JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Improved Uptake Models of Nonionized Pesticides to Foliage and Seed of Crops

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The residual amount of nonionized pesticides incorporated to foliage and stem (foliage) and seed (fruit) of crops via root hairs from the water phase was estimated using the uptake models newly including metabolic parameters by which the amount of intact pesticide remaining in crops was considered with its proportion in a transpiration stream. A new parameter was also introduced for the seed model that accounts for the pesticide loss by adsorption to the inner surface of xylem tissue. Validation of the model was conducted using six pesticides with soybean and spinach plants. The ratio of the predicted concentration of pesticide to the measured one was 0.44−1.49 and 0.57−2.93 with foliage and seed models, respectively, showing that these improved models would be effective as a prediction tool.

KEYWORDS: Plant uptake model; pesticide; transpiration stream concentration factor; metabolism

INTRODUCTION

A number of plant uptake models for pesticides have been developed (*1*−*8*) to elucidate their distribution mechanism and residual profiles in crops. The major concept adopted in these models is the partition-based theory. The overall plant uptake process is driven by the external water concentration and is considered to consist of a series of partition uptakes within the plant and external water. Incidentally, government authorities for pesticide registration in the United States and European Union (EU) have recently adopted a tiered approach in which more important roles are allocated to the computer simulations in many scientific fields as a screening tool (*9*) to handle vast numbers of pesticides. For the plant uptake model in particular, EU authorities recently notified the usage of the PLANT X model developed by Trapp and Matthies (*1*) in the European Union System for Evaluation of Substances (EUSES) (*10*−*12*).

Although these models have successfully exhibited the most probable distribution of a pesticide in crops, the metabolic factor and the distribution route in plants have not been fully taken into account. From this viewpoint, we have improved the partition-based concept, first, by considering the metabolism rate. Second, we have developed the seed model, which accounts for pesticide uptake via xylem with a new parameter expressing the pesticide loss by adsorption onto the inner surface of xylem. For this paper, we conducted model simulation using improved plant uptake models of pesticides to foliage and seed.

MATERIALS AND METHODS

Chemicals. Furametpyr (**1**), diethofencarb (**2**), procymidone (**3**), diclocymet (**4**), diniconazole-M, (**5**), and pyriproxyfen (**6**), uniformly labeled with ^{14}C at the phenyl ring (**Figure 1**) were all synthesized in our laboratory. The specific activities of **1**, **2**, **3**, **4**, **5**, and **6** were 2.18, 2.37, 3.01, 3.56, 2.08, and 2.85 GBq/mmol, respectively, and the radiochemical purities were 99.1, 98.2, 97.3, 98.6, 98.2, and 100%. The non-radiolabeled authentic standards of **1**−**6** with the chemical purity of >98% were also synthesized in our laboratory. Other reagents used in the study were of the purest grade commercially available. Fertilizer, Hyponex with an N:P:K ratio of 5:10:5,was purchased from Takii & Co., Ltd.

Plant Material. Soybean (*Glycine max* Merr.) and spinach (*Spinacia oleracea* L.) were sown to cultivation soil (Kureha Chemical Industry Co., Ltd.) and grown in a greenhouse at 22 °C for 1 month. The plant samples of fourth-leaf stage were used for calculation of parameters and validation of the foliage model. Soybean was also grown for 3 months to obtain plant samples at the growth stage of seed bearing, which were used for validation of the seed model. Plants at an appropriate growth stage were carefully taken out from the cultivation soil, and their roots were thoroughly washed with running tap water prior to being used in the experiment.

Plant Exposure. The parameters in the model were each calculated from the experiment using pesticides with different octanol/water partition coefficients, log K_{ow} [**1**, 2.36 (*14*); **2**, 3.02 (*15*); **3**, 3.14 (*15*); **4**, 3.97 (*15*); **5**, 4.30 (*15*); **6**, 5.37(*16*)].

