Comparison of soil sorption parameters of pesticides measured by batch and centrifugation methods using an andosol

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We compared the soil sorption coefficient (K_d) measured by batch and centrifugation methods using a Japanese andosol and ten pesticides. Although the K_d values measured by both methods increased with time, those obtained via the batch method tended to be higher during the test period. The difference in K_d values between the two methods affected pesticide concentrations estimated in the soil solution, and the results estimated using K_d values obtained via the batch method underestimated the observed trends.

Keywords: pesticides, soil sorption, soil solution, centrifugation method, andosol.

Electronic supplementary material: The online version of this article contains supplementary material (Supplemental Tables S1–S7 and Figs. S1–S2), which is available at http://www.jstage.jst.go.jp/browse/jpestics/

Introduction

The soil sorption coefficient, K_d, describes the distribution of pesticides between the water phase and soil particles and is one of the most important input parameters of mathematical models predicting the fate of pesticides in environments. The K_d values are generally determined by the batch method, in which slurry conditions are used, that is, the soil:solution ratio is in the range of 1:2 to 1:100. However, such slurry conditions are quite different from the soil moisture conditions of upland fields and so the K_d values may not adequately express the actual soil sorption ability of pesticides. Recent studies suggest that such K_d values are greater than the K_d values measured at realistic soil:solution ratios using the centrifugation method (K_d,C) to obtain the soil solution. However, there are no reports comparing K_d and K_d,C for Japanese soils. Japanese upland fields are characterized by andosols with high organic carbon content. Although andosols cover only 0.8% of the earth’s surface, they cover approximately half of all upland fields in Japan. Therefore, it is important to determine the difference between K_d and K_d,C for Japanese andosols. Furthermore, our previous study indicated that the K_d values of many pesticides increased with time and were proportional to the square root of time. The changes in K_d,C with time should also be investigated for more realistic evaluation of the soil sorption ability of pesticides.

On the other hand, in Japan, some pesticides applied to crops remain in the soil and are detected in succeeding crops. Pesticide concentrations in succeeding crops occasionally exceed the uniform residue limit of 0.01 ppm set by the Japanese Positive List System. In order to prevent the production of crops exceeding the uniform residue limit, mathematical models are required to predict the residue concentrations in succeeding crops, which are affected by many variable factors such as soil type, pesticide type and weather conditions. It is assumed that some pesticides sorbed to soil particles are eluted into the soil solution and subsequently taken up by plant roots, so that predicting the pesticide concentrations in a soil solution using K_d is an essential process in such models. The K_d,C values can express the actual soil sorption ability of pesticides in upland fields more precisely than K_d values. If there is a discrepancy between K_d,C and K_d, then predicting pesticide concentrations in the soil solution and in succeeding crops using K_d without appropriate correction is inadequate.

The objectives of this study are to compare the parameters regarding time-dependent sorption between the batch and centrifugation methods using a Japanese andosol and to investigate the effect of the difference in sorption parameters between the two methods on estimated concentrations of pesticides in the soil solution.

Materials and Methods

The details of the field study were described in our previous report. In brief, the study began on May 12, 2015, and was performed in triplicate in an upland andosol field located at the Institute for Agro-Environmental Sciences, NARO, Tsukuba City, Japan. The physicochemical properties in the surface soil (0–10 cm depth) were pH 6.3, organic carbon (OC) 4.93%, cation exchange capacity 26.0 cmol(+)/kg and a texture of silty loam (clay 7.3%, silt 46.6% and sand 46.1%). Ten pesticides (dinotefuran, imidacloprid, clothianidin, thiacloprid, foshizate, metalaxyl, fenobucarb, flutolanil, procymidone and tolclofos-
methyl; Supplemental Table S1) were chosen based on hydrophobicity, i.e., the range of their octanol–water partition coefficients (log $P_{ow}$). The commercial formulations of the pesticides (Supplemental Table S1) were added to a plastic container and diluted with water. One liter of the mixed solution (200 mg/L each) was evenly applied to each plot (1 m × 1 m) using a watering can, and the soil surface was tilled. Four cores were taken from each plot for the soil depth of 0–10 cm at 0 (immediately after tilling), 2, 7, 14, 21, 28, 35, 42, 49, 56, 63, 70, 77 and 84 days after application of the pesticides. The cores were combined for each plot and were mixed well.

To determine the $K_d$ values, a sequential extraction of soils was conducted. Distilled water (25 mL) was added to the sampled soil equivalent to a 5 g of dry weight (DW) in a 50 mL glass centrifuge tube. The tubes were agitated on a thermostat shaker (TATIEC, Saitama, Japan) for 24 hr at 25±2°C in darkness. After shaking, the mixtures were centrifuged at 1200 × g for 30 min, and 15 mL of supernatant was taken and used to quantify the water extracts. In addition, 30 mL of acetone was added to the remaining sample, the tubes were shaken in a thermostat shaker for 20 min at 25±2°C and centrifuged at 1200 × g for 10 min, and the supernatant was carefully decanted. This extraction procedure was repeated twice more. The collected supernatants were evaporated in a rotary evaporator to reduce the volume to approximately 15 mL and then used to quantify the acetone extracts.

To determine the $K_{d,c}$ values, the soil solution in the sampled soil was collected by centrifugation with double tubes (Hitachi Koki, Tokyo, Japan). The soil was placed into four inner tubes (capacity 100 mL), and the inner tubes were inserted into outer tubes with a glass fiber filter included. The tube assembly was centrifuged at 15,800 × g for 1 hr corresponding to pF 4.2 (i.e., the permanent wilting point of plants) using a soil dehydrating rotor (Hitachi Koki). The collected soil solution was used to quantify the pesticide concentration.

The aliquots of water extracts, the concentrates of acetone extracts from soils and the collected soil solutions were cleaned using a diatomite column (InertSep K-solute 20 mL; GL Sciences, Tokyo, Japan). Then the following solid-phase extraction cartridges were used: a PSA column (500 mg; Supelco, Bellefonte, PA, USA) and an ENVI-Carb II/PSA column (500 mg/500 mg; Supelco) for analytical groups A (dinofuran, imidacloprid, clothianidin, thiacloprid, fosfathiazate and metalaxyl) and B (fenobucarb, flutolanil, procymidone and tolclofos-methyl), respectively. The cleaned samples were analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) for group A and gas chromatography-mass spectrometry (GC-MS) for group B (Supplemental Tables S2–S5). In the case of the high matrix effects of cleaned samples, quantifications of pesticides using GC-MS were carried out using matrix-matched standards. Pesticide recovery tests were performed with distilled water (spiked with a pesticide concentration of 1 ng/mL) and the field soil (spiked with a pesticide concentration of 5 and 3 ng/g for groups A and B, respectively) using the above-mentioned methods. The mean recovery for groups A ($n$ = 4) and B ($n$ = 5) were in the range of 82.2–96.1% for all compounds; the coefficients of variation (CVs) were ≤ 14.4%. The limits of quantification (LOQs) for all compounds in distilled water and field soil were in the ranges of 0.16–1.29 ng/mL and 0.60–3.62 ng/g, respectively.

The mass fraction of water-extractable pesticides in the soil measured using the batch method, $C_w$ (µg/g DW), was calculated using the following equation:

$$ C_w = C_{aq} \cdot (V_{add} + V_{sw}) / M $$

where $C_{aq}$ (µg/mL) is the mass concentration of the pesticide in the aqueous phase after shaking for 24 hr, $V_{add}$ is the volume of added distilled water (mL), $V_{sw}$ is the volume of soil solution (mL) calculated based on soil moisture content and $M$ is soil dry mass (g). The mass fraction of the total extractable pesticide in the soil measured using the batch method, $C_T$ (µg/g DW), was represented by the following equation:

$$ C_T = (C_{aq} \cdot V_{add} + m_b) / M $$

where $V_{add}$ is the volume of the aliquot taken from the supernatant (mL) and $m_b$ is the mass of the pesticide extracted by acetone from the remaining sample after $V_{add}$ was removed (µg).

The mass fraction of the water-extractable pesticide in the soil measured using the centrifugation method, $C_{w,c}$ (µg/g DW), was calculated using the following equation:

$$ C_{w,c} = C_{sw} \cdot V_{sw,c} / M $$

where $C_{sw}$ (µg/mL) is the mass concentration of the pesticide in the soil solution and $V_{sw,c}$ is the volume of soil solution (mL) collected by centrifugation.

$K_d$ (mL/g) and $K_{d,c}$ (mL/g) are apparent sorption coefficients and were determined using Eq. 4 and Eq. 5, respectively, on the assumption that acetone-extractable pesticides in soils represented soil-sorbed pesticides:

$$ K_d = C_{sorb} / C_{aq} = (C_T - C_w) / C_{aq} $$

$$ K_{d,c} = C_{sorb} / C_{sw} = (C_T - C_{w,c}) / C_{sw} $$

where $C_{sorb}$ is the mass fraction of soil-sorbed pesticides (µg/g DW).

**Results and Discussion**

The comparison between $K_d$ and $K_{d,c}$ of the 0-day incubation sample is shown in Fig. 1 and Supplemental Tables S6–S7. The $K_{d,c}$ values tended to be lower than the $K_d$ values, although the discrepancy between them differed according to pesticide type. The $K_{d,c}/K_d$ ratios ranged from 0.24 for thiacloprid to 1.43 for procymidone, and the geometric mean of the ratios was 0.66. There were especially low ratios (≤ 0.35) for three neonicotinoids: imidacloprid, clothianidin and thiacloprid. Kah and Brown investigated the discrepancy between the batch and centrifugation methods using six pesticides, which included acidic compounds and sulfonylureas, and nine soils
respectively. Thus, the variation range of carbofuran in eight soils (OC = 0.7–3.5%) were 0.56 and 0.22, d,C of 1-day incubation samples, and OECD method and the K measured using the batch and centrifugation (b,C) methods. The reasons the d,C values of the 1-day incubation sample and that the means of Kd,C/Kd ratios in nine soils ranged from approximately 0.6 to 1.3. Similarly, Yazgan et al.3 compared the Kd obtained with the OECD method and the Kd,C of 1-day incubation samples, and found that the means of the Kd,C/Kd ratios of imidacloprid and carbofuran in eight soils (OC = 0.7–3.5%) were 0.56 and 0.22, respectively. Thus, the variation range of Kd,C/Kd ratios in previous reports was similar to that of a Japanese andosol. Kah and Brown4 reported that the Kd,C/Kd ratios were negatively correlated with the levels of sorption (estimated by Kd) for a limited number of pesticides and soils—the difference between Kd,C and Kd tended to increase with greater sorption strength. However, the present study showed that the Kd,C/Kd ratios for the andosol were not correlated with Kd, so sorption strength alone was insufficient to explain the degree of difference between Kd,C and Kd. On the other hand, Brücher et al.14 indicated that linuron sorption to soils was influenced by temperature, and the sorption strength of linuron at 15°C tended to be higher than that at 23°C. In the present study, the daily mean temperature (18.7°C) on the first soil sampling (i.e., day 0) for obtaining the soil solution was lower than the equilibrium temperature (25°C) in the batch method. Therefore, the discrepancy between Kd and Kd,C (i.e., Kd,Kd,C) could not be explained by the difference in temperature. Three neonicotinoids with especially low values of Kd,C/Kd ratio tended to have low log Po for water solubility; i.e., such pesticides may be less easily distributed to the hydrophobic phase (Supplemental Fig. S1). For such pesticides, the vigorous shaking of the batch equilibrium method probably enhances the sorption to hydrophobic regions of soil and may give rise to the discrepancy between Kd and Kd,C, although further studies using a greater variety of pesticides are necessary to verify this. In contrast to three neonicotinoids, the Kd,C values of metalaxyl and procymidine were higher than the Kd values, and the Kd,C/Kd ratios were 1.31 and 1.43, respectively (Fig. 1). The reasons the Kd,C/Kd ratios were greater than 1 are not clear. However, the variability of Kd,C values was higher than that of Kd values, and the CVs of the Kd,C values ranged from 20.4 to 40.9% (Supplemental Tables S7). Thus, it is possible that the measurement errors for the Kd,C values affect the variance of the Kd,C/Kd ratios.

The values of Kd,C increased with time, in agreement with the results of Walker and Jurado-Exposito2 and Kah and Brown.4 Our previous report7 indicated that the time-dependent changes in the Kd values of all tested pesticides, except for fenobucarb and procymidine, were represented by the following equation:

\[
K_d(t) = a + b \cdot t^{0.5}
\]

where Kd(t) is the Kd value after t days, a and b are empirical parameters and t is the time of incubation. In the present study, the time-dependent changes in the Kd,C of all pesticides, except for fenobucarb and procymidine, were also fitted to Eq. 6 (Supplemental Fig. S2). This result implies that the changes in Kd,C with time were also estimated by Eq. 6, as with Kd. The Kd,C values of fenobucarb and procymidine were extremely high on days 28 and 56 (and afterward), respectively, because their concentrations in the soil solution were at low levels near the LOQ at these times. Therefore, the fit to Eq. 6 for these two pesticides was poor (R2<0.3 and p>0.01; Supplemental Fig. S2). Although Eq. 6 has no theoretical basis, it has been suggested that the amounts of sorbed chemicals, which are controlled by diffusion, are proportional to the square root of time.15 Hence, the time-dependent increase of Kd is presumably associated with the diffusion of pesticides into the solid phase of organic matter and the nanopores (i.e., inaccessible internal sites) of soil particles.16 However, Cox et al.17 mentioned that the time-dependent increase in Kd values for imidacloprid was caused by degradation in the soil solution and on accessible external sites of soil particles when the degradation rate exceeded the desorption rate from inaccessible internal sites. Thus, two processes (diffusion and degradation) are thought to contribute to the time-dependent increase in Kd.

A comparison of the b values of Eq. 6 (i.e., the increase rate of Kd with time) between the centrifugation and batch methods for all pesticides except fenobucarb and procymidine is shown in Fig. 2. The ratios of b values of the centrifugation method (b,C) to those of the batch method ranged from 0.18 for metalaxyl...
to 1.11 for flutolanil, and the geometric mean of the ratios was 0.54. Thus, the $b_C$ values were lower than the $b$ values of the batch method, similar to the relationship between $K_d$ and $K_{d,C}$. The $b_C/b$ ratios of metalaxyl and fosthiazate were especially low, 0.18 and 0.34, respectively. These two pesticides had a relatively high log $P_{ow}$ in spite of high water solubility, which was in contrast to the three neonicotinoids: imidacloprid, clothianidin and thiacloprid (Supplemental Fig. S1). However, the relationship between such physicochemical properties of pesticides and the variability of the $b_C/b$ ratios remains unexplained.

The $a$ values of Eq. 6, which represent $K_d$ at time zero, were approximated as the measured values of 0-day incubation samples. Hence, Eq. 6 can be rewritten by using $K_d$ as follows:

$$K_d(t) \equiv K_d + b \cdot t^{0.5}$$

To estimate pesticide concentrations in the soil solution, it is effective to modify the $C_T$ values (i.e., pesticide concentrations in soil) by using time-dependent $K_d$. Therefore, the pesticide

Fig. 3. Comparisons between calculated and measured concentrations in the soil solution. Cases 1 and 2 indicate the estimated results using sorption parameters of the batch and centrifugation methods, respectively, and Case 3 indicates the results estimated by compensating for the difference in sorption parameters between the batch and centrifugation methods. Error bars indicate the standard error. The measured values of tolclofos-methyl were less than the LOQ at and after 63 days.

![Graphs showing comparisons between calculated and measured concentrations in the soil solution.](image-url)
Concentration in the soil solution after \( t \) days \( (C_i(t), \mu g/mL) \) was estimated using the following equation:
\[
C_i(t) = \frac{C_i(t)}{\theta} + \left[K_d + b \cdot t^{0.5}\right] \tag{8}
\]
where \( C_i(t) \) was calculated using a double-first-order in parallel (DFOP) model as described in our previous report. \( \theta \) is the volumetric soil water content (dimensionless) and \( \rho_b \) is the bulk density of the soil (g/mL). The mean value of \( \theta/\rho_b \) during test period \( (i.e., 0.21 \text{ mL/g}) \) was used in Eq. 8. Because the \( K_d \) and \( b \) values were higher than the \( K_{d,C} \) and \( b_C \) values, respectively, the \( C_{sw} \) values for upland fields estimated using \( K_d \) and \( b \) based on Eq. 8 may underestimate the measured values. The goodness of fit for each estimation method was assessed using the percent bias (PBIAS, %)

