

ATRAZINE AND NITRATE-NITROGEN LEACHING THROUGH UNDISTURBED SOIL COLUMNS AS AFFECTED BY LIME APPLICATION

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ABSTRACT. Farm operators need information that enable them to select a combination of farming systems that minimizes the movement of agricultural chemicals into water sources. Agricultural lime (CaCO_3) applied to the soil to reduce soil acidity, can affect the movement and fate of agricultural chemicals in the soil. A laboratory study was conducted to determine the effects of three application rates of lime (0, 5 and 10 Mg ha^{-1}) on atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5 triazine) and nitrate-nitrogen ($\text{NO}_3\text{-N}$) transport through undisturbed-unsaturated soil columns. Urea (H_2NCONH_2) and atrazine were applied on the surface of soil columns one month after mixing lime in the top 20 mm of surface soil of these columns. Five different irrigations, totaling 36.5 cm of distilled deionized water, were used in this study. The results indicate that lime application had no significant effect on the leachate depth and pH. An increase in lime application rate increased the concentrations of Ca and $\text{NO}_3\text{-N}$ in the leachate. The concentration of $\text{NO}_3\text{-N}$ in the leachate increased with increased irrigation events for limed soil columns. The concentration of atrazine in the leachate increased significantly with increased lime application rates and decreased with subsequent irrigation events.

Keywords. Leaching, Lime, Atrazine, Nitrate-nitrogen.

In the agricultural sector, farmers use different types of chemicals for various cropping systems in order to increase yields and maximize benefits. Pesticide application, ammonium-nitrogen fertilization, and liming are common agricultural practices aimed at improving soil environment for plant growth and development. However, some of these chemicals may potentially pollute surface water and groundwater resources if not properly applied. Groundwater contamination by agricultural chemicals was reported by over 800 of the 1437 counties in the U.S. (National Research Council, 1989). The rate at which agricultural chemicals dissipate in the soil is influenced by many factors, including the method of application, chemical and physical properties of the soil, and the soil management history (Weed et al., 1995).

Agricultural chemicals left on the soil surface are lost through plant uptake, leaching, volatilization, photodegradation, chemical and microbial degradation, and transport in surface runoff (Smith and Wills, 1985). Surface applied fertilizers and pesticides are particularly susceptible to loss through surface runoff or downward movement into the soil profile by leaching with water

(Kanwar et al., 1990). Pesticides that migrate into no-till surface soil may be adsorbed and degraded more quickly than in conventionally tilled soil, due to more organic material and a more active microbial population (Fermanich and Daniel, 1991). Weed et al. (1995) reported that the fast rate of alachlor [2-chloro-2', 6'-diethyl-N-(methoxy-methyl) acetanilide] degradation prevented it from leaching as deeply as atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5 triazine) which was the most frequently detected pesticide in rural drinking wells in Iowa and other groundwater studies (Hallberg, 1989).

The application of agricultural chemicals also change physical and chemical conditions of the soil. Smith and Wills (1985) reported more than 30-fold DDT [1, 1, 1-trichloro-2, 2-bis-(P-chlorophenyl) ethane] leached when alkaline urea fertilizer was added. The downward movement of DDT was attributed to the fact that alkaline urea increased the pH, thereby enhancing the dispersion and leaching of humic acids that serve as carrier substances for DDT. The authors also found concentrations of metribuzin in the leachate decreased with an increase in anhydrous NH_3 . The decrease in metribuzin was attributed to the fact that alkali-solubilized humic substances promote decomposition of metribuzin and atrazine in fulvic acid solutions.

Ammonium-forming fertilizers added to soils that are not naturally acidic, slowly decrease the pH (Clay et al., 1993). Soils also become more acidic when there is leaching of nitrate nitrogen, build-up of organic matter, and removal of crop produce. Acidification leads to significant changes in microbial dynamics and consequently in nitrification rates. Some soils have large amounts of natural "lime" to convert H^+ (acidic conditions) into water and they have lots of organic matter and clay to bind the H^+ removing it (temporarily) from the soil solution. Other soils quickly lose the ability to buffer the H^+ in the soil,

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and allow the H⁺ to build up in the soil water. Once the soil has lost its ability to deactivate H⁺, it is likely to become even more acidic if H⁺ is added to it.

