Loss Pathways of *N*-Nitrosodimethylamine (NDMA) in Turfgrass Soils

M. Arienzo,* J. Gan, F. Ernst, S. Qin, S. Bondarenko, and D. L. Sedlak

ABSTRACT

N-nitrosodimethylamine (NDMA) is a potent carcinogen that is often present in municipal wastewater effluents. In a previous field study, it was observed that NDMA did not leach through turfgrass soils following 4 mo of intensive irrigation with NDMA-containing wastewater effluent. To better understand the loss pathways for NDMA in landscape irrigation systems, a mass balance approach was employed using in situ lysimeters treated with ^{14}C-NDMA. When the lysimeters were subjected to irrigation and field conditions after NDMA application, very rapid dissipation of NDMA was observed for both types of soil used in the field plots. After only 4 h, total ^{14}C activity in the lysimeters decreased to 19.1 to 26.1% of the applied amount, and less than 1% of the activity was detected below the 20-cm depth. Analysis of plant materials showed that less than 3% of the applied ^{14}C was incorporated into the plants, suggesting only a minor role for plant uptake in removing NDMA from the vegetated soils. The rapid dissipation and limited downward movement of NDMA in the in situ lysimeters was consistent with the negligible leaching observed in the field study, and suggests volatilization as the only significant loss pathway. This conclusion was further corroborated by rapid NDMA volatilization found from water or a thin layer of soil under laboratory conditions. In a laboratory incubation experiment, prolonged wastewater irrigation did not result in enhanced NDMA degradation in the soil. Therefore, although NDMA may be present at relatively high levels in treated wastewater, gaseous diffusion and volatilization in unsaturated soils may effectively impede significant leaching of NDMA, minimizing the potential for ground water contamination from irrigation with treated wastewater.

The increasing use of treated wastewater to irrigate golf courses and landscaped lands may pose a threat to ground water quality due to the potential for organic pollutants such as *N*-nitrosodimethylamine (NDMA) to leach into the ground water (Sedlak et al., 2000; Sedlak, 2003; WateReuse Foundation, 2005). NDMA is a member of the chemical class of *N*-nitrosoamines and a probable carcinogen (Agency for Toxic Substances and Disease Registry, 1989; Mitch et al., 2003; USEPA, 2005). NDMA is soluble in water, does not adsorb to soil, and has a moderate to long persistence in soils, suggesting a high potential to leach through a soil profile to reach ground water (Tate and Alexander, 1975, 1976; Oliver et al., 1979; Mallik and Tesfai, 1981; Kaplan and Kaplan, 1985; Gunnison et al., 2000; Yang et al., 2005). Under laboratory conditions, NDMA was found to leach through saturated soil columns at nearly the same rate as the inert tracer chloride (Dean-Raymond and Alexander, 1976). The mobility and persistence of NDMA is also evidenced by NDMA detection in ground water downgradient from industrial sites where large volumes of NDMA-contaminated water were infiltrated to ground water through unlined percolation pits (Gunnison et al., 2000; Mitch et al., 2003; WateReuse Foundation, 2005). Contrary to expectations based on data from industrial sites, NDMA was largely absent in the leachate from mature turfgrass plots that were heavily irrigated with NDMA-containing wastewater effluent (Gan et al., 2006). Incubation experiments conducted with soils from the field site further showed that NDMA was relatively persistent in the turfgrass soils, suggesting that mechanisms other than degradation or adsorption were responsible for the rapid NDMA removal and low leaching in the turfgrass plots.

The purpose of this study was to evaluate the importance of plant uptake and volatilization in NDMA dissipation from turfgrass soils. Plants play an important role in water movement in the vadose zone. In addition, plants could serve as a sink for NDMA. For example, Dean-Raymond and Alexander (1976) showed that lettuce and spinach plants were capable of taking up NDMA from soil or sand in containers. Furthermore, NDMA is a semivolatile compound with a low boiling point (152°C) and relatively high vapor pressure (2.67 mm Hg at 25°C) (International Programme on Chemical Safety, 2002), suggesting a high potential for gas phase transport and volatilization. Under laboratory conditions, NDMA was found to volatilize readily after application in dichloromethane to the soil surface, but NDMA volatilization decreased greatly when it was incorporated into the soil (Oliver, 1979). The role of plant uptake and volatilization in preventing NDMA from leaching is unknown for field conditions and merits further investigation.

It is known that when a soil is repeatedly exposed to a chemical, the soil may develop a capability to degrade the chemical at an enhanced rate as the microorganisms become acclimated (Alexander, 1994). However, it is unknown if long-term irrigation of NDMA-containing wastewater would result in accelerated transformation of NDMA in the irrigated soil. The second objective of this study was therefore to determine if NDMA persistence changes after soil is irrigated with wastewater for extended periods.

MATERIALS AND METHODS

Chemicals

N-[methyl-^{14}C] NDMA (specific activity 57 mCi mmol^{-1}; radioactive purity $>$ 99%) was purchased from Moravek Biochemicals in Brea, CA. Unlabeled NDMA (>99% pure)

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Published in J. Environ. Qual. 35:285–292 (2006).
Technical Reports: Organic Compounds in the Environment
doi:10.2134/jeq2005.0265

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Abbreviations: NDMA, *N*-nitrosodimethylamine.

was purchased as a neat liquid from Sigma-Aldrich (Milwaukee, WI). The deuterium-labeled NDMA (d6-NDMA, 98%) was purchased from Cambridge Isotope Laboratories (Andover, MA) and used as a surrogate in NDMA analysis.

