal products from internal or foreign origin, because they must be within adequate requirements for the population consumption.

It is evident that the use of pesticides in fruit production increases fruit yielding, and also the potential consumption of fruits and derivates. However, consumers need to be informed about the risks of consuming fruits from production fields managed with pesticides. In the integrated production system, a list of recommended pesticides and technical procedures for application and monitoring are always suggested, aiming at reducing risks of food and environmental contamination. Nevertheless, managers, technicians, administrators and researchers involved in the integrated production systems ought to have the know-how to estimate the pesticide cumulative potential in fruits in order to monitor and suggest new technologies for a sustainable fruit production.

Mathematical models can contribute to predict the substance uptake by plants and can be used to indicate which substances must be monitored in vegetal product samples of Good Agricultural Practices Programs (GAPs). Several models have been developed with such objectives and among them the following works are mentioned: Fujisawa *et al.* (2002), Trapp *et al* (2003), Trapp (2004), McKone and Maddalena (2007), Trapp, (2007) and Paraíba (2007).

An organism substance bioconcentration describes the increase in the organism substance concentration in relation to the substance concentration in the medium. The organism substance bioconcentration factor (BCF) is a number that expresses the bioconcentration process and it represents the substance partition coefficient between the organism and the medium. In the chemical equilibrium state, this coefficient is the quotient between the substance concentration in the organism and the medium. According to Paraíba (2007), the BCF is determined by the limit quotient between the substance concentration in the organism and the medium, when time tends to infinite. A pesticide BCF in apples is an important indicator of the apple-pesticide affinity and it might allow selecting pesticides to be monitored and help to improve the integrated apple production systems.

Therefore, this work objective was to estimate thirty six pesticide BCF in apples, used in the Brazilian integrated apple production systems (IAP) and indicate the priority pesticides to be monitored. For that, a hypothetical apple orchard was assumed,

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cultivated with pesticides used in the IAP system, and a model approach according to Paraíba (2007) was adopted to estimate BCF in apples.

Materials and Methods

The studied pesticides and their physical-chemical properties required to estimate BCF are presented in Table 1. These data were obtained from Gebler (2004) and Girardi and Bender (2003). The pesticides' half-life times in the soil were obtained from Hornsby *et al.* (1996) or Tomlin (2000). And the pesticide octanol-water partition coefficients were obtained from Tomlin (2000). When calculating BCF, it was assumed steady-state equilibrium into the pesticide/soil solution/plant system and that the pesticide dissipation in the soil/plant system occurred via plant growth, plant metabolism and pesticide degradation in the soil. BCF was estimated by the expression $BCF = \dfrac{Q\,Q_f TSCF}{Q + k_{egs}\,K_{wood,w}\,M}$, where BCF ($l\ kg^{-1}$) is the pesticide bioconcentration factor in the apple, Q ($l\ day^{-1}\ ha^{-1}$) is the apple-tree daily water transpiration rate, Q_f ($l\ kg^{-1}$) is the water total volume required for the plant to produce one kilogram of fresh fruit, TSCF is the transpiration stream concentration factor of pesticide, k_{egs} (day^{-1}) is the pesticide dissipation rate in the soil-plant system, $K_{wood,w}$ is the pesticide stem-water partition coefficient and M ($kg\ ha^{-1}$) is the apple plant total dry biomass per hectare. Steady-state equilibrium of the quotient between the fruit pesticide concentration and the soil solution pesticide concentration was assumed to obtain equation 1 (Paraíba, 2007). The pesticide dissipation rate in the soil-plant system was calculated by $k_{egs} = k_e + k_g - k_s$, where k_e, k_g and k_s (day^{-1}) are, respectively, the pesticide metabolism rate in the plant, the plant growth rate, and the pesticide degradation rate in the soil. The TSCF was estimated from the pesticide octanol-water partition coefficient using the equation given by (Burken and Schnoor, 1998) $TSCF = 0.756 \times e^{\left(\frac{-(\log K_{ow} - 2.50)^2}{2.58}\right)}$, where $\log K_{ow}$ is the logarithm of pesticide octanol-water partition coefficient and TSCF is the transpiration stream concentration factor of pesticide. The $K_{wood,w}$ value was estimated using an equation that relates the logarithm of the octanol-water partition coefficient (K_{ow}) with the logarithm of the stem-water partition coefficient given by (Trapp *et al*, 2001) $\log K_{wood,w} = -0{,}27 + 0{,}632 \times \log K_{ow}$.

