Soil Column Mobility of Metribuzin from Alginate-Encapsulated Controlled Release Formulations

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The mobility of metribuzin [4-amino-6-(1,1-dimethylethyl)-3-methylthio)-1,2,4-triazin-5(4*H*)-one] from alginate-encapsulated controlled release (CR) formulations was investigated in four contrasting soil profiles. Two CR formulations based on sodium alginate (1%), kaolin (10%), and Tween 20 (0.5%) were compared to technical grade (TG) metribuzin and to a commercial liquid (CL) metribuzin formulation (Sencor 4L). In addition to the basic components, the CR-Oil formulation contained 4% linseed oil and the CR-N formulation did not. All herbicide treatments were labeled with [^{14}C]-metribuzin and were applied to duplicate soil columns containing a surface and a subsoil horizon. Each horizon was packed to a depth of 12.5 cm, giving a total column length of 25 cm. The columns were leached with 21 (420 mL) to 30 cm (600 mL) of 0.01 M $CaCl_2$ for a period of 7–10 days. For the TG treatment, the total amounts of [^{14}C]metribuzin leached were 85, 62, 66, and 58% for the Evesboro, Ochlocknee, Conover, and Commerce soils, respectively. This is compared to 91, 52, 51, and 43% for the CL formulation. The CR-Oil formulation leached 9, 13, 9, and 9% of the applied [^{14}C]metribuzin, compared to 49, 53, 41, and 48% for the CR-N formulation. The CR-Oil formulation also increased the amount of [^{14}C]metribuzin retained in the soil surface horizon (13–27%), compared to the CR-N (2–5%), TG (2–3%), and CL (1–2%) formulations.

Keywords: *Herbicides; leaching; linseed oil; groundwater*

INTRODUCTION

The safety of public and private drinking water supplies continues to be an important environmental issue. Agrochemicals, including herbicides, pesticides, and fertilizers, have all been found in groundwater and surface water supplies. Fertilizers, particularly nitrogen and phosphorus, appear to result in the most widespread contamination (U.S. EPA, 1990). However, contamination by herbicides and pesticides has been demonstrated in many localities (U.S. EPA, 1989). These concerns may lead to additional legislation that would further restrict the use of some herbicides.

Metribuzin is a triazine herbicide that is widely used in Louisiana and the Mid South area in sugarcane production. The triazines are the most widely applied herbicide class with an estimated market size of $1425 million (Parry, 1989). Sorption of metribuzin, a weak base, to soils and sediments will be governed, to a large extent, by the soil pH. Sorption of metribuzin has been shown to increase with decreasing pH. This increase in sorption is accompanied by a decrease in metribuzin phytotoxicity (Ladlie et al., 1976).

Several alternative pest control strategies have been investigated in an attempt to reduce the amount of chemical pesticide used. Examples include biological control systems, integrated pest management and CR formulations. CR formulations may provide a viable, environmentally sound alternative to many of the current herbicide formulations (Schreiber, 1989). CR formulations have several advantages over standard herbicide formulations, including ease and safety in handling and reduced leaching potentials (Lewis and Cowsar, 1977). It is possible that the application rates may be decreased with CR formulations, although this has not always found to be the case. In addition, Taylor and Glotfelty (1988) have suggested that CR formulations may also reduce herbicide volatilization losses.

Many procedures have been evaluated for the preparation of CR formulations. These include, but are not limited to, alginate encapsulation (Connick, 1982; Connick et al., 1984), starch encapsulation (Shasha et al., 1976; Wing, 1989; Wing et al., 1987), cyclodextrin complexation (Dailey, 1991; Szejtil, 1985), and lignin entrapment (Riggle and Penner, 1987, 1988).

Pepperman et al. (1991) have described a series of alginate–kaolin-based metribuzin CR formulations. In a water release study, the authors reported little effect on release due to alginate type or to various organic adsorbents. Greater control of release rates could be obtained with the addition of charcoal, although this resulted in some irreversible adsorption. In another water release study (Pepperman and Kuan, 1993), the authors demonstrated that much greater control of metribuzin release rates could be obtained with the addition of linseed oil to the CR formulation. The authors attributed their observations to a combination of effects. First, a partitioning of the metribuzin occurs between the oil and the surrounding water. Also, the linseed oil forms a polymeric film upon aging, which serves as a diffusional barrier.

Riggle and Penner (1987) investigated the controlled release of alachlor and metribuzin from pine kraft lignins utilizing soil thin layer chromatography (STLC). The authors reported a significant decrease in the mobility of both alachlor and metribuzin on the STLC plates. In a related study (Riggle and Penner, 1988), the authors investigated the mobility of chloramben, metribuzin and alachlor in a soil column leaching study. The pine kraft lignin, PC940C, was found to control release of all three herbicides and to decrease their mobility significantly in soil columns. The PC940C lignin was immobile in soil columns. Recently, the same authors (Riggle and Penner, 1992), studied the adsorption of metribuzin by various kraft lignins. The authors reported that the controlled release properties of the

Table 1. Selected Soil Properties for the Evesboro, Ochlocknee, Conover, and Commerce Soils[a]

soil series horizon	pH	OM (%)	sand (%)	silt (%)	clay (%)	0.33 bar (%)	texture	K_d (L kg^{-1})
Evesboro								
Ap	5.3	0.94	71	16	13	9.6	sandy loam	0.24
C	5.3	0.24	81	6	13	8.2	sandy loam	0.09
Ochlocknee								
A	4.9	1.09	67	21	12	15.0	sandy loam	0.41
C	4.8	0.27	86	3	11	5.3	loamy sand	0.06
Conover								
Ap	6.6	1.79	60	20	20	20.6	sandy loam	0.47
Btg	6.6	1.21	61	19	20	20.8	sandy loam	0.28
Commerce								
Ap	5.2	1.52	41	33	26	28.6	loam	0.60
Bw	5.5	1.28	41	31	28	29.5	loam	0.47

[a] pH, pH of 1:1 soil/deionized water suspension; OM, soil organic matter content; 0.33 bar, water content (g/100 g dry soil) at 0.33 bar of pressure; texture, soil textural class; K_d, soil sorption distribution coefficient.

lignins could be explained by a combination of adsorption of the herbicides to the lignin surfaces and macromolecule formation. Street et al. (1987) investigated the effects of several adjuvants, including linseed oil, on the behavior of metribuzin in soil. Linseed oil was found to reduce metribuzin mobility slightly on STLC plates when applied in combination with the adjuvant ARD 54. The combination of linseed oil and the adjuvants did not decrease soybean yield; however, linseed oil plus ARD 1836 significantly decreased control of sicklepod at two locations. Fleming et al. (1992a) reported that starch encapsulated metribuzin formulations resulted in a decreased leaching potential in soil columns. These formulations had a limited effect on metribuzin movement in the field. The objective of this study was to determine the influence of two alginate-encapsulated CR formulations of metribuzin on herbicide mobility in soil columns, compared to a commercial liquid formulation and TG metribuzin.

MATERIALS AND METHODS

Soils. The soils investigated in this study included an Ap and Bw horizon of a Commerce silty clay (fine-silty, mixed, nonacid, thermic Aeric Fluvaquent) and an A and C horizon of an Ochlocknee sandy loam (coarse-loamy, siliceous, acid, thermic Typic Udifluvent), from East Baton Rouge parish, Louisiana, an Ap and C horizon of an Evesboro loamy sand (coarse-loamy, siliceous, mesic Aquic Hapludult) from Sussex county, Delaware, and an Ap and Btg horizon of a Conover loam soil (loamy, mixed, mesic Udollic Ochraqualf) from Ingham county, Michigan. The horizon designation Ap indicates that the soil has been cultivated and the designation A indicates that the soil has not been cultivated. The B horizons are subsoils, with the Bt horizon indicating an accumulation of clay, the Btg indicating an accumulation of clay with strong gleying (an indication of that the horizon has been saturated with water at some time), and the Bw indicating a horizon that has been only slightly modified as compared to the surface horizon. Finally, the C designation indicates a subsoil that is composed of parent material (Soil Survey Staff, 1987). Soils were air-dried and then crushed to pass a 4-mm sieve for column studies and to 2 mm for chemical and physical analysis. The following properties were determined on all soil horizons: particle size (soil texture) by the hydrometer method (Day, 1965); 0.33 bar moisture content by pressure plate analysis; soil pH (in deionized water); and organic matter by Walkley-Black wet oxidation (Nelson and Sommers, 1982). Soil properties are presented in Table 1.

Metribuzin sorption K_d values were determined by a standard batch equilibrium method, with the exception that the centrifuge tubes were pre-equilibrated with the [^{14}C]metribuzin solution for 24 h, prior to soil addition. This procedure was utilized to account for any sorption to the centrifuge tubes. Stock 10^{-4} M solutions were prepared in 0.01 M $CaCl_2$ with technical and [^{14}C]metribuzin to obtain an activity of 20 000 Bq L^{-1}. Five grams of soil was equilibrated with 20 mL of [^{14}C]metribuzin solution at concentrations of 15, 30, and 60 μM L^{-1}. The samples were equilibrated on a rotary shaker at a speed of 150 rpm for 24 h. After equilibration, the samples were centrifuged at 2000g for 0.5 h. A 0.2-mL aliquot was then taken from the supernatant and placed in 4 mL of scintillation fluid (Scintiverse TM E, Fisher Scientific) and counted on a Beckman LS 1800 liquid scintillation spectrophotometer. Counting efficiency was 90%. The difference between the supernatant concentration and the amount of herbicide initially added was assumed to be sorbed (after correction for soil blanks). Sorption results are reported as K_d values (Table 1).

Controlled Release Formulations. Technical-grade metribuzin and [^{14}C]metribuzin were obtained from Miles Inc., Kansas City, MO, and E. I. du Pont, Wilmington, DE, respectively. Commercial metribuzin (Sencor 4L) was obtained from Dr. Clyde Dowler, USDA, ARS, Georgia Coastal Plain Experiment Station, Tifton, GA. Controlled release formulations were prepared to contain 1% sodium alginate (Kelgin MV, Kelco, Division of Merck and Co., San Diego, CA), 10% kaolin (Thiele Kaolin Co., Wrens, GA), 0.5% Tween 20 (Sigma Chemical Co., St. Louis, MO), TG, and [^{14}C]metribuzin. The controlled release formulations were prepared by a method similar to that of Pepperman and Kuan (1993). Technical and [^{14}C]metribuzin were first dissolved in the Tween 20, water, and linseed oil, if present. Kaolin was gradually added and the slurry was stirred on a magnetic stir plate for 1 h to obtain a homogeneous mixture. The pH of the mixture was then adjusted to approximately 7.8 with NaOH. This was done to prevent decomposition of the metribuzin due to increased acidity (Pepperman and Kuan, 1992). The alginate was slowly added to prevent clumping and the mixture stirred for 0.50 h. The pH was then readjusted to approximately 7.8 and the mixture was stirred for a final 0.25 h. The formulation mixture was then dropped into the gellant solution (0.25 M $CaCl_2$) with the aid of a peristaltic pump (Manostat Cassette) at a rate of approximately 80 mL h^{-1}. The beads were dropped into the gellant solution in two batches of 0.25 h. After an additional 5-min period, in which the beads were allowed to harden further, they were vacuum filtered through Whatman No. 2 filter paper, rinsed with an additional 30 mL of deionized water, and allowed to dry for 72 h. The CR-N formulation contained 1.74% ai, and the CR-Oil formulation contained 1.46% ai. The CR-Oil formulation also contained raw linseed oil (T&R Chemicals, Inc., Clint, TX) (4% of formulation mixture).

Metribuzin Treatments. The herbicide treatments used in this study were radiolabeled with [^{14}C]metribuzin. The treatments were applied at a rate equivalent to 40 kg of ai ha^{-1} with 49 950 Bq column^{-1}. This rate was required to achieve adequate surface coverage in our scaled down system. Also, this amount was required to achieve an adequate ^{14}C-labeling rate at this lower metribuzin formulation loading rate. Finally, this high rate would also simulate a worst case scenario in the field. For the TG and CR formulations, TG and [^{14}C]metribuzin were combined, and for the CL treatments [^{14}C]metribuzin was mixed with Sencor 4L.

Column and Soil Preparation. Soil columns were prepared from clear Plexiglas pipe, 5 cm i.d. × 30 cm long. The columns were split longitudinally and resealed with silicone sealant and duct tape to allow easy sampling of the column after the leaching process was completed. The bottom of each column was covered with Whatman No. 4 filter paper, followed by a piece of 200-mesh stainless steel wire cloth. Each column contained a surface soil and a subsoil. The soil horizons were packed to a depth of 12.5 cm each, for a total of 25 cm. The soil columns were packed at the following bulk densities: Commerce Ap, Bw (1.3, 1.3), Conover Ap, Btg (1.3, 1.3), Ochlocknee A, C (1.5, 1.5), Evesboro Ap, C (1.5, 1.5). These bulk densities resulted in pore volumes of 0.11 L for the Evesboro and Ochlocknee soils and 0.13 L for the Commerce and Conover soils. The pore volume is approximately equivalent to the total volume of voids present in the soil, after correction for moisture content. Prior to application of the herbicide treatments, the columns were saturated with tap water via capillarity and then allowed to drain free for 24 h.

Chemical Preparation and Application. All herbicide treatments were applied to duplicate soil columns. The TG and CL formulations were applied in 5 mL of MeOH and 5 mL of deionized water, respectively, in a cross-hatched pattern on the soil surface. Significant movement of the applied herbicide due to this application was not observed. The CR formulations were evenly distributed on the soil surface as determined by visual inspection. After herbicide application, an additional 2 cm of air-dried soil was added to the top of the column, followed by a disk of Whatman No. 4 filter paper covering the applied herbicide treatments. The herbicides were allowed to equilibrate with the soil for 24 h prior to initiation of the leaching procedure.

Leaching and Leachate Collection. The leaching solution used in all experiments was 0.01 M $CaCl_2$. This was done to simulate the soil solution and to prevent dispersion of the soil during the leaching procedure. The Ochlocknee, Conover, and Commerce soils were leached with 30 cm (600 mL) of solution over a period of 10 days (3 cm day^{-1}). Due to its higher leaching rate, the Evesboro soil was leached with 21 cm (420 mL) of solution over a period of 7 days (3 cm day^{-1}). The time and volume of each leachate were recorded. A 0.2-mL aliquot was then taken from the leachate and placed in 4 mL of scintillation fluid (Scintiverse TM E, Fisher Scientific) and counted on a Beckman LS 1800 liquid scintillation spectrophotometer. Counting efficiency was 90%. At the termination of the leaching procedure, the columns were allowed to drain for 72 h.

Soil Analysis. The columns were split vertically and the soil was removed in 5-cm increments, placed in plastic bags, mixed, labeled and sealed. Subsamples (50 g, oven dry weight equivalent) of each sampling increment were extracted for 2 h with 100 mL of HPLC grade MeOH, filtered through Whatman No. 42 paper, and analyzed by LS techniques, as described above.

Statistics. Metribuzin breakthrough data were fit to linear, quadratic, and cubic equations. The best fit was selected based on comparison of r^2 and P values and an analysis of residuals. An analysis of covariance was then used to make pairwise comparisons between formulations for each soil. Soil distribution data were analyzed with a repeated measures analysis of variance, with soil and formulation as the subject effects and depth as the repeated measure. Data were ranked by soil and depth and means were separated on the ranked data by the Kruskal–Wallis test.

RESULTS AND DISCUSSION

Herbicide Sorption. Metribuzin was only weakly retained by the soils investigated, with K_d values ranging from 0.06 for the Ochlocknee C horizon to 0.60 for the Commerce Ap horizon (Table 1). These values are consistent with those in the literature. Bouchard et al. (1982) reported metribuzin distribution coefficients of 0.57 and 0.32 for a Toloka silt loam surface and subsoil. Harper (1988) reported Freundlich K_f values for metribuzin that ranged from 0.78 to 1.34 for various depths of a Dundee silty clay loam soil. Sorption K_ds were positively correlated with silt content, organic matter content, 0.33 bar moisture content, and clay content with r^2 values of 0.95***, 0.91***, 0.89**, and 0.76*, respectively. A negative correlation ($r^2 = -0.91$***) was noted between sorption K_ds and sand content. A significant correlation was not noted between sorption K_ds and pH.

Herbicide Leaching. Distinct differences were noted in the leaching patterns of the soils investigated. Averaged across formulation the ranking of the soils, in terms of percent [^{14}C]metribuzin leached, was Evesboro (58%) > Ochlocknee (45%) > Conover (42%) > Commerce (40%). There was not a significant correlation between sorption K_ds and percent [^{14}C]metribuzin leached; however, a relation was noted ($r^2 = -0.84$, $P = 0.12$). Marked differences were also observed in the leaching patterns of the formulations investigated. Averaged across soils the ranking of formulations, in terms of percent leached, was TG (68%) > CL (60%) > CRF-N (48%) > CRF-Oil (10%).

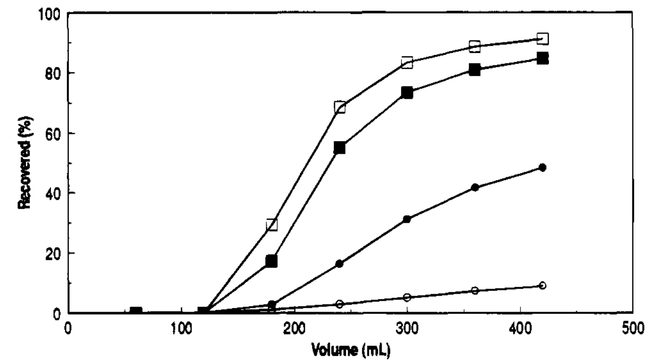

Figure 1. Cumulative [^{14}C]metribuzin leached from TG (■), CL (□), CR-N (●), and CR-Oil (○) formulations in an Evesboro soil.

The Evesboro soil is a coarse-textured, low organic carbon content, Atlantic Coastal Plain soil. This soil has a limited ability to retain metribuzin, with Kd values of 0.24 in the Ap horizon and 0.09 in the C horizon. Significant differences were noted between all herbicide treatments. For the TG and CL metribuzin treatments, ^{14}C was first detected in the leachate at approximately 0.18 L or slightly over 1.5 pore volumes (Figure 1). The amount leached increased steadily over time to approximately 91% for the CL formulation and 85% for the TG-metribuzin at the termination of the experiment (3.8 pore volumes). For the CR formulations, ^{14}C was also detected in the leachate at 1.5 pore volumes. The amount leached from the CR-N formulation increased to 49% of that applied by the termination of the leaching procedure. The CR-Oil formulation was leached to a much smaller extent, with a total amount leached of 9%.

The Ochlocknee soil is a coarse-texture, riparian zone soil. This soil has a slightly higher organic carbon content than the Evesboro soil and a lower pH but is similar in soil texture. The surface Ap horizon has a K_d value of 0.41, almost twice that of the Evesboro Ap. The C horizon, however, has a K_d of 0.06, indicating minimal sorption. There were significant differences between the TG and CL metribuzin treatments and between the two CR formulations. For the TG and CL metribuzin treatments, ^{14}C was first detected in the leachate at approximately 2.2 pore volumes (Figure 2). The amount leached from this soil increased to approximately 52% for the CL formulation and 62% for the TG-metribuzin by the end of the experiment (5 pore volumes). For the CR formulations, ^{14}C was detected in the leachate at 2.2 pore volumes. The amount leached increased to 13.0% for the CR-Oil formulation and 53% for the CR-N formulation.

The Conover soil is loamy, glacial till soil, with a high organic carbon content in the surface and subsoil. The K_ds for this soil are 0.47 for the Ap horizon and 0.28 in the Btg horizon. There were significant differences between the TG and CL treatments and between the CR formulations. For the TG and CL metribuzin treatments, ^{14}C was first detected in the leachate at

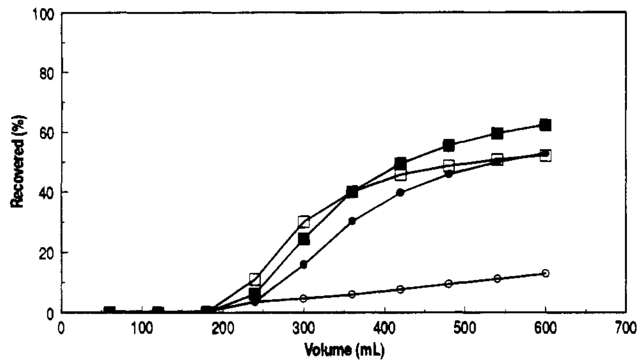

Figure 2. Cumulative [^{14}C]metribuzin leached from TG (■), CL (□), CR-N (●), and CR-Oil (○) formulations in an Ochlocknee soil.

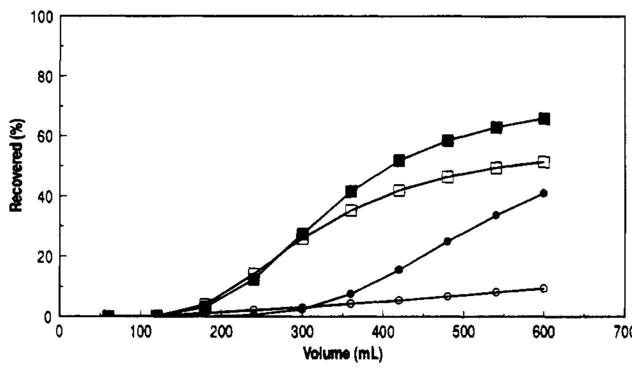

Figure 3. Cumulative [^{14}C]metribuzin leached from TG (■), CL (□), CR-N (●), and CR-Oil (○) formulations in a Conover soil.

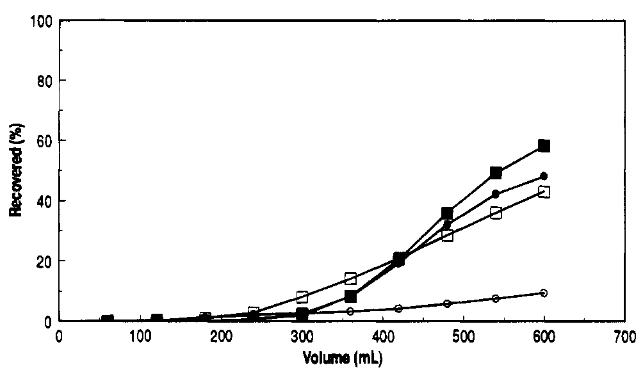

Figure 4. Cumulative [14C]metribuzin leached from TG (■), CL (□), CR-N (●), and CR-Oil (○) formulations in a Commerce soil.

approximately 1.4 pore volumes and increased to 66% for the TG-metribuzin and 51% for the CL formulation by the end of the experiment (Figure 3). For the CR-Oil formulation ^{14}C appeared in the leachate at 1.8 pore volumes and for the CR-N formulation at 2.3 pore volumes. The total amount leached was 9.2% for the CR-Oil formulation and 41% for the CR-N formulation.

The Commerce soil is a fine-textured, Mississippi alluvial soil that also possesses a high organic carbon content and would be expected to have the lowest leaching potential of the four soils investigated. There were significant differences noted between all herbicide treatments for this soil. For the TG and CL treatments, ^{14}C was first detected in the leachate at approximately 1.4 pore volumes and increased to 58% for the TG-metribuzin and 43% for the CL formulation by the end of the experiment (Figure 4). For the CR-Oil formulation ^{14}C appeared in the leachate at 1.8 pore volumes and for the CR-N formulation at 2.3 pore volumes. The total amount leached was 9.4% for the CR-Oil formulation and 48% for the CR-N formulation.

Table 2. Distribution of ^{14}C from TG, CL, CR-N, and CR-Oil Formulations of Metribuzin in Four Soil Profiles As Estimated by Soil Methanol Extractions[a]

		Formulation[b] (%)			
soil	depth (cm)	TG	CL	CR-N	CR-Oil
Evesboro	0−5	1.95b	1.24c	2.18b	19.54a
	5−10	0.87bc	0.72c	1.32a	1.10b
	10−15	0.82bc	0.66c	1.13b	1.35a
	15−20	1.16a	0.82a	0.96a	1.10a
	20−25	1.26a	1.05a	1.10a	1.26a
Ochlocknee	0−5	3.23b	1.71c	4.86b	26.58a
	5−10	2.15a	1.10b	2.36a	2.63a
	10−15	1.88a	1.11a	1.88a	1.58a
	15−20	1.29a	0.95a	1.53a	1.26a
	20−25	1.80a	1.14a	1.90a	1.44a
Conover	0−5	1.87bc	1.34c	3.59ab	18.34a
	5−10	1.28b	1.02b	3.28a	1.19b
	10−15	1.43b	1.02d	2.97a	1.17c
	15−20	1.65ab	1.23b	3.98a	1.26b
	20−25	2.17b	2.19b	5.30a	1.19c
Commerce	0−5	2.54b	1.49d	1.91c	13.01a
	5−10	1.46ab	0.83c	1.25b	2.22a
	10−15	1.55b	1.72ab	1.32c	2.44a
	15−20	3.08a	3.31a	2.72a	2.09a
	20−25	5.96a	6.37a	5.12ab	2.19b

[a] Means within a row followed by the same letter are not significantly different at $P = 0.05$. [b] TG, technical grade; CL, Sencor (4L); CR-N, 1% alginate, 0.5% Tween 20, 10% kaolin; CR-Oil, 1% alginate, 0.5% Tween 20, 10% kaolin, 4% linseed oil.