The nominal concentrations of pesticide in exposure solution were 0.5 ppm for **1**−**5** and 0.05 ppm for **6**, which are below the water solubility [**1**, 225 ppm (*14*); **2**, 26.6 ppm (*15*); **3**, 4.5 ppm (*15*); **4**, 6.4 ppm (*15*); **5**, 4.3 ppm (*15*); **6**, 0.37 ppm (*16*)]. The exposure solution was prepared in a 200-mL flask covered with aluminum foil by fortifying 100 μL of acetonitrile solution of ^{14}C compound into 200 mL of distilled water with Hyponex. Soybean and spinach plants at the fourth-leaf stage were transferred to the exposure flask, and their roots were completely dipped into the solution. The open end of the flask was covered with Parafilm to prevent loss of water other than through transpiration. The plants were incubated in the greenhouse at 22 °C, and sampling was mostly conducted 1, 3, and 7 days post-treatment. All of the experiments were done in duplicate.

10.1021/jf010985j CCC: $22.00
Published on Web 01/05/2002

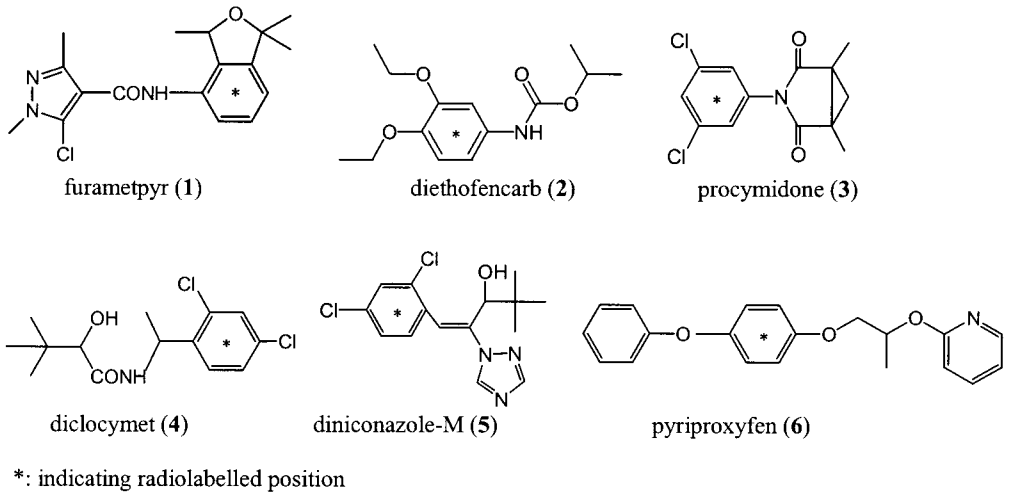

Figure 1. Chemical structures of pesticides.

For calculation of parameters related to degradation factors, independent experiments were conducted. First, soybean and spinach plants at fourth-leaf stage were each treated in a 200-mL flask with exposure solution for 4 days. Successively, the plants were transferred to the flask filled with fresh water and grown in the greenhouse for 1, 3, and 7 days. All of the experiments were done in duplicate.

Validation of the mathematical model was conducted by comparing the measured figures of pesticides in foliage and seed with those of predicted ones. The procedure to obtain measured figures was same as the one used to obtain parameters except for the exposure condition. The plants of fourth-leaf stage were treated with 300 mL of exposure solutions with their nominal concentrations of 2.0 (**1**), 2.5 (**2**), 0.2 (**3**), 0.5 (**4**), 0.5 (**5**), and 0.02 ppm (**6**) for soybean foliage and 2.0 (**1**), 3.0 (**2**), 0.2 (**3**), 0.5 (**4**), 0.3 (**5**), and 0.037 ppm (**6**) for spinach foliage. This concentration setting is effective to show that the model is able to express the uptake phenomena unanimously despite the difference in concentration. The plants were mostly incubated for 1, 3, and 7 days for soybean and for 19 h for spinach. Each sample was extracted to measure the residual amount of intact pesticide.

With the seed model, soybean plants of seed bearing stage were treated with 800 mL of exposure solutions with their nominal concentrations of 1.0 (**1**−**4**), 0.5 (**5**), and 0.02 ppm (**6**). Soybean was exposed to pesticide for 7 days and on the sampling day 5−7 g of seeds (∼25−45 seeds) were collected from a single plant. The seeds were extracted, and the total residual amount of pesticide per seed was obtained.

