The fate of pesticide on tea plant and the prediction of pesticide residue in fresh leaves of tea plant

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Abstract

The degradative kinetics of pesticides on tea plant surface are characterized by an initial rapid degradation which follows a first-order kinetics, then transferred to a more slower degradative rate. The degradative process mainly consists of photodegradation, evaporation, rainfall elution and growth dilution. The influencing parameters of these processes were investigated on tea plant. The predictive model of the initial concentration, photodegradation rate constant, evaporation rate constant, rainfall elution rate, growth dilution rate and the total degradative rate was discussed and verified in four locations situated in the range of 25° -30° N latitude, and acceptable results were obtained.

1. Introduction

Industrialization of modern society has led to a progressive deterioration in the quality of the earth's environment. As with other crops, control of pests by pesticides is widely used in tea plantations. Tea is an unusual crop for the following reasons. Firstly, the product of economic importance from the tea plant is the portion, which is sprayed directly with the pesticides. The shoots of the tea plant are thin and tender, and the surface area per unit weight of leaf is relatively larger than with other crops (Table 1). Secondly, the tea bush is harvested several times per year. Thirdly, the interval period between the spraying date and the plucking date is shorter than with other crops, and the plucking shoots are processed directly without washing. So, in comparison with other crops, the residue level of pesticide in tea shoots is higher under the same applied dosage. Fourthly, as a beverage, the pesticide residue in the processed tea

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may be extracted into the infusion during the brewing process.

Table 1 Area-to-weight ratio of tea leaves and various vegetables

Plant	Area-to-weight ratio (cm^2g^{-1})
Cabbage leaves	18.7
Cabbage	0.8
Cucumber	0.7
Tomato	0.6
Spinach	27.7
Celery	38.2
Edible amaranth	53.9
Tea:tender leaf	41.7
Tea:mature leaf	15.9

2. Degradative dynamics of pesticide on tea plant

After pesticides are sprayed on the canopy of the tea plant, most of them are degraded in two stages (Chen et al, 1975,1980,1981, 1983a,1983b,1984, 1986,1988). The first stage is the rapid degradative process dominated by the mechanism of evaporation, then followed by a slower degradative process (Figure 1). It can be expressed by a fiest-order kinetic equation: $\mathbf{C_t = C_o e^{rt}}$, where $\mathbf{C_t}$ is the pesticide residue at time **t** (mg/kg), $\mathbf{C_o}$ is the initial pesticide deposit (mg/kg), **r** is the degradative rate constant of pesticide (sec^{-1} or day^{-1}) and **t** is the time after the pesticide application (day). Table 2 represents the degradative rate constant of pesticides in the tea garden and the half-life (HL_{50}) of pesticides on tea leaves. The **r** values of organophosphate pesticides are generally within the range of 5×10^{-6} sec^{-1} to 40×10^{-6} sec^{-1}, while those of pyrethroids are mostly lower than 4×10^{-6} sec^{-1} (Chen 1983,1984,1988,1997).

The factors inducing the degradation of pesticides on tea plant include growth dilution, photolysis, evaporation and elution by rainfall. The direct photodegradation of pesticide is a consequence of the absorption of energy by the chemical molecule. The energy source of photodegradation is mainly provided from the absorption of phototons from solar radiation. The proportions of absorbed photons used in the degradation of functional groups of pesticides are different for various pesticides. The ratio is called the quantum yield (Φ). The larger the value, the higher the photodegradative rate. Other parameters related to the photodegradation of pesticides are extinction coefficient of pesticide ($\mathbf{A}_\lambda$) and irradiance intensity of sunlight

(**Eo**$_\lambda$). The quantum yield and the extinction coefficient are the physical properties of pesticide and the last factor is an external environmental factor. According to the equation of $\mathbf{E} = \boldsymbol{hc}\,\lambda$, the shorter the wavelength of radiated light , the higher the photon energy. However, when the sunlight passes through the atmosphere, its intensity is decreased through absorption by ozone. Actually, the wavelength of radiated light is mainly in the range of 280 to 350 nm. Almost all the short-wave radiation (< 295 nm) is filtered by the ozone layer. Photodegradation plays a significant role in the total degradation of pesticides with high photosensitivity, such as Phoxim.

