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A Simple Adsorption/Dilution Model for Rice Herbicides

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As environmental fate computer models increase in complexity, it is more difficult to evaluate their validity. Because increasing model complexity allows for a wider range of possibilities for model behavior, it becomes easier to fit a model to an experimental data set and most soil transport and transformation models require calibration in order to be used (Jury and Ghodrati 1988). As a response to these considerations, this work was conducted to develop and evaluate a simple simulation model used in rice culture, which mimics a minimal set of processes: adsorption and dilution. Degradation, volatilization and uptake processes were omitted from the model in order to simplify and reduce parameters. Moreover, model output would be compared to field data, without calibration.

The environmental fate of pesticides used in California rice culture is perhaps easier to model than in other forms of agriculture because soil and water conditions during the growing season are relatively constant. The performance of the model developed in this paper was compared using 3 rice herbicides; thiobencarb and molinate, used primarily for control of barnyardgrass (Echinochloa crus-galli L.(Beauv.)) and bentazon, used for control of various broadleaf weeds. These compounds are usually aerially applied, post-flood. Their use requires various water holding periods in order to reduce downstream pollution from field runoff (Lee 1989). Environmental fate studies conducted in California rice fields with clay loam soils provided a convenient data set for comparing model predictions to measured values (Ross and Sava 1986, Ross et al. 1989). Model development in this work was constrained by estimating all input parameters independently from data used for validation.

MATERIALS AND METHODS

To define the model the following assumptions were made: (1) degradation and volatilization were unimportant over the 32-day field studies (2) adsorption was instantaneous, reversible and represented by a linear isotherm (3) water moved in a downward piston flow (3) the soil was saturated and homogenous.

The linear adsorption coefficient, KD (cm^3/g), is a common method used in models to describe the partitioning between soil and water (Carsel et al. 1985, National Research Council 1990, Wagenet and Hutson 1987).

$$KD = \frac{CS}{CW} \qquad (1)$$

where CS and CW are concentrations (µg/g) of herbicides in soil and water.

Equation 2 was used to describe herbicide concentrations in the soil. It divides the amount of compound adsorbed (A in ug/ha) by the mass of soil contained in a solid 1 ha x depth to which the compound has leached. The depth of leaching is expressed by (IR x T)/V, which assumes a steady downward water flow (Jury et al. 1987).

$$CS = \frac{A}{\frac{IR * T}{V} * BD * K1} \qquad (2)$$

where IR = infiltration rate (cm/day), T = time (days), V = dimensionless fraction of voids (as estimated by saturated water content), BD = soil bulk density (g/cm^3), K1 = 10^8 (cm^2/ha) converts hectares to cm^2.

Equation 3 represents herbicide concentrations in surface and soil water. The numerator is the difference between the amount of active ingredient applied and the amount adsorbed. The denominator is the total water which has infiltrated into the soil cube (IR x T) plus the surface water, W.

$$CW = \frac{(K2 * APP) - A}{(IR * T + W) * K1} \qquad (3)$$

where the new terms are K2 = 10^9 (µg/kg) converts kg to µg, APP = the application rate (kg/ha), and W = surface water depth (cm).

To run the model, equations 1, 2 and 3 are solved for A, which gives equation 4. CS and CW are then computed using A and the other known constants.

$$A = \frac{K2 * APP * KD * BD * [\frac{IR * T}{V}]}{(IR * T + W) + KD * BD * [\frac{IR * T}{V}]} \qquad (4)$$

These 4 equations comprise the model. Parameters were estimated from sources other than the validation data sets found in Ross and Sava (1986) and Ross et al. (1989). Adsorption coefficients (KD) were based on batch adsorption studies using soils similar in texture to clay loam (Table 1). The downward piston flow of water was estimated using an infiltration rate of 2.56 cm/day for clay loam which was based on an extensive soil data base (Carsel and Parrish 1988). Slow infiltration is necessary to establish ponded rice-paddy conditions. Bulk density was estimated as 1.25 g/cm^3 and saturated water content as 0.41 (Carsel and Parrish 1988).

Field data collected in 2 studies conducted in rice fields were used for validation (Ross and Sava 1986; Ross et al. 1989). In these studies initial mass balance recoveries compared to application rates were 70% for thiobencarb, 100% for molinate (based on amount present at second application) and 33-58% for bentazon. Field concentrations were divided by initial mass recovery rates (or mass present just after second application for molinate) so that application rate was equal to initial mass recovery rates. Field 1 in Ross et al. (1989) was omitted since soil samples were not taken. Following initial herbicide application, fields were flooded for 6 and 10 days, subsequently drained, refilled and maintained at a constant level of 10 and 17 cm for thiobencarb and molinate, respectively. For bentazon, surface water was not drained and was maintained at 3 cm during the 32 day sampling period. Field drainage for molinate and thiobencarb was simulated by reducing the application rate by the mass lost in surface water. For thiobencarb and molinate, mean and standard deviations were calculated over samples within 1 field. For bentazon, volume weighted average concentrations were calculated within a field over paddies and averaged between fields. Since soil concentrations in these field studies were expressed on a dry soil weight basis, the model-estimated soil concentrations were increased by adding (V*CW)/BD=(0.41*CW)/1.25. This represents the additional herbicide mass contributed by the soil water to the concentration in the mass contained in the soil.

Table 1. Physicochemical characteristics of 3 rice herbicides. Except where noted, the tabulated values were provided by chemical companies which followed EPA guidelines for determining these properties (EPA 1982). Columns are MW (molecular weight g/mole), Sol (solubility ppm), VP (vapor pressure mmHg), Koc (linear Freundlich adsorption coefficient cm^3/g organic carbon), KD (linear Freundlich adsorption coefficient cm^3/g), AP (aqueous photolysis half life days), Hyd (water hydrolysis half life days), AE and AN (soil aerobic & anaerobic metabolism half life days), Kh (Henry's Law constant atm m^3/mole). NA indicates data not found.

Herbicide	MW	Sol	VP	Koc	KD	AP	Hyd	AE	AN	Kh
Thiobencarb	258	30	2.2E-5	1380	9.3[a]	190[b]	>160	37	222	2.7E-7
Molinate	187	970	5.0E-3	186	1.76[a]	>4[bc]	>30	NA	66[d]	1.3E-6
Bentazon[e]	240	530[f]	<0.8E-7	31	0.35[a]	1-5	>30	45	>365[g]	<4.8E-11

[a] Based on studies using soils with clay loam texture
[b] Natural photosensitizers may accelerate photolysis (Crosby 1983)
[c] At least 91% remaining after 4 days of natural sunlight (Deuel et al. 1978)
[d] Imai and Kuwatsukula 1982
[e] Forms anion in water, pKa approximately 3.2 (Abernathy and Wax 1973)
[f] Solubility of sodium bentazon formulation is 2.5E6 ppm
[g] 93% of parent material left after 1 year

Sensitivity analysis was performed utilizing the modified Biplot technique (Huson 1982). APP, IR, T, BD, V, KD, and W were varied as input parameters with a coefficient of variation of 20% from a normal distribution. Six simulations, day 2 and day 32 conditions for the 3 compounds, were each calculated with 10000 iterations. The resulting Biplots included the 7 input parameters and the 2 output variables, CW and CS.

RESULTS AND DISCUSSION

Model estimates were 4-7 times lower than measured thiobencarb water concentrations during the first week following application (Figure 1A). After 2 weeks, the model estimates converged to measured values. Measured soil

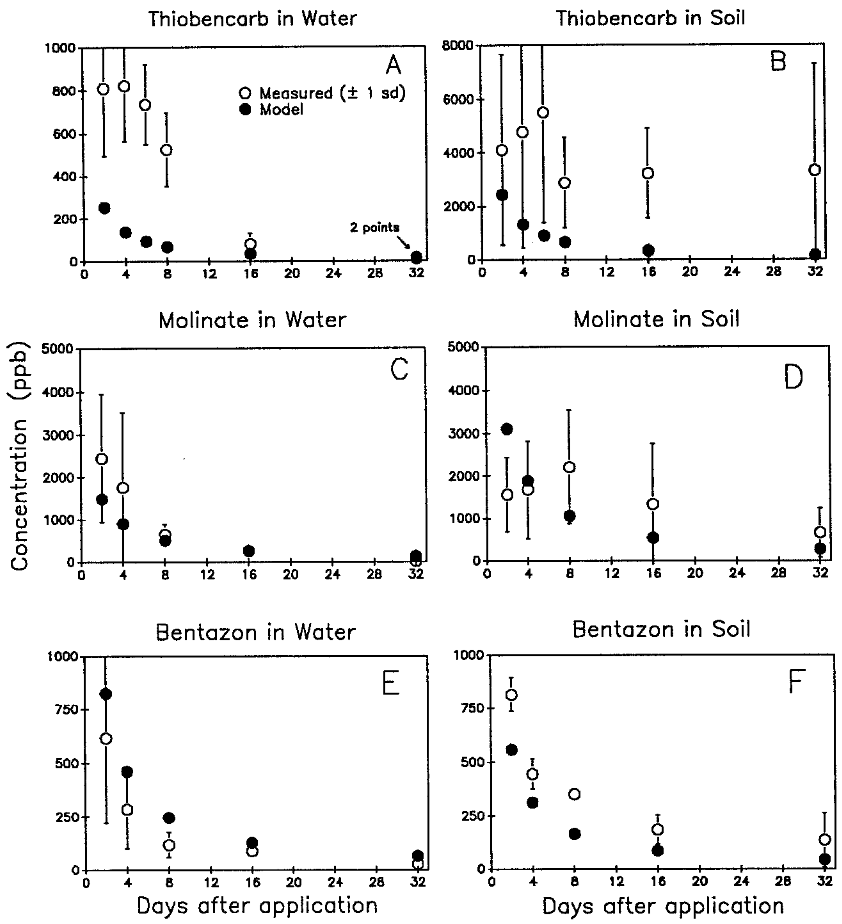

Figure 1. Comparison of model predictions with measured values. Measured values have been adjusted by recovery rate. Error bars represent +/- 1 standard deviation.

concentrations increased during the first week and remained relatively constant thereafter (Figure 1B). The model underestimated thiobencarb concentration in the soil. Model estimates fell below 1 standard deviation of the field mean in 4 of 6 and 3 of 6 comparisons for water and soil, respectively.

The model underestimated molinate water concentration but not as severely as in the case of thiobencarb (Figure 1C). The first 3 model estimates fell within 1 standard deviation of mean measured values. Both field data and the model exhibited a declining concentration over time. Measured concentrations of molinate in soil increased during the first week, then declined (Figure 1D). Following the initial measurement, the model remained within 1 standard deviation of mean soil concentrations.

Bentazon water concentrations declined over time and were somewhat overestimated by the model (Figure 1E). Soil concentrations, however, were underestimated by the model with 4 of 5 model estimates falling below 1 standard deviation from the mean value (Figure 1F).

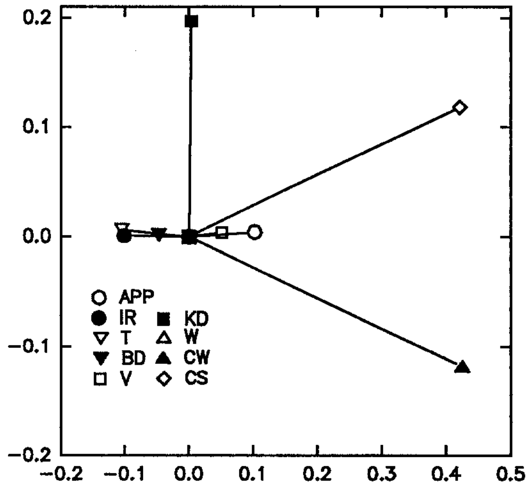

Figure 2 Biplot sensitivity analysis for bentazon at day 32 with CV=0.2 and 10000 iterations. See text for variable abbreviations.

For thiobencarb and molinate the model tended to underestimate both soil and water concentrations. For bentazon the model underestimated soil but overestimated water concentrations. A possible explanation lies in the different formulations used with these pesticides. The granular formulation of thiobencarb and molinate may have resulted in a slower release, which maintained high concentrations in the upper soil, led to higher surface water concentrations, and reduced the amount leached downward. Sodium salt of bentazon, however, was applied in a liquid formulation which dispersed more quickly. Also, the model assumed perfect diffusion and mixing throughout the soil and water infiltration volume. Mixing rates would be faster in surface water than in soil water. Consequently, the pesticides may have loaded up in the surface soil before leaching downward.

The greatest underestimates occurred for thiobencarb. Thiobencarb with a high KD may have concentrated preferentially in the upper soil horizon where organic matter content was probably the highest (Marade and Segawa 1988). Both molinate and bentazon had low KD partition coefficients compared to thiobencarb (Table 1) and did not exhibit this degree of surface concentration compared to model predictions. Solubility is relatively unimportant since environmental concentrations in water are always well below solubility limits.

The possible modes for degradation or dissipation include aerobic or anaerobic metabolism, aqueous photolysis or, for molinate with a relatively high vapor pressure, volatilization (Table 1). Anaerobic conditions in rice paddies effectively reduce or eliminate aerobic metabolism (Patrick and Delaune 1972; Ponnamperuma 1955). The anaerobic half-lives for all 3 compounds are considerably longer than the 32-day field studies and therefore probably not important during this time period (Table 1). For thiobencarb and molinate, photolysis rates are slow, but may increase in the presence of photosensitizers (Crosby 1983). The photolysis half-life for molinate is approximately 29 days, based on a maximum of 9% degradation after 4 days (Table 1). Volatilization of molinate can be a significant avenue of dissipation (Soderquist et al. 1977). For bentazon, laboratory measurements of aqueous photolysis result in estimated half-lives of less than 1 week (Table 1). However, under field conditions, water turbidity, canopy shading or infiltration into the soil may reduce or eliminate photolysis (Deuel et al. 1978). Inclusion of differing combinations of infiltration, photolytic degradation or volatilization rates in the model might provide closer fits between the model and site specific field data. However, the adsorption/dilution processes modeled here provide a parsimonious hypothesis for the dominant behavior of these compounds in rice fields.

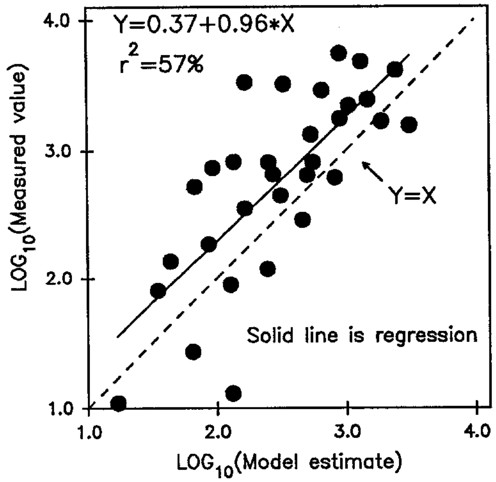

Figure 3. Combined model performance for 3 rice herbicides in soil and water shown on log-log plot. Dashed line Y=X represents perfect prediction.

In the Biplot technique, the sensitivity of an output vector to variation in an input vector is related to both the angle between the two vectors and the length of the input vector (Huson 1982). Since all 6 Biplots were very similar, only one is shown (Figure 2). APP, IR, T, BD, V were nearly collinear with respect to their influence on the 2 output vectors, CW and CS (Figure 2). Increasing IR, T, or BD decreased concentrations since they were negatively correlated to CW and CS, while the converse was true for APP and V. KD was orthogonal to the other 6 input variables in terms of its affect on CW and CS. Increasing KD increased CS and decreased CW. In the thiobencarb Biplot, the angle between KD and CS decreased slightly compared to Figure 2. This decrease indicated a stronger influence of variations in KD on soil concentrations for thiobencarb, a natural conclusion since the magnitude of KD for thiobencarb was larger than for bentazon and molinate.

Overall the model captured 57% of the variability of the data for these 3 compounds on a log-log plot (Figure 3). Comparison of the regression of measured vs predicted to the line X=Y, representing perfect model performance, indicates 2 parallel lines with a small consistent bias towards underestimation. The underestimation was contrary to expectation since all degradation and volatilization processes were omitted. Generally the model predicted concentrations within 1 order of magnitude of observed data, which should be evaluated in light of the complete independence of model parameters and validation data. The model supports the hypothesis that adsorption/dilution processes in rice growing areas are important components of the environmental fate of herbicides used in the rice culture.

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