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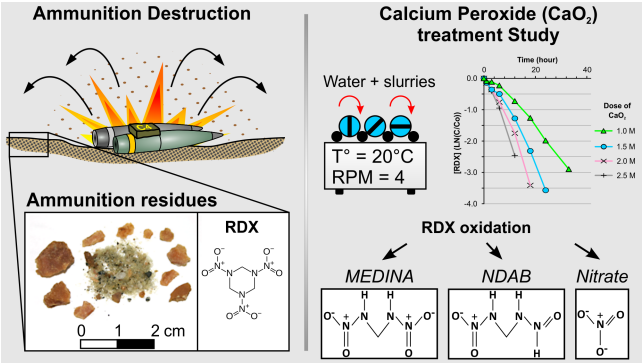

RDX DEGRADATION BY CHEMICAL OXIDATION USING CALCIUM PEROXIDE IN BENCH SCALE SLUDGE SYSTEMS

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Abstract

The ability of calcium peroxide (CaO_2) to degrade hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in contaminated soil slurries using CaO_2-based modified Fenton oxidation was investigated. Results showed that increasing the CaO_2 dose increased degradation rates of RDX and pH. RDX concentrations decreased to below detection after 18 hours with 2 M and 2.5 M CaO_2, after 30 hours with 1.5 M CaO_2, after 54 hours with 1 M CaO_2, but 0.1 M CaO_2 achieved no significant RDX removal. Increasing the soil organic matter content decreased the rate and extent of RDX degradation. RDX degradation products 4-nitro-2,4-diazabutanal (NDAB) and methylenedinitramine (MEDINA) were quantified, and the greater accumulation of NDAB than MEDINA suggests denitration of RDX was the most likely initial degradation step. Isotopic ratios for nitrogen and oxygen associated with RDX oxidation are also consistent with either nitrification of NH_4^+ from soil or precipitation. Existing technologies merely only extract energetics from soils for treatment *ex situ*, whereas the approach introduced herein destroys RDX *in situ* with a one-step application.

Keywords

RDX degradation; calcium peroxide; chemical oxidation; energetics-contaminated soil; isotopes

1. Introduction

Originally patented for medical use in 1899, mass production of 1,3,5-trinitro-1,3,5-triazine (RDX) began, and its properties became fully understood during World War II (Anderson, 2010, Akhavan, 2004). Since then the manufacture and use of this toxic compound (Robidoux et al.,

2002, Talmage et al., 1999) in munitions has contaminated soils, surface waters, and groundwater, particularly at military training ranges (Clausen et al., 2004, Hewitt et al., 2005, Albano et al., 2010, Lapointe et al., 2017).

Current remediation strategies for explosive-contaminated soils include incineration, landfilling, composting, bioaugmentation, and phytoremediation. Excavation for treatment is expensive and disrupts site ecology (Environment Protection Authority, 1996). Microbes introduced during bioaugmentation typically cannot compete with native soil bacteria, requiring additional amendments and increasing remediation time and costs (Michalsen et al., 2016). Phytoremediation often requires exceedingly long treatment times (Anderson, 2010).

Chemical oxidation is widely used for the treatment of water, wastewater and soils contaminated with a wide range of organic compounds. *In Situ* Chemical Oxidation (ISCO) has been increasingly used in the last decade to treat contaminated sites (Baciocchi, 2013). This technology relies upon generating a reactive zone in the subsurface by introducing oxidants and other amendments that degrade organic contaminants and has proven effective in both the saturated and unsaturated zones. Common ISCO chemistries include those based on hydrogen peroxide (modified Fenton chemistry) (Watts and Teel, 2005, Liou et al., 2003, Zoh and Stenstrom, 2002, Bier et al., 1999, Bose and Glaze, 1998), permanganate (Chokejaroenrat et al., 2011, Adam et al., 2004), persulfate (Oh et al., 2016) and, ozone (Adam et al., 2006, Bose et al., 1998).

Oxidant formulations based on hydrogen peroxide (H_2O_2) have been widely employed for the treatment of a wide variety of contaminants (e.g., hydrocarbons, PAHs, PCBs, chlorinated solvents, explosives, etc.). Conventional Fenton chemistry (**Reaction 1**), used for wastewater

treatment, introduces a stoichiometrically-limiting amount of H_2O_2 into a tank with excess Fe^{2+} (Zoh and Stenstrom, 2002, Bier et al., 1999, Haber and Weiss, 1934), which forms a suite of radical species capable of non-selectively oxidizing a wide range of organic pollutants (Watts and Teel, 2005, Kiwi and al., 2000). The oxidizing species include H_2O_2 itself (1.776 V), the hydroxyl radical (•OH; 2.59 V), the superoxide radical ($•O_2^-$; -0.33 V), and the perhydroxyl radical ($HO_2•$; 1.495 V) (Watts and Teel, 2005, Siegrist et al., 2011). Of these, the hydroxyl radical is the most desirable for contaminant degradation because it is both the strongest oxidant and the least selective (Watts and Teel, 2005, Siegrist et al., 2011). Conventional Fenton chemistry yields 100% hydroxyl radical from H_2O_2, Soil applications of H_2O_2 are referred to as modified Fenton chemistry, because the catalysts (Fe^{2+} and Mn^{2+}) are stoichiometrically limiting and H_2O_2 is in excess. Modified Fenton systems yield less than 100% hydroxyl radical from H_2O_2 but also generate significant amount of the superoxide and perhydroxyl radicals (Watts and Teel, 2005, Siegrist et al., 2011).

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + Fe^{3+} + HO^{\cdot} \qquad \textbf{Reaction 1}$$

The effectiveness of modified Fenton oxidation of contaminants in soils varies widely. Radicals can be scavenged by species such as carbonates and organic matter (Siegrist et al., 2011). H_2O_2 can also undergo disproportion to water and molecular oxygen, which do not contribute to chemical oxidation, and this reaction is increasingly favored as temperature increases. The short half-life of H_2O_2 (min to h) is the most important limitation of modified Fenton treatment. However, stabilisers (e.g. citrate, malonate, phytate) may be added to increase the persistence of H_2O_2 in the soils (Watts et al., 2014).

Solid sources of H_2O_2 such as sodium percarbonate (Na_2CO_3•1.5 H_2O_2) and magnesium and calcium peroxide (MgO_2 and CaO_2) release H_2O_2 into the aqueous phase and can be used as alternatives to liquid H_2O_2 (Davis-Hoover et al., 1991, Vesper et al., 1994, Weast, 1998, Bianchi-Mosquera et al., 1994, White et al., 1998, Cassidy and Irvine, 1999). When liquid H_2O_2 is applied to soils, all the H_2O_2 is present in the aqueous phase and available to react at once. This leads to a scenario in which the H_2O_2 is in stoichiometric excess and Fe^{2+} and Mn^{2+} are stoichiometrically limiting, which decreases the yield of the hydroxyl radical. The advantage of using solid sources of H_2O_2 is that the release of H_2O_2 to the aqueous phase is auto-regulated by the rate of dissolution of the solid. This reduces disproportionation and minimizes the stoichiometric excess of H_2O_2 relative to the metal catalysts in soil, thereby increasing the yield of the hydroxyl radical and enhancing chemical oxidation of contaminants. The high solubility of sodium percarbonate often requires it to be encapsulated to slow the release of H_2O_2 (Waite et al., 1999). CaO_2 and MgO_2 are much less soluble, providing a slow release of H_2O_2. Both CaO_2 and MgO_2 release H_2O_2 which increase the pH of the medium into which they are introduced, and higher the pH, the more slowly H_2O_2 is released from these solid peroxides (Vol'nov, 1966). To the point, quantifying the H_2O_2 content of CaO_2 and MgO_2 involves adding them to a solution with a pH less than 2, which completely dissolves the peroxides and releases all the H_2O_2 (Vol'nov, 1966). MgO_2 releases less hydrogen peroxide per weight than CaO_2 (White et al., 1998). Moreover, commercial CaO_2 is considerably less expensive than MgO_2, and is easily produced in the field by heating lime with diluted H_2O_2 (Walawska et al., 2007). Northup and Cassidy (2008) compared the performance of CaO_2 with liquid H_2O_2, using organic probe compounds to identify the relative yield of the hydroxyl radical to superoxide and perhydroxyl radicals. This study demonstrated, in both aqueous and soil systems, that CaO_2 generates a

96 greater yield of hydroxyl radical and a greater rate and extent of chemical oxidation than liquid
97 H_2O_2.

