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Stability of Nitroguanidine in Moist, Unsaturated Soils

Nathan D. Mulherin, Thomas F. Jenkins, and Marianne E. Walsh February 2005

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ABSTRACT

The stability of nitroguanidine (NQ) was evaluated in three moist, unsaturated soils under laboratory conditions. The three soils were fortified using an aqueous spiking solution and the residual concentration of NQ was measured after storage for 0, 1, 2, 4, and 8 days at 20ºC in the dark. The results yielded a range in the half-life decay estimates for nitroguanidine from 7.5 to 56 days, depending on the soil type. No attempt was made to determine environmental transformation products of NQ.

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CONTENTS

ILLUSTRATIONS

TABLES

PREFACE

This report was prepared by Nathan D. Mulherin, Research Physical Scientist, Snow and Ice Branch, Engineer Research and Development Center-Cold Regions Research and Engineering Laboratory (ERDC-CRREL), Hanover, New Hampshire; Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch (ESB), CRREL; and Marianne E. Walsh, Chemical Engineer, ESB, CRREL.

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NATHAN D. MULHERIN, THOMAS F. JENKINS, AND MARIANNE E. WALSH

1 INTRODUCTION

Propellants and explosives are energetic compounds that are released into the environment through military activities. These compounds include nitrate esters, such as nitroglycerin and nitrocellulose; nitroaromatics, such as trinitrotoluene; and nitramines, such as RDX and HMX. The persistence of many energetic compounds in soils has been studied under a variety of laboratory and field conditions (Brannon and Myers 1997; Brannon et al. 1998; Grant et al. 1993; Jenkins et al. 2004; Maskarinec et al. 1991; Miyares and Jenkins 2000; Pennington et al. 2004; Price et al. 1997, 1998, 2000, 2001).

A study was conducted at Oak Ridge National Laboratory by Maskarinec et al. (1991) in which nitroaromatic and nitramines explosives were fortified into several test soils using acetonitrile and held for periods up to a year to estimate analytical holding times. Their results indicated that nitroaromatics had much shorter half-lives than nitramines such as RDX, but later results have shown that the use of acetonitrile to fortify the soil can influence the stability of some compounds (Ringelberg et al. 2003). At CRREL, a series of studies have been performed where various unsaturated soils were fortified with energetic compounds using small amounts of aqueous spiking solutions. These studies were also initially performed to determine holding times for analytical samples that were stored moist at –15ºC, 2ºC, and 22ºC (Grant et al. 1993), and later to determine half-lives for components of the chemical vapor signature of landmines in soil (Miyares and Jenkins 2000). The results of these studies showed that nitroaromatics were relatively unstable, with half-lives ranging from a day or less in some soils for TNB and TNT to 26 days for 2,4-DNT in soils stored at 22ºC. In contrast, the nitramines such as RDX and HMX were much more persistent in unsaturated soils. A later study with similar experimental design, but at one temperature (22ºC) and using soils from Army training ranges, showed that two nitrate esters, nitroglycerin (NG) and pentaerythritol tetranitrate (PETN), have very short half-lives (less than three days) and should not pose a threat to

groundwater, but confirmed that nitramines such as RDX, HMX, and CL20, a new R&D explosive, have half-lives in the hundreds of days (Jenkins et al. 2004).

Nitroguanidine (NQ) is a component, along with NG and nitrocellulose, of triple-base gun propellants used with several munitions, including 155-mm howitzers. NQ has a relatively high water solubility (2.6 ± 0.1 g/L), a low Henry's constant ($< 7 \times 10^{-6}$), and a low soil sorption coefficient ($K_p < 0.1$) (Haag et al. 1989). Because of these factors, if NQ is stable in the environment, it has the potential to leach through surface soils and contaminate underlying groundwater aquifers.

