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Pilot-Scale Destruction of TNT, RDX, and HMX on Contaminated Soils Using Subcritical Water

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Subcritical (hot/liquid) water was used in a simple static (nonflowing) vessel to treat two soils from former defense sites which were contaminated with the explosives TNT (12 wt %) or RDX (0.32 wt %) and HMX (0.08 wt %). Laboratory studies demonstrated that significant degradation of RDX began at 100 °C and at 125 °C for TNT and HMX. For highly contaminated soils, the bulk of the undegraded explosives remained in the soil rather than in the water phase. Based on HPLC/UV analysis, intermediate degradation products formed but quickly degraded at <250 °C. Pilot-scale remediations (4–6 kg soil) using 4-L of water at 275 °C for 1 h (with 2-h heat-up time) of real soils resulted in >99.9% destruction of TNT and RDX and ca. 98% destruction of HMX. None of the mutagenic nitroso derivatives of RDX and HMX were formed. "Microtox" acute toxicity tests with *Vibrio fischeri* showed no significant (compared to background) residual toxicity in either the process wastewaters or leachates from the treated soils.

Introduction

Soils contaminated with high explosives such as TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) pose significant risk to human health (1). Incineration is the most effective remediation method but is expensive, destroys soil fertility, and generates concern about air emissions (1, 2). Bioremediation is often effective but does not apply well to highly contaminated sites, requires long treatment times, and often produces toxic and/or mutagenic products (2–7).

Recently, subcritical water (hot water under sufficient pressure to maintain the liquid state) has been used for the remediation of kilogram quantities of soils historically contaminated with several hundred mg/kg levels of polycyclic aromatic hydrocarbons (PAHs) and pesticides (8). In that study, dynamic (flowing) water was used to extract the contaminants from soil. Additional studies demonstrated that some pesticides degrade rapidly in subcritical water at temperatures >175 °C (9). Most notably, trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) and pendimethalin (*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine) degrade in pure water at temperatures above 150 °C, and complete degradation occurs at 250 °C in <30 min (9).

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Degradation of these pesticides is interesting because of their chemical similarity to many high explosives. Therefore, we investigated the degradation of TNT, RDX, and HMX on historically contaminated soils at the lab scale (2–40 g) and pilot scale (4–6 kg) using only pure water and contaminated soils placed in heated stainless steel vessels under static (no water flow) conditions.

Experimental Section

Soils. TNT-contaminated soil was from a Ministry of Defense site in the United Kingdom and contained 12 wt % (120 000 mg/kg) of TNT but no significant levels of other explosives. The soil was used as received for the 2-g and 40-g laboratory experiments. Since only limited quantities of this soil could be obtained, the soil was diluted 1/10 with clean sand for the pilot-scale run. Soil contaminated with both RDX (3200 mg/kg) and HMX (750 mg/kg) was obtained from a military storage site in Texas (U.S.A.), sieved to <6 mm to remove rocks and sticks, and mixed for 2 h in a concrete mixer to ensure homogeneity. Concentrations of the explosives on both soils were based on the analysis of eight 2-g subsamples of each homogenized bulk soil sample. Particle size distributions for the TNT and RDX/HMX soils were 1–6 mm (19 and 26 wt %, respectively), 0.5–1 mm (23 and 41 wt %), 0.25–0.5 mm (19 and 22 wt %), 0.125–0.25 mm (19 and 8 wt %), and <0.125 mm (20 and 3 wt %), and water contents were 14 and 8 wt %, respectively. An uncontaminated agricultural soil (obtained locally) was used for spiking experiments and contained 8 wt % organic carbon, ca. 2 wt % water, and particle sizes of 1–6 mm (37 wt %), 0.5–1 mm (29 wt %), 0.25–0.5 mm (14 wt %), 0.125–0.25 mm (9 wt %), and <0.125 mm (11 wt %).