Extraction. Each sample was cut into pieces, put into plastic or glass vials, and subjected to extraction by adding acetone/water (4:1, v/v). The mixtures were stored in the refrigerator for 3 days, and then the extract and residue were separated using filter paper. The residue was washed two additional times with acetone/water (4:1, v/v), and the extracts were combined. The aliquot of the recombined extracts (0.1 mL), bound residue (25 mg), and exposure water (0.5 mL) were individually subjected to radioassay in duplicate. Extracts were also analyzed with HPLC to determine the remaining rate of pesticide in each plant part.

Radioassay. The radioactivity in plant extracts and exposure water was measured by mixing an aliquot of the liquid sample into 10 mL of Packard Emulsifier-Scintillator Plus and quantified by liquid scintillation counting (LSC) with Packard model 2000CA liquid scintillation analyzer. Unextractable residues were air-dried at room temperature, weighed with Mettler model AE 240, and the aliquots were subjected to combustion analysis using a Packard model 306 sample oxidizer. $^{14}CO_2$ produced was absorbed into 9 mL of Packard Carb-CO_2 absorber, mixed with 15 mL of Packard Permafluor oxidizer scintillator, and the radioactivity was quantified with LSC.

High-Performance Liquid Chromatography (HPLC). The plant extracts were analyzed with reversed phase HPLC to determine the residual ratio of parent compound. The HPLC chromatographic system consisted of a Hitachi L-6200 pump, a Rheodyne 7125 injection valve with a 1-mL injection loop, and a Hitachi model L-4000 UV detector set at 254 nm. Separation was carried out on a Sumipax ODS A-212 (5 μm, 6 mm × 15 cm) packed column. Elutions were performed at ambient temperature at a flow rate of 1 mL/min using the gradient system with acetonitrile (solvent A) and 0.01% trifluoroacetic acid (solvent B). The gradient system started with 20% solvent A and linearly increased to 80% in 30 min. The radioactivity of the column effluent was monitored with a Packard Flow-one/Beta A-120 radiochromatography detector equipped with a 200 μL liquid cell using Ultima-Flo AP as a scintillator. Identification was done by HPLC cochromatography comparing the retention times of the peaks of non-radiolabeled authentic standards detected by UV detector and the ones of ^{14}C material by radiodetector. Typical retention times were 13.5 (**1**), 17.5 (**2**), 21.5 (**3**), 24.8 (**4**), 29.0 (**5**), and 29.8 min (**6**).

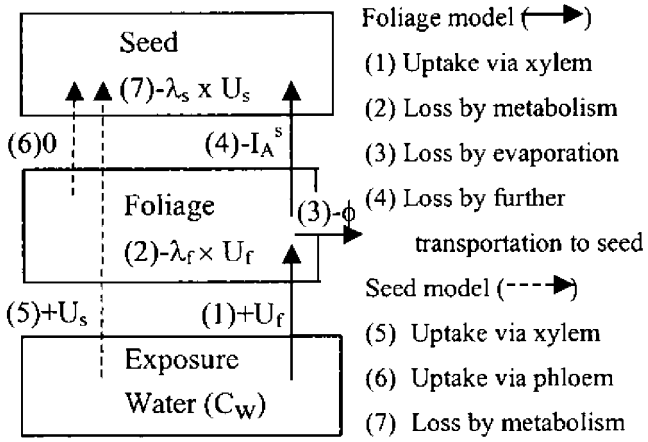

Figure 2. Schematic view of the model concept.

Foliage Model. The four main factors that affect the residual amount in foliage were defined as pesticide transfer to foliage from soil with transpiration stream via root hairs (I), loss by metabolism/degradation (II), loss by evaporation from plant surface and stomata (III), and loss by further transportation to seed (IV) (**Figure 2**).

Using the transpiration stream concentration factor (TSCF) described by Shone and Wood (*17*) and Briggs (*18*, *19*), the concentration of pesticides in transpiration stream is expressed as TSCF × C_w (g·mL^{-1}). C_w is the pesticide concentration in external water. The proportion of intact pesticides in the transpiration stream (γ) should be considered especially when pesticide is susceptible to metabolic degradations. Total uptake of the pesticides into foliage (U_f, g·s^{-1}) via the transpiration stream can be described as

$$U_f = Q_w(\mathrm{TSCF})\gamma C_w$$

where Q_w (cm^3·s^{-1}) is the total mass flow of the transpiration stream.