Several studies have been conducted that provide information on the stability of NQ in the environment. Using aerobic cultures inoculated with activated sludge, Kaplan et al. (1982) reported that nitroguanidine was stable over a seven-day experiment at concentrations from 50 to 100 mg/L. Haag et al. (1989) reported that NQ underwent aerobic biotransformation via a cometabolic process in natural waters and estimated a half-life of about 85 days in a quiescent water body containing 1×10^6 organisms and a low nutrient concentration. The rate of reaction was found to be a function of the concentrations of organic nutrients. Recently, Pennington et al. (2004) conducted a study in which three test soils were fortified with NQ and slurried with one part soil to four parts water, and shaken for periods up to 140 hours. Their results indicated that NQ was stable under these conditions and conclude "Nitroguanidine would not be expected to degrade in either aerobic or aquifer soils." Because NQ is the major component of triple-base propellants, it may be present in surface soils at Army training ranges and hence its environmental fate may be important. To our knowledge, NQ has not been detected in groundwater samples at DoD training ranges, but the number of samples that have been analyzed for NQ is unknown. The objective of the study presented here is to provide an initial estimate of the half-life of NQ in several unsaturated surface soils using the protocol developed by Grant et al. (1993) to determine whether NQ will be attenuated by natural soil processes.

2 EXPERIMENTAL METHODS

Chemicals

The NQ standards were prepared from a Standard Analytical Reference Material (SARM) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Aqueous stock for all solutions and the RP-HPLC eluents was from a Milli-Q Type-1 Reagent-Grade Water System (Millipore Corporation). The pure-water eluents were vacuum-filtered through 0.45-μm nylon membranes to degas the eluent and remove particulates. Calcium chloride, used in a 5-g/L aqueous solution for settling turbidity during sample extraction, was reagent grade (JT Baker).

Calibration solutions and analyte spiking solution

An intermediate 1.00-g/L aqueous NQ stock solution was made by weighing 0.100 g of dried NQ crystals into a 100-mL volumetric flask and filling to the mark with reagent-grade water. This flask was then covered with aluminum foil to shield from daylight and placed on a stir plate at room temperature for approximately 24 hours to ensure complete dissolution. After stirring, the solution was syringe-filtered through a Millex-HV (0.45-μm) filter. Diluting 2.50 mL of this 10.0-g/L stock to 250 mL produced our second intermediate 10.0-mg/L stock solution. This 10.0-mg/L solution also served as our spiking solution. We made a 5.0-mg/L calibration standard by diluting 56.5 mL of 10.0-mg/L stock to 113 mL. We made up our 2.0-mg/L-calibration standard by diluting 20.0 mL of 10.0-mg/L stock to 100 mL. Similarly, our other calibration standards (0.8, 0.2, 0.1, and 0.04 mg/L) all were made by diluting from the 2.0-mg/L solution. The stock, spiking, and calibration solutions all were transferred to 120-mL amber bottles and refrigerated at 4 ± 0.5ºC when not needed. Dilution ratios are shown in Table 1. The standards were each analyzed by RP-HPLC to check their concentrations with respect to the concentration of the 10.0-mg/L spiking solution. The analyte elution peaks appeared between 3.05 and 3.19 minutes after sample injection.

Table 1. Volume and concentration of components of stock, spiking, and calibration solutions.

Volume of stock solution (mL)	Concentration of starting solution (mg/L)	Volume of dilution flask (mL)	Concentration of final solution (mg/L)
2.50	1000	250	10.0
56.5	10.0	113	5.0
20.0	10.0	100	2.0
40.0	2.0	100	0.8
20.0	2.0	100	0.4
10.0	2.0	100	0.2
5.00	2.0	100	0.1
2.00	2.0	100	0.04

3 SOILS

The soils used in this study were Lebanon Landfill from New Hampshire, Fort Edwards Clay from New York, and Yakima Composite-67 from Washington. A summary of physical properties of these soils is presented in Table 2.

Table 2. Properties of soils used in stability tests.

Soil	TOC%[1]	CEC[2] (meq/100 g)	pH	Clay (%)	Sand (%)	Silt (%)
Yakima	1.06	23.6	6.8	15	40	45
Lebanon Landfill	0.3		6.6	5	45	50
Fort Edwards Clay	0.6		8.4	81	5	14