Subcritical Water Apparatus. Two laboratory and one pilot (8-L) reactors were used for the degradation studies. The 5 mL reactors for 2-g samples were constructed from 77-mm long, 7-mm i.d. (12-mm o.d.) 316 stainless steel pipe with national pipe threads (npt) and end caps sealed with Teflon tape (10). These cells were loaded with 2 g of soil and 2 mL of HPLC-grade water (which had been purged with nitrogen to remove dissolved oxygen) and capped. This procedure left ca. 1.5 mL of headspace in the cell. The 75 mL reactor was constructed from 316 stainless steel tubing (2.22 cm i.d., 3.17 cm o.d. × 17.1 cm) with welded conversion fittings to 1 in. (2.54 cm) "Swagelok" tubing fittings. "Swagelok" caps were used to seal both ends. Each reaction used 40 g of soil and 40 mL of water. Cells were placed in a GC oven (Hewlett-Packard 5890, series II) for heating. After heating, the cells were cooled to room temperature and opened, and the soil and water were recovered separately for analysis.

The pilot-scale reactor was a type 304 stainless steel 8.2-L tubular reactor (10.2 cm i.d., 12.7 cm o.d. × 100 cm long reactor from High-Pressure Equipment, Erie, PA) wrapped with six 620-W heat tapes, which were controlled in three zones with separate thermocouples. A thermocouple was inserted into the center of the soil column through a 1/4 in. "Swagelok" tee fitting on one of the reactor's end caps. This tee was also attached to a pressure relief valve (Nupro ss 177-R3A-K1-D) set at ca. 100 bar and a pressure monitoring gauge. A second pressure relief valve was mounted on a tee on the other end of the reactor, and the other leg of this tee was attached to a 1/4-in. vent line (4.9 mm i.d. × 6.4 mm o.d. × 15 m long stainless steel tubing) which was coiled in a barrel of cool water to condense the vented steam for collection in a separate water container. Venting was

controlled by a manual shut-off valve (ss 10-11AF4, High-Pressure Equipment Co.) mounted in the vent line.

Two pilot-scale runs (one with each soil) were conducted using 4 kg of soil and 4 L of tap water with the reactor in the horizontal position. Since no water flow is used during the process, and the soil is loaded as a soil/water slurry, no channeling can occur in the system. After the heating was completed, the reactor was allowed to cool overnight before opening, and the soil and water were recovered for analysis. One additional run was performed with 6 kg of soil and 4 L of water with the reactor in the vertical position. At the end of the heating period, the vent line was opened to release the water as steam in order to more rapidly cool the soil to ca. 100 °C, allowing the reactor to be opened only ca. 2 h after the heating was completed.

Safety note: All static (nonflowing) reaction vessels must contain a sufficient headspace so that the pressure inside the vessel is controlled by the steam/liquid equilibrium. A full vessel must never be used since the pressures could reach several thousand bar (11). For these studies where the highest temperature was 275 °C (resulting in a pressure of ca. 60 bar), ca. 20% (or more) of the vessel volume was left empty to ensure adequate headspace.

Analysis. All untreated soils, treated soil residues, and wastewaters from every degradation experiment were analyzed using EPA method 8330. Soils were extracted with acetonitrile by sonication for 18 h, and water samples were diluted 1:1 in acetonitrile before analysis by HPLC with UV detection (HPLC/UV) at 254 nm with isocratic elution with 82/18 water/2-propanol for TNT and 95/5 water/2-propanol for HMX and RDX. Solvent programming from 85/15 water/methanol to 100% methanol was used to obtain higher resolution in order to analyze selected samples for intermediate products. All separations were conducted with a Waters HPLC (model 2487 dual wavelength UV/Visible detector, and model 515 pump) equipped with a "Nova-Pak" C-18 HPLC column (15 cm long, 4 mm i.d., with 4 μ m packing). Peak identifications and quantitations were based on the injection of known compounds.