98 CaO_2 reacts with water form H_2O_2 and $Ca(OH)_2$ (**Reaction 2**). The calcium carbide type
99 structure of CaO_2 is known to liberate a maximum of 0.47 g H_2O_2/g CaO_2 (Vol'nov, 1966) and -
100 23.55 kJ/mol of heat (Zhao et al., 2013).

101 $$CaO_{2(s)} + 2H_2O \rightarrow H_2O_2 + Ca(OH)_{2(s)}$$ **Reaction 2**

102 The production of hydrated lime ($Ca(OH_2)$) can dramatically increase the pH in poorly buffered
103 soils (Cassidy and Irvine, 1999). However, this side-effect is desirable in our application because
104 RDX can also be degraded by alkaline hydrolysis (Hwang et al., 2006, Balakrishnan et al.,
105 2003). While many of the end products of the alkaline hydrolysis of RDX are known (Heilmann
106 et al., 1996, Hoffsommer et al., 1977), little information is currently available on decomposition
107 mechanisms or by-products in the degradation of RDX by modified Fenton chemistry,
108 particularly with CaO_2 application. To evaluate CaO_2-based modified Fenton oxidation of RDX
109 and optimize performance, degradation steps and intermediate products must be identified.

110 Laboratory experiments on the chemical oxidation of RDX with CaO_2-based modified Fenton
111 chemistry were conducted. Aqueous systems and batch slurry reactors were used to demonstrate
112 the ability of CaO_2 to oxidize RDX, to monitor known RDX transformation products, and to
113 illuminate degradation steps. A wide range of CaO_2 doses were tested and nitrous RDX
114 derivatives and ring cleavage products were quantified. The presence of organic matter (OM) in
115 RDX oxidation systems was investigated to better understand if and how OM affects RDX
116 degradation by potentially scavenging the radicals generated in modified Fenton chemistry.

Because RDX is rarely the only energetic material (EM) present at an EM contaminated site, the concentration stability of known EM in the presence of CaO_2 during analyses was also evaluated to ascertain the accuracy of results. Mineralization of RDX was also demonstrated by measuring stable isotopes of nitrogen and oxygen liberated from RDX degradation. Existing technologies extract energetics from soils so they can be removed and treated *ex situ*, whereas chemical oxidation with CaO_2 is capable of *in situ* destruction of RDX with a one-step application.

2. Materials and Methods

2.1. Chemicals

RDX was provided by Defence Research & Development Canada (DRDC Valcartier). Methylenedinitramine (MEDINA), 4-Nitro-2,4-diazabutanal (NDAB), hexahydro-3,5-dinitro-1-nitroso-1,3,5-triazine (MNX), hexahydro- 5-nitro-1,3-dinitroso-1,3,5-triazine (DNX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) were provided by the National Research Council of Canada-Biotechnology Research Institute (NRC-BRI). Calcium peroxide (CaO_2) was purchased from Chemco, Inc. (Quebec, QC, Canada). Standards for nitroaromatics and nitramines (EPA standard S11627) and sea salts were purchased from Sigma-Aldrich (Oakville, ON). Deionized water was obtained with a Milli-QUV plus (Millipore) system. ACS-certified EDTA salt (S311-100) was from Fisher Scientific (Mississauga, ON, Canada). Other chemicals were reagent grade.

2.2. Chemical Analyses

2.2.1. Energetic materials

The analytical determination of explosives was performed using EPA 8330B HPLC method (U.S. EPA, 2006).The detection limit was between 0.05 and 0.5 μg/L, depending on the analyte. RDX and its nitroso products MNX, DNX, and TNX were analyzed by reverse phase HPLC as reported by Paquet et al. (2011) with limits of detection and quantification of 0.05 and 0.1 μg/L, respectively. RDX ring-cleavage products, MEDINA and NDAB, were analyzed via HPLC system with an AnionSep Ice-Ion-310 Fast organic acids column (St Louis, MO, USA), maintained at 35°C (Paquet et al., 2011). The mobile phase was acidified water (pH=2.0) at a flow rate of 0.6 mL/min. Chromatograms were taken at a wavelength of 225 nm. The detection limit was 0.05 μg/L. To avoid measurement bias in the analysis of RDX in soils treated with CaO_2, the use of acetonitrile or acetone rather than water was necessary (see section 1 in **Supplementary material**).

2.2.2. Nitrate and nitrite

Nitrate (NO_3^-) and nitrite (NO_2^-) were analyzed by ion chromatography (IC) according to US EPA Method 300.0 (1993) using a Dionex ICS-2000 chromatograph (Sunnyvale, CA) equipped with a 4 mm x 50 mm AG18 guard column and a 4 mm x 250 mm PAC AS18 ion exchange resin analytical column. Maintaining a constant temperature of 30 °C, NO_3^- and NO_2^- ions were eluted at a flow rate of 1 mL/min with 23 mM KOH. Ions were quantified by suppressed conductivity detection. The detection limit was 0.05 mg/L NO_3^- and 0.01 mg/L NO_2^-.

2.2.3. Stable isotope ratios of nitrogen and oxygen

Samples were prepared according to the method presented by Smirnoff et al. (2012), designed for samples with low NO_2^- and NO_3^- concentrations (> 0.1 mg/L NO_2^--N or NO_3^--N). After

158 removing RDX from samples by passing through Sep-Pak® Porapak® RDX Vac 6cc Cartridges
159 (500 mg Sorbent, 125-150 µm Particle Size), each sample volume was diluted to 0.1 mg/L NO_3^--
160 N using ultra-pure water, and then 7.5 mL of 0.05 M sodium chloride-EDTA solution and 2.9 g
161 NaCl (to increase ionic strength) were added. The pH was adjusted to 8.5 using a 0.5 N NaOH
162 solution. To complete reduction of NO_3^- to NO_2^-, samples were passed through a glass column
163 filled with cadmium-copper pellets at a flow rate of 7 mL/min (Wood et al., 1967). Five mL were
164 used to measure NO_2^- concentrations using a color reagent prepared from sulphanilamide (Sigma-
165 Aldrich, S9251- 500 G) and N-(1-naphthyl) ethylenediamine dihydrochloride (Sigma-Aldrich,
166 N9125-25 G) and a photometer with a 543 nm wavelength (Genesys 10 UV, Thermo Scientific,
167 Madison, WI, USA).

168 On the day of the analysis, sodium azide (NaN_3) was carefully introduced with a syringe into each
169 bottle to chemically reduce NO_2^- to nitrous oxide (N_2O). After being placed for 15 min into a 30°C
170 water bath, N_2O production was stopped by adding 0.3 mL of 6M NaOH to each sample.

171 The N_2O was analyzed using isotopic ratio mass spectrometry (IRMS). The gaseous N_2O taken
172 from sample headspace was injected into a modified pre-concentration system (Pre-Con, Thermo
173 Scientific) equipped with a gold reduction furnace and two GC columns: a pre-furnace column
174 (HP6890A, Thermo Scientific, Bremen, Germany) ensures that only pure N_2O enters the 875 °C
175 gold-wire furnace, and a main, post-furnace column (HP-Molsieve, silica-fused, 5 Å, 0.32 mm,
176 25 µm film thickness, 30 m, J&W Scientific, Agilent Technologies Canada, Mississauga, ON,
177 Canada) which separates N_2 from O_2 after N_2O decomposition from the furnace. These two gases
178 were then passed through a GC interface (Thermo Scientific, Bremen, Germany), and finally
179 issued into a mass spectrometer (Delta Plus XL from Thermo Scientific, Bremen, Germany).

After the isotope analyses were complete, the results of all the analytical runs were normalized using typical calibration lines, for which the equations were developed after averaging out measured values for duplicate standards.

2.3. Bench-scale batch soil treatment reactors

Ten grams of sieved soil (< 2 mm diameter) from a Canadian military demolition site were weighed in 25 amber, 40 mL glass bottles (VWR North America, Cat No. 89093-842). The soil consisted of (on a wt. % basis) 2.6 clay, 15.2 silt, 73.5 fine sand, and 0.8 organic matter. Twenty-five mL of a solution containing 16 mg/L RDX was added to each bottle, with different doses of CaO_2. All bottles were then placed on a New Brunswick Rollacell (New Brunswick Scientific, New Jersey, USA) which rotates the bottles at 4.25 rpm. This experiment was conducted at room temperature (19°C ± 1°C) and started when CaO_2 was added.