A five-year-old apple orchard was supposed, with one thousand plants per hectare and a total dry weight estimated in 50,000 $kg\ ha^{-1}$ ($M = 50{,}000$). Plant transpiration was estimated in 8,220 $l\ day^{-1}\ ha^{-1}$ ($Q = 8{,}220$) (300 $mm\ year^{-1}$ of evapotranspiration) and an average daily plant growth rate of $2.74 \times 10^{-5}\ day^{-1}$ ($k_g = 2.74 \times 10^{-5}$) (0.01 per year). According to Trapp *et al.* (2003), the water volume required for apple trees to produce one kilogram of fresh fruits was estimated in 3.5 $l\ kg^{-1}$ ($Q_f = 3.5$). The pesticide degradation rate in the soil was estimated from the pesticide half-life time in this medium and using the expression $k_s = 0.693 / t_{1/2}$. The pesticide degradation rate in the plant was estimated from the pesticide half-life time in soil and using the relation term $k_e = k_s / 16$ (Juraske *et al.*, 2008). The pesticide half-life time values in the soil-plant system were estimated by the expression $t_{1/2}(\text{s-p}) = 0.693 / k_{egs}$ and used to evaluate the pesticide BCF in apples.

Table 1. Thirty six pesticides of the integrated apple production systems (IAP) and their respective parameters used to estimate and evaluate pesticide BCF in apples: agronomic function; chemical class; octanol-water partition coefficient ($\log K_{ow}$); half-life time in soil ($t_{1/2}$) and soil sorption coefficient (K_{oc}).

Pesticide	agronomic function	chemical class	$\log K_{ow}^{*}$	$t_{1/2}$	$K_{oc}^{\S}$
abamectin	insecticide & acaricide	avermectin	4.40	28^{+}	36644
bitertanol	fungicide	triazole	4.1	30^{*}	20941
carbaryl	insecticide	carbamate	2.36	10^{+}	816
chlorothalonil	fungicide	chloronitrile	4.00	60^{*}	17378
chlorpyrifos	fungicide	organophosphorus	3.05	30^{+}	2955
cyprodinil	fungicide	anilinopyrimidine	4.96	30^{*}	104136
diazinon	insecticide & acaricide	organophosphorus	3.81	40^{+}	12193
difenoconazole	fungicide	triazole	4.30	145^{*}	30409
dodine	fungicide	guanidine	1.15	20^{+}	85
fenarimol	fungicide	pirymidine	3.60	360^{+}	8241
fenitrothion	insecticide	organophosphorus	3.30	4^{+}	4710
fenpyroximate	acaricide	pyrazole	5.01	50^{*}	114314
fluazinam	fungicide	phenylpyridinamine	3.56	62^{*}	7649
fluquinconazole	fungicide	triazole	3.24	300^{*}	4211
folpet	fungicide	phthalimide	2.85	4.3^{*}	2035
imibenconazole	fungicide	triazole	4.94	28^{*}	100323
kresoxim-methyl	fungicide	oximinoacetate	3.40	3^{*}	5675
malathion	insecticide & acaricide	organophosphorus	2.36	1^{+}	816
mancozeb	fungicide	dithiocarbamate	1.33	70^{+}	119
metiram	insecticide & acaricide	dithiocarbamate	0.3	20^{+}	17
myclobutanil	fungicide	triazole	2.94	66^{*}	2407
phosmet	fungicide	organophosphorus	2.78	19^{+}	1786
prochloraz	fungicide	imidazole	4.10	120^{+}	20941
pyrazophos	fungicide	phosphorothiolate	3.80	21^{*}	11967
pyridaben	insecticide & acaricide	-	6.37	21^{*}	1444442
pyrimethanil	fungicide	anilinopyrimidine	2.84	54^{*}	1997

simazine	herbicide	1,3,5-triazine	2.18	60^{+}	583
spirodiclofen	acaricide	-	5.80	5.5^{*}	498884
tebuconazole	fungicide	triazole	3.70	28^{*}	9931
tebufenozide	insecticide	diacylhydrazine	0.83	30^{*}	47
thiophanate-methyl	fungicide	benzimidazole	1.40	10^{+}	136
triadimefon	fungicide	triazole	2.77	26^{+}	1753
trichlorfon	insecticide	organophosphorus	0.51	10^{+}	26
triflumizole	fungicide	imidazole	1.40	14^{+}	136
triforine	fungicide	piperazine	2.20	21^{+}	605

**Data obtained from Tomlin (2000); ⁺Data obtained from Hornsby et al. (1996).§ValuesL estimated by* $\log K_{oc} = 0.81\times\log K_{ow}+0.1$ *(EUSES, 1996).*

esults and Discussion

For each pesticide listed in Table 1, the following variables were estimated: half-life time in the soil-plant system; transpiration eam concentration factor; stem-water partition coefficient; and BCF in apples (Table 2). Sixteen of the thirty six pesticides show og $K_{ow} > 3.5$, what means there is an expressive affinity between pesticide and soil organic carbon or plant woody material, as licated by the soil sorption coefficients and the stem-water partition coefficients (Tables 1 and 2). Thus, the pesticides fluazinam, narimol, tebuconazole, pyrazophos, diazinon, chlorothalonil, prochloraz, bitertanol, difenoconazole, abamectin, imibenconazole, prodinil, fenpyroximate, spirodiclofen and pyridaben might be found mainly in the soil or woody part of plants.