[1] Total organic carbon
[2] Cation exchange capacity

Soil sample preparation

While the Lebanon Landfill (LL) soil was used without additional preparation, the Fort Edwards (FE) and Yakima Composite (YC) soils varied greatly in particle size and were further processed before use. The FE soil was first ground with mortar and pestle to break up balls of clay on the order of 1–5 mm in diameter. The YC soil also had a small amount of grass root and stem intermixed. Both FE and YC soils were sieved (Lab sieve #30 [600 μm]) immediately prior to sample portioning in order to better standardize the particle size and, in the case of YC soil, to remove the grassy debris. Replicate 5-g soil amounts were weighed into 72 20-mL glass scintillation vials (24 of each soil type). This number allowed one blank sample and a spiked triplicate of each soil type for six different time periods of interest. The mean weights $\pm$ the standard deviations for the LL, FE, and YC samples were 5.0021 $\pm$ 0.0054, 5.0138 $\pm$ 0.0021, and 5.0060 $\pm$ 0.0031 g, respectively. Each of the 72 samples was then wetted with a 1.00-mL pipetted aliquot of water, capped tightly, and stored in darkness at room temperature (20 $\pm$ 1ºC). Two days later, another 1.00 mL of water was added to each Fort Edwards (FE) and Yakima Composite (YC) soil sample, and 0.50 mL of water was added to each Lebanon Landfill (LL) soil sample, so that they were fully moistened but without standing water. The first LL sample actually received a full milliliter of water at this time, but this amount flooded the sample and standing water resulted. The 72 samples were recapped and stored in the dark at room temperature for another three days to allow microbial activity to become

fully established before adding the NQ analyte, in the manner of Maskarinec et al. (1991).

Spiking of soil samples

To check the accuracy and repeatability of the analyte spiking method, 1.00-mL aliquots of water were pipetted into weighed scintillation vials, after which the vials were reweighed and the fluid weight from each delivery was calculated. The results of this experiment are shown in Table 3. The mean weight $\pm$ the standard deviation of the measured aliquots was 1.0120 $\pm$ 0.0036 g (RSD = 0.36%).

Table 3. Spiking accuracy and repeatability.

Vial #	Weight of vial + H_20 (g)	Weight of vial (g)	Weight of H_20 (g)
1	17.6424	16.6324	1.0100
2	18.0214	17.0117	1.0097
3	18.1564	17.1478	1.0086
4	17.6240	16.6112	1.0128
5	17.9910	16.9752	1.0158
6	17.5968	16.5847	1.0121
7	17.9490	16.9332	1.0158
8	17.7547	16.7462	1.0085
9	18.0448	17.0262	1.0186
10	18.1314	17.1230	1.0084
Mean			1.0120
St. Dev.			0.0036
% RSD			0.36%

A set of four samples of each soil type was randomly selected for each of six time periods of interest. One of each set served as a blank, whereas the other three served as a spiked triplicate. The blank samples each received a 1.00-mL aliquot of plain water. The triplicate samples each received a 1.00-mL aliquot of 10.0-mg/L NQ spiking solution. The first blank and triplicate set of samples were immediately placed into coldroom storage (–29 $\pm$ 1 ºC) to freeze, and hereinafter are referred to as the Day_0 sample set. Freezing the samples ended any further microbial degradation of NQ until such time that all the samples could be extracted and analyzed together. After vortexing for five seconds, the samples for

the remaining time periods of interest were stored in darkness at room temperature to allow microbial activity, and resulting NQ degradation, to occur.

Based on the above-described weights and volumes, the theoretical concentration of NQ in each of the LL samples, for example, was as follows:

(0.0010120 L × 10.0 mg/L) of NQ / 0.0050021 kg of soil = 2.02 mg NQ / kg of LL soil.

The results of similar calculations for the FE and YC soils are summarized in Table 4.

Table 4. Theoretical NQ concentration in fortified soils.

Soil type	Volume of analyte spike (mL)	Concentration of analyte spike (mg/L)	Mean weight of soil sample (g)	Calculated soil NQ concentration (mg/kg)
LL	1.012 ± 0.0036	10	5.0021 ± 0.0054	2.02 ± 0.01
FE	1.012 ± 0.0036	10	5.0138 ± 0.0021	2.02 ± 0.01
YC	1.012 ± 0.0036	10	5.0060 ± 0.0031	2.02 ± 0.01

Aging of spiked samples

The Day_0 samples were frozen immediately after spiking to prevent NQ degradation. One day after spiking, the Day_1 blank and spiked triplicate samples were frozen to stop microbial activity and end NQ degradation. Two days after spiking, the Day_2 blank and spiked triplicate samples were frozen, and four days after spiking, the Day_4 blank and spiked triplicate samples were similarly frozen. Eight days after spiking, the Day_0, Day_1, Day_2, and Day_4 samples were removed from the freezer, thawed, and along with the Day_8 samples, were extracted and analyzed. It should be pointed out that the treatment of the Day_8 samples differed in that they were not frozen and thawed prior to extraction and analysis.