Several interesting trends appear in the herbicide leaching data. First, only the CR-Oil formulation resulted in significant reductions in leaching of metribuzin in all of the soils investigated. The CR-N formulation only reduced leaching in the Evesboro and Conover soils, compared to TG and CL treatments. In the Ochlocknee soil, the CR-N formulation leached the same amount as the CL treatment and in the Commerce soil the CR-N formulation was leached to a greater extent than the CL formulation. These data are supported by the literature reports. Pepperman and Kuan (1991) found that alginate−kaolin formulations alone resulted in only moderate control of release rates. However, addition of linseed oil significantly reduced the water release rates of metribuzin from their alginate−kaolin formulations. The leaching trends for the CR-Oil formulation are similar to other reported results. Gish et al. (1991) found that starch encapsulation reduced leaching of atrazine compared to technical grade atrazine in soil columns. After 16.1 pore volumes, 35, 10, 3, and <1% of the available atrazine was leached from the technical grade, borate, pearl, and waxy starch formulations, respectively. In a related study, Boydston (1992) also reported significant decreases in leaching from starch encapsulated norflurazon and starch encapsulated simazine formulations. Norflurazon and simazine applied as commercial dry flowable or water dispersible granules leached to a depth of 15 cm in loamy sand soil columns, compared to 2.5 cm for starch granule formulations.

Herbicide Distribution. The distribution of herbicides in the soil columns at the termination of the leaching procedure is presented in Table 2. Total recoveries (leached + extracted) of [^{14}C]metribuzin from the soil was variable, ranging from 96% for the Evesboro CL treatment to 31% for the Commerce CR-Oil treatment. The low recoveries for the CR formulations are to be expected, because the [^{14}C]metribuzin must be extracted not only from the soil but also from the alginate beads. The very properties of the formulations that allow for controlled release, also decrease the extraction efficiency. Despite the variation in recoveries, distinct, significant differences were still noted in the absolute quantity of MeOH extractable [^{14}C]metribuzin from the different formulations. Mass balance calculations were performed in an attempt to account for unextracted [^{14}C]metribuzin. For this procedure, the total recoverable herbicide for a given soil was taken to be the amount recovered (leached + extracted) for the TG-metribuzin treatment. The difference between this amount and the amount recovered from the CR formulations was assumed to be retained in the CR formulations.

In the Evesboro soil, the [^{14}C]metribuzin remaining in the columns, as determined MeOH extraction, from the TG, CL, and CR-N formulations was uniformly distributed with depth throughout the soil profile, approximately 6% remaining in the profile for the TG, 4% for the CL formulation, and 7% for the CR-N formulation (Table 2). The CR-Oil formulation retained a significantly greater percentage of [^{14}C]metribuzin in the surface (0−5 cm) as compared to the TG, CL, and CR-N formulations (Table 2). The remainder of the [^{14}C]metribuzin from the CR-Oil formulation (5%) was also uniformly distributed with depth. Mass balance calculations indicate that the surface retention for the CR formulations was 38% for the CRF-N and 77% for the CR-Oil formulation.

In the Ochlocknee soil, the distribution of ^{14}C from the TG- and CL-metribuzin treatments was similar to the Evesboro soil. There was a trend, at all depths, indicating that the TG resulted in a slightly higher retention of [^{14}C]metribuzin, as compared to the CL formulation. However, this trend was only significant in the 0−5- and 5−10-cm depths. Approximately 10% of the [^{14}C]metribuzin from the TG and 6% from the CL treatments remained in the profile at the end of the experiment as determined by MeOH extraction (Table 2). The distribution of ^{14}C from the CR-N formulation was not significantly different from the TG. The CR-N formulation did result in a significantly greater retention in the 0−5- and 5−10-cm depths, as compared to the CL treatment. The CR-Oil formulation retained a significantly greater amount of [^{14}C]metribuzin in the soil surface (0−5 cm) as compared to the TG, CL, and formulation (Table 2). The remaining [^{14}C]metribuzin from the CR-Oil formulation (6%) was uniformly distributed with depth and was not significantly different from the other treatments. Mass balance calculations yield surface concentrations of 12 and 53% for the CRF-N and CRF-Oil formulations, respectively.

