Types of Selective Action by Herbicides which Inhibit Photosynthesis

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Various sources are involved in the selective action of herbicides which inhibit photosynthesis, ranging from gross morphological differences connected with the availability of the herbicide to the foliar or root surface, to differential absorption, translocation and inactivation in the tissues of various plants species, and finally to differences in susceptibility at the chloroplast level. Their significance is reviewed with respect to the selectivity in the field.

Introduction

The difference in response between plant species to herbicides is by far the most important basis for the development of chemical weed control. It makes selective herbicide application to a useful tool in the destruction or suppression of growth of undesired plants in a population without causing harm to the other plants.

To analyse the selective action of herbicides under field conditions three types of differences between weed and crop plants should be distinguished:

a) the extent of availability of the herbicide to the plant surface,
b) its degree of accumulation at the site of action, and
c) differential sensitivity at the site of action.

Although selectivity in the field is seldom the result of one single property, its analysis may help towards an easier interpretation of selective chemical weed control. This review deals with about half the number of herbicides, *viz.* those known to interfere with the process of photosynthesis.

Availability to the plant surface

The first step of application to the plant surface seems uncomplicated, but is subject to a number of variables that may determine selectivity. Only a broad outline can be given here. For more details the reader is referred to the textbooks (*e.g.* [1]).

Foliage treatment

The availability for intake of a herbicide by the foliage may differ between plant species because of differences in interception and retention of the spray solution. Gross differences in interception are obvious when crop and weeds are separated in time or space. For example, applications of herbicides with exclusively contact action against young plants are selective, when made before the crop has emerged. Exposure of the crop to the herbicide spray is also more or less prevented, when the weeds are under trees or other tall crops.

Even with overall treatments the interception may differ from one plant species to the other, especially where they differ in leaf angle and arrangement. For instance, erect leaves of cereal plants will intercept less of the spray than the more horizontal leaves of dicotyledonous weeds.

At equal interception, differences in retention of spray droplets between plant species may also produce selectivity. Fewer droplets will adhere to the erect leaves. The nature of the leaf surface (arrangement of wax particles and hairiness) may affect its wettability. In addition, changes in properties of the spray solution, such as droplet size and surface tension may cause considerable variation in retention, and thus produce selectivity.

Root exposure

Difference in availability to roots or other belowground organs between crop and weed plants is often the main source of selectivity of many soil-applied herbicides. As they are usually adsorbed to soil

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Abbreviations: For common names and abbreviations of the herbicides the reader is referred to Weed Res. **18**, 319 (1978).

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constituents such as humus and clay, and little soluble in water, they tend to be retained in the top soil. Low penetration of a herbicide into the soil combined to differences in the depth of germination or rooting horizon between crop and weed plants often permit selective application of residual herbicides. This depth protection is obvious in established deep-rooted crop plants associated with shallow-germinating annual weeds. It may also be important in crops germinating only a little deeper or developing roots that rapidly penetrate into the soil.

Deeper penetration of the herbicide may harm the crop, so that it is risky to depend on this type of selectivity alone on light soils or during heavy rainfall. The selectivity of residual herbicides in perennial fruit crops may depend to a large extent on depth protection. This undoubtedly applies also to the selective use of triazines and ureas in large-seeded, deep-sown crops, although additionally physiological tolerance may make such treatments less risky. Protection of the crop might be increased by placing a band of activated carbon above the row with crop seeds. Dipping the roots into a slurry of carbon also increases tolerance [2].

Degree of accumulation in the leaves

With photosynthesis inhibitors the site of action is in the leaves. Both direct absorption by the foliage and root uptake followed by translocation to the leaves may differ between plant species. Differential inactivation is another important factor.

Absorption by the foliage

There is considerable variation in cuticle structure and composition between plant species. Size and distribution of stomata also vary. Both may induce differences in penetration of herbicides. The selectivity of ioxynil correlated with penetration [3], and that of bentazon could at least partly be attributed to differences in uptake [4, 5]. Other workers [6], however, found no great difference in penetration rates between tolerant and susceptible plants. Various additives to the spray solution may affect herbicide penetration into the leaf, and so modify selectivity [1]. In recent years oils have been used to increase leaf uptake, for instance of atrazine in a new post-emergence selectivity for the maize crop. Effects of oil on bentazon uptake also differed between species [4].

Root absorption and translocation to the leaves

With all soil-applied herbicides the tissue concentration attained may vary with differences in seed size among plant species [7], but root absorption is certainly involved in the selectivity displayed by some photosynthesis inhibitors. Usually it is not possible to differentiate between uptake and translocation to the foliage. There are a few indications of different transport of triazines [8, 9]. More simazine accumulation was found in the leaves as the plants were more susceptible [10 – 12]. In contrast, concentrations of prometryne were not higher in plant species susceptible to this herbicide (*e.g.* [13]).

