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Tillage and Controlled Drainage-subirrigated Management Effects on Soil Persistence of Atrazine, Metolachlor, and Metribuzin in Corn

By:
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MANAGEMENT PERSPECTIVE

The occurrence of herbicides in surface waters necessitates the development of management practices to reduce herbicides loss through tile drainage and surface runoff. Many factors, such as soil carbon, soil texture, and pH, affect persistence of herbicides in soil. These factors control the availability of the herbicides to microbial or chemical alteration and their potential to appear in surface and ground water.

This paper investigates herbicide persistence under two drainage regimes with four tillage-intercrop treatments including moldboard plow, moldboard plow with rye grass intercrop, soil saver, and soil saver with rye grass intercrop. The two water table management treatments were free drainage and controlled drainage-subirrigation. The input of herbicides was 50% less by strip application compared to an entire area application.

Results suggested that tillage combined with intercrop treatment had little effect on soil residues of the herbicide at 0 to 10 cm depth. Most consistent effects in herbicide dissipation occurred with controlled drainage treatment even in a dry year.

Make recommendations and on farm demonstration to farmers on the potential for drainage control to enhance herbicide dissipation in soil, which could improve water quality by reducing transport to surface waters.

Interactions entre les particules touchant la stabilité de flocs de boues

B. Q. Liao, D. G. Allen, G. G. Leppard, I. Droppo et S. N. Liss

Sommaire à l'intention de la direction

Public visé : Ce manuscrit présente les résultats obtenus grâce à une subvention de recherche stratégique du Conseil de recherches en sciences naturelles et en génie du Canada. Cette étude a également bénéficié du soutien direct d'Environnement Canada, ainsi que d'un programme-cadre à long terme d'EC, du CRSNG et de l'industrie, qui lui a permis d'obtenir de l'aide en R et D de dix industries canadiennes et de trois universités de l'Ontario. Les objectifs à long terme de ces recherches, qui s'insèrent dans les secteurs d'activité Nature et Un environnement sain, sont l'amélioration et la réduction des coûts des traitements des eaux usées.

Sommaire des résultats : Ces recherches ont permis de mettre au point un modèle de floc de boues qui établit des liens entre 1) la nature chimique et l'entassement de substances polymériques extracellulaires (SPE) colloïdales dans une matrice de floc, 2) la stabilité d'une population de floc donnée et 3) des interactions physico-chimiques spécifiques entre les sous-éléments du floc et les agents utilisés pour manipuler leurs milieux d'eau libre. On propose une matrice de floc constituée de deux zones physiquement distinctes, définies par la disposition tridimensionnelle et la chimie des SPE colloïdales. Ces zones distinctes subissent des changements selon les temps de rétention des solides des flocs de boue (TRS); c'est pour cette raison que les flocs à TSR différents sont touchés de façon différente par les divers agents utilisés pour la manipulation des flocs artificiels. Ces résultats semblent indiquer qu'on peut obtenir, dans les réservoirs de traitement, une population des flocs à propriétés de décantation optimales par un simple réglage du TRS.

État du projet : Il s'agit du 9[e] article de publication qui rend compte de travaux réalisés grâce à six années consécutives de soutien du CRSNG, et d'autres sont en cours de rédaction. Pour donner suite à ces recherches, il faudra 1) transférer notre expertise en manipulation des flocs de boues des petites installations de laboratoire aux systèmes de traitement de l'eau en vraie grandeur et 2) créer des modèles de flocs améliorés permettant la production de flocs spécialement conçus pour diverses industries environnementales.

ABSTRACT

The occurrence of herbicides in surface waters necessitates the development of management practices to reduce herbicide loss through tile drainage and surface runoff. Four tillage-intercrop systems: moldboard plow (MB), moldboard plow with rye grass (*Lolium multiflorum* Lam.) intercrop (MB+IC); soil saver (SS), and soil saver with rye grass intercrop (SS+IC), and two water table management treatments: controlled drainage-subirrigation (CDS) and no control drainage (D) were investigated for their effect on herbicide persistence. Atrazine [2-chloro-4-ethylamino-6-isopropylamnino-s-triazine] (1.1 kg ha^{-1}), metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(*4H*)-one] (0.5 kg ha^{-1}), and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methlylethyl) acetamide (1.68 kg ha^{-1}) were strip applied in a corn (*Zea mays* L.) management system to reduce herbicide inputs 50%. Tillage-intercrop system had little consistent effect on soil residues of the herbicides at 0- to 10-cm depth. Control drainage-subirrigation decreased half-life of atrazine and metolachlor in one of two years. Half-life for atrazine ranged from 34 to 56 d, metribuzin 24 to 35 d, and metolachlor 40 to 79 d, with longer half-life in dry years. Des-ethyl atrazine [2-chloro-4-amino-6-isopropylamino-*s*-triazine], the major metabolite of atrazine, persisted along with atrazine and metolachlor to the next planting season. Less than 10% of the original herbicide application was recovered the year following application. It was concluded that environmental factors such as rain affect herbicide residues more than cultivation practices.

Résumé

Lors d'une expérience de traitement par lots, on a étudié en laboratoire les interactions entre les particules qui influent sur la stabilité de flocs de boues, prélevés dans des cuves de traitement séquentiel par lots pour divers temps de rétention des solides (TRS), dans diverses conditions de pH, de force ionique, de valence des cations et de concentrations d'urée et d'EDTA dans les solutions de suspension. On a observé l'ultrastructure des surfaces des flocs de boues par microscopie électronique à transmission (MET). Les changements dans les constantes de dissociation des flocs de boues dans différentes conditions ont indiqué que des interactions ioniques et des liaisons hydrogène maintenaient la cohésion des flocs et compensaient l'influence négative des interactions électrostatiques sur la stabilité des flocs de boues. Les interactions ioniques et les liaisons hydrogène étaient les deux forces dominantes qui maintenaient la stabilité des flocs de boues à faibles TRS. Par contre, pour celles à plus grands TRS, d'autres mécanismes, comme les interactions dues à l'enchevêtrement physique et aux forces de van der Waals et/ou aux forces hydrophobes, jouaient un rôle plus important dans la régulation de la stabilité des flocs. Aux plus grands TRS (16 et 20 jours), les flocs des boues avaient une plus grande stabilité physique qu'aux plus petits TRS (4 et 9 jours). On propose un modèle théorique de structure de floc, basé sur des interactions entre les particules, pour décrire la stabilité des flocs de boues. Selon la matrice proposée, ceux-ci seraient constitués de deux zones physiquement distinctes, définies par la disposition des substances polymériques extracellulaires (SPE). Ces deux zones devraient être touchées de façon différente par les agents utilisés pour manipuler les forces interparticulaires. Ainsi, l'hétérogénéité de l'entassement et le type de SPE reflètent la stabilité d'un floc.

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Tillage and Controlled Drainage–Subirrigated Management Effects on Soil Persistence of Atrazine, Metolachlor, and Metribuzin in Corn

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ABSTRACT

The occurrence of herbicides in surface waters necessitates the development of management practices to reduce herbicide loss through tile drainage and surface runoff. Four tillage–intercrop systems: moldboard plow (MB), moldboard plow with rye grass (*Lolium multiflorum* Lam.) intercrop (MB+IC), soil saver (SS), and soil saver with rye grass intercrop (SS+IC), and two water table management treatments: controlled drainage–subirrigation (CDS) and no control drainage (D) were investigated for their effect on herbicide persistence. Atrazine [2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine] (1.1 kg ha^{-1}), metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(*4H*)-one] (0.5 kg ha^{-1}), and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide] (1.68 kg ha^{-1}) were strip applied in a corn (*Zea mays* L.) management system to reduce herbicide inputs 50%. Tillage–intercrop system had little consistent effect on soil residues of the herbicides at 0- to 10-cm depth. Control drainage–subirrigation decreased half-life of atrazine and metolachlor in one of two years. Half-life for atrazine ranged from 34 to 56 d, metribuzin 24 to 35 d, and metolachlor 40 to 79 d, with longer half-life in dry years. Des-ethyl atrazine [2-chloro-4-amino-6-isopropylamino-*s*-triazine], the major metabolite of atrazine, persisted along with atrazine and metolachlor to the next planting season. Less than 10% of the original herbicide application was recovered the year following application. It was concluded that environmental factors such as rain affect herbicide residues more than cultural practices.