The TG and CL treatments had a similar distribution in the Conover soil with the exception that a slight increase in ^{14}C was noted in the 15−20- and 20−25-cm depths (Table 2). A significantly greater amount of [^{14}C]-metribuzin was retained in the soil surface (0−5-cm) with the CR-Oil formulation as compared to the TG and CL formulations (Table 2). There was not a significant difference between the two CR formulations, although a trend indicating greater retention by the CR-Oil formulation in the surface was noted. When compared to the CL formulation, the CR-N formulation resulted in significantly higher percentages of [^{14}C]metribuzin at all depths. Significantly greater percentages were found in three of five depths when compared to the TG (Table 2). The [^{14}C]metribuzin remaining in the soil profile from the TG, CL, and CR-N treatments tended to increase with depth, indicating that the columns were not at equilibrium and further leaching could have occurred. A total of 23% of the [^{14}C]metribuzin remained in the soil profile with the CR-Oil formulation, compared to 19%, 8%, and 7%, for the CR-N, TG, and CL formulations, respectively. Mass balance calculations give a surface concentration of 18 and 60% for the CRF-N and CRF-Oil formulations.

The distribution pattern exhibited by the Commerce soil was also different from those of the coarse-textured Evesboro and Ochlocknee soils. The Commerce soil would be expected to have the lowest leaching potential of the four soils investigated. This is most clearly indicated by the increase in retention noted in the 15−20- and 20−25-cm depths (Table 2). A significantly greater amount of MeOH extractable [^{14}C]metribuzin was obtained in the soil surface (0−5-cm) from the CR-Oil formulation as compared to the TG, CL, and CRF-N formulations (Table 2). The amount of [^{14}C]metribuzin remaining in the soil profile from the CR-Oil formulation was relatively constant with depth, while the [^{14}C]-metribuzin from the other formulations increased with depth. At the 20−25-cm depth the TG and CL treatments resulted in significantly greater amounts of [^{14}C]-metribuzin, as compared to the CR-Oil formulation (Table 2). Thus, the primary difference between the TG, CL, and CR-Oil formulations in this soil is increased retention in the soil surface. Mass balance calculations yield surface concentrations of 14 and 54% for the CRF-N and CRF-Oil formulations. These combined data indicate that there is still an advantage to CR formulations in soils that are at less risk to groundwater pollution.

Several researchers have demonstrated increased surface concentrations of herbicide with CR formulations (Gish et al., 1991; Riggle and Penner, 1988). Fleming et al. (1992b) reported that 99% of the applied starch encapsulated atrazine was retained in the top 5 cm of soil compared to 18 and 13% for a dry flowable atrazine formulation when 0.44 and 0.88 pore volumes of water were applied over 2 and 4 h, respectively. When the leaching regime was extended to 12 days, 81% of the starch-encapsulated atrazine was retained in the top 5 cm, compared to only 5% of the dry flowable. Boydston (1992) demonstrated that all of the applied norflurazon and simazine was retained in the soil surface (0−2.5 cm) with CR starch granules, in soil column experiments.

The CR-Oil formulation increased the concentration of [^{14}C]metribuzin in the soil surface, as compared to TG and CL formulations. The CR-Oil formulation also resulted in a decreased leaching potential for [^{14}C]-metribuzin in all soils investigated, including two soils of high leaching potential. These combined effects would ensure that the herbicide will be less of a threat to groundwater supplies since more would be retained at the surface until it is degraded.

The sources of the observed controlled release effects have been discussed by Pepperman and Kuan (1993). The authors have attributed the controlled release of metribuzin from alginate formulations to both physical and chemical factors. Light micrographs of the CR-Oil formulations have shown a polymeric film on the surface of the bead. This would act as an additional diffusional barrier for the herbicide. Release of metribuzin from the CR-N formulations is also controlled by diffusion, however without the linseed oil polymeric film the diffusion occurs more rapidly. Also it is evident that a partitioning of the metribuzin occurs between the linseed oil present in the CR-Oil formulation and the water surrounding the bead. This is supported by water release experiments in which the established equilibrium has been disturbed. In this case, additional metribuzin has been shown to be released, until a new equilibrium point is established.

Increasing the surface concentration of a herbicide is important from an efficacy standpoint. It is also important, however, that the herbicide be available for weed control and not in a bound form. Evidence from water release studies (Pepperman and Kuan, 1993) and the breakthrough data from this paper indicate that the metribuzin present in the CR-Oil formulation will be gradually released. Experiments are currently underway to determine if sufficient metribuzin will be available for adequate weed control under field conditions.

LITERATURE CITED

Baur, J. R. Release characteristics of starch xanthide herbicide formulations. *J. Environ. Qual.* 1980, *9*, 379–382.

Bouchard, D. C.; Lavy, T. L.; Marx, D. B. Fate of metribuzin, metolachlor and flumeturon in soil. *Weed Sci.* **1982**, *30*, 629–632.

Boydston, R. A. Controlled release starch granule formulations reduce herbicide leaching in soil columns. *Weed Technol.* **1992**, *6*, 317–321.

Connick, W. J., Jr. Controlled release of the herbicides 2,4-D and dichlobenil from alginate gels. *J. Appl. Polym. Sci.* **1982**, *27*, 3341–3348.

Connick, W. J., Jr.; Bradow, J. M.; Wells, W.; Steward, K. K.; Van, T. K. Preparation and evaluation of controlled-release formulations of 2,6-dichlorobenzonitrile. *J. Agric. Food Chem.* **1984**, *32*, 1199–1205.

