

Rye Cover Crop and Nitrogen Fertilization Effects on Nitrate Leaching in Inbred Maize Fields

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ABSTRACT

Nitrate leaching from maize (*Zea mays* L.) fields fertilized in excess of plant requirements continue to threaten water quality even though many agronomists have recommended reducing N fertilization rates to contain this environmental risk. Inbred maize has lower N uptake than conventional hybrid maize; therefore, inbred maize production exposes soils to even greater ground water pollution risks by nitrates. A 3-yr field experiment was conducted on sandy loam soils in southwestern Michigan to investigate the combined effects of N fertilization rates and rye (*Secale cereale* L.) cover crops on NO₃ leaching in inbred maize fields. Inbred maize was fertilized at 0, 101, and 202 kg N ha⁻¹. Annual NO₃ leaching losses were 7 kg N ha⁻¹ higher in fields fertilized at 101 kg N ha⁻¹ than in nonfertilized controls. Annual NO₃ leaching losses to ground water between May 1995 and April 1998 from lysimeters fertilized at 202 kg N ha⁻¹ averaged 88 kg NO₃-N ha⁻¹. Rye interseeded with inbred maize fertilized at 202 kg N ha⁻¹ sequestered from 46 to 56 kg ha⁻¹ of excess fertilizer N. Rye scavenged little residual fertilizer N in plots fertilized at 101 kg N ha⁻¹. Well established rye cover crops in 1996 reduced NO₃ leaching by as much as 65 kg N ha⁻¹ when the previous crop was fertilized with 202 kg N ha⁻¹. Therefore, rye cover crops sequestered substantial amounts of soil NO₃ in heavily fertilized inbred maize fields.

GROUND WATER contamination by nitrates leached from maize fields fertilized in excess of plant uptake has been reported by numerous groups (Ferguson et al., 1991; Jemison and Fox, 1994; Kladyko et al., 1991; Sexton et al., 1996). Nitrate leaching from fertilized maize fields remains a problem though many agronomists have recommended reducing N fertilization rates applied to maize to contain environmental risks within acceptable limits (Peterson and Corak, 1993; Sexton et al., 1996; Williams et al., 1992). Several studies reported that N fertilizer application in excess of maize requirements is necessary to reach maximum grain yields (Liang and MacKenzie, 1994; Sexton et al., 1996) and maximum economical yields (Liang and MacKenzie, 1994; Jemison and Fox, 1994). Many seed producers apply high N fertilization rates to their inbred fields as inexpensive insurance against high N losses by leaching during wet growing seasons and to reach maximum yields during especially favorable growing seasons (Martin, 1992). Nonleguminous cover crops have been used to remove residual NO₃ left in the soil profile of fertilized maize fields after harvest (Ball-Coelho and Roy, 1997; Brandi-Dohrn et al., 1997; Ranells and Waggoner, 1997). Dry growing seasons generate greater accumulation of soil NO₃ from maize production because of reduced N

uptake by water-stressed maize plants and insufficient water drainage to displace soil nitrates (Ranells and Waggoner, 1997). Fall planted cover crops were found efficient at removing residual soil nitrates following a dry growing season (Davies et al., 1996; Ranells and Waggoner, 1997). Numerous studies have reported that rye cover crops reduce NO₃ leaching in maize production systems (Ball-Coelho and Roy, 1997; Brandi-Dohrn et al., 1997; Shepherd and Lord, 1996; Ranells and Waggoner, 1997). Similar effects were obtained with ryegrass covers (*Lolium multiflorum* Lam.), which were efficient at sequestering soil inorganic N during the cold season (Kuo et al., 1997; Shipley et al., 1992).

Inbred maize accounts for a substantial portion of agricultural production from St. Joseph County in southwestern Michigan. Inbred maize is produced in the county on approximately 20 000 ha. The region presents favorable climatic conditions and soil types, mostly sandy loams and sands, and has abundant irrigation water. In the last decade, NO₃-N concentrations above the USEPA's maximum contaminate level of 10 mg NO₃-N L⁻¹ were found in ground water used for public water supply of one community, which raised concerns about the impact of maize production on ground water quality.

The lower N uptake by inbred maize than hybrid maize plants increases the risk of excessive N fertilization and subsequent ground water pollution by NO₃-N leaching (Peterson and Corak, 1993; Wilhem et al., 1995). We hypothesized that rye cover crops could substantially reduce ground water contamination by nitrates by scavenging residual fertilizer N from inbred maize fields. Opposite to hybrid maize, the canopy of inbred maize never reaches closure, which allows for an early interseeding of a rye cover crop with inbred maize. In hybrid maize systems, best results were obtained when rye was planted as early as possible following a maize crop harvested as silage (Ditsch et al., 1993). As inbred maize sequesters less N than hybrid and is suitable for summer interseeding with a cover crop, there are potentially great benefits to interseeding a rye cover crop with inbred maize. This article reports a 3-yr field experiment started in 1995 that was designed to investigate the effects of rye cover crops on soil inorganic N fluxes within the soil profile of inbred maize fields receiving different rates of N fertilization.

