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Adsorption of the Herbicides Diuron, Terbacil, and Simazine to Blueberry Mulches

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Abstract. Samples of soil, mulch, and the soil/mulch interface zone were collected from commercial highbush blueberry *(Vaccinium corymbosum* L.) fields typical in their use of mulch under Arkansas conditions. Mulches included 1-year-old hardwood sawdust, 5-year-old hardwood sawdust, and 1-year-old pine needle mulch. Herbicide adsorption (Kd values) of the samples was determined for diuron, terbacil, and simazine. The soils, mulches, and interfaces adsorbed nearly 10 times as much diuron and more than twice as much simazine as terbacil. Adsorption of the herbicides was three to five times greater to the mulches than to the soils. Adsorption was significantly correlated with the organic matter content of the mulch. Adsorption was not related to herbicide solubility. Although no statistical differences were found among the three mulch materials, adsorption coefficients (Kd values) were numerically lower for each chemical on the 5-year-old hardwood mulch than on the 1-year-old hardwood or pine mulch. Chemical names used: 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron); 3- *tert* -butyl-5-chloro-6-methyluracil (terbacil); 2-chloro-4,6-bis(ethylamine)- *s* -triazine (simazine).

Blueberries in northern Arkansas are mulched heavily with either hardwood sawdust or pine needles to retain moisture and moderate soil temperature. The use of mulch alone does not provide adequate weed control (Talbert et al., 1975). Herbicides recommended for application to the mulched surface of the bed include diuron, terbacil, and simazine, which generally provide adequate control of most annual and some perennial weeds (Baldwin and, Boyd, 1989). However, an apparent loss of herbicide activity has been observed 3 to 4 months after application. Since herbicide rates are based on soil texture or organic matter, questions have been raised regarding the chemical availability of these herbicides when applied to the mulch surface.

Adsorption of herbicides by soil tends to reduce their phytotoxicity and movement in the soil (Harris and Warren, 1964). The importance of soil organic matter content to herbicide adsorption is well documented (Bailey and White, 1979; Grover, 1971; Rhodes et al., 1970; Upchurch, 1966; Walker and Crawford, 1968); however, undecayed plant material often does not adsorb triazine herbicides (Erback and Lovely, 1975; Grover, 1971; Walker and Crawford, 1968). Other research indicates surface residue can adsorb appreciable herbicide and, subsequently, affect phytotoxicity and uniformity of weed control (Eleftherhorinos et al., 1985; Toth and Milham, 1975). Adsorption increases as the plant material incubates with soil, and plant material was most adsorptive when completely humified (Grover, 1971; Walker and Crawford, 1968).

The adsorption (Rhodes et al., 1970), leaching (Murray et al., 1969), and degradation (McCormick and Hiltbold, 1966) of diuron in soils have been recorded. The importance of microbial decomposition and soil organic matter content in diuron persistence was demonstrated by the work of McCormick and Hiltbold (1966). More herbicide was inactivated per unit of metabolized soil carbon in a loamy sand than in a clay loam. Amending soil with organic matter high in N accelerated diuron decomposition (Murray et al., 1969). Other evidence shows chemical degradation to be of minor importance (McCormick and Hiltbold, 1966; Murray et al., 1969). Diuron phytotoxicity was found to be inversely correlated with soil organic matter and cation exchange capacity (Upchurch, 1958). A higher rate of diuron was required to reduce the growth of ryegrass *(Lolium* spp.) as soil organic matter increased.

Liu et al. (1971) found an organic soil more adsorptive for terbacil and atrazine, a herbicide chemically related to simazine, than sandy loam soils. Kratky and Warren (1973) found ≈19 times more terbacil was needed to give 30% control of sorghum *(Sorghum bicolor* L.) in a Chalmers silty clay loam with 24% organic matter than in a Bloomfield fine sand with only 0.3% organic matter. Organic materials in soil were much more adsorptive than clays for simazine and other *s* -triazine herbicides (Talbert and Fletchall, 1965).

The study reported here was initiated to compare the adsorption of the three herbicides most frequently used in blueberry culture in northern Arkansas to the mulch materials and soils.

Two composite samples were collected from each of three commercial blueberry fields typical in their use of mulch under Arkansas conditions. Soil/mulch strata sampled were: 1) the surface mulch of the bed, 2) the soil/mulch interface zone beneath the bed, and 3) the soil adjacent to the bed. The soil at one location was a Linker loam (fine loamy, siliceous, thermic, Typic Hapludults). Here, the mulch was a combination of 1-year-old hardwood shavings and sawdust with a well-developed interface zone consisting of partially decomposed sawdust. The second location had been mulched 5 years previously with hardwood sawdust. The soil was a Captina silt loam (fine silty, mixed, mesic, Typic Fragiudalf). The soil/mulch interface zone was shallow (<0.5 cm deep), the mulch being largely decomposed. The third field was a Zanusville silt loam (fine silty, mixed, mesic, Typic Fragiudalf) overlying sandstone. Samples of 1-year-old pine needle mulch, soil/mulch interface zone, and soil were collected. The interface zone at this location was also shallow with little decomposition of the pine needles. A considerable amount of sandy soil was included in the interface zone sample from this location.