Many factors, such as soil carbon, soil texture, and pH, affect persistence of herbicides in soil. These factors control the availability of the herbicides to microbial or chemical alteration and their potential to appear in surface and ground water. Other factors such as soil water content and temperature relate to the kinetics of persistence (Walker, 1991). For example, increasing the soil temperature from 5 to 35°C decreased the half-life (the time for herbicide concentration to be reduced 50%) of atrazine from 210 d to 28 d and metolachlor from 257 to 43 d at 25% field capacity. Increasing water content from 25% of field capacity to field capacity reduced atrazine half-life by 27 d and metolachlor by 43 d at 25°C. Cultural practices such as tillage may or may not have an effect on herbicide persistence depending upon how they affect soil temperature and water content. Gaynor et al. (1987) found greater persistence of atrazine in ridge tillage tops than in valleys in some years because of the reduced water content of the ridge tops. Extended studies on the same clay loam soil verified this effect with tillage for atrazine and metolachlor (Gaynor et al., 1998). Ghadiri et al. (1984) found no difference in half-life for atrazine between conventional and no-till treatments on an acidic soil. Bauman and Ross (1983), on the other hand, found higher atrazine residue in surface soil from no-till than conventional and chisel tillage after five years of application.

The mobility of an herbicide in soil depends in part upon its adsorption–desorption characteristics and solubility (Walker, 1987, 1991). No-till increases infiltration of rainfall because of greater crop residue on the surface, which reduces runoff velocity (Unger, 1990; Locke and Bryson, 1997). Higher water content in no-till may reduce soil temperatures (Stone et al., 1989) and increase persistence. The increase in herbicide persistence in no-till may predispose this cultural practice to increased probability of surface and ground water impairment. Herbicides with high water solubility and low affinity for soil leached to deeper depths in no-till than conventional tillage culture (Isensee et al., 1990; Sadeghi and Isensee, 1992). Herbicides can move rapidly through structured and unstructured soil through cracks, worm and root channels, and other macropores or through finger or funnel flow (Gish et al., 1991; Kung, 1993; Rice et al., 1991; Edwards et al., 1993).

Many agricultural soils have impaired drainage characteristics because of texture or water table conditions. Productivity is improved by installation of subsurface drains to remove excess rain during planting, crop establishment, or harvest. Herbicide residues are most vulnerable to transport during planting (Gaynor et al., 1992, 1995a; Olson et al., 1998). Controlled drainage has been adopted to reduce tile drainage to conserve water for crop growth early in the season or during the winter months. Controlled drainage coupled with conservation tillage and subirrigation effectively reduces nitrate losses and increases crop yield (Drury et al., 1996). Since herbicide persistence is directly correlated to soil water content and soil temperature (Walker, 1987, 1991) the effect of controlled drainage–subirrigation on herbicide persistence is of interest. We followed the persistence of atrazine, metolachlor, and metribuzin in soil for three years in corn culture under drained and controlled drainage–subirrigation conditions in the presence and absence of a ryegrass intercrop. Our purpose was to determine if tillage, controlled drainage, and ryegrass intercrop would alter herbicide dissipation, which may affect surface water quality. The occurrence of des-ethyl

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Abbreviations: CDS, controlled drainage–subirrigation; D, drained; MB, moldboard plow; MB+IC, moldboard plow with ryegrass intercrop; SS, soil saver; SS+IC, soil saver with ryegrass intercrop.

atrazine, the predominant metabolite of atrazine, was also followed.

MATERIALS AND METHODS

Site Description

The study incorporated two drainage regimes with four tillage–intercrop treatments, replicated twice on plots 15 m wide by 67 m long (Tan et al., 1993; Drury et al., 1996). The four tillage–intercrop treatments were: moldboard plow, moldboard plow with rye grass intercrop, soil saver, and soil saver with rye grass intercrop, and the two water management treatments were: drained only and controlled drainage–subirrigation.

The poorly drained Brookston clay loam (fine-loamy, mixed, mesic Typic Argiaquoll) represents more than 80% of the soil type in Essex County, Ontario, Canada. The Ap horizon is a dark brown clay loam, 30 cm deep with 2.5% organic matter. The B horizon had a clay texture to a depth of 1.5 m. Two 104-mm diameter tile lines at 7.5-m spacing and 0.6-m depth provided drainage for each plot. Risers fitted to the drain tile outlet controlled the water table in the subirrigated treatments (Tan et al., 1993). The risers were set to control the water level at 30 cm below ground level during the growing season. When water level dropped below 30 cm, subirrigation was initiated. Risers were removed before harvest in the fall and before planting in spring to facilitate these operations. Risers were reinstalled after harvest to control drainage at 30 cm for the winter and spring periods and no subirrigation was applied. When required, subirrigation began in June of each year and continued to September. Water table depths and depth of subirrigation have been reported previously (Drury et al., 1996). An overflow pipe removed excess rain when the water table was higher than the preset level (30 cm).

Agronomy

The preemergence herbicides atrazine, metribuzin, and metolachlor were applied as tank mixes at 1.1, 0.5, and 1.68 kg ha^{-1}, respectively. The herbicides were applied to each plot on 14 May 1992, 17 May 1993, and 13 May 1994 in a 38-cm band over the seeded row (76 cm spacing) so that 55 g atrazine, 25 g metribuzin, and 84 g metolachlor were applied to each treatment. These amounts represent a 50% reduction in the amount of herbicide applied as compared with broadcast application. A Chelsea sprayer (Turner Ltd., Blenheim, OH) was equipped with 8004 EVS Tee Jet flat fan nozzles (Sprayer Systems Co., Wheaton, IL), which delivered the herbicides in 270 L ha^{-1} water.

The MB plots were plowed to a depth of 15 cm in fall with a moldboard plow and disced in spring for seedbed preparation. The SS plots were prepared with a Glencoe soil saver implement (Model F551-A, Series 3, Glencoe, Farmhand Div, Excelsior, MN) equipped with seven-35 cm sweeps at 38 cm spacing, which disturbs the soil to a depth of 15 cm. No further spring seed bed preparation was performed before planting. A four-row Kinze planter (Kinze Manufacturing Co., Williamsburg, IA) seeded corn (Pioneer 3573) at 65 000 seeds ha^{-1} in 75-cm wide rows. Fertilizer (8–32–16, N–P–K) was band applied beside the seed at a rate of 132 kg ha^{-1}. A brush applicator applied urea (46–0–0, N–P–K) at the six-leaf stage at a rate based on the average nitrate soil test (Drury et al., 1996). The annual ryegrass was seeded as an intercrop in the interrow with a Brillion seeder (Brillion Iron Works, Brillion, WI).

Table 1. Theoretical and measured herbicide application rates (±SE). Rate calculated from residue in petri plates (n = 96 per plot).