According to Paraíba (2007), pesticides with $1.5 \le \log K_{OW} \le 3.5$ present the ideal attributes for translocation from soil fruits. The fruit bioconcentration depends also on the half-life time in the soil-plant system, because the BCF value (equation 1) is versely proportional to the pesticide degradation rate in the soil-plant system. The longer the half-life time, the lower the degradation te in the soil-plant system and the higher the BCF. Therefore, considering the three parameters, half-life time in the soil-plant system, CF and $K_{wood,w}$ the following pesticides can be considered priority pesticides for apple monitoring (in decreasing order): mancozeb > bufenozide > simazine > fluquinconazole > dodine > metiram > fenarimol > triflumizole > trichlorfon > myclobutanil (Table 2). These e also the ten pesticides with higher BCF values in apples.

Mancozebe and metiram are dithiocarbamate class pesticides and have been found in apples and vegetables (Cesnik *et al.*, 06, Caldas *et al*, 2004, ANVISA, 2003, Ripley *et al*, 2000, Dogheim *et al.*, 1999, EU, 2001, IUPAC, 1994). They are recommended by O (2004) as priority pesticides for fruit and vegetable monitoring.

Sharma and Nath (2005) analyzed 327 apple samples collected from orchards of Himachal Pradesh, India, and found 101 mples contaminated with dithiocarbamates, whereas 33 from 286, 20 from 246 and 9 from 97 samples were contaminated with ganochlorides, organophosphorates and carbamates, respectively. According to Chamberlain *et al* (1998), dodine is a systemic ngicide, what means it might bioconcentrate in apple fruits. The dodine fungicide is one of the priority pesticides indicated by FAO 004) for vegetal-originated food monitoring.

Table 2. Parameter estimates for twenty six pesticides of the integrated apple production system (IAP): $t_{1/2}$(s-p): half-life time in the soil-plant system; TSCF: concentration factor in the transpiration stream; $K_{wood,w}$: stem-water

partition coefficient; and BCF: bioconcentration factor in apples.

Pesticide	$t_{1/2}$ (s-p) (days)	TSCF	$K_{wood,w}$ (l kg^{-1})	BCF (l kg^{-1})
mancozeb	2	0.445	4	0.3210
tebufenozide	2	0.256	2	0.1687
simazine	1	0.727	13	0.1576
fluquinconazole	4	0.611	60	0.1407
dodine	2	0.373	3	0.1169
metiram	2	0.116	1	0.1005
fenarimol	3	0.473	101	0.0789
triflumizole	9	0.473	4	0.0760
trichlorfon	1	0.163	1	0.0631
myclobutanil	23	0.701	39	0.0579
pyrimethanil	< 1	0.723	33	0.0566
triforine	3	0.730	13	0.0564
thiophanate-methyl	4	0.473	4	0.0551
triadimefon	19	0.735	30	0.0310
phosmet	< 1	0.733	31	0.0224
carbaryl	2	0.750	17	0.0222
chlorpyrifos	< 1	0.672	45	0.0219
fluazinam	< 1	0.489	95	0.0156
prochloraz	4	0.280	210	0.0079
diazinon	1	0.389	137	0.0056
difenoconazole	4	0.215	280	0.0055
chlorothalonil	1	0.316	181	0.0052
tebuconazole	8	0.433	117	0.0051
folpet	1	0.721	34	0.0045
pyrazophos	1	0.393	135	0.0030
malathion	3	0.750	17	0.0022
bitertanol	4	0.280	210	0.0020

fenitrothion	< 1	0.590	65	0.0018
kresoxim-methyl	2	0.552	76	0.0011
abamectin	2	0.187	324	0.0008
fenpyroximate	1	0.066	788	0.0002
cyprodinil	2	0.072	732	0.0001
imibenconazole	1	0.075	711	0.0001
spirodiclofen	1	0.011	2487	0.0000
pyridaben	1	0.002	5700	0.0000

nclusions

The BCF - bioconcentration factor - values in apples were estimated for thirty six pesticides of the integrated apple production :tems (IAP). Such estimates allowed indicating the following priority pesticides for apple monitoring (in decreasing order of BCF ues): mancozeb, tebufenozide, simazine, fluquinconazole, dodine, metiram, fenarimol, triflumizole, trichlorfon and myclobutanil. This ication is corroborated by the apple pesticide monitoring through residue analysis and it is according to recommendations of julatory international organisms.

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