Each sample was air-dried and then sieved through a 2.4-mm screen. Four subsamples from each of the two samples from each field were taken for analysis. Determination of herbicide adsorption was by the standard procedure of Talbert and Fletchall (1965), which provides a distribution coefficient (Kd) value or adsorption ratio for each chemical. Ten ml of an aqueous solution of ^{14}C-labeled diuron (1.0 ppmw, specific activity 9.12 µCi/mg; 1 Ci = 37 GBq), ^{14}C-labeled terbacil (0.6 ppmw, specific activity 9.12 µCi/mg), or ^{14}C-labeled simazine (1.0 ppmw, specific activity 33.9 µCi/mg) were equilibrated with 0.5 g of sample in a 15-ml glass centrifuge tube. The tubes were sealed with an aluminum foil-covered cork to prevent adsorption by the stopper. The tubes were placed on a rotating rack, allowed to equilibrate for 24 hr, and then centrifuged to separate the supernatant. A 2-ml aliquot of the supernatant was removed and placed in 5 ml of Insta-Gel counting solution (Packard Instrument Co., Downers Grove, Ill.). Samples were counted on a Packard Tri-Carb model 2650 liquid scintillation spectrometer. The distribution coefficient was calculated by the fol-

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Table 1. Adsorption of three herbicides on soils and mulches.[z]

Media	Herbicide			Mean	Organic matter (%)
	Diuron	Terbacil	Simazine		
			Kd values		
Mulches	97.7	11.6	21.2	43.5	47.3
Interface zones	71.9	6.6	17.4	32.0	23.0
Soils	18.0	2.1	6.6	8.9	4.4
Mean	62.5	6.8	15.1		

[z] $LSD_{0.05}$ among chemicals 11.7; among media 17.5; interactive 20.5.

lowing equation: Kd = (dpm standard – dpm equilibrium solution)/(dpm equilibrium solution) × (ml total solution)/(g adsorbent). Appropriate statistical analysis was performed as a modified split-split plot design; main plots were fields with mulches as the sub-plots and chemicals as sub-subplots. Correlation coefficients were determined for the adsorption of each herbicide to the organic matter of the various media. Percent organic matter was based on the percent total carbon, as determined by the Lindberg dry combustion analyzer (Storer, 1984).

Adsorption (Kd) varied for the herbicides tested (Table 1). Diuron was the most strongly adsorbed of the three herbicides, having eight to 11 times more adsorption on the three mulches than did terbacil, the least strongly adsorbed of the herbicides. Adsorption of simazine was similar to that of terbacil, but the average for simazine was two to three times greater over the three soil/mulch samples. These results were similar to the report of Liu et al. (1971), in which the triazine herbicide atrazine was adsorbed consistently more to soils than was terbacil. Ivey and Andrews (1965) found diuron, although much more soluble than simazine, was less subject to leaching. They postulated that this difference was due to diuron being more readily adsorbed to soil colloids than the triazines.

Adsorption of each herbicide to various soils and mulches was significantly correlated with the organic matter (total carbon) content of the media (diuron, $r = 0.73$, 18 df; simazine, $r = 0.75$, 18 df; terbacil, $r = 0.87$, 18 df). Herbicide adsorption was not related to water volubility (diuron = 42 ppm; simazine = 5 ppm; terbacil = 710 ppm at 25C).

Each herbicide was more adsorbed to the mulches, including the interface zone, than to the soils. Mulches were five times more adsorptive than soils for both diuron and terbacil and three times more adsorptive than the soils for simazine (Table 1). The mulches as a group contained nearly 12 times more organic matter than the soils (Table 1). These data indicate that plant residues on the soil surface, whether sawdust or pine needles, can adsorb an appreciable amount of herbicide. In general, herbicide rates are based on the soil texture or organic matter content. When these herbicides are to be applied to a mulched surface on low organic matter soils, it may be necessary to increase the application rate to obtain weed control comparable to nonmulched surfaces. Haramaki et al. (1969) found weed control increased in woody ornamental with increased simazine concentration or when the herbicide was incorporated on oak bark mulch and a greater depth of mulch was applied. However, Bing (1965) found no increase in the rate of diuron or simazine required to obtain effective weed control when using various mulches, including salt marsh hay and cocoa hulls. It is possible in these cases that the depth of mulch compensated for decreased herbicide availability, a situation which we have not experienced.

Herbicides did not differ significantly in adsorption to different types of mulch or soil found in the three fields, although there was consistently one-third less adsorption to the 5-year-old hardwood mulch and underlying soil (data not shown).

The pattern of herbicide adsorption in various media for different mulch types was also constant, with one exception. Diuron was the only herbicide showing appreciably greater adsorption by the partially decomposed interface zone than by the surface of the mulch or the soil (Table 1, LSD = 17.1). Recently, Madhun et al. (1986) found a stronger tendency for diuron (vs. simazine) to complex with water soluble soil organic material (WSSOM) resembling fulvic acid and typical of soil humates. Our results may reflect a higher proportion of humates or WSSOM in the decomposing interface.

The behavior of each herbicide suggests that each will be adsorbed similarly to each of the soils within the narrow range of soils evaluated. However, when herbicide is applied to the mulched surface, its adsorption may be considerably greater than that of the soil, depending on chemical applied and, perhaps, mulch type. Additional research is warranted to establish more firmly the relationship of herbicide adsorption to mulch materials and its subsequent availability, persistence, and phytotoxicity.

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