At pre-selected times, pH and oxidation-reduction potential (ORP) were measured in all bottles with a pH/Ion/Conductivity meter (Orion 9206BN, Thermo Scientific, USA) and a Cole-Parmer double junction, sealed, with a BNC Connector probe (Cat No. S-59001-77) connected to an Accumet Excel XL50 Dual Channel pH/Ion/Conductivity meter from Fisher Scientific). Each bottle was sacrificed and left standing vertically for 5 min to allow soil to settle. Fifteen mL of supernatant was passed through a 0.45 μm nylon filter (Cat No. 28145-489, VWR international) and transferred into a 50 mL polypropylene tube (Sarstedt Inc.). Ten μL of 37% HCl was added to the 15 mL samples to lower the pH. Two, 150 μL aliquots were transferred to two different 14 mL culture tubes (Cat No. 47729-576 from VWR, Canada). Equal volumes of water (for ring-cleavage product analyses) or methanol (for nitroso derivative product analyses) were added and

the samples were homogenized (Maxi Mix II, Bansted Thermolyne type 37600). Solutions were filtered with a 0.45 µm nylon filter (Cat No. 28145-489, VWR international) and then transferred to1.5 mL amber glass vials equipped with a micro-volume insert for EM analysis purposes.

The remaining water sample was used for isotopic analyses, prepared as follows. The water sample was passed through a Sep-Pak® Porapak® RDX Vac 6cc Cartridge (500 mg Sorbent, 125-150 µm particle size) to capture RDX. The presence of RDX in water samples is undesirable because it releases NO_3^- not originally present in the sample during the ion chromatography (IC) and preparation of samples for isotopic analyses (Bordeleau et al., 2012). Therefore, RDX was removed from solution before performing those analyses. Each cartridge was previously conditioned with 5 mL acetonitrile (ACN) followed by 15 mL of ultra-pure water. Cartridges were vacuum dried and effluent was collected into a 15 mL polypropylene tube (Sarstedt Inc.). Aliquots of 150 µL were taken to measure RDX, MEDINA and NDAB. The remaining volumes were separated in two; 4.85 mL for Dionex ICS-2000 analysis for NO_2^- and NO_3^- and 10 mL for isotopic analysis.

2.3.1. Effects of soil organic matter

Eleven, 1 L, wide mouth HDPE bottles were used, with 1%, 5% and 10% of organic soil added to natural soil (< 2 mm diameter) to obtain 100 g of soil total. Then 250 mL of RDX-contaminated water (26 mg/L) was added to each bottle with 10 g of CaO_2. The bottles were placed on a New Brunswick rollacell (New Brunswick Scientific, New Jersey, USA) rotated at 4.25 rpm. Experiments were done at room temperature (19°C ± 1°C).

221 At preselected times, the pH in all bottles was measured and 300 µL aliquots of supernatant were
222 taken. The aliquots were passed through a 0.45 µm nylon filter (Cat No. 28145-489, VWR
223 international) and transferred to 14 mL culture tubes (Cat No. 47729-576 from VWR, Canada),
224 where 1.5 µL of HCl 37% was gauged to stop the alkaline hydrolysis reaction and lower the
225 solution pH. Afterwards, culture tubes were homogenized (Maxi Mix II, Bansted Thermolyne
226 type 37600) and the solution was again passed through a 0.45 µm nylon filter. A 1:1 volume
227 (sample:methanol) was transferred into two separate 1.5 mL amber glass vial for analysis of
228 RDX and its nitroso derivatives, as well as for MEDINA and NDAB ring cleavage products.

229 **2.4. EM stability analyses**

230 See Supplementary material section 1 for the method description and obtained data.

231 **3. Results and Discussion**

232 **3.1. Batch soil slurry reactors**

233 **Fig. 1** shows a plot of ln-normalized aqueous concentrations of RDX over time relative to initial
234 concentrations in batch soil slurry reactors receiving different doses of CaO_2. The degradation of
235 RDX followed 1st-order kinetics (**Eq. 1**), where C_x is the concentration at time (t_x), C_0 is the
236 initial concentration at time-zero, e is the Neper constant (2.718281), and k is the rate constant.

237 $$C_x = C_0 e^{-kt_x} \qquad \textbf{Eq. 1}$$

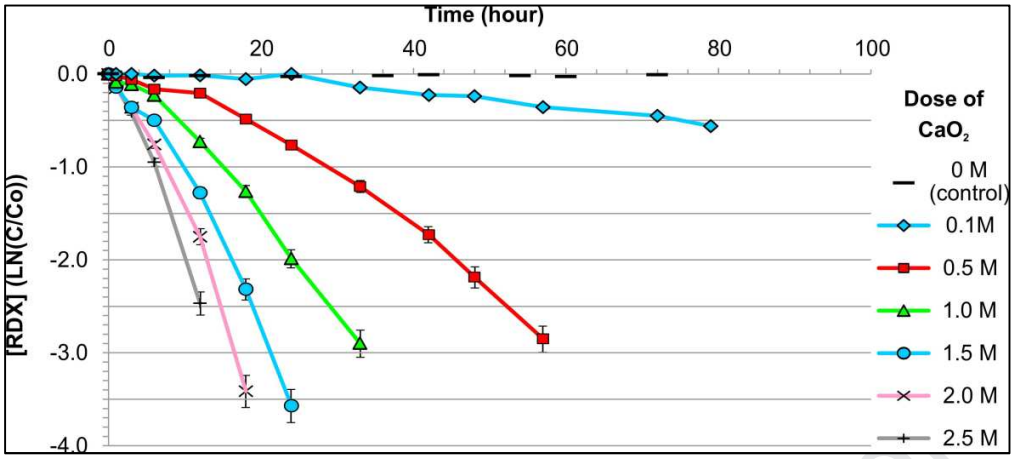

Fig. 1. The ln-normalized aqueous concentrations of RDX over time in batch soil slurry reactors with different doses of CaO_2 (in color).

Eq. 1 was transformed to a linear form ($y= mx+b$) by converting to neperian logarithm on both sides. The result is **Eq. 2**, where $\ln(C_x)$ is the natural log of concentration at time x; k is the slope of the line; and $\ln(C_0)$ is the y-intercept.

$$\ln(C_x) = -kt_x + ln(C_0) \qquad \textbf{Eq. 2}$$

The half-life ($t_{1/2}$) was then calculated from the rate constant ($-k$), using **Eq. 3**.

$$t_{1/2} = ln(2)/k \qquad \textbf{Eq. 3}$$

First-order degradation constants (K_1) were calculated for each CaO_2 dose. All data uncertainties (error ranges) were calculated at the 95% confidence level using the Student t-tests. For individual data points of EM concentrations, the uncertainty was calculated from the standard deviation between replicates. Error bars are not visible for data points having an error bar smaller than the symbol for the data point. The values of all the kinetic constants are listed in **Table 1**.

Table 1. Kinetic constants for RDX degradation in batch slurry reactors with different doses of CaO_2.

[CaO_2] (mole)	**pH**			**[OH^-]**	**K_1 (min^{-1})**	**R^2**	**$T_{1/2}$ (hour)**
	After 1	**After**	**Average**				

	hour	72 hours					
0.0	6.48 ± 0.10	6.56 ± 0.08	6.56 ± 0.18	3.63E-08	6.67E-06	0.96	1733
0.0*	10.17 ± 0.04	10.29 ± 0.04	10.22 ± 0.04	1.66E-04	8.17E-04	0.95	849
0.0*	11.82 ± 0.03	11.98 ± 0.03	11.92 ± 0.03	8.24E-03	9.48E-04	0.95	12
0.1	10.80 ± 0.07	11.09 ± 0.09	10.84 ± 0.16	6.92E-04	1.07E-04	0.82	108
0.5	12.10 ± 0.12	12.16 ± 0.12	12.10 ± 0.24	1.26E-02	7.20E-04	0.95	16
1.0	12.36 ± 0.10	12.41 ± 0.10	12.37 ± 0.19	2.34E-02	1.35E-03	0.97	9
1.5	12.37 ± 0.10	12.44 ± 0.22	12.41 ± 0.32	2.57E-02	2.25E-03	0.97	5
2.0	12.42 ± 0.10	12.58 ± 0.10	12.58 ± 0.19	3.80E-02	2.86E-03	0.97	4
2.5	12.66 ± 0.08	12.78 ± 0.08	12.73 ± 0.15	5.37E-02	3.22E-03	0.98	4

***Alkaline hydrolysis only**

The results demonstrate that the half-life of RDX in the reactors decreased (i.e., degradation rates increased) with increasing dose of CaO_2. H_2O_2 concentrations were measured 1 h and 72 h after the experiment started, using Indigo H_2O_2 test strips (0-100 ppm). Over 50 ppm H_2O_2 was detected in all reactors 1 h after the experiment began, and over 50 ppm H_2O_2 was detected after 72 h in the 0.1 M CaO_2 reactor and 3 ppm H_2O_2 in the 1 M CaO_2 reactor. These results show that the CaO_2 released H_2O_2 and that the H_2O_2 was available for modified Fenton reactions during the entire course of the experiments. Values of pH also increased with increasing CaO_2 dose, which is consistent with the generation of $Ca(OH)_2$ (**Reaction 2**). RDX concentrations were reduced to below detection (< 0.5 µg/L) after 18 h with 2 M and 2.5 M of CaO_2, after 30 h with 1.5 M CaO_2, after 54 h with 1 M CaO_2. No appreciable RDX degradation was observed with 0.1 M CaO_2. **Fig. S1** (provided in the Supplementary material) shows that systems with 0.1 M CaO_2 had lower ORP than systems with higher CaO_2 doses. This is consistent with the lowest CaO_2 dose (0.1 M) resulting in the lowest reduction in RDX concentrations. For all doses, the ORP diminished moderately over the course of the experiments.