Bacterial Toxicity. "Microtox" tests were conducted on water leachates of the treated and untreated soils and on the process wastewaters by a commercial laboratory (AquaTox Research, Inc., Syracuse, NY) using the luminescent bacteria *Vibrio fischeri* (12, 13). Test waters were diluted until the luminescence of the bacteria was one-half that of nontoxic controls (EC_{50}).

Results and Discussion

Lab-Scale. Initial testing with TNT, RDX, and HMX spiked onto 2 g of clean soil at ca. 25 mg/kg was conducted for 15 and 60 min at temperatures ranging from 50 to 200 °C. As shown in Figure 1, no detectable degradation occurred at 50 °C, while some degradation (ca. 10–25%) occurred after 1 h at 100 °C for all three compounds. The mildest conditions for >99% destruction were 175 °C for 15 min for RDX and HMX and 1 h at 200 °C for TNT.

Based on these spiked explosive results, analogous studies were performed using the historically contaminated soils. Since shake-down tests with the 8-L reactor showed a heating rate of ca. 2.5 °C/min, the lab-scale tests were performed by temperature programming the GC oven used to heat the small reactors from 25 °C to 275 °C at 2.5 °C/min. Several identical reactor cells (each containing the same amounts of soil and water) were placed in the oven, and individual cells were removed as the oven reached various temperatures so that the remaining explosives in the soil and water at each temperature could be determined.

Figure 2 shows the concentrations of the explosives in the individual reactors removed from the oven at various temperatures. TNT began to show substantial degradation

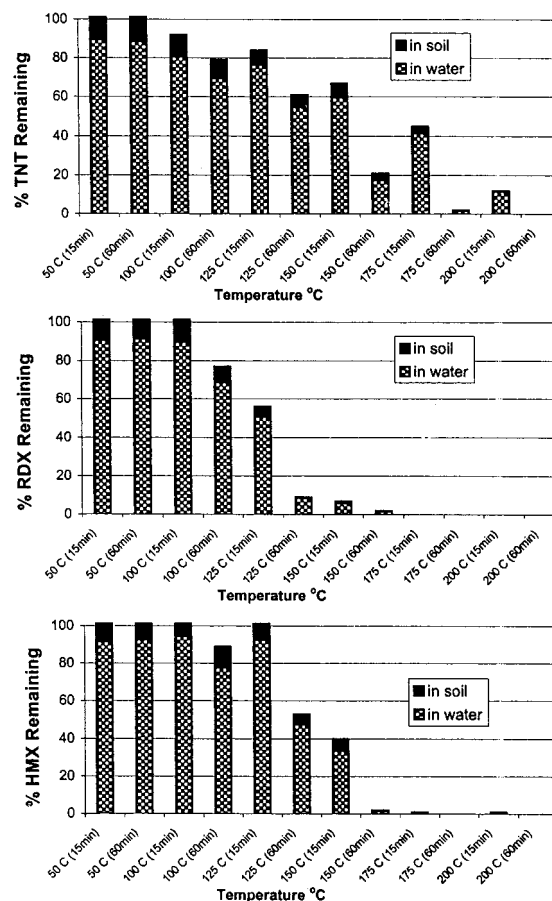


FIGURE 1. Degradation of TNT (top), RDX (middle), and HMX (bottom) spiked at 25 mg/kg on clean soil and exposed to subcritical water at different temperatures. Each sample was heated rapidly to the test temperature and then held for 15 or 60 min.

in the reactor heated to 200 °C, and nearly complete degradation in the reactor heated to 250 °C. Similar behavior was observed for RDX and HMX on the second soil, although significant degradation began at somewhat lower temperatures than for TNT (Figure 2). All three explosives were completely degraded (based on analysis of both the treated soils and the wastewaters) when the reactors were allowed to reach 275 °C (Figure 2). The largest quantities of nondegraded compounds were found in the soil phase (compared to small amounts in the wastewater), possibly because solvated molecules (that had not degraded) repartitioned to the soil upon cooling, or because the explosives degraded rapidly once solvation in the water occurred. Alternatively, the degradation reactions could occur primarily on the soil surface, although rapid degradation of the explosives spiked into water (with no soil present) also occurs, demonstrating that the soil is not necessary for the degradation reactions.

Based on the results shown in Figures 1 and 2, additional lab-scale trials were performed using reactors heated to mimic the pilot-scale unit, i.e., the GC oven was programmed at 2.5 °C/min and then held at 275 °C for 1 h. In addition, since the amount of TNT soil available at the 12 wt % contamination level was not enough for pilot-scale tests, triplicate degradation experiments were performed using 40 g of the 12 wt % TNT soil and 40 mL of water in the 75-mL reactor to provide sufficient treated soil for the biological testing.

The results of these lab-scale experiments (triplicate reactions at each condition) performed to mimic the pilot-scale runs are shown in Table 1. For the 2-g samples, all of the TNT, RDX, and HMX (and the intermediate products

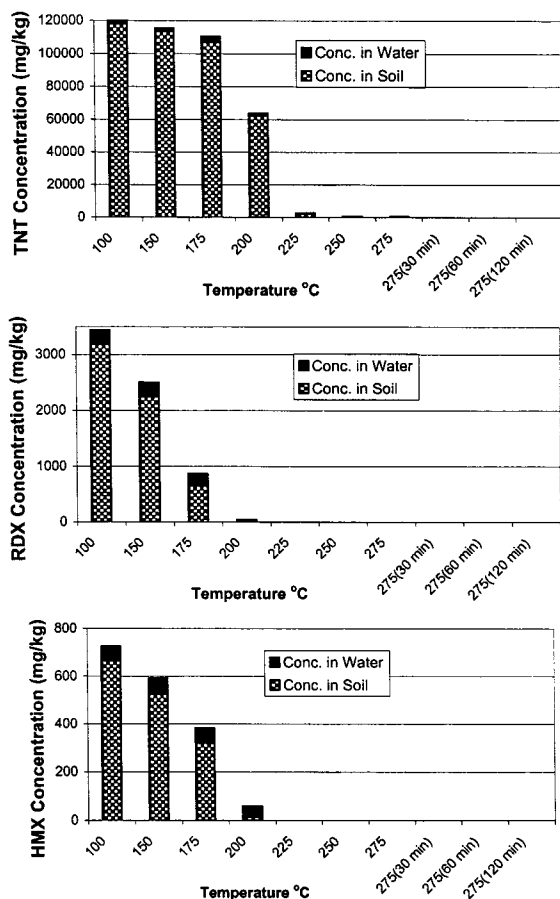


FIGURE 2. Degradation of TNT (top), RDX (middle), and HMX (bottom) on contaminated soils exposed to subcritical water at different temperatures. Heating was performed from 25 to 275 °C at 2.5 °C/min to mimic the pilot-scale unit. Reaction cells were removed from the oven when the temperature shown on the figure was reached.

discussed below) were degraded below their analytical detection limits of 1 mg/kg in the water and the soil. Triplicate treatments of 40-g subsets of the 12 wt % TNT soil (with 40 mL water) resulted in only low mg/kg levels of TNT remaining in the soil and wastewater (Table 1).

Intermediate Reaction Products. HPLC/UV analysis of the soil residue and water phases from the spiked and real-world soils did show some intermediate reaction products. The reaction product with the highest concentration came from the TNT-contaminated soil, with its appearance beginning at 200 °C (Figure 3) and its maximum concentration reaching ca. 24% of the total TNT concentration (assuming the UV response factor for the degradation product is the same as for TNT) in the reactor heated to 225 °C. However, the concentration of this product dropped rapidly as the reaction temperatures were increased and disappeared when the reactor was exposed to 275 °C for 60 min or longer. Only one significant degradation product from the RDX/HMX-contaminated soil was observed, with a maximum concentration (assuming the same HPLC/UV response factor as RDX) of ca. 20% of the total RDX concentration in the reactor heated to 150 °C. This intermediate product also quickly disappeared as the reactors were exposed to higher temperatures.