Table 2 Degradative rate constant and half-lives (HL_{50}) of pesticides on fresh tea leaves

Pesticide	Degradative Rate Constant (x 10^{-6} sec^{-1})	Half-life (days)
Dichlorvos	**40.1**	**0.20**
Phoxim	**33.3**	**0.24**
Trichlorfon	**23.6**	**0.34**
Malathion	**21.6**	**0.37**
Fenitrothion	**16.0**	**0.50**
Dimethoate	**8.5**	**0.95**
Phosmet	**6.9**	**1.15**
Quinalphos	**5.8**	**1.39**
Cypermethrin	**3.2**	**2.50**
Permethrin	**3.0**	**2.70**
***Cis*-Cypermethrin**	**2.8**	**2.90**
Fenvalerate	**2.6**	**3.10**
Deltamethrin	**2.5**	**3.20**
Bifenthrin	**2.5**	**3.20**
Cyhalothrin	**2.4**	**3.40**
Dicofol	**2.1**	**3.85**

Table 3 is the quantum yield value and the photolysis rate constant.

Table 3 Photolysis rate constant and quantum yield for photolysis of solid-phase pesticides under 313nm monochromatic light

Pesticide	Photolysis rate constant (hr^{-1})	Photo-quantum yield (Φ_{313})
Fenvalerate	**0.20100**	**0.09390**
Dimethoate	**0.00153**	**0.05020**
Dicofol	**0.01324**	**0.04510**
Buprofezin	**0.00286**	**0.03820**
Cypermethrin	**0.00230**	**0.03010**
Malathion	**0.00415**	**0.01980**
Quinalphos	**0.04500**	**0.00091**
Parathion-methyl	**0.04500**	**0.00075**

Evaporation is another important factor causing the loss of pesticides, especially those which possess a higher vapour pressure (v.p.). Under the environmental condition of high air temperature, the rate of evaporation can be expressed by the following equation: $\mathbf{K_E = C.\ VP.\ \surd M}$, where $\mathbf{K_E}$ is the rate of evaporation, **C** is the constant which depends on the mobile state of atmosphere in the system, **VP** is the vapour pressure of pesticide and **M** is the molecular weight of pesticide. So, in the same system, for pesticides which have a similar molecular weight, the rate of evaporation depends mainly on the vapour pressure. Table 4 presents results from an investigation on the evaporation rate constant of different pesticides in a phytotron. Results showed that the larger the vapour pressure value, the more pesticide is evaporated,.

Rainfall elution is important during the first few days after application, for those pesticides, which have a high water solubility. An experiment with simulated rainfall on various pesticides with different water solubility proved that the rate of rainfall elution is closely related to the water solubility of pesticides. In addition, the rate of elution is negatively correlated with the interval between the time of spraying and onset of rain (Chen 1993). The rainfall shortly after the application of pesticide has a significant effect of elution on the pesticide. The elution percentage by 15 mm rainfall at 1 hr after application of Dichlorvos, Dimethoate, Malathion and Quinalphos ranged from 82.9-94.6%, that of Cypermethrin was 73.6%. For those pesticides with high water solubility, such as Dichlorvos, Malathion and dimethoate, the elution rate under the 5 mm rainfall was as high as more than 85%. For pesticides with low water solubility, such as Cypermethrin, the elution rate under the same condition was less than 50% (Chen 1989). However, the correlation is decreased in the treatment with heavy rain (15 mm rainfall). This is because the role of mechanical washing due to rainfall is larger than the soluble action of rainwater. Some low polarity pesticides gradually penetrate into the wax layer of leaves from surface. However, the systemic pesticide can be translocated to the upper part of plant via the transpirative flow. Thus, the dissolution and mechanical washing action of rainfall are gradually diminished with time. It was also shown that the amount of rainfall was far less important than that of the interval between the spraying date and the onset of rain.

Table 4 Relationship between vapour pressure of pesticides and evaporation rate constant

Pesticide	Vapour pressure (mbar)	Evaporation rate constant (hr^{-1})	
		30° C	40° C
Dichlorvos	1.2 x 10^{-2} (20° C)	3.8340	10.4450
Fenitrothion	1.6 x 10^{-4}(25° C)	0.1230	0.2034
Malathion	3.2 x 10^{-4}(25° C)	0.0314	0.1387
Quinalphos	3.0 x 10^{-4} (25° C)	0.0304	0.1306
Dimethoate	3.0 x 10^{-5}(25° C)	0.0180	0.0995
Bifenthrin	1.8 x 10^{-7}(25° C)	0.0019	0.0133
Fenvalerate	2.8 x 10^{-7}(25° C)	0.0004	0.0006
Cypermethrin	3.2 x 10^{-8}(25° C)	0.0002	0.0007