In order to reduce or neutralize soil acidity and maintain proper pH for crop production, agricultural lime (CaCO₃) is added to replace the hydrogen ions by mass action (Follett et al., 1981). Lime reduces aluminum (Al) and manganese (Mn) to subtoxic levels, and affects the soil's ability to retain anions and cations. Liming increases nitrification rates (expressed as percentages of NH₄-N added) from 27% for untreated (0 kg ECCE ha⁻¹) to 76% for treated (17920 kg ECCE ha⁻¹) soils (Senwo, 1995). Senwo concluded that liming stimulated the microbial population responsible for nitrification in soils. Azevedo et al. (1996) investigated the movement of NO₃-N and atrazine through soil columns as affected by lime application and found that atrazine and NO₃-N concentrations in leachate were higher for limed soil columns compared with unlimed soil columns.

Studies on the interaction of lime, fertilizers, and pesticides applied to the soil are needed to determine management practices for better strategies in manipulating the soil-plant system for improved soil, water, and environmental quality. Farm operators need information that will enable them to select a combination of farming systems that will minimize the movement of agricultural chemicals into water sources (Kanwar et al., 1990). Azevedo et al. (1996) investigated atrazine and urea applied to soil columns immediately after lime application. However, samples were limited to two days after lime application. This procedure did not allow enough time for the agricultural lime to interact completely with the soil and chemicals. Thus, the objective of this study was to lengthen the interaction time and conduct leachate studies on atrazine and urea. The specific objects were to investigate the effect of lime on the movement of NO₃-N and atrazine through undisturbed soil columns under unsaturated soil moisture conditions.

MATERIALS AND METHODS

EXPERIMENTAL SITE

Soil columns were collected from a research farm located at the Iowa State University Agronomy and Agricultural Engineering Research Center near Boone, Iowa. The site was under no-till continuous corn (*Zea mays* L.) production between 1984 and 1991 receiving an annual application of 175 kg N ha⁻¹. Since 1992, the field has been under a chisel plow management system and a yearly rotation of corn and soybeans (*Glycine max* L.), with corn in odd-numbered years and soybean in even-numbered years. Since 1992, alachlor has been applied to both corn and soybean plots at a rate of 2.2 kg ha⁻¹ active ingredients (a.i.), cyanazine and nitrogen fertilizer have been applied to corn plots at rates of 2.8 kg ha⁻¹ and 112 kg N ha⁻¹, respectively, and metribuzin has been applied to soybean plots at 0.45 kg ha⁻¹. During the study year (1996) the field was planted in soybeans. The soils at the research farm are classified as Nicollet-loam in the Clarion-Nicollet-Webster Soil Association and are characterized as fine loamy, mixed mesic aquatic Hapludoll with moderate permeability and somewhat poor drainage and 3% organic matter (table 1).

Table 1. Selected properties of the soil at the experimental site

Soil Properties Measured	Depth of Soil Sampling (cm)		
	0-15	15-30	30-60
Saturated hydraulic conductivity (K, cm s ⁻¹)	3.6E-8	3.45E-8	1.92E-8
Bulk density (g cm ⁻³)	1.46	1.51	1.51
Particle density*	2.61	2.61	2.61
Volumetric moisture content (%)	17.20	19.50	19.70
C: N ratio†	14.10	13.80	12.2
Soil pH	5.50	5.30	5.00
Texture*			
Sand (% by volume)	48.4	50.3	60.3
Course silt (% by volume)	17.8	16.6	14.6
Fine silt (% by volume)	13.3	12.8	8.8
Clay (% by volume)	20.5	20.3	16.3
Atrazine conc. (µg L ⁻¹)	0.02	0.01	0.01
NO ₃ -N conc. (mg L ⁻¹)	2.88	2.73	2.10

* From Azevedo et al., 1996.

† From Senwo, 1995. C:N ratios of the extracted soil organic matter.

These soils are derived from glacial till and have a slope of less than 3% (Kanwar et al., 1990).

SOIL COLUMN COLLECTION PROCEDURES

In July of 1996, nine undisturbed soil columns 20.3 cm in diameter and 60 cm in length were randomly collected from the field. In order to obtain an undisturbed soil column from the field, a circular trench was dug with hand shovels to a depth of 70 cm, leaving an undisturbed pedestal of soil about 50 cm × 50 cm in the center of the trench. A furnace pipe (20.3 cm in diameter and 60 cm in length) was placed in the center of the undisturbed pedestal of soil. Before the furnace pipe was pushed into the soil, the soil pedestal was shaved off to form a pedestal of about 20 cm in diameter and 15 cm in length. The furnace pipe was then gently slid downward to encase the column. Care was taken to avoid compaction of the soil column. The soil column was shaved off to another 15-cm depth-increment and the pipe was slid down to encase another 15 cm of undisturbed soil column. This process was continued until the desired 60-cm-long column was obtained without any soil compaction. The soil column was cut below the 60-cm depth and trimmed evenly at the end of the pipe without any smearing. Styrofoam™ blocks and tape were used to tightly secure both ends of the column. The entire column was then placed in a large polyethylene bag and sealed to ensure no loss of moisture. The columns were taken to the laboratory and stored in a cooler at 4°C until used in laboratory experiments.

SOIL SAMPLING PROCEDURES

Twenty-four soil samples and 24 small soil cores (7.6 cm in diameter and 15 cm in length) (two at each depth) were collected at depths of 15, 30, and 45 cm close to where soil columns were collected. Soil core sampler was used to collect soil cores. Some soil compaction could have occurred thereby affecting the saturated hydraulic conductivity (table 1). Soil samples were used to determine the general characteristics (like pH, moisture content, atrazine, and NO₃-N concentrations) of the soils at the experimental site. The soil cores were used for laboratory analysis of bulk density and saturated hydraulic conductivity. The average soil moisture content determined

from the soil samples was used to calculate the bulk density and then average pore volume for the soil columns.

SOIL CHEMICAL ANALYSIS

Soil samples were analyzed for NO₃-N, atrazine, Ca, and pH at the Water Quality Laboratory of the Agricultural and Biosystems Engineering Department, Iowa State University, Ames, Iowa. Analysis of soil pH was done using a pH meter. Each soil sample was mixed with distilled water and shaken for an hour before measuring the pH. An electrode, connected to a pH meter, was placed in the mixture for about 10 s before a stable pH reading was recorded.

The atrazine concentrations were determined by mixing 25 g of soil with 50 mL of toluene in a flask and then shaken for 1 h on an automatic shaker at a speed of 2500 rpm. The samples were allowed to settle for 24 h, after which toluene was decanted into 10 mL test tubes. Toluene extracts were analyzed using a Tracor Model 560 gas-liquid chromatograph, equipped with a "nitrogen-phosphorus" detector, a Model 730 autosampler, and a 3% OV-1, 0.63-cm diameter × 1.8-m long packed column. Flow rates of 18 cm³ min⁻¹ were maintained for helium (carrier gas), 2.5 cm³ min⁻¹ for hydrogen (reaction gas), and 100 cm³ min⁻¹ for air (reaction gas). Splitless injections of 8 µL were made with the injector maintained at 245°C, the oven temperature at 160°C, and the detector temperature at 245°C. The detector output was connected to a chart recorder, and the data were processed with a SP Model 4270 integrator where the area data for the atrazine peaks were obtained.

The concentration of NO₃-N was measured by mixing 25 g of soil with 110 mL of 2 N (normal) potassium chloride (KCl) solution. The mixture was stirred for 1 h on an automatic shaker, and then allowed to settle for 24 h. After settling, the clear liquid (extract) was decanted into test tubes. The extract was later analyzed with a Lachat Model AE ion analyzer that converted the colorless NO₃-N in the filtrate to a pink water-soluble dye. The analyzer then measured the color intensity (absorbance) using a spectrophotometer. The color intensity was proportional to NO₃-N concentrations in the extract.

PREPARATION OF SOIL COLUMNS FOR LEACHING STUDIES

In the laboratory, the furnace pipe was carefully opened and removed to expose the soil column. A metal pipe 20 cm in diameter and 60 cm in length (1.9 × 10⁴ cm³) was centered around the soil column and slid down until the whole soil column was inside the metal pipe. Any gap between the soil column and metal pipe was filled with molten paraffin wax to prevent boundary flow (Singh and Kanwar, 1991; Weber et al., 1986). After sealing the gaps, a regular wire screen, cheese cloth and 10-mesh wire (2 mm) were placed at the bottom of the soil column in order to hold the soil and to minimize collection of sediment in the leachate. Soil columns were then covered with aluminum foil to minimize moisture loss by evaporation.

Lime, Nitrogen, and Atrazine Application. On 22 July 1996, agricultural lime was applied at rates of 5 Mg effective calcium carbonate equivalent (ECCE) ha⁻¹ (29.2 g-lime per soil column) to three soil columns; 10 Mg ECCE ha⁻¹ (58.4 g-lime per soil column) to three other soil columns, and no lime was applied to the remaining three

soil columns. The source of the agricultural liming material applied in the soil columns had an effective calcium carbonate equivalent of 55.4%. Lime was incorporated into the top 20 mm of the soil using a spatula. After lime application, soil columns were covered with aluminum foil to minimize loss of moisture and were kept in the lab at room temperature (25°C) for one month. The one-month period was necessary for the lime to react with the soil.

