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Attenuation mechanisms of *N*-nitrosodimethylamine at an operating intercept and treat groundwater remediation system

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Abstract

The North Boundary Containment System (NBCS), an intercept-and-treat system, was established at Rocky Mountain Arsenal (RMA), Commerce City, CO, to remove low-level organic contaminants from a groundwater plume exiting RMA to the north and northwest. *N*-nitrosodimethylamine (NDMA) was detected in groundwater collected from the dewatering and recharge zones of the NBCS system. Concern over the fate of NDMA, in terms of potentially exiting the boundaries of the arsenal, prompted an investigation to evaluate potential attenuation mechanisms for NDMA within the alluvial aquifer system and within the NBCS itself. Groundwater, soil, and granular activated carbon (GAC) samples were taken from key locations in the NBCS system. Soil and GAC samples were assayed for sorption kinetics and for adsorption and desorption properties using ^{14}C-labeled NDMA. NDMA biodegradation experiments were conducted by following $^{14}CO_2$ evolution from ^{14}C-labeled NDMA in soils and GAC samples under aerobic and anaerobic conditions. The sorptive capacity of the site soils for NDMA was insignificant. Furthermore, the adsorption of the NDMA by the soil was almost completely reversible. Evaluation of the degradation potential of the native microbial consortia indicated a high level of NDMA mineralization when measured using bench-scale microcosms. The native consortia had capability to mineralize the NDMA under both aerobic and anaerobic incubations, indicating facultative characteristics. Testing of the local groundwater chemistry revealed that the area of the aquifer of interest was microaerobic and neutral in pH. These conditions were optimal for NDMA removal.

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While sorption was insignificant, degradation was a significant attenuation mechanism, which may be the reason that no NDMA has migrated off-site. This gives rise to the potential of a long-term sink for attenuating NDMA within the recharge zone of the treatment system.

Keywords: *N*-Nitrosodimethylamine; Natural attenuation; Biodegradation; Sorption; Adsorption

1. Introduction

Rocky Mountain Arsenal (RMA) occupies more than 6880 hectares in Adams County near Denver, CO. During World War II, RMA manufactured and assembled weapons containing intermediate and toxic chemical end-products and incendiary munitions. Activities since that time have included blending of hydrazine compounds for the manufacture of rocket fuels for the US Air Force, and civilian use of the arsenal for the manufacture of pesticides and herbicides. As a consequence of these activities, a number of contaminants have migrated into portions of the shallow alluvial aquifers underlying the ground surface. Among the organic contaminants that have been detected at the Arsenal, *N*-nitrosodimethylamine (NDMA [$(CH_3)_2HNO$]) is present at some subsurface locations within RMA because of the microbiological conversion of hydrazine-based compounds into NDMA in the soil. The presence of NDMA in groundwater is of concern because of the carcinogenic and many other biologically harmful properties of nitrosamines exhibited at small concentrations [1–3].

NDMA (CAS No. 67-75-9; specific gravity = 1.005@4°C; molecular weight = 74.08) is a yellow, oily liquid that is fully soluble in water [3,4]. Environmental sources of NDMA include microbial transformation of *N*-precursors within feedlots [5] and incomplete oxidation of hydrazines [6,7]. NDMA is a common organic chemical present in many exposure routes to the general population including drinking water [8], groundwater [9], beer [10], meats [11,12] during human digestive activity in vivo [13], cheese [11], and in pickles [14]. Concerns over the presence of NDMA within human exposure vectors have prompted the evaluation and development of analytical techniques that have pushed the detection limit of NDMA using these techniques to the low ng/kg levels [15].

Remedial investigations at the Arsenal indicated a low-level organic contaminant plume exiting RMA to the north and northwest directions. The primary pollutants detected within this plume were diisopropylmethylphosphonate, organochloropesticides, and chloroform. To prevent further contamination of areas outside of the Arsenal boundaries, RMA operates an intercept-and-treat system with a flow rate of approximately 1136 l/min. This system, known as the North Boundary Containment System (NBCS), captures contaminated groundwater flowing northward across the arsenal using a soil–bentonite slurry wall. Groundwater extraction (dewatering) wells remove the groundwater, which is then pumped into an influent sump prior to treatment by adsorption onto granular activated carbon (GAC) (Fig. 1). The effluent from adsorption treatment is collected in a common effluent sump prior to discharge into a system of 15 groundwater recharge trenches. Years of analytical monitoring of the groundwater and

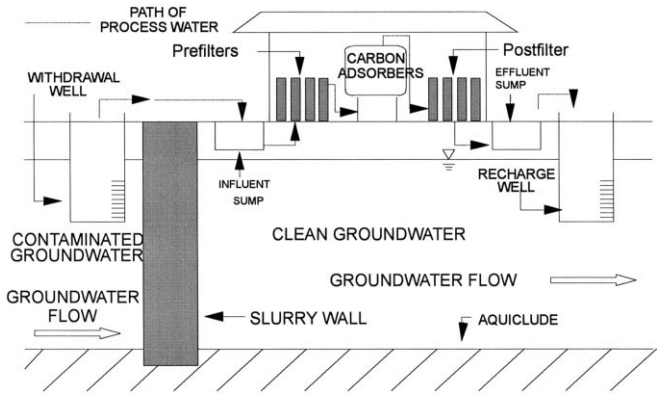

Fig. 1. Schematic of NBCS process flow path.

treatment system indicate that the NBCS is effective in removing the pollutants to within current regulatory levels. However, recent chemical analysis of the groundwaters around and within the NBCS indicates the presence of NDMA within the system waters. These analytical detections were found within the groundwater collected from monitoring wells on the ''contaminated'' side of the NBCS and in the NBCS influent and effluent. Mean levels of NDMA in the influent and effluent waters were 0.35 and 0.20 μg/l, respectively, suggesting that the existing GAC units, as operated, are not highly effective in removing NDMA from the system influent. This is consistent with the observations of Kaplan and Kaplan [16] and of Fleming et al. [9], which show a relatively low adsorption capacity of activated carbon for NDMA. Adsorption processes are effective in removal of non-polar hydrophobic compounds in contrast to the more polar, water-soluble contaminants, such as NDMA [17,18]. Fortunately, chemical analysis of the groundwater outside of the RMA boundary (i.e., north of the northern boundary) did not detect any NDMA. This indicates either a slow progression of NDMA toward the boundary, potentially resulting in eventual contamination of areas outside the Arsenal bounds and/or the presence of an attenuation activity preventing migration of the NDMA off-post. However, continual monitoring for NDMA around and within the NBCS indicates no migration of the NDMA off-site. Therefore, it was postulated that some mechanism around and/or within the NBCS was providing significant attenuation of the NDMA, thereby, preventing the further migration of the NDMA off-site.