It is important to note that these intermediate products are not the toxic (and sometimes mutagenic) reaction products such as the nitroso derivatives of RDX (based on the lack of detectable mono-, di-, and trinitroso derivatives of TNT, RDX, and HMX compared to the HPLC/UV behavior of standard compounds). Indeed, the fact that our method

TABLE 1. Lab- and Pilot-Scale Degradation of TNT, RDX, and HMX on Historically-Contaminated Soils with Subcritical Water at 275 °C for 1 h

		concn after treatment, mg/kg \pm SD ^b			
		original concn, mg/kg \pm SD ^a	soil	waste- water	total % degraded ^c
TNT Soil					
2 g		120000 \pm 10000	<1	<1	>99.99
40 g		120000 \pm 10000	2 \pm 2	4 \pm 3	99.99
4 kg		12000 \pm 1300	<1	5 \pm 2	99.96
RDX/HMX Soil					
2 g	RDX	3200 \pm 400	<1	<1	>99.9
	HMX	750 \pm 140	<1	<1	>99.7
4 kg	RDX	3200 \pm 400	<1	2 \pm 1	99.9
	HMX	750 \pm 140	1 \pm 1	15 \pm 3	97.9
6 kg	RDX	3200 \pm 400	<1	4 \pm 1	99.9
	HMX	750 \pm 140	2 \pm 1	27 \pm 4	97.3

^a Original concentrations were based on the analysis of eight 2-g subsamples of each homogenized bulk soil sample. ^b Standard deviations are based on triplicate degradation runs for the 2- and 40-g runs and on the extraction and analysis of triplicate soil and water subsamples from the pilot-scale runs. ^c Total percent degraded was determined by comparing the sum of the explosive concentrations in the wastewater plus their concentrations in the soil after treatment to the concentrations in the soil before treatment.

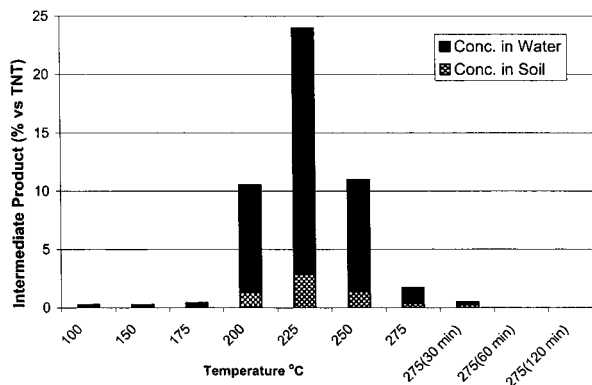


FIGURE 3. Production and degradation of an intermediate reaction product from soil contaminated with 12 wt % of TNT using subcritical water at various temperatures. Heating was performed from 25 to 275 °C at 2.5 °C/min to mimic the pilot-scale unit. Reaction cells were removed from the oven when the temperature shown on the figure was reached.

uses no added oxidant (note that the water for the lab-scale experiments was purged to remove dissolved oxygen) makes formation of the nitroso-derivatives unlikely compared to oxidative approaches such as wet air oxidation, supercritical water oxidation, and bioremediation (2–7, 14–18).

Unfortunately, no degradation products could be identified by GC/MS in methylene chloride (CH_2Cl_2) extracts of any of the TNT or RDX/HMX soil or water samples, results which demonstrate that the intermediates are too polar to be amenable to GC separations. However, the intermediate degradation products elute on reverse-phase HPLC much earlier than TNT, indicating that it is more polar (more water soluble), as is consistent with attack by hydroxy groups on the aromatic TNT ring. Although little information has been published on organic reactions in subcritical water, hydrolysis (not oxidation) and acid- or base-catalyzed reactions are known to be greatly enhanced by the higher temperatures because of the increase in hydronium and hydroxide ions (i.e., increased self-ionization) which occurs as water is heated (19). Two recent papers have shown that alkaline hydrolysis at room temperature can effectively degrade TNT, RDX, and

HMX (20, 21) results which are consistent with hydrolysis of the explosives under the conditions used in our study.