Atrazine and urea (H₂NCONH₂) were applied on 22 August 1996 (1 month after applying lime). Urea in granular form was surface applied to each soil column at a rate of 200 kg-N ha⁻¹ (1.4 g-urea per soil column) and was incorporated into the top 20 mm of soil with a spatula. Then, atrazine (80% active ingredient in wettable powder formulation) was applied on the surface of each soil column in a granular form at a rate of 2.8 kg atrazine ha⁻¹ (11.3 mg per soil column). The atrazine granules were also incorporated into the top 20 mm of soil with a spatula. Soil columns were then covered with aluminum foil and were allowed to incubate for 1 week at 25°C.

Column Leaching. After incubation, five different irrigations using deionized distilled water were applied to the columns for leaching experiments. These water quantities were chosen to represent comparable rainfall amounts received during the spring months in Iowa (Sallade and Sims, 1993). The first irrigation (117 mm) was applied on 27 August 1996 (five weeks after the application of lime and one week after the application of atrazine and urea) over a 3-h period. The subsequent four irrigation events were applied at one-week intervals, at a rate of 62 mm over a 2-h period. During each irrigation event, water was applied to the surface continuously with a Marriott bottle arrangement without letting any water pond on the surface until all the water had infiltrated the column.

Leachate samples were collected at the bottom of each soil column using glass bottles. For each irrigation event, leachate samples were collected at 30, 60, 120, 180, and 360 min. These time intervals were used because not enough leachate for atrazine analysis could be collected in less than those time intervals due to low flow rates. After each irrigation event, soil columns were covered with aluminum foil to minimize evaporation. The leachate samples were kept in a cooler at 4°C until the analyses for pH, atrazine, Ca, and NO₃-N concentrations were conducted in the laboratory.

CHEMICAL ANALYSIS OF WATER SAMPLES

Leachate samples for each irrigation event were analyzed for atrazine using different extraction ratios with toluene. For the first irrigation, 50 mL of leachate sample was mixed with 100 mL of toluene; for the second and third irrigation events, 50 mL of leachate sample was mixed with 50 mL of toluene; and for the fourth and fifth irrigation events, 100 mL of leachate sample was mixed with 25 mL of toluene. The extraction ratios were chosen because the concentration of atrazine in the leachate was expected to decrease for each additional irrigation event. The mixture was shaken on an automatic shaker for 1 h at a speed of 2500 rpm. After shaking, the mixture was allowed to set for 24 h, and then toluene was decanted into 10-mL glass test tubes. The concentration of atrazine was then analyzed by using a gas-liquid chromatograph.

The concentration of NO₃-N in the leachate was analyzed using an automated cadmium-reduction method (Standard Methods 4500 NO₃-F) and a Technicon Autoanalyzer II. The NO₃-N in the samples was reduced to nitrite-nitrogen (NO₂-N). The NO₂-N was diazotized with sulfanilamide and then reacted with N- (1-naphthyl)-ethylenediamine dihydrochloride at a pH of 8.5 to form a colored (pink to red) azo dye. The dye's absorbance was measured at a wavelength of 520 nm with a colorimeter. Then the NO₂-N was determined by comparing sample absorbance with those obtained from a calibration curve comprised of standards containing NO₂-N concentrations of 0.125 to 2.00 mg L⁻¹. The results of NO₃-N concentration by this method and the previously discussed Lachat Model AE method were the same.

The concentration of Ca in the leachate was analyzed by using the direct air-acetylene flame method (Standard Methods 3111 B) with atomic absorption spectrometry equipment. Analysis of leachate pH was completed using a pH meter. An electrode connected to a pH meter, was placed in the leachate sample for about 10 s before a stable pH reading was recorded.

STATISTICAL ANALYSIS

The concentrations of atrazine, Ca, and NO₃-N in the leachate were converted into flow weighted concentrations and then analyzed using a split-plot analysis. The amount of leachate and its pH data were also analyzed using split-plot analysis.

RESULTS AND DISCUSSION

LEACHATE FLOW

Statistical analysis of data on the amount of leachate indicate that there was no significant difference between the leachate amounts for different lime application rates (table 2). The results also show that for all treatments, the amount of leachate collected during the first 30- and 60-min time intervals from the beginning of the leaching event, were higher compared with the leachate amounts from the subsequent sampling time intervals (table 2). This trend was due to the fact that at the beginning of irrigation, the soil was relatively dry and the presence of more macropores resulted in higher infiltration (normal infiltration characteristics of soil). The data also show that irrigation events had no significant effect on the depth of leachate in all treatments. The amount of leachate drained for each treatment (expressed as a percent of the amount of irrigation water added to the columns) ranged from 75.5 to 91.5% for soil columns with no lime application rate, 75.3 to 94.0% for soil columns treated with 5 Mg ha⁻¹ lime application rate, and 63.7 to 91.0% for soil columns treated with 10 Mg ha⁻¹ lime application rate. These results show that an increase in volumetric water content in the soil columns ranged from 9.1% for non-limed soil columns to 12.1% for soil columns treated with 10 Mg ha⁻¹ lime application rate.

