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Summer Cover Crops Reduce Atrazine Leaching to Shallow Groundwater in Southern Florida

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At Florida's southeastern tip, sweet corn (*Zea Mays*) is grown commercially during winter months. Most fields are treated with atrazine (6-chloro-*N*-ethyl-*N'*-[1-methylethyl]-1,3,5-triazine-2,4-diamine). Hydrogeologic conditions indicate a potential for shallow groundwater contamination. This was investigated by measuring the parent compound and three degradates—DEA (6-chloro-*N*-[1-methylethyl]-1,3,5-triazine-2,4-diamine), DIA (6-chloro-*N*-ethyl)-1,3,5-triazine-2,4-diamine, and HA (6-hydroxy-*N*-[1-methylethyl]-1,3,5-triazine-2,4-diamine)—in water samples collected beneath sweet corn plots treated annually with the herbicide. During the study, a potential mitigation measure (i.e., the use of a cover crop, Sunn Hemp [*Crotalaria juncea* L.], during summer fallow periods followed by chopping and turning the crop into soil before planting the next crop) was evaluated. Over 3.5 yr and production of four corn crops, groundwater monitoring indicated leaching of atrazine, DIA, and DEA, with DEA accounting for more than half of all residues in most samples. Predominance of DEA, which increased after the second atrazine application, was interpreted as an indication of rapid and extensive atrazine degradation in soil and indicated that an adapted community of atrazine degrading organisms had developed. A companion laboratory study found a sixfold increase in atrazine degradation rate in soil after three applications. Groundwater data also revealed that atrazine and degradates concentrations were significantly lower in samples collected beneath cover crop plots when compared with concentrations below fallow plots. Together, these findings demonstrated a relatively small although potentially significant risk for leaching of atrazine and its dealkylated degradates to groundwater and that the use of a cover crop like Sunn Hemp during summer months may be an effective mitigation measure.

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An assessment conducted across the continental USA in the 1990s found that about 60% of shallow groundwater samples collected in urban and agricultural land use areas contained detectable residues of one or more pesticides or pesticide degradates (Gilliom et al., 2006). The herbicide atrazine and its degradate, desethylatrazine (DEA), were the most commonly reported. These results are consistent with other studies and have identified a need to quantify groundwater quality risks in atrazine use areas and implement mitigation measures when adverse impacts are indicated (USEPA, 2003).

Risks appear high at the southeastern tip of peninsular Florida, where various crops are produced in a 32-km^2 area that is bounded by the City of Miami to north, Biscayne Bay National Park to the east, and the Everglades National Park to the south and west. Sweet corn is grown on about 2000 ha, with 65 to 78% of fields treated annually with atrazine (Degner et al., 2002; USDA-NASS, 2006). Mineral soils used for corn production are carbonatic, shallow, and gravely, with low organic carbon (C) content (<10 g kg^{-1}), high hydraulic conductivity, and atrazine soil organic C water partition coefficient about one third of reported literature values for noncarbonatic soils (Noble et al., 1996; Nkedi-Kizza et al., 2006; Ritter et al., 2007). In addition, the water table residing in the underlying porous limestone bedrock is within 1 to 3 m of the soil surface throughout the year (Fish and Stewart, 1991). Together, the soil and hydrogeologic conditions indicate that shallow groundwater is vulnerable to atrazine contamination.

The area's surficial aquifer is part of the Biscayne aquifer system, which provides potable water for nearly all of south Florida's rapidly growing population (Wilcox et al., 2004). Another concern is that agricultural practices, which contribute to water quality impairment, have the potential to adversely affect the massive project focused on restoring south Florida's Everglades ecosystem (Perry, 2004). Restoration plans have identified a need to minimize agricultural

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Abbreviations: COV, cover crop; CT, chlorotriazines; DACT, diaminochlorotriazine; DEA, desethylatrazine; DGRD, downgradient; DIA, desisopropylatrazine; ET, evapotranspiration; HA, hydroxyatrazine; LTA, long-term average; MCL, maximum contaminant level; MDL, method detection limit; MS, mass spectrometry; NOCOV, no cover crop; $t_{1/2}$, soil half-life; UGRD, upgradient.