In Situ Lysimeter Experiment

At the conclusion of the previous field irrigation study in early October 2004, an in situ lysimeter experiment was performed to understand the loss mechanisms of NDMA from turfgrass soils. About 10 mo before the in situ lysimeter experiment, galvanized aluminum tubing (5-cm i.d. and 30 cm long) was inserted into six turfgrass plots (three plots for each soil type) that were planted with a hybrid Bermuda grass (*Cynodon dactylon* × *transvaalensis*) and allowed to acclimatize under field conditions. These plots were irrigated with plain water before the lysimeter experiment. For treatment, ^{14}C-NDMA was dissolved in water and 50 mL of the solution (166 Bq mL^{-1}, or 200 μg L^{-1} in total NDMA concentration) was uniformly applied to the top of each lysimeter using a glass pipette. To ensure accurate treatment, the treatment area was secured with an aluminum collar when ^{14}C-NDMA was applied. The plots with the treated lysimeters were then subjected to standard irrigation practices at three irrigation events per week with plain water. From the time ^{14}C-NDMA was applied until the end of the experiment (14 d or 336 h), the total amount of irrigation water applied was 48 mm, which was 103% of the total evapotranspiration rate (46.4 mm) for the site. As irrigation occurred three times a week, each irrigation event introduced an average of 8.0 mm of water into the test plots. A precipitation event (18 mm) occurred about 12 d after the treatment. The average air temperature for the 2-wk period after the treatment was 19.5°C and the average soil temperature at the 15-cm depth was 20.0°C. These temperatures were lower than those recorded during the previous irrigation study, but the overall climate for the test period was still relatively warm and dry.

Triplicate lysimeters from each soil type were removed at 0, 4, 8, 12, 28, 72, 168, and 336 h after the treatment. Both ends of the soil column were immediately closed with adhesive aluminum foil and stored in a freezer at −20°C until extraction. For extraction, the frozen soil column was cut into 0- to 5-, 5- to 10-, 10- to 20-, and 20- to 30-cm increments. Plant and roots were carefully separated from soil, washed with deionized water, and cut into small pieces. The soil contained in each segment was weighed and mixed, after which aliquots were removed for determination of water content. The whole plant sample or 40 g of wet soil was individually placed in Soxhlet extraction cups, spiked with 0.1 mL of 10 mg L^{-1} d6-NDMA, and extracted with 300 mL dichloromethane for 8 h. The solvent extract was passed through a layer of anhydrous sodium sulfate and condensed to 10 mL on a vacuumed rotary evaporator. Duplicates of 0.5-mL aliquot of the extract were mixed in 6 mL of Ultima Gold scintillation cocktail (Packard BioScience, Meriden, CT) and measured for ^{14}C radioactivity on a Beckman (Fullerton, CA) LS 1800 liquid scintillation counter (LSC). Following solvent extraction, ^{14}C associated with the extracted sample matrix was also determined by combusting 50 mg of air-dried plant tissues or 1.0 g of air-dried soil on a R.J. Harvey (Hillsdale, NJ) OX-500 biological oxidizer. The evolved ^{14}CO$_2$ was trapped in a basic solution and the activity was measured by LSC. The fraction of ^{14}C measured in the methylene chloride extract was defined as extractable ^{14}C, while the ^{14}C measured after the extraction was considered non-extractable ^{14}C. The sum of these two fractions was further defined as total ^{14}C. It must be noted that as NDMA was not distinguished from its potential metabolites, the measured ^{14}C activity could overestimate the actual NDMA concentration. Therefore, information on ^{14}C would serve as a conservative estimation for the behavior of NDMA.

Volatilization Experiments under Controlled Conditions

Volatilization of NDMA from water and soil was further evaluated in the laboratory using controlled conditions. In the first experiment, ^{14}C-NDMA was spiked into 200 mL of 0.01 *M* CaCl$_2$ solution in wide-mouth glass containers (12.5-cm i.d.) at an initial NDMA concentration of 72.5 μg L^{-1}. Three replicates were prepared, and the containers were placed on magnetic plates (600 rpm) in a fume hood at the ambient temperature (20 ± 1°C). At 0, 0.5, 1, 2, 4, 8, 24, 48, and 72 h after the treatment, each container was individually weighed to determine water loss from evaporation, and aliquots of 1.0 mL were removed from each container for measurement of ^{14}C radioactivity by LSC. In the second experiment, a sandy loam soil with 0.91% organic carbon content was sieved through 1 mm and air-dried to about 6% water content. Two hundred grams of soil (dry weight) was placed in open mouth glass containers (12.5-cm i.d.), and uniformly treated with 12 mL of an aqueous solution of ^{14}C-NDMA. Three replicates were prepared, and the initial NDMA concentration in the soil was about 3.8 μg kg^{-1}. The treated soil containers were equilibrated in a fume hood at ambient temperature. At 0, 0.5, 1, 2, 4, 8, 24, 48, and 72 h after the treatment, 1.0 g soil was removed and immediately combusted on the biological oxidizer and the released ^{14}C activity was determined by LSC. Losses of NDMA were calculated as percentage of the initial applied amount and used for analysis of NDMA volatilization kinetics.

NDMA Degradation in Turfgrass Soils

The long-term application of NDMA-containing wastewater effluents may have selectively influenced soil microbial populations capable of degrading NDMA. A separate laboratory incubation experiment was therefore performed to determine the potential effect of wastewater irrigation on NDMA persistence in soil. Immediately following the previous wastewater irrigation study (Gan et al., 2006), soil samples were taken with an auger from turfgrass plots that were previously irrigated with wastewater for approximately 4 mo. Soil samples were simultaneously taken also from adjacent plots that were irrigated only with plain water. The soil cores were divided into 0- to 10-, 10- to 25-, and 25- to 50-cm layers. The soil samples were passed through a 2-mm sieve after slight air-drying. The basic physicochemical properties of the soils were measured using standard methods and are given in Table 1. The initial water content of the soil samples was adjusted to 10% (w/w) by adding deionized water. Ten grams (dry weight

Table 1. Selected soil properties of turfgrass grass plots used in the study.

Depth	pH	Organic C	Sand	Silt	Clay
cm		%			
			Sandy loam		
0–10	6.6	1.33	0.76	0.20	0.04
10–25	7.5	0.40	0.76	0.17	0.07
25–50	7.0	0.33	0.78	0.16	0.06
			Loamy sand		
0–10	7.2	0.98	0.77	0.19	0.04
10–25	6.9	0.10	0.82	0.15	0.03
25–50	7.4	0.09	0.85	0.12	0.03

equivalent) of soil was weighed into 125-mL glass serum bottles (Wheaton, Millville, NJ) and spiked with 0.5 mL of 2 mg L^{-1} NDMA aqueous solution to give an initial NDMA concentration of 100 μg kg^{-1}. To ensure homogeneous distribution of NDMA, the spiked soil was thoroughly stirred with a stainless steel spatula for 1 min. The spiked samples were immediately closed by capping with aluminum seals and Teflon-lined butyl rubber septa. The sample bottles were then incubated in the dark at room temperature (20 ± 1°C) and triplicate samples were removed 0, 3, 7, 14, 21, 28, and 56 d after the treatment for analysis of NDMA. For extraction, each soil sample was spiked with 0.1 mL of d6-NDMA in dichloromethane (10 mg L^{-1}) and then extracted with 50 mL dichloromethane by shaking at high speed for 4 h. The solvent extract was filtered through a funnel containing 20 g anhydrous sodium sulfate, and the dried extract was concentrated to a final volume of about 1 mL under a stream of dry nitrogen. An aliquot of the final extract was analyzed by gas chromatography–mass spectrometry (GC–MS). The recovery of NDMA was determined to be 38.5 ± 5.1% for the turfgrass soil. However, as d6-NDMA was used as a surrogate, the results were not corrected for recovery. Detailed analytical conditions used for quantification of NDMA in the final extract were the same as in the proceeding paper (Gan et al., 2006). The detection limit of NDMA using the above protocol was 0.20 μg kg^{-1}.

RESULTS AND DISCUSSION

Dissipation of Carbon-14-NDMA in In Situ Lysimeters

Dissipation of total ^{14}C activity (sum of extractable and non-extractable ^{14}C activity) in the in situ lysimeters is shown in Fig. 1. When the soil and plant tissues were analyzed immediately after the treatment, about 80 and 87% of the added activity were recovered from the sandy loam soil lysimeters and the loamy sand soil lysimeters, respectively, indicating good mass recoveries for the overall protocol. The dissipation of total ^{14}C was almost instantaneous for both soil types. At 4 h after the treatment, only 19.1 ± 5.2% of the applied ^{14}C still remained in the sandy loam lysimeters, and 26.1 ± 6.0% in the loamy sand lysimeters. After 72 h, the total ^{14}C decreased to less than 3% of the mass applied in all lysimeters. The dissipation of total ^{14}C activity closely followed a first-order decay model (Fig. 1). The estimated first-order dissipation half-life (DT_{50}) was 2.2 h for the sandy loam soil ($R^2 = 0.98$; $P = 0.0002$) and slightly longer at 2.6 h for the loamy sand soil ($R^2 = 0.95$; $P = 0.0014$). Under the experimental conditions, the time required for 95% dissipation, or DT_{95}, was 9.4 h for the sandy loam soil, and 11.1 h for the loamy sand soil.

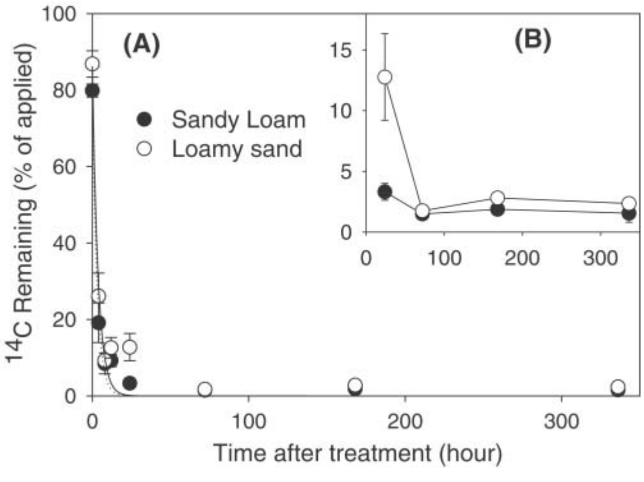

Fig. 1. Dissipation of total ^{14}C activity from ^{14}C-NDMA-treated in situ lysimeters in turfgrass plots under field conditions. (A) Overall dissipation trends. (B) Dissipation kinetics from 28 h after ^{14}C-NDMA application. Vertical lines are standard errors of measurements from three replicated lysimeters.