Table 1 presents two different sets of data from the alkaline hydrolysis of RDX, where the pH is above 10 and no CaO_2 was added. The reactors with an alkaline pH of 11.92 ± 0.03 and no CaO_2

had an RDX half-life of 12 h, compared to reactors dosed with 0.5 M CaO_2 and having a similar pH (12.10 ± 0.24) which had an RDX half-life of 16 h. This finding shows that alkaline hydrolysis in oxidative system is effective in degrading RDX, which is also supported by Lapointe et al. (2013) and Lapointe and Martel (2014).

Similar results were obtained when RDX was introduced as solid particles into batch soil slurry reactors (see Supplementary material **Fig. S2**). RDX concentrations in solution remained stable for hours before any significant degradation occurred, indicating that solid RDX must first dissolve before it can be chemically oxidized. This observation is also supported by the fact that RDX added in excess of its aqueous solubility (~80 mg/L) never showed aqueous concentrations even close to this concentration, suggesting RDX was oxidized as soon as it was dissolved.

RDX degradation by CaO_2 did not produce detectable amounts of the nitroso derivatives MNX, DNX and TNX. MNX is the most acutely toxic of the nitro-reduced degradation products of RDX, and causes mild anemia at high doses (Jaligama et al., 2013). The only degradation products detected were MEDINA and NDAB (**Fig. 2**). MEDINA concentrations increased linearly when the CaO_2 concentration was 0.1 M (y= 0.0071x; R^2= 0.9916), indicating that this dose was insufficient to degrade MEDINA, even though RDX was degraded. The 0.1 M CaO_2 dose clearly did not generate sufficient radicals to oxidize MEDINA, allowing it to accumulate. In general, the higher the CaO_2 dose, the faster MEDINA was produced and accumulated, except for the reactions with 0.1 M and 0.5 M CaO_2, where a greater CaO_2 dose resulted in a lower maximum MEDINA concentration. This is consistent with higher doses of CaO_2 providing more radical species to oxidize MEDINA. The 0.5 M CaO_2 dose degraded MEDINA at a rate

comparable to that for RDX, with the MEDINA concentration temporarily peaking and then decreasing at the same rate as RDX degraded.

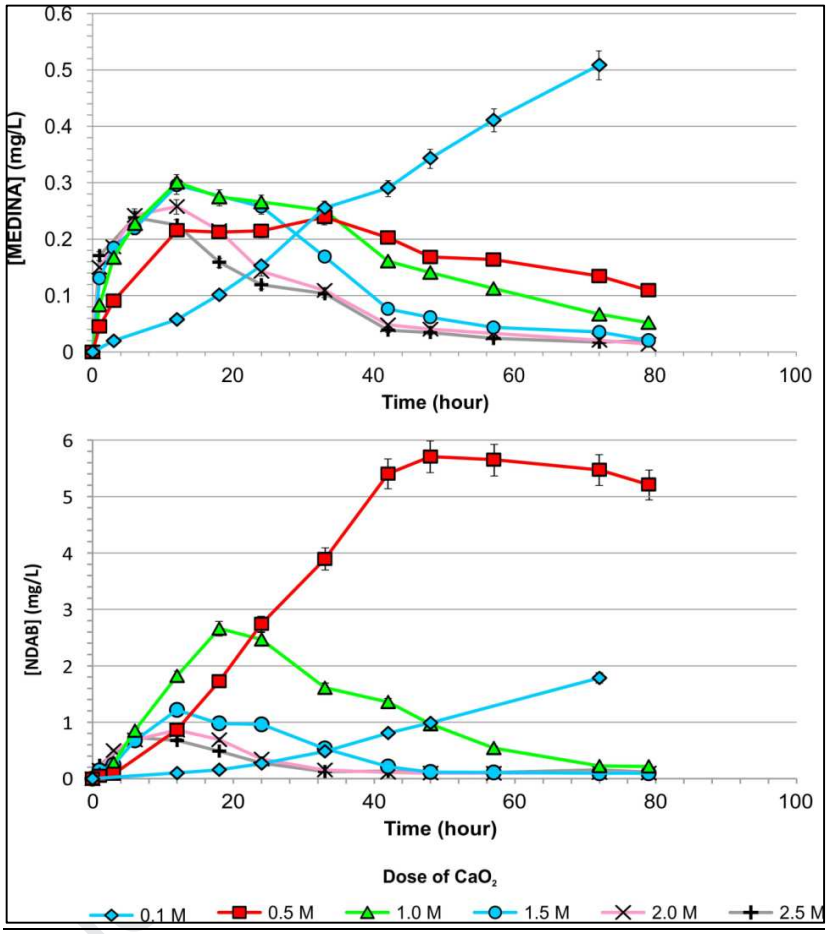

Fig. 2. MEDINA and NDAB aqueous concentrations over time during RDX chemical oxidation by different doses of CaO_2 in soil slurry reactors (in color).

Measured concentrations of NDAB were 10 times greater than MEDINA (**Fig. 2**). The greater accumulation of NDAB than MEDINA suggests that RDX denitration under aerobic conditions from CaO_2 decomposition is likely the initial degradation step. This observation is supported by Sunahara et al. (2009) and is also consistent with the formation of NDAB during aerobic degradation. NDAB production was exponential for 0.1 M CaO_2. But as CaO_2 doses increased, the maximum concentrations of NDAB measured decreased, probably due to decomposition of NDAB to N_2O, HCHO, NH_3, and HCOOH under alkaline conditions (pH $\geq$ 12.3) at room

304 temperature (Balakrishnan et al., 2003, Halasz et al., 2010). However, none of these
305 decomposition products were analyzed in this study and stable isotopes of nitrate were the only
306 ones quantified to support complete mineralization of RDX. Both MEDINA and NDAB were
307 detected after 1 h in all reactors, but in systems with a 0.1 M CaO_2 dose NDAB only appeared
308 after 12 h, whereas MEDINA after 3 h. The appearance of MEDINA before NDAB in systems of
309 0.1 M CaO_2, coupled with the observed positive ORP values confirm that 0.1 M CaO_2, the
310 lowest dose tested, did not provide enough oxidant to mineralize RDX, and should be considered
311 the lower limit of CaO_2 doses for RDX oxidation.

312 **3.1.1. Stable isotopes of nitrogen and oxygen associated to nitrate produced by**
313 **RDX degradation**

314 Isotopic ratios are reported in per mil (‰). This expresses the difference in the ratio of heavy to
315 light isotopes ($^{15}N/^{14}N$, $^{18}O/^{16}O$) between the sample and an international standard, shown in **Eq.**
316 **4**, where "*x*" is the sample, and "ref" the standard. Standards are atmospheric N_2 and the Vienna
317 Standard Mean Ocean Water (VSMOW) for N and O, respectively. The precision is 0.6 ‰ for
318 both $\delta^{15}N$ and $\delta^{18}O$ values.

319 $$\delta^{15}N(‰) = \left(\frac{\left[\left({}^{15}N/_{14}N \right)_x - \left({}^{15}N/_{14}N \right)_{ref} \right]}{\left({}^{15}N/_{14}N \right)_{ref}} \right) \times 1000 \qquad \textbf{Eq. 4}$$

320 **Table S2** (see Supplementary material) lists the calculated ratios of $\delta^{15}N$ and $\delta^{18}O$ associated with
321 RDX degradation. Because NO_2^- released from nitroaromatics during chemical oxidation is

322 immediately oxidized to NO_3^- (Delwiche and Steyn, 1970, Cassidy et al., 2009), the $\delta^{15}N$ values
323 represent the sum of both species (NO_2^- and NO_3^-). The measurement of NO_2^- and NO_3^-
324 concentrations by ICS-2000 Dionex demonstrates that RDX is mineralized by contact with 1 M
325 CaO_2, as both ions from RDX degradation were detected from the RDX mother solution. The ratios
326 of $\delta^{15}N$ and $\delta^{18}O$ remained quite similar throughout the experiment, but the sum of NO_2^- + NO_3^-
327 (NO_x^-) decreased slightly after 60 h.