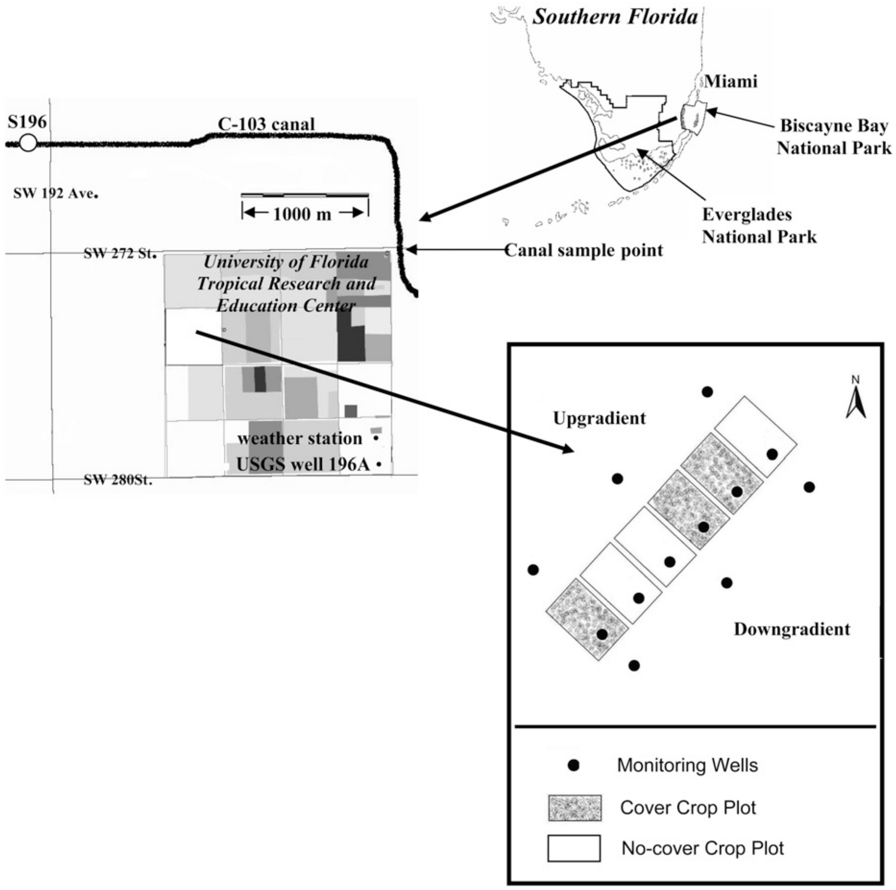

Fig. 1. Location of study site, research plots, and water sample collection points.

nonpoint source water pollution (CERP, 2002). Few assessments provide data on groundwater quality directly beneath farmer's fields; thus, the affects of common agricultural practices such as atrazine use are uncertain (McPherson et al., 2000).

Because groundwater quality may be threatened, surface water quality in the region's network of drainage canals may be at risk. These canals intersect the water table and promote short groundwater flow paths (Genereux and Slater, 1999). Harman-Fetcho et al. (2005) associated the detection of atrazine and selected degradates in canal water samples with nearby sweet corn production. This observation suggested that leaching to groundwater and groundwater discharge to the canal was an atrazine transport pathway.

In this article, a 3.5-yr study conducted in this crop production region is described. Potential affects of atrazine use on water quality were studied by measuring atrazine and selected degradate concentrations in groundwater directly beneath sweet corn plots treated annually with the herbicide. Use of a cover crop, Sunn Hemp (*Crotalaria juncea* L.), on plots during summer fallow periods followed by chopping and turning cover crop residue into soils was evaluated to determine whether this practice may reduce the affects. Cover crops typically increase soil biological activity and organic matter (Reeves, 1994); as a result, herbicide leaching and groundwater contamination may be reduced (Bottomley et al., 1999; Gaston et al., 2003). Sunn Hemp has been shown to be a highly vigorous and effective cover crop for vegetable production systems in subtropical environments like South Florida provided a reliable and low-cost seed source can be developed (Wang et al., 2005; Cherr et al., 2006). Growers are being encouraged to plant cover crops, although the practice is not widespread and fields are often left fallow during summer wet seasons (Li et al., 2006).

A companion laboratory study examined atrazine dissipation kinetics in soil samples collected at the study site. Kinetic parameters related to the dissipation of atrazine are discussed in this article. Relationships between land management and groundwater nitrate dynamics at the study site were described by Ritter et al. (2007).

Materials and Methods

Study Area and Management

Investigations were conducted on a flat 4-ha field 0.5 km south of the South Florida Water Management District's C-103 canal between November 1999 and April 2003 at the University of Florida Tropical Research and Education Center located about 5 km northwest of Homestead, FL (Fig. 1). In the 3 yr before beginning the study, a variety of vegetable crops were produced in portions of the field. Metribuzin was applied to cultivated areas in December 1996, and cyromazine was used in March 1999. Records do not indicate the use of other triazines.

Field soils are in the Krome series (loamy-skeletal, carbonatic, hyperthermic Lithic Udorthents) (Ritter et al., 2007). Properties (average ± SD) of composite samples ($n = 6$) collected to the limestone surface (0–20 cm) before planting the first corn crop were as follows: gravel (>2 mm), 669 ± 52; sand, 194 ± 6.2; silt, 75 ± 11; clay, 61 ± 8.4; organic C, 11 ± 1.0 g kg^{-1}: and organic nitrogen (N), 0.6 ± 0.1 g kg^{-1}. The median pH was 8.1.

Sweet corn, var. Attribute (Rodgers Seeds, Boise, ID), was planted in a 192 by 47 m rectangular strip positioned diagonally across the field and perpendicular to the predominant direction of groundwater flow, NW-SE (Ritter et al., 2007). At the beginning of the study, the strip was divided equally into six subplots (27 by 47 m), with the longer dimension NW–SE. Three plots each were randomly assigned to cover (COV) and no-cover crop (NOCOV) treatment groups (Fig. 1). Each year, corn was planted in October to November and harvested in February to March. This corresponded to the winter dry season and followed normal agronomic practice in the region. After tillage and 1 to 2 wk before planting each crop, *Atrazine 4L* was broadcast applied with a tractor-mounted sprayer. The atrazine application rate (target 2.0 kg ha^{-1}) was measured by analysis of spray targets ($n = 4$ per plot) or composite soil samples (see below) collected to the bedrock surface on each plot after each application. During growing seasons, plots were irrigated with a solid-set system. The water supply was a 25-cm diameter unlined borehole drilled to 10 m into the limestone about 30 m due south (hydraulically downgradient) of plots. Local growers commonly use boreholes of this type for irrigation supplies. Irrigation (17–25 mm at 3- to 5-d intervals), fertility, and pest management followed recommended commercial practices (Hochmuth et al., 2000).

Each year, the number of marketable ears and their length and weight were evaluated on each plot. Yields were comparable to the most successful growers in the region, with no significant difference ($P = 0.05$) in yield, ear length, or weight when COV and NOCOV plot means were compared by two-way ANOVA (Schaffer, unpublished data). After harvest, all plots were mowed and disced repeatedly to turn corn stover into the soil. At the beginning of the following rainy season (early May), Sunn Hemp (Pleasant Valley Farms, Grass Valley, CA or USDA-NRCS, Hilo, HI) was seeded on COV plots at 55 kg ha^{-1}. When the Sunn Hemp was about 1 m tall (end of June), it was mowed to a height of about 0.1 m. By early October, it had regrown to about 1.5 m. The crop was again mowed, and residues were chopped and turned into the soil by repeated discing. In all years, NOCOV plots were left fallow. They were disced before planting and periodically during fallow periods to control weeds. Weeds in the remaining area within the field were managed similarly.

Hydrologic Monitoring and Sample Collection

Rainfall and water table elevation data were obtained from automated monitoring stations located 1 km west of plots (FAWN, 2006; USGS, 2006). Groundwater samples were collected from 18 monitoring wells constructed for the study within field boundaries. Well screens intersected the water table surface. Six wells were located within sweet corn plots, four between plots, and four (each) at upgradient (UGRD) and downgradient (DGRD) locations (Ritter et al., 2007). Groundwater flow direction was verified, and velocity estimates (3–9 m d^{-1}) were determined during three groundwater tracer studies and by continuous water table elevation measurements in a network of perimeter wells during 2002 and 2003 (Potter, unpublished observation; Ritter et al., 2007).

Canal samples were collected from the bridge crossing the C-103 canal about 0.6 km NW of the field (Fig. 1). This was the closest available canal access point. From December 1999 to May 2000, well and canal samples were collected monthly. Thereafter, samples were collected bimonthly. During the 2002 wet season (May–October), seven "storm-event" samples were collected from wells within plots. The criteria used for sample collection was a 25-cm rain within a 24-h period provided the rain occurred at least 2 d before or 7 d after a "scheduled" biweekly sample. Before sample collection, wells were purged (about 40 L) with a portable pump. Water levels were allowed to stabilize (5–10 min), and samples were secured with a bailer. A field blank, prepared by rinsing the bailer with distilled-deionized water, was included with each sample set. Starting in January 2001, the sample from one NOCOV plot well was collected in triplicate. This provided field duplicates and a sample for matrix spiking (see below). Sample containers were 500-mL glass bottles that were washed with soap and water, rinsed with distilled-deionized water and acetone, and baked for 2 h at 125°C before each use. Screw caps were lined with Teflon.

About 2 h after the first atrazine application in 1999, a composite soil sample was collected on each plot. A second set of samples were collected from the COV and NOCOV plots in the center of the cultivated strip 1 d before the forth atrazine application in 2002. Portions of these and the samples collected in 1999 were used in soil incubations conducted to assess atrazine dissipation kinetics. Composite soil samples were also collected from all plots in November 2001, in February 2002, and after harvest of the fourth corn crop in April 2003. All water and the soil samples used in incubation studies were refrigerated overnight and were shipped within 24 h to the analytical laboratory. The other soil samples were frozen and shipped in bulk.

Soil Incubations

Subsamples (50 g) of soil passing a 2-mm stainless sieve were placed in 250-mL square glass bottles. Bottles were sealed with Teflon-lined screw caps and incubated in the dark at 25 ± 1°C. Before beginning incubations of soil samples collected in 1999 (after first atrazine application), the soil water content was adjusted to field capacity (15% gravimetric) with deionized water. During incubations, methanol (50 mL) was added to one bottle containing soil from each plot after 0, 4, 8, 18, 22, 35, 51, 80, and 108 days. Before incubation of COV and NOCOV plot soil collected in 2002 (before spraying), an aqueous solution of atrazine was added to achieve an atrazine concentration of 1 μg g^{-1} of soil. Sufficient deionized water was then added to bring the soil water content to field capacity. During incubation of these samples, 50-mL methanol was added to three bottles, each containing the COV and NOCOV soil after 0, 1, 4, 7, 14, 21, 28, 42, 63, 91, and 119 days. After methanol addition, all bottles were recapped and stored in a −20°C freezer.

Sample Analysis and Quality Control

Spray targets (7-cm diameter cellulose filter paper) were shaken for 1 h with 25 mL of methanol. A 1-mL aliquot was reserved for analysis. Bottles containing soil and methanol were brought to room temperature and shaken for 1 h on a rotating bed shaker. The methanol was decanted and vacuum filtered (70-mm Whatman GFF filters). Two repeat extractions were made with 50-mL aliquots of methanol. The combined extracts were concentrated to 10 mL under a stream of N_2 gas. Soil organic C and N was measured by dry combustion using a Carlo-Erba NA1500 II CN-analyzer (CE-Elantech Inc., Lakewood, NJ). Before analysis, samples were sieved (2 mm), stirred with 3 N HCl overnight to remove carbonates, filtered, rinsed with deionized water, and oven-dried. The same measurements were made on samples collected in November 1999 without prior acidification. As a result, organic C measurements in these samples were anomalously high due to interference by soil carbonates.

Water samples were vacuum filtered (70-mm Whatman GFF filters). Filtrate was extracted using 6-mL (200 mg) Oasis HLB cartridges (Waters, Milford, MA) followed by sequential elution with 3 mL methanol and 3 mL methylene

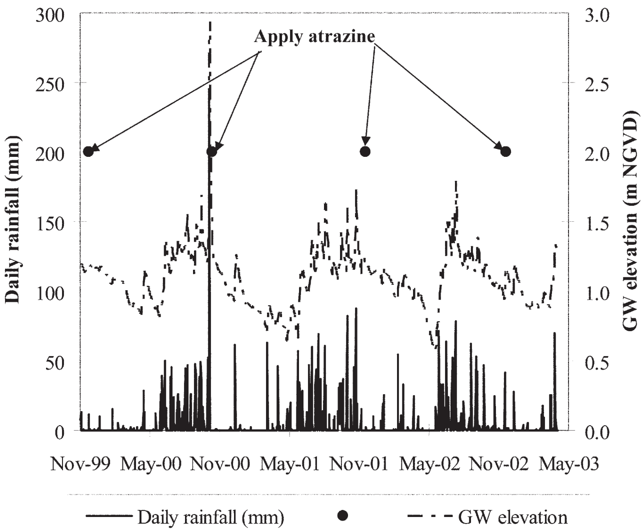

Fig. 2. Rainfall, water table elevation, and timing of atrazine applications. NGVD, National Geodetic Vertical Datum of 1929.

chloride. Eluents were combined and concentrated to 1 mL by evaporation under N_2 gas.

