

**Fig. 1.** Pesticide concentrations in komatsuna shoots. Columns with the same letter are not significantly different at  $p < 0.05$ , according to ANOVA-protected Tukey's multiple range testing. Error bars indicate standard deviations ( $n = 4$ ). Reprinted from Ref. 25.

ported that OCs in soils include black carbons (BCs) such as char and soot, which are products of the incomplete combustion of vegetation by wildfires or human activity.<sup>9–12</sup> Because BCs strongly sorb organic chemicals including pesticides, the BC content in soils may affect the overall sorption of pesticides in soils.<sup>13</sup> However, there are no reports about the effect of the OC quality on the sorption properties of pesticides in Japanese soils, including andosol, which is the major upland soil.

The  $K_d$  values are generally determined in accordance with the Organization for Economic Cooperation and Development (OECD) test guidelines, which is the standard batch method.<sup>14</sup> In this method, the  $K_d$  values are measured by shaking the soil with an aqueous solution for about 24 hr after pesticide application, and daily and weekly time courses of  $K_d$  values are not taken into account. However, it is reported that the  $K_d$  values of various pesticides increased with time.<sup>15–24</sup> Therefore, if the aging effect on the  $K_d$  values is not considered, the concentrations of water-extractable pesticides predicted using the  $K_d$  values seem to be higher than the actual values.

In order to develop a method for estimating the residue concentrations of pesticides in succeeding crops using those in soils, the present study investigated (i) the relationships between pesticide concentrations in komatsuna (*Brassica rapa* var. *perviridis*) and water-extractable concentrations in soils; (ii) the dissipation behavior of water-extractable concentrations in soils, influenced by time-dependent sorption; and (iii) the effects of OC quality, such as the chemical composition of OC and the presence of BC, on  $K_{oc}$  variability.

## 1. Plant Uptake of the Extractable Pesticides in Soils<sup>25)</sup>

### 1.1. Relationships between pesticide concentrations in komatsuna and the extractable concentrations in soils

The relationship between pesticide concentrations in komatsuna shoots and the extractable concentrations in soils, which were quantified by a sequential soil extraction with water and acetone, was investigated in 8 pesticides and 4 soils.

The residue concentrations of a given pesticide in komatsuna shoots, which were cultivated on pesticide-applied soil, varied

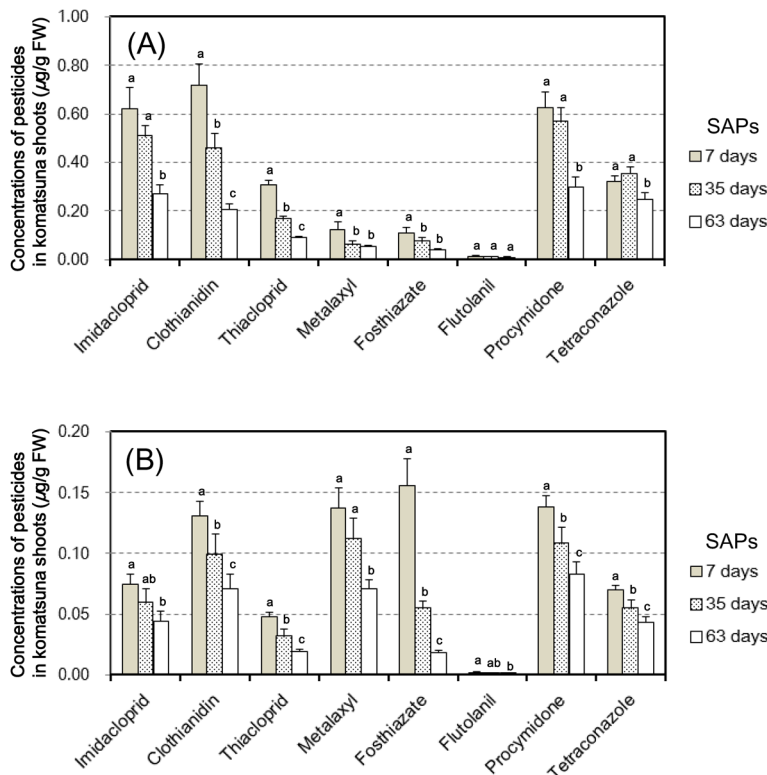
among test soils (Fig. 1), and the coefficients of variation (CVs) of the concentrations for a given pesticide ranged from 17.6% for metalaxyl to 123.5% for thiachloprid. Overall, the shoot concentrations for two andosols, which have relatively high OC content and strong sorption of pesticides, were lower than those for non-andosols. On the other hand, for metalaxyl and fosthiazate, which have very weak sorption by soils, the variability of concentrations in komatsuna shoots was especially low; the CVs of these pesticides were less than 30%. Therefore, one reason for the high variability of the shoot concentrations is considered to be the differences in the soil sorption strength.