328 **Fig. 3** is a plot of the $\delta^{15}N$ ratio vs. the $\delta^{18}O$ ratio measured in the NO_3^- liberated during the
329 degradation of RDX and shows a distinct pattern. Ratios of NO_3^- released from RDX degradation
330 are lighter with respect to $\delta^{15}N$ and heavier with respect to $\delta^{18}O$ values than the non-fractionated
331 ratios of the nitro ($-NO_2$) group on RDX. The heavier $\delta^{18}O$ ratio is due to the release of O_2 from
332 CaO_2. A lighter $\delta^{15}N$ ratio may be due to a kinetic isotope effect, but more likely indicates that
333 NO_3^- released from RDX does not accumulate. The latter is consistent with the decreased NO_x^-
334 concentrations observed after 60 h (**Table S2**). Denitrification or exchange of NO_3-N with soil
335 particles would cause an increase in $\delta^{15}N$ values of residual NO_3^- (Delwiche and Steyn, 1970,
336 Fogg et al., 1998, Bernstein et al., 2010). Therefore, the decrease in $\delta^{15}N$ observed here can only
337 be satisfactorily explained by processes related to RDX degradation and NO_3^- chemically
338 binding with other compounds in the soil slurry system.

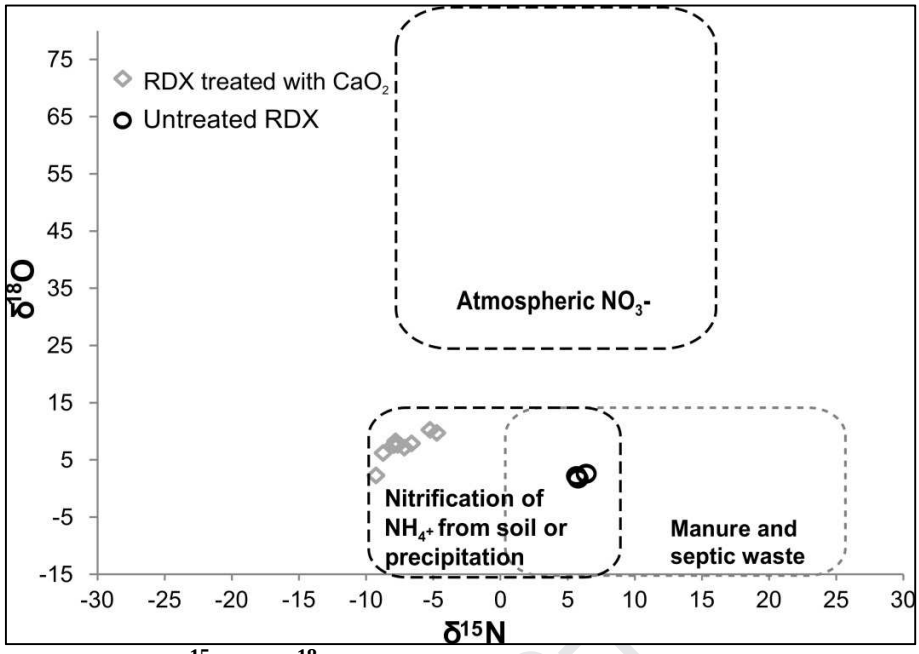

Fig. 3. Isotopic ratios of $\delta^{15}N$ vs. $\delta^{18}O$ measured in NO_3^- released during RDX degradation with 1 M CaO_2.

The isotopic ratios obtained in **Fig. 3** were compared with those reported by Kendall et al. (2007) for common NO_3^- sources. The ratios obtained from CaO_2 oxidation of RDX overlap with nitrification of ammonium (NH_4^+) from soil or precipitation, both ubiquitous processes in soils. Therefore, if stable isotopes for NO_3^- are to be used as a means to follow *in situ* RDX degradation by CaO_2, one should keep in mind that other NO_3^- sources may coexist on site and that a classic dual isotopic plot does not suffice to infer if RDX releases those $\delta^{15}N$ and $\delta^{18}O$ ratios only from its chemical oxidation.

3.1.2. Effects of soil organic matter

Aqueous concentrations of RDX over time in batch soil slurry reactors having different percentage of OM are shown in **Fig. 4**. RDX degradation by CaO_2 with the presence of soil and/or OM did not produce detectable amounts of the nitroso derivatives MNX, DNX and TNX.

The only degradation products detected were only MEDINA and NDAB, and their concentrations over the course of the experiment are plotted in **Fig. 5**.

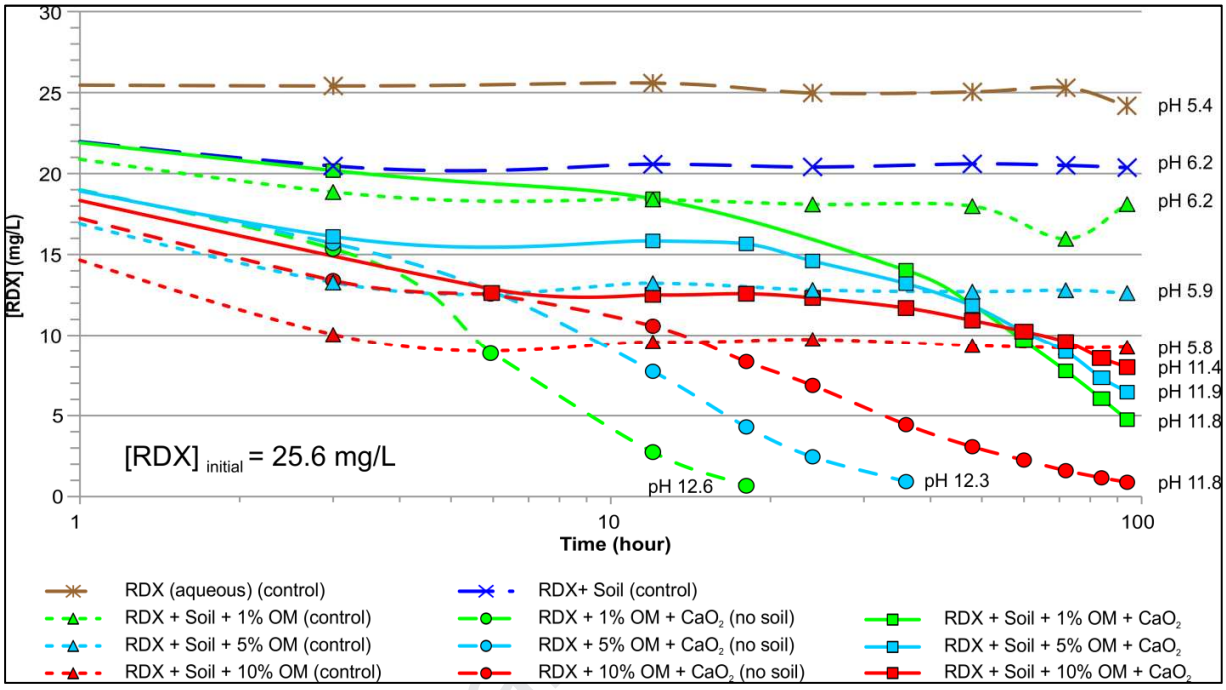

Fig. 4. Aqueous concentrations of dissolved RDX over time in soil slurries reactors containing CaO_2 and different organic matter (OM) content (in color).

In the control reactors with no CaO_2, aqueous concentrations of RDX in soil decreased over the first 3 h and then levelled off. The final RDX concentration decreased steadily as the OM content increased from 1% to 5% to 10% (**Fig. 4**). This can be explained by RDX partitioning into the OM. Card and Autenrieth (1998) observed that RDX sorption and desorption depends on the OM content in soils. They found that approximately 2% of the RDX in a soil-water environment partitioned to soil for each incremental 1% of OM. When comparing steady state aqueous RDX concentrations in these experiments, in the presence of soil alone and soil with OM contents ranging from 1% to 10%, the relationship of RDX partitioning was non-linear. It was found that only 20% of RDX partitioned onto soil with no OM, 31% partitioned with 1% OM; 50% partitioned with 5% OM, and 63% partitioned with 10% OM.

