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## Research article

## Use of dilute ammonia gas for treatment of 1,2,3-trichloropropane and explosives-contaminated soils

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## ABSTRACT

Laboratory studies were performed to test a novel reactive gas process for in-situ treatment of soils containing halogenated propanes or explosives. A soil column study, using a 5% ammonia-in-air mixture, established that the treatment process can increase soil pH from 7.5 to 10.2. Batch reactor experiments were performed to demonstrate contaminant destruction in sealed jars exposed to ammonia. Comparison of results from batch reactors that were, and were not, exposed to ammonia demonstrated reductions in concentrations of 1,2,3-trichloropropane (TCP), 1,3-dichloropropane (1,3-DCP), 1,2-dichloropropane (1,2-DCP) and dibromochloropropane (DBCP) that ranged from 34 to 94%. Decreases in TCP concentrations at 23° C ranged from 37 to 65%, versus 89–94% at 62° C. A spiked soil column study was also performed using the same set of contaminants. The study showed a pH penetration distance of 30 cm in a 2.5 cm diameter soil column (with a pH increase from 8 to > 10), due to treatment via 5% ammonia gas at 1 standard cubic centimeter per minute (scm) for 7 days. Batch reactor tests using explosives contaminated soils exhibited a 97% decrease in 2,4,6-trinitrotoluene (TNT), an 83% decrease in nitrobenzene, and a 6% decrease in hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). A biotransformation study was also performed to investigate whether growth of ammonia-oxidizing microorganisms could be stimulated via prolonged exposure of soil to ammonia. Over the course of the 283 day study, only a very small amount of nitrite generation was observed; indicating very limited ammonia monooxygenase activity. Overall, the data indicate that ammonia gas addition can be a viable approach for treating halogenated propanes and some types of explosives in soils.

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## 1. Introduction

1,2,3-Trichloropropane (TCP) is an emerging contaminant that is present at U.S. Department of Defense (DoD) sites through its application as a solvent for cleaning and maintenance, paint and varnish removal, and degreasing (ATSDR, 1992). Sources also include chemical manufacturing processes, and use in pesticides and/or soil fumigants (USEPA, 2014; ATSDR, 1992; Konnecker and Schmidt, 2003). TCP is a suspected human carcinogen, and emerging DoD contaminant, that is difficult to treat via conventional remediation processes. The notification level established by the California Department of Public Health (CDPH) has been set at 0.005 µg/L for TCP in drinking water, based on a  $1 \times 10^{-6}$  lifetime

excess cancer risk, and CDPH has set a public health goal of 0.0007 µg/L (CDPH, 2010, 2013).

2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-triazine (RDX) are common munitions constituents (MC) which are often found in soil and groundwater at former MC manufacturing facilities, former load-assembly-and-pack facilities, active installations, and DoD testing and training ranges. RDX is generally a greater concern for groundwater contamination and transport than TNT because it is much more mobile in soil and groundwater (Yamamoto et al., 2010; Alavi et al., 2011). The health advisory level for RDX in groundwater is 0.1 mg/L (USEPA, 2014). RDX is classified as a Class C, possible human carcinogen, based primarily on toxicity studies with mice (USEPA, 1990). TNT is considered a Class C, possible human carcinogen, for which mutagenic activity has been observed (USEPA, 1989).

Alkaline hydrolysis (AH) is a process for treatment of contaminated media that relies on raising the pH of the media to promote

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destruction of contaminants. Use of AH to promote destruction of explosives in surface soils was pioneered by the Engineering Research and Development Center (ERDC), of US Army Corps of Engineers more than a decade ago (Brooks et al., 2003; Davis et al., 2007a,b,c). Laboratory studies and field demonstrations revealed that incorporation of lime into shallow soils is effective for treating various explosives, including RDX and TNT. Variations of the process involve using sodium hydroxide, instead of lime, to promote AH (Britto et al., 2010).

Solid amendments, such as lime or sodium hydroxide, are well suited for treatment of shallow soils, where contamination lies primarily within the first meter of the soil surface, as various mixing approaches can reach these depths (e.g., Topolnicki, 2004). However, for treatment of contaminants trapped at intermediate and deep levels within the subsurface, other strategies are needed.

The reactive gas process entails injection of a blend of air and gaseous ammonia ( $\text{NH}_3$ ) in order to raise the pH of soil, and to promote destruction of contaminants via AH (Coyle et al., 2016). When  $\text{NH}_3$  is added to soil, it combines with  $\text{H}_2\text{O}$  to produce ammonium ion ( $\text{NH}_4^+$ ) and hydroxide ion ( $\text{OH}^-$ ), subsequently increasing soil pH. Many different types of contaminants are amenable to AH; including halogenated propanes, explosives, and some pesticides and herbicides among others (e.g., Balakrishnan et al., 2003; Ali and El-Dib, 1971; Sarathy et al., 2010; Torrento et al., 2014). As a secondary effect, at the edge of the reactive zone, or after the pH begins to decline, the process has the potential to induce cometabolic degradation reactions via the ammonia monooxygenase (AMO) enzyme. AMO is used by nitrifying bacteria to transform  $\text{NH}_3$  into hydroxylamine ( $\text{NH}_2\text{OH}$ ), which is the first step in the ultimate conversion of the  $\text{NH}_3$  into nitrite ( $\text{NO}_2^-$ ) and ultimately nitrate ( $\text{NO}_3^-$ ) as a final reaction product (USEPA, 2002). AMO is capable of degrading a wide range of chlorinated hydrocarbons via cometabolism, including: dichloromethane, dibromomethane, chloroform, bromoethane, 1,2-dibromoethane, 1,1,2-trichloroethane, 1,1,1-trichloroethane, vinyl chloride, *cis*- and *trans*-1,2-dichloroethene, trichloroethene, and TCP among others (Hyman et al., 1988; Vannelli et al., 1990).

Ex-situ treatment is often cost prohibitive, and becomes technically impractical at depth. Contaminated soils underlying foundations and paved areas, also pose additional difficulties for ex-situ treatment. The presence of unexploded ordinance (UXO) on active installations, as well as site access issues for active training ranges, can also make ex-situ treatment impractical. Ex-situ treatment processes require excavation, usually followed by off-site disposal. A potential advantage of the  $\text{NH}_3$  gas treatment processes is that it allows for in-place contaminant destruction. In contrast, soil vapor extraction and in situ thermal treatment, typically require extraction and capture of contaminