Hydrophobicity of Buprofezin and Flutolanil in Relation to Their Soil Adsorption and Mobility in Rice Plants

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INTRODUCTION

Both adsorption with soil and mobility in rice plants are very important physicochemical characters governing the biological availability of pesticides, especially when they are directly applied to the soil surface. Estimation of these characters is extremely useful for optimization of practical pesticidal activities.

Recently, the adsorption and mobility in soil and rice plants of a series of fungicidal compounds was found to be nicely related to their hydrophobicity, $\log P$. If these relationships can be extended to various classes of compounds, their adsorption with soil and mobility in rice plants may be predictable from a measure of the hydrophobicity, $\log P$. Here, we will assess the extensibility of these relationships to other classes of compounds and their application to predict such behavior in soil and plants, using structurally unrelated compounds such as 2-tert-butylimino-3-isopropyl-5-phenyl-3,4,5,6-tetrahydro-2H-1,3,5-thiadiazin-4-one (buprofezin) and 3'-isopropoxy-2-(trifluoromethyl)benzanilide (flutolanil), which are respectively an insecticide and a fungicide.

MATERIALS AND METHODS

1. Compound

Buprofezin and flutolanil were synthesized in the Chemical Research Center of this Company and were highly purified before use by repeated recrystallizations.

2. Analysis of the Compounds

The instrument used was a Shimadzu GC 6A gas chromatograph equipped with an ECD of $^{60}$Ni (10 mCi). A 1.5 m glass column (ø 0.3 cm) packed with 2% OV-1 on Chromosorb W, HP (80–100 mesh) was used at 230°C with N$_2$ gas as the carrier (60 ml/min). The retention times of buprofezin and flutolanil were 3.6 and 3.1 min, respectively. For quantitative analysis, the calibration curves (the plots of $\log$ peak height against the $\log$ value of the
concentration in the injected solution) were prepared just before analysis. The injected volume was fixed at 8 µl using an automatic operation controller system, Shimadzu AOC-6. To determine the amount of compounds in 1-octanol, water and rice plants, samples were diluted or extracted with acetone or benzene and the resulting homogeneous solutions or organic layers were analyzed by gas chromatography.

3. Log P
The partition coefficient between 1-octanol and water, P, was determined in a manner similar to those reported previously. The initial concentration added to the 1-octanol phase was 200-2,000 mg/l. For each compound, at least two runs with different concentrations were made and the values were averaged. The log P values are shown in Table 1.

4. Adsorption Constant (K) with Soil from Aqueous Solutions
The soil used in this study was collected from the surface of a paddy field in Kawachi-Nagano, Osaka and stored at -20°. Analysis data of the soil (alluvial, clay loam) has been shown in our previous paper. Adsorption constant, K, with Osaka soil was determined according to the method reported previously. The initial concentration of the compounds in the solution ranged from 0.05 to 0.5 mg/l. The obtained log K values are shown in Table 1.

5. Affinity to Rice Plants
A rice plant column was prepared as described previously. Ten ml of an aqueous solution of buprofezin (0.2×10^-6 M) and flutolanil (0.2×10^-6 M) was put on the rice plant column. The log of elution volume, log V_e, of the compounds is used as affinity to the plant. The larger log V_e value the compound has, the higher would be its affinity to the packed material (rice plants). Obtained log V_e values are listed in Table 1.

6. Mobility in Rice Plants
Compound mobility, log µ, was determined according to the method reported previously. The roots of five rice plants of the 3- to 4-leaf stage were immersed in 20 ml of nutrient solution containing 1 mg NH₄NO₃, 1 mg K₂HPO₄ and 0.2×10^-6 M of the compounds at 25° for 1 and 2 days. After being washed in running tap water for 1 min, the plants were divided into 7 parts based on the distance from the root system: I (root), II (0-3 cm), III (3-6 cm), IV (6-9 cm), V (9-12 cm), VI (12-15 cm) and VII (15-18 cm). From the distribution patterns of the compounds in the plants, the mobility, log µ, was derived using the following Eq. (1). The obtained log µ values are shown in Table 1.

\[ \log \mu = \log \left( \frac{\text{concentration in Part II}}{\text{concentration in Part I}} \right) + \left( \frac{1}{2} \right) \sum_{n=1}^{7} \{ \log (\text{concentration in Part } n) / \text{concentration in Part } n) \} \]
RESULTS AND DISCUSSION

1. Hydrophobicity (log P)

The log P value of flutolanil was 3.70, but that of buprofezin varied with pH: 1.20 (pH 1) and 4.31 (pH 6.5-12).

Since the log P at pH 1 was identical to that of buprofezin hydrochloride, the lower value must be due to the salt formation or protonation of the buprofezin molecule.

2. Soil Adsorption Constant (K)

The log K of flutolanil was 0.90, but that of buprofezin again varied from 2.69 at pH 1, then 1.86 at pH 6.5 and finally to 1.48 at pH 12. The positive charge of protonated molecules can interact with negative charges on soil particles so that acidic conditions gave higher log K values. Indeed, many cationic compounds have been known to be strongly adsorbed with soil components. Thus, the log K of buprofezin would be 1.48 for its neutral molecules and 2.69 for its protonated molecules.

A good relationship between log K and log P has been obtained for a series of neutral fungicides Eq. (2). In this and the following equations, n is the number of compounds studied, s is the standard deviation, r is the correlation coefficient and the figures in the parentheses are the 95% confidence intervals.

\[
\log K = 0.41 (\pm 0.06) \log P - 0.40 (\pm 0.24)
\]

\[n=12, \ s=0.150, \ r=0.980 \] (2)

From this equation and log P values, the log K of buprofezin and flutolanil could be calculated and compared with those observed: Calculated 1.37 and observed 1.48 for neutral buprofezin, and calculated 1.12 and observed 0.90 for flutolanil. Thus, in each case the calculated and the observed log K were almost identical to each other. The relationship between log K and log P of the fungicides seemed to be extendible to these structurally unrelated compounds. Therefore, soil adsorption of other classes of compounds would be predictable from log P, but not for ionized compounds such as buprofezin hydrochloride, whose log K value was 0.09 (calculated) or 2.69 (observed).

3. Affinity to Rice Plants

The affinity to rice plants, log \( V_E \), of buprofezin and flutolanil was 2.02 and 1.81, respectively. Both well coincided with those (2.04 and 1.72, respectively) estimated by using Eq. (3), which was originally obtained for the neutral fungicides. Thus, Eq. (3), showing the relationship between log \( V_E \) and log P of the neutral fungicides, was also applicable to buprofezin and flutolanil.

\[
\log V_E = 0.53 (\pm 0.09) \log P - 0.24 (\pm 0.33)
\]

\[n=9, \ s=0.111, \ r=0.981 \] (3)

4. Mobility in Rice Plants

Compound mobility in rice plants of the neutral fungicides has been delineated not only with affinity to rice plants, log \( V_E \), but also with hydrophobicity, log P (Eqs. (4) and (5)).

\[
\log a = -0.64 (\pm 0.13) \log P + 1.95 (\pm 0.46)
\]

\[n=9, \ s=0.156, \ r=0.974 \] (4)

\[
=-1.18 (\pm 0.27) \log V_E + 1.16 (\pm 0.44)
\]

\[n=9, \ s=0.174, \ r=0.968 \] (5)

As mentioned above, the relationship between log \( V_E \) and log P (Eq. (3)) for the fungicide analogs was found to be applicable to other classes of compounds such as buprofezin and flutolanil. Therefore, the extensibility of the other relationship between compound mobility in rice plants and log P (Eq. (4)) can be expected. The log \( \mu \) calculated using Eq. (4) were \(-0.77\) for buprofezin and \(-0.53\) for flutolanil. The observed values were \(-0.69\) and \(-0.53\), respectively (Table 1). Although the exact value of buprofezin was not obtained mainly due to the limited sensitivity to the GC detector (63Ni-ECD), the observed log \( \mu \) of the compounds well coincided with the calculated ones.

Thus, the relationships between log P and the compound behavior in soil and plants for the neutral fungicides were shown to be extendible to other classes of compounds (buprofezin and flutolanil). This in turn means that the behavior is predictable from the
correlations expressed as Eqs. (2)-(4) and log \(P\). The predictability was also confirmed for such compounds as buprofezin and flutolanil. However, the behavior, especially in soils of ionized compounds, should be estimated not only from the correlations with log \(P\) but also from other parameters concerning ionic effects.

Highly hydrophobic buprofezin was strongly adsorbed with the soil and was hardly mobile in rice plants. The residual effectiveness of submerged buprofezin against two major rice planthoppers, \(N{\text{i}}l{\text{a}}p{\text{a}}r{\text{v}}a{\text{t}}a ~l{\text{u}}g{\text{e}}{\text{n}}s ~S{\text{t}}{\text{å}l}\) and \(S{\text{o}}g{\text{a}}t{\text{e}}l{l}{\text{l}}{\text{a}} ~f{\text{u}}r{\text{c}}i{\text{f}}e{\text{r}}a ~H{o}{\text{r}}v{\text{å}}{\text{t}}{\text{h}}\), which usually live on the lower parts of the plants, are attributable to these behavioral characters. Flutolanil, which was not highly hydrophobic, was not strongly adsorbed with the soil but was quite mobile in the plants. Indeed, flutolanil applied to paddy water shows a systemic activity against the rice sheath blight caused by \(Riz{\text{o}}c{\text{t}}{\text{o}}n{\text{i}}a ~s{\text{o}}l{\text{a}}{\text{n}}i\).{\text{5}})

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要 約

Buprofezin および flutolanil の疎水性と土壤 吸着およびイネ体内移行

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Buprofezin および flutolanil の土壤吸着とイネ体内 移行性を調べた。疎水性の高い buprofezin は土壤に強 く吸着され、またイネ体内ではほとんど移行しない。疎 水性の低い flutolanil は土壤吸着も強くなく、植物 体内での移行もみられた。イソプロテオラン誘導体の土 壤吸着やイネ体内移行性は疎水性と非常によく相関する が、構造的に関連のない両化合物もこの相関性をよく満 たした。したがって、土壤吸着やイネ体内移行性はその log \(P\) 値より一般に予測可能であることになろう。