

DEVELOPMENT OF SIMPLE MODELS FOR AGRICHEMICAL UPTAKE INTO PLANT FOLIAGE

J.A. ZABKIEWICZ and W.A. FORSTER

Plant Protection Chemistry_{NZ} Forest Research, PB 3020, Rotorua

Corresponding author: jaz@forestresearch.co.nz

ABSTRACT

Pesticide uptake into plants is typically reported as percentage uptake of the amount applied, but in studies of the mechanism of cuticular penetration, this approach has not been helpful. It can be shown that relating percentage uptake to initial dose of bentazone applied to *Vicia faba* foliage cannot provide pertinent relationships that can be used to explain cuticular uptake mechanisms. However, applying the principles of Fick's Law, and using mass or molar quantities, does provide excellent linear relationships between mass uptake and initial dose applied. Universal equations can be derived that relate dose uptake to initial dose applied onto plant leaves.

Keywords: cuticular uptake, mechanism, spread areas, initial dose, models.

INTRODUCTION

Pesticide formulations are typically compared on the basis of the percentage uptake of the active ingredient (a.i.) into plant foliage. This approach has also been used in efforts to understand the principal factors affecting cuticular uptake. However, apart from providing general guidelines in relation to a.i. or adjuvant combinations, little progress has been made towards a mechanistic interpretation. Since cuticular uptake of xenobiotics is considered to be a diffusion process, it should follow Fick's first law of diffusion. This principle has been applied, with some success, to studies of cuticular diffusion using isolated cuticles. It has resulted in the production of an equation based on three main factors, the solute mobility of the a.i., the driving force (involving the concentration and partition coefficients of the a.i.) and the cuticle tortuosity (Schonherr et al 1999). This equation is not easy to apply in practice, due to difficulties in measuring each parameter, and may not be altogether appropriate for *in vivo* situations where the applied quantity is a finite dose (from a droplet deposit). Since the initial solution deposit (droplet) rapidly becomes a deposit residue due to droplet evaporation, the initial concentration becomes irrelevant. A good approximation in that case is the total initial mass of a.i. in the deposit, expressed as a dose (taking droplet spread area into account). This is much easier to determine and should be proportional to the initial driving force.

The present studies use previously published data to test this proposed relationship, and its potential for modelling mass uptake, by relating the mass uptake to the initial dose of a.i. per unit leaf area.

MATERIALS AND METHODS

Standard methods were used to determine the uptake of radiolabelled bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide) into bean (*Vicia faba* cv. Evergreen) foliage after 24 h. The surfactants used were all non-ionic, and covered a wide range of hydrophile and hydrophobe structures. Their identities are given in Table 1. The experimental details for plant propagation, herbicide and radiolabelled herbicide, surfactants and uptake determinations have been presented fully elsewhere (Liu & Zabkiewicz 2001). Briefly, bean plants were grown in a controlled environment (20°C/15°C day/night temperature and 70% RH) for four weeks prior to use.

^{14}C -bentazone solution of known radioactivity was added to a commercial formulation (Basagran) containing bentazone sodium salt. Just before use aqueous dispersions or solutions of surfactants were added to form the required treatment formulations. Droplets of solutions were applied by microsyringe to the adaxial surfaces of a single, third bean leaf per plant (five replicates per treatment). Uptake was determined by washing residual bentazone from treated leaf surfaces at 24 h after application and calculating the amount absorbed.

The droplet spread areas for the different formulations were measured by image analysis (mean of 10 determinations) and compared using the least significant difference test (LSD) after performing stabilising transformations ($1/\sqrt{\text{spread area}}$). Regressions on graphed data were produced in Microsoft PowerPoint.

RESULTS AND DISCUSSION

The results from the uptake trials (Liu & Zabkiewicz 2001) provided a range of a.i. concentrations, surfactant types and percentage uptake results. These are presented in Table 1. The droplet spread areas range from 1.37 mm² to 9.48 mm² (a seven-fold range) for droplets of 0.24 μl . The consequence is that the initial dose of a.i. per unit area (1 mm²) varies from 0.0729 to 3.6841 nMoles/mm². This is a 50-fold range, whereas the actual concentration range of bentazone in solution is only 20-fold.

TABLE 1: Bentazone uptake (%) at 24 h, the spread area (mm²) of a 0.24 μl droplet, initial dose (nMoles/mm²) and mass uptake of bentazone (nMoles/mm²) in different formulations.

Bentazone % conc.	Surfactant (0.5% final conc.)	% Uptake	Spread area	Initial dose	Mass uptake
0.01	AO5 (C ₁₃₋₁₅ alkanol/5EO)	87	2.64 cd ¹	0.0378	0.032902
0.05	None	20	2.36 d	0.2115	0.042305
0.05	None	17	2.36 d	0.2115	0.035959
0.05	AO5 (C ₁₃₋₁₅ alkanol/5EO)	83	6.84 ab	0.0730	0.060575
0.05	A14 (C ₁₃₋₁₅ alkanol/14EO)	54	3.71 bc	0.1346	0.072660
0.05	AO5 (C ₁₃₋₁₅ alkanol/5EO)	83	6.84 ab	0.0730	0.060575
0.05	A14 (C ₁₃₋₁₅ alkanol/14EO)	54	3.71 bc	0.1346	0.072660
0.05	ON110 (C ₁₀ alkanol/11EO)	43	2.50 d	0.1997	0.085862
0.05	AO10 (C ₁₃₋₁₅ alkanol/10EO)	73	4.28 bc	0.1166	0.085144
0.05	AT11 (C ₁₆₋₁₈ alkanol/11EO)	46	2.69 d	0.1856	0.085365
0.05	TX-100 (Octylphenyl/10EO)	27	6.01 ab	0.0831	0.022427
0.05	NP1000 (Nonylphenyl/10EO)	36	5.17 b	0.0966	0.034761
0.2	None	23	2.04 d	0.9788	0.225129
0.2	None	22	2.04 d	0.9788	0.215341
0.2	ON110 (C ₁₀ alkanol/11EO)	34	1.37 e	1.4575	0.495556
0.2	AO10 (C ₁₃₋₁₅ alkanol/10EO)	47	6.70 ab	0.2980	0.140074
0.2	AT11 (C ₁₆₋₁₈ alkanol/11EO)	22	2.40 d	0.8320	0.183040
0.2	TX-100 (Octylphenyl/10EO)	25	9.48 a	0.2106	0.052658
0.2	NP1000 (Nonylphenyl/10EO)	27	4.99 b	0.4001	0.108043
0.2	AO5 (C ₁₃₋₁₅ alkanol/5EO)	62	6.43 b	0.3105	0.192537
0.2	A14 (C ₁₃₋₁₅ alkanol/14EO)	40	2.52 d	0.7924	0.316952
0.2	ON50 (C ₁₀ alkanol/5EO)	42	4.34 b	0.4601	0.193239
1.0	AO5 (C ₁₃₋₁₅ alkanol/5EO)	72	2.71 cd	3.6841	2.652576

¹Treatments with no letter in common are significantly different (P=0.05).

Previous studies have shown the importance of increasing initial dose in relation to increasing glyphosate uptake (Liu & Zabkiewicz 1997), as well as the influence of surfactant structure and concentration (Liu & Zabkiewicz 1999). Examination of the

current data series does not show any obvious relationship of percentage uptake to initial dose (Fig. 1; best fit $R^2 = <0.2$). Other data (W.A. Forster & J.A. Zabkiewicz, unpubl. data) confirm that no sensible correlation or regression can be developed when using a wider range of a.i.s or surfactants. The use of percentage uptake in relation to a wide range of physico-chemical characteristics of the a.i. has at best provided only trends within a narrow data set, or completely failed to provide insights into the mechanism of xenobiotic uptake (Baker et al 1992).

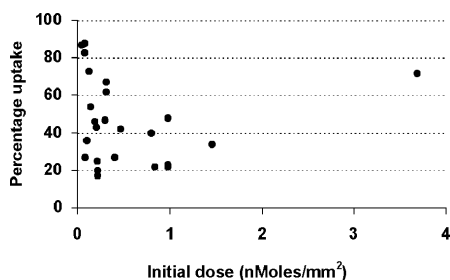


FIGURE 1: Percentage uptake of bentazone into *V. faba* after 24 h from different formulations in relation to initial dose (nMoles/mm²) applied.

Since uptake through a leaf cuticle is in most cases a diffusion process (Price 1982), then Fick's law of diffusion should apply. This is based on the flux per unit area, i.e. the amount of solute that diffuses through a unit area per unit of time, and can be expressed as $J = M/At$, where J is the flux, M is moles (or mass), A the area across which diffusion occurs and t is the time. Uptake at a specific time (Jt) can be determined in terms of moles uptake per unit area, and can be considered with respect to the initial molar quantity, which is proportional to the driving force.

Therefore it is more appropriate to compare uptake among a range of xenobiotics or formulations in molar amounts. Accordingly, when the mass (molar) uptake of bentazone is related to initial dose, a completely different relationship emerges, as illustrated in Figure 2. This provides a linear relationship, plotted on a log-log scale, with a good correlation coefficient of $R^2=0.8609$. It also shows that mass uptake of bentazone in the surfactant formulations lies well above the bentazone only formulation. This data set includes a very wide range of surfactant structures and if only one surfactant series is considered, then the correlation can be even better ($R^2=0.9976$) as shown in Figure 3. An alternative presentation is to plot the relationship on a linear-linear scale (Fig. 4) which permits easier comprehension of the actual doses involved. Although this format tends to compress the presentation of the low dosage treatments, it again shows an excellent correlation ($R^2=0.9999$).

CONCLUSIONS

Current studies show clearly that using percentage uptake data to develop an understanding of xenobiotic uptake mechanism into plant foliage is totally inadequate if tested across a range of a.i.s, formulations and plant species (Forster et al. 2003). Instead, excellent relationships can be developed between the initial dose applied and xenobiotic uptake, if mass or molar quantities are used, and compared on a per unit area basis. These relationships provide equations that can be used to model the dose uptake of a xenobiotic. Although the illustration presented in this paper is only for bentazone, a much wider range of xenobiotics of varying lipophilicities have been tested, on several plant species and a wide range of adjuvant systems (W.A. Forster & J.A. Zabkiewicz, unpubl. data). Provided that the adjuvants are of a similar capability, and the uptake

interval is 24 h, simple model equations can be derived to explain and forecast mass uptake in relation to initial dose applied. This is a significant progression in the understanding of the mechanisms of cuticular uptake into living plant foliage.

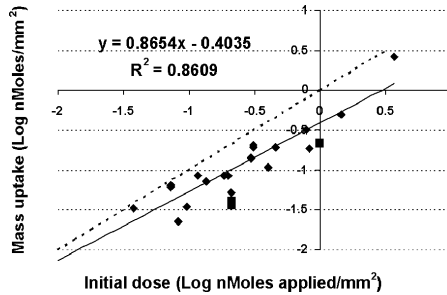


FIGURE 2: Mass uptake (log nMoles/mm²) of bentazone into *V. faba* from different formulations in relation to initial dose (log nMoles/mm²) applied. Bentazone formulations are indicated by a square symbol. Maximum uptake is indicated by the dotted line.

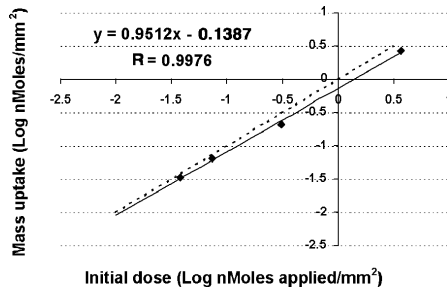


FIGURE 3: Mass uptake (log nMoles/mm²) of bentazone into *V. faba* in presence of AO 5 surfactant in relation to initial dose (log nMoles/mm²) applied. Maximum uptake is indicated by the dotted line.

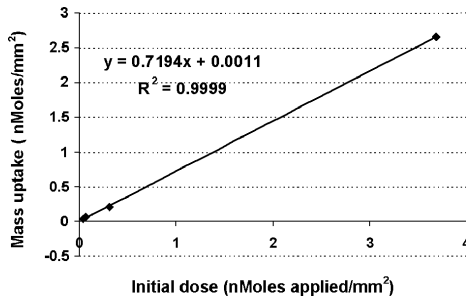


FIGURE 4: Mass uptake (nMoles/mm²) of bentazone into *V. faba* in presence of AO 5 surfactant in relation to initial dose (nMoles/mm²) applied. Maximum uptake is indicated by the dotted line. Note that these are the data from Figure 4 plotted on a linear-linear scale.

ACKNOWLEDGEMENT

We wish to thank B. Nanayakkara for the droplet spread area determinations. This work was supported by the Foundation for Research, Science and Technology.

REFERENCES

- Baker, E.A.; Hayes, A.L.; Butler, R.C. 1992: Physicochemical properties of agrochemicals: their effects on foliar penetration. *Pesticide Sci.* 34: 167-182.
- Forster, W.A.; Zabkiewicz, J.A.; Riederer, M. 2003: Mechanisms of agrichemical uptake into living plant foliage. *In: 3rd Pan Pacific Conference on Pesticide Science, Honolulu, Hawaii, P-234.* p. 101.
- Liu, Z.Q.; Zabkiewicz, J.A. 1997: Cuticular uptake of glyphosate into wheat with organosilicone surfactant. *Proc. 50th N.Z. Plant Prot. Conf.:* 129-133.
- Liu, Z.Q.; Zabkiewicz, J.A. 1999: Influence of surfactant mixtures on cuticular uptake of glyphosate into grasses. *Proc. 52nd N.Z. Plant Prot. Conf.:* 228-233.
- Liu, Z.Q.; Zabkiewicz, J.A. 2001: Uptake of bentazone in relation to surfactant structures and surfactant uptake. *In: de Ruiter, H. ed. Sixth Int. Symp. Adjuvants for Agrochemicals. ISAA 2001 Foundation, Amsterdam.* Pp. 139-144.
- Price, C.E. 1982: A review of the factors influencing the penetration of pesticides through plant leaves. *In: Cutler, D.F.; Alvin, K.L.; Price, C.F. ed. The Plant Cuticle, Academic Press, London.* Pp. 237-252.
- Schönherr, J.; Baur, P.; Buchholz, A. 1999: Modeling foliar penetration: its role in optimising pesticide delivery. *In: Brooks, G.T.; Roberts, T.R. ed. Pesticide Chemistry and Bioscience, Proc. 9th Int. Congress on Pesticide Chemistry. Royal Society of Chemistry, London.* Pp.134-151.