This selectivity seems to occur more frequently with phenylureas. A difference in translocation of chloroxuron was observed between plant species [14]. Indirect evidence of limited translocation of linuron to carrot leaves after root exposure was obtained by measuring photosynthesis [15]. Using radioactive herbicide confirmed that linuron was retained in the roots of tolerant carrots and parsnips, but distributed more evenly over the organs of more sensitive plant species [16, 17]. For other evidence on the relation between partition and susceptibility the reader is referred to Geissbühler *et al.* [18].

Similar differences have been observed for terbacil. Retention is higher in the roots of tolerant citrus [19] and peppermint [20] than in susceptible plant species. Besides, tolerant plants show accumulation round the veins, whereas the more sensitive species show a fairly even distribution in the leaves. Absorption and translocation are also involved in the tolerance of cotton to norflurazone and metflurazone [21].

Differences in transpiration rate may also affect the differential absorption and translocation in susceptible and tolerant plants, but it is usually not recorded. The sensitivity of some trees to simazine and the absorption of this herbicide have been related with water uptake [11]. According to Singh *et al.* [13] accumulation of prometryne coincided with the CO_2 fixation pathway in susceptible (C_3) and tolerant (C_4) species, but this could also be due to a difference in transpiration rates between these plants which largely determines the effect of root-absorbed herbicides on photosynthesis [22]. Other reported differences in sensitivity to triazines between intact C_3 and C_4 species [23, 24] could also be related to different transpiration rates.

Inactivation in the leaves

Inactivation of a herbicide in the leaves may prevent or reduce its accumulation at the site of action, and is certainly an important source of selectivity of herbicides which inhibit photosynthesis. In most studies on inactivation in tolerant plants its biochemical nature has been demonstrated. Here only a general indication can be given of the type of conversion involved in some important groups of these herbicides.

There is much information on triazines (see *e. g.* [8]) where different pathways may lead to loss or decrease in phytotoxicity. The longest-known hydrolysis of chlorotriazines could not satisfactorily explain the selectivity in various plants [9]. Conjugation with glutathione not only appears important to the tolerance of maize and sorghum [25, 26], but also to that of various grass weeds [27, 28]. In addition, N-dealkylation could be significant in the selectivity of intermediately susceptible plants, and contribute to the selectivity in tolerant plants. The responses of soybean [29] and tomato [30] cultivars to metribuzin were almost entirely related to metabolism in the leaves, while inactivation by deamination in the leaves of tolerant plants has been demonstrated for metamitron [31].

Inactivation of substituted ureas in the leaves suggest an effect on selectivity (see *e. g* [18]). The pathway is not yet elucidated, although dealkylation seems important here [32, 33]. The selectivity of terbacil should at least partly be ascribed to differential metabolism [20]. That of chloridazon is mainly attributed to metabolism in tolerant plants by conjugation with glucose [34, 35].

Hydrolysis of propanil occurs in the leaves of rice plants (*e. g.* [36]). The selectivity of the leaf-applied biscarbamate phenmedipham is also due to inactivation in the leaves of the tolerant sugar beet, but details are still unknown [37]. Inactivation is probably not important in the selectivity of dinitrophenols, while that of phenylethers is not clear. For another foliage-absorbed herbicide, bentazon, metabolism is a main factor in the selective phytotoxicity, *e. g.* in rice [6, 38] and in soybean cultivars [5].

There is increasing evidence that enzymes are involved in the metabolism of these herbicides in plants. The enzyme aryl acylamidase regulates the hydrolysis of propanil in rice. Hence, its inhibition by some insecticides will increase the phytotoxicity of propanil in this plant. The role of enzymes in the metabolism of pyrazon is less certain, but arylamine N-glucosyltransferase is possibly involved [36]. The enzyme system responsible for the metabolism of chlorotriazines in tolerant plants, glutathione S-transferase, has been isolated and partially characterized. The metabolism of urea herbicides appears related to the presence of N-demethylase which induces a gradual detoxification [39]. Genetic factors may play a role *e. g.* in a rice mutant susceptible to propanil [40] and a maize line susceptible to atrazine [26], thus supporting the view that artificial selection and breeding for tolerance may be successful (see *e. g.* [9]).

The elucidation of herbicide metabolism in plants by chemical methods is time-consuming. However, in the case of inhibitors of photosynthesis, inactivation in the leaves can be readily established with equipment suitable for continuous measurement of photosynthesis. Usually a distinct inhibition of photosynthesis indicates that a toxic amount of the herbicide has entered the leaf. When then uptake is stopped, subsequent recovery from inhibition is a measure of herbicide inactivation in the leaves provided that contribution of new leaf growth is negligible during a test period of sufficiently short duration. However, no evidence as to the nature of the inactivation is obtained.