MATERIAL AND METHODS

Experimental Design and Treatments

A field experiment was conducted from spring 1995 to spring 1998 on an Elston sandy loam (coarse-loamy, mixed

Abbreviations: LSD, least significant difference; NC, no cover; RC, rye cover; 101 and 202 N, 101 and 202 kg N ha⁻¹.

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mesic Typic Argiudolls) at Constantine, St. Joseph County in southwestern Michigan. Different rates of N fertilizer application and cover cropping with rye were tested on the inbred maize variety 'Pioneer P38'. Treatments were 0 kg N ha⁻¹ with rye cover (RC), 0 kg N ha⁻¹ with no cover (NC), 101 kg N ha⁻¹ with rye cover (101 N RC), 101 kg N ha⁻¹ with no cover (101 N NC), 202 kg N ha⁻¹ with rye cover (202 N RC), and 202 kg N ha⁻¹ with no cover (202 N NC). Experimental plots were installed in a randomized complete block design with four replications. Nitrogen was applied in the form of NH₄-NO₃ (34-0-0), with a preplant application of 34 kg N ha⁻¹ for all 101 N and 202 N treatments. Sidedress applications of 67 kg N ha⁻¹ for 101 N treatments and 168 kg N ha⁻¹ for 202 N treatments were conducted between the sixth and the eighth leaf stage. Measurements in the 0 N RC treatment were restricted to rye biomass and N content. The rye cover was interseeded with maize at maize-V6 stage at a rate of 125 kg seed ha⁻¹, which corresponds to about 450 seeds m⁻². This early interseeding was chosen for two reasons: (i) the canopy of inbred maize is generally smaller than that of hybrid maize (Martin, 1992; Orr et al., 1997), which leaves more solar radiation available to reach cover crops in the interrow of inbred fields compared with hybrids; and (ii) delayed cover crop planting following maize harvest can lead to poor stand establishment (Monks et al., 1997). Rye stands were destroyed by tillage before preparation of the inbred maize seedbed.

Experimental plots had been under inbred maize production and had received the same N treatments, as described in this study, since 1989. Plots were 6.1-m long and comprised 10 rows of inbred maize. Inbred maize was planted at 74 074 plants ha⁻¹ in 0.76-m rows at a depth of 0.045 m. Plots were chisel plowed in April, planted in May, and cultivated between maize rows in June of each year. Maize seed production from inbred plants was simulated by planting one inbred variety per plot. Two blocks of four inbred rows were designated as productive *female* plants, while the remaining two maize rows of each plot were assigned as *male* plants for pollination. Maize plants from *female* rows were detasseled, while *male* plants were cut at soil level after silking of *female* plants was completed. Plots were irrigated according to computer software scheduling that uses precipitation and temperature data from the research site to estimate soil water balance. An inoperative irrigation system prevented irrigation of research plots following rye sowing in 1997, which resulted in very poor rye emergence. Consequently, this article reports effects on NO₃ leaching from N fertilizer applications made in 1995, 1996, and 1997, and from rye cover crop for 1995 and 1996 only.

Instrumentation and Measurements

Five in situ nonweighing field lysimeters, 0.91 m by 3.80 m by 1.83 m deep, were installed in 1988, as described by Kalmbach (1995). The width of lysimeters corresponded with five rows of maize. Four lysimeters were disturbed and one was undisturbed. Three years following lysimeter installation, Kalmbach (1995) observed no significant difference in water drainage and NO₃ leaching among disturbed and undisturbed lysimeters subjected to identical treatments. This study was started 8 yr after lysimeter installation in the field. Lysimeters were buried with their upper edge at a 0.30-m depth so that normal field operations could be conducted. Lysimeter soil water drained into a collecting container through a 0.0127-m diameter pipe located at the lowest point in the lysimeter wall. One lysimeter was in one plot of the following treatments: 0 N NC, 101 N NC, 101 N RC, 202 N NC, and 202 N RC. Collection and sampling of drainage water from each lysimeter were manually completed with a water pump on a bimonthly basis. Water

samples from lysimeters were analyzed for NO₃ by flow injection technique using a QuickChem automated ion analyzer (Lachat Instruments, Milwaukee, WI). Drainage volumes were multiplied by NO₃ concentrations to compute total NO₃ leaching losses over time.

