Sorption of the Herbicides Isoxaben and Oryzalin to Soils and Container Media[1]

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Abstract

The herbicides isoxaben (Gallery) and oryzalin (Surflan) are commonly used to prevent weed emergence around ornamental plants in nurseries and landscapes. Saturated batch experiments were conducted in the laboratory to generate equilibrium sorption isotherms for these herbicides in soils and container media. Soils consisted of [A] a sandy loam containing 1.24% organic matter (by wt) after sieving, and [B] a silt loam containing 1.36% organic matter (by wt) after sieving. Container media obtained from nurseries consisted of [C] a mixture of 50% peat and 50% sand (by vol) containing 18.5% organic matter (by wt) after sieving, and [D] a mixture of 70% bark, 25% peat, and 5% fine stone (by vol) containing 34.9% organic matter (by wt) after sieving. Sorption isotherms were generated from these data. Based on sorption coefficients (K_d, K_f), container mix D sorbed both herbicides to a much greater extent than did the other substrates. Oryzalin sorption was greater than isoxaben sorption in each soil and container mix. For oryzalin, organic carbon partition coefficient (K_{oc}) values in the soils were greater than those in the container mixes. Compositional differences in organic matter between soils and container media may account for differences in herbicide sorption in these media.

Index words: adsorption, leaching, organic carbon, organic matter, potting mix.

Chemicals used in study: Gallery (isoxaben, technical grade), N-[3-(1-ethyl-1-methylpropyl)-5-isoxazolyl]-2,6-dimethoxybenzamide; Surflan (oryzalin, technical grade), 4-(dipropylamino)-3,5-dinitrobenzenesulfonamide.

Significance to the Nursery Industry

The activity and fate of an organic chemical in the soil environment is determined by the relative affinities of the chemical for soil and water. The binding of a chemical to solid substrates is known as adsorption, or sorption. Organic chemicals such as herbicides are attracted to the surfaces of organic matter and/or clay particles in soils. After a herbicide is applied, an equilibrium is attained in which a certain percentage of the total herbicide content is sorbed to the solid phase (soil or container mix) and the remaining herbicide is in the aqueous phase (water). In general, greater herbicide sorption results in less off-site movement (runoff, leaching, volatilization), and may increase herbicide persistence but decrease herbicide uptake by plant roots. The sorption properties of herbicides can thus be used to predict their biological activity and environmental fate.

Laboratory experiments were conducted to determine the sorption properties of isoxaben (active ingredient in Gallery 75DF and a component of the granular herbicide Snapshot 2.5TG) and oryzalin (active ingredient in Surflan AS and a component of the granular herbicides Rout and XL 2G). These herbicides are widely used to prevent weeds in nursery fields and containers, landscape beds and/or turf. In four soils and container media, sorption of both herbicides was greatest in the container mix containing the most organic matter. Oryzalin sorption exceeded isoxaben sorption in all substrates. Thus, one would expect oryzalin to be more resistant than isoxaben to off-site movement, and both herbicides to be more mobile in field soils than in container media having substantial organic matter content. Determination of sorption properties for these and other herbicides is useful for optimizing application rates in different soils and mixes, and for predicting environmental impacts such as leaching and runoff potentials.

Introduction

Preemergence herbicides are routinely used in the landscape and nursery industry to prevent weeds in field and container plantings. Off-site movement of herbicides in water can result in contamination of surface water (via runoff) or groundwater (via leaching) in addition to dissipation of herbicidal efficacy at the site of application. The most important and predictive factors determining the environmental fate of a chemical are its sorption parameters (6). Thus, the strength of binding (sorption) of a herbicide to soils or container media is the dominant factor affecting its potential for off-site movement (3, 6). Sorption also affects other processes such as herbicide availability for uptake by plant roots, biodegradation rates and volatilization. Thus, knowledge of the sorption properties of herbicides is a crucial component of models that predict environmental fate of pesticides.

