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Coupled Abiotic/Biotic Degradation of N-Nitrosodimethylamine in Subsurface Sediments

Jim E. Szecsody (jim.szecsody@pnl.gov), James P. McKinley,
Andrew Breshears, Ravi K. Kukkadapu, and Carolyn Burns
(Pacific Northwest National Laboratories, Richland, Washington)

ABSTRACT: N-nitrosodimethylamine (NDMA) is a byproduct of propellant manufacture, which, even at trace levels (0.7 parts per trillion), poses a considerable threat to health and ecology. Unintentional surface and subsurface releases of NDMA in water results in rapid subsurface transport due to minimal NDMA sorption and negligible degradation. In this study, abiotic, biotic, and coupled degradation/mineralization processes were investigated, with the field application of a permeable reactive barrier. When subsurface sediments are chemically reduced, abiotic surface phase reactions rapidly degraded NDMA to nontoxic dimethylamine (DMA), primarily by adsorbed Fe(II). The NDMA mineralization rate and extent in oxic systems was oxygen dependent, which was indicative of microbial oxygenase pathway(s) promoting mineralization. Propane addition did promote more rapid oxic NDMA mineralization. Mineralization rates were ~10x slower under iron reducing conditions for the same sediment, but the NDMA mineralization extent was still significant (10% to 15% for reducing systems, 35% to 65% for oxic systems). Results suggest that while abiotic NDMA degradation to DMA may be sufficient for remediation, sequential abiotic NDMA degradation (in reduced sediment) to intermediates followed by down gradient biotic mineralization of intermediates (in oxic sediment) may yield the most rapid rates for complete mineralization of NDMA mass to field-relevant (ppt) concentrations.

INTRODUCTION

N-nitrosodimethylamine (NDMA) is a byproduct of propellant manufacture, which, even at trace levels (0.7 parts per trillion), poses a considerable threat to health and ecology. Unintentional surface and subsurface releases of NDMA in water results in rapid subsurface transport due to minimal NDMA sorption and slow or negligible degradation in both aerobic and anaerobic environments. However, some early studies showed that NDMA can be degraded by aerobic environmental consortia (Kaplan and Kaplan, 1983) and soil microcosms (Mallik and Testai, 1981). Recent studies with microbial isolates show that NDMA is degraded by specific methane-, propane-, and toluene-4-monooxygenase enzymes (Sharp et al., 2005). NDMA is also mineralized most rapidly in oxic bioreactors (Schaefer et al., 2007) and oxic sediment systems (Gunnison et al., 2000). Because ex-situ degradation of NDMA by zero valent iron and Ni-Fe mixed metal (Odziemkowski et al., 2000), it is possible that initial abiotic degradation followed by biotic mineralization of NDMA could most rapidly mineralize NDMA. An in situ reducing environment can be created by zero valent iron injection/barrier installation or chemical reduction of aquifer sediments using sodium dithionite (Szecsody et al., 2005, Vermeul et al., 2007).

For zero valent iron and Ni/Fe mixed metal, three possible mechanisms for NDMA degradation have been proposed: (1) direct electron transfer from zero valent iron,

(2) electron transfer from adsorbed Fe^{2+}, and (3) catalyzed hydrogenolysis by H_2 produced from iron corrosion. While degradation of many compounds appears to occur via the first or second mechanism, recent evidence suggests that the third mechanism was most likely (Gui et al., 2000), based on several lines of evidence. First, the direct reduction of NDMA by zero valent iron was judged to be unlikely, based on electrochemical potentials of the two species. Chemical evidence also supported the conclusion that surface hydrogenation degraded NDMA. The direct electrochemical reduction of NDMA produces dimethylamine (DMA) and nitrous oxide (i.e., proposed degradation products for mechanism #1), but the batch and column experiments conducted by Odziemkowski et al., (2000) with zero valent and Ni/Fe mixed metals produced the products of hydrogenation: DMA and ammonia. Electron transfer from zero-valent iron hydrolyzes water to yield hydrogen. This hydrogen adsorbs to the iron surface and reacts with NDMA via catalytic hydrogenation. In addition, because most of the zero valent metals are coated with a magnetite (Fe_3O_4) film (Odziemkowski et al., 2000), the proposed mechanism involves magnetite.