Rye was sampled six times from August 1995 to April 1996, and four times from July 1996 to April 1997. All aboveground rye biomass was collected from two randomly selected 0.76-m² areas of each plot. Samples were dried at 65°C, weighed, finely ground (<0.5 mm), and analyzed for total N by dry combustion method (Kirsten, 1983) using a C/N/S analyzer NA1500, Series 2 (Carlo Erba Stumentazione, Milano, Italy). Rye samples collected on 21 Apr. 1997 were mishandled and were not analyzed for total N. Maize grain yields were measured by collecting all ears from two *female* rows from each plot at harvest. Kernels were detached from ears, weighed, and subsampled for moisture content. Maize grain yields were computed on a per total land area basis and reported at 15.5% moisture content.

Destructive soil sampling was conducted to 1.25-m depths in fall 1996 and 1997, spring 1997, and 1998 with a Giddings hydraulic probe with a 0.075-m core diameter (Giddings Machines Co., Ft. Collins, CO). Two cores, one between and one within the maize rows, were extracted from each plot and visually divided into Ap, B, C₁, and C₂ horizons. Gravimetric soil water contents were determined on subsamples oven dried for 24 h at 105°C. Field moist 20 g subsamples were extracted for NO₃-N and NH₄-N by shaking for 1 h in 50 mL of 1 M KCl solution. Solutions were filtered and analyzed for NO₃-N and NH₄-N with a QuickChem automated flow injection ion analyzer.

Statistical Analyses

Statistical analyses were conducted using the general linear model of the SAS system (SAS Inst., 1989). Mean separation tests for rye biomass and N content, and maize yields were conducted using Fisher's least significant differences (LSD_{0.05}) when global *F* tests were significant; LSD_{0.05} could not be calculated for 26 Oct. 1996 because of missing data. Within treatment variability of soil extraction data was too great for graphical representation of LSD_{0.05}; therefore, standard errors were used as error bars. Field lysimeters were not replicated; therefore, statistical comparison of means could not be performed. Linear regression analyses were performed on lysimeter data for cumulative NO₃ leaching vs. cumulative drainage.

RESULTS

Maize yields were not significantly modified by rye cover crops for any of the growing seasons (Table 1). For a low-yield growing season (i.e., 1995) grain yields

Table 1. Grain yields of inbred maize at Constantine for the 1995 to 1997 period.

N rate	Cover	Grain yields		
		1995	1996	1997
kg ha ⁻¹		kg ha ⁻¹		
0	no	1153a [*]	4684c	2075b
101	no	1308a	5047bc	2928ab
101	rye	1188a	5328abc	3002ab
202	no	1167a	6211a	3407a
202	rye	1156a	5632ab	3622a
LSD _{0.05}		353	944	1264

* Means indexed with the same letter are not significantly different at *P* = 0.05.