Few papers have been published on the sorption characteristics or mobility of ornamental herbicides, especially in container media. Horowitz and Elmore (5) found greater movement of the herbicide oxyfluorfen in a container mix containing bark:sand (3:1, by vol) than in a mix containing peat:sand (1:1, by vol). Leaching of metolachlor and simazine through containers with several different media was not simply a function of organic matter content (8). Greater leaching of oxadiazon occurred in coarser textured container media (11), and less oryzalin movement occurred in a peat-based container mix than in native soils (12). Camper et al. (2) detected little to no pendimethalin, oryzalin or oxyfluorfen in runoff water from container production areas into a pond. Sorption of oryzalin increased with greater contact time in four soils (7). No leaching of isoxaben occurred in contain-

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ers filled with sphagnum peat consisting of 92.3% organic matter (10).

I chose to study the sorption of isoxaben and oryzalin, two common herbicides in the nursery and landscape industries, by conducting experiments under controlled laboratory conditions to maximize uniformity of procedures and to minimize confounding factors. In this way, these two herbicides could be evaluated in a direct comparison in a range of substrates (two soils, two container media). No published scientific research has generated sorption isotherms for isoxaben or oryzalin in container media. Sorption coefficients for isoxaben and oryzalin in each of these substrates were derived from equilibrium sorption isotherms. These data can be used to predict the potential for off-site movement (leaching, runoff) and activity of these herbicides in various soils and container media.

Materials and Methods

Technical grade samples of isoxaben and oryzalin were provided by Dow AgroSciences. Stock solutions of each herbicide were prepared in methanol.

Soils were collected from research farms of The Connecticut Agricultural Experiment Station: Valley Laboratory in Windsor, CT (Soil A) and Lockwood Farm in Hamden, CT (Soil B). Soil was taken from the top 15 cm (6 in) in fields that had not been treated previously with isoxaben or oryzalin. Container media were obtained from two nurseries [Summer Hill Nursery, Madison, CT (Mix C); and Prides Corner Farms, Inc., Lebanon, CT (Mix D)]. Soils and container media were air dried and sieved through a 2-mm screen before any analyses were conducted. Samples were sent to A&L Analytical Laboratories, Inc. (Memphis, TN) for determination of organic matter (OM) content by a modified Walkley-Black method, and to A&L Eastern Agricultural Laboratories, Inc. (Richmond, VA) for quantification of cation exchange capacity (CEC) by a modified ammonium saturation method. Soil and container media pH values were determined in an equal volume of distilled water. Table 1 contains pH, CEC and OM data for each of the substrates.

Soil A was a Merrimac sandy loam containing 1.24% OM (by wt), and Soil B was a Cheshire silt loam containing 1.36% OM (by wt). Container Mix C consisted of long-fiber Canadian peat (50% by vol) and washed sand (50% by vol). Mix C contained 18.5% OM (by wt). Container Mix D consisted of northern softwood bark (70% by vol), Canadian peat (25% by vol), and finely ground stone (5% by vol). Mix D contained 34.9% OM (by wt). Organic matter contents may be lower than expected for container media because samples contained only particles that had passed through a 2-mm screen. Thus, larger pieces of bark and peat were removed prior to organic matter determination. The larger particles removed by sieving would have a low ratio of surface area to mass, and would therefore be much less active in terms of herbicide sorption. Also, the sand (Mix C) and finely ground stone (Mix D) components of these media comprised a higher percentage on a weight basis than on the reported volume basis, thereby reducing organic matter content based on weight.

Each batch sorption experiment was set up as a randomized complete block design with four replicates. Each experiment was conducted twice. A 10-µl aliquot of a herbicide stock solution (in methanol) was added to 200 ml of 0.01 M $CaCl_2 \cdot 2H_2O$ (prepared with distilled water) in a 250-ml wide-mouth Teflon (PTFE) centrifuge bottle (Nalge Co., Rochester, NY). Initial concentrations of isoxaben or oryzalin in bottles were 0, 0.1, 0.25, 0.5 or 1.0 mg/liter. Concentrations were limited to this 10-fold range because of approaching detection limits at the low end and approaching herbicide solubility limits on the high end. Reported solubility in water at 25C (77F) of isoxaben is 1 mg/liter and of oryzalin is 2.6 mg/liter (1).