This project was initiated to determine whether the coupled abiotic/biotic degradation of NDMA could be a viable remediation alternative to ‘pump and treat’ methods currently in use, specifically at the Aerojet, California site, which has NDMA groundwater contamination. The general objective of the project is to stimulate NDMA degradation through combined biotic and abiotic processes in natural, contaminated aquifer sediments. We hypothesize that an initial degradative environment can be readily induced in the subsurface through the injection of sodium dithionite. The reduction in the sediment of structural iron in sediment minerals will produce a porous reactive barrier that can degrade NDMA. We further hypothesize that the complete mineralization of NDMA will require or be facilitated by the in situ microbial community, if it is appropriately stimulated by the addition of an electron donor. Abiotic degradation mechanisms of NDMA in chemically reduced sediment was investigated by: a) NDMA reactions with isolated iron minerals identified in reduced sediment, and b) reduced sediment with specific iron phases removed or added. NDMA mineralization (abiotic/biotic) was additionally investigated in oxic, reduced, and sequential reduced, then oxic sediments with the addition of trace nutrients and electron donors.

MATERIALS AND METHODS

Experiments. Aquifer sediment from Aerojet (Sacramento, CA) well 30053 255’ depth and Ft Lewis (Logistics Center, Tacoma, WA) 60’ depth were reduced by 0.01 to 0.1 mol/L sodium dithionite for 1 week (Szecsody et al., 2004), then washed with groundwater (10 pore volumes). Sediments were modified with addition of iron oxides or removal of iron phases by chemical treatment. Batch NDMA experiments consisted of mixing 0.1 to 5 g of sediment with 10 to 50 mL of NDMA-laden water (2.5 ppm to 10 ppt initial concentration). Experiments were typically sampled at times ranging from minutes to 100s of hours and analyzed for NDMA and degradation products (described below). Column experiments consist of injecting NDMA-laden water at a constant flow rate into a 1-D column (0.76 cm diameter × 10 to 25 cm length) packed with sediment and collecting effluent samples for analysis. Column experiments are at ~100 times higher sediment/water ratio relative to most batch experiments, so observed degradation rates are more rapid.

NDMA and Degradation Product Analysis. NDMA at 0.1 to 50 mg/L concentration was measured by high performance liquid chromatography (HPLC). This method consists of injecting a 50 microliter sample into a 40% methanol, 60% water mobile phase at 0.8 mL/minute into a C-18 column (250 mm x 4.6 mm), with UV detection at 230 nm. The NDMA retention time under these conditions was 5.6 minutes, with a detection limit of 0.05 mg/L. Significantly lower NDMA concentrations were analyzed by liquid scintillation counting using 14C-labeled NDMA (56 mCi/mmol specific activity). For this low level analysis, a 1 mL sample was injected into a preparatory scale HPLC column (476 mM x 11 mm) with a 12% methanol/88% water mobile phase at 5.0 mL/minute. The analytical column was used to separate NDMA from other aqueous degradation products. The NDMA was separated in the column effluent (7.8 to 10.4 min. retention time) and then counted for 180 minutes on a liquid scintillation counter. The detection limits was 0.5 ppt.

A degradation product of NDMA, dimethylamine (DMA) was analyzed by HPLC after derivatization using 9-fluorenymethylchloroformate (Lopez et al., 1996) or 2,4-dinitroflorobenzne (DNFB, Gui et al., 2000). The original DNFB method with the DNFB/DMA molar ratio of 50:1 with additional reagents (acetonitrile and NaOH) was modified to have a DNFB/DMA ratio of 20:1 so that lower DMA concentrations could be more accurately measured.

RESULTS AND DISCUSSION

Aqueous Stability. Aqueous solutions of NDMA at a concentration of 2.3 mg L^{-1} was stable for 700 h at pH 3.5 to 14. Some NDMA degradation was observed at pH 2.5. Aqueous solutions of NDMA at different redox conditions induced by H_2 bubbling in water (Eh = -597 mV, -310 mV, -230 mV, and +100 mV) was also stable for 100s of hours. NDMA did, however, slowly degrade in 0.1 mol/L sodium dithionite solution (chemical reductant, Eh = -560 mV) with a half-life of 230 h. Although there was no photodegradation of NDMA in fluorescent light, experiments were conducted in amber glass vials or stainless steel columns. NDMA does photodegrade in UV light.