	Herbicide		
	Atrazine	Metribuzin	Metolachlor
	g plot^{-1} (kg ha^{-1})		
Theoretical	55 (1.1)	25 (0.50)	84 (1.68)
1992	42 ± 5 (0.8 ± 0.1)	17 ± 2 (0.34 ± 0.4)	65 ± 11 (1.3 ± 0.20)
1993	72 ± 3 (1.4 ± 0.1)	35 ± 5 (0.70 ± 0.10)	85 ± 12 (1.7 ± 0.20)
1994	47 ± 8 (0.9 ± 0.2)	26 ± 4 (0.52 ± 0.08)	80 ± 14 (1.6 ± 0.30)

Herbicide Analyses

For each plot, soil residues at each sampling date (seven to nine times throughout the growing season) were determined from analysis of 21 composited cores collected from each plot with a 2.5-cm diameter probe with acetate sleeve. Since soil water content over the tiles would differ from that between the tiles because of drainage–subirrigation treatment and low hydraulic conductivity of the soil (4.7 cm d^{-1}), two-thirds of the composite samples (14 cores) were collected in the corn row over the drain tiles and one-third (seven cores) in the corn row midway between the two tiles. Samples were sectioned in the field at 0- to 10-cm, 10- to 15-cm and 15- to 20-cm increments. Although herbicide was detected in tile effluent at 60 cm, we did not measure residues below 20 cm because most of the residue is in the 0- to 20-cm depth (Gaynor et al., 1998) and soil at 20- to 30-cm over the tile in the subirrigated treatment was too wet to sample consistently. The increments from each core were composited by plot and stored at −10°C for up to 2 mo before analysis. The weight of the bulk samples was recorded, a subsample was taken for water content, and the bulk density calculated as the ratio between dry weight and combined volume of the cores. To determine herbicide concentration at time zero, six glass Petri plates were placed in each plot and the spray residue (removed with methanol) analyzed on a Varian 3400 gas chromatograph (Varian Canada, Mississauga, ON, Canada). Analytes were separated on a 15 m DB-5 capillary column (J&W Scientific, Folsom, CA), temperature programmed from 70 to 210°C. A thermionic sensitive detector operating in N mode was used to detect and quantify the herbicides. Soil samples were prepared as follows: soil (132 g wet weight) was mixed with 100 ml methanol and water (95:5 v/v) on a New Brunswick shaker (Model V, New Brunswick Scientific, New Brunswick, NJ) for 1 h. The samples were filtered through #5 Whatman paper and the residue leached with methanol. The combined filtrates were reduced to 10 ml on a Buchler evaporator (PTFE-1-6, Fisher Scientific, Nepean, ON, Canada) at 40°C, then the residue was dissolved in 100 ml distilled water. Herbicide in the water was concentrated on a preconditioned cyclohexyl extraction column (Baker Cat. No. 7212-03, Mallinckrodt Baker, Phillipsburg, NJ). After herbicide loading, the column was dried and the herbicide eluted with 1.5 mL methanol for injection into the gas chromatograph. Herbicide recovery from soil fortified with 1 and 50 μg kg^{-1} of the respective herbicides and des-ethyl atrazine was greater than 80%. All values are reported on a dry weight basis without correction for recovery.

Soil Properties

Soil pH was determined in a saturated paste in water with a glass electrode. Carbon content was determined by dry combustion in a Leco Induction Furnace (Model CR12, Leco Corp., St. Joseph, MI). Particle size determination was by

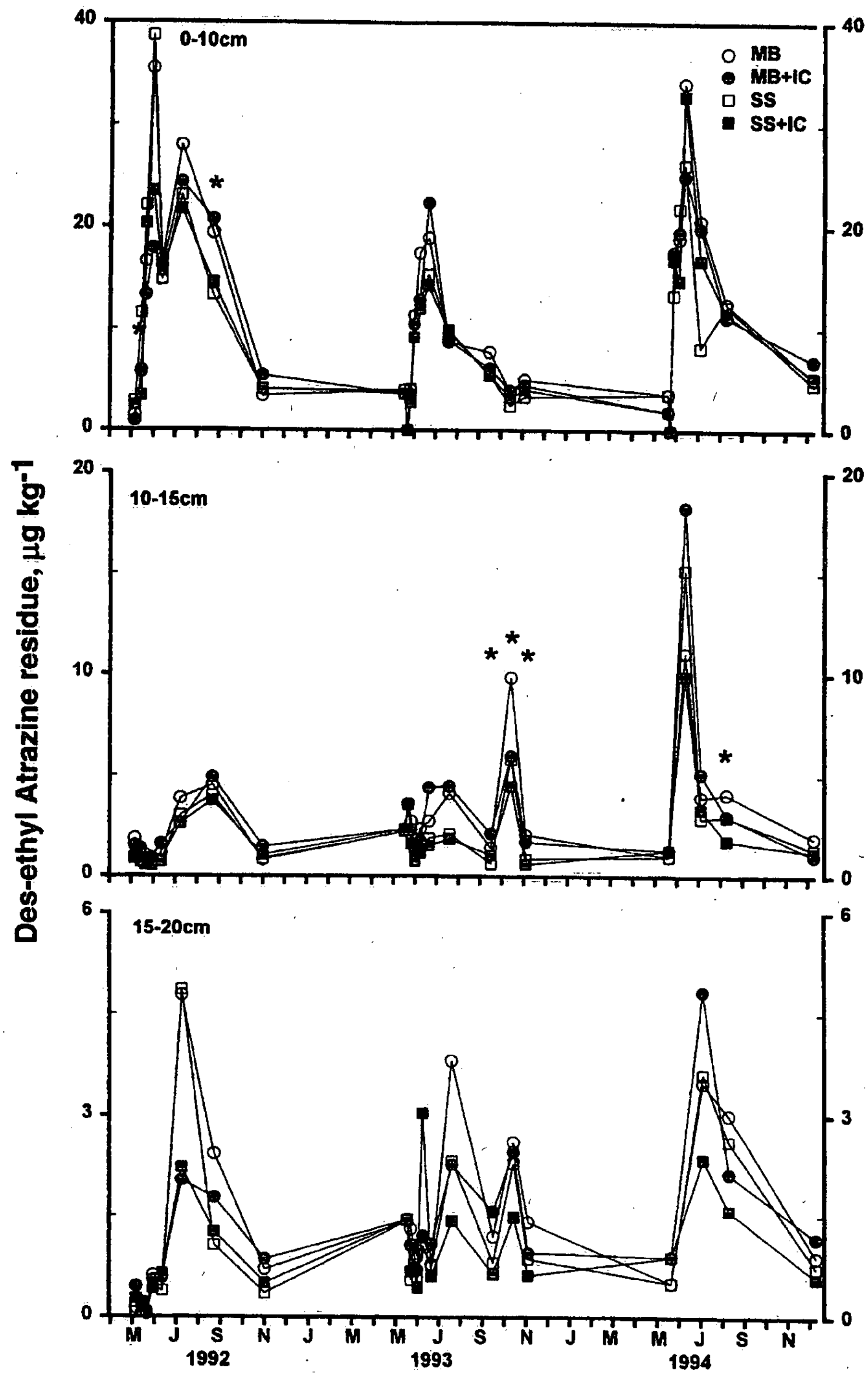

Fig. 1. Des-ethyl atrazine residues in Brookston soil as affected by tillage–intercrop treatment. Asterisk denotes significant difference ($p = 0.05$) in residue among tillage treatment at the indicated sampling date. Data are averaged by tillage–intercrop treatment ($n = 4$).

pipette method after dispersion in sodium hexametaphosphate.