\[
PBIAS = 100 \left( \frac{1}{n} \sum_{i=1}^{n} (O_i - P_i) / \sum_{i=1}^{n} O_i \right) \tag{9}
\]
where \( P_i \) and \( O_i \) are the predicted and observed values, respectively, and \( n \) is the number of observations. The optimal value of PBIAS is 0.0. The lower the absolute value of PBIAS, the better the goodness-of-fit. Positive and negative values of PBIAS indicate underestimation bias and overestimation bias, respectively.

Temporal changes in observed and estimated \( C_{sw} \) values in the field study are shown in Fig. 3, and Table 1 shows the PBIAS values and the ratios of the geometric mean of estimated values to that of measured values during the test period \( (R_{GM}) \). The \( C_{sw} \) values estimated using the parameters of the batch method (Case 1) underestimated the observed trend. In Case 1, the PBIAS values of all pesticides were positive, and the \( R_{GM} \) values ranged from 0.41 for fosthiazate to 0.95 for dinotefuran. Unsurprisingly, the \( C_{sw} \) values estimated using the parameters of the centrifugation method (Case 2), \( K_{d,C} \) and \( b_C \), showed good agreement with the observed values. The absolute values of PBIAS were lower in Case 2 than in Case 1. The \( R_{GM} \) values in Case 2 ranged from 0.89 for fosthiazate to 1.22 for dinotefuran and clothianidin. Although the \( K_{d,C} \) and \( b_C \) values are needed for the precise estimation of \( C_{sw} \) values, there are very few data on \( K_{d,C} \) and \( b_C \). To precisely estimate \( C_{sw} \) values, it appeared effective to correct the difference in sorption parameters between the batch and centrifugation methods. The \( K_d \) and \( b \) values of the batch method were corrected \( (i.e., \text{multiplied}) \) by the geometric mean of the \( K_{d,C}/K_d \) ratios \( (0.66) \) and the \( b_C/b \) ratios \( (0.54) \), respectively, and the \( C_{sw} \) values were estimated (Case 3). The \( R_{GM} \) in Case 3 ranged from 0.71 for fosthiazate to 1.54 for flutolanil. The estimated values in Case 3 resulted in less underestimation of the observed values as compared to Case 1, although the absolute values of PBIAS were higher in Case 3 than in Case 2. As mentioned above, the variation in \( K_{d,C}/K_d \) ratios and \( b_C/b \) ratios could not be explained by the physicochemical properties of pesticides. This implied that the estimation of \( C_{sw} \) using the mean values of \( K_{d,C}/K_d \) ratios and \( b_C/b \) ratios \( (i.e., \text{the estimation in Case 3}) \) is a realistic approach for the time being, although further investigations using a greater number of chemicals are required.

Thus, the difference in sorption parameters between the centrifugation and batch methods affected the variation in estimated \( C_{sw} \) values. Although numerous data for sorption parameters measured using the batch method are available, the estimation of \( C_{sw} \) using data measured by the batch method tended to underestimate actual dissipation trends in upland fields. If underestimated \( C_{sw} \) values are used for mathematical models predicting the residue concentrations in succeeding crops, the values predicted by the models also become underestimates. Underestimation of the residue concentrations in succeeding crops leads to producing crops in which the pesticide concentrations exceed the uniform residue limit of 0.01 ppm. Therefore, when estimating \( C_{sw} \) using the sorption parameters of the batch method, particular attention must be paid to the difference from those of the centrifugation method, in which the sorption parameters take into account the actual moisture content in upland fields.

References

1) OECD: “Guidelines for Testing of Chemicals,” Section 1 (106),

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\( a \) Estimation using the sorption parameters of the batch method. \( b \) Estimation using the sorption parameters of the centrifugation method. \( c \) Percent bias (%). \( d \) Ratio of geometric mean of estimated values to that of measured values during the test period.