LEACHATE pH

Statistical analysis of leachate pH indicate that there were no significant differences between lime application rates (table 3). This could be due to the fact that the soil had high buffering capacity to resist change in pH and/or

Table 2. Statistical analysis of the average amount of leachate (mm) as a function of lime application

Sampling Time	Irrigation Event					Total*
	1	2	3	4	5	
	-----Leachate (mm)-----					
0 Mg ha⁻¹ lime						
30	81.3	27.8	26.9	27.4	28.7	192.2a
60	14.4	19.4	22.4	27.4	19.6	99.3b
120	6.5	3.4	2.8	23.5	2.1	17.3c
180	1.5	3.1	1.4	2.1	1.2	8.5c
360	2.0	1.9	2.2	1.3	1.8	10.3c
Irrigation total†	105.6a	56.1a	55.9a	56.5a	53.5a	
Treatment total‡		327.5a				
5 Mg ha⁻¹ lime						
30	72.2	27.6	25.9	27.1	27.6	180.4a
60	10.7	17.7	21.7	24.7	22.0	96.8b
120	2.6	3.4	2.1	2.3	2.0	12.4c
180	1.2	2.2	1.5	1.4	1.4	7.8c
360	1.5	2.3	2.5	2.5	2.2	11.0c
Irrigation total	88.1a	53.3a	53.8a	57.9a	55.3a	
Treatment total		308.4a				
10 Mg ha⁻¹ lime						
30	63.6	27.6	24.9	27.6	27.7	171.4a
60	6.2	19.6	21.5	20.9	22.0	90.2b
120	2.2	2.7	2.3	2.2	2.1	11.6c
180	1.1	2.2	1.7	1.7	1.7	8.5c
360	1.6	3.1	3.0	3.1	2.7	13.6c
Irrigation total	74.7a	55.2a	53.6a	55.6a	56.3a	
Treatment total		295.3a				

* Total values with the same letters are not significantly different at 0.05 level of significance.

† Irrigation means with the same letters are not significantly different at 0.05 level of significance.

‡ Treatment totals with the same letters are not significantly different at 0.05 level of significance.

Table 3. The average pH in leachate from soil columns under unsaturated moisture conditions as a function of lime application

Sampling Time	Irrigation Event					Average*
	1	2	3	4	5	
	-----pH-----					
0 Mg ha⁻¹ lime						
30	6.04	5.53	6.23	6.03	5.23	5.81a
60	5.77	5.80	6.23	6.07	5.70	5.91a
120	5.58	5.57	6.10	5.60	5.47	5.66c
180	6.00	5.60	6.00	5.63	6.33	5.91a
360	5.80	5.97	6.20	6.13	6.10	6.04a
Irrigation mean†	5.84d	5.69d	6.15a	5.89b	5.77d	
Treatment mean‡		5.87a				
5 Mg ha⁻¹ lime						
30	5.97	6.13	5.93	6.10	5.73	5.97a
60	6.20	5.53	5.97	5.97	5.87	5.91a
120	6.17	5.73	5.97	5.87	5.60	5.87a
180	5.97	5.83	6.03	5.97	6.27	6.01a
360	6.00	6.27	6.30	5.93	6.20	6.14a
Irrigation mean	6.06b	5.90b	6.04b	5.97b	5.93b	
Treatment mean		5.98a				
10 Mg ha⁻¹ lime						
30	6.55	6.03	5.63	5.90	5.53	5.93a
60	6.47	6.03	5.77	5.93	5.73	5.99a
120	6.30	5.87	5.87	5.77	5.83	5.93a
180	5.83	6.00	5.90	5.90	6.03	5.93a
360	5.80	6.07	6.33	5.97	6.27	6.09a
Irrigation mean	6.19a	6.00b	5.90b	5.89b	5.88b	
Treatment mean		5.97a				

* Average values with the same letters are not significantly different at 0.05 level of significance.

† Irrigation means with the same letters are not significantly different at 0.05 level of significance.