Herbicide Adsorption Study

Soil (10 g) from three depths (0 to 10, 10 to 30, and 30 to 60 cm) was mixed with a 0.01 *M* $CaCl_2$ solution (100 mL) containing 0, 0.1, 1, 10, and 100 mg L^{-1} of each herbicide. The herbicides were added as their formulated materials, namely, 96 EC (emulsifiable concentrate) for metolachlor, 75 WG (wettable granules) for metribuzin, and 90 WG for atrazine, to achieve these concentrations. These depths do not correspond to our sampling depths for residues except for the 0-

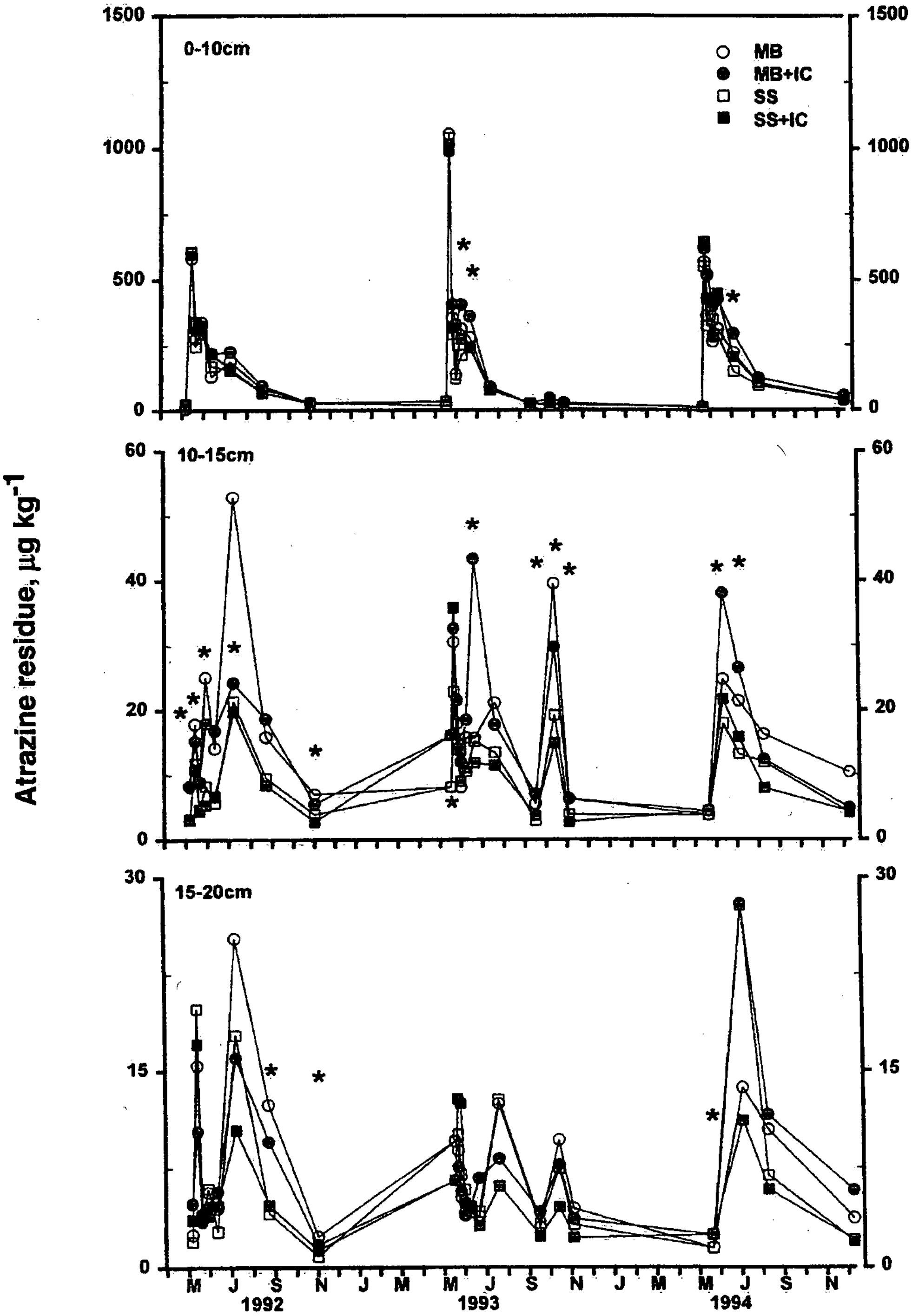

Fig. 2. Atrazine residues in Brookston soil as affected by tillage–intercrop treatment. Asterisk denotes significant difference ($p = 0.05$) in residue among tillage treatment at the indicated sampling date. Data are averaged by tillage–intercrop treatment ($n = 4$).

to 10-cm depth because we were interested in the adsorptive capacity of the Ap (0–30 cm) and B (30–60 cm) horizons to the tile drains. The samples were equilibrated in triplicate in Erlynmeyer flasks on a New Brunswick shaker at 25°C overnight. Flasks with herbicide solution but no soil were also included. It was determined that equilibrium was reached after 10 h and that no herbicide loss occurred in the absence of soil. The samples were filtered on #5 Whatman paper and the filtrate analyzed for herbicide residue by concentrating the filtrate on the preconditioned cylclohexyl columns as previously stated. The herbicide in the column eluate was analyzed by gas chromatography as above. Herbicide adsorbed

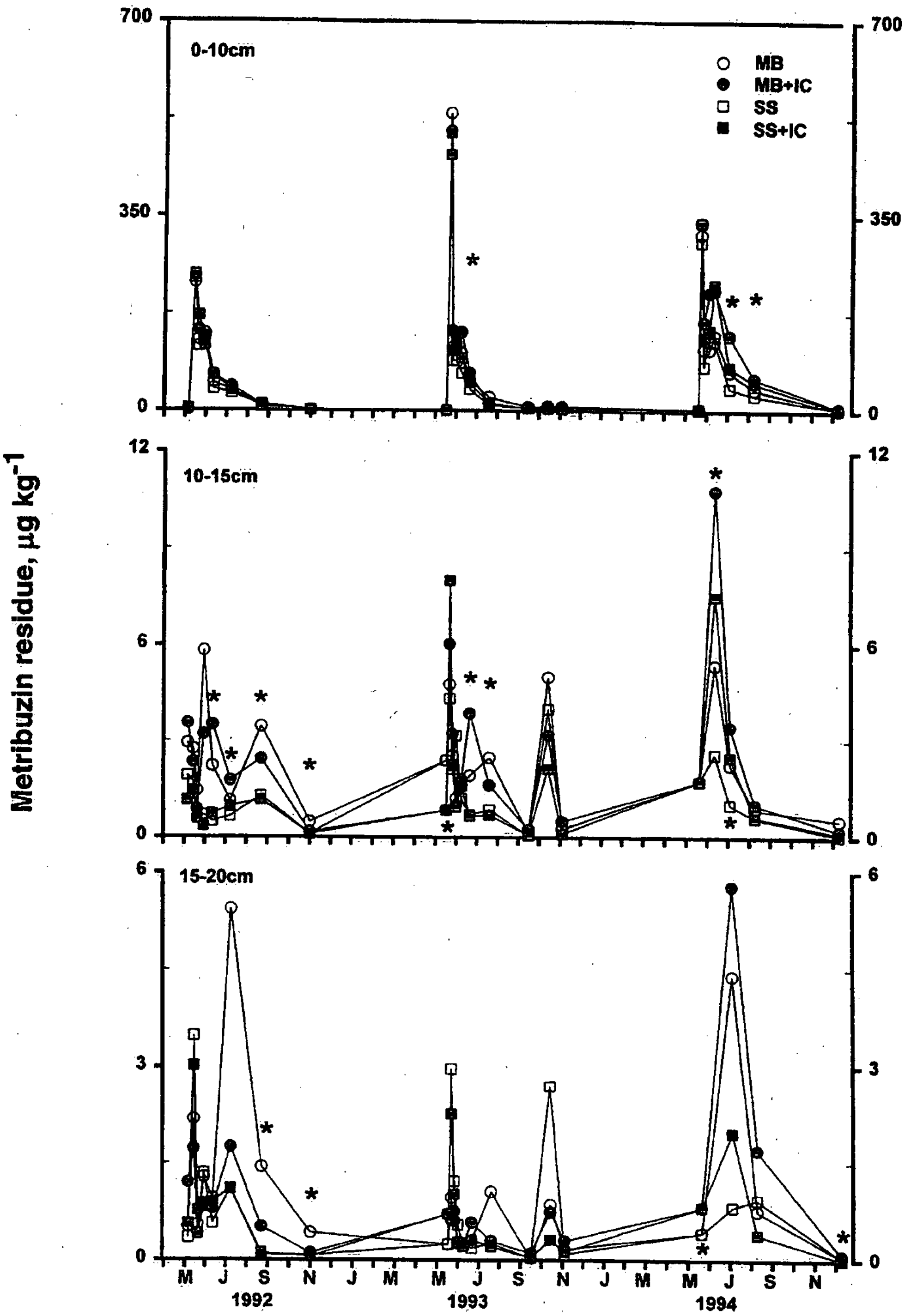

Fig. 3. Metribuzin residues in Brookston soil as affected by tillage–intercrop treatment. Asterisk denotes significant difference (p = 0.05) in residue among tillage treatment at the indicated sampling date. Data are averaged by tillage–intercrop treatment (n = 4).

was determined by difference between initial and final amount in the equilibrating solution. The linearalized form of the Freundlich equation:

$$\log x/m = n \log S + \log K_f$$

where x/m = amount adsorbed, S = equilibrium solution concentration, and K_f is the Freundlich constant derived from the intercept. The Freundlich constants K_f and n represent adsorption capacity and intensity of adsorption, respectively, of the herbicides by soil (Celis et al. 1997).