Soil or container mix was added to the bottle (Soil A and Soil B, 20 g; Container Mix C, 10 g; Container Mix D, 5 g). In all cases, the mixture in the bottle was within a pH range of 5.0 to 6.0. Bottles were shaken on their sides for 6 hr at 150 rpm and 25C in a Precision 66800 reciprocal shaking bath (Precision Instruments, Winchester, VA). Preliminary experiments indicated that 6 hr was sufficient shaking time for sorption equilibrium to be reached for these herbicides and sorbents. Bottles were then set upright in the water bath overnight (approximately 12 hr) to allow solid particles to precipitate.

A solid-phase extraction (SPE) procedure utilizing a six-port extraction station was used to extract herbicide from the aqueous fraction (supernatant). Riley and Keese (9) reported the advantages of solid-phase extraction cartridges and disks compared to traditional liquid-liquid extraction procedures. Bakerbond™ Speedisk C_{18} disks (J.T. Baker, Mallinckrodt-Baker, Inc., Phillipsburg, NJ), that contain a C_{18} sorbent powder, were pre-conditioned with the following solutions applied in order (disks vacuumed to dryness after each step): 10 ml methanol; 10 ml methanol plus 10 ml water; and 10 ml water. From each sample bottle, 150 ml of aqueous fraction were poured carefully through a 300-mesh screen and through a SPE disk under vacuum. Disks were placed in an oven set at 38C (100F) for 2 hr to remove residual water.

Sorbed chemicals were extracted from disks with two 10-ml methanol washes into the same collection vial. For each wash, disks were soaked with methanol for 1 minute prior to vacuuming liquid into the vial.

The combined methanol extract was poured into a 50-ml evaporation flask. Methanol was removed from the flask by rotary evaporation using a Rotavapor R-124 (Büchi Labortechnik AG, Flawil, Switzerland) under vacuum at 100 rotations/min and water bath temperature of 30C (86F). The dried extract was resuspended by swirling 1.0 ml of methanol:water (1:1, by vol) around the inner wall of the flask. The extract was passed through a 0.45-µm filter attached to a syringe body, and was collected in a chromatography vial.

Herbicide content of samples was determined by high-performance liquid chromatography (HPLC). An Integral 4000 chromatograph (PerkinElmer Analytical Instruments, Shelton, CT) equipped with an autosampler, ultraviolet light detector and an integrator was employed. A 50-µl sample

Table 1. Properties of soils and container media used in sorption experiments. Analyses were conducted on screened samples that passed through a 2-mm sieve.

Soil/container media	pH	Cation exchange capacity (meq/100 g)	Organic matter (g/100 g)
Field Soil A	6.4	3.0	1.24
Field Soil B	5.3	6.1	1.36
Container Mix C	4.5	13.2	18.5
Container Mix D	4.8	21.4	34.9

was injected onto a Supelcosil LC-18 reverse-phase column (25 cm × 4.6 mm) heated to 35C (95F). For isoxaben samples, the following solvent program (% methanol/% water, vol/vol) was used: 0 to 4 min (50/50); 4 to 9 min, linear gradient (75/25); 9 to 17 min (75/25); 17 to 20 min (50/50). For oryzalin samples, the following solvent program (% methanol/% water, vol/vol) was used: 0 to 4 min (50/50); 4 to 9 min, linear gradient (80/20); 9 to 17 min (80/20); 17 to 20 min (50/50). The detector was set at a wavelength of 254 nm for isoxaben samples, and at 285 nm for oryzalin samples. Approximate retention time for isoxaben was 11.9 min and for oryzalin was 13.5 min. Isoxaben or oryzalin concentrations were automatically quantified from peak area integration based on linear regression of peak areas from a series of standards.

In each experiment, a set of bottles was included that contained soil or container mix but no herbicide. Chromatographic peaks produced by naturally occurring compounds extracted from the aqueous phase sometimes were identified as isoxaben or oryzalin. The concentration generated for an untreated blank was subtracted from the concentrations calculated for the herbicide-treated samples containing that same soil or container mix. In bottles containing neither soil nor container mix, recoveries of isoxaben and oryzalin ranged from 83 to 97%.