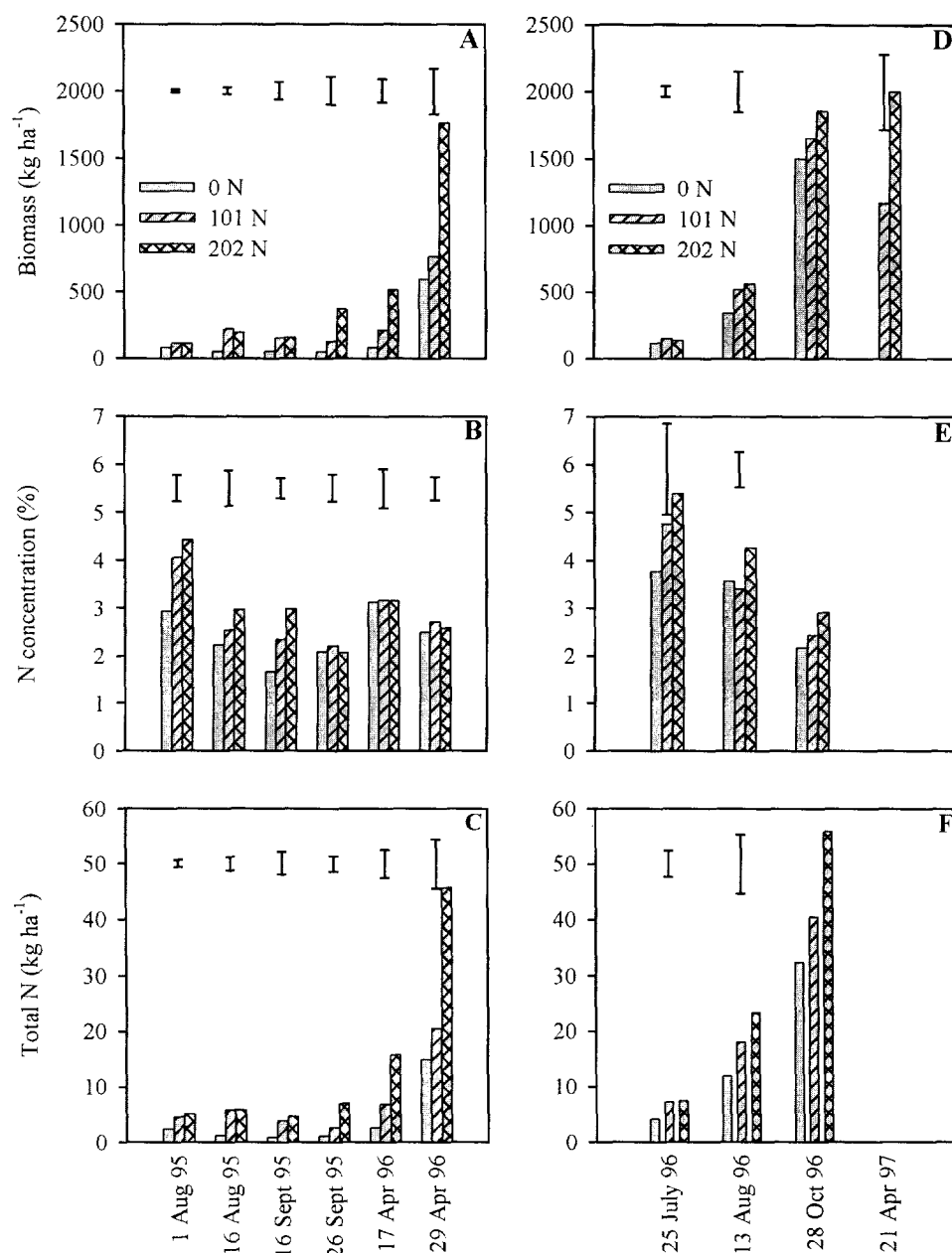


Fig. 1. (A-D) Biomass, (B-E) N concentration, (C-F) and total N of rye cover crops interseeded with inbred maize during the 1995-1996 and 1996-1997 growing seasons, and fertilized at rates of 0, 101 and 202 kg N ha⁻¹; LSD_{0.05} given for four replicates.

were not significantly improved by N fertilization. For the two following growing seasons (i.e., 1996 and 1997) grain yields were significantly increased by 202 N compared with the nonfertilized treatment. Grain yields were not significantly increased by application of 202 kg N ha⁻¹ compared with 101 kg N ha⁻¹, except for the noncover cropped plots in 1996.

Rye biomass measured in April 1996 and April 1997 were significantly greater in the 202 N treatment than in the 0 N and 101 N treatments (Fig. 1A and 1D). Rye biomass did not significantly differ between the 0 N and the 101 N treatments, except soon after rye planting in 1995. Similar amounts of rye biomass was present on 29 Apr. 1996 and 21 Apr. 1997. Nevertheless, rye accumulated up to 1800 kg ha⁻¹ of biomass on 28 Oct. 1996,

while less than 500 kg ha⁻¹ of biomass were observed on 26 Sept. 1995 and 17 Apr. 1996. The rye N concentrations varied depending on season, year, and treatment, generally decreasing as the rye matured (Fig. 1B and 1E). Rye cover crops contained greater quantities of total N in plots fertilized at 202 kg N ha⁻¹ than in plots receiving 0 or 101 kg N ha⁻¹ (Fig. 1C and 1F). This difference in total plant N from fertilizer treatment was more a function of rye yield than N tissue concentration.

Substantial quantities of extractable inorganic N (i.e., NO₃-N and NH₄-N) were present in the top 1.25 m of the soil profile of 202 N treatments in October 1996, particularly in the C₁ and C₂ horizons (Fig. 2). The B_t horizon displayed only a slight increase in inorganic N, while concentrations in the Ap horizon matched base-

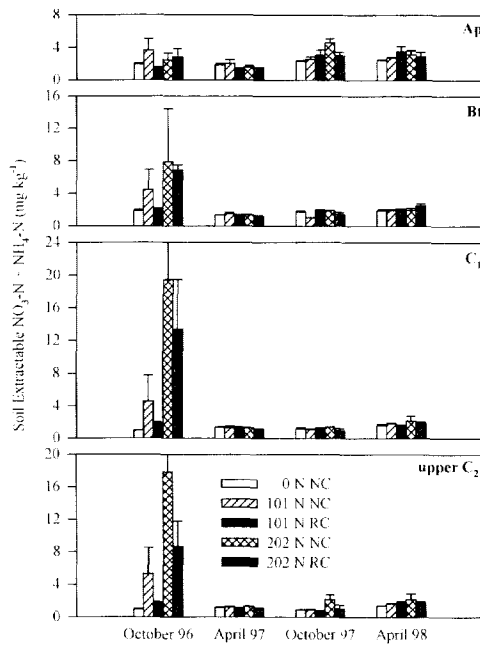


Fig. 2. Soil inorganic N concentrations in the Ap, Bt, C₁, and C₂ horizons of soils under inbred maize fertilized at 0, 101, and 202 kg N ha⁻¹, followed by bare fallow or interseeded with a rye cover crop. Error bars are standard errors for four replicates.

line levels observed for other dates and treatments. The high levels of soil inorganic N observed in October 1996 were not found in April 1997, October 1997, or April 1998. Total inorganic N content per horizon in kg N ha⁻¹ was estimated from the inorganic N concentrations and soil water content. This estimate suffers from imprecision related to exact depths of the soil horizons, which varied from plot to plot, and uncertainties related to bulk densities. Estimated quantities of inorganic N contained in the upper 1.25 m of the soil profile in October 1996 were decreased by the rye cover crop by 41 and 75 kg N ha⁻¹ in 101 N and 202 N treatments, respectively.