368 In the absence of soil, reactors dosed with CaO_2 and OM showed lower aqueous RDX
369 concentrations over time than the controls with no CaO_2, demonstrating that CaO_2 degraded
370 RDX. The RDX degradation rate decreased with increasing OM content. This phenomenon may
371 be due to RDX partitioning to OM, making less of the RDX available to react. OM may also
372 have competed with RDX for the radicals responsible for chemical oxidation. Ca^{2+} released from
373 CaO_2 would be expected to compete with RDX for sorption sites on solids and OM due to cation
374 exchange capacity (CEC), which is greater for OM than mineral solids because of all abundance
375 of negative charges on OM. This mechanism would increase the presence of RDX in the aqueous
376 phase and enhance the chemical oxidation of RDX. As shown in **Fig. 4**, the reduction in RDX
377 concentrations achieved after 3 h increased with increasing OM content in soil systems (21%
378 reduction for 1% OM, 37% for 5% OM and 50% for 10% OM). This indicates that even if Ca^{2+}
379 is competing with RDX for sorption, some RDX would have remained sorbed to the OM.

380 Generally, the presence of soil did not appreciably influence RDX degradation by CaO_2 during
381 the first 3 h, because the RDX concentrations are quite similar in systems with and without soil
382 (16.1 mg/L with soil and 15.7 mg/L without soil for 5% OM; 12.9 mg/L with soil and 13.4 mg/L
383 without soil for 10% OM). The sole exception was with the 1% OM reactors, which showed
384 RDX concentrations of 20.2 mg/L with soil and 15.4 mg/L without soil. After 3 h, the amount of
385 RDX degraded decreased as the OM content increased, with and without soil present. The RDX
386 half-life in soil with OM was 40 h, 45 h, and 128 h, in presence of 1%, 5% and 10% OM,
387 respectively. The RDX half-life in the absence of soil was 4 h, 7 h, and 21 h, with 1%, 5% and
388 10% OM, respectively. It can therefore be concluded that the presence of both OM and soil
389 decreased RDX degradation after 3 h, and this decrease was proportional to the OM content.

Aqueous concentrations of MEDINA were higher without soil (as high as 3 mg/L), compared with reactors with soil (< 0.2 mg/L) (**Fig. 5**). MEDINA was released more gradually with 10% OM in the absence of soil than with lower OM contents. With 5% OM, MEDINA concentrations peaked at 3 mg/L after 48 h and then decreased over time to nearly the detection limit after 94 h. This indicates that MEDINA could have been further chemically oxidized as the reactions triggered by CaO_2 progressed. When soil was present, MEDINA concentrations were below detection until 60 h, with 5% and 10% OM, and until 94 h with 1% OM. The presence of soil resulted in less MEDINA accumulation because soil decreased the rate of RDX degradation.

Fig. 5 clearly shows that higher OM content in reactors with soil and dosed with CaO_2 decreased the rate of NDAB production, which is consistent with RDX degradation rates being lower as OM content increased. NDAB accumulated to higher peak concentrations than MEDINA in systems with and without soil, reaching a concentration of 9 mg/L with 10% OM (**Fig. 5)**. This observation suggests that some aerobic degradation of RDX occurred as its aerobic degradation pathway leads to the formation of NDAB (Sunahara et al., 2009). NDAB continuously accumulated in reactor vessels containing soil and OM, indicating that the CaO_2 dose was too low to mineralise NDAB in those systems. In absence of soil, NDAB production rate decreased as the OM content decreased. NDAB degradation took place and it stopped accumulating in all systems with no soil. NDAB was below detect after 48 h with 1% OM, continuously decreased over time after 18 h with 5% OM, and plateaued by the end of the experiment with 10% OM system. This indicates that the chemical oxidation of RDX did occur to an extent beyond the step generating NDAB, though rates of RDX degradation decreased with increasing OM content.

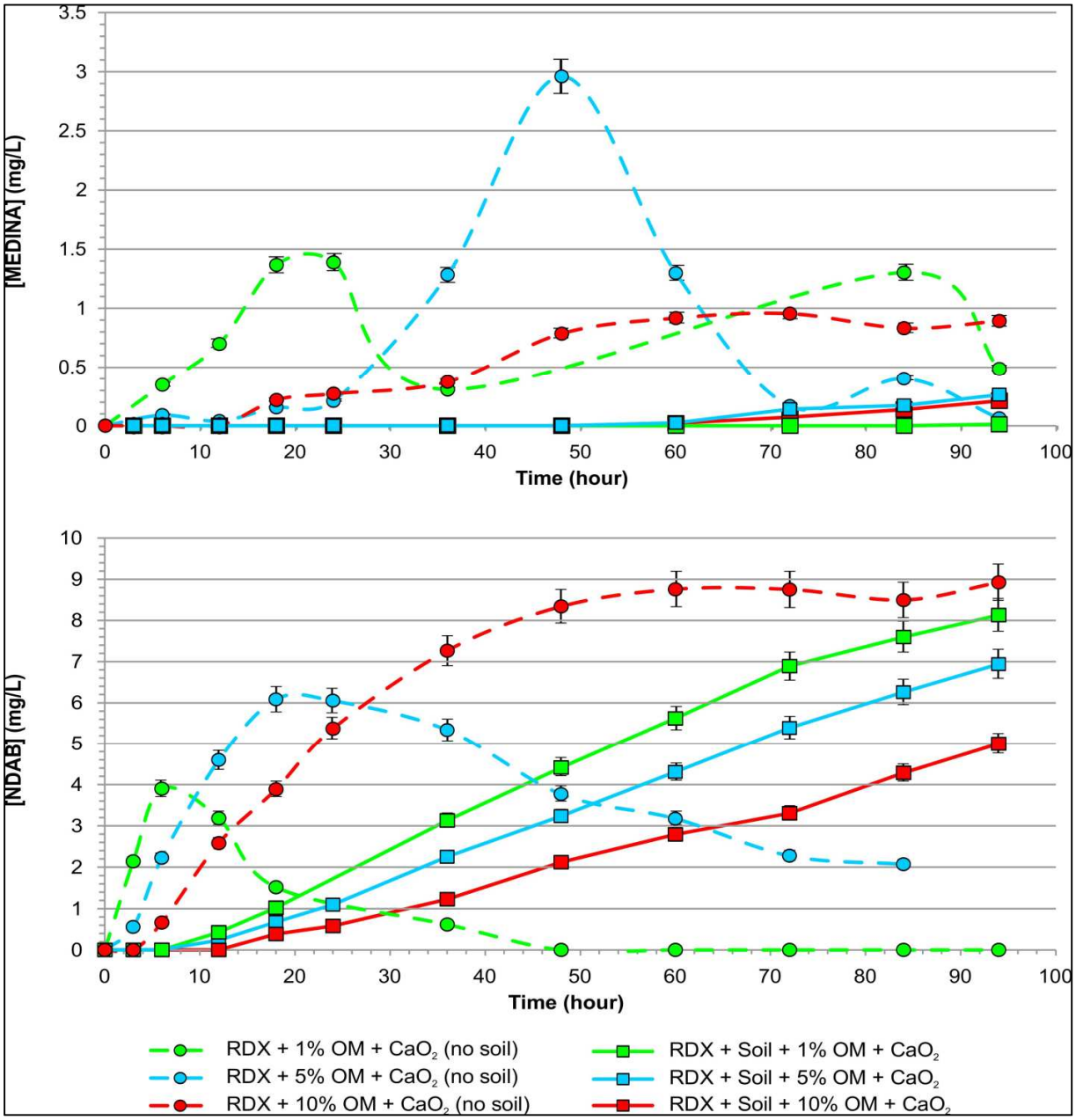

Fig. 5. MEDINA and NDAB aqueous concentrations during RDX chemical oxidation by CaO_2 in soil slurries containing different percentages of organic matter (OM) (in color).

4. Conclusions

The primary objective of this study was to conduct laboratory investigations of the ability of CaO_2-based modified Fenton chemistry to degrade RDX in soil systems with and without OM.

Batch tests in soil slurry reactors demonstrated that RDX was readily chemically oxidized by CaO_2 within 20 hours. The half-life of RDX oxidation decreased with increasing CaO_2 dose, from 108 hours with a CaO_2 dose of 0.1M to 4 hours with a CaO_2 dose of 2.5 M. CaO_2 also increased pH values, which further promoted RDX degradation via alkaline hydrolysis. RDX was chemically oxidized by CaO_2 even in the presence of OM as high as 10%. Nitroso derivatives of RDX (i.e., MNX, DNX, TNX) were below detection levels in all the experiments, indicating that sequential reduction of RDX nitro groups did not occur. Denitration of RDX did occur, evidenced by the formation of MEDINA and NDAB in all the soils treated with CaO_2. The mineralization of RDX by chemical oxidation was demonstrated using stable isotope ratios of the nitrate generated. This paper demonstrates that CaO_2-based modified Fenton chemistry can be used to treat soils contaminated with RDX at munitions training ranges and RDX production facilities.