The herbicide concentration in the sample vials (corrected for percent recovery) was used to calculate the herbicide content (μg) of the aqueous phase at sorption equilibrium. The sorbed herbicide content (μg) at equilibrium was determined by difference [(initial μg in aqueous phase) – (μg in aqueous phase at equilibrium)]. Sorption isotherms were generated by plotting aqueous phase concentrations [C_w (μg/ml)] vs. sorbed concentrations [C_s (μg/g)]. The distribution coefficient (K_d) was derived from the Freundlich adsorption equation (4): $C_s = K_f C_w^{1/n}$. For linear isotherms, $1/n = 1$, thus $K_f = C_s/C_w = K_d$. The slope of a sorption isotherm line, determined by linear regression analysis, is equal to the K_d value. The organic carbon partitioning coefficient (K_{oc}) was calculated as follows: $K_{oc} = [(100)(K_d)] / (\% \text{ organic carbon})$.

Statistical analyses were performed on K_d values using the Number Cruncher Statistical Systems (NCSS) 2000 program (J.L. Hintze, Kaysville, UT). Analyses of variance were conducted on the square root of treatment means, and means were separated by Fisher's Protected LSD test (P = 0.05). Non-transformed means are reported in Table 2.

Results and Discussion

The K_d value represents the affinity or sorption potential for a chemical in a substrate (3, 4, 6). The higher the K_d is for a herbicide in a soil, the greater will be the percentage of herbicide that is sorbed or bound to the soil. Sorption reduces herbicide movement in water passing through the soil (leaching) and reduces off-site movement in water passing over the soil surface (runoff). Strongly sorbed herbicides will remain near the surface of the soil, thus optimizing herbicidal activity and minimizing off-site environmental impacts. However, if a herbicide were completely bound or sorbed, it could be unextractable by weed roots and thus be inactivated.

Within the range of concentrations tested, linear sorption isotherms were obtained for isoxaben and oryzalin in each soil and container mix (Figs. 1 and 2). Sorption distribution coefficients (K_d values) in Table 2 were equal to the slopes of sorption isotherms.

Based on K_d values, oryzalin was sorbed to a greater extent than isoxaben in all soils and container mixes (Table 2). In particular, oryzalin sorption was nine to ten times greater than isoxaben sorption in the soils. Isoxaben sorption was not significantly different in Soil A and Soil B, which varied more in soil texture and cation exchange capacity than in organic matter content. Otherwise, K_d values for isoxaben and oryzalin increased with increasing organic matter contents of the sorbents.

Both herbicides were most strongly bound to Container Mix D, which contained the highest percentage (34.9%) of organic matter. Organic matter is usually the constituent that determines the capacity of a soil to adsorb organic chemicals (3, 4, 6). The organic carbon partitioning coefficient (K_{oc}) is defined simply as the distribution coefficient (K_d) divided by the fraction of organic carbon in the sorbent. Soil organic matter is generally considered to contain 57% organic carbon on average (4). For chemicals that are sorbed predominately to organic matter components, the K_{oc} value should be somewhat consistent in a range of soil types. However, organic matter in different soils, or especially in different container mixes, is not homogenous in chemical or physical properties. For example, organic matter that is highly decomposed (humus) will have a greater surface area per unit mass than minimally decomposed organic matter. In soils containing similar percentages of organic matter (weight basis), the soil containing the greater surface area of organic matter will generally have a greater sorptive capacity (3, 4).

For both herbicides, the calculated K_{oc} values in the two soils were similar, which suggests that organic matter was the primary sorptive component. The average K_{oc} in these soils was 163 for isoxaben and 1530 for oryzalin (Table 2). The reported range of K_{oc} values is 190 to 570 for isoxaben, and 93 to 2700 for oryzalin (1). For oryzalin sorption in four soils, Krieger et al. (7) calculated a K_{oc} range of 880 to 1115. Reported K_d and K_{oc} values for isoxaben and oryzalin are based on a relatively small set of data in soils only (not container media). In general, herbicides with greater solubility in water tend to be less strongly sorbed to organic matter. However, compared to isoxaben, oryzalin has slightly higher water solubility (1) but had stronger affinity for organic matter [K_{oc}] (Table 2).