Growth dilution plays an important role in the degradation of pesticides on/in plant surface,especially those plant with rapid growth rate, such as vegetables and tea plant. The results of an investigation on the degradative rate of Cypermethrin on tea shoots at different developmental stages showed that the degradative rate of pesticide is proportional to the growth rate of tea shoots (r-0.98) (Table 5). The younger the tea shoots, the faster the growth rate and the larger contribution of growth dilution to the pesticide degradation on tea shoots. For persistent pesticides, such as pyrethroids and organochlorine pesticides, growth dilution contributes around 40-50% of reduction in concentration (Xue and Chen, 1992).

Table 5 Degradative rate constant of Cypermethrin on/in tea shoots at different developmental stages

Growth stage	Growth rate constant of tea shoot (day^{-1})	Degradative rate constant of Cypermethrin on tea shoot ($day^{-1)}$
Bud	**0.159**	**0.292**
Bud and 1 leaf	**0.131**	**0.214**
Bud and 2 leaves	**0.084**	**0.202**
Bud and 3 leaves	**0.070**	**0.142**

3. Prediction on the degradative rates of pesticide on tea fresh leaves

As discussed earlier, the degradation of most pesticides on plant surface follows first-order kinetics. The equation can be expressed as $\mathbf{C = C_0\ e^{-k\ t}}$, where **C** is the concentration after time **t**,$\mathbf{C_0}$ is the initial concentration and **k** is the rate constant. According to the results of investigation on more than 30 pesticides , the main degradative processes under field conditions include the photodegradative rate constant ($\mathbf{k_p}$), evaporative rate constant ($\mathbf{k_E}$), elution rate by rainfall ($\mathbf{k_R}$)and growth dilutive rate constant of tea shoots ($\mathbf{k_G}$). Thus, the total degradative rate constant (**k**) is the summation of the individual rate constant, expressed as the following equation: $\mathbf{k = k_p + k_E + k_R + k_G}$.

Hence, the prediction on the degradative rates of pesticide on plant surface relies on the prediction of those parameters including $\mathbf{C_0}$, $\mathbf{k_p}$, $\mathbf{k_E}$, $\mathbf{k_R}$, and $\mathbf{k_G}$.

A. Prediction on the initial concentration (C_0)of pesticide on tea plant

The initial concentration of pesticides on tea plant after application in the most important parameter for prediction. The initial deposit of pesticide intercepted by tea plant is mainly dependent on the dosage of application, vapour pressure of the pesticide and environmental temperature. Investigation on more than 30 pesticides including organochlorine, organophosphate, pyrethroid and carbamate pesticides showed that the organochlorine and pyrethroid pesticides are closely related with the applied dosage due to the low VP of these compounds(Xue and Chen, 1992). The predictive equation on the $\mathbf{C_0}$ of these two groups of pesticides on tea shoots after application are listed as follows:

Organochlorine pesticides: $\mathbf{C_0 = 0.432 \times 10^3 . F . I . L^{-1} - 8.31}$

Pyrethroid pesticides: $\mathbf{C_0 = 0.289 \times 10^3 . F . I . L^{-1} - 0.70}$

The organophosphate pesticides, however, have rather high VP , so that the $\mathbf{C_0}$ of organophosphate pesticides is not only dependent on the applied dosage, but also influenced by the environmental temperature and the VP of the compound. The predictive equation is as follows:

Organophosphate pesticides: $\mathbf{C_0 = 1.57 \times 10^6 . F . I . L^{-1} . (273+t)^{-2}(\ln P) - 5.57}$

In the above equations, **F** is the liquid volume (liter) of pesticide applied per hectare, **I** is the active ingredient in the pesticide formulation (%), **L** is the dilution, **t** is the environmental temperature (°C) and **P** is the vapour pressure of pesticide (mbar).