The relationship between the pesticide concentrations in komatsuna shoots and the extractable concentrations in soils was analyzed using linear regression analysis (Table 1). Although the coefficient of determination ( $R^2$ ) values differed according to the type of pesticide, the concentrations of pesticides, except for metalaxyl and fosthiazate, in komatsuna shoots were more strongly correlated with the concentrations of water-extractable pesticides ( $C_W$ ) than those of total extractable pesticides ( $C_T$ ). Therefore, this result implies that the  $C_W$  values, which are influenced by the soil sorption of pesticides, can be available for evaluating the phytoavailability of residual pesticides in soils and

**Table 1.** Linear regression analysis<sup>a)</sup> between pesticide concentrations in komatsuna shoots and extractable concentrations<sup>b)</sup> in four soils

Compound	No. soils	$R^2$	
		Water-extracts	Total-extracts
Imidacloprid	4	0.733	0.332
Clothianidin	4	0.918 <sup>c)</sup>	0.462
Thiachloprid	4	0.975 <sup>d)</sup>	0.123
Metalaxyl	4	0.648	0.844 <sup>c)</sup>
Fosthiazate	4	0.466	0.732
Flutolanil	4	0.566	0.543
Procymidone	4	0.714	0.489
Tetraconazole	4	0.976 <sup>d)</sup>	0.334

<sup>a)</sup> Regression lines were calculated using data containing the point (0, 0), i.e.,  $n = 5$ . <sup>b)</sup> Mean values during the period between sowing and harvest. <sup>c)</sup> Significant at  $p < 0.05$ ; <sup>d)</sup> significant at  $p < 0.01$ .



**Fig. 2.** Effect of soil-aging periods (SAPs) on residue concentrations of pesticides in komatsuna shoots cultivated in a gray lowland soil (A) and an andosol (B). Columns with the same letter are not significantly different at  $p < 0.05$ , according to ANOVA-protected Tukey's multiple range testing. Error bars indicate standard deviations ( $n=4$ ). Reprinted from Ref. 25.

estimating the residual concentrations in succeeding crops.

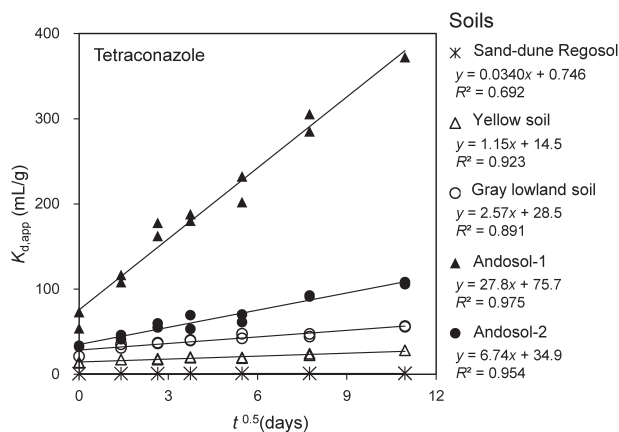
### 1.2. Influence of soil-aging periods (SAPs) on pesticide concentrations in komatsuna

The effects of soil-aging periods (SAPs)—the periods between pesticide applications and sowing—on pesticide concentrations in komatsuna shoots were investigated. Figure 2 shows the relationships between the shoot concentrations and three different SAPs—7-day, 35-day, and 63-day—for a gray lowland soil and an andosol. Shoot concentrations decreased with increasing SAPs. The ratios of the residue concentrations in komatsuna shoots cultivated in soils with a 63-day SAP as compared to those with a 7-day SAP were 29–90% (mean=50%) and 12–69% (mean=51%) in a gray lowland soil and an andosol, respectively. As a result of correlation analysis between pesticide concentrations in komatsuna shoots cultivated in soils with three different SAPs and the extractable concentrations in these two soils, the  $R^2$  values of the regression lines calculated using the  $C_W$  values were higher than those using the  $C_T$  values, except for metalaxyl and fosthiazate. These results suggest that estimating pesticide concentrations in crops based on the  $C_W$  values and setting appropriate SAPs lead to preventing the production of succeeding crops contaminated with pesticide residues in the soil.

## 2. Estimation of the Dissipation Behavior of Phytoavailable Pesticides in Soils<sup>(26)</sup>

### 2.1. Dissipation behavior of extractable pesticides in soils

To estimate the pesticide concentrations in succeeding crops contaminated by pesticide residues in soils, the dissipation behavior of water-extractable pesticides, *i.e.*, phytoavailable pesticides, in soils should be investigated. Therefore, a laboratory



**Fig. 3.** Time-dependent changes in apparent sorption coefficient ( $K_{d,app}$ ) of tetraconazole. Reprinted with permission from Ref. 26. Copyright (2016) American Chemical Society.

incubation study using 27 pesticides and 5 Japanese soils was conducted. The soil samples were sequentially extracted using water and acetone, and the  $C_W$  and  $C_T$  values were quantified.

The dissipation behavior in soils was clearly different between water- and total extractable pesticides. That is, the  $DT_{50}$ , which is the time taken for a 50% decrease, of  $C_W$  was shorter than that of  $C_T$  for all test soils except a sand-dune regosol having an extremely low OC content (<0.1%), and the dissipation of  $C_W$  was better fitted by biphasic models as compared with a single first-order (SFO) model applied to the dissipation of  $C_T$ . Furthermore, the dissipation rate of  $C_W$  varied depending on the OC content of soils, and the dissipation of  $C_W$  in two andosols having high OC contents and high pesticide sorption ability was faster than that of other soils. Therefore, it is possible that the sorption of pesticides to OCs affects the dissipation of  $C_W$ .

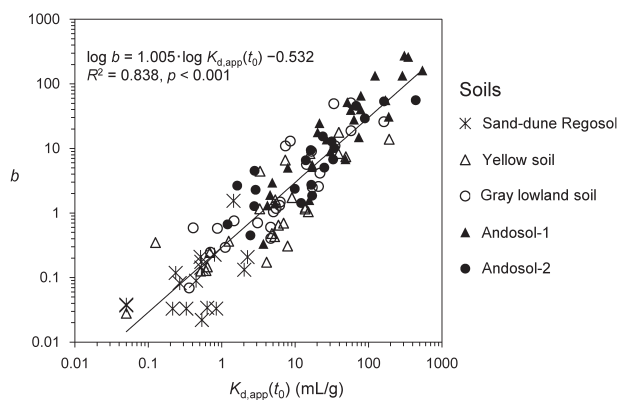
## 2.2. Time-dependent sorption of pesticides in soils

The previous studies<sup>15–24</sup>) reported that the apparent sorption coefficients ( $K_{d,app}$ , mL/g), which are calculated by taking the dissipation of  $C_T$  and  $C_W$  over time into account, of many pesticides increased with increasing incubation time. According to previous reports,<sup>19,21,23</sup>) changes in  $K_{d,app}$  over time could be represented as

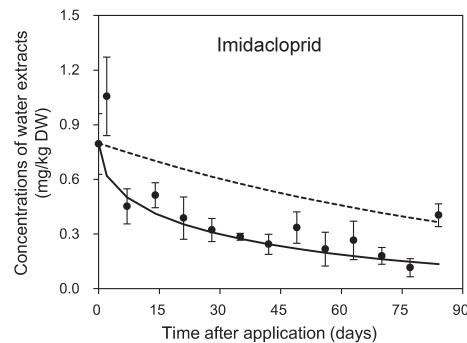
$$K_{d,app} = a + bt^{0.5} \quad (1)$$

where  $a$  and  $b$  are empirical parameters, and  $t$  is the time of incubation. Figure 3 shows an example of tetraconazole to illustrate time-dependent changes in sorption.  $K_{d,app}$  values were strongly correlated with the square root of time, and the  $a$  and  $b$  values were relatively high with the condition that the OC content of soils and the octanol–water partition coefficients ( $\log P_{ow}$ ) of pesticides were both high.

Parameters  $a$  and  $b$  play an important role in the prediction of time-dependent changes in  $K_{d,app}$  values. The  $a$  values, which represent  $K_{d,app}$  at time  $t=0$ , were approximated as the measured  $K_{d,app}$  values of the 0-day incubation sample ( $K_{d,app}(t_0)$ ). Moreover, the  $b$  values were proportional to the  $K_{d,app}(t_0)$  values, as



**Fig. 4.** Fitted parameter  $b$  for Eq. 1 plotted as function of apparent sorption coefficient at 0-day incubation ( $K_{d,app}(t_0)$ ). Reprinted with permission from Ref. 26. Copyright (2016) American Chemical Society.



**Fig. 5.** Comparisons between predicted and measured concentrations of water extracts from a field soil. (●) measured values, (—) values predicted using apparent sorption coefficients calculated by Eq. 2 and (---) values predicted using apparent sorption coefficient at 0-day incubation. Error bars indicate the standard error. Reprinted with permission from Ref. 26. Copyright (2016) American Chemical Society.

shown in Fig. 4. This result suggests that parameter  $b$  can be estimated using the  $K_{d,app}(t_0)$  values. Therefore, the empirical relationships between  $K_{d,app}(t_0)$  and the parameters of Eq. 1 ( $a$  and  $b$ ) allow us to rewrite Eq. 1 by using  $K_{d,app}(t_0)$  as

$$K_{d,app} = K_{d,app}(t_0) + 0.294K_{d,app}(t_0)^{1.005}t^{0.5} \quad (2)$$

Thus, it appears possible to estimate time-dependent changes in the  $K_{d,app}$  values using the  $K_{d,app}(t_0)$  values.

## 2.3. Predicting the dissipation of water-extractable pesticides in a field soil

As described in Section 2.1., the dissipation behaviors of  $C_W$  and  $C_T$  differed. It was considered that the time-dependent increase in soil sorption affected the dissipation of  $C_W$ . Therefore, the dissipation of  $C_W$  was predicted by compensating for the dissipation of  $C_T$  using the time-dependent  $K_{d,app}$  according to the following equation:

$$C_W = C_T \frac{r}{(r + K_{d,app})} \quad (3)$$

where  $C_T$  was calculated using the SFO model, and  $r$  is the ratio of the solution to the soil (mL/g) of water extraction. The  $K_{d,app}$  calculated by Eq. 2 and  $K_{d,app}(t_0)$  were used in Eq. 3 with and without consideration of time-dependent sorption, respectively. Figure 5 shows an example of imidacloprid for a comparison of the measured  $C_W$  and the predicted  $C_W$  values with and without consideration of the time-dependent increase in  $K_{d,app}$ . In the case of pesticides having high  $K_{d,app}(t_0)$  values (>6 mL/g), such as clothianidin, imidacloprid, and flutolanil, the differences between the values predicted using the  $K_{d,app}(t_0)$  values and the measured values were large. In contrast, the  $C_W$  values predicted using  $K_{d,app}$  estimated by Eq. 2 showed good agreement with the  $C_W$  values measured.

These results indicated that the dissipation rate of  $C_W$  was higher than that of  $C_T$ , and the time-dependent increase in  $K_{d,app}$  affected the difference in the dissipation rate between  $C_W$  and

**Table 2.** Coefficients of variation (CV) of  $K_{oc}$  values and correlation coefficients ( $r$ ) between the log  $K_{oc}$  values of pesticides and proportions of aromatic carbon in soils

Compound	No. soils	CV (%) of $K_{oc}$ values	$r$
Imidacloprid	7	124.9	0.93 <sup>a)</sup>
Dimethoate	4	82.4	0.60
Clothianidin	7	113.8	0.97 <sup>a)</sup>
Thiacloprid	7	115.4	0.94 <sup>a)</sup>
Metalaxyl	6	70.2	0.28
Fosthiazate	6	46.9	0.07
Methidathion	7	93.8	0.98 <sup>a)</sup>
Fenobucarb	5	92.2	0.76
Flutolanil	7	65.9	0.39
Procyimidone	7	84.9	0.57
Fenitrothion	7	76.3	0.75
Tetraconazole	7	50.2	0.30
Chloroneb	7	117.0	0.89 <sup>a)</sup>
Diazinon	7	48.7	−0.40
Cadusafos	7	59.9	0.40
Tolclofos-methyl	7	45.8	0.26
Tetradifon	7	29.5	−0.36

<sup>a)</sup> Significant at  $p < 0.01$ .

$C_T$ . Therefore, it is possible that the dissipation of  $C_W$ , which is important for evaluating the phytoavailability, is predicted by correcting the dissipation of  $C_T$  by time-dependent  $K_{d,app}$ .

### 3. Factors Influencing the Sorption of Pesticides to Soils<sup>27)</sup>

#### 3.1. Variability of the OC-normalized sorption coefficient ( $K_{oc}$ )

As described in Section 2 above, to estimate the dissipation behavior of water-extractable pesticides—phytoavailable pesticides—in soils, the  $K_{d,app}(t_0)$  should be measured. However, when the  $K_{d,app}(t_0)$  was compared to the  $K_d$  measured by OECD test guidelines,<sup>14)</sup> these values were approximately equal. Therefore, the elucidation of factors influencing the  $K_d$  variability and the estimation of  $K_d$  values using these factors leads to predicting the dissipation of phytoavailable pesticides in soils. The  $K_d$  values of 17 pesticides in 7 typical Japanese soils were measured in accordance with OECD test guidelines, and the relationships between the  $K_d$  values and the properties of pesticides and soils were investigated.

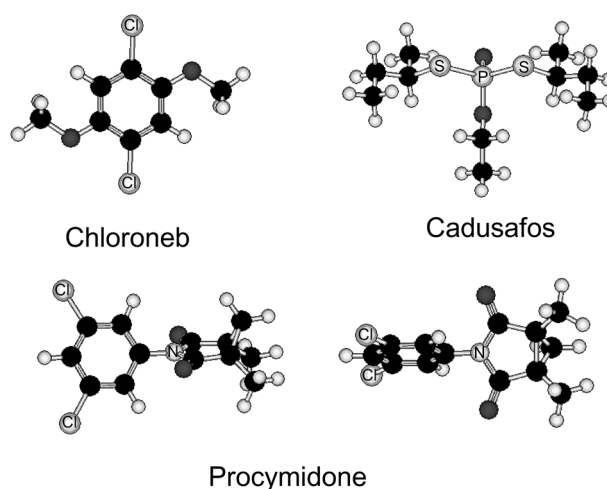
Previous sorption studies using foreign soils suggested that the variability of the  $K_d$  values of nonionic pesticides is strongly affected by the OC content in soil and the hydrophobicity, *i.e.*, the log  $P_{ow}$ , of pesticides.<sup>4)</sup> Therefore,  $K_{oc}$  values are known to have low variability among soils and can be estimated using the log  $P_{ow}$  of pesticides. However, the  $K_{oc}$  values measured in 7 Japanese soils of a given pesticide exhibited high variability among soils, *i.e.*, the CVs of the  $K_{oc}$  values of a pesticide ranged from 29.5 to 125% and the CVs of the  $K_{oc}$  values for 11 pesticides exceeded 60% (Table 2). Wauchope *et al.*<sup>4)</sup> reviewed the variability of the  $K_{oc}$  values in the literature mainly for foreign soils and re-

ported that the typical CVs of the  $K_{oc}$  values of a given pesticide range from 40 to 60%. This result implies that the variability of the  $K_{oc}$  values in Japanese soils was higher than that in foreign soils. On the other hand, the correlation between the log  $K_{oc}$  and log  $P_{ow}$  was poor, especially for two test andosols because the  $K_{oc}$  values varied depending on the molecular structures of pesticides, *i.e.*, the  $K_{oc}$  values of the aromatic compounds were larger than those of non-aromatic compounds. These results imply that the sorption of pesticides to soils is affected not only by hydrophobic interaction but also by interactions involving aromatic rings such as  $\pi$ – $\pi$  interaction.

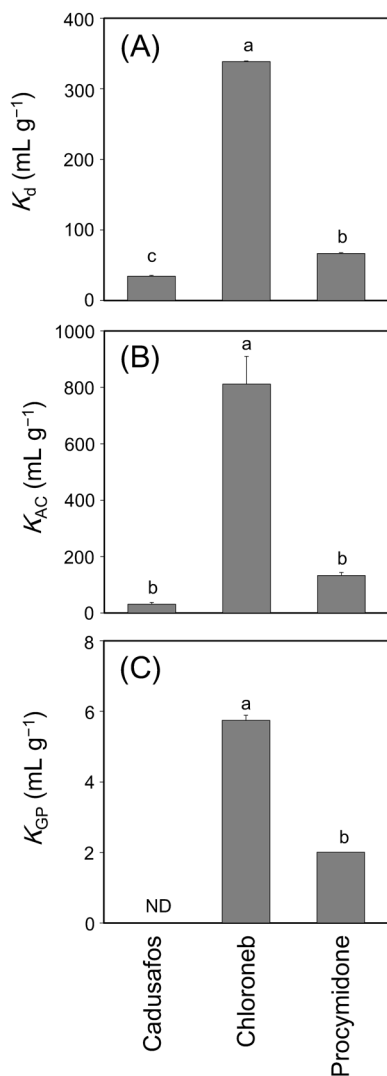
#### 3.2. Effect of OC quality on the $K_{oc}$ variability of pesticides

Solid-state <sup>13</sup>C nuclear magnetic resonance was performed to elucidate the effect of OC quality, *i.e.*, the relative proportions of each carbon type (alkyl carbon, *O*-alkyl carbon, aromatic carbon, and carboxyl carbon), on  $K_{oc}$  variability. The proportion of aromatic carbons, which correspond to lignin, tannin, BC, and so on, exhibited the greatest variability among test soils, ranging from 12.6 to 41.3%. Two test andosols in particular exhibited greater proportions of aromatic carbon than did other soils. In addition, the  $K_{oc}$  values of almost all pesticides for an andosol, which had the highest aromatic carbon content, were substantially higher than those for other soils. Focusing on the relationship between the  $K_{oc}$  and the proportion of aromatic carbon, the log  $K_{oc}$  values for several pesticides were positively correlated with the proportions of aromatic carbon. The correlation coefficients ( $r$ ) increased with the increasing CVs of the  $K_{oc}$  values for a given pesticide (Table 2).

The sorption of organic chemicals to BC is influenced by hydrophobicity, the presence of aromatic rings, and the planarity of the molecular structure.<sup>28–30)</sup> In other words, given the same log  $P_{ow}$  value, the sorption of planar aromatics to BC is higher



**Fig. 6.** Molecular structures of pesticides optimized using the PM7 semi-empirical Hamiltonian function in the MOPAC 2012 package.<sup>31)</sup> Reprinted from Ref. 27. ○—Hydrogen atom, ●—oxygen atom, ●—carbon atom, (P)—phosphorus atom, (Cl)—chlorine atom, (N)—nitrogen atom, (S)—sulfur atom.



**Fig. 7.** (A) Soil–water distribution coefficients ( $K_d$ ) for an andosol, (B) activated carbon–acetone distribution coefficients ( $K_{AC}$ ), (C) graphite–acetone distribution coefficients ( $K_{GP}$ ). Columns with the same letter are not significantly different at  $p < 0.05$  by ANOVA with Tukey's multiple range test for (A) and (B) and unpaired 2-sided  $t$ -tests for (C). Error bars indicate standard deviations ( $n=3$ ). ND: not detectable. Reprinted from Ref. 27.

than that of aliphatics or non-planar aromatics. For an andosol, in which the highest aromatic carbon content may be involved in the abundance of BC, the  $K_d$  values of chloroneb (a planar aromatic) were higher than those of cadusafos (an aliphatic) and procymidone (a non-planar aromatic with a torsional structure) (Figs. 6 and 7); this is in spite of the fact that the  $\log P_{ow}$  of chloroneb is nearly the same as that of procymidone and lower than that of cadusafos. Similar to the results for the andosol, the sorption of chloroneb to activated carbon and graphite carbon as a model substance of BC was significantly greater than that of cadusafos or procymidone (Fig. 7). Therefore, it is possible that the BC contained in the andosol greatly affects the sorption behavior of pesticides.

## Concluding Remarks

To develop a method for estimating the pesticide concentrations in succeeding crops on the predicted concentrations in soils, the dissipation behavior of phytoavailable pesticides in soils should be evaluated. The present study reveals that (i) the concentrations of water-extractable pesticides in soil can be used to evaluate the phytoavailability of pesticides in soils and (ii) the dissipation behavior of water-extractable pesticides in soils is estimated using the dissipation rates of total extractable pesticides in soils and the time-dependent  $K_{d,app}$ , which is predicted on the basis of the  $K_d$  measured in accordance with OECD test guidelines. Furthermore, the present study suggests that the  $K_d$  can be more precisely predicted by considering not only the OC content in soil and the hydrophobicity of pesticides but also the BC content in soil and the molecular structure of pesticides. Regrettably, no standard method for quantifying the BC in soils has been established. Therefore, further studies are needed to isolate and quantify the BC in soils.

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