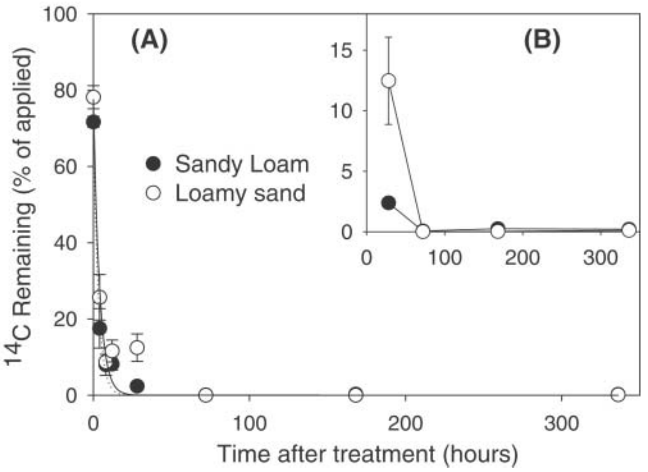

Fig. 2. Dissipation of dichloromethane extractable ^{14}C activity from ^{14}C-NDMA-treated in situ lysimeters in turfgrass plots under field conditions. (A) Overall dissipation trends. (B) Dissipation kinetics from 28 h after ^{14}C-NDMA application. Vertical lines are standard errors of measurements from three replicated lysimeters.

The dissipation of extractable ^{14}C activity from the lysimeters as a function of time is shown in Fig. 2. Dissipation of extractable ^{14}C closely followed the same trend as total ^{14}C for both soil types (Fig. 2). The DT_{50} for extractable ^{14}C was estimated to be 2.2 h for the sandy loam soil ($R^2 = 0.99$; $P < 0.0001$), and slightly longer at 2.7 h for the loamy sand soil ($R^2 = 0.95$; $P = 0.0013$). The respective DT_{95} values were 9.6 and 11.8 h for the two soil types. After 72 h, the total ^{14}C in the lysimeters remained at 1.5 to 3% until the end of the experiment (Fig. 1B). However, the extractable fraction of ^{14}C in the lysimeters decreased to less than 0.3% of the applied mass at ≥72 h after the treatment (Fig. 2B). This suggests that the non-extractable fraction accounted for the majority of the total ^{14}C activity in the lysimeters after the initial rapid dissipation of NDMA. During the first 24 h after the treatment, the extractable fraction accounted for 72 to 94% of the total ^{14}C in the sandy loam lysimeters, and 90 to 98% in the loamy sand lysimeters. However, from 72 to 336 h, the ratio of the non-extractable ^{14}C contributed for 84 to 95% of the total ^{14}C in the sandy loam lysimeters, and 95 to 99% in the loamy sand lysimeters. Therefore, even though trace levels of ^{14}C were present in the lysimeters after 72 h, the residue was mostly in the non-extractable form and would have little potential for leaching.

Distribution of Carbon-14-NDMA in In Situ Lysimeters

The vertical distribution patterns of total and extractable ^{14}C at different times after the treatment are shown in Fig. 3 for the sandy loam soil lysimeters and in Fig. 4 for the loamy sand soil lysimeters. The initial distribution showed that ^{14}C-NDMA percolated into the 10- to 20-cm layer, and for the loamy sand soil, a small amount (3.4%) even reached the 20- to 30-cm segment (Fig. 3 and 4). The application of 50 mL of solution in each lysimeter was equivalent to 25 mm irrigation, which was higher than the average irrigation rate (8.0 mm) used for the test period, but was within the range of irrigation rates (8–31 mm) used in the previous field study (Gan et al., 2006). In the lysimeters, most of the activity initially resided in the 0- to 10-cm section, and about 10.2 and 5.1% were found in the 10- to 20-cm layer for the sandy loam soil and the loamy sand soil, respectively (Fig. 3 and 4). However, both total and extractable ^{14}C dissipated quickly from all depths for both soil types. At 4 h after the treatment, less than 0.3% of the original activity was detected in the soil below 20 cm (Fig. 3 and 4). As the first irrigation event did not occur until 16 h from the time of ^{14}C-NDMA application, it may be concluded that irrigation did not cause leaching of ^{14}C-NDMA beyond the 30-cm depth. The precipitation event occurred at about 12 d after the treatment, and therefore should have had no effect on the overall distribution or dissipation trends of ^{14}C-NDMA. It is also evident from Fig. 3 and 4 that the amount of non-extractable ^{14}C was small compared to the total ^{14}C in the soil during the first 28 h. However, at ≥72 h after the treatment, the trace amounts of ^{14}C detected in the soil were predominantly in the form of non-extractable ^{14}C, possibly indicating partial degradation and reduced leaching risk for the small amounts of remaining residue.