Statistics

Plots were arranged in a four by two factorial randomized complete block design. All statistical analysis was done with

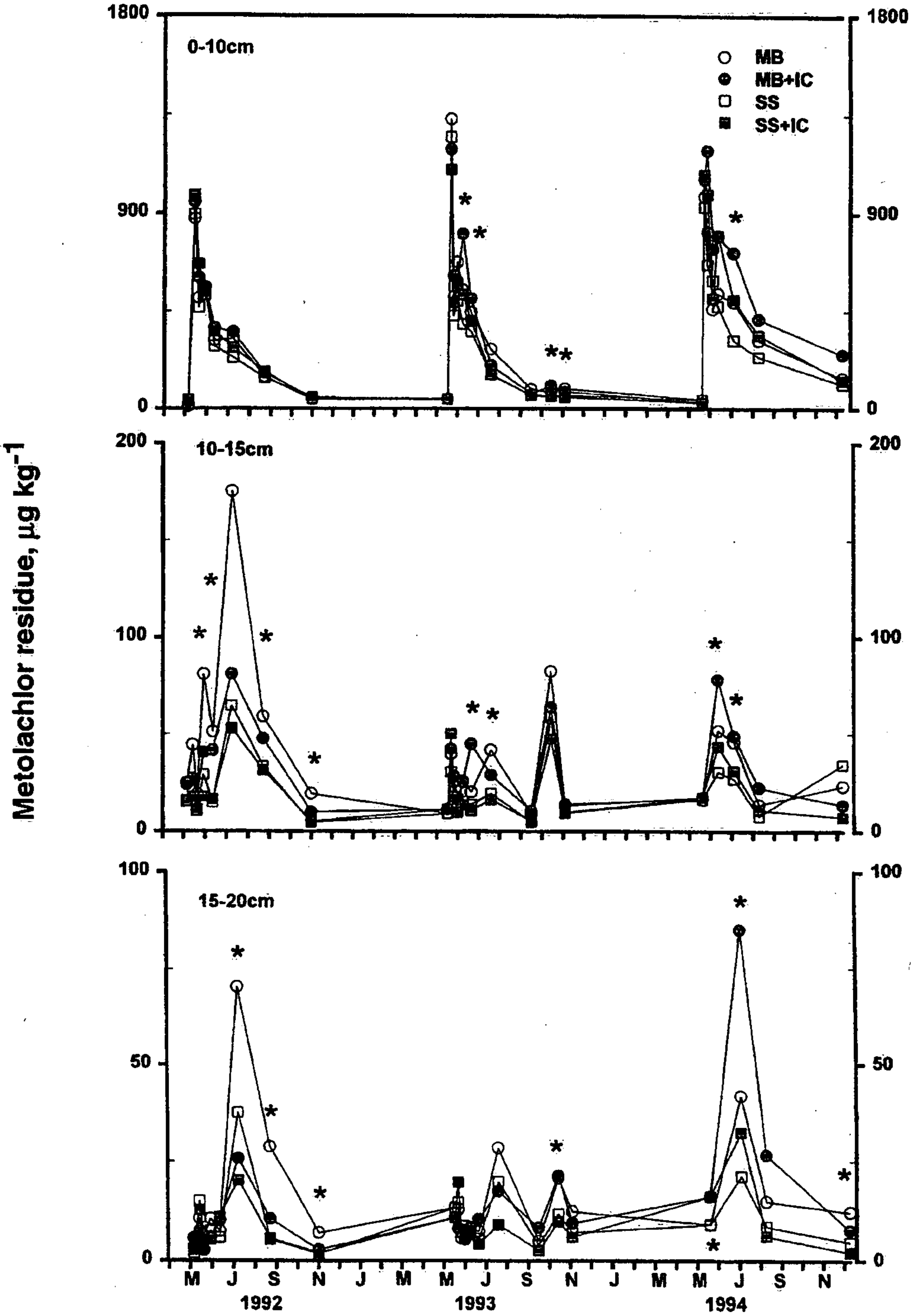

Fig. 4. Metolachlor residues in Brookston soil as affected by tillage–intercrop treatment. Asterisk denotes significant difference (p = 0.05) in residue among tillage treatment at the indicated sampling date. Data are averaged by tillage–intercrop treatment (n = 4).

SAS Version 6.12 (SAS Institute, 1989). Statistical significance is reported at the 0.05 level. No significant interactions for any of the parameters tested were found.

Herbicide residue in the 0- to 10-cm depth was fitted, using proc REG, to the first order reaction equation:

$$\log C = mt + \log C_0 \, .$$

where C_0 and C = initial soil residue and soil residue at time t and m is the rate constant for residue decline. Half-life ($t_{1/2}$), the time required for herbicide concentration in soil to be