All extracts were fortified with 5 μg of 2-chlorolepidine and analyzed by high-performance liquid chromatography–mass spectrometry (HPLC-MS) using a Thermoquest–Finnigan LCQ DECA ion trap mass spectrometer system equipped with an Atmospheric Pressure Chemical Ionization interface (Thermo-Fisher Scientific, San Jose, CA). The HPLC column was a Beckman Ultrasphere ODS (4.6 mm i.d. × 150 mm) (Beckman-Coulter Inc., Fullerton, CA). Column temperature was maintained at 40°C. Gradient elutions at 1 mL min^{-1} were made with 0.026 *M* formic acid (pH adjusted to 3.5 with NH_4OH) (A) and methanol (B). Initial conditions, 90% A–10% B held 1 min, were changed linearly to 10% A–90% B in 14 min. Conditions were then held isocratic for 2 min. Before each use, the MS response was optimized on $m/z^+ = 198$ while infusing a 10 μg mL^{-1} mixture of hydroxyatrazine (HA), atrazine, DEA, and desisopropylatrazine (DIA) dissolved in methanol. These compounds were targeted in all analyses. Base peaks of MS spectra (HA, $m/z^+ = 198$; atrazine, $m/z^+ = 216$; DEA, $m/z^+ = 188$' and DIA, $m/z = 174^+$) were used for quantitation. The method detection limit (MDL) for all analytes, 0.010 μg L^{-1}, in water samples was estimated from the lowest concentration standard used in calibrations and extraction and concentration of 500-mL water sample to 1 mL. Detections in selected samples were confirmed by operating the MS in the MS–MS mode while monitoring fragments produced by collisionally induced dissociation of $(M+H)^+$. The MS–MS data obtained from analysis of sample extracts closely matched data obtained during analysis of standards.

Matrix spikes for water samples were prepared by fortifying one of the three replicate well samples obtained with scheduled sample sets with a mixture of the target compounds. The spiking rate was equivalent to increasing the concentration of each analyte by 1 μg L^{-1}. Matrix spike recoveries ($n = 54$) averaged 103 ± 9.4% for DIA, 97 ± 12% for HA, 100 ± 12% for DEA, and 99 ± 13% for atrazine. The average relative percent deviations of duplicates were as follows: DIA, 16 ± 13%; HA, 19 ± 17%; DEA, 17 ± 16%; and ATZ, 14 ± 14%. Analytical spike recovery and relative percent deviation met generally accepted quality assurance criteria (USEPA, 2000). None of the target analytes was detected in field blanks. The time-zero samples from incubations using soil samples collected in 2002 were used as matrix spikes. Atrazine recoveries were 98 ± 3.3% for COV and 97 ± 1.3% for NOCOV samples, respectively.

Data Analysis

Data from canal samples and the six wells within plot boundaries and the three UGRD and DGRD wells nearest plots were evaluated by analyte, year, and season (dry or wet) when samples were collected (Fig. 1). The dry season was defined as the period between 1 May and 31 October, and the wet season was defined as the period between 1 November and 30 April. One UGRD well was damaged during tillage, which prevented sample collection on 35 occasions during 2000 and 2001. A new well was drilled at the end of 2001. A small number of samples (<1.5%) from COV, NOCOV, and DGRD well groups was lost during shipment. No adjustments in data were made for missing or lost samples. The MDL (0.010 μg L^{-1}) was substituted for all < MDL results. Medians were compared by sample group, analyte, and season (wet and dry) by Kruskal-Wallis ANOVA on ranks. This procedure was used because preliminary testing showed that data sets were not normally distributed. Pair-wise comparisons of COV and NOCOV plot sample means of the sum of chlorotriazines (CT) (i.e., atrazine plus DEA and DIA concentrations expressed as "atrazine equivalents") were made for each date that samples were collected using unpaired *t* tests. Testing showed that all but two of the 83 data sets met normality and equality of variance assumptions. The probability used to determine that means or medians were significantly different was $P = 0.05$. All test statistics were computed using SigmaStat 3.1. Soil incubation data were to fit to a first-order rate equation. In these calculations, data obtained from samples collected in 1999 before installation of treatments were pooled across all plots.

Results and Discussion

Rainfall and Water Table Response

Rainfall during the study period followed the region's monsoonal pattern with a wet season in May to October and dry season in November to April (Fig. 2). Eighty-seven percent to 94% of total annual rainfall was received during wet seasons and 6 to 13% in dry seasons, and seasonal and annual rainfall totals were close to long-term averages (LTA) (Table 1). The exception was the 2000–2001 dry season when rainfall was about one third the LTA. Although this dry season had relatively little rainfall, the following wet season had slightly more rain than the wet season LTA; thus, annual totals were relatively close to the LTA (Table 1).

The same seasonal trends were observed when the number of large (>25.4 mm) storm events were evaluated (Table 1). Most (86–100%) occurred during wet seasons, and seasonal and annual totals of the number of these events were close to the regional LTAs (Table 1). Large events were notable because they likely exceeded the water-holding capacity of the soil, thereby promoting leaching. The volumetric water con-

Table 1. Total irrigation applied to sweet corn and rainfall and number of storm events >25.4 mm during wet and dry seasons and corresponding long-term averages at University of Florida Tropical Research and Education Center, Homestead, FL.†

Period	Dry season			Wet season		12-mo total	
	Irrigation	Rain	Events‡	Rain	Events	Rain	Events
	——mm——			mm		mm	
1999–2000	208	224	0	1437	19	1661	19
2000–2001	336	87	2	1361	23	1448	23
2001–2002	455	159	2	1542	12	1701	14
2002–2003	533	228	3	–			
Long-term average§		250	2.4	1333	15.2	1583	18

† Dry season: November to April; wet season: May to October; 12 mo total: November to October.

‡ Number of events >25.4 mm rainfall.

§ Summarized from National Climate Data Center Records for the period 1948–1988 (NCDC, 2006).

tent of Krome soils at field capacity was reported to be 0.18 to 0.20 $m^3\ m^{-3}$, and bulk density and soil depth to the limestone were typically 1400 Mg m^{-3} and 0.15 m, respectively (Noble et al., 1996; Al-Yahyai et al., 2006). These data indicate that water held in the soil profile after free drainage is about 25.4 mm of rain (i.e., the minimum depth of a “large event”).

Trends in water table elevation tracked rainfall patterns (Fig. 2). During dry seasons, there was a steady decline in elevation, with little perturbation due to rainfall. During wet seasons, elevation trended higher and was more variable responding rapidly to rainfall recharge. Comparison of rainfall and water elevation records for the study period showed that large events (>25.4 mm) produced on average a corresponding rise in the water table of 2.5 times the rainfall depth within 24 h. This value agreed with estimates of near-surface porosity (about 0.42 $m^3\ m^{-3}$) of the limestone (Schmoker and Halley, 1982).

Seventeen to 25 mm of water was applied to corn crops every 3 to 5 d during growing seasons with the water drawn from a 25-cm diameter borehole drilled to a depth of 10 m about 30 m downgradient of the plots. Total irrigation amounts were 208 to 533 mm, 0.9 to 3.8 times total rainfall during corresponding dry seasons (Table 1). Pumping during irrigation had the potential to influence local groundwater gradients. However, given pumping rates (about 13 L s^{-1}) and aquifer properties, any impact on gradients was likely small and transient. Using aquifer parameter data and the Neuman unconfined well function equation, estimated drawdown in the monitoring well that was nearest the irrigation borehole was less than 0.3 mm at the end of irrigation periods (Freeze and Cherry, 1979; Genereux and Guardiaro, 1998; Bolster et al., 2001).

Together, rainfall and water table elevation data showed that climatic and hydrologic conditions during the study reflected long-term regional trends with most rainfall and groundwater recharge occurring during wet seasons between May and October. During dry seasons (November–April), when corn crops were produced, combined rainfall and irrigation were about threefold less than wet-season rainfall. This pattern explained water table elevation response, with elevations steadily declining during dry seasons when crops were produced and increasing during summer fallow periods.

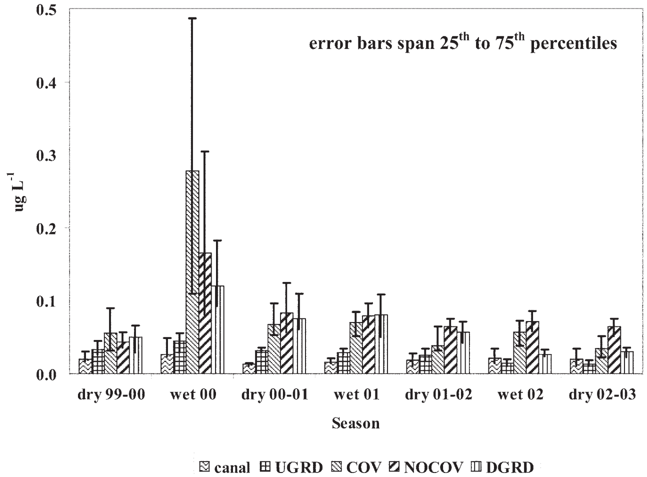

Fig. 3. Median atrazine concentration in canal and well samples by season (wet and dry) and year when samples were collected.

Atrazine Inputs

Measured atrazine application rates (average ± 1 SD) were 2.2 ± 1 kg ha^{-1} in 1999, 2.5 ± 0.5 kg ha^{-1} in 2000, 1.8 ± 0.4 kg ha^{-1} in 2001, and 2.1 ± 0.5 kg ha^{-1} in 2002. In total, each plot received 1.1 ± 0.2 kg atrazine. This was close to the target amount of 1.0 kg. The percent relative SD (20–45%) also indicated that applications were relatively uniform.

Trends in Atrazine and Degradates Concentration in Water Samples

Initially and throughout the first dry season, atrazine and degradates concentrations in canal and groundwater samples were nearly equal across the study site, with low concentrations (<0.1 μg L^{-1}) of all compounds detected in nearly all samples (Fig. 3–6). Differences in medians were small and not significant. Hydroxyatrazine predominated, accounting for 53 to 69% of total measured atrazine residues on a molar basis.

These observations suggest that residues detected in canal and

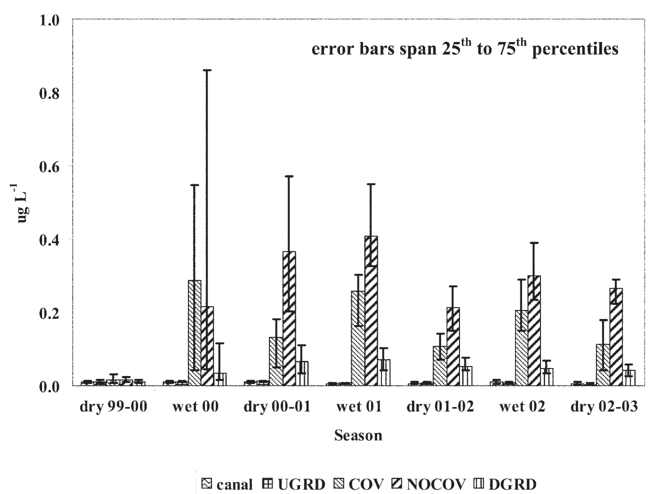

Fig. 4. Median desethylatrazine concentration in canal and well samples by season (wet and dry) and year when samples were collected.

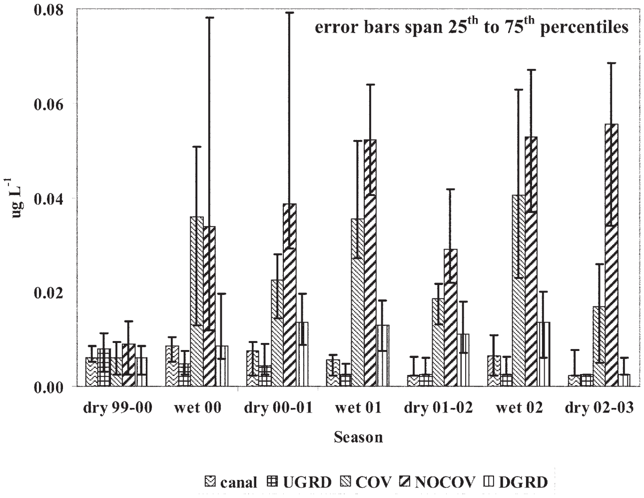

Fig. 5. Median desisopropylatrazine concentration in canal and well samples by season (wet and dry) and year when samples were collected.

groundwater samples had a common source. Exchanges of water between the water table aquifer and canals are a common feature of the region, with the direction of flow governed by water levels in canals (Genereux and Slater, 1999). During most of the year, water levels in the canal that was sampled were above the water table elevation at the study site (Muñoz-Carpena, unpublished data), which created a gradient from the canal to the surrounding aquifer. Thus, it seems that atrazine and degradates in canal water and infiltration into the aquifer contributed the low-levels of these compounds detected in groundwater.

During successive wet and dry seasons, atrazine and degradates concentration in canal and UGRD samples followed the same trend. Concentrations were low, with HA the predominant form of atrazine detected. The only significant difference observed was greater median (about 1.5-fold) HA in canal samples during wet seasons (Fig. 6). The greater HA concentration in wet-season canal samples was likely explained by the manner in which canal flow was regulated. As needed, the local water management authority opened canal gates to route storm water through the regional canal network. When gates were opened, water from upstream locations flowed eastward in the canal sampled in this study, and when gates were closed, some of the water originating from crop production and residential areas to the west and north of the study site was retained behind the gates. The water retained presumably contained HA and/or residual atrazine that was converted to HA. Because in general the canal was hydraulically upgradient, water flowed from the canal into the aquifer S-SE toward the study site. During transport in the shallow groundwater, HA concentration was likely reduced by dilution and/or attenuation, resulting in lower median concentrations in the UGRD wells.

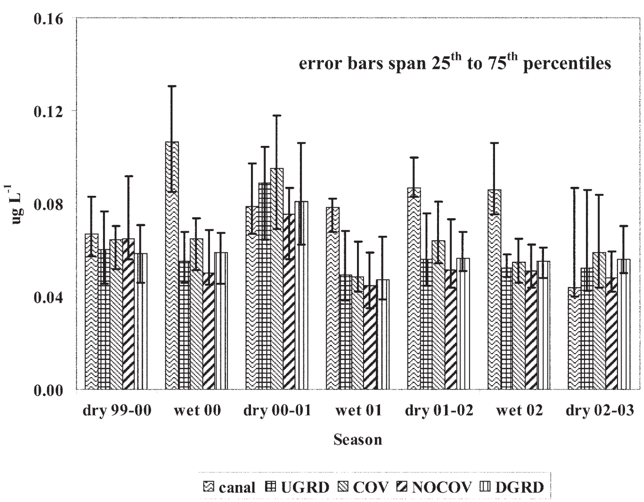

Fig. 6. Median hydroxyatrazine concentration in canal and well samples by year season (wet and dry) when samples were collected.

The HA median concentration in UGRD samples closely matched the medians of the NOCOV, COV, and DGRD well samples in all seasons (Fig. 6). Differences were small and not significant. It seems HA detected in wells beneath and downgradient of plots had an upgradient source rather than being from formation transformation and leaching from treated soil. This behavior is consistent with reports of high soil sorption and persistence in surface and groundwater and low leaching potential when compared with atrazine, DEA, and DIA (Lerch et al., 1999).

Hydroxyatrazine behavior contrasted with atrazine, DIA, and DEA. Their leaching was clearly indicated during the first wet season (2000) after atrazine application. Median concentrations of these compounds in NOCOV and COV plot and DGRD well samples were three- to tenfold greater than corresponding UGRD well sample medians and were significantly different (Fig. 3–5). Atrazine and DEA medians in these samples were approximately equal and were about fourfold greater than the DIA median. In the following dry season (2000–2001), the DEA median remained relatively high, and proportionally the DIA median fluctuated little. However, the atrazine median decreased about fourfold. This pattern persisted during the remainder of the study (Fig. 3).

Atrazine is more strongly sorbed by soil and sediment than DEA and DIA; thus, lower leaching rates were expected (Oliver et al., 2005). However, reported differences in sorption do not seem to explain the results because relatively high atrazine concentrations were found in groundwater samples beneath NOCOV and COV plots in the first wet season (Fig. 3). A more likely reason was an increase in atrazine degradation rate in soil as the number of atrazine applications increased. Repeated atrazine application reportedly enhanced atrazine degradation in many studies (Vanderheyden et al., 1997; Ostrofsky et al., 1997; Houot et al., 2000). Houot et al. (2000) observed that as few as two successive annual atrazine applications accelerated degradation in some soils. Desisopropylatrazine and DEA have also been reported to be more persistent in soils than atrazine (Bottoni et al., 1996); thus, these compounds may have remained in the soil longer and available for leaching.

Laboratory incubations of soil collected after the first atrazine application and of soil collected before the fourth application and spiked with atrazine seemed to confirm this hypothesis. The soil half-life ($t_{1/2}$) determined for the later samples was 13 d for spiked COV and NOCOV samples. The $t_{1/2}$ for the other samples (78 d) was sixfold greater. The first-order rate model fit data well, with a somewhat better fit (r^2 = 0.95) for samples collected after spraying at the beginning of the study versus $r^2 = 0.82$ to 85 for the samples that were collected 1 d before the fourth spray and spiked in the laboratory. The poorer data "fit" for the later samples was due to relatively rapid atrazine dissipation at the beginning of the incubations. This type of behavior is often observed when acclimated pesticide degrading populations develop (Shelton and Doherty, 1997).

The $t_{1/2}$ measured in incubations was in general agreement with other studies. For example, Ostrofsky et al. (1997) reported that $t_{1/2}$ (mineralization) in soil samples without prior atrazine exposure or from fields in a 4-yr rotation with other crops was 27 to 53 d. The $t_{1/2}$ for soil from a field in continuous corn that received annual atrazine applications was 4 d.

Although the data supported the enhanced degradation hypothesis, it is possible that differences in dissipation rates observed in our study were due to the way in which atrazine was applied (field spray versus laboratory spike) to incubated soil. Confirmatory studies may be required.

Because plots were irrigated with groundwater that contained low concentrations of atrazine and selected degradates, there was a second potential source of these compounds to the cropped area. Setting atrazine and degradates concentrations in the irrigation water to maximum levels observed in DGRD wells and using irrigation amounts, total inputs from irrigation were less than 0.15% of atrazine applied. These computations indicated that amounts contributed by irrigation were small when compared with the atrazine application rate.

Water Quality Implications

Atrazine and degradates concentrations were low relatively compared with the USEPA drinking water atrazine maximum contaminant level (MCL) (USEPA, 2003). Atrazine was below the MCL (3 $\mu g\ L^{-1}$) in all samples, and the sum of measured chlorotriazines expressed in atrazine equivalents (CT) exceeded the MCL in only 0, 0, 0.4, and 2% of UGRD, DGRD, COV, and NOCOV samples, respectively. Examination of temporal trends also showed that all but one of the samples in which CT concentration exceeded the MCL was collected during the first wet season after beginning the study (Fig. 3–5). In all subsequent seasons, CT in all samples was less than the MCL. This pattern was likely explained by enhanced atrazine degradation as described previously.

Spalding et al. (2003) found much higher levels of atrazine, DEA, and DIA in shallow groundwater immediately downgradient of atrazine treated fields in central Nebraska. The CT concentration in all cases was greater than the MCL. This was observed even though the unsaturated zone was a 1.1-m thick layer of well drained silt loam and the organic C content of the surface soil was 10 to 15 $g\ kg^{-1}$. At our study site, soil properties indicated a much lower potential for atrazine retardation and retention in the unsaturated zone. Countering this were climatic and cropping patterns that contributed little leaching during the 4 to 6 mo after herbicide application and potential for substantial dilution in the highly productive Biscayne aquifer.

Recently, the USEPA determined that atrazine and its chlorotriazine degradates DEA, DIA, and the fully dealkylated product (2,4-diamino-6-chloro-s-triazine) (DACT) were equivalent in terms of their toxic potential. Based on this logic, the

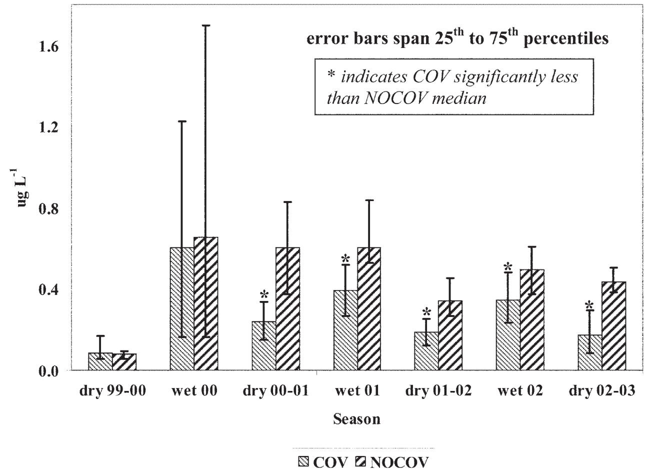

Fig. 7. Median measured chlorotriazine concentration in no cover crop plot and cover crop plots well by season. Chlorotriazine (CT) level is expressed in "atrazine equivalents." COV, cover crop plots. NOCOV, no cover crop plots.

sum of atrazine and these degradates was compared with the MCL to evaluate drinking water quality risks (USEPA, 2003). The degradate DACT was not targeted in our analyses in part because the compound is a challenging analyte that is not readily detected with methods commonly used for atrazine, DEA, and DIA (Huang et al., 2003). Unpublished registrant data have indicated that DACT was commonly detected in groundwater at atrazine use sites (USEPA, 2003). More complete characterization of drinking water quality risks from atrazine use in South Florida may require future DACT measurements.

Cover Crop Impacts

Because data showed that atrazine applications resulted in increased atrazine, DEA, and DIA concentration in groundwater, the affects of the cover crop treatment were evaluated on the basis of their sum, CT. During the study's first year, NOCOV and COV plots behaved similarly. There was little difference in CT medians in groundwater when compared by season (wet and dry), and these differences were not significant (Fig. 7). None of the sample sets (by date collected) had means that differed significantly (Table 2). This was anticipated because the first cover crop was not planted

Table 2. Percentage of cover crop plots (COV) and no cover crop plots (NOCOV) sample sets ($n = 83$) with means significantly different ($P = 0.05$) when compared by season and cover crop management‡

	Percentage of total sample sets¶	
Season	COV > NOCOV	NOCOV > COV
Dry, 1999–2000 ($n = 6$)†	0	0
Wet, 2000 ($n = 13$)	0	0
Dry, 2000–2001 ($n = 11$)	0	27
Wet, 2001 ($n = 11$)	0	18
Dry, 2001–2002 ($n = 12$)	0	50
Wet, 2002 ($n = 19$)	0	36
Dry, 2002–2003 ($n = 13$)	0	69

† Dry season: November to April; wet season: May to October.
‡ Unpaired *t* test.
¶ COV = cover crop plots, NOCOV = no cover crop plots.

Table 3. Average (SD) soil organic carbon.

Date collected	Organic carbon	
	COV‡	NOCOV
	g kg^{-1}	
November 1999 (n = 6)†	11 (0.9)	11.4 (1.0)
November 2001 (n = 9)	16.1* (1.1)	13.8 (1.9)
February 2002 (n = 3)	19.4* (1.8)	14.7 (1.6)
November 2002 (n = 3)	17.4* (0.2)	14.1 (0.8)
April 2003 (n = 3)	14.2 (0.7)	12.2 (1.6)

* Difference in means was significant (P = 0.05).

† Organic carbon content of samples collected in 1999 was estimated using the measured total organic nitrogen content and the average carbon to nitrogen ratio (18) in all NOCOV samples.

‡ COV, cover crop; NOCOV, no cover crop.

until about 6 mo after the first atrazine application; thus, there was little potential for the crop to influence atrazine environmental fate.

In subsequent years, the cover crop biomass was tilled into the soil 3 to 4 wk before atrazine application. Studies by Li et al. (2006) have indicated that Sunn Hemp typically yields about 5 Mg ha^{-1} in South Florida, making it one of the highest-yielding cover crops suitable for use in the region. Incorporation of the dry matter into soil during our study apparently contributed to much lower (two- to threefold) median CT concentrations in groundwater beneath COV plots. The COV plot well medians were significantly less than corresponding NOCOV values beginning in the dry season of 2001 (Fig. 7).The number of samples sets (by date) in which the NOCOV was significantly greater than COV mean also increased progressively. During the last sample period in which samples were collected (the 2002–2003 dry season), the NOCOV was significantly greater than the COV mean nearly 70% of the time (Table 2).

The close agreement in HA results across the study site (Fig. 6) also suggested that groundwater flow beneath plots was uniform; thus, lower CT loading of groundwater beneath COV plots was inferred. The potential loading difference when compared with NOCOV plots was estimated by numerical integration of the areas under the curves of the CT–date of sample collection plots. The COV was 33% lower than the mean of the NOCOV, but the difference was not significant. The one-tail test of NOCOV > COV yielded P = 0.15.

Soil C measurements suggest that CT concentration differences in groundwater were linked to increased atrazine soil sorption. Soil organic C showed an increasing trend in samples from COV and NOCOV plots, with the greatest increase on COV plots (Table 3). In three out of four sets of samples collected in years after cover crops were planted and residues turned into soil, COV plot soil organic C means were significantly greater than NOCOV plot means (Table 3). The mean difference, although modest (2.0–4.7 g kg^{-1}), was apparently enough to retard atrazine, DIA, and DEA leaching. Retardation presumably retained the compounds in the biologically active zone near the soil surface where degradation was more likely. Increased soil organic C content on COV plots would have increased soil water holding capacity and reduced leaching.

Bottomley et al. (1999) and Gaston et al. (2003) reported that planting cover crops and turning residues into soil increased soil organic C and soil sorption of 2,4-D and fluometuron. Degradation rates of these compounds were increased when cover crop and no cover crop treatments were compared. Increased rates of degradation on the COV versus the NOCOV plots may have occurred during our study, but this was not indicated in laboratory soil dissipations. Incubations of samples collected from COV and NOCOV plots 1 d before the fourth atrazine application and spiked with atrazine gave identical $t_{1/2}$ (13 d). This value was about sixfold less than the value obtained from incubations of soil collected immediately after the first atrazine application. The change in rate, which was attributed to the development of enhanced degradation conditions, likely overwhelmed any effects that may have been observed due to increased biological activity on COV plots.

Another possible effect of the cover crop was increased evapotranspiration (ET). Increased ET had the potential to decrease leaching. If increased ET affected CT concentrations in groundwater, it is anticipated that the magnitude of the difference in medians between COV and NOCOV samples would have been greater in wet seasons when compared with dry seasons. This trend was not observed; thus, the potential for increased ET on cover crop plots to affect CT concentrations was likely small. Atrazine was applied at the beginning of dry season, and there was a period of approximately 6 mo before cover crops were established. During this period, extensive atrazine degradation was indicated. When wet seasons began and cover crops were established, there was little atrazine or degradates in soil available for leaching.

Conclusions

Data indicated that atrazine use for sweet corn production may negatively affect groundwater quality in southern Florida. The greatest threat was from DEA, which was the principal form of atrazine detected in groundwater samples. Hydroxyatrazine leaching was not observed.

Although the potential for adverse water quality effects was indicated, few (<3%) samples collected directly beneath treated plots had CT levels that exceeded the drinking water MCL in spite of the fact that the soil at the study site was shallow and porous and the water table surface was typically 1 to 3 m below the soil surface. Climatic and cropping patterns and relatively rapid atrazine degradation in soil and high dilution rates in the aquifer were likely controlling factors.

Results also showed that the use of a cover crop during summer fallow periods contributed to significantly lower atrazine and degradates concentration in groundwater. Up to 33% lower CT loading was indicated if groundwater flow beneath plots was assumed uniform. Growers in the region should be encouraged to adopt this practice more widely to minimize water contamination associated with normal agricultural use of atrazine. Others benefits anticipated include enhanced soil quality and reduction in the leaching of other pesticides.

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