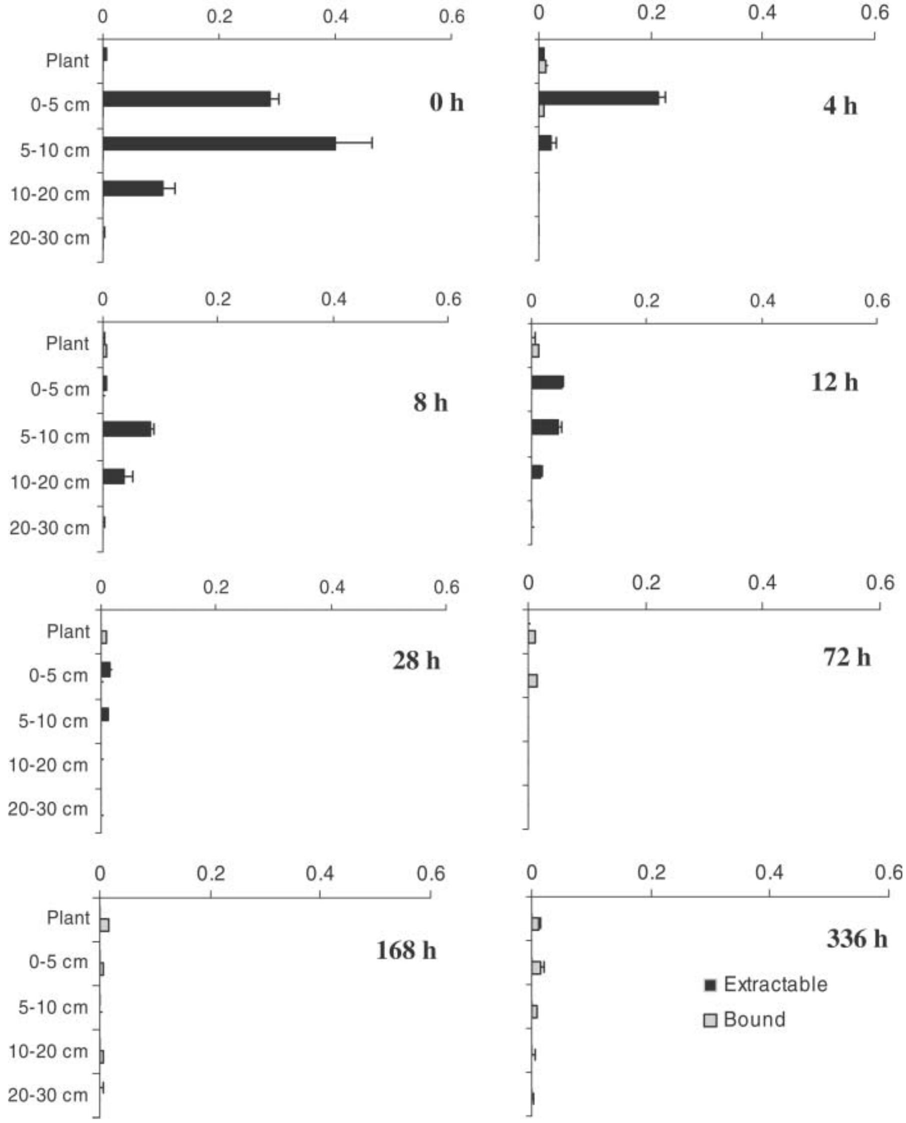

Fig. 3. Vertical distribution of total and extractable ^{14}C activities at different times in ^{14}C-NDMA-treated in situ sandy loam lysimeters in turfgrass plots under field conditions. Bars are means of three replicates and lines are standard errors.