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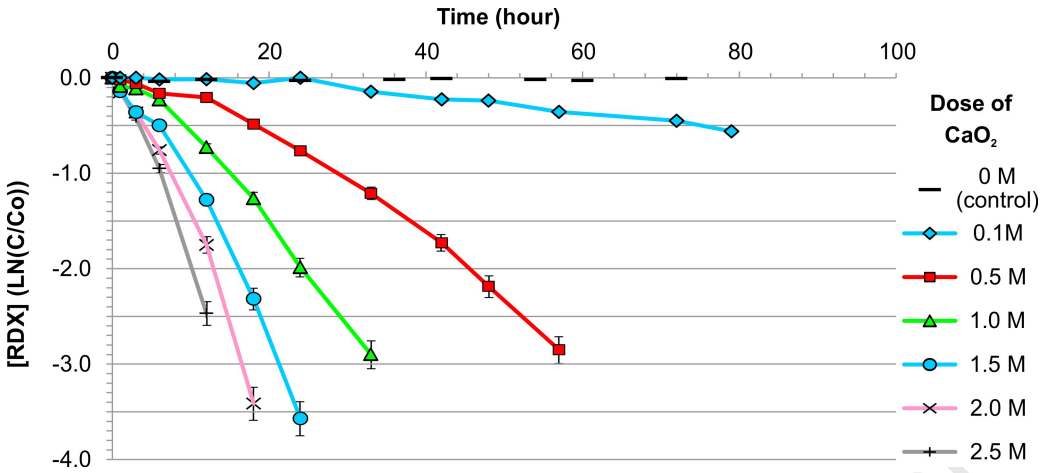
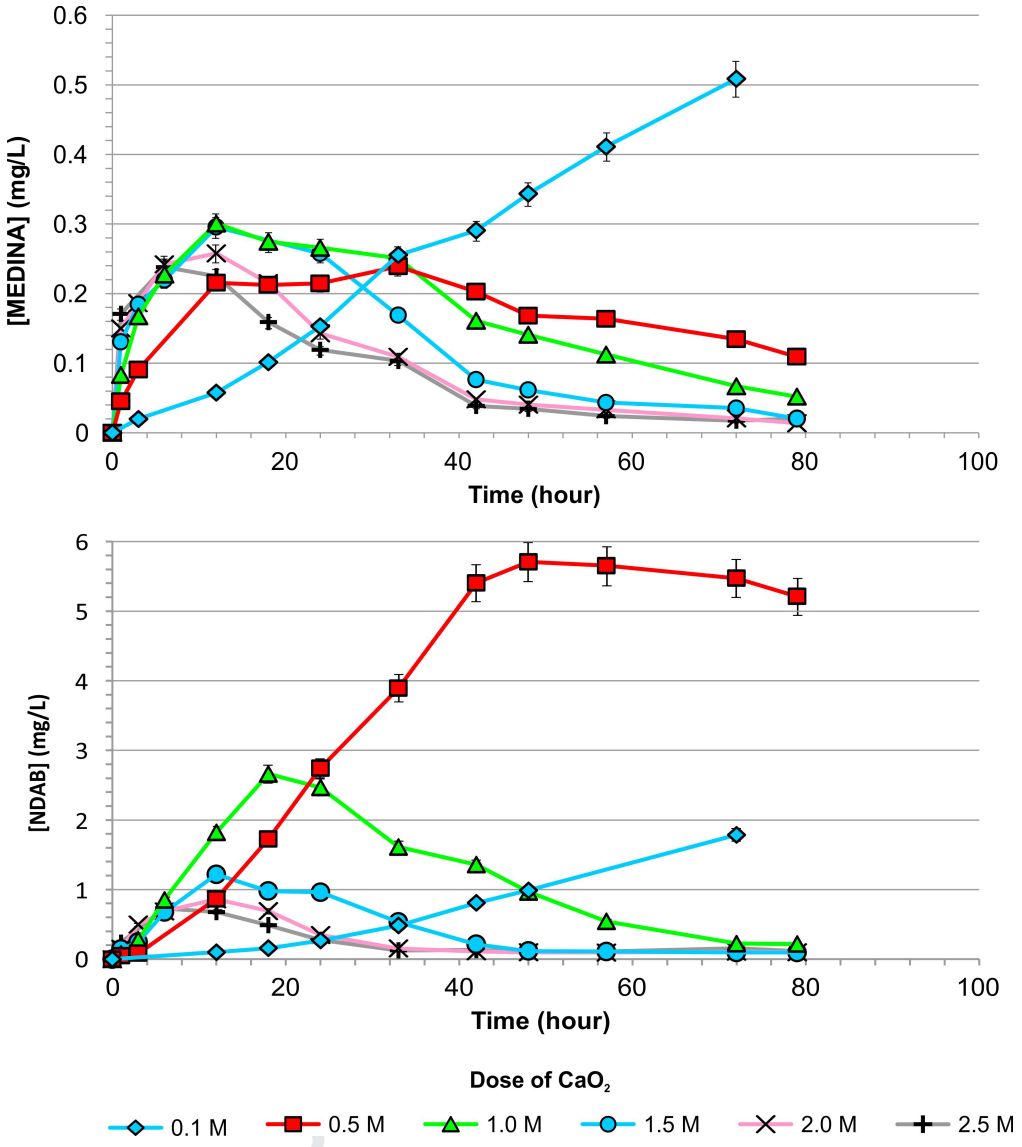
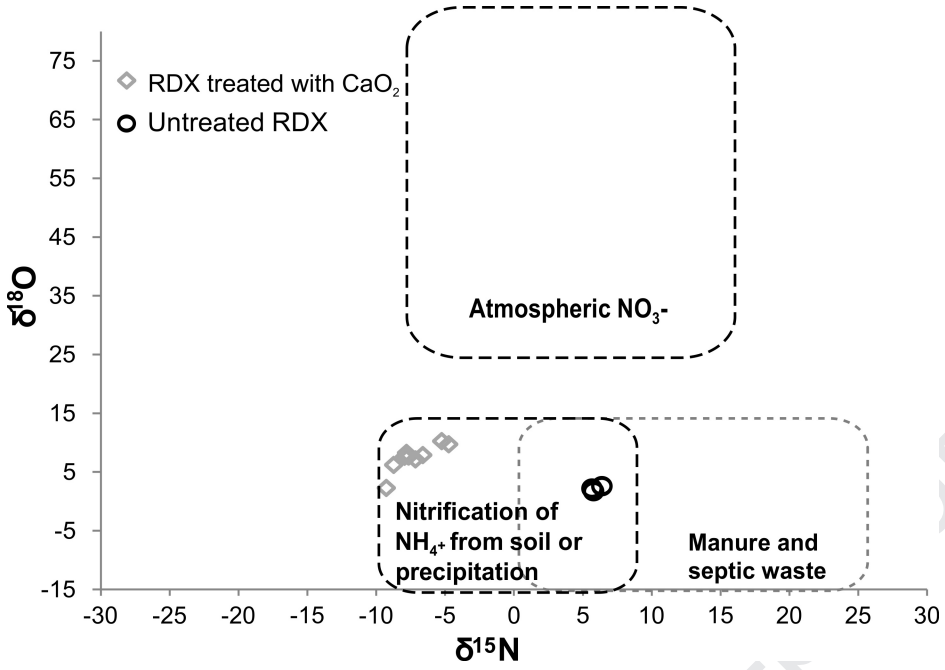
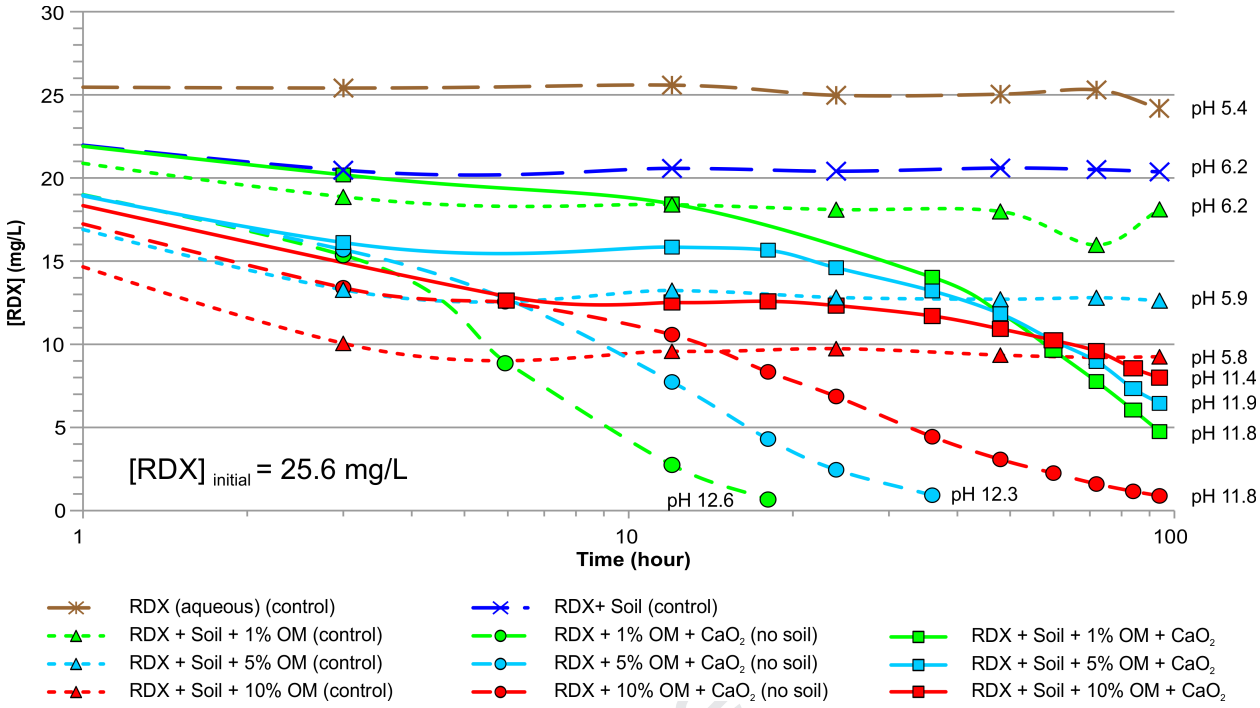
$[CaO_2]$ (mole)	pH			$[OH^-]$	K_1 (min^{-1})	R^2	$T_{1/2}$ (hour)
	After 1 hour	After 72 hours	Average				
0.0	6.48 ± 0.10	6.56 ± 0.08	6.56 ± 0.18	3.63E-08	6.67E-06	0.96	1733
0.0*	10.17 ± 0.04	10.29 ± 0.04	10.22 ± 0.04	1.66E-04	8.17E-04	0.95	849
0.0*	11.82 ± 0.03	11.98 ± 0.03	11.92 ± 0.03	8.24E-03	9.48E-04	0.95	12
0.1	10.80 ± 0.07	11.09 ± 0.09	10.84 ± 0.16	6.92E-04	1.07E-04	0.82	108
0.5	12.10 ± 0.12	12.16 ± 0.12	12.10 ± 0.24	1.26E-02	7.20E-04	0.95	16
1.0	12.36 ± 0.10	12.41 ± 0.10	12.37 ± 0.19	2.34E-02	1.35E-03	0.97	9
1.5	12.37 ± 0.10	12.44 ± 0.22	12.41 ± 0.32	2.57E-02	2.25E-03	0.97	5
2.0	12.42 ± 0.10	12.58 ± 0.10	12.58 ± 0.19	3.80E-02	2.86E-03	0.97	4
2.5	12.66 ± 0.08	12.78 ± 0.08	12.73 ± 0.15	5.37E-02	3.22E-03	0.98	4