Nitrogen fertilization rate of 202 kg N ha⁻¹ applied to noncover cropped inbred maize resulted in the highest NO₃-N concentrations in lysimeter leachates (Fig. 3A). Nitrate concentration of lysimeter leachates from the 202 N lysimeter peaked at 70 mg NO₃-N L⁻¹ in August and September 1997. Nitrate concentrations in lysimeter leachate were less than 20 mg NO₃-N L⁻¹ in the 101 N treatment and less than 11 mg NO₃-N L⁻¹ in the 0 N treatment from May 1995 to May 1997. Drainage differed substantially among the three lysimeters without rye cover (Fig. 3B). The nonfertilized treatment consistently displayed highest cumulative drainage. In 1995 and 1996, 101 N NC and 202 N NC lysimeters drained comparable volumes of soil solution. For the two subsequent years, drainage was about 85% greater for the 202 N NC than for the 101 N NC lysimeter. Cumulative amounts of NO₃ leached below the root zone between May 1995 and April 1998 were 76, 98, and 264 kg NO₃-N ha⁻¹ for 0 N NC, 101 N NC, and 202 N NC lysimeters, respectively (Fig. 3C). A peak of NO₃ leaching was observed in July and August 1995 and 1997, while the rate of NO₃ leaching was more even during the 1996

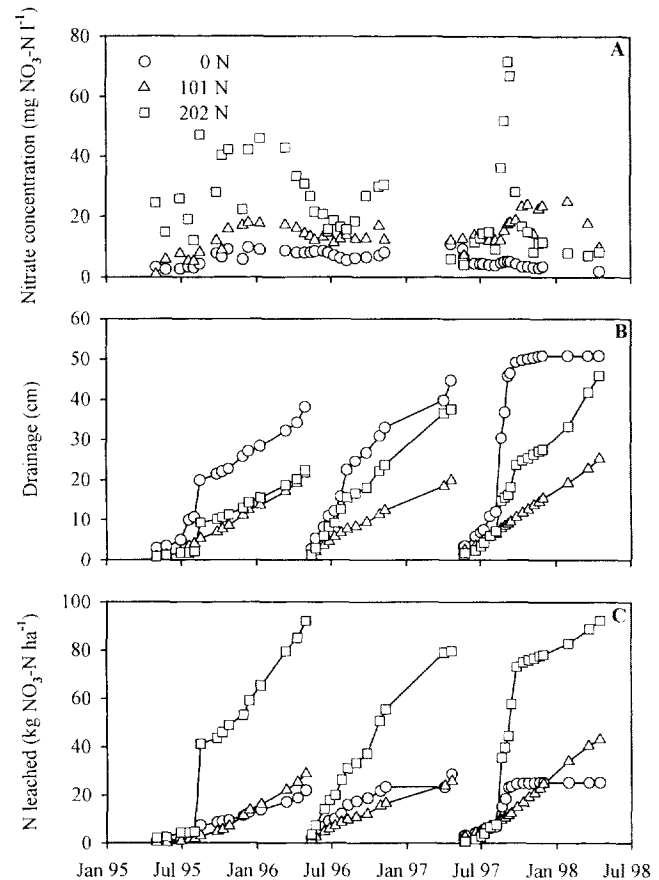


Fig. 3. (A) Nitrate concentration of leachates, (B) cumulative drainage, and (C) total N leached from noncover cropped lysimeters under inbred maize fertilized at 0, 101 and 202 kg N ha⁻¹.

growing season. Weather data from a nearby station indicated that July 1996 was dryer than July 1995 and 1997 (Fig. 4).