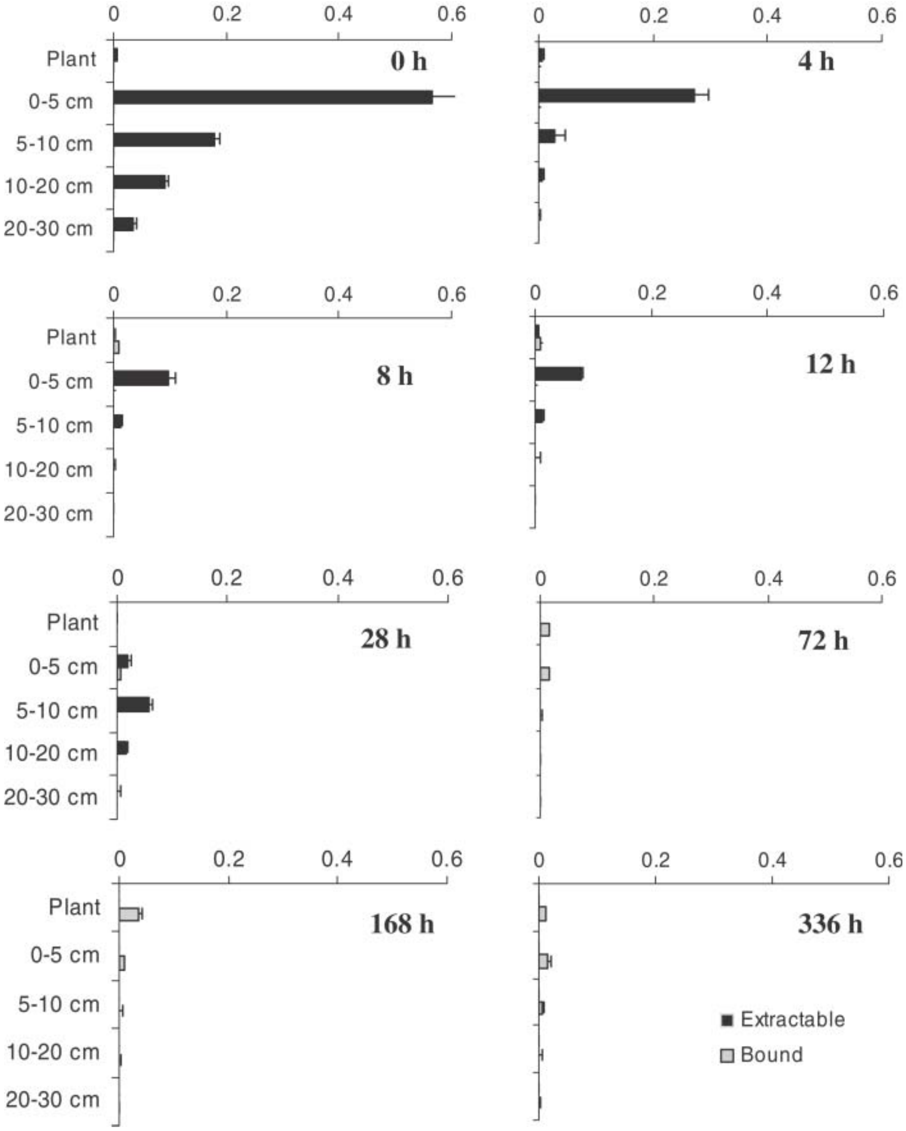

Fig. 4. Vertical distribution of total and extractable ^{14}C activities at different times in ^{14}C-NDMA-treated in situ loamy sand lysimeters in turfgrass plots under field conditions. Bars are mean of three replicates and lines are standard errors.

The turfgrass leaves and roots were analyzed for extractable and non-extractable ^{14}C activities over time. Contrary to the patterns observed for soil samples, the total ^{14}C found in the plant tissues did not exhibit a clear decreasing trend, as shown in Fig. 5 for the sandy loam soil. The total ^{14}C in plant tissues varied from 0.45 to 1.65% in the sandy loam lysimeters, and from 0.07 to 2.85% in the loamy sand lysimeters. It is evident that while the extractable ^{14}C accounted for a significant fraction of the total ^{14}C in the plant tissues within the first 28 h, the majority of the detected ^{14}C (97–100%) was in the non-extractable fraction at ≥72 h after the treatment (Fig. 5). Overall, uptake of ^{14}C-NDMA by turfgrass appeared to be relatively insignificant, and the absorbed ^{14}C was rapidly converted into the non-extractable form. Plant uptake of NDMA was previously studied using lettuce and spinach seedlings grown in containers either with soil, sand, or water (Dean-Raymond and Alexander, 1976). The uptake rate as percentage of applied ^{14}C activity ranged from 0.02 to 5.06%, which is consistent with the limited uptake by turfgrass observed in this study. The current study showed that although turfgrass had extensive root systems, plant uptake of NDMA by turfgrass seemed to be rather limited and should have contributed negligibly to NDMA removal in the previous field study.

Loss Pathways of NDMA in Turfgrass Soils

In the previous field study, NDMA was only detected sporadically at very low concentrations in the leachate during 4 mo of intensive irrigation with NDMA-containing wastewater. A concurrent incubation experiment further suggested that the limited NDMA leaching was not attributable to degradation in the soil profile, as NDMA exhibited a moderate to long persistence in the turfgrass soils (Tate and Alexander, 1975, 1976; Oliver et al., 1979; Mallik and Tesfai, 1981; Kaplan and Kaplan,

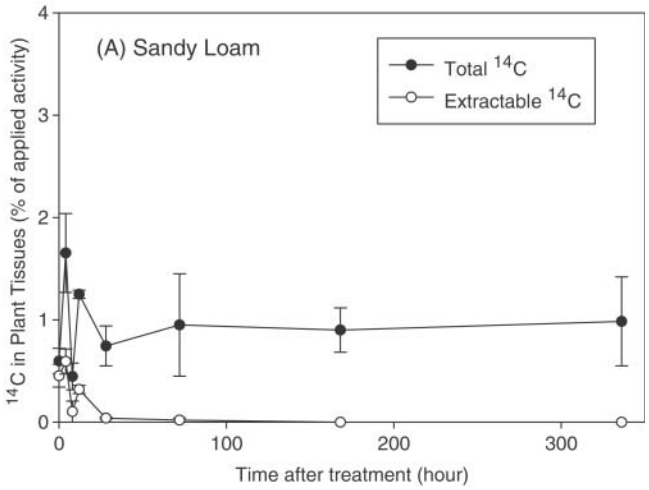

Fig. 5. Total and dichloromethane extractable ^{14}C activity in plant tissues from ^{14}C-NDMA-treated in situ lysimeters in turfgrass plots. Vertical lines are standard errors of measurements from three replicated lysimeters.