The degradation rate of pesticide in foliage (M_f, g·s^{-1}) is expressed with the equation $M_f = \lambda_f V_f C_f$, where λ_f is the degradation rate constant (s^{-1}), V_f is the volume (cm^3), and C_f is pesticide concentration (g·cm^{-3}) of foliage. As C_f could be described as U_f/V_f, M_f is transformed to $\lambda_f U_f$.

On the basis of these considerations, the pesticides (g) accumulated to foliage in the period of t (s) can be expressed by the equation $I_A{}^f$ as

$$I_A{}^f = (U_f \phi t - M_f t) - I_A{}^s = (\phi - \lambda_f) U_f t - I_A{}^s$$

ϕ is the recovery rate of radioactivity from the test system during incubation, and $I_A{}^s$ is the pesticide further translocated to seed.

γ and λ are both calculated as follows. The plant was exposed to pesticide for 4 days, transferred to fresh water, and incubated for another 1−7 days. When the concentration of remaining intact pesticide in the plant was plotted against time, it decreased according to pseudo-first-order kinetics, which is expressed with the following equations

$$C_t = C_{t,0}\, e^{(-\lambda t + s)}$$

$$\ln (C_t / C_{t,0}) = -\lambda t + s$$

C_t is the calculated concentration of pesticide at time t obtained by experimental results, $C_{t,0}$ is the theoretical concentration at time 0, λ is a slope, and s is the y-axis intercept. $C_t/C_{t,0}$ is conveniently expressed as $R_t/100$ using the ratio of intact pesticide remaining in the plant obtained at time t from HPLC analysis of the plant extracts. The λ and s values that minimized the sum of the squared differences between the variable values in the model equations and the experimental ones were calculated using the software curve-fitting program SigmaPlot (version 6.0, SPSS Inc.) with Marquardt−Levenberg algorithm. λ is a degradation rate constant. γ (= $R_0/100$) which describes the ratio of intact pesticide in the transpiration stream, is calculated from the y-intercept ($t = 0$) as $\gamma = e^s$.

Seed Model. The three main factors that affect the residual amount in seed (fruit) were defined as pesticide transfer to seed/fruit with transpiration stream via xylem (I), transfer to seed/fruit by phloem (II), and loss by metabolism/degradation (III) (**Figure 2**).

It is a well-known fact that the concentration of pesticide in the transpiration stream that goes into the seed is totally different from the simple TSCF (*13*, *20*), as pesticide is adsorbed to the inner surface of xylem tissue. Concretely, the concentration in the upper stream of transpiration is lower than the one in the basin area, especially when lipophilic pesticides are considered. To cope with this issue, the revised TSCF was introduced as a new arithmetic parameter, UTSCF (upstream TSCF). UTSCF is calculated as "total radioactive residue in leaf (g)/volume of transpiration stream (mL)". Total uptake of pesticide into seed (U_s, g·s^{-1}) through the transpiration stream is then expressed as

$$U_s = (\mathrm{UTSCF}) \beta Q_{sw} \gamma C_w$$

where Q_{sw} is total water supplied (cm^3·s^{-1}) to the seed and β is the fraction of water supplied by the transpiration stream.

Mobility through phloem was considered to be insignificant (= 0) for nonionized pesticides (*21*−*23*). It is postulated that very polar nonionized compounds do not enter the phloem vessel and so are not translocated. More lipophilic compounds (log K_{ow} = 1−3), which cross membranes very readily, can enter phloem easily but immediately diffuse back into the greater volume of xylem. Furthermore, chemicals with high log K_{ow} values will be trapped in the cell membrane while translocated, as phloem is the consolidated form of cell in lines.

The rate of pesticide loss by metabolism (M_s, g·cm^{-3}) is expressed as $M_s = \lambda_s V_s C_s$, where λ_s is the degradation rate constant (s^{-1}), V_s is volume (cm^3), and C_s is pesticide concentration (g·cm^{-3}) of seed. As C_s could be described as U_s/V_s, M_s is transformed to $\lambda_s U_s$.

On the basis of these considerations, the pesticides (g) accumulated to seed in the period of t (s) can be expressed by the equation $I_A{}^s$ as

$$I_A{}^s = (U_s - M_s)t = (1 - \lambda_s) U_s t$$

RESULTS

Parameters Commonly Used for Foliage and Seed Models. From HPLC analysis of the exposure water, >95% of the radioactivity was confirmed as intact pesticide for **1**−**6**, which shows they are stable in the exposure water under the test conditions.

The water concentration of **1**−**4** did not fluctuate much (standard deviation ± 10.1%) throughout the exposure period; thus, the average of the measured concentration was determined as pesticide concentration in water (C_w). To the contrary, the measured concentration dropped to two-thirds and one-fourth of the nominal one within <5 h for **5** and **6**, respectively. However, the once-dropped concentration was constant (standard deviation ± 18.3%) afterward. Thus, C_w values of **5** and **6** were conveniently defined as the average of the measured concentration after it reached equilibrium (**Tables 1**−**3**).

Table 1. Major Parameters Used in Foliage Model of Soybean

	TSCF	γ	C_w (g·cm^{-3})	Q_w (cm^3·s^{-1})	λ (s^{-1})	ϕ
1	0.303	0.854	2.00×10^{-6}	1.33×10^{-4}	0.036	1.000
2	0.350	0.148	2.50×10^{-6}	1.33×10^{-4}	0.802	0.869
3	0.687	1.000	2.08×10^{-7}	1.33×10^{-4}	0.000	0.956
4	0.385	0.490	5.03×10^{-7}	1.33×10^{-4}	0.204	0.948
5	0.330	1.000	3.26×10^{-7}	1.33×10^{-4}	0.040	0.941
6	0.185	1.000	5.20×10^{-9}	1.33×10^{-4}	0.046	0.873

Table 2. Major Parameters Used in Foliage Model of Spinach

	TSCF	γ	C_w (g·cm^{-3})	Q_w (cm^3·s^{-1})	λ (s^{-1})	ϕ
1	0.629	0.221	2.10×10^{-6}	2.02×10^{-5}	0.270	1.000
2	0.540	0.406	3.13×10^{-6}	2.02×10^{-5}	0.743	0.929
3	0.734	0.730	2.19×10^{-7}	2.02×10^{-5}	0.281	1.000
4	0.710	0.407	6.36×10^{-7}	2.02×10^{-5}	0.260	1.000
5	0.587	1.000	2.33×10^{-7}	2.02×10^{-5}	0.000	0.953
6	0.090	1.000	1.43×10^{-8}	2.02×10^{-5}	0.000	0.932

Table 3. Major Parameters Used in Seed Model of Soybean

	UTSCF	γ	C_w (g·cm^{-3})	Q_{sw} (cm^3·day^{-1})	β	λ (day^{-1})
1	0.274	0.854	1.23×10^{-6}	6.43×10^{-3}	0.6	0.036
2	0.234	0.148	1.02×10^{-6}	6.43×10^{-3}	0.6	0.802
3	0.240	1.000	1.35×10^{-6}	6.43×10^{-3}	0.6	0.000
4	0.253	0.490	9.65×10^{-7}	6.43×10^{-3}	0.6	0.204
5	0.130	1.000	2.98×10^{-7}	6.43×10^{-3}	0.6	0.040
6	0.040	1.000	3.83×10^{-8}	6.43×10^{-3}	0.6	0.046

Parameters for Foliage Model. The TSCF figure was originally obtained at each sampling time, and the average TSCF of three sampling points was used as the parameter (**Tables 1** and **2**). The maximum standard deviation was ±20.1% when the average TSCF was considered as 100%.

The degradation rate constant (λ) and the proportion of parent compound in the transpiration stream (γ) were calculated using computer software (**Tables 1** and **2**). The correlation coefficient (r^2) of curve-fitting exceeded 0.85, which shows good correlation between the measured value and the predicted linear line. Compounds **2** and **6** degraded at the same rate in both plants having λ values of 0.74−0.80 and 0.20−0.26, respectively. On the other hand, the degradation rate constant drastically differed between spinach (λ = 0.28) and soybean (λ = 0.00) for **3**. The γ values of **4**−**6** were relatively similar in both plants, but a fairly big difference was observed for **1**−**3** due to the difference in plant species.