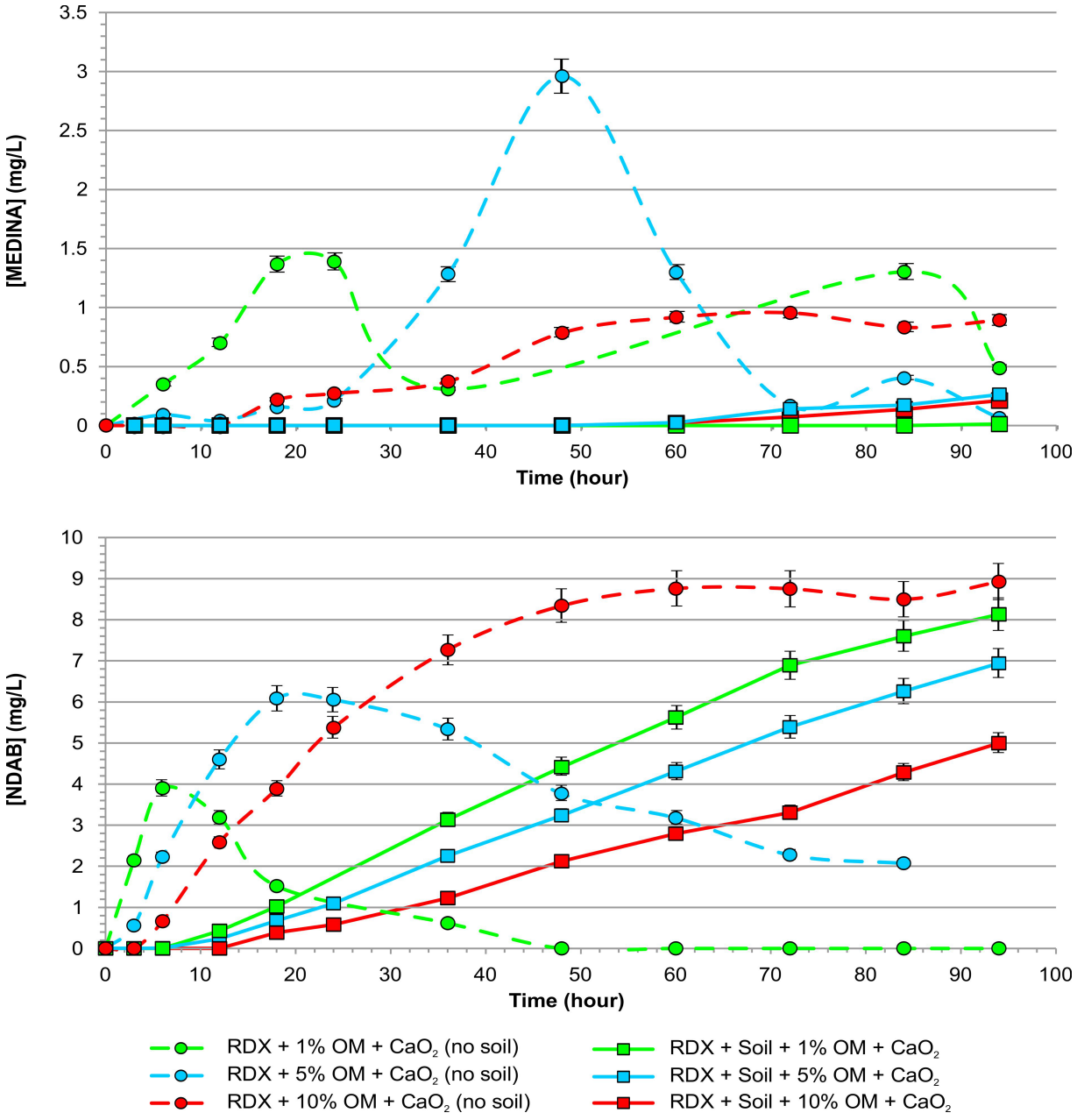
***Alkaline hydrolysis only**




[MEDINA] (mg/L)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Time (hour)
[NDAB] (mg/L)
6
5
4
3
2
1
0
0
20
40
60
80
100
Time (hour)
Dose of CaO2
0.1 M
0.5 M
1.0 M
1.5 M
2.0 M
2.5 M






[MEDINA] (mg/L)
Time (hour)
[NDAB] (mg/L)
Time (hour)
RDX + 1% OM + CaO2 (no soil)
RDX + 5% OM + CaO2 (no soil)
RDX + 10% OM + CaO2 (no soil)
RDX + Soil + 1% OM + CaO2
RDX + Soil + 5% OM + CaO2
RDX + Soil + 10% OM + CaO2

Highlights:

1. Increasing dose of CaO_2 in soil slurry reactors increased the degradation rates of RDX.
2. RDX denitration by CaO_2 is likely the initial degradation step.
3. RDX in solid form must first dissolve before it can be chemically oxidized.
4. Isotopic ratios for nitrogen and oxygen from RDX oxidation overlap with another common domain.
5. Soil samples containing CaO_2 shall be preserved in 100% solvent to avoid the underestimation of RDX.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: