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ScienceDirect
Pesticide Biochemistry and Physiology 87 (2007) 1–8
PESTICIDE Biochemistry & Physiology
www.elsevier.com/locate/ypest

Foliar uptake of pesticides—Present status and future challenge

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Received 31 January 2006; accepted 17 April 2006
Available online 19 May 2006

Abstract

Uptake of pesticides into plant foliage varies with plants and chemicals, and can be greatly influenced by adjuvants and environmental conditions. It is known that the penetration of pesticides into plant leaves is related to the physicochemical properties of the active ingredients, especially molecular size and lipophilicity. However, the uptake rate of a compound cannot be predicted by either of them or even combination of them. For a specific chemical, uptake varies greatly with plant species and there is no simple method at the moment to quickly evaluate the leaf surface permeability of a plant. Various adjuvants are being used to increase the penetration of pesticides into target plant foliage, but their effects vary with chemicals and plant species. The mechanisms of action of adjuvants in enhancing pesticide uptake remain unclear despite the effort made during the last three decades. Modern analytical and microscopic techniques provide powerful tools to deepen our understanding in this field. However, a more multidisciplinary approach is urgently needed to elucidate the transcuticular diffusion behaviour of pesticides and the mode of action of adjuvants. A better understanding of the foliar uptake process should lead to a more rational use of pesticides and minimize their negative impact on the environment.

Keywords: Adjuvants; Ammonium salts; Foliar uptake; Oils; Pesticides; Surfactants

1. Introduction

Despite the negative perception of the public, pesticides are still going to be used for many decades to ensure the food supply for the ever growing world population. The simple reason for this is that alternative methods for plant protection are either inefficient or too costly for farmers. The global pesticide production in 2000 amounted to over three million tons of active ingredients (AIs) [1]. It is estimated that of the total amount of pesticides applied for weed and pest control, only a very small part (<0.1%) actually reaches the sites of action [2], with the larger proportion being lost *via* spray drift, off-target deposition, run-off, photodegradation and so on. This not only increases the cost in crop protection, but also causes serious environmental pollution. It is clear that, although pesticides remain indispensable in agriculture and forestry in a foreseeable future, great potential still exists to improve their efficiency, and thus reducing their input into the environment and food chain.

One of the most important ways to improve the efficacy of pesticides and minimize their impact on off-target organisms is through increasing the penetration of AIs into plant foliage. If foliar uptake is important for the efficacy of systemic fungicides and insecticides, then diffusion into plant tissues is a prerequisite for the activity of foliar-applied herbicides, growth regulators, and defoliants. Foliar uptake of pesticides is a complex process, depending on leaf surface characters of plants, physicochemical properties of the chemicals, types and concentration of the additives, and environmental conditions. How each of these factors influences the uptake is only partially understood, despite an urgent demand for efficient use of pesticides.

The aim of this review is to summarize the major progress made especially during the last 15 years or so in the understanding of pesticide uptake into plant foliage and the

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doi:10.1016/j.pestbp.2006.04.004

influence of adjuvants, and to highlight the critical problems to be solved. It is not our intention to provide an exhaustive compilation of research reports in this field. However, it is hoped that this paper will serve to highlight the complexity of foliar uptake of pesticides and encourage a more multidisciplinary approach in the future.

2. Physicochemical properties of AIs in relation to pesticide uptake

2.1. Molecular weight

Foliar uptake of pesticides is a diffusion process across the epicuticular wax, the cuticle, and the plasma membrane of epidermal cells. The diffusion rate of both lipophilic and hydrophilic compounds across isolated leaf cuticles was negatively correlated with their molecular weight (MW), or molecular size [3,4]. A similar trend was somewhat observed for the uptake of chemicals into plant leaves [5]. However, in the latter case, the results were obtained with a range of pesticides and model compounds which differed both in molecular weight and in polarity. A study on the foliar uptake of chemicals with identical or similar polarity but differing molecular size is still lacking.

Yu et al. [6] reported that Congo Red (MW: 697) did not show any uptake into cucumber or rice leaves, even in the presence of various surfactants. In addition, the plasmodesmata of plants can only allow free circulation of molecules smaller than 1 kDa [7]. It is thus not a coincidence that most foliar-applied herbicide have a molecular weight between 100 and 500 [8], as any out-ranged molecules would be eliminated at the screening stage if they cannot enter plant leaves or move between cells.

Within the 100–500 molecular weight range, the effect of molecular size on pesticide uptake into plant foliage may not be of great importance, as molecular weight is not the sole factor affecting chemical uptake. Moreover, the use of suitable adjuvants may greatly reduce the size effect of chemicals in transcuticular diffusion [9].

2.2. Lipophilicity

Lipophilicity is probably the single most important property of pesticides related to foliar uptake. Generally, an octanol/water partition coefficient ($\log o/w$ or $\log P$) is used to describe the lipophilicity of a compound. Chemicals with $\log P < 0$ are considered as hydrophilic and those with $\log P > 0$ lipophilic. Due to the lipoidal nature of the epicuticular wax and the cuticle, foliar uptake tends to increase with increasing lipophilicity of the chemicals [5,10]. A best example showing this is the faster uptake of 2,4-D ester (lipophilic) compared to 2,4-D salt (hydrophilic) [11].

However, like molecular size, $\log P$ is not the only property that determines the foliar penetration. Indeed, based on the uptake data obtained with 26 chemicals and four plant species, only a moderate correlation (R^2: 24–45%) was found between $\log P$ and the foliar uptake of chemicals [5]. Therefore, it would be wrong to conclude that all lipophilic compounds are taken up faster by plant foliage than hydrophilic ones. Some hydrophilic compounds, such as paraquat, are actually able to penetrate into plant leaves very fast (Liu, unpublished). A systematic study on the foliar uptake of a wide range of chemicals with identical or similar molecular weight and identical ionic charge but differing $\log P$ would provide definite information on the relationship between chemical lipophilicity and foliar penetration.

3. Physicochemical properties of the spray mixtures in relation to pesticide uptake

3.1. Concentration of AIs

Foliar uptake of chemicals is a diffusion process, depending on both the concentration gradient of the solutes across the leaf surface and the permeability of the cuticle. The concentration of AIs in the spray mixture that determines the ultimate concentration gradient after droplet dry-down is expected to have an influence on pesticide uptake. However, the influence of AI concentration on pesticide uptake has been systematically investigated only with glyphosate. It is well established now that the uptake of glyphosate is closely related to its concentration in the spray mixture: the higher the AI concentration, the greater the uptake [12,13]. However, through a systematic study, Liu [14] found that glyphosate uptake into grasses depends actually on the AI dose formed on the leaf surface (μg AI/mm^2), rather than the AI concentration *per se*. The former is a function of both the AI concentration in the spray solution and the droplet spread area. By contrast, only fragmentary information is available for a few other chemicals. Knoche and Bukovac [15] found that the uptake of gibberellic acid and 2,4-D into bean (*Phaseolus vulgaris*) leaves was negatively correlated with the AI concentration. A negative correlation was also obtained between the AI concentration and the uptake of triclopyr ester into quaking aspen [16], and the uptake of bentazone sodium salt into broad bean (*Vicia faba*) leaves in the presence of surfactants [17].

The influence of AI concentrations on pesticide uptake has important implications, but has been largely neglected in the past. Due to the fact that the recommended doses for pesticide application are given on the basis of the treatment area (kg AI/ha), AI concentrations in the spray mixtures can be manipulated through changing the spray volumes. In the case of glyphosate, its efficacy increases as spray volume decreases, a fact that is well documented [18]. Unfortunately, for most foliar-applied agrochemicals, the possible influence of AI concentrations on foliar uptake remains less clear or largely unknown.

3.2. Carrier pH

Most post-emergence herbicides are weak acid compounds. The dissociation of the acid group depends on the pH of the medium. It is generally believed that for weak