From these results, it is clear that the precise degradation factor which has a great impact on predicting the residual amount of intact pesticide in plants is very difficult to obtain by any means of assumption and is available only by conducting experiments.

Table 4. Pesticide Uptake Rate

	soybean foliage[a] ($g \cdot s^{-1}$)	spinach foliage[a] ($g \cdot s^{-1}$)	soybean seed[b] ($g \cdot day^{-1}$)
1	6.63×10^{-11}	4.30×10^{-12}	1.07×10^{-9}
2	1.15×10^{-12}	2.58×10^{-12}	2.69×10^{-11}
3	1.82×10^{-11}	1.70×10^{-12}	1.25×10^{-9}
4	9.39×10^{-12}	2.74×10^{-12}	4.88×10^{-10}
5	1.29×10^{-11}	2.63×10^{-12}	1.43×10^{-10}
6	1.06×10^{-13}	2.42×10^{-14}	4.80×10^{-12}

[a] Pesticide uptake rate per plant of fourth-leaf stage. [b] Pesticide uptake rate per seed.

Besides, the average total weight increase of the plant during experiments obtaining degradation rate figures was within 4.4% of the total weight of the plant. From this fact, the effect of a growth rate of the plant is considered to be negligible in terms of calculating degradation rate figures.

For transpiration rate (Q_w), the ratio of water loss from the flask (g) during the incubation period (s) was calculated at each sampling point and an average figure of eight sampling points was obtained. The Q_w value was $1.33 \times 10^{-4} \pm 2.1 \times 10^{-5}$ ($cm^3 \cdot s^{-1}$) for soybean and $2.02 \times 10^{-5} \pm 2.50 \times 10^{-6}$ ($cm^3 \cdot s^{-1}$) for spinach.

Parameters for Seed Model. The UTSCF figure was originally obtained at each sampling time, and the average UTSCF of three sampling points was used as the parameter (**Table 3**). The maximum standard deviation was ±15.5% when the average UTSCF was considered as 100%. The disparity of TSCF and UTSCF figures was well recognized in accordance with the increase in lipophilicity of pesticide, as the UTSCF values of **5** and **6** were half and one-tenth of the TSCF, respectively.

The Q_{sw} value was calculated as the ratio of water increase (g) in seed during the incubation period (day) at each sampling point, and an average figure of eight sampling points was obtained. The Q_{sw} was $6.43 \times 10^{-3} \pm 5.01 \times 10^{-4}$ ($cm^3 \cdot day^{-1}$). The ratio β was determined as 0.6 from the experimental result shown by Layzell et al. (*24*). The γ and λ of the foliage model were used as substitutions for degradation factors in the seed model.

In summary, parameters used for calculation are shown in **Tables 1−3** and I_A^f ($g \cdot s^{-1}$) and I_A^s ($g \cdot day^{-1}$) of each pesticide are expressed in **Table 4**.

Validation. The predicted and measured figures of each pesticide in foliage and seed and the ratio of "predicted/measured" are summarized in **Tables 5−7**. The "predicted/measured" figures of foliage and seed model were 0.44−1.49 and 0.57−2.93, respectively.

DISCUSSION

Foliage Model. Although every existing model contained a parameter regarding the pesticide loss by metabolism/degradation, there were few studies explaining the actual method to obtain the rate constant. Our results summarized in **Tables 5** and **6** clearly show that the metabolism/degradation parameters (λ and γ) are especially important when accurate prediction of the residual amount of intact pesticide is required for a rapidly degradable one. For example, the predicted/measured ratios of **2** in soybean and spinach were 46.83−92.15 and 5.46, respectively, calculated from the model neglecting the degradation parameters ($\lambda = 0$, $\gamma = 1$). To the contrary, the corresponding ratio drastically improved to 0.59−1.05 and 0.44 when degradation factors from the experiment were used. Our simple experiment for degradation factors may be useful and important, as experiment is the only way to obtain the precise degradation parameters at this moment.