Soil extraction

On the eighth day after spiking, the Day_0, Day_1, Day_2, and Day_4 series were removed from the freezer and thawed at room temperature. Beginning approximately one hour after removal from the freezer, each set of samples was processed sequentially starting with the Day_0 series. They were processed as follows: a 7.00-mL aliquot of water was added to each of the FE and YC blanks and spiked samples, whereas a 7.50-mL aliquot of water was added to the LL blank and spiked triplicate. The samples were then recapped and vortexed for one minute each, and placed in an ultrasonic water bath (maintained at less than 25ºC) for two hours. The Day_1, Day_2, and Day_4 series blank and spiked triplicate

samples were successively and similarly treated. The Day_8 series was extracted without prior freezing.

Maintaining the sequence of operations, each series of samples was successively removed from the ultrasonic water bath after two hours, and a 1.00-mL aliquot of 5-g/L aqueous $CaCl_2$ flocculating solution was added to each sample to help in settling suspended solids. The samples were allowed to settle for at least 30 minutes, after which the supernatant in each LL and YC sample was poured into a 10-mL syringe and filtered through a Millex-HV (0.45-µm) filter. The FE samples were still too cloudy to filter and so these were each centrifuged for five minutes at 1500 rpm, to allow the supernatant to be poured off. The first milliliter of each syringed filtrate was discarded and the remainder was collected in new scintillation vials. Amber, 2-mL, auto-analyzer vials were filled with each filtrate and immediately analyzed using RP-HPLC.

To summarize, the treatments received by the soil samples up to the point of RP-HPLC analysis included the initial and second soil wettings with water, the spiking with 10.0-mg/L aqueous NQ, water extraction, and the addition of 5-g/L aqueous $CaCl_2$ flocculating solution. These aqueous additions totaled 11 mL. The water added to the various soil types at each step of treatment for each of the time series is summarized in Table 5.

Table 5. Aqueous additions of water to soils, in milliliters.

Soil type	1st soil wetting	2nd soil wetting	Spiking	Extracting	Flocculating	Total
LL	1.0	0.5	1.0	7.5	1.0	11.0
FE	1.0	1.0	1.0	7.0	1.0	11.0
YC	1.0	1.0	1.0	7.0	1.0	11.0

RP-HPLC analysis

Our analysis was conducted as described by Walsh (1989) on a modular system composed of a Spectra Physics SP8810 Precision Isocratic pump with the flow rate set at 1.5 mL/minute, and the rise time and range set at 0.10 and 0.001, respectively. We used a 4.6- × 250-mm Mixed Mode RP18 Cation 100A-7-U column (Alltech) and a Spectra Physics 100 variable wavelength detector set at 263 nm. The autosampler (Dynatech Precision Sampling Corporation) was programmed to cycle each sample through in five minutes, beginning with a 45-second flush, and then overfilling a 100-µL precision sample loop injector.

The water used as eluent was prepared by vacuum-filtering through a microfiber filter nylon membrane (0.45 μm). Air was removed from the eluent by continuous helium-sparging throughout the RP-HPLC process.

Prior to sample analysis, we ran calibration standards ranging in concentration from 0.1 to 5.0 mg/L. Between each time series of samples, we analyzed a blank water sample, and a 0.8-mg/L standard. At the end of the run, a final set of calibration standards was analyzed, ranging from 0.1 to 5.0 mg/L. The Day_0 through Day_8 samples all were analyzed together eight days after spiking, thereby eliminating any uncertainty due to slight day-to-day calibration differences. The NQ-peak elution times ranged from 3.05 to 3.12 minutes during the seven-hour-long analysis period.

Experimental parameters and data analysis

The test parameters for this investigation are summarized in Table 6. In all cases, our reported mean and standard deviation values for NQ concentration in the soil are based on the three spiked samples. No samples were excluded.

The mean concentrations for each storage time were plotted as ln (C/C_0) with respect to time t (in days), where C_0 is the mean concentration in a given soil type at time 0, and C is the mean concentration for that same soil type measured at the end of any other storage time. The least-squares, best-fit, straight line was fitted to these data and its slope was computed. For a first-order rate of depletion, the computed slope of this line is the rate constant for loss of NQ in that soil type.