B. Prediction on the Photodegradative rate constant (k_p) of pesticide

According to the investigation, the photodegradative rate on tea plant is dependent upon three factors: Quantum yield (Φ)for photodegradation of pesticide in the solid state, extinction coefficient of pesticide (ε_λ) and radiation intensity of sunlight ($\mathbf{I_{0\lambda}}$) (Tao & Chen, 1994). The former two factors are physical properties of the pesticide, the last factor is an environmental factor. The quantum yield represents the fraction of photons absorbed that result in photoreaction and can be determined in the laboratory. The Φ value can be calculated by the following equation (Tao & Chen, 1994).

$$\Phi_{313} = \frac{\mathbf{K_{313} . D}}{\mathbf{2.303} . \ \varepsilon_{313} . \ I_{0\lambda}}$$

where K_{313} is the photodegradative rate constant of pesticide on glass surface at 313 nm radiation, **D** is the specific gravity of pesticide (mol . cm^{-2}), ε_{313} is the absorptivity of pesticide at 313 nm, and $\mathbf{I_0}$ is the radiation intensity of sunlight (photo . cm $^{-2}$. s^{-1}) which varies with different latitudes and seasons. The absorptivity can be determined by spectrophotometry and the radiation intensity is obtained from Bener (1972). The photodegradative rate constant ($\mathbf{k_p}$) can then be obtained by the following equation (Tao & Chen, 1994).

$$\mathbf{k_p = 2.303 . \ \Phi_{313} . M . J^{-1}. W^{-1} .} \ \sum_{\lambda=295\,nm}^{380} \mathbf{I_\lambda} . \ \varepsilon_\lambda$$

where **M** is the molecular weight of pesticides, **J** is the Einstein constant ($\mathbf{6.023 \times 10^{-23}}$ **photon . Einstein**$^{-1}$) and **W** is the mass of pesticide (g . cm^{-2}), $\mathbf{I_\lambda}$ is the radiation intensity at wavelength λ and ε_λ is the absorptivity.

C. Prediction on the evaporative rate constant (k_E) of pesticide

A predictive equation of evaporative rate constant ($\mathbf{k_E}$) was developed by using the parameter of vapour pressure and molecular weight of pesticides as well as the environmental temperature.

When the VP of pesticide is higher than 10^{-7} mbar:

$$\mathbf{k_E = 4.94 \times 10^{-3} + 3.61 \times 10^{-4} . \ln (P \surd M) + 9.88 \times 10^{-4} T + 7.22\ 10^{-5} . \ln (P \surd M) . T}$$

When the VP of pesticide is less than 10^{-7} mbar:

$$\mathbf{k_E = 1.26 \times 10^{-3} + 8.29 \times 10^{-4} . \ln (P \surd M) + 2.0 \times 10^{-4} T + 1.66 \times 10^{-5} . \ln (P \surd M) . T}$$

According to the investigation carried out on tea plant, the $\mathbf{k_E}$ value of Malathion is 0.60 day^{-1}, $\mathbf{k_E}$ of Dimethoate is 0.36 day^{-1} and $\mathbf{k_E}$ of pyrethroids is 0.02-0.05 day^{-1}. The total degradative rate constant of organophosphate pesticides under field conditions ranged from 0.6-1.2 day^{-1} (Chen et al 1990,1991). By comparing these two figures, the role of evaporation on the total degradation is more important in organophosphate pesticides than in pyrethroids.

It must be noted that the evaporative rate of pesticides after spraying on tea plant is uneven. The evaporative rate is relatively fast in the first day after application. Then it slows down. It is therefore advisable to predict the $\mathbf{k_{E\,1}}$ in the first after application and the subsequent days ($\mathbf{k_{E\,2}}$) separately (Chen, 1992). Regression analysis on the prediction of $\mathbf{k_{E\,1}}$ and $\mathbf{k_{E\,2}}$ are listed as follows:

$$\mathbf{Log\ k_{E\,1} = 1.40 + 0.260\ [\log P + 0.04\ (T - 24.5)]}$$

$$\mathbf{Log\ k_{E\,2} = 0.938 + 0.339\ [\log P + 0.04\ (T - 24.5)]}$$

D. Prediction on the rainfall elution rate (k_R) of pesticide on tea shoot

The prediction of rainfall elution rate ($\mathbf{k_R}$) of pesticide should include those parameters such as water solubility of pesticide, amount of rainfall and the interval between the spraying date and raining date. Each parameter is divided into 2-4 classes, and the elution rate of pesticide on tea plant by rainfall can be obtained from the various combinations of the above parameters (Xia and Chen, 1989) (Table 6,7).

Table 6　Parameters for the prediction of loss rate of pesticide by rainfall and their grouping

Class	Water solubility (mg.kg^{-1})	Rainfall amounts (mm)	Interval between spraying and rainfall (hr)
1	>50	>5	<12
2	5-50	<5	12-36
3	<5		>36
4	systemic		

Table 7　Prediction on elution rate under different combinations of three parameters

Combination	Elution rate (%)
$A_1B_1C_1$　$A_4B_1C_1$	95 ± 5
$A_1B_2C_1$　$A_2B_1C_1$　$A_4B_2C_1$	80 ±10
$A_1B_1C_2$　$A_2B_1C_2$	75 ± 10
$A_1B_2C_2$　$A_3B_2C_1$	70 ± 10
$A_1B_1C_3$　$A_3B_1C_1$　$A_4B_1C_2$	50 ± 10
$A_2B_2C_2$	45 ± 10
$A_1B_2C_3$　$A_3B_1C_2$　$A_4B_1C_2$	40 ± 5
$A_2B_1C_3$　$A_3B_2C_1$　$A_4B_1C_3$	35 ± 5
$A_3B_1C_3$　$A_3B_2C_2$	25 ± 5
$A_3B_2C_3$	20 ± 5
$A_4B_1C_3$	5 ± 3
$A_4B_2C_3$	< 5

E.　Prediction on the growth dilution rate (k_G) of pesticide by tea shoot

Growth dilution is a distinctive degradative mechanism of leafy crops. The pesticide sprayed on tea shoots is diluted by the growing process of the shoots. In general, the shoots with one bud and two to three leaves are plucked. Hence, when the pesticide is sprayed on the unfolded buds, its concentration will be diluted with the extension of the shoots. The normal shoot of tea plant possesses the periodic rhythm in growth. It starts with the sprouting of the bud, then the emerging of the first leaf. After 3-5 leaves have fully appeared, the growth ceases, and the *banjhi* is formed. It is a full growth cycle. Investigation showed that the younger the developmental age in the initial state, the faster the growth rate, and the larger the contribution of growth dilution to the dissipation of pesticide on the tea plant (Xue and Chen,1992). Bedsides, the value of **k_G** varies with the different culticars, season and growing stages. The growth dilution rate can be expressed by the following equation:

$$\mathbf{k_G = \sum_{i=0}^{3} X_i \, . \, r_i}$$

where **X_0** is the proportion of shoot with one bud in the total shoots (%), **X_1** is the proportion of ‘one bud and one leaf’ shoot in the total shoots (%), and so on. This figure can be obtained via the survey in tea garden during spraying. From the results of field experiments, the r values are as follows:

$r_0 = 0.145 \pm 0.003$ day^{-1} (spring, autumn); 0.140 ± 0.005 (summer)

$r_1 = 0.135 \pm 0.003$ day^{-1} (spring, autumn); 0.130 ± 0.005 (summer)

$r_0 = 0.120 \pm 0.003$ day^{-1} (spring, autumn); 0.115 ± 0.005 (summer)

$r_0 = 0.110 \pm 0.003$ day^{-1} (spring, autumn); 0.100 ± 0.005 (summer)

F. Prediction on the total degradative rate constant of pesticide on tea plant

The total degradative rate constant of pesticide in the first day after application (**k_1**) can be expressed by the following equation:

$$\mathbf{K_1 = k_{E\,1} + k_P + k_R + k_G}$$

Then from the equation **$C_1 = C_{01} e^{-k_1 t}$**, the concentration of pesticide on/in tea plant on the first day of application can be obtained. Accordingly, the concentration of pesticide on /in tea shoots on the subsequent days (**k_2**) after application can be obtained from the following equation:

$$\mathbf{K_2 = k_{E\,2} + k_P + k_R + k_G}$$

in which, **$k_{E\,1}$, $k_{E\,2}$** ,**k_P** and **k_G** can be predicted by the above equation, and **k_R ,** a discrete factor, can be predicted separately.

4. Validation of the predictive model

For the purpose of evaluating the correctiveness of model, the experiments on the prediction of pesticide residues on/in tea shoots were carried out in Hangzhou (30.5° N latitude), Changsha (28° N latitude), Fuan (27° N latitude) and Guiling (25.5° N latitude) in 1999-2000 respectively. By comparing the results from the validation experiments and the predictive value, the average error on the prediction of initial pesticide deposit ($\mathbf{C_0}$) on tea shoots was 18.9%. the errors on the prediction on the total degradative rates were 31.5% ($\mathbf{K_1}$) and 18.9% ($\mathbf{K_2}$), respectively. It can be regarded as acceptable from the viewpoint of pesticide residue analysis, because the acceptable range of error in this kind of analysis *per se* is 20-100%.

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