Pathway and Reactive Surface Phase. When subsurface sediments are chemically reduced, abiotic surface phase reactions rapidly degraded NDMA (8 h half-life for high reduction, 600 h half-life for low reduction, Figure 1a) to nontoxic dimethylamine (DMA, Figure 1b). DMA was degraded further at longer time periods. Higher sediment reduction resulted in a higher mass of the surface phases (ferrous oxides, carbonates, and sulfides) and a more alkaline pH. The reductive capacity of the dithionite-reduced sediment is ~80 umol/g, or 0.44% iron per gram of sediment. The reactivity of these different iron phases was investigated (McKinley et al., 2007). Alkaline hydrolysis by itself (to pH 11) did not degrade NDMA. Alkaline hydrolysis with the oxic or anaerobic sediment (as a catalyst) also did not degrade NDMA (i.e., a reactive phase in the reduced sediment appears to be involved in electron transfer). Iron sulfides, while present in the reduced sediment, did not promote significant NDMA degradation, as additions did not change the NDMA degradation rate. Iron(II) carbonate (siderite) removal also did not change the NDMA degradation rate (Figure 1c).

Magnetite by itself (no sediment) did not promote NDMA degradation, but magnetite removal from the reduced sediment (Figure 1d) decreased the NDMA degradation half-life from 8 h to 25 h (i.e., significant, but there was still remaining reactivity). It is likely that the dithionite-treated magnetite contains some altered surface phase such as adsorbed ferrous iron or sulfides. When this dithionite-treated magnetite that was removed from one experiment was added to another experiment, the NDMA degradation reactivity increased. Magnetite removal from the Aerojet sediment prior to dithionite reduction showed a slower NDMA degradation rate (30 h half-life) compared to just dithionite-reduced sediment (8 h half life). Therefore, magnetite itself appears to not be the primary reduce phase that degrades NDMA, but if present, possibly surface phases on magnetite promote degradation. In one study with zero-valent iron and -alent iron/nickel metals, it was hypothesized that magnetite on zero-valent iron would be promoting NDMA degradation to DMA (Odziemkowski et al., 2000).

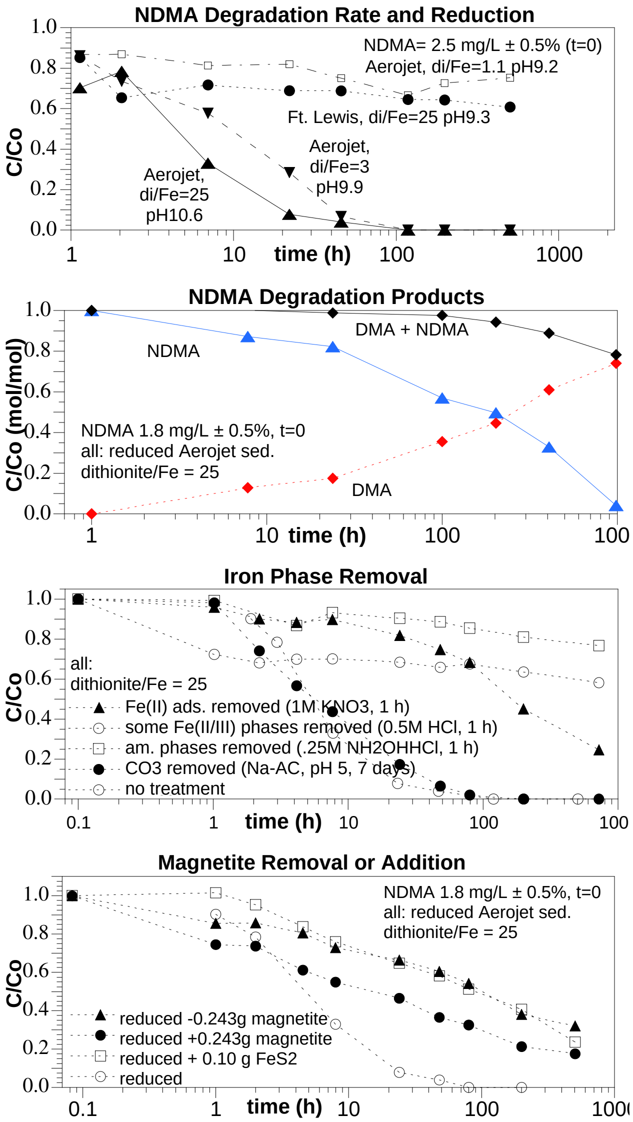

FIGURE 1. 2.5 mg/L NDMA degradation in dithionite-treated Aerojet sediment (pH 10.5): a) using different dithionite conc., b) moderate dithionite conc, and c) reduced, with some Fe phases removed, d) reduced with magnetite removed/added.

Removal of adsorbed ferrous iron from the dithionite-reduced Aerojet sediment (Figure 1c) resulted in a 15x decrease in the NDMA degradation rate from 8 h to 115 h half-life. When the fully reduced Aerojet sediment (at pH 10.5) was altered to pH 9.3, 8.4, and 7.5, there was a substantial decrease in the resulting NDMA reactivity. In addition, if the pH was decreased for 24 h, then increased back to pH 10.5, the NDMA reactivity was still significantly lower. Assuming ferrous iron was not oxidized during these manipulations, if the reactive surface phase was adsorbed ferrous iron, then the decrease and subsequent increase in pH back to 10.5 should result in the initial rapid NDMA degradation. Conversely, if the reactive surface phase was some other ferrous phase (green rust, iron sulfide…), the pH decrease, then increase may not result in the phase reappearing. Therefore, most evidence indicates that adsorbed Fe(II) is the reactive surface phase for NDMA, although some data may indicate other ferrous phases are also contributing to the redox reactivity.

NDMA Degradation Rate. NDMA can be degraded as rapidly as a 8 h half-life (Figure 1a). NDMA degradation increased with the ratio of ferrous iron to NDMA in various sediment/water systems, and the rate of NDMA degradation was predictable from the intrinsic NDMA degradation rate and this ferrous iron/NDMA ratio (Figure 2a). NDMA degradation rates observed in batch experimental systems were slow (100s to 1000s of hours), but more rapid in column systems (10s of hours) because of a higher ferrous iron/NDMA ratio in columns. Rates observed in columns (similar sediment/water ratio as aquifer) that are < 200 h are viable for field scale remediation. Of greatest interest in this study are NDMA degradation experiments conducted at a starting concentration of 100 ppt and 10 ppt (Figure 2b), which, while successful (< 4.7 h half-life), NDMA degraded so fast, it could not be accurately measured.

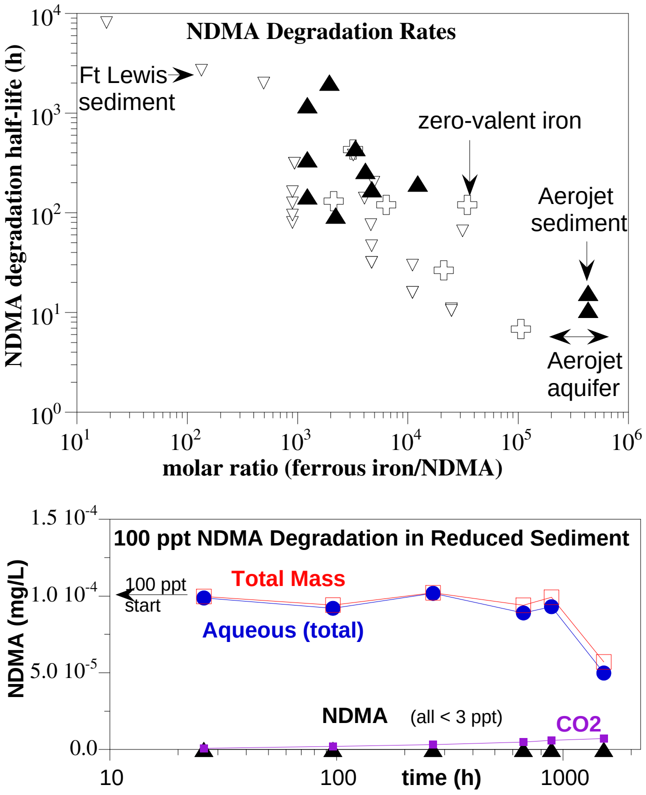

Figure 2. a) NDMA degradation half-life and iron/NDMA ratio, and b) 100 ppt NDMA degradation.

NDMA Mineralization. Degradation of NDMA to dimethylamine (DMA) in reduced sediment systems could be a viable remediation strategy only if DMA was the sole and final degradation product. Because DMA is further degraded in reduced sediment systems, alternate combination abiotitc-biotic sediment system treatments were investigated (coupled, sequential) in order to optimize a system with the most rapid NDMA mineralization rate and greatest mineralization extent. NDMA mineralization was investigated in sediments at differing NDMA concentration (2.5 ppm to 2.5 ppt) in oxic systems, in anoxic/reducing systems (more common in aquifers), and in sequential reduced, then oxic systems (representing NDMA degradation in a reduced zone and downgradient oxic zone). The observed mineralization rate was the same or slower and extent less at higher NDMA concentration (Figure 3a, 3c). The NDMA mineralization rate and extent in oxic systems was oxygen dependent, which was indicative of microbial monooxygenase pathway(s) promoting mineralization (Figure 3a). Propane addition with prestimulation in oxic sediments did promote more rapid NDMA mineralization (i.e., propane monooxygenase enzymes mineralizing NDMA, Figure 3b), but methane and toluene additions did not. Acetylene addition also did not block mineralization. Yeast addition in oxic systems also showed a slight increase in NDMA mineralization. NDMA mineralization by 2000 h in oxic Aerojet sediment averaged (n = 10) 51.0% mineralization with 17.8% species remaining aqueous, 2.0% sorbed to sediment, 0.7% sorbed to microbes, and 5.7% NDMA carbon mass incorporated into microbes (total mass balance 80.0%). NDMA oxic minerali-zation was as high as 82% in the Ft Lewis sediment. This high carbon mass balance in the oxic systems is indicative of significant microbial control, which was confirmed by bactericide addition to the oxic sediment resulting in no NDMA mineralization (Figure 3a, circles).

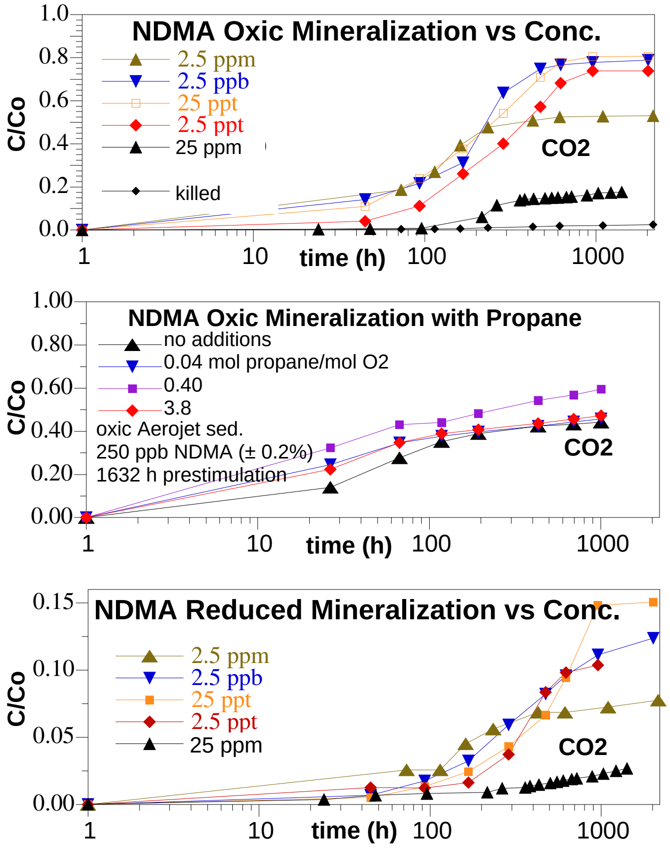

FIGURE 3. NDMA mineralization in a) oxic Ft Lewis sediment, b) oxic Aerojet sediment with prestimulation and propane additions, and c) reduced Ft Lewis sediment.

For anoxic and reduced sediment (Figure 3c), carbon additions normally associated with increasing monooxygenase pathways (propane, methane, toluene) had no influence on NDMA mineralization, as expected, indicating this pathway was not mineralizing NDMA. Other carbon additions (humic acid, yeast extract, trace nutrients) did not increase mineralization, indicating that reduced system mineralization could have significant abiotically control and/or limiting nutrients were not found (i.e., initial NDMA degradation to DMA is an abiotic reaction). Reduced Aerojet sediment carbon mass balance at 2000 h (n = 7) showed 40.2% aqueous, 9.9% mineralized, 0.35% sorbed to sediment and microbes, and 0.18% incorporated into microbes. The low carbon mass (from NDMA) sorbed to and incorporated into microbes is likely caused by the low biomass concentration. The total mass balance was 50.6%, (compared with oxic sediment mass balance of 80%) so volatile intermediates such as formaldehyde, methylamine, formate could represent a significant amount of mass.

Mineralization rates were an order of magnitude slower under iron reducing conditions for the same sediment (mineralization half-life in oxic Aerojet sed.= 342 ± 36 h, reduced Aerojet sed. = 3475 ±504 h; oxic Ft Lewis sed. = 282 h, anaerobic Ft Lewis sed. = 611 h, reduced Ft Lewis sed. = 2330 h), but the NDMA mineralization extent was still significant (6-17% for reducing systems, 35-82% for oxic systems) by an unidentified microbial enzyme pathway in reduced systems. In addition, NDMA could be mineralized in a natural reduced sediment (Puchack, NJ, 283’ depth, 28.4% mineralization, half-life 770 h, Vermeul et al., 2006) likely by the reduced 2:1 clays or natural organic matter present. Sequential reduced, then oxic sediment systems were slower and with less mineralization extent compared to oxic sediment.

Trends of the NDMA mineralization rate and extent (Figure 4) showed which treatment systems are most viable. For the Aerojet aquifer sediment (255’ depth), various oxic treatments (red squares) gave mineralization half lives from 130 h to 1200 h (~10x more rapid than reduced systems), and mineralization extent ranging from 20% to 61%. Anoxic sediment (yellow squares; the natural Aerojet aquifer system has several zone, and is primarily suboxic) shows slower and less mineralization. Reduced Aerojet sediment (green squares) has mineralization rates ranging from 2000 to 10,000 h half-life, and mineralization extent from 6% to 15%. Trends in the Ft Lewis aquifer sediment were similar (diamonds, McKinley et al., 2007) and Rocky Flats sediment (triangles, Gunnison et al., 2000). In addition, sequential reduced system, then oxic system mineralization (purple triangles) rate and extent were about the same as the reduced system. Specific microbial isolates (Figure 4, crosses) showed a significant range of mineralization rate and extent (all oxic), likely depending on efficiency of oxygenase enzyme pathways.

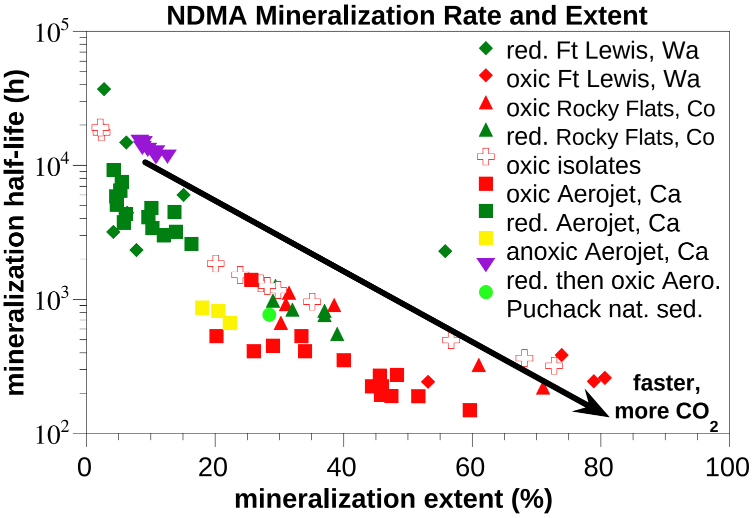

FIGURE 4. Intrinsic NDMA degradation rate for minerals and reduced sediments.

CONCLUSIONS

Results suggest that while the rapid (8 h half-life at ppm concentration) in situ abiotic NDMA degradation in reduced sediment to DMA may be sufficient for remediation, because DMA is degraded further, ultimately NDMA mineralization should be evaluated. Some NDMA mass is slowly mineralized in reduced systems, but the extent is low (< 20%) and rate slow (1000s of h) and efforts have been unsuccessful at increasing these rates. A dithionite-treated aquifer zone would therefore be viable to degrade NDMA to DMA, but reactions are too slow to consider mineralization. In contrast, addition of oxygen to the Aerojet aquifer sediment resulted in moderately rapid NDMA mineralization (342 h half-life). Propane and yeast addition did increase the mineralization rate a small extent. Sequential abiotic NDMA degradation (in reduced sediment) to intermediates followed by down gradient biotic mineralization of intermediates (in oxic sediment) may yield the most rapid rates for complete mineralization of NDMA mass to field-relevant (ppt) concentrations.

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