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 (Kd) measured by batch and centrifugation methods using a Japanese andosol and ten pesticides. Although the Kd 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 Kd values between the two methods affected pesticide concentrations estimated in the soil solution, and the results estimated using Kd 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, Kd, 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 Kd 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 Kd values may not adequately express the actual soil sorption ability of pesticides. Recent studies2–4) suggest that such Kd values are greater than the Kd values measured at realistic soil:solution ratios using the centrifugation method (Kd,C) to obtain the soil solution. However, there are no reports comparing Kd and Kd,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,5) they cover approximately half of all upland fields in Japan.6) Therefore, it is important to determine the difference between Kd and Kd,C for Japanese andosols. Furthermore, our previous study7) indicated that the Kd values of many pesticides increased with time and were proportional to the square root of time. The changes in Kd,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.8) 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 Kd is an essential process in such models.9) The Kd,C values can express the actual soil sorption ability of pesticides in upland fields more precisely than Kd values.3) If there is a discrepancy between Kd,C and Kd, then predicting pesticide concentrations in the soil solution and in succeeding crops using Kd 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.7) 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, fosthiazate, metalaxyl, fenobucarb, flutolanil, procymidone and tolclofos-
tubes (capacity 100 mL), and the inner tubes were inserted into Supelco) for analytical groups A (dinotefuran, imidacloprid, clo- 
dardis.12) Pesticide recovery tests were performed with distilled matrix effects of cleaned samples, quantifications of pesticides group B (Supplemental Tables S2–S5). In the case of the high A and gas chromatography-mass spectrometry (GC-MS) for thianidin, thiacloprid, fosthiazate and metalaxyl) and B (fen -
tridges were used: a PSA column (500 mg; Supelco, Bellefonte, using a diatomite column (InertSep K-solute 20 mL; GL Scienc -
was centrifuged at 15,800 g, the permanent wilting point of plants) using a soil de -
hydrating rotor (Hitachi Koki). The collected soil solution was ×g for 1 hr corresponding to pF 
Kd,C values, a sequential extraction of soils was conducted.7) 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 (TAITEC, 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 Kd values, the soil solution in the sampled soil was collected by centrifugation with double tubes (Hitachi Koki, Tokyo, Japan).10,11) The soil was placed into four inner tubes with (Hitachi Koki, Tokyo, Japan). Then the following solid-phase extraction car -
tridges 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 (dinotefuran, imidacloprid, clo -
thiainidin, thiacloprid, fosthiazate and metalaxyl) and B (feno -
bucarb, flutolanil, procymidine and tolclofos-methyl), respecti -
vel.7) The cleaned samples were analyzed via liquid chroma -
tography-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.12) 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 coe 
ficients of variation (CVs) were ≤ 14.4%. The limits of quantifi -
cation (LOQs)13) 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, Cw (µg/g DW), was calcu -
lated using the following equation:

\[ C_w = C_{aq} \cdot (V_{add} + V_{sw}) / M \] (1)

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:

\[ C_T = (C_{aq} \cdot V_{aliq} + m_k) / M \] (2)

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

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

\[ C_{wjc} = C_{sw} \cdot V_{swjc} / M \] (3)

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

K_d (mL/g) and K_{djc} (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 repre -
sented soil-sorbed pesticides:

\[ K_d = C_{norb} / C_{aq} = (C_T - C_w) / C_{aq} \] (4)

\[ K_{djc} = C_{norb} / C_{swjc} = (C_T - C_{wjc}) / C_{swjc} \] (5)

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

**Results and Discussion**

The comparison between K_d and K_{djc} of the 0-day incubation sample is shown in Fig. 1 and Supplemental Tables S6–S7. The K_{djc} values tended to be lower than the K_d values, although the discrepancy between them differed according to pestic -
type. The K_{djc}/K_d ratios ranged from 0.24 for thiacloprid to 1.43 for procymidine, and the geometric mean of the ratios was 0.66. There were especially low ratios (≤ 0.35) for three neonicotinoids: imidacloprid, clothianidin and thiacloroprid. Kaah and Brown10 investigated the discrepancy between the batch and centrifugation methods using six pesticides, which included acidic compounds and sulfonylureas, and nine soils
carbofuran in eight soils (OC = 0.7–3.5%) were 0.56 and 0.22, d,C of 1-day incubation samples, and measured using the batch and centrifugation (K ratios were 1.31 and 1.43, respectively (Fig. 1). The reasons the present study showed that the d,C/Kd values of metalaxyl and procymidone, were represented by the following equation:

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

where $K_d(t)$ is the $K_d$ 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 $K_{d,C}$ of all pesticides, except for fenobucarb and procymidone, were also fitted to Eq. 6 (Supplemental Fig. S2). This result implies that the changes in $K_{d,C}$ with time were also estimated by Eq. 6, as with $K_d$. The $K_{d,C}$ values of fenobucarb and procymidone 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 ($R^2 < 0.3$ 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. Hence, the time-dependent increase of $K_d$ 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. However, Cox et al. mentioned that the time-dependent increase in $K_d$ 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 $K_d$.

A comparison of the $b$ values of Eq. 6 (i.e., the increase rate of $K_d$ with time) between the centrifugation and batch methods for all pesticides except fenobucarb and procymidone is shown in Fig. 2. The ratios of $b$ values of the centrifugation method ($b_{c,C}$) 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 $P$ 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:

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

(7)

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
concentration in the soil solution after \( t \) days \((C_w(t), \mu g/mL)\) was estimated using following equation:

\[
C_w(t) = \frac{C_f(t)}{\theta} + \left[ K_d + b \cdot t^{0.5} \right] 
\]

where \( C_f(t) \) was calculated using a double-first-order in parallel (DFOP) model as described in our previous report\(^7\), \( \theta \) 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 mL/g) was used in Eq. 8. Because the \( K_d \) and \( b \) values were higher than the \( C_w \) (volumetric soil water content (dimensionless) and \( C_{GM} \) values were underestimation bias and overestimation bias, respectively. \( PBIAS \) of all pesticides were positive, and the \( PBIAS \) values of Case 1 underestimated the observed trend. In Case 1, the \( PBIAS \) values were lower in Case 2 than in Case 1. The \( PBIAS \) values in Case 3 ranged from 0.89 for fosthiazate to 1.22 for dinotefuran and clothianidin. Although the \( K_d \) and \( b \) values are needed for the precise estimation of \( C_w \) values, there are very few data on \( K_{GM} \) and \( K_d \). To precisely estimate \( C_w \) 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., multiplied) by the geometric mean of the \( K_{GM}/K_d \) ratios (0.66) and the \( b_{GM}/b \) ratios (0.54), respectively, and the \( C_{GM} \) 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 \( K_{GM}/K_d \) and \( b_{GM}/b \) ratios could not be explained by the physicochemical properties of pesticides. This implied that the estimation of \( C_w \) using the mean values of \( K_{GM}/K_d \) ratios and \( b_{GM}/b \) ratios (i.e., 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 \( C_w \) values. Although numerous data for sorption parameters measured using the batch method are available, the estimation of \( C_w \) using data measured by the batch method tended to underestimate actual dissipation trends in upland fields. If underestimated \( C_w \) 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 \( C_w \) 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.

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### Table 1. Goodness-of-fit between the measured and estimated concentrations of pesticides in soil solution

| Compound         | Case 1 \(^{a}\) | Case 2 \(^{b}\) | Case 3 \(^{c}\) |
|------------------|----------------|----------------|----------------|
|                  | \( PBIAS^{d} \) | \( R_{GM}^{e} \) | \( PBIAS^{d} \) | \( R_{GM}^{e} \) | \( PBIAS^{d} \) | \( R_{GM}^{e} \) |
| Dinofuran        | 9.7            | 0.95           | -10.4          | 1.22           | -33.5          | 1.44           |
| Clothianidin     | 44.6           | 0.67           | -9.6           | 1.22           | 12.2           | 1.08           |
| Imidacloprid     | 50.1           | 0.62           | -6.3           | 1.18           | 19.8           | 1.02           |
| Thiacloprid      | 71.3           | 0.46           | 6.8            | 1.16           | 54.3           | 0.78           |
| Metalaxyl        | 41.5           | 0.44           | 5.5            | 1.12           | 10.1           | 0.75           |
| Fosthiazate      | 43.5           | 0.41           | 24.1           | 0.89           | 15.8           | 0.71           |
| Flutolanil       | 17.8           | 0.93           | 3.3            | 1.02           | -33.3          | 1.54           |
| Tolclofos-methyl | 14.6           | 0.86           | -4.6           | 1.09           | -36.2          | 1.42           |

\(^{a}\) Estimation using the sorption parameters of the batch method. \(^{b}\) Estimation using the sorption parameters of the centrifugation method. \(^{c}\) Estimation using the corrected sorption parameters of the batch method with respect to the difference between the batch and centrifugation methods. \(^{d}\) Percent bias (%). \(^{e}\) Ratio of geometric mean of estimated values to that of measured values during the test period.
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