Intentionally, a new model did not provide the stem and leaf models individually, but a foliage model as a consolidated form. Governmental authorities require the pesticide residual amount in so-called raw agricultural commodities (RACs), which in most cases indicate foliage as an important commodity. Furthermore, the accuracy of the model improves drastically by simplifying the actual plant phenomenon in a rational way and successively decreasing the number of factors to be expressed with arithmetic terms. Also, the effect of a growth factor of the plant could be precisely reflected to our model by simply adjusting the amount of transpiration stream, as our model is centered on calculating the total weight (g) of the intact pesticide taken up by plants, not the concentration.

Table 5. Validation of Foliage Model for Soybean

	time (days)	without λ and γ parameters: pesticide (g) predicted	measured	ratio	with λ and γ parameters: pesticide (g) predicted	measured	ratio
1	1	6.71×10^{-6}	3.85×10^{-6}	1.74	5.73×10^{-6}	3.85×10^{-6}	1.49
	4	2.69×10^{-5}	1.99×10^{-5}	1.35	2.29×10^{-5}	1.99×10^{-5}	1.15
	7	4.70×10^{-5}	3.47×10^{-5}	1.35	4.01×10^{-5}	3.47×10^{-5}	1.16
2	1	8.74×10^{-6}	1.70×10^{-7}	51.42	9.97×10^{-8}	1.70×10^{-7}	0.59
	3	2.62×10^{-5}	5.60×10^{-7}	46.83	2.99×10^{-7}	5.60×10^{-7}	0.53
	7	6.12×10^{-5}	6.64×10^{-7}	92.15	6.98×10^{-7}	6.64×10^{-7}	1.05
3	1	1.57×10^{-6}	2.65×10^{-6}	0.59	1.57×10^{-6}	2.65×10^{-6}	0.59
	3	4.70×10^{-6}	5.46×10^{-6}	0.86	4.70×10^{-6}	5.46×10^{-6}	0.86
	7	1.10×10^{-6}	1.30×10^{-5}	0.85	1.10×10^{-5}	1.30×10^{-5}	0.85
4	1	2.11×10^{-6}	1.08×10^{-6}	1.95	8.11×10^{-7}	1.08×10^{-6}	0.75
	4	8.43×10^{-6}	4.74×10^{-6}	1.78	3.25×10^{-6}	4.74×10^{-6}	0.69
	7	1.48×10^{-5}	4.69×10^{-6}	3.15	5.68×10^{-6}	4.69×10^{-6}	1.21
5	1	1.16×10^{-6}	1.90×10^{-6}	0.61	1.11×10^{-6}	1.90×10^{-6}	0.59
	5	5.81×10^{-6}	1.95×10^{-6}	0.63	5.57×10^{-6}	9.31×10^{-6}	0.60
	7	8.13×10^{-6}	1.95×10^{-5}	0.62	7.80×10^{-6}	1.32×10^{-5}	0.59
6	1	9.65×10^{-9}	1.56×10^{-8}	0.62	9.14×10^{-9}	1.56×10^{-8}	0.59
	3	2.90×10^{-8}	1.92×10^{-8}	1.51	2.74×10^{-8}	1.92×10^{-8}	1.43
	7	6.76×10^{-8}	5.26×10^{-8}	1.28	6.40×10^{-8}	5.26×10^{-8}	1.22

Table 6. Validation of Foliage Model for Spinach, 19-h Exposure

	without λ and γ parameters			with λ and γ parameters		
	pesticide (g)			pesticide (g)		
	predicted	measured	ratio	predicted	measured	ratio
1	1.83×10^{-6}	6.66×10^{-7}	2.74	2.94×10^{-7}	6.66×10^{-7}	0.44
2	2.17×10^{-6}	3.97×10^{-7}	5.46	1.76×10^{-7}	3.97×10^{-7}	0.44
3	2.22×10^{-7}	1.17×10^{-7}	1.91	1.17×10^{-7}	1.17×10^{-7}	1.00
4	6.24×10^{-7}	1.78×10^{-7}	3.51	1.88×10^{-7}	1.78×10^{-7}	1.06
5	1.80×10^{-7}	1.95×10^{-7}	0.92	1.80×10^{-7}	1.95×10^{-7}	0.92
6	1.66×10^{-9}	1.30×10^{-9}	1.27	1.66×10^{-9}	1.30×10^{-9}	1.27