Table 6. Experimental factors and levels for this soil stability study.

Factors	Number of levels	Levels
Analytes	1	NQ
Concentration	1	2 mg/kg
Soils	3	Lebanon Landfill, Fort Edwards Clay, Yakima Composite-67
Storage temp. (ºC)	1	20º $\pm$ 1ºC
Storage time (days)	5	0, 1, 2, 4, 8
Replicates	3	a, b, c

4 RESULTS AND DISCUSSION

Instrument calibration

The mean concentration values for the calibration standards are plotted in Figure 1. The least-squares linear model with zero intercept for the standards over the range from 0.04 to 5.0 mg/L was y = 6.629E-06x. This relationship had an $r^2 = 0.99999$, indicating that the linear model with zero intercept was adequate over the entire concentration range.

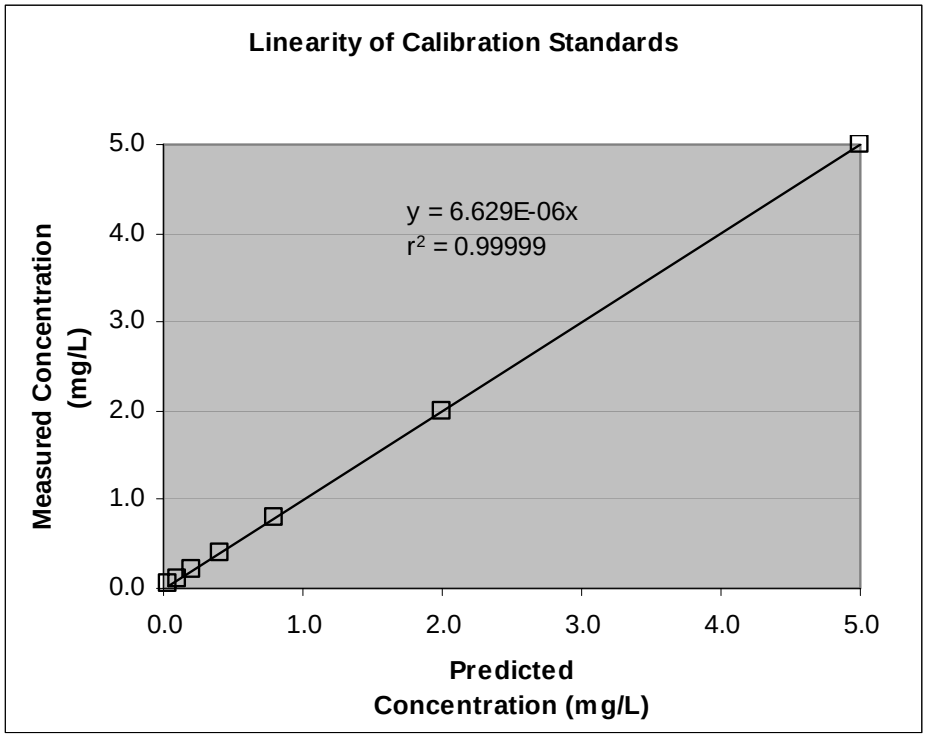

Figure 1. Calibration standards linearity. The trend line through the data is the least-squares best fit.

NQ concentration as a function of time

The mean and standard deviations for the NQ concentrations for each time series and soil type are shown in Table 7. All soil blanks tested negative for NQ except for the Day_8 YC sample, which yielded a 0.169-mg/kg-equivalent NQ peak at the retention time for NQ.

Table 7. Statistical summaries for NQ concentration, and relative NQ concentration (C/C_0), as a function of storage time.