Rye cover crops planted in the 202 N lysimeter reduced NO₃ leaching compared with noncover cropped lysimeter from May 1995 to May 1997 (Fig. 5). Nitrate leaching was reduced by 26 kg NO₃-N ha⁻¹ in 1995 and 1996 and 54 kg NO₃-N ha⁻¹ in 1996 and 1997. As drainage varied substantially among lysimeters in this study (Fig. 3), cumulative NO₃-N losses were expressed

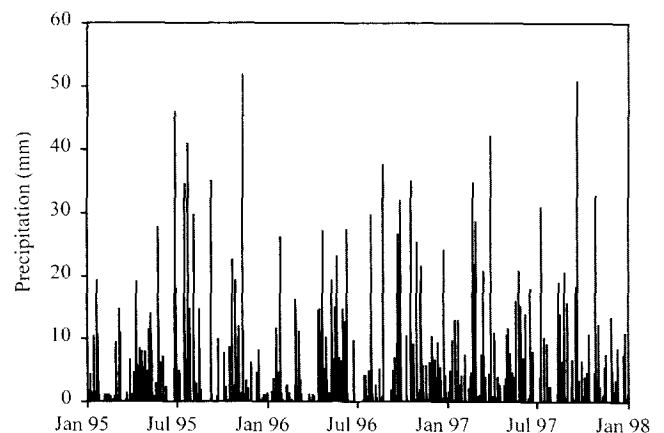


Fig. 4. Precipitation for 1995, 1996, and 1997 at Three Rivers, MI.

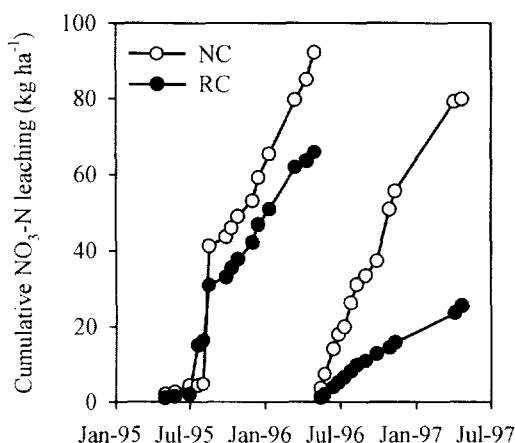


Fig. 5. Total N leached from lysimeters under inbred maize fertilized at 202 kg N ha⁻¹, (NC) with no cover crop or (RC) with a rye cover crop.

as a function of cumulative drainage rates (Fig. 6). Cumulative NO₃-N leaching was a linear function of cumulative drainage volumes for the 0 N and 101 N treatments, becoming less linear as fertilization rates increased to 202 kg N ha⁻¹. Flow-weighted NO₃-N leaching was highest for the 202 N NC treatment, and lowest for the 0 N NC treatment. The three other treatments (i.e., 101 N NC, 101 N RC, and 202 N RC) presented fairly similar slopes of flow-weighted NO₃-N leaching (Fig. 6).

DISCUSSION

Different responses of maize yields to rye cover cropping have been reported in the literature. Some researchers found that maize yields are decreased by rye cover crops (Karlen and Doran, 1991; Raimbault et al., 1990; Tollenaar et al., 1993), while others observed no significant effects of rye cover crops on maize yields (Abdin et al., 1998; Ball-Coelho and Roy, 1997; Ranells and Wagger, 1997; Schroder et al., 1997). Our data support that rye cover crops do not modify inbred maize

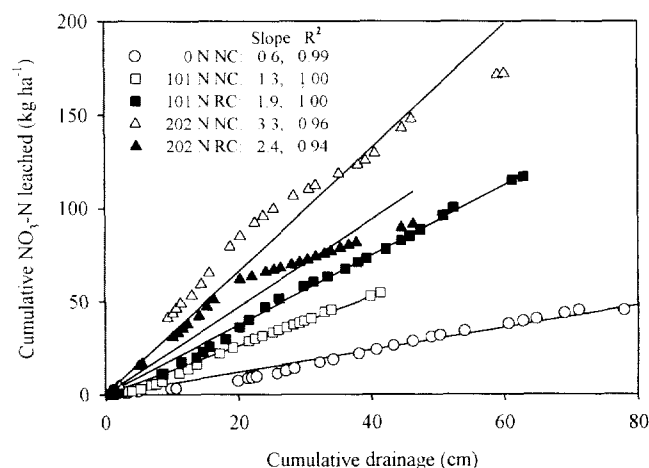


Fig. 6. Cumulative NO₃-N leaching as a function of cumulative drainage flow for the May 95 to May 97 period, in lysimeters fertilized at 0, 101, and 202 kg N ha⁻¹, (NC) with no cover crop or (RC) with a rye cover crop.

yields, which is crucial for adoption by farmers of rye cover cropping for removing residual NO₃ from soil profiles.

Scavenging of residual N by rye cover crops and associated reduction of NO₃ leaching rates were assessed by measurements of rye biomass N, soil extractable N, and lysimeter NO₃-N leaching. For the 202 N treatment, maximum rye N contents averaged 46 kg N ha⁻¹ in 1995 and 1996 and 56 kg N ha⁻¹ in 1996 and 1997 (Fig. 1). Extractable soil inorganic N contents in October 1996 were decreased by 75 kg N ha⁻¹ when a rye cover crop was applied to plots fertilized at 202 kg N ha⁻¹ (Fig. 2). Measurements conducted in the 202 N lysimeters indicated that rye cover cropping reduced NO₃ leaching by 26 kg NO₃-N ha⁻¹ in 1995 and 1996 and 54 kg NO₃-N ha⁻¹ in 1996 and 1997 (Fig. 5). These three methods for assessing the N scavenging potential of rye cover crops gave results comprised within a fairly narrow range (i.e., from 26 to 44 kg N ha⁻¹) in 1995 and 1996 and from 54 to 75 kg N ha⁻¹ in 1996 and 1997. We infer from these measurements that rye cover crops reduced N leaching from inbred maize plots fertilized at 202 kg N ha⁻¹ by about 35 kg N ha⁻¹ in 1995 and 1996 and 65 kg N ha⁻¹ in 1996 and 1997. These results are similar to published data for N uptake and reduction of NO₃ leaching by rye and ryegrass cover crops in hybrid-maize production systems. Reported values for N contents of rye cover crops averaged 64 kg N ha⁻¹ when following maize fertilized at 168 kg N ha⁻¹ (Ditsch et al., 1993), and 70 kg N ha⁻¹ when following maize fertilized at 224 kg N ha⁻¹ (Burket et al., 1997). Ryegrass following maize fertilized at 200 kg N ha⁻¹ was reported to decrease NO₃ leaching by 70 kg N ha⁻¹ (Martinez and Guiraud, 1990). Spring soil inorganic N content was reduced by an estimated 81 kg N ha⁻¹ by a preceding rye cover crop compared with bare fallow following a maize crop fertilized at 168 kg N ha⁻¹ (Ditsch et al., 1993). Brandt-Dohrn et al. (1997) reported that rye cover crops decreased NO₃ leaching from fertilized maize fields by 32 to 69 kg N ha⁻¹. Our results indicate that rye cover crops reduced NO₃ leaching in inbred maize fields, but not to a greater extent than reductions reported in the literature for hybrid maize fields. We had expected that rye would have performed particularly well in inbred maize systems because of the early interseeding of rye, which is rendered possible because inbred maize canopy never reaches closure. From this study we cannot conclude that rye cover cropping presents greater benefits in inbred than hybrid maize systems.

Little benefit of rye cover crops was observed for the 101 N treatment. Maximum rye N contents in 101 N plots averaged 20 kg N ha⁻¹ in 1995 and 1996 and 41 kg N ha⁻¹ in 1996 and 1997 (Fig. 1). These values were not significantly different from total N contents of rye crops grown in the nonfertilized plots. This result suggests the rye cover crop did not substantially benefit from the 101 N treatment. Rye planted at the time of maize-V6 stage appeared to be out competed by maize for NO₃ uptake. Nonreplicated lysimeter data suggested that rye cover cropping did not help prevent NO₃ leaching. A small increase in NO₃-N leaching rate was ob-

served in the 101 N RC lysimeter compared with the 101 N NC lysimeter, which probably resulted from individual lysimeter variability. The only positive indicator of rye effects on residual fertilizer N was the soil extraction conducted in October 1996, which showed a substantial decrease (41 kg N ha^{-1}) in inorganic soil N when a rye cover crop was applied to plots fertilized at 101 kg N ha^{-1} . We infer from these results that the benefit of rye cover cropping for the scavenging of residual N was much reduced for the 101 N treatment compared with the 202 N treatment.

The reduced impact of rye cover crops on NO_3 leaching from 101 N plots can better be understood when leaching data from the three noncover cropped lysimeters are compared. Cumulative amounts of NO_3 leached below the root zone between May 1995 and April 1998 were 76, 98, and $264 \text{ kg NO}_3\text{-N ha}^{-1}$ for 0 N, 101 N, and 202 N lysimeters, respectively (Fig. 3C). These results imply that residual fertilizer N susceptible to being leached during a 3-yr period was 22 kg N ha^{-1} for 101 N and 188 kg N ha^{-1} for 202 N. Therefore, rye cover crops appeared inefficient at removing residual fertilizer N in the 101 N plots because little N was left to be removed at this fertilization rate. These results also confirm that fertilization of inbred maize fields at a rate of about 100 kg N ha^{-1} is an environmentally sound practice, while 202 kg N ha^{-1} is excessive and leads to ground water pollution, as previously reported by Peterson and Corak (1993) and Rasse et al. (1999).

Most of the NO_3 was leached from the soil profile during the 1995 and 1997 summers, while late fall and early spring are generally reported as being the periods when substantial leaching occurs in the northern Corn Belt (Chichester, 1977). Eighty percent of total annual leaching from 1997 to 1998 had already occurred by August 1997 (Fig. 3). This observation explains why no residual fertilizer N was detected in soil extractions conducted in October 1997 and April 1998, as near complete leaching had already taken place during the summer. A dry summer in 1996 (Fig. 4) prevented soil nitrates from being leached from the soil profile by October of the same year (Fig. 2). While lowest rates of NO_3 leaching during the summer were observed in 1996, highest yields were also measured (Table 1). We hypothesize from these observations that the irrigated sandy soils of southwestern Michigan are susceptible to summer NO_3 leaching, which might negatively impact inbred maize yields.