Table 7. Validation of Seed Model of Soybean, 7-Day Exposure

	with TSCF parameter			with UTSCF parameter		
	pesticide (g) per seed			pesticide (g) per seed		
	predicted	measured	ratio	predicted	measured	ratio
1	8.28×10^{-9}	6.78×10^{-9}	1.22	7.49×10^{-9}	6.78×10^{-9}	1.10
2	2.82×10^{-10}	1.65×10^{-10}	1.71	1.88×10^{-10}	1.65×10^{-10}	1.14
3	2.47×10^{-8}	3.79×10^{-9}	6.52	8.77×10^{-9}	3.79×10^{-9}	2.31
4	5.19×10^{-9}	5.95×10^{-9}	0.87	3.41×10^{-9}	5.95×10^{-9}	0.57
5	2.55×10^{-9}	3.43×10^{-10}	7.43	1.00×10^{-9}	3.43×10^{-10}	2.93
6	1.54×10^{-10}	3.19×10^{-11}	4.83	3.36×10^{-11}	3.19×10^{-11}	1.05

Seed Model. Uchida (*20*) and Briggs (*19*) found that the pesticide concentrations in the transpiration stream are different when those in basin and upper areas are compared. Concretely, the concentration decreases rapidly in the upper stream due to the pesticide adsorption to stem, especially with lipophilic compounds. McCardy (*25*) also showed that pesticide transportation through xylem is akin to column chromatography as pesticide was more strongly retained to plant tissue according to an increase in the K_{ow} value. However, few of the existing plant uptake models considered this factor as a parameter in their model. Trapp (*2*) expressed this adsorption phenomenon in his model with a partitioning coefficient of pesticide between stem and xylem sap based on the assumption that the plant material is made from equal and homogeneous constituents, lipid and water. However, strictly speaking, because the stem consists of different cells in nature (xylem, phloem, epidermis, cambium, etc.) and the pesticide is adsorbed onto lignin (*13*), which has a quite different chemical character compared to lipid, there may be a discrepancy when the theory is generalized. Within this paper, a simple UTSCF figure was introduced as a new parameter to cope with the issue. Fundamentally, as the UTSCF figure could easily be obtained from the same experiment used to calculate the TSCF, there will be no additional workload required. The effect of the UTSCF could be recognized when pesticides with high lipophilicity are considered. For example, the predicted/ measured ratios of **3**, **5**, and **6** were 6.5, 7.4, and 4.8, respectively, when calculated with the model using TSCF, but the corresponding figures were improved to 2.3, 2.9, and 1.0 with the model using UTSCF (**Table 7**).

In summary, the parameter setting of the model is very important in the prediction of the residual amount of intact pesticide in crops. This fundamental fact can be applied to any other existing mathematical models. For example, with the pesticide root zone model/exposure analysis model system (PRZM/EXAM) (*26*, *27*), which is widely used for evaluating ecotoxicological concerns and drinking water contamination, it is well recognized that the key parameters such as degradation rate constant and adsorption/desorption coefficient of soil have to be obtained from the experiments at least to conduct meaningful prediction. Herein, we propose that transpiration (UTSCF and TSCF) and degradation factors (λ and γ) are the two important parameter groups which determine the accuracy of prediction figures, especially when rapidly degradable and lipophilic pesticides are considered.

Validation of the Model. The ratio of predicted/measured shows that the model is effective as a prediction tool. The aberration between the predicted and measured figures may be explained for model needs to simplify the actual phenomena of pesticide uptake into plant and to express it with the mathematical arithmetic term.

Conclusion. The arithmetic model for calculation of intact pesticides in foliage and seed was developed with some new concepts in a parameter setting. Validation of the model was conducted using six pesticides with soybean and spinach plants. Although there are some hypotheses used in the model that need to be further investigated before the model's reliability is fully confirmed, this model is useful when the intact pesticide residues in foliage and seed are considered, as it could be calculated using a personal computer with a few input parameters.

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Received for review July 26, 2001. Revised manuscript received October 22, 2001. Accepted November 7, 2001.

JF010985J