The HPLC/UV results on our treated soils and resultant wastewaters (Table 1) also show that no detectable UV-absorbing organics are left either in the extracts from the soil residues or in the process wastewaters, results which demonstrate that the ring structures of the explosives were broken during subcritical water treatment. In any case, these intermediate products degrade rapidly in subcritical water and are not found in detectable quantities in the treated soils and wastewaters after the 275 °C treatment.

While the final degradation products have not been identified, it is interesting to note that a great deal of gas escapes upon opening the cooled reaction vessels (either from the lab or pilot-scale studies), as is consistent with earlier reports using alkaline hydrolysis (20, 21). The pH of the wastewaters is ca. 6.5, consistent with dissolved carbon dioxide. Addition of HCl to the wastewaters causes much more evolution of gas, demonstrating the presence of carbon dioxide as a major reaction product. Analyses of the wastewaters from the 275 °C treatment of the 12% TNT-contaminated soil for nitrate and nitrite showed only ca. 60 mg of nitrate per kg of soil treated (corresponding to only 60 mg of nitrate from 120 g of TNT) and no detectable nitrite. However, significant amounts of ammonia (2.4 g/kg soil) were detected in the process wastewater. Total conversion of nitrogen would yield ca. 25 g ammonia per kg soil. Since (as discussed above) much gas is lost when the reaction vessels are vented, it appears that ammonia is a major product from the TNT degradation, a result which further indicates that subcritical water destruction is not oxidative.

Pilot Scale. Based on the results of the lab-scale studies, the pilot-scale remediations were performed on both soils by heating the reactor to 275 °C (requiring ca. 100 min) and holding the temperature for 1 h. Pressures and temperatures measured inside the reactor during the heating step agreed with those expected from the steam/water equilibrium (e.g., ca. 5 bar at 150 °C and 60 bar at 275 °C).

As shown in Table 1, the results from the pilot-scale runs agreed well with those of the lab-scale studies, and overall destruction of the TNT, RDX, and HMX was very high. Final concentrations of the explosives in the soils were sufficient to meet typical target treatment values of a few mg/kg [e.g., 30–50 mg/kg in ref 22] suggested for TNT, RDX, and HMX. The wastewaters appear sufficiently clean to allow reuse for additional soil treatments, since each wastewater had only traces of residual explosives, a pH of ca. 6.5, and no odor of ammonia.

Bacterial Toxicity. "Microtox" assays demonstrated a 1700-fold reduction in the toxicity of soil leachates from the 12 wt % TNT-contaminated soil after subcritical water treatment (EC_{50} of 0.0006% for untreated soil and 1.0% for treated soil). The RDX/HMX soil leachates showed a 35-fold reduction in toxicity (EC_{50} of 0.03% for untreated soil and 1.0% for treated soil). Bacterial toxicity of the wastewaters was also low (EC_{50} values of 3% and 52% for the HMX/RDX and TNT wastewaters, respectively). The EC_{50} values obtained for the leachates and wastewaters from both treated soils are in the range typically found for pore waters from sediments (12, 13). In contrast, it is noteworthy that wet air oxidation studies of TNT-contaminated waters can result in increased in bacteria toxicity (17, 18).