‡ Treatment means with the same letters are not significantly different at 0.05 level of significance.

the five-week incubation period was not long enough for the lime to react with the soil. The results also indicate that the leachate pH were not significantly different between sampling time intervals for soil columns treated with 5 and 10 Mg ha⁻¹ lime application rates. For soil columns treated with 10 Mg ha⁻¹ lime application rate, the leachate pH was highest during the first irrigation event compared with subsequent irrigation events. For soil columns treated with 5 Mg ha⁻¹ lime application rate, irrigation events had no significant effect on leachate pH.

LEACHING OF CALCIUM AS AFFECTED BY LIME APPLICATION

Soil columns treated with 5- and 10-Mg-ha⁻¹ lime application rates had significantly higher Ca concentrations in the leachate compared with soil columns that had 0-Mg ha⁻¹ lime application rate (table 4). Sampling time intervals and irrigation events had no significant effect on the concentration of Ca in the leachate for soil columns with no lime application rate. Soil columns treated with 5-Mg ha⁻¹ lime application rate, had significantly lower concentrations of Ca in the leachate during the first and third irrigation event compared with the other irrigation events. Soil columns treated with 10-Mg-ha⁻¹ lime application rate had significantly lower concentration of Ca in the leachate during the first and second irrigation events compared with subsequent irrigation events. This trend was also observed for the sampling time intervals (for soil columns treated with 5- and 10-Mg-ha⁻¹ lime application rates) whereby the concentration of Ca was significantly

lower during the 30, 60, and 120 min sampling time intervals compared with subsequent time intervals. For soil columns without lime application, sampling time had no effect on Ca concentrations.

The low concentration of Ca in the leachate at the beginning of the irrigation period, could have been due to the dilution of Ca by the high amount of water applied and/or due to preferential flow through macropores that resulted in Ca being bypassed by the water. The concentration of Ca in the leachate increased with subsequent irrigation events due to the fact that it takes time for the center of mass of Ca to reach the bottom of the column. Another explanation could be due to the fact that the cation exchange capacity (CEC) of the soil was close to being saturated with Ca cations and the excess cations were being leached out with the leachate.

NO₃-N CONCENTRATIONS IN THE LEACHATE AS AFFECTED BY LIME APPLICATION

The concentrations of NO₃-N in the leachate significantly increased with increased lime application rate (table 5). Table 5 shows that the NO₃-N concentrations in the leachate were not significantly different between sampling time intervals for all treatments. All treatments had significantly lower concentrations of NO₃-N during the first and second irrigation events compared with subsequent irrigation events. A similar trend was reported by Chae and Tabatabai (1986) regarding N mineralization in soils amended with various sludges, animal manure, and plant materials. They reported that N mineralization during

Table 4. The average calcium concentration in leachate from soil columns under unsaturated moisture conditions as a function of lime application

Sampling Time	Irrigation Event					Average*
	1	2	3	4	5	
	-----Ca (mg L ⁻¹)-----					
0 Mg ha ⁻¹ lime						
30	6.18	10.94	11.07	10.87	11.43	10.10f
60	9.42	13.87	12.80	13.96	12.57	12.52f
120	10.33	12.00	16.07	18.12	16.35	14.57f
180	11.99	13.46	16.93	19.22	16.62	15.64f
360	13.67	17.44	19.79	19.41	17.84	17.63f
Irrigation mean†	10.32c	13.54c	15.33c	16.32c	14.96c	
Treatment mean‡	14.09b					
5 Mg ha ⁻¹ lime						
30	32.97	16.17	16.68	24.43	20.82	22.21b
60	23.54	15.74	20.23	29.29	27.63	23.29b
120	17.77	16.45	22.74	32.38	35.75	25.02b
180	22.39	86.19	24.88	33.95	38.72	41.23a
360	28.49	23.79	27.70	36.06	45.01	32.21a
Irrigation mean	25.03d	31.67a	22.45d	31.22a	33.59a	
Treatment mean	28.79a					
10 Mg ha ⁻¹ lime						
30	19.72	14.45	26.53	34.41	32.21	25.46b
60	21.76	16.58	29.55	39.57	35.06	28.50b
120	16.65	17.47	28.23	41.55	40.26	28.83b
180	19.59	25.03	32.09	42.58	40.88	32.03a
360	36.21	20.64	27.03	39.97	43.73	33.52a
Irrigation mean	22.79d	18.83h	28.69b	39.62a	38.43a	
Treatment mean	29.67a					

* Average values with the same letters are not significantly different at 0.05 level of significance.

† Irrigation means with the same letters are not significantly different at 0.05 level of significance.

‡ Treatment means with the same letters are not significantly different at 0.05 level of significance.

Table 5. The flow-weighted average concentration of NO₃-N in leachate water from soil columns under unsaturated soil moisture condition

Sampling Time	Irrigation Event					Average*
	1	2	3	4	5	
	-----NO ₃ -N (mg L ⁻¹)-----					
0 Mg ha ⁻¹ lime						
30	3.80	8.09	9.40	10.11	9.95	8.27d
60	7.64	9.33	12.00	12.08	11.63	10.54d
120	6.96	10.46	12.71	12.40	11.87	10.88d
180	6.01	9.81	12.79	11.15	11.71	10.29d
360	7.11	10.42	13.29	13.91	13.73	11.69d
Irrigation mean†	6.30d	9.62d	12.04e	11.93e	11.78e	
Treatment mean‡	10.33c					
5 Mg ha ⁻¹ lime						
30	6.77	6.69	13.70	22.85	20.02	14.01b
60	7.93	9.39	16.54	27.63	25.65	17.43b
120	8.65	7.97	16.13	25.07	27.97	17.16b
180	5.85	10.27	16.14	28.67	29.72	18.13b
360	9.07	10.55	17.96	29.02	32.88	19.90a
Irrigation mean	7.65d	8.98d	16.09d	26.65b	27.25b	
Treatment mean	17.32b					
10 Mg ha ⁻¹ lime						
30	5.20	9.22	22.35	29.49	28.82	19.02a
60	7.22	10.79	26.48	35.83	31.83	22.43a
120	6.12	10.42	22.38	32.71	32.69	20.86a
180	6.18	9.99	20.49	31.75	34.17	20.52a
360	7.51	9.92	21.37	33.57	36.93	21.86a
Irrigation mean	6.45d	10.07d	22.61c	32.67a	32.89a	
Treatment mean	20.94a					

* Average values with the same letters are not significantly different at 0.05 level of significance.

† Irrigation means with the same letters are not significantly different at 0.05 level of significance.

‡ Treatment means with the same letters are not significantly different at 0.05 level of significance.

incubation studies followed a pattern whereby there was immobilization of N during the initial period and then a steady, linear release with time over the incubation period.

The increase in NO₃-N concentrations in the leachate with time was due to an increase in nitrification rates of ammonium ions from applied urea to NO₃-N form. Thus, nitrification rates increased because urea (like other ammonium forming fertilizers) increased the nitrifiers populations responsible for nitrification in soils and/or that urea fertilizer increased nitrifiers adaptations and efficiency by changing soil pH and inducing the enzymes responsible for oxidizing NH₄⁺ to NO₃⁻ in soils (Senwo, 1995; Tlustos and Blackmer, 1992). Another explanation could be due to more mixing and reaction of lime with the soil that resulted in the reduction in the number of positive charges in the soil, and consequently, anion exclusion (NO₃⁻) from the soil matrix (Curtin and Smillie, 1983). Total NO₃-N loss with leachate (expressed as a percent of the total NO₃-N added) ranged from 15.3% for soil columns without lime application to 29.0% for soil columns treated with 10-Mg-ha⁻¹ lime application rate (table 6).

ATRAZINE CONCENTRATIONS IN THE LEACHATE AS AFFECTED BY LIME APPLICATION

Soil columns treated with 5- and 10-Mg-ha⁻¹ lime application rate had significantly higher atrazine concentrations in the leachate compared with non-limed soil columns (table 7). This trend can be explained by the fact that Ca was affecting the structure of organic matter which in turn affects the sorption of atrazine through H bonding and hydrophobic attractions (Alva and Singh, 1990). Since the pH values in this study ranged from 5.87 to 5.98 (which are 5 pH units above the 1.7 pKa value for atrazine), atrazine ionization was probably slightly affected. The application of urea fertilizer, which had to be converted to NH₄⁺ and NO₃-N, could also have contributed to leaching of atrazine. Smith and Wills (1985) observed an increase in leaching of insecticides with an increase in anhydrous NH₃. This was attributed to the fact that soil humic substances, solubilized by NH₃, serve as pesticide carriers.

Concentrations of atrazine were significantly higher during the first, second, and third irrigation events compared with the subsequent irrigation events for soil

Table 6. Mass balance for NO₃-N for soil columns under unsaturated moisture conditions based on average values from three soil columns

	Lime Application Rate (Mg ha ⁻¹)		
	0	5	10
Initial amount in the soil columns*	9.2	9.2	9.2
Applied amount in the soil columns	644	644	644
Total amount in the soil columns	653.2	653.2	653.2
Amount leached with first irrigation	21.6	21.9	15.6
Amount leached with second irrigation	17.5	15.5	18.0
Amount leached with third irrigation	21.8	28.1	39.3
Amount leached with fourth irrigation	21.9	50.1	58.9
Amount leached with fifth irrigation	20.4	48.9	60.1
Total lost with leachate	103.2	164.5	191.9
Amount remaining in the soil columns	550.0	488.7	461.3

* Estimated from concentrations in the soil samples collected at the same spot as soil columns.