Studies with chloroplasts (*e. g* [41] and unicellular algae (*e. g.* [42]) indicated that the effect on photosynthesis is reversible; recovery from inhibition was obtained by removing the herbicides by washing. In intact higher plants, accumulation can be stopped by transfer to herbicide-free nutrient solution. In this case subsequent recovery from inhibition must indicate inactivation in the leaves, because translocation from these leaves to other plant parts is unlikely. Shimabukuro and Swanson [43] assumed equilibrium between the reversibly-bound atrazine in the chloroplast and the atrazine pool in the cytoplasm. Metabolism of atrazine in the cytoplasm of sorghum will have the effect of "washing" the chloroplast to reduce its atrazine concentration, and explains the recovery from photosynthesis inhibition. Similar correlations between herbicide metabolism and recovery from photosynthesis inhibition were observed for atrazine in various grasses [27], linuron in parsnip [16], terbacil in peppermint [20] bentazon in wheat, rice and soybean [38, 44] and metamitron in sugar beet [31].

If recovery from photosynthesis inhibition occurs, inactivation of the herbicide in the leaves is obvious, independent of further knowledge about its pathway of degradation [45]. Such tests may also indicate whether further studies on metabolism are useful. The interpretation is simplified by applying the herbicide in nutrient solution, and allowing root absorption to proceed until an equal degree of inhibition is attained by the plants under study. Then, the relative rates of recovery in the plants are directly comparable (*e.g.* [46]). It is also possible to assess the safety of various herbicides in different crops [47], *e.g.* if selective application is freely permitted on the seed-bed (at high inactivation), certain restrictions in soil type or depth of sowing are necessary (at weak inactivation), or if the result mainly depends on depth protection of the crop (no inactivation). Hilton *et al.* [48] studied differences in detoxification of pyridazone herbicides in this way, and Jensen *et al.* [49] the inactivation of some triazines in various grasses.

Foliar application of a photosynthesis inhibitor may result in a more or less constant level of inhibition. Here too, recovery in due time may indicate herbicide inactivation, provided that it occurs fast enough to exclude dilution of the herbicide in the tissue by growth as another reason for recovery. In this way inactivation in particular plants could be demonstrated for foliage-acting herbicides such as phenmedipham [50], propanil [51], bentazon [38, 52] and metamitron [46]. The results are not so easily comparable, because absorption by the plants may vary between species.

Differential sensitivity of chloroplasts

Herbicides may affect the photosynthetic reactions of chloroplasts in various ways (for surveys see *e.g.* [53, 54]), but the majority has been qualified as electron transport inhibitors probably acting at the same site close to photosystem II [55]. Moreland and Hilton [54] classified some other herbicides as inhibitory uncouplers, while a few others act as electron acceptors.

Most of the information concerns electron transport inhibitors. In studying the selective action of these compounds on different plant species it was soon realized that differences in sensitivity of the chloroplasts between these species could be involved. However, until recently no differences were observed between chloroplasts of tolerant and susceptible plants with regard to simazine [41], linuron [17], terbacil [19], chloridazon [34], phenmedipham [50], bentazon [52, 56] and metamitron [31]. This could easily lead to the conclusion that no differences exist between tolerant and sensitive plants at the chloroplast level.

Lately it has been demonstrated that this is not the case. Yearly repeated applications of simazine and atrazine produced a selection of resistant strains in susceptible weed populations of *Senecio vulgaris* [57, 58], *Amaranthus retroflexus* [59] and *Chenopodium album* [60]. Differences in uptake, translocation or metabolism between resistant and sensitive strains were absent or too small to account for the difference in tolerance [61, 62].

Further studies indicated that atrazine did not inhibit the photochemical activity of chloroplasts from resistant biotypes of these weeds, whereas it severely inhibited that of chloroplasts from sensitive biotypes [63–65]. Yet, chloroplasts from both resistant and sensitive biotypes of *Chenopodium album* were equally inhibited by diuron [65]. Chloroplasts from the atrazine-resistant biotype were also resistant to other triazines, and it has been suggested that their photosystem II complex is modified into one with a decreased binding affinity to triazines [66]. A comparable type of chloroplast tolerance is acquired by growing *Euglena gracilis* in a medium containing diuron. Here too, the tolerance was not due to detoxification of diuron or to selective permeability of chloroplast membranes [67].

It is not clear why tolerance of the chloroplasts in these weed populations has evolved instead of the detoxification mechanism, and why it has not yet been observed in tolerant crops.

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