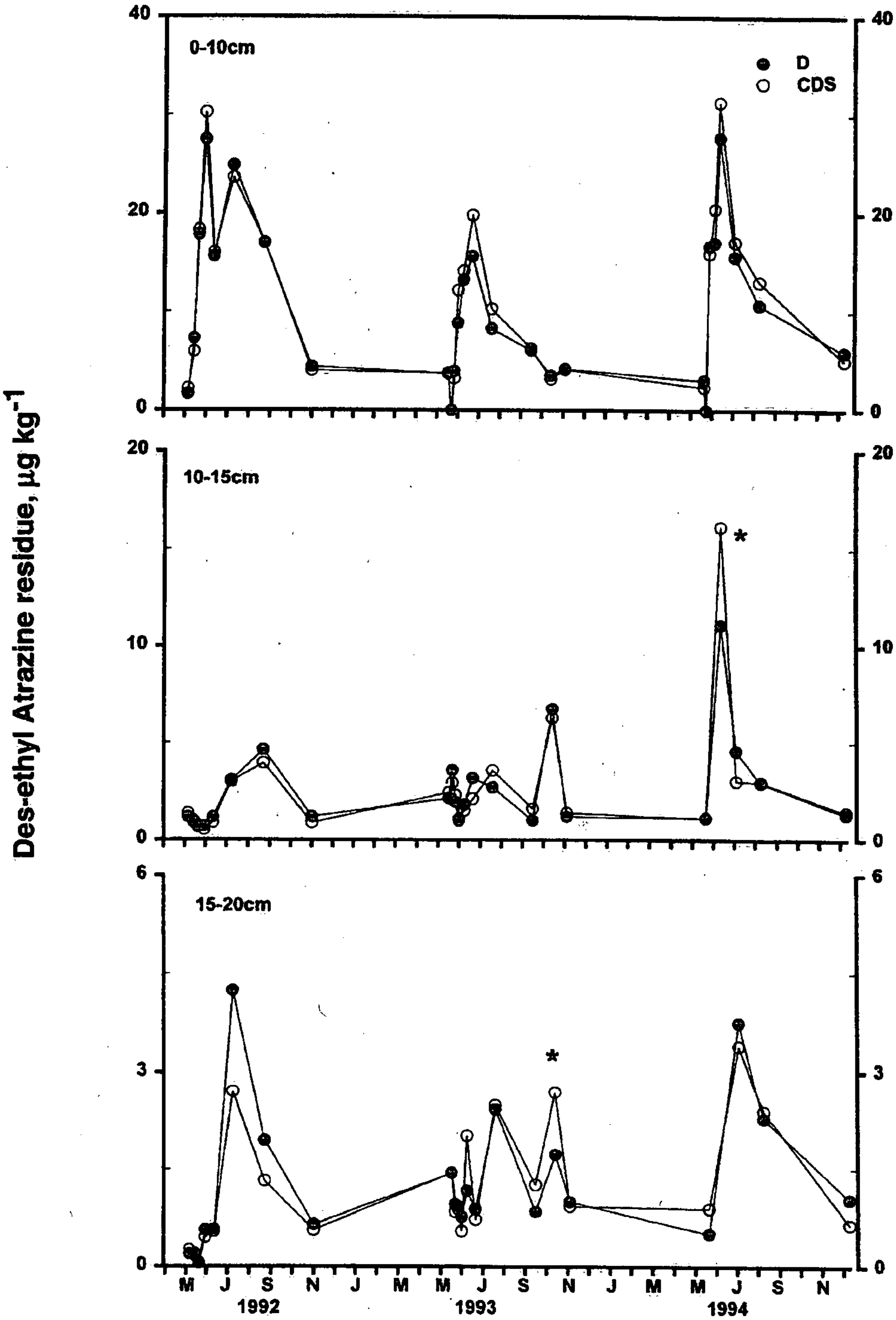

Fig. 5. Des-ethyl atrazine residues in Brookston soil as affected by drainage control. Asterisk denotes significant difference ($p = 0.05$) in residue between drainage treatments at the indicated sampling date. Data are averaged by drainage control ($n = 8$).

reduced to half its initial value, was calculated from the rate constant as:

$$t_{1/2} = 2.303 \log (0.5)/m$$

Differences among half-lives were assessed by ANOVA using proc GLM with the factorial randomized complete block design.

RESULTS AND DISCUSSION

Herbicide residue recovered from Petri plates at time of application indicated that the rate of application for metolachlor was fairly consistent in each of the three years (1.3 to 1.7 kg ha^{-1}, Table 1) but that atrazine (range 0.8 to 1.4 kg ha^{-1}) and metribuzin (range 0.3 to

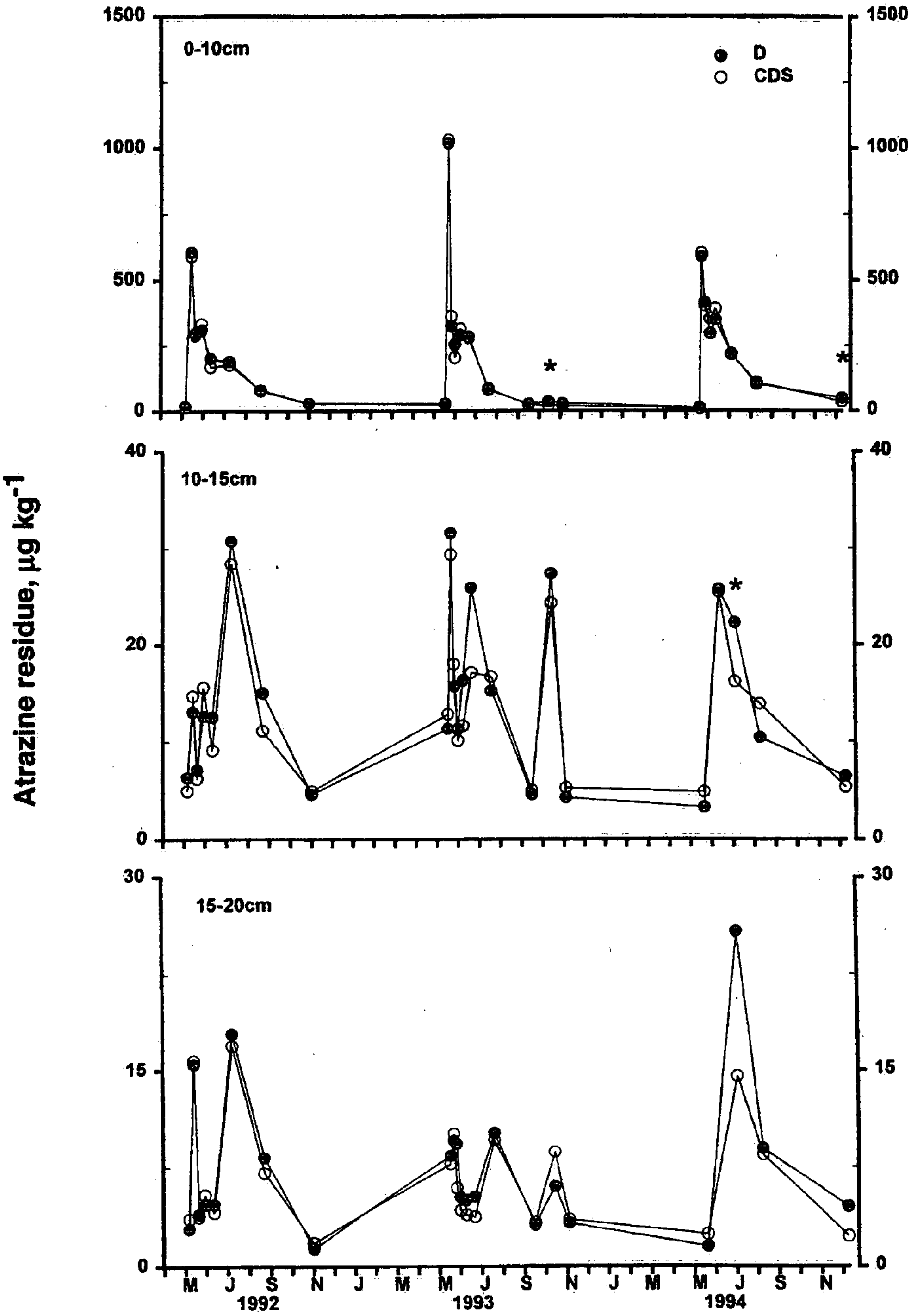

Fig. 6. Atrazine residues in Brookston soil as affected by drainage control. Asterisk denotes significant difference (p = 0.05) in residue between drainage treatments at the indicated sampling date. Data are averaged by drainage control (n = 8).

0.7 kg ha^{-1}) were more variable. These herbicides have a low vapor pressure and no significant volatile losses were expected. Whang et al. (1993) reported volatile losses for atrazine of 1 to 2% of application from no-till. Strek and Weber (1982) found 19% volatile loss of metolachlor in 3 d when applied to straw in Petri dishes under greenhouse conditions. In a field study, Prueger et al. (1999) reported 22% loss of metolachlor in 10 d when applied broadcast preemergence to corn and 6% volatilization when applied in a 0.25-m band over a 0.75-m corn row.

Herbicide residues in the 0- to 10-cm depth declined with time according to the first order rate equation (R^2 > 0.60, n = 7). Residue patterns were characterized by an initial rapid decline within 28 d after application followed by slower dissipation (Fig. 1–8). Others have re-

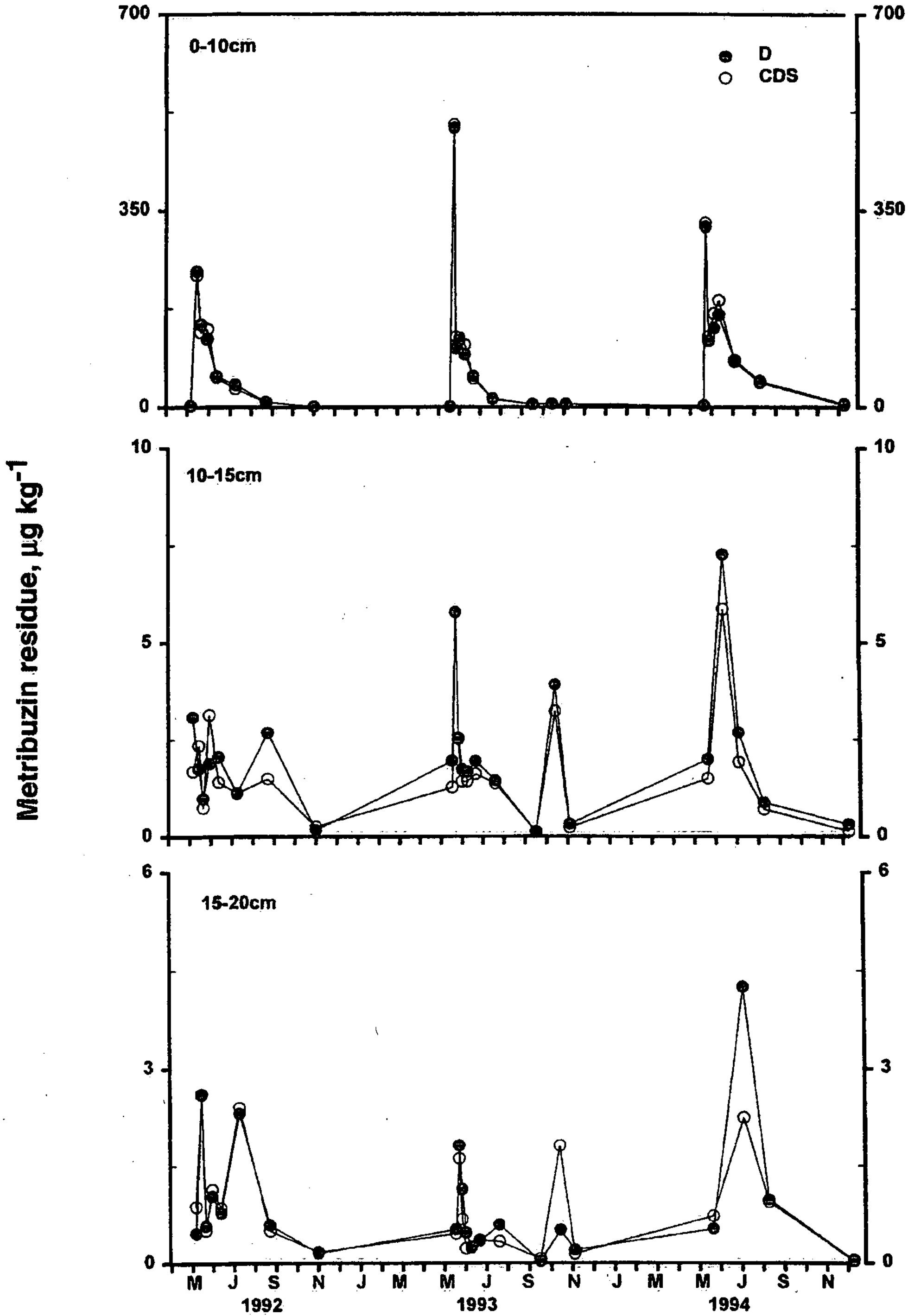

Fig. 7. Metribuzin residues in Brookston soil as affected by drainage control. Asterisk denotes significant difference ($p = 0.05$) in residue between drainage treatments at the indicated sampling date. Data are averaged by drainage control ($n = 8$).

ported a similar pattern for these herbicides (Burgard et al., 1994; Weed et al., 1995; Gaynor et al., 1998) and have described their rate of decline with either a single first order rate equation or a two-step reaction order. Analysis of variance for half-life detected no interaction between treatment and water table control (Table 2). Therefore, Fig. 1 through 4 report data averaged by tillage–intercrop treatment and Fig. 5 through 8 by water table control.

Herbicide residues in the 0- to 10-cm depth did not differ among tillage–intercrop treatments in 1992, a wet year, or with few exceptions in 1994, a dry year (Fig.

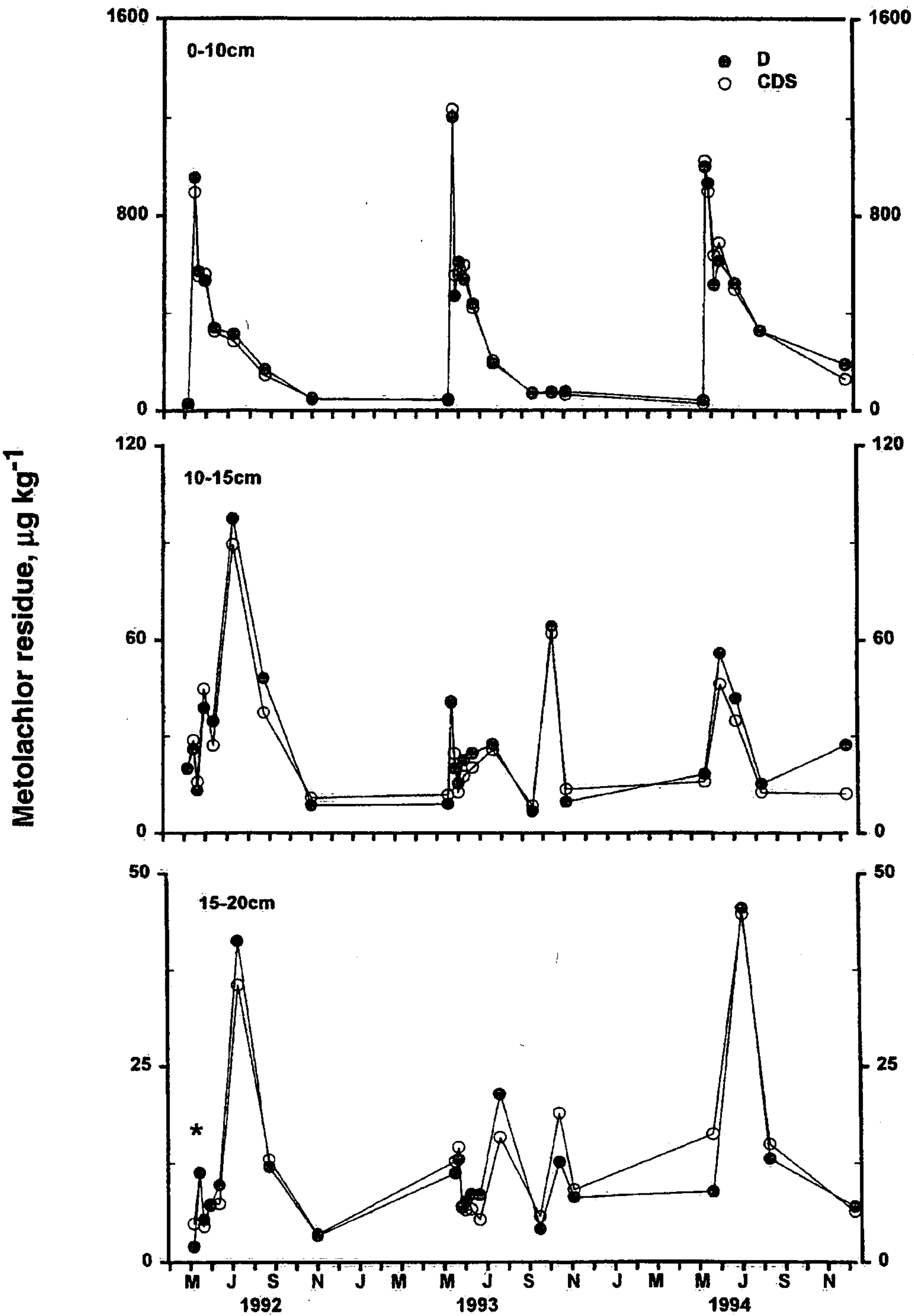

Fig. 8. Metolachlor residues in Brookston soil as affected by drainage control. Asterisk denotes significant difference (p = 0.05) in residue between drainage treatments at the indicated sampling date. Data are averaged by drainage control (n = 8).

1–4). There were some differences in residue concentrations among tillage–intercrop treatments in 1993 at some sampling dates. Residues of atrazine and metolachlor averaged by drainage control were higher in D than CDS treatments on some sampling dates in 1994 but not in other years.

The rate of decline in herbicide concentration over the growing season is reflected by half-life (Table 2). Tillage–intercrop treatment had no effect on the half-life of these herbicides in the 0- to 10-cm depth. Analysis of the half lives detected longer persistence of atrazine and metolachlor in D than CDS treatments in 1994. This result is not unexpected because 1994 was a relatively dry year and subirrigation increased water content

Table 2. Half-life for atrazine, metribuzin, and metolachlor persistence in the top 10 cm of Brookston clay as affected by tillage–intercrop treatments and water table control.

	Atrazine			Metribuzin			Metolachlor		
	1992	1993	1994	1992	1993	1994	1992	1993	1994
	Half-life, days								
	Tillage–Intercrop Treatments (TMT)								
MB†	46	34	54	23	29	32	42	45	79
MB + IC	44	35	59	24	29	37	44	44	97
SS	45	36	56	24	27	34	46	42	72
SS + IC	40	33	54	24	26	36	42	40	69
	Water Table (WT)								
D	43	37	60	24	29	37	43	44	91
CDS	45	32	52	24	27	32	44	42	67
Year	44	34	56	24	28	35	44	43	79
	Probability > *F*								
Source									
TMT	0.87	0.70	0.52	0.96	0.61	0.68	0.75	0.50	0.13
WT	0.73	0.10	0.02	0.96	0.51	0.10	0.63	0.35	0.02
TMT*WT	0.89	0.83	0.47	0.99	0.59	0.36	0.90	0.79	0.76

† MB, moldboard plow; MB + IC, moldboard plow with ryegrass intercrop; SS, soil saver; SS + IC, soil saver with ryegrass intercrop; D, drained; CDS, controlled drainage–subirrigation.

in the CDS treatment, which favored herbicide degradation. Water table control had no effect on herbicide dissipation in 1992 because rainfall was adequate to support herbicide dissipation. Jebellie and Prasher (1998) recovered more metribuzin from soil maintained at 0.85- than 0.4-m water table control, which they attributed to lower soil water content.

Residues of these herbicides were found in the 10- to 15- and 15- to 20-cm depths in all years (Fig. 1–8). Greater residues were found in the 10- to 15- than the 15- to 20-cm depths. Residues peaked after periods of high rainfall, then rapidly declined because of leaching and degradation. Greater herbicide residues were found for MB and MB+IC treatments than SS and SS+IC treatments in all years at the 10- to 15-cm depth but the effect was not consistent for all sampling dates. At the 15- to 20-cm depth MB or MB+IC had larger residues than the other treatments in 1992 but no discernible patterns were noted in 1993. Although these herbicides have a wide range in water solubility (33 mg L^{-1} for atrazine to 1500 mg L^{-1} for metribuzin) they appeared to be equally mobile in this soil and residue concentration was in proportion to the rate of application.

Des-ethyl atrazine was found at all depths with greatest concentrations following atrazine application (Fig. 1 and 5). Although there were some differences among treatments and water table control in the level of residue found, no consistent trends were readily apparent. The results are consistent with those reported by others in that des-ethyl atrazine does not accumulate over years, it readily leaches to greater depths with rainfall, and

Table 3. Properties of Brookston clay loam soil to determine sorptive capacity.

Depth	Horizon	C	pH	Silt	Clay
cm		%		%	%
0–10	Ap	1.83	5.4	30	39
10–30	Ap	1.55	5.5	28	41
30–60	B	0.25	6.5	28	38

Table 4. Adsorption capacity (K_f) and intensity of adsorption (slope) of atrazine, metribuzin, and metolachlor on Brookston clay loam from three depths.

Herbicide	Soil	Depth	Slope	K_f	R^2
		cm	L kg^{-1}	mg kg^{-1}	
Atrazine	Brookston	0–10	0.80 ± 0.04	4.68 ± 0.54	0.98
		10–30	0.83 ± 0.05	4.34 ± 0.56	0.97
		30–60	0.81 ± 0.07	2.37 ± 0.52	0.95
Metolachlor	Brookston	0–10	0.81 ± 0.04	7.25 ± 0.93	0.98
		10–30	0.81 ± 0.06	6.80 ± 0.91	0.96
		30–60	0.82 ± 0.07	3.60 ± 0.54	0.97
Metribuzin	Brookston	0–10	0.76 ± 0.05	2.03 ± 0.35	0.92
		10–30	0.78 ± 0.03	1.97 ± 0.30	0.91
		30–60	0.74 ± 0.08	1.28 ± 0.41	0.88

consistent, low concentrations are found throughout the year (Jayachandran et al., 1994; Gaynor et al., 1995a,b, 1998).

Herbicide Adsorption

Leaching and persistence of an herbicide is dependent upon its adsorption characteristics. The three depths of the Brookston soil provided a range in carbon content (0.3 to 1.8%, Table 3) and pH (5.4 to 6.5), but texture was uniform (clay content 38 to 41%). The capacity of a soil to adsorb an herbicide can be assessed from the K_f value derived from the Freundlich equation as noted above. The capacity of the Brookston soil from the 0- to 10-cm depth to adsorb these herbicides increased in the order metribuzin < atrazine < metolachlor (Table 4). A similar order was observed for the 10- to 30- and 30- to 60-cm depths. The 0- to 10- and 10- to 30-cm depths of soil had similar adsorption capacity for these herbicides (K_f metribuzin = 2.00, atrazine = 4.51, metolachlor = 7.03) because these depths are from the Ap horizon, where carbon content was greater than 1.5% (Table 3). The 30- to 60-cm depth (part of the B horizon to the tile drain) had a lower affinity (K_f = 1.28, 2.37, and 3.60, respectively) for these compounds, probably because of the low carbon content (0.3%). Adsorption of these herbicides has been related to soil carbon content and soil texture (Chesters et al. 1989; LeBaron et al. 1988; Sharom and Stevenson 1976). An increase in soil carbon and clay content increases adsorption. For our study, the low carbon content of the soil from the 30- to 60-cm depth (Table 3) relative to the other depths from the Ap horizon would account for the reduced adsorption of these herbicides, since clay content was similar. Atrazine and metolachlor were adsorbed with equal intensity (0.81 L kg^{-1}) by all depths of the Brookston soil but metribuzin was adsorbed with less intensity (0.76 L kg^{-1}) than the other herbicides. Thus, metribuzin should have greater potential to leach or be degraded in the Brookston soil. A shorter half-life was calculated for metribuzin than the other herbicides (Table 2), but no conclusions on differences among herbicides for leaching can be formed from the data because of the differences in application rate and persistence.

In conclusion, cultural practice had little consistent effect on dissipation of these herbicides. Generally, greater soil residues of these herbicides were found with MB or MB+IC than SS or SS+IC treatments, probably because of the greater water content of the SS treatment (Stone et al., 1989). The greater herbicide residues associated with the MB treatments could increase probability of these residues in surface runoff and tile drainage. Most consistent effects in herbicide dissipation occurred with drainage control. In a dry year (1994), CDS increased dissipation (decrease in $t_{1/2}$ of 5 d for metribuzin, 8 d for atrazine, and 24 d for metolachlor). Thus, the potential exists for drainage control to enhance herbicide dissipation in soil, which could improve water quality by reducing transport to surface waters.

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