1985; Gunnison et al., 2000; Yang et al., 2005). It was therefore postulated that plant uptake and volatilization were the main causes for the limited NDMA leaching. In the current study, distribution and dissipation of ^{14}C-NDMA in in situ lysimeters in similar turfgrass plots showed that NDMA rapidly dissipated after application, and NDMA did not move below the 30-cm depth after irrigation and precipitation. As ^{14}C was used as a tracer and both temporal and spatial distribution trends were monitored, this study provided strong experimental evidence supporting the hypothesis that surface-applied NDMA was not transported into deeper soil layers in unsaturated soil systems. Moreover, measurement of ^{14}C in plant tissues in this study indicated that uptake of ^{14}C-NDMA by the turfgrass plant, although measurable, was a relatively small sink for NDMA. This analysis leaves volatilization as the most predominant cause for NDMA elimination from the soil.

The significant NDMA volatilization loss was likely a result of both rapid NDMA volatilization at the soil–air interface, and active upward transport of NDMA due to efficient gaseous phase diffusion and negative water potential gradients expected under dry, warm conditions in the soil. Volatilization of NDMA from water was measured under ambient conditions. As shown in Fig. 6A, volatilization loss of NDMA from water at 20°C was rapid under the relatively static conditions, with a first-order half-life of about 25 h. From the measured volatilization kinetics, Henry's Law constant K_H was estimated to be 1.45×10^{-3} using a chemical property estimation method (Lyman et al., 1990). This value was in close agreement with that (1.4×10^{-3} at 25°C) reported by the International Program on Chemical Safety (International Programme on Chemical Safety, 2002). It is known that for organic compounds with $K_H > 10^{-4}$, chemical movement in unsaturated soils is dominated by gaseous phase diffusion and can thus be highly efficient (Jury et al., 1991). Rapid volatilization loss of NDMA was further observed to occur from a layer of moist soil under similar laboratory conditions, with a first-order half-life of only 10.3 h (Fig. 6B).

Much more rapid volatilization may be expected to occur in the field where volatilization at the soil–air interface is facilitated by much greater wind speed and higher temperatures. Furthermore, under field conditions, in addition to gas phase transport, the water-miscible NDMA may also move along with soil water. As active upward movement of water may occur in unsaturated soils under dry conditions, the water flow may have transported NDMA upward, further facilitating NDMA volatilization loss (Spencer and Cliath, 1973). The distribution patterns observed at the different depths following the treatment of ^{14}C-NDMA also support the conclusion that active upward transport of NDMA occurred in the unsaturated turfgrass systems. For instance, in the sandy loam lysimeters, although the highest ^{14}C level was found in the 5- to 10-cm layer, at 4 h after the treatment, the peak concentration was found in the 0- to 5-cm surface layer, indicating upward movement of ^{14}C-NDMA along the lysimeter (Fig. 3). Similar patterns were also observed in the loamy sand lysimeters, where the highest ^{14}C distribution was consistently found in the surface layer, while the amount of ^{14}C in the lower layers was negligibly small. Saunders et al. (1979) compared the leaching behavior of ^{14}C-*N*-nitrosodipropylamine (NDPA), an analog to NDMA, in small columns (1.0-mm i.d.) under

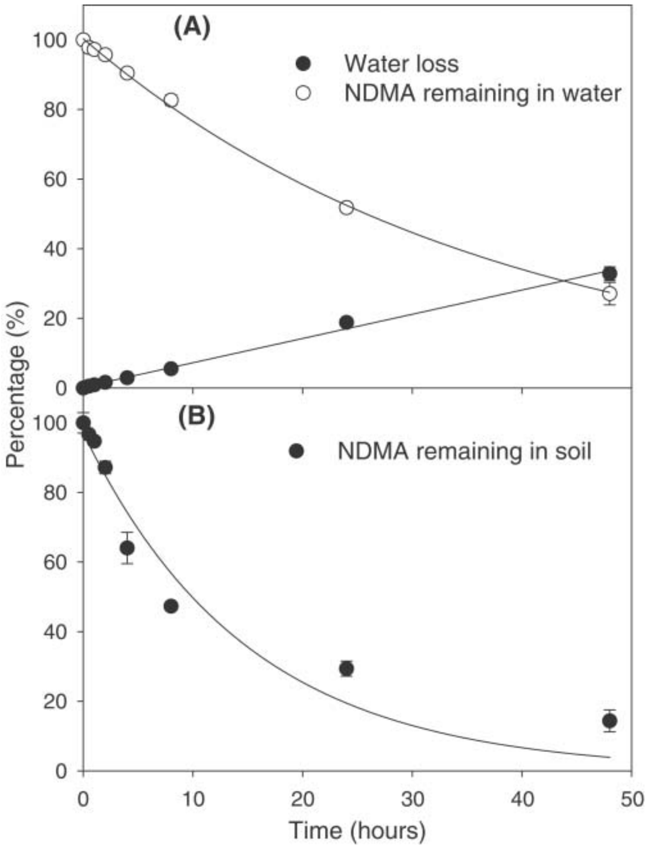

Fig. 6. Volatilization of ^{14}C-NDMA from water and soil under laboratory conditions at 20°C. (A) NDMA volatilization loss from water. (B) NDMA volatilization loss from a sandy loam soil.

laboratory and field conditions. Under laboratory conditions, after application of 60 cm water, the majority (88–94%) of the applied ^{14}C was recovered in the leachate. However, under field conditions, ^{14}C-NDPA did not leach below the 20-cm depth despite frequent rainfall events over a time period of 124 d (Saunders et al., 1979). The difference was consistent with the rapid NDMA leaching observed in the laboratory leaching experiments (Dean-Raymond and Alexander, 1976) and the limited leaching found under field conditions in this study. The difference may be attributed to the fact that in the laboratory leaching experiments, the soil columns were always saturated and water was forced to move in a single direction, which effectively eliminated NDMA volatilization and vapor phase transport.

Transport of NDMA under other conditions may differ greatly from what was observed in this and previous studies. For example, long-term water ponding may occur during furrow irrigation or at wastewater spreading grounds, and the saturated soil conditions may diminish the role of gas phase transport of NDMA and enhance its leaching. To reduce potential NDMA leaching in these operations, periodic site drying may be useful, as drying creates unsaturated soil conditions and facilitates gas phase diffusion and volatilization. The behavior of NDMA under these conditions should be further evaluated. In addition, this and the previous studies (Gan et al., 2006) were conducted under relatively dry and warm conditions. The leaching behavior of NDMA may be different under other climatic and soil conditions and should also be evaluated.

Effect of Wastewater Irrigation on NDMA Persistence

In a separate laboratory incubation experiment, the potential effect of long-term wastewater irrigation on NDMA persistence was evaluated using soil samples taken from the turfgrass plots previously irrigated with NDMA-containing wastewater. The dependence of NDMA concentration in soil as a function of time was fitted to a first-order decay model to estimate the degradation rate constant (k) and half-life ($T_{1/2}$) (Tables 2 and 3). There was little or no difference in NDMA degradation rates between the two soil types. Irrigation with treated wastewater for 4 mo did not result in significantly enhanced NDMA degradation in the soil when compared to soils that did not receive wastewater irrigation. After wastewater irrigation, the persistence of NDMA in the 0- to 10-cm layer was shorter for the sandy loam soil, but was statistically similar to the plain water irrigated samples for the loamy sand soil as well as for the other depths for both soil types. The $T_{1/2}$ was generally short in the surface layers, and consistently increased in the deeper layers. It is well known that the thatch layer of turfgrass contains high levels of organic matter and is biologically more active than in the underlying layers (Sears and Chapman, 1979). The high organic matter and microbial activity may have contributed to the enhanced NDMA degradation in the surface layer. Many studies show that degradation of organic compounds in soil generally decreases with increasing soil depth (Dobbins et al., 1987; Moorman and Harper, 1989). For example, Alexander et al. (1989) and Lavy et al. (1973) showed that as depth within the soil profile increased, various soil microbial populations decreased by 10- to 1000-fold, resulting in greatly reduced microbial activity.

Table 2. First-order constants for NDMA degradation in turfgrass soils previously irrigated with NDMA-containing wastewater.

Depth	k	$T_{1/2}$	R^2
cm	d^{-1}	d	
		Sandy loam	
0–10	0.62 ± 0.102	1.1	0.92
10–25	0.113 ± 0.017	6.1	0.90
25–50	0.052 ± 0.007	13.3	0.90
		Loamy sand	
0–10	0.170 ± 0.027	5.0	0.90
10–25	0.124 ± 0.015	5.6	0.93
25–50	0.012 ± 0.003	59.2	0.40

Table 3. First-order constants for NDMA degradation in turfgrass soils with previous plain water irrigation.

Depth	k	$T_{1/2}$	R^2
cm	d^{-1}	d	
		Sandy loam	
0–10	0.225 ± 0.021	3.1	0.97
10–25	0.122 ± 0.014	5.7	0.94
25–50	0.070 ± 0.010	9.9	0.88
		Loamy sand	
0–10	0.209 ± 0.017	3.3	0.97
10–25	0.130 ± 0.011	5.3	0.97
25–50	0.053 ± 0.007	13.1	0.87

In summary, results from this study support the hypothesis that the limited leaching of NDMA observed in the companion field study was mainly attributable to volatilization. ^{14}C-NDMA was found to dissipate rapidly from turfgrass soils under field conditions, and essentially no NDMA moved below the 30-cm depth, suggesting that the rapid dissipation effectively impeded NDMA leaching in the unsaturated soil. The results strongly suggest that the rapid NDMA dissipation was caused predominantly by NDMA transport through gas phase diffusion and upward water movement through soil capillaries, and subsequent volatilization near the soil surface. Plant uptake, degradation, and adsorption played insignificant roles relative to volatilization. As both studies were conducted in highly sandy soils and the soil thickness examined was small (<100 cm), it may be concluded that NDMA has little or no leaching risk when NDMA-containing wastewater is used for irrigating turfgrass systems such as golf courses, parks, or residential lawns under comparable conditions. In addition, NDMA persistence in soil was not affected by long-term application of wastewater. However, as NDMA behaviors in soil likely depend closely on the state of soil saturation, the leaching risk of NDMA may be higher in saturated soils.

ACKNOWLEDGMENTS

This work was supported by WateReuse Foundation Award WRF-02-002.

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