CONCLUSIONS

Application of 101 kg N ha^{-1} to inbred maize line P38 resulted in little additional NO_3 leaching compared with nonfertilized plots. At this N fertilization rate, soil extraction and lysimeter data were inconsistent with respect to rye cover-crop effects on NO_3 leaching. Therefore, we would not recommend rye cover cropping for the purpose of sequestering residual fertilizer N in inbred maize fields fertilized at rates of approximately 100 kg N ha^{-1} . At a N fertilization rate of 202 kg N ha^{-1} , substantial NO_3 leaching to ground water was ob-

served. At this fertilization rate, interseeding a rye cover crop with inbred maize substantially reduced NO_3 leaching. Many seed producers apply high N fertilization rates to their inbred fields as inexpensive insurance against climatic adversity and to reach maximum yields during especially favorable growing seasons. At high N fertilization rates, we advocate the use of rye cover crops, which substantially reduced NO_3 leaching during the cold season. Nevertheless, we do not recommend to fertilize inbred maize fields in excess of plant requirements.

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Bentonite and Humic Acid as Modifying Agents in Controlled Release Formulations of Diuron and Atrazine

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ABSTRACT

The herbicides diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and atrazine [6-chloro-N²-ethyl-N⁴-isopropyl-1,3,5-triazine-2,4-diamine] were incorporated in alginate-based granules to obtain controlled release (CR) properties. The basic formulation [sodium alginate (14.0 g kg⁻¹)-herbicide(6.0 g kg⁻¹)-water] was modified by addition of sorbents. The effect on diuron and atrazine release rate, caused by incorporation of natural bentonite and humic acid in the alginate formulation, was studied by immersion of the granules in water under static conditions. The release of the active ingredient from alginate-based CR granules in water was affected by the addition of natural bentonite, and to a greater extent, by the addition of the humic acid. The water uptake, permeability, and the time taken for 50% of active ingredient to be released into water, T_{50} , were calculated for the comparison of the preparations. Addition of both bentonite and humic acid samples to the basic alginate-based formulation produced the higher T_{50} values (43.11 and 50.49 d for diuron and atrazine formulations, respectively), indicating a slower release of herbicide. Based on parameters of an empirical equation used to fit the herbicide release data, it appears that the release of diuron and atrazine from the various formulations into water is controlled by a diffusion mechanism. Sorption capacity of the sorbent and the permeability of the formulations (ranging from 3.77 to 20.83 mg d⁻¹ mm⁻¹) were the most influential factors affecting herbicide release.

IN PEST MANAGEMENT, the majority of soil-acting pesticides are applied by spraying formulations in which the active ingredient is dispersed in fine particles. Losses can occur due to spray drift, and the risk of leaching is greater as the pesticide is quickly dissolved in the soil

solution. The main objectives of controlled release (CR) technology in this area are to improve efficiency and reduce the environmental impact associated with the use of pesticides (Wilkins, 1995). Some recent work indicates beneficial effects related to the use of CR formulations (Johnson and Pepperman, 1996; Cotterill et al., 1996; Fernández-Pérez et al., 1998). The use of natural polymers in the preparation of CR systems is of special interest, because of the possible biological degradation of the matrices, and the relatively low costs of some of the raw materials (Pfister et al., 1986). Although the use of alginate in CR technology has been mainly focused in the development of formulations with medical applications, this natural polymer has also been used as a matrix for the controlled release of pesticides (Barret, 1978; Pepperman et al., 1991; Pepperman and Kuan, 1993). Besides the benefits of a delayed release of the pesticide, alginate formulation do not disintegrate in soil, as it has been observed in other formulations of related nature (Connik et al., 1984; Wienhold and Gish, 1992; Fernández-Pérez et al., 1999).

Diuron and atrazine are general-applied herbicides (Tomlin, 1994) and have been identified as potential leachers by using the ground water ubiquity score (GUS) modeling technique (Guftanson, 1989). Furthermore, atrazine has been widely detected in ground water

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Abbreviations: T_{50} , time taken for 50% of active ingredient to be released into water; CR, controlled-release; B, bentonite; H, humic acid; HPLC, high performance liquid chromatography; AA₁, atrazine-alginate formulation; AA₁B, atrazine-alginate-bentonite formulation; AA₁BH, atrazine-alginate-bentonite-humic acid formulation; DA₁, diuron-alginate formulation; DA₁B, diuron-alginate-bentonite formulation; DA₁BH, diuron-alginate-bentonite-humic acid formulation.