Practical Considerations. The treatment of soils with subcritical water has several attractive features. No catalysts, oxidants, or additives of any kind are used. The equipment is very simple i.e., only a pressure vessel constructed of stainless steel, a source of water, and a source of heat are required. No pumping system is needed to maintain the system pressure, since pressure is automatically controlled by the steam/water equilibrium. Based on the conditions

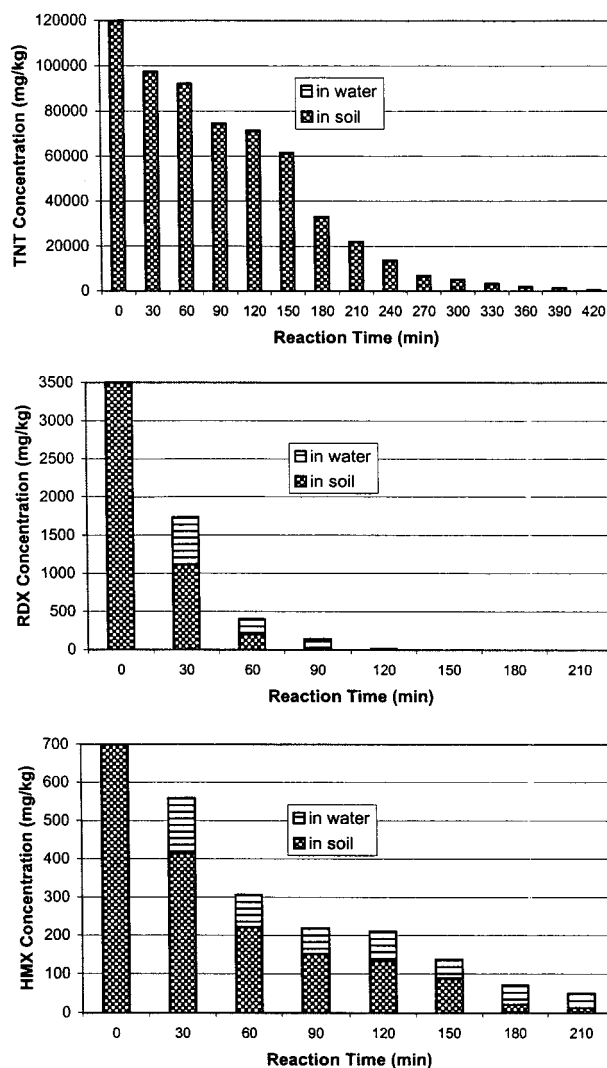


FIGURE 4. Degradation of TNT (top), RDX (middle), and HMX (bottom) on contaminated soils exposed to subcritical water at 150 °C.

used in our study, estimates based on the approach of Montero et al. predict a cost of \$125/ton compared to \$125–210/ton for composting, \$220–650/ton for supercritical water oxidation, and ca. \$1600/ton for incineration (23). These estimates were based on our pilot-scale study which used rather harsh conditions (275 °C, which results in 60 bar pressure); it may be possible to use much lower temperatures (and thus much lower pressure requirements) and longer contact times to decrease the process costs. For example, lab-scale studies of the two contaminated soils performed at 150 °C (Figure 4) show that 98% destruction of TNT on the 12% contaminated soil could be achieved with ca. 6 h of treatment, >99% destruction of HMX can be achieved in 2–3 h, and ca. 95% destruction of RDX could be achieved with 3 and 1/2 h of treatment. Since treatment at 150 °C requires much less heat, and the pressure vessel only must hold the equilibrium pressure of 5 bar (plus a safety factor), the overall process may be less costly, especially for easily degraded compounds.

The process should be safe since (after the reactor is filled), operation is performed from a remote location by simply turning the power to the unit on at the beginning of the run and off after the run is completed. Corrosion should be minimized (e.g., compared to supercritical water oxidation (16)), since lower temperatures are used, and no reactive additives are needed. The low contaminant concentrations found in the process wastewaters indicate that a single volume

of water can be used to treat multiple soil samples. In addition, our initial studies demonstrate that very highly contaminated soils can be rapidly treated to very low contaminant levels, without the production of more toxic derivatives.

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