	Storage time (days)	NQ concentration (mg/kg soil)		RSD (%)	(C/C_0)
		Mean	Standard deviation		
LL samples	0	2.02	0.009	0.44	Actual spiked amount
	0	2.10	0.002	0.12	1.000
	1	2.05	0.016	0.78	0.977
	2	2.01	0.031	1.53	0.956
	4	1.96	0.039	1.97	0.934
	8	1.93	0.008	0.41	0.921
FE samples	0	2.02	0.008	0.40	Actual spiked amount
	0	1.89	0.030	1.57	1.000
	1	1.92	0.017	0.87	1.017
	2	1.90	0.033	1.74	1.006
	4	1.81	0.004	0.22	0.960
	8	1.68	0.172	10.3	0.888
YC samples	0	2.02	0.008	0.40	Actual spiked amount
	0	1.94	0.167	8.61	1.000
	1	1.49	0.057	3.86	0.765
	2	1.35	0.025	1.87	0.692
	4	1.24	0.038	3.09	0.636
	8	1.03	0.129	12.5	0.529

The repeatability for the triplicate samples at each storage time was good for all soil types as illustrated by the relative standard deviations. Except for the FE and YC samples at Day_8 and FE Day_0, RSDs were all less than 4%. The RSDs for LL soils never exceeded 2% of their mean values.

Table 7 shows that the mean NQ concentration in the LL samples decreased continuously as expected. However, the Day_0 and Day_1 values (2.10 and 2.05 mg/kg, respectively) slightly exceeded the theoretical spiked amount of 2.02 mg/kg, i.e., by approximately 3.7 and 1.4%, respectively.

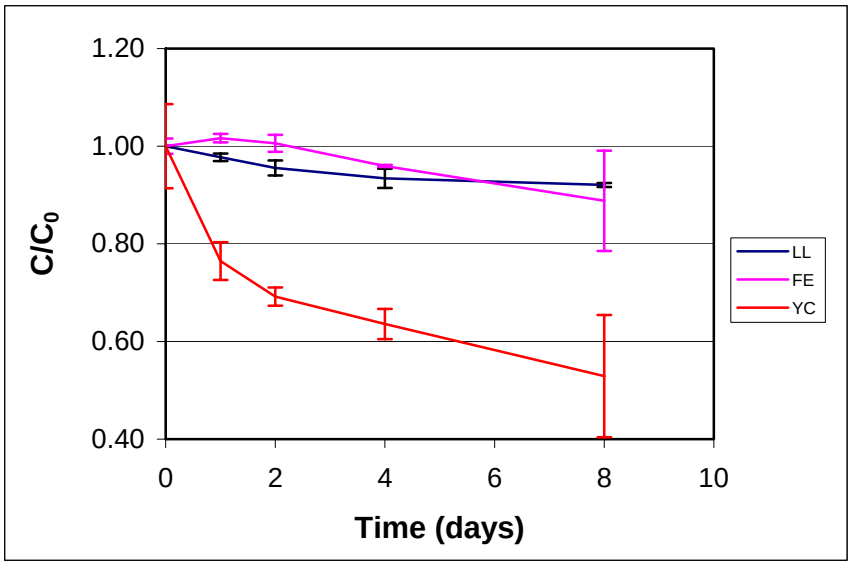

Figure 2. Mean relative NQ reduction as a function of time. Each data point is the mean of three sample measurements. Error bars are ± one relative standard deviation (RSD).

In the case of the FE soils, the Day_1 and Day_2 values both exceed the Day_0 amount by 1.6 and 0.6%, respectively. This feature is illustrated by the slight rise of the FE curve on Day 1 as shown in Figure 2. The overlapping standard deviations indicate that the NQ concentrations were not significantly different from the initial concentration for the first two days.

While all three soils showed time-related reduction in NQ soil concentration, the YC samples showed the greatest rate of loss. The average rates of NQ reduction for the LL and FE soils were nearly equivalent, and after eight days the remaining concentration was about 90% of their Day_0 values. For the YC soil, however, there appears to be fairly rapid loss of NQ to about 70% of the initial concentrations after the first day, and then a reduced rate of loss of NQ over the final six days to about 50% of its Day_0 value.

Loss rate and NQ half-life estimation

To further investigate the rate of loss of NQ and estimate the half-life in these soils, we plotted ln (C/C_0) as a function of time (Fig. 3). When this type of relationship is linear, the loss mechanism can be assumed to be a first-order process and the half-life can be estimated from $-(1/k)\ \ln 2$ where k is the slope of the best-fit line. The relationships for the LL and FE soils appear linear and we estimate half-lives of 56.4 and 54.2 days, respectively, for NQ in these soils (Table 8).

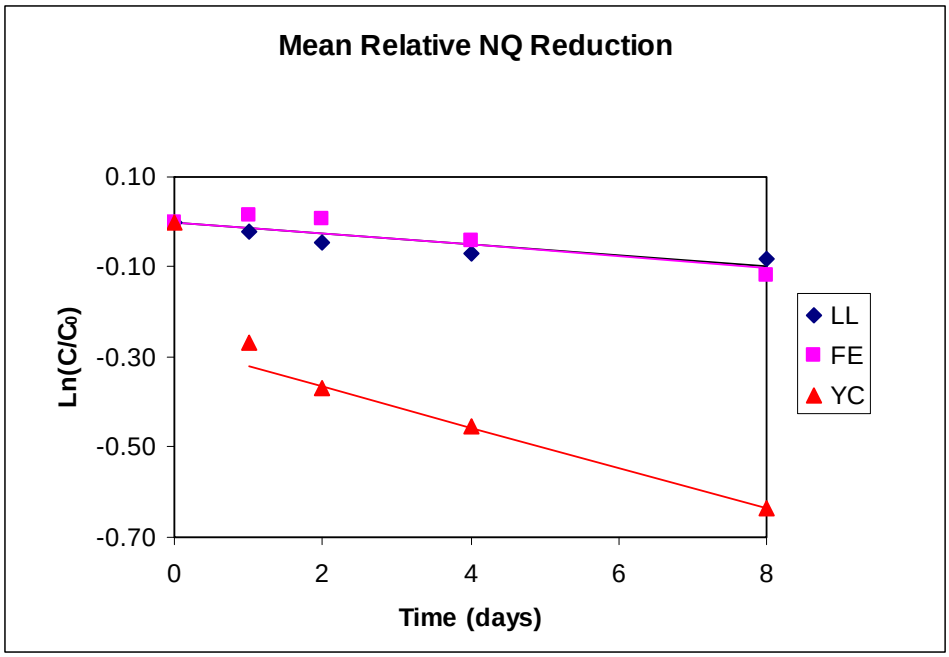

Figure 3. Logarithmic analyte loss with respect to time. Each data point is the mean of three sample measurements. The LL and FE trendlines, overlying one another, are least-square linear fits with zero y-intercepts.

Table 8. Rate constants and half-life estimates for NQ in three test soils.

Soil type	Rate constant (slope value)	Measure of linear fit (r^2 value)	Half life (days)
LL	–0.0123	0.7410	56.4
FE	–0.0128	0.8203	54.2
YC	–0.0449	0.9996	15.4

The relationship of ln ($C/C_{0)}$ versus time for the YC soil, however, is clearly non-linear and thus the degradative process does not appear to follow first-order kinetics in this soil. The YC soil had the highest organic carbon content of the three soils tested, and the observed loss of NQ may be due to a cometabolic process associated with the degradation of the natural organic matter as described by Haag et al. (1989). However, a close inspection of the plot of ln (C/C_0) indicates that the loss of NQ does appear to be fairly linear from Day_1 to Day_8, and it is this rate of loss that may be sustained over longer periods of time. The slope of the best-fit line for the data from Day_1 to Day_8 is 0.045, from which we estimate a half-life of about 15.4 days.

5 CONCLUSIONS

This study was conducted to provide an estimate of the stability of NQ in unsaturated soil that was shielded from light. We fortified our soils using aqueous solutions of NQ that would simulate the introduction of NQ into the soil pore water as solid NQ residues dissolve and migrate. The rate of loss of NQ was found to be slow, but measurable, with half-lives ranging from 15 to 56 days. Because the rate of loss may be related to soil organic carbon content, the rate of degradation is expected to be reduced as NQ leaches deeper into the soil profile where organic carbon concentrations are reduced. Because NQ is non-volatile and has little affinity for soil, it appears that it could, under some circumstances, migrate through the vadose zone to underlying aquifers.

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U.S. Army Engineer Research and Development Center
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14. ABSTRACT

The stability of nitroguanidine (NQ) was evaluated in three moist, unsaturated soils under laboratory conditions. The three soils were fortified using an aqueous spiking solution and the residual concentration of NQ was measured after storage for 0, 1, 2, 4, and 8 days at 20ºC in the dark. The results yielded a range in the half-life decay estimates for nitroguanidine from 7.5 to 56 days, depending on the soil type. No attempt was made to determine environmental transformation products of NQ.

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