K_{oc} values were more divergent when calculated from herbicide sorption to the container mixes. K_{oc} values for oryzalin were much lower in the container mixes than in the soils. In contrast, for isoxaben the highest K_{oc} value was for Container Mix D. For both herbicides, the lowest K_{oc} was for sorption to Container Mix C, which contained equal volumes of peat

Table 2. Distribution coefficients (K_d) and organic carbon partitioning coefficients (K_{oc}) for isoxaben and oryzalin in two soils and two container media.

Soil/container Media	K_d (L kg^{-1})		K_{oc} (L kg^{-1})	
	Isoxaben	Oryzalin	Isoxaben	Oryzalin
Field Soil A	1.11f^z	9.64de	157	1360
Field Soil B	1.30f	13.20cd	168	1700
Container Mix C	7.19e	16.60c	68	157
Container Mix D	102.00b	121.00a	512	607

^{z}Means followed by the same letter are not significantly different based on Fisher's Protected LSD test (P = 0.05) performed on the square root of the treatment means. Non-transformed means are presented in this table.

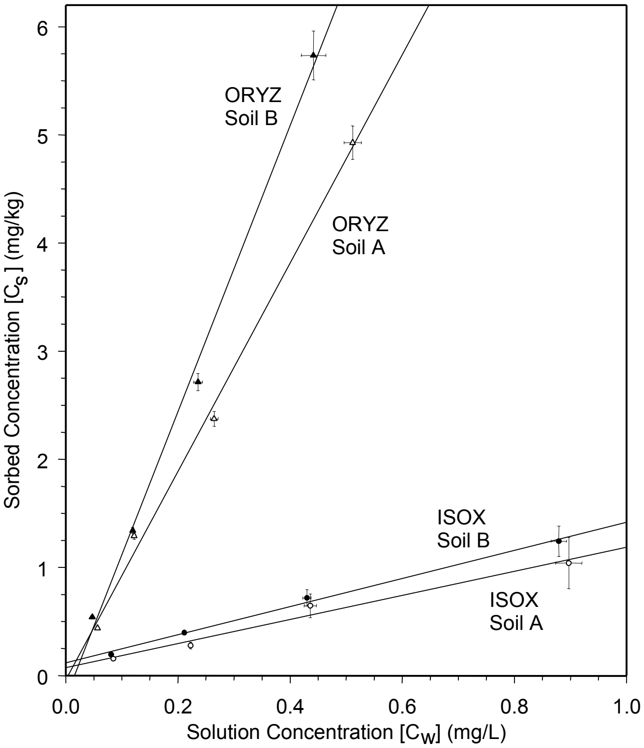

Fig. 1. **Sorption isotherms for isoxaben (ISOX) and oryzalin (ORYZ) in Soils A and B. Error bars represent the standard error about the mean for both the sorbed concentration (C_s) and the solution concentration (C_w). The slope of each regression line equals the distribution coefficient (K_d) of the specified herbicide in the specified soil. Linear regression equations are the following: Isoxaben/Soil A: $y = 1.11x + 0.07$ ($R^2 = 0.71$); Isoxaben/Soil B: $y = 1.30x + 0.12$ ($R^2 = 0.85$); Oryzalin/Soil A: $y = 9.64x - 0.04$ ($R^2 = 0.97$); Oryzalin/Soil B: $y = 13.2x - 0.21$ ($R^2 = 0.94$)**