Table 7. The flow-weighted average concentration of atrazine in leachate from soil columns under unsaturated soil moisture condition

Sampling Time	Irrigation Event					Average*
	1	2	3	4	5	
-----Atrazine (mg L ⁻¹)-----						
0 Mg ha ⁻¹ lime						
30	0.451	0.087	0.056	0.042	0.029	0.133b
60	0.168	0.088	0.053	0.042	0.028	0.076c
120	0.183	0.087	0.063	0.053	0.037	0.085c
180	0.206	0.088	0.064	0.059	0.039	0.091c
360	0.250	0.102	0.068	0.058	0.040	0.104c
Irrigation mean†	0.252c	0.091e	0.061e	0.051e	0.035e	
Treatment mean‡						0.098c
5 Mg ha ⁻¹ lime						
30	0.536	0.149	0.111	0.083	0.081	0.192b
60	0.366	0.192	0.136	0.123	0.094	0.182b
120	0.314	0.214	0.163	0.137	0.112	0.188b
180	0.292	0.196	0.162	0.139	0.116	0.181b
360	0.285	0.202	0.190	0.098	0.126	0.180b
Irrigation mean	0.359b	0.191d	0.152d	0.116f	0.106f	
Treatment mean						0.185b
10 Mg ha ⁻¹ lime						
30	0.895	0.122	0.123	0.141	0.117	0.280a
60	0.599	0.205	0.136	0.108	0.077	0.225a
120	0.563	0.236	0.419	0.107	0.068	0.279a
180	0.555	0.254	0.164	0.115	0.088	0.235a
360	0.567	0.261	0.170	0.135	0.091	0.245a
Irrigation mean	0.636a	0.216c	0.202c	0.121f	0.088f	
Treatment mean						0.253a

* Average values with the same letters are not significantly different at 0.05 level of significance.

† Irrigation means with the same letters are not significantly different at 0.05 level of significance.

‡ Treatment means with the same letters are not significantly different at 0.05 level of significance.

columns treated with 5- and 10-Mg-ha⁻¹ lime application rate (table 7). For non-limed soil columns, the concentration of atrazine in the leachate was significantly higher during the first irrigation compared with subsequent irrigation events. The concentration of atrazine in leachate was lowest during the last irrigation events likely due to the fact that most of the atrazine was leached out with the previous irrigation events and/or some atrazine may have started degrading with time. The higher concentration of atrazine during the first irrigation could have been due to preferential flow and the higher amount of water added during the first irrigation.

These results agree with the observations by Baker and Lafen (1983), and Bowman (1989) who reported the greatest loss of most surface-applied pesticides, like atrazine, with the first watering following pesticide application. The results in table 7 also show that there was no significant difference in the concentration of atrazine in the leachate between sampling time intervals for soil columns treated with 5- and 10-Mg-ha⁻¹ lime application rates. Soil columns treated with 0-Mg-ha⁻¹ lime application rate had significantly higher concentration of atrazine in the leachate during the 30-min time interval compared with subsequent time intervals.

CONCLUSIONS

The following conclusions were drawn from the study:

1. The results of this study indicate that the application of lime had no significant effect on the amount of leachate from the soil columns. However, the

leachate depth collected during the first 60 min was significantly higher compared with the other time intervals, which was due to the normal infiltration characteristics of the soil and also due to preferential flow through the soil columns.

2. The application of lime resulted in higher concentration of calcium in the leachate. Also, the concentration of calcium in the leachate was significantly high during the last two irrigation events for soil columns treated with 10 Mg ha⁻¹. However, for the study soils an increase in the application rate of lime had no significant effect on leachate pH.
3. An increase in the application rate of lime resulted in increased concentration of NO₃-N in leachate. The concentration of NO₃-N in the leachate increased with irrigation events for soil columns treated with 5-Mg-ha⁻¹ and 10-Mg-ha⁻¹ lime application rates.
4. An increase in lime application rate resulted in increased concentrations of atrazine in leachate. Also, in limed and non-limed soil columns, significantly higher concentrations of atrazine were observed in the leachate during the first irrigation event compared with subsequent irrigation events.

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