Dailey, O. D. Preparation and Characterization of Cyclodextrin complexes of selected herbicides. In *Biotechnology of amylodextrin oligosaccharides*; Friedman, R. B., Ed.; American Chemical Society: Washington, DC, 1991.

Day, P. R. Particle fractionation and particle size analysis. In *Methods of Soil Analysis. Agronomy No. 9, Part 1*; American Society of Agronomy: Madison, WI, 1965; pp 545–567.

Fleming, G.; Simmons, F. W.; Wax, L. M.; Wing, R. E.; Carr, M. E. Atrazine movement in soil columns as influenced by starch-encapsulation and acrylic polymer additives. *Weed Sci.* **1992a**, *40*, 465–470.

Fleming, G.; Wax, L. M.; Simmons, F. W.; Felsot, A. S. Movement of alachlor and metribuzin from controlled release formulations in a sandy soil. *Weed Sci.* **1992b**, *40*, 606–613.

Gish, T. J.; Schoppet, M. J.; Helling, C. S.; Shirmohammadi, A.; Schreiber, M. M.; Wing, R. E. Transport comparison of technical grade and starch-encapsulated atrazine. *Trans. ASAE* **1991**, *34*, 1738–1744.

Harper, S. S. Sorption of metribuzin in surface and subsurface soils of the Mississippi Delta Region. *Weed Sci.* **1988**, *36*, 84–89.

Ladlie, J. S.; Meggit, W. F.; Penner, D. Effect of pH on metribuzin activity in the soil. *Weed Sci.* **1976**, *24*, 505–507.

Lewis, D. H.; Cowsar, D. R. Principles of controlled release pesticides. In *Controlled release pesticides*; Scher, H. B., Ed.; American Chemical Society: Washington, DC, 1977; pp 1–16.

Nelson, D. W.; Sommers, L. E. Total carbon, organic carbon and organic matter. In *Methods of Soil Analysis. Agronomy No. 9, Part 2*; American Society of Agronomy: Madison, WI, 1982; pp 539–577.

Parry, K. P. Herbicide use and invention. In *Herbicides and plant metabolism*; Dodge, A. D., Ed.; Cambridge University Press: Cambridge, U.K., 1989.

Pepperman, A. B.; Kuan, J-C. W. Slow release formulations of metribuzin based on alginate-kaolin-linseed oil. *J. Controlled Release* **1993**, *26*, 21–30.

Pepperman, A. B.; Kuan, J-C. W.; McCombs, C. Alginate controlled release formulations of metribuzin. *J. Controlled Release* **1991**, *17*, 105–112.

Riggle, B. D.; Penner, D. Evaluation of pine kraft lignins for controlled release of alachlor and metribuzin. *Weed Sci.* **1987**, *35*, 243–246.

Riggle, B. D.; Penner, D. Controlled release of three herbicides with the kraft lignin PC940C. *Weed Sci.* **1988**, *36*, 131–136.

Riggle, B. D.; Penner, D. Kraft lignin adsorption of metribuzin as a controlled-release function evaluation. *J. Agric. Food Chem.* **1992**, *40*, 1710–1712.

Schreiber, M. M. Overview of controlled release herbicides. *Proc. Int. Symp. Controlled Release Bioact. Mater.* **1989**, *16*, 30.

Shasha, B. S.; Doane, W. M.; Russell, C. R. Starch-encapsulated pesticides for slow release. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 417–420.

Soil Survey Staff. *Keys to Soil Taxonomy*; SMSS Technical Monograph 6; Cornell University: Ithaca, NY, 1987.

STORET. STORET water quality file, Office of Water, U.S. EPA (data file search conducted in May 1988).

Street, J. E.; Wehtje, G.; Walker, R. H.; Patterson, M. G. Effects of Adjuvants on behavior of metribuzin in soil and soybean injury. *Weed Sci.* **1987**, *35*, 422–426.

Szejtli, J. Cyclodextrins in pesticides. *Starch/Staerke* **1985**, *37*, 382–386.

Taylor, A. W.; Glotfelty, D. E. Evaporation from soils and crops. In *Environmental chemistry of herbicides*; Grover, R., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. 1, pp 90–129.

Trimnell, D.; Shasha, B. S. Controlled release formulations of atrazine in starch for potential reduction of groundwater pollution. *J. Controlled Release* **1990**, *12*, 251–256.

U.S. EPA. *Drinking water health advisory: Pesticides*; Lewis Publishers: Chelsea, MI, 1989.

U.S. EPA. *National pesticide survey: Phase I report*; Office of Water, Office of Pesticides and Toxic Substances; EPA 570/9-90-015; U.S. Govt. Printing Office: Washington, DC, 1990.

Wing, R. E. Cornstarch encapsulated herbicides show potential to reduce groundwater contamination. *Proc. Int. Symp. Controlled Release Bioact. Mater.* **1989**, *16*, 430–431.

Wing, R. E.; Maiti, S.; Doane, W. M. Effectiveness of jet-cooked pearl starch as a controlled release matrix. *Starch/Staerke* **1987**, *39*, 422–425.

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