This research was conducted to evaluate potential attenuation mechanisms of NDMA within the alluvial aquifer system around the treatment system and within the NBCS itself. The movement of NDMA through the aquifer soils and the respective bioavailability of this compound for degradation are governed by interactions of the contaminant with the soil. Potential abiotic interactions that have been encountered during subsurface transport of contaminants include advection, adsorption, and chemical reaction, such as hydrolysis [18]. Biodegradation may also account for a significant fraction of natural attentuation [19]. Based on the work of Kaplan and Kaplan [16], who studied the biodegradation of NDMA within a variety of microcosms incubated under differing conditions and NDMA dosed at varying levels, NDMA biodegradation may be feasible

within bioreactors using aerobic consortia. Mallik and Testai [20] compared the removal of NDMA to diphenylnitroamine and nitrosopiperidine within amended soil microcosms. Their results indicated that the dosed NDMA was degraded to levels exceeding 30% removal; however, activity ceased within 30 days of incubation. Both diphenylnitroamine and nitrosopiperidine appeared to be more biodegradable than NDMA. Partial mineralizations to carbon dioxide and partial by-products of formaldehyde, methylamine, and methylhydrazine have been reported [5].

Two mechanisms of attenuation, biodegradation (aerobic and anaerobic) and adsorption, onto aquifer solids were selected for investigation in this study. Little information was available in literature to assist in the assessment of these key attenuation mechanisms. Therefore, the study was divided into two primary phases: microbiological fate and soil sorption experiments. Advection was being evaluated under another study using a particle-tracking groundwater model under development that was specific for the unique geohydraulic system found within the NBCS system. The purpose of the microbiological portion of the evaluation was to assess: (1) the rate and extent of microbial mineralization of NDMA in the saturated soil and one of the GAC columns using microorganisms that were native (i.e. already present) within these media (i.e. no seeding with exotic organisms) and (2) the ability of environmental conditions present in the alluvial aquifer around the NBCS to support active NDMA degradation in situ also using the native microbial consortia. GAC had been previously reported to provide little sorptive capacity based on the results reported by the USEPA [19] and chemical analysis of the adsorber influent and effluents. These results were consistent with the findings of Zappi et al. [7] who found GAC to be marginally effective for removing low levels of NDMA from a treated water produced after several hours of UV/chemical oxidation treatment. Therefore, this study focused on evaluating soil attentuation mechanisms within the sub-surface environments surrounding the NBCS. The sorption evaluation was conducted to determine the NDMA sorption capacity of the saturated alluvial aquifer soils within the NBCS dewatering and recharge zones. It was hoped that these experiments would provide critical insight as to the fate of NDMA in terms of potential off-site migration and possibly in situ management (i.e. natural attenuation) of the NDMA within the NBCS groundwater injection zone (the trenches and nearby aquifer recharge zones).

2. Materials and methods

2.1. Water samples

Groundwater samples were aseptically collected from representative dewatering wells, recharge wells, and recharge trenches (Fig. 2). Subsurface (aquifer) soil sampling locations used during this study were selected based on the past history of NDMA contamination. NBCS system influent water samples were collected from system post-filtration lines prior to entering the GAC adsorbers (13,610 kg pulsed-bed adsorbers). Effluent samples were obtained from the exit line of the absorbers. All samples were collected in sterile 250-ml Nalgene bottles, labeled, and placed on ice until

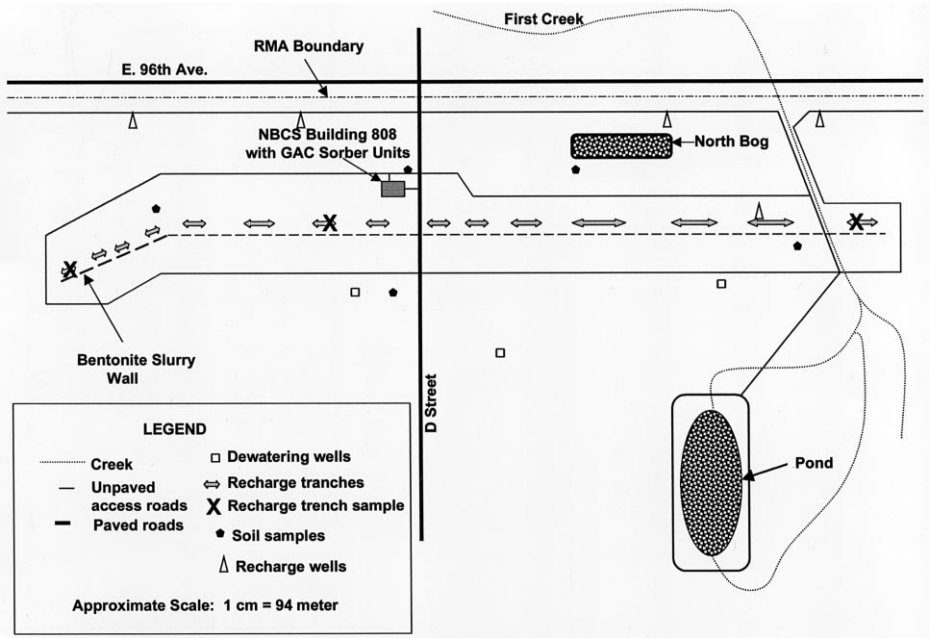

Fig. 2. Planar view of the NBCS area at RMA showing groundwater and subsurface soil sampling locations.

delivery to US Army Engineer Waterways Experiment Station (WES) within 24 h following collection.