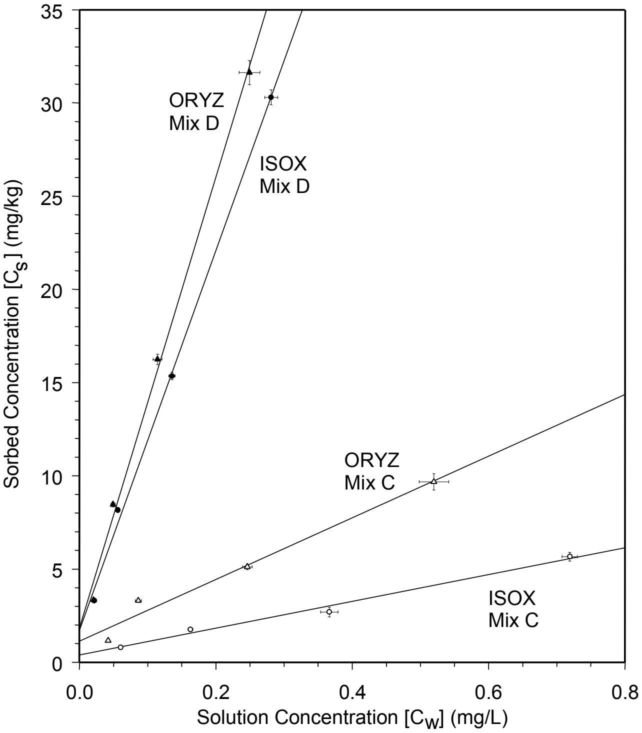

Fig. 2. **Sorption isotherms for isoxaben (ISOX) and oryzalin (ORYZ) in Container Media C and D. Error bars represent the standard error about the mean for both the sorbed concentration (C_s) and the solution concentration (C_w). The slope of each regression line equals the distribution coefficient (K_d) of the specified herbicide in the specified container media. Linear regression equations are the following: Isoxaben/Mix C: $y = 7.19x + 0.38$ ($R^2 = 0.94$); Isoxaben/Mix D: $y = 102x + 1.69$ ($R^2 = 0.98$); Oryzalin/Mix C: $y = 16.6x + 1.12$ ($R^2 = 0.92$); Oryzalin/Mix D: $y = 121x + 1.81$ ($R^2 = 0.95$)**

and sand. A possible explanation is that the organic matter in Mix C has a low ratio of surface area to mass, and thereby less sorptive capacity.

Under the moderately acidic conditions (pH 5 to 6) of the sorption experiments, isoxaben and oryzalin are both uncharged compounds of minimal polarity (1), thus their solubility and sorption characteristics would not be affected significantly by pH. Oryzalin is slightly basic [pK_a of 8.6 to 9.4 (1)], but it would only possess a positive charge under alkaline conditions.

The cation exchange capacity of a substrate refers to the prevalence of exchange sites for inorganic or organic cations. These cation exchange sites are generally on negatively charged surfaces of clay and organic matter surfaces. Cation exchange capacity values for the soils and container media are reported in Table 1. Again, because both isoxaben and oryzalin would have been in a non-polar state under the experimental conditions, one would not expect cation exchange to contribute to sorption of these herbicides.

Compositional differences in organic matter between soils and container media may account for the wide range in K_{oc} values. Even though particles larger than 2 mm were excluded from the sorption experiments, much of the peat and bark-derived organic fraction in these mixes was still larger and less completely decomposed than the organic matter found in the soils. Highly decomposed organic matter, or humus, has a greater surface area per unit mass, and thus has greater capacity to sorb organic chemicals. Mahnken et al. (8) concluded that generalizations about relative herbicide mobility cannot be made across container media due to undetermined compositional differences. Herbicide sorption to container media may not be easily predicted based on sorption data generated in soils. This study demonstrates that the percentage of organic matter in a container mix is not the only factor that affects herbicide sorption. The physical and chemical properties of the organic matter, and possibly other factors, may have significant impact on the sorption process.

The results of this study suggest that oryzalin will have lower mobility (leaching and runoff potentials) than isoxaben, especially in field soils. Both herbicides should be less mobile in container media than in field soils. However, container nursery production involves much greater input of water (irrigation) than do field situations. With greater movement of water through the containers, it is important to use a container mix having sufficiently high sorptive capacity to minimize herbicide leaching or runoff.

Herbicidal activity is also affected by sorption. A herbicide could potentially be bound so tightly to organic matter that its biological activity would be reduced. In this case, weeds might not be controlled because such a small percentage of the herbicide would be present in soil solution to be taken up by roots. However, the extent to which isoxaben and oryzalin are sorbed, even in Container Mix D, is not enough to reduce activity of these herbicides when applied at recommended dosages, provided that sufficient moisture is present (Mervosh, personal observation). In fact, if a preemergence herbicide is strongly bound to soils or container media, more of the herbicide will remain near the surface where it can effectively prevent weed emergence over a greater length of time.

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