2.2. Collection and handling of soil samples

Subsurface soil samples were collected using a truck-mounted drill rig equipped with a 10.2-cm auger drive. Drilling locations were selected based on the samples being collected from within areas of potential NDMA exposure and on information gained from historical geolithology (stratigraphy) charts with the intent of varying samples according to soil type and fabric to the extent possible within the limited NBCS area. Subsurface soil samples were obtained by drilling until the auger indicated the presence of a saturated zone of the unconfined, alluvial aquifer, drilling an additional 61-cm into the saturated zone, and collecting the aquifer material using a push-type 10.2-cm Shelby tube. These subsurface soils were named for the areas from which they were collected, termed West End, East End, Bog, and D Street (Fig. 2). Soil cores were removed from the coring device using a hydraulic piston mounted on the drill rig for core extraction. Extracted cores were placed into an acrylic glove box, 1.83 $(L) \times 0.91$ $(W) \times 0.91$ m (H), which was continuously purged with analytical grade nitrogen gas to limit atmospheric oxygen introduction. To preserve the anaerobic integrity of the core, the outer 2.54 cm of soil was trimmed from the cores in the glove box, after which, the soil cores from each sample location were pulverized, mixed, and then transferred into sterile 500-ml Nalgene bottles and sealed. Soil samples were transported on ice to WES via

overnight delivery and then stored at 4°C until used. Soil samples were analyzed at WES for NDMA, pH, total organic carbon, particle size distribution, and cation exchange capacity (CEC). All the soil samples were typical of the local aquifer materials, yielding neutral pH, sandy or loamy sand textural content and relatively small total organic carbon content (Table 1). The concentration of NDMA in the soils was less than the detection limit of 0.8 μg/kg.

2.3. GAC samples

GAC samples were collected from one of the two operational adsorbers of the NBCS (Adsorber B) using a 0.91 m (length) × 0.635 cm (diameter) (OD) stainless steel tube fitted with a ball valve on the clean end. The tube was inserted into the adsorber via one of the bed sample taps located along the side of the tank. Once the tube was inside the tank to approximately a 61.0-cm radial location, the valve was opened; pressure within the bed forced the GAC sample out into the sample container. GAC samples were collected and maintained under aerobic conditions in airtight containers, prior to shipment on ice to WES and subsequent storage at 4°C.

2.4. Physical and chemical analyses

The subsurface samples were analyzed for NDMA using the methods described in EPA SW-846 Method 8270 [21]. Particle size determinations were made using the methods of Day [22] as modified by Patrick [23]. Organic carbon levels were assessed with the complete combustion method of Nelson and Sommers [24]. CEC was established by summation of base nutrients and acidity [25], and pH was measured with the standard electrode technique [40CFR 796.2750(c)(9)].

2.5. Radiological analysis

For adsorption and sequential desorption experiments, soil–water slurries spiked with ^{14}C-NDMA were separated after equilibration by centrifugation at a relative centrifugal

Table 1
Characteristics of the subsurface soil samples

Soil	pH	%TOC[a]	Particle size			Textural classification[b]	CEC[c]
			% Sand (> 50 μm)	% Silt (50–2 μm)	% Clay (< 2 μm)		(meq/100 g)
West End	7.7	0.177	72.5	20.0	7.5	Sandy loam	45.7
D Street	7.7	0.172	95.0	5.0	0.0	Sand	1.78
Bog	7.5	0.254	97.5	0.0	2.5	Sand	3.12
East End	7.3	0.237	92.5	7.5	0.0	Sand	5.36
South Side	7.4	0.270	87.5	10.0	2.5	Loamy sand	4.23

[a] Percent total organic carbon.
[b] Classification based on US Department of Agriculture method using mechanical analysis.
[c] Cation exchange capacity.

force of $7796 \times g$ for 30 min at 4°C. The radiation remaining in the water was quantified by liquid scintillation spectrometry (LSC) on a Packard 2500 Liquid Scintillation Spectrometer (Packard Instruments, Downer's Grove, IL). Soil phases were analyzed by complete combustion of 1 g of soil in a Packard Sample Oxidizer (Packard Instruments), trapping the released $^{14}CO_2$ in Ultima Gold™ scintillation cocktail (Packard Instruments), and counting the $^{14}CO_2$ by LSC. Radiolabeled ^{14}C from ^{14}C-NDMA biodegradation studies were measured by trapping the respired $^{14}CO_2$ in 1 N KOH. One milliliter aliquots of 1 N KOH samples were mixed with 15 ml of Ultima Gold™ scintillation cocktail (Packard Instruments) and were counted by LSC.

2.6. Adsorption and sequential desorption experiments

All studies were conducted in triplicate and all data presented represent the mean of three replicates. Preliminary testing to select an appropriate soil-to-water ratio for use in batch adsorption experiments was conducted on West End and D Street subsurface soils. One microgram *N*-[methyl-^{14}C]-nitrosodimethylamine (^{14}C-NDMA) was added aseptically to sterile soil–water (S/W) mixtures at ratios of 1:3, 1:4, 1:5, and 1:6 S/W and shaken for 24 h at room temperature (24°C) on a reciprocating shaker. Soil samples were sterilized by treatment with 2 Mrad of irradiation with ^{60}Co. ^{14}C-NDMA remaining in the aqueous phase of the soil–water slurries was measured as described above.

West End and D Street subsurface soils were selected to generate adsorption kinetics based on their clay and organic matter contents (Table 1). Each 1:4 (g/l basis) soil–water mixture was mixed in the presence of 1-μg ^{14}C-NDMA for time intervals of 0.5, 1, 2, 24 and 48 h and then separated by centrifugation and quantified as described above. Desorption kinetics were evaluated on the same subsurface soils after equilibration times of 0.5, 1, and 2 h.

After establishing the equilibration times, partitioning experiments were conducted to assess soil sorptive capacity. Adsorption isotherms were generated by exposing 0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 μg of ^{14}C-NDMA to each of the six test soils at concentrations of 30% [(soil to total volume (l) slurry] and counting residual radiolabel in the aqueous phase by LSC. The soil phase from the 2-μg test was also analyzed by complete combustion and LSC, as described above. Sequential batch desorption testing was conducted for a total of three cycles. The entire solution phase was removed and replaced after each cycle. Each of the solution phases was analyzed after each cycle; however, the soil phase was also analyzed after the third cycle.

2.7. Biodegradation experiments

Biodegradation of NDMA was studied in 250-ml Bellco respirometer flasks (Belco Glass, Vineland, NJ). Six-gram oven-dry weight (ODW) of contaminated material was added to each sterile flask along with sufficient sterile deionized water to produce a 20-ml, 30% (w/v) slurry. Poisoned controls were prepared by dosing with $HgCl_2$ to a final concentration of 5 mM. The flasks were incubated on an orbital shaker at 75 rpm for 30 min. West End and South Side subsurface soils were also vortexed to further break up clumps.

One microgram [^{14}C]-NDMA (equivalent to 50 μg NDMA/l) was added to each flask to conduct the mineralization studies. The effect of initial concentration on NDMA mineralization was studied by spiking with solutions of 1 and 10 μg radiolabeled NDMA/ml to obtain 50 μg/l, 500 μg/l, 5 mg/l, and 50 mg/l final concentrations. An anaerobic atmosphere was achieved in the flasks by flushing with purified N_2 gas for 60 s prior to sealing the units with rubber stoppers, and then sealing the stoppers with weather-stripping cement. Poisoned flasks were incubated for 2 days prior to the addition of radiolabeled NDMA. Spiked flasks were incubated for 30 days at 75 rpm and 25°C. 1 N KOH was used in the respirometer sidearms to capture carbon dioxide produced; this solution was replaced after 6 h, and then after 1, 2, 3, 5, 10, 15, and 30 days. At 30 days, the KOH was replaced, the slurries were acidified by the addition of six drops of conc. H_3PO_4, and the biometers were incubated for 6 additional hours prior to separation of the soil and liquid phases by centrifugation as above. One milliliter of the KOH sample and 1 ml of the resulting supernatant were each counted in 15 ml Ultima Gold, as described above. One gram of the remaining soil or GAC material was placed into a tared aluminum weighing dish, dried, and reweighed prior to combustion of a 0.1-g aliquot in a sample oxidizer, and counting of the released $^{14}CO_2$, as described above.

To establish the rate and extent of NDMA mineralization occurring at different initial concentrations of NDMA, 30% slurries of Bog and West End subsurface soils were established as described above, except that slurries were dosed with 10-μg [^{14}C]-NDMA and either 0, 90, or 990 μg of unlabeled NDMA, giving total NDMA concentrations of 10, 100, and 1000 μg NDMA/20 ml of 30% (w/v) slurry. Data obtained from the previous comparison of NDMA mineralization rates in subsurface soils and GAC were used as the source of data for 1 μg of NDMA/20 ml of slurry.

3. Results and discussion

3.1. Adsorption isotherms

Adsorption and desorption concentrations for each of the five subsurface soils generally fit along the same straight line (Fig. 3). Correlation coefficients for West End, D Street, Bog, East End, and South Side subsurface soils ranged from 0.70 to 0.92. Adsorption isotherms were also run on the five subsurface soils. Results conformed well to a linear model ($r^2 > 0.90$) [26]. Correlation coefficients for West End, D Street, Bog, East End, and South Side subsurface soils were 0.94, 0.95, 0.94, 0.90, and 0.91, respectively (data not shown). This model has been successfully used for modeling the equilibrium sorptive state (liquid–solid partitioning) of a wide model, the distribution coefficient, K_d, expresses the partition of a solute between the solid and the solution phases and is measured by equilibrating soil with a series of increasing concentrations. The model is illustrated below:

$$q = K_d * C \quad (1)$$

where q = soil concentration (mg/kg), K_d = distribution coefficient (l/kg), and C = liquid phase concentration (mg/l). The larger the partitioning coefficient, the greater the

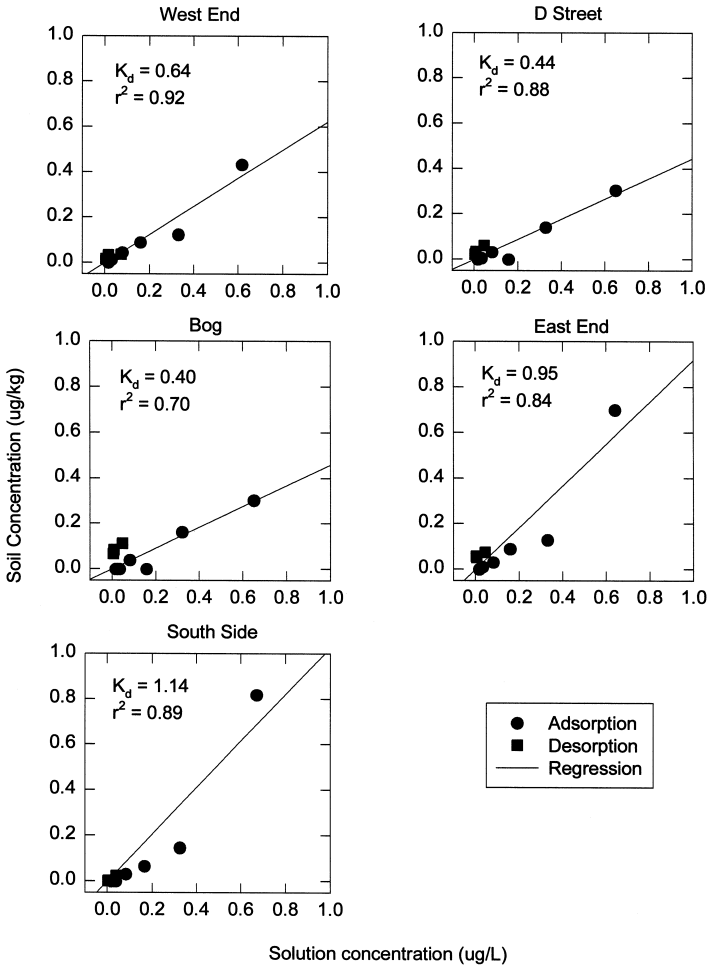

Fig. 3. Adsorption and sequential desorption isotherms for five subsurface soils from the NBCS, RMA. K_d and r^2 values include data for both adsorption and desorption.

affinity of the compound for the solid or soil phase, which means that the abiotic attenuation effect is greater. Contaminants having distribution coefficients in excess of 100,000 are considered highly adsorbable, while those having distribution coefficients between 10 and 100,000 are considered slightly to moderately adsorbable, and those having coefficients less than 10 are not considered very adsorbable [18].

The adsorption data for East End and South Side subsurface soils indicated that the highest concentration leveled-off as the sorption capacity of the soil was approached. When regression analysis was applied to the five remaining adsorption data points for these two soils, r^2 values improved from 0.90 to 0.94 and from 0.91 to >0.99, respectively. A five-point regression analysis of the other subsurface soils did not improve their r^2 values. The adsorption distribution coefficients ranged from 0.5 to 1.2

l/kg. The distribution coefficients (K_ds) for all of the subsurface soils (Fig. 3) were low compared to those of other organic compounds [27]. Results of a Pearson Product Moment Correlation Analysis of distribution coefficients with the chemical and physical characteristics of the soil indicated no significant relationship between adsorption K_d and percent sand, silt, clay, total organic carbon, pH, cation exchange capacity ($p > 0.050$). Therefore, none of these properties impacted the mobility potential of NDMA in these subsurface materials. The high aqueous solubility of NDMA is likely to govern mobility in these soils.

In order to ensure that the sorptive capacities measured with these soils were indeed abiotic, cultures were run on the subsurface soil samples following sterilization. No growth of microorganisms was observed during the period of isotherm data generation. Therefore, all NDMA loss from the water was attributable to adsorption rather than to biodegradation.

3.2. Sequential batch desorption

Results of sequential desorption tests indicated that nearly all adsorbed NDMA desorbed after one cycle. Desorption isotherms were approximately linear ($r^2 > 0.92$), except for West End data, for which r^2 for the linear regression was 0.55 (data not shown). Distribution coefficients were also low and similar to adsorption distribution coefficients (Fig. 3). These results indicated that the small amount of NDMA that adsorbed to subsurface soils was readily and completely removed when challenged with water containing lower levels than those used for initially establishing sorptive equilibrium. Results of correlation analysis of desorption K_d values with soil properties yielded no relationship. Therefore, as was the case for adsorption, desorption from these subsurface soils was not governed by the local subsurface soil properties, but was likely the result of the aqueous solubility of NDMA.

3.3. Rate and extent of NDMA mineralization from biodegradation

Cumulative mineralization, calculated from radiolabeled carbon dioxide ($^{14}CO_2$) measurements made during the aerobic and anaerobic incubations, ranged from about 30% to > 60% over a period of 30 days in subsurface soils and the GAC sample (Fig. 4). These data were analyzed for initial rates, average rates, and mineralization rate constants using several degradation models. These models are listed below:

$$\frac{dC}{dt} = -k_0 \quad \text{(Zero order degradation)} \tag{2}$$

$$\frac{dC}{dt} = -k_1 C \quad \text{(first order degradation)} \tag{3}$$

$$\frac{dC}{dt} = -k_2 C^2 \quad \text{(second order degradation)} \tag{4}$$

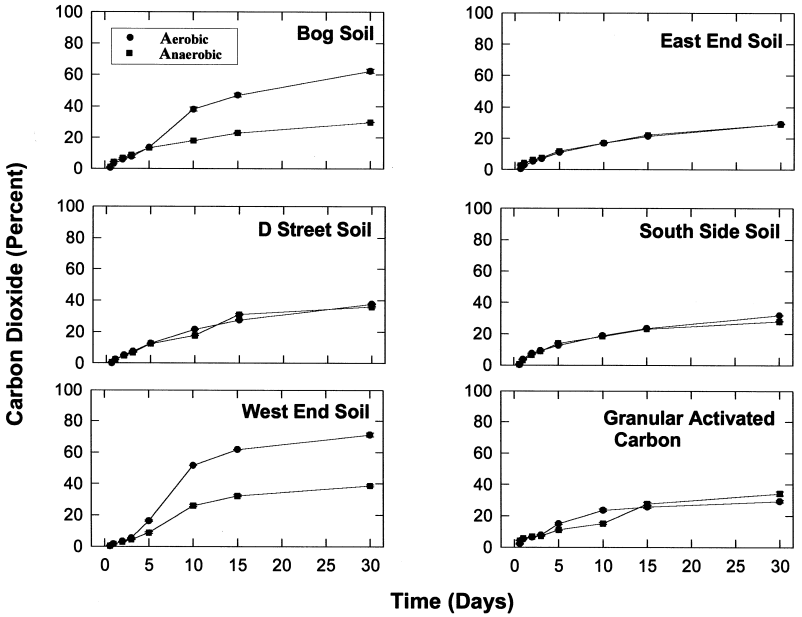

Fig. 4. Mineralization curves resulting from addition of 50 μg of NDMA/l of 30% slurries of subsurface soil and GAC in water.

Here, k_0, k_1, and k_2: zero, first, and second order rate constants, respectively.

$$\frac{dC}{dt} = -k\frac{C}{K_M + C} \quad \text{(Michaelis–Menten degradation kinetics)} \tag{5}$$

Here, concentration (C) of NDMA in liquid phase $(\mu g/ml)$ is defined as

$$C = \frac{m_0(1 - \text{fraction mineralized})}{\left(V_{slurry} - m_{soil}/2.5\right) + m_{soil}K_d}$$

Where m_0: amount of NDMA added initially (μg); V_{slurry}: volume of slurry (ml); m_{soil}: mass of soil in the slurry (g); K_d: partition coefficient of NDMA between soil and slurry (ml/g); K_M: the Michaelis constant, a measure of affinity between NDMA and the microorganism; k: the maximum velocity of NDMA degradation.

These expressions are based on the following assumptions.

(a) The microbial cell concentration does not change appreciably during the course of the study. This assumption was justified given the small concentration of NDMA (carbon and energy source) in this study (50 μg NDMA/ml of slurry). Consequently, cell concentration does not appear explicitly in any of the expressions, but is implicit in the rate constants.

(b) The uptake of NDMA by the cells occurs only from the dissolved form. Hence, the rate expressions considered are based on solution–phase concentrations of NDMA.

(c) Solid and liquid phases exist in a state of instantaneous equilibrium. The NDMA adsorption/desorption results indicated that equilibrium was attained rapidly (within

hours) in these subsurface soils and practically all the adsorbed NDMA can be desorbed by repeated washing. Given the long period (days) between samples in this work, the assumption of instantaneous equilibrium appeared to be justified.

The integral method was used to analyze the data. Parameters were estimated by a linear-least squares procedure, after linearization of the integrated equations. The Michaelis–Menton kinetics was eliminated from consideration, because one of the constants in the equation was invariably estimated to be negative. The negative estimate is perhaps an aberration resulting from the linear-least squares estimation procedure employed in this study. Zero-order kinetics, which are equivalent to suggesting that the degradation rate remains constant, were an excellent fit when the 30-day measurements were excluded from the analysis. However, when all the experimental data were used, zero-order kinetics yielded the worst fit, meaning that they are not suitable for this application. Among the first- and second-order degradation kinetics, agreement between predictions and experimental data improved as the order of reaction was increased, although the improvement between first- and second-order was marginal. Hence, first-order degradation was considered a satisfactory fit. Considering the small concentration of NDMA in this part of the study, and the fact that biological processes are involved, first-order degradation was also mechanistically sound. When replicate sets of each of the slurries were treated with mercuric chloride, no radiolabeled carbon dioxide was formed. This indicated that NDMA was not degraded to volatile products under abiotic conditions.

Based on an evaluation of the first-order degradation constants, the largest rates of mineralization occurred with Bog and West End subsurface soils incubated with 50-μg radiolabeled NDMA/l under aerobic conditions (0.032 ± 0.002 and 0.043 ± 0.004 per day, respectively) (Table 2). The smallest rates of mineralization were obtained from Bog, East End, and South Side subsurface soils and GAC under anaerobic conditions

Table 2
First-order mineralization constants and correlation coefficients for subsurface soils and GAC exposed to 50 μg NDMA/l of slurry

Sample	Incubation	First-order mineralization rate ± std. error (day^{-1})[a]	Half-life of NDMA in soil or GAC slurry (days)[b]	r^2 (%)[c]
Bog soil	Aerobic	0.032 ± 0.002	15.6	0.96
	Anaerobic	0.014 ± 0.002	35.7	0.82
D Street soil	Aerobic	0.018 ± 0.001	27.8	0.94
	Anaerobic	0.017 ± 0.002	29.4	0.90
East End soil	Aerobic	0.013 ± 0.001	35.0	0.89
	Anaerobic	0.014 ± 0.001	38.5	0.84
South side soil	Aerobic	0.015 ± 0.001	33.3	0.86
	Anaerobic	0.014 ± 0.002	35.7	0.76
West End soil	Aerobic	0.043 ± 0.004	11.6	0.92
	Anaerobic	0.019 ± 0.002	26.3	0.90
GAC	Aerobic	0.015 ± 0.002	33.3	0.68
	Anaerobic	0.016 ± 0.001	31.2	0.89

[a] Measured in a 30% (w/v) slurry at 25°C.
[b] Determined as the time required for 50% of the added NDMA to be mineralized from the slurry at 25°C.
[c] Correlation coefficient for linear fit of predictions to experimental data.

and East End subsurface soil under aerobic conditions. In East End soil under aerobic conditions, cumulative mineralization at 30 days amounted to less than 43% of the initial radiolabeled NDMA added. Nearly identical mineralization patterns were obtained, both aerobically and anaerobically, for D Street, East End, and South Side subsurface soils and for GAC, indicating that the microorganisms active on NDMA may have been facultative anaerobes. Bog and West End subsurface soils were selected for additional study because of their large mineralization rates.

Half-life values for each of the soil slurries at the 50-μg NDMA ranged from 11.6 to 38.5 days, with West End soil incubated under aerobic conditions having the shortest half-life value (Table 2). Since these values were generated in laboratory vessels, predictions made for field use must be treated with caution. Laboratory values generated using slurries under ideal conditions in small containers are likely to be greater than those that will be found in nature.

3.4. Impact of NDMA concentration on mineralization

The Bog and West End subsurface soils were selected for further study because they had the largest mineralization rates under aerobic conditions. These soils were examined for mineralization obtained for different initial levels of NDMA. The data describing mineralization starting at these different levels of [^{14}C]-NDMA were analyzed using a pseudo first-order equation similar to Eq. 3. In the absence of a better model describing mineralization rates at various NDMA concentration levels, the use of these rate constants (or the specific mineralization rates) should be constrained within the concentration ranges of each serial concentration only.

For both the Bog and West End subsurface soils, the specific mineralization rates decreased nearly 3-fold between the 50 μg/l and 50 mg/l levels (Table 3). A decrease in rate at the larger NDMA concentrations suggests some inhibition of mineralization, but does not indicate whether this was the result of NDMA toxicity, lack of sufficient nutrients (i.e. nitrogen, phosphate, trace minerals) needed to support larger degradation rates, or to an overload of existing microbial degradation capabilities. For the Bog subsurface soil, the largest decrease occurred between 500 μg/l and 5 mg/l treatments,

Table 3
First-order mineralization constants at serial NDMA concentrations for Bog and West End subsurface soils

Soil	NDMA concentration	Mineralization rate ± std. error (day^{-1})[a]	(r^2)[b]
Bog soil	50 μg/l	0.032 ± 0.002	0.96
	500 μg/l	0.025 ± 0.003	0.90
	5 mg/l	0.013 ± 0.002	0.91
	50 mg/l	0.010 ± 0.001	0.97
West End soil	50 μg/l	0.043 ± 0.004	0.92
	500 μg/l	0.019 ± 0.002	0.93
	5 mg/l	0.014 ± 0.009	0.96
	50 mg/l	0.011 ± 0.001	0.96

[a] Measured in a 30% (w/v) slurry at 25°C.
[b] (r^2) = Correlation coefficient for linear fit of predictions to raw data.

and for the West End subsurface soil, the most pronounced decrease occurred between the 50 and 500 μg/l treatments.

Inhibition of mineralization by NDMA levels above 500 μg/l to 50 mg/l did not indicate a lack of mineralization. Rather, the total amount of NDMA mineralized with each 10-fold increase in NDMA also increased by an order of magnitude (Fig. 5). Therefore, the 500 mg/l NDMA treatment mineralized nearly 360 times more NDMA than the 50 μg/l NDMA treatment. The decrease in mineralization rate with increase in NDMA concentration is very similar to the observations of Kaplan and Kaplan [16] for a topsoil exposed to serial increases in NDMA. They found that the extent of mineralization and the rate constants were largest for the two smallest concentrations [10 ng and 1 μg NDMA/g of soils (our comparable concentrations were 167 ng/g and 1.67 μg NDMA/g of soil, respectively)]. By contrast, the data also indicated that even at NDMA levels of 50 μg/l, the subsurface soil microflora can mineralize substantial levels of the NDMA initially present. However, at some point less than this concentration, NDMA may become so scarce as to prevent the microorganisms carrying out the degradation from sustaining significant rates of mineralization, unless NDMA can be co-metabolized at the expense of other more abundant sources of carbon and energy.

3.5. Other considerations

When the rate constants obtained for the different initial NDMA concentrations were plotted against the initial NDMA concentration, the result for each subsurface soil was a hyperbolic graph typical of what would be expected from inhibition of degradation or from Monod kinetics. In making this comparison, several factors can affect the rates, ranging from inhibition by NDMA toxicity to potential sorption of increasing levels of NDMA as the concentration increases.

Kaplan and Kaplan [16] conducted studies for 74 days using 100 μg of NDMA/g of soil at moisture levels ranging from dry soil to 25%, 50%, 75%, and 100% of saturation. While almost all mineralization activity was inhibited in dry soil, the amount of NDMA

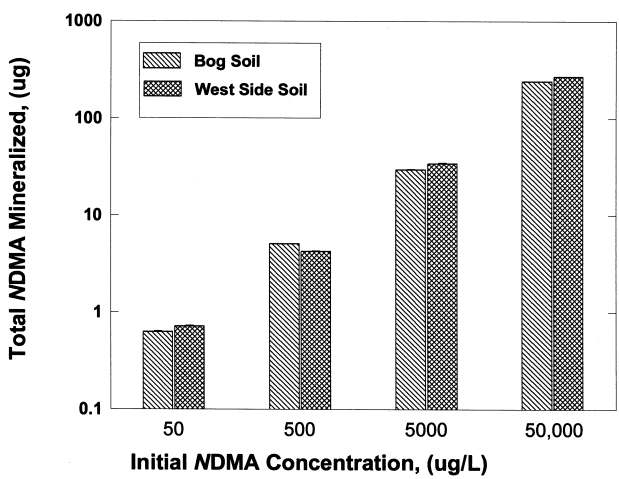

Fig. 5. Comparison of total NDMA mineralized with the total NDMA initially added.

Table 4
Correlation of mineralization rates with subsurface soil parameters[a]

Independent variable	r^2
pH	0.30
Organic matter concentration	0.44
Cation exchange capacity	0.43
Sand content	0.27
Silt content	0.45
Clay content	0.18

[a]Correlations were determined for each first-order mineralization rate presented in Table 2.

mineralized (between 47.6% and 57.0%) was similar at all other moisture levels. Our study was conducted with subsurface soil and GAC as slurries, because we were interested in determining mineralization rates under saturated conditions and because the subsurface soil samples came from aquifers. The additional water may have enhanced NDMA mineralization somewhat over that expected in saturated soils. However, because NDMA undergoes such a limited amount of sorption in the μg/kg range, data from our subsurface soils at field moisture capacity were expected to be similar to the slurry data.

Kaplan and Kaplan [16] also examined the effect of soil organic matter on NDMA mineralization kinetics using 100 μg of NDMA/g of soil. Using the same soil amended with 2.6% to 36.0% organic matter (a topsoil was treated with equal parts of carbon-free (acid-washed) sea sand and bentonite to adjust the organic matter levels), they found that the amount of organic matter did not significantly affect NDMA mineralization kinetics. Although we did not examine the impact of varying organic matter levels, we did not find significant correlations between subsurface soil (or GAC) organic matter level or any of the other soil parameters and the mineralization rates obtained for 50 μg NDMA/l of soil slurry (Table 4).

3.6. Environmental regulation of NDMA degradation

A study was conducted to evaluate the oxidative conditions of various components of the NBCS at the same time the samples for the remainder of the study were taken. This includes average data from the system influent and effluent, a recharge trench, a recharge well, and a dewatering well summarized as follows:

Source of data	Dissolved oxygen level (mean mg/l ± SD)	Oxidation–reduction potential (mean mg/l ± SD)
Adsorber system influent	1.9 ± 0.0	138 ± 3
Adsorber system effluent	0.1 ± 0.0	134 ± 4
Recharge trench	0.0 ± 0.0	32 ± 2
Recharge well	0.9 ± 0.1	94 ± 2
Dewatering well	2.0 ± 0.1	139 ± 1

Thus, the data indicate that NBCS waters generally were slightly oxidized (microaerophilic). These conditions are most conducive to supporting the types of microorganisms isolated from the various matrices sampled. Teeter et al. [28] observed that the overall oxidative state of the NBCS was very sensitive in terms of rapidly changing from slightly reduced to oxidized conditions. They observed rapid oxidation of reduced iron within the waters sampled from the system influent and dewatering system (wells and trenches). This indicated that respiration at the NBCS can easily change from reduced to oxidized conditions or in the other direction, depending on such external influences as air permeation into the ground, long-term exposure while remaining within the recharge system, or influx of organic substrate during release of spent carbon fines into the trenches and/or wells. Another factor that can be used in characterizing the overall ecological state of the NBCS in terms of supporting microbial activity is pH. Teeter et al. [28] determined that the waters within and around the NBCS were neutral, which is appropriate for supporting biological growth.

In summary, environmental conditions within and around the NBCS should be conducive to supporting an active bacterial population, as indicated by the results of this study. The results of this study strongly support the ability of microbial communities present to degrade NDMA. Moreover, addition of nutrients and increasing the levels of electron acceptors may stimulate the native microflora and increase degradation rates. A brief nutrient amendment study indicated that addition of small to moderate levels of nitrogen and phosphorus (small = 0.100 g of nitrate and 0.015 g of phosphate; moderate = 1.00 g of nitrate and 0.150 g of phosphate) resulting in a cumulative increase in NDMA mineralization of 7- to 100-fold, respectively. Thus, while natural processes seem to be capable of attenuating the NDMA observed in this study, in situ biotreatment obtained by addition of small levels of nitrate and phosphate may ensure rapid removal of any residual amounts of NDMA. These findings supported the results reported by Rubin and Alexander [29] who found that the amending of nutrients did enhance the removal of trace organic compounds from aqueous microcosms.

4. Engineering significance

The results of this study indicated that removal of NDMA within the aquifer by adsorption onto the aquifer solids is not a significant attenuation factor. However, the presence of NDMA-degrading microorganisms with facultative characteristics does offer the potential for natural attenuation to provide significant removal of the NDMA. However, the ability to demonstrate substantial mineralization in the laboratory only confirms that the potential for mineralization is present. These criteria satisfy one of the three major criteria recently cited by the USEPA [19] as indicating that natural attenuation is an acceptable alternative to more active forms of treatment for removal of hazardous substances from the environment. It was perplexing why NDMA was being transported through the aquifer up until interception and passage through the treatment system. This indicated limited attenuation capacity for NDMA within this region of the aquifer (within the ''dirty'' side). However, once the NDMA was introduced into the

treatment plant and passed through into the recharge zone, NDMA was being attenuated, as indicated by the lack of detectable NDMA within the many observation wells placed down-gradient of the NBCS within the off-post areas. It was possible that the changes in chemical composition of the water that occur within the treatment plant, such as increased REDOX, and/or removal of some chemicals may provide key growth factors or removal of an inhibitory agent by the GAC that enhances the attenuation capacity of the recharge zones. Engineers involved in the bioremediation of contaminated sites would question the viability of an aquifer biomass that can be catabolically maintained using NDMA as a substrate at such low levels. However, the work of Boethling and Alexander [30] provided supporting evidence as to the ability of microorganisms to degrade substrates at very low concentrations. They observed mineralization of ^{14}C-labeled glucose at levels less than 20 ng/l using *Pseudomonas* sp. obtained from enrichment culture and incubated in sterilized lake water. These glucose levels were degraded at rates for greater than those predicted by the Michaelis–Menten Equation.

These results offer an additional interesting option to site managers in that localized area of enhanced biological activity, established by addition of nutrients and possibly additional electron acceptors, may be utilized as a safeguard against loss of NMDA across the site boundaries. However, any effort to add nutrients to stimulate growth of microbial communities within the NBCS must be done carefully to avoid biofouling of the recharge zones. Teeter et al. [28] identified significant losses in recharge capacity of recharge wells resulting from excessive bacterial growth. Careful scheduling and formulation of injection fluids along with intensive monitoring of recharge systems should allow for bacterial stimulation without excessive biofouling.

5. Conclusions

Sorption is not extensive in the RMA soils for NDMA levels in the parts per billion (ppb) range. Distribution coefficients for all of the subsurface soil samples were approximately 2 l/kg. Adsorption was reversible. The NDMA will likely remain in the aqueous phase, eliminating accessibility as a problem for long-term removal via continual pumping of the groundwater. Moreover, NDMA was not detected in the subsurface soil samples at the RMA, indicating that NDMA was not accumulated in the aquifer soils.

Biodegradation is a major attenuation mechanism for NDMA. Native microorganisms cultured from both subsurface soils and GAC samples were found to mineralize substantial (about 30% to more than 60%) NDMA under both aerobic and anaerobic conditions. First-order kinetics were found to best describe NDMA removal. Based on the serial mineralization studies, the role of NDMA concentration as a factor in regulating NDMA the rate of degradation does not appear to have an effect until levels reach the mg/kg range, although NDMA was mineralized over the entire range of concentrations examined. The levels of nutrients or co-factors necessary for the degradation process present in the Bog and West End subsurface soil field samples were evidently capable of supporting microbial mineralization of NDMA in the 50 to 500 μg/kg range, as indicated by the destruction of from 40% to 70% of the added NDMA

within 30 days. For this reason, it was concluded that natural biodegradation processes are likely able to remove all of the NDMA moving in the groundwater aquifer at RMA. However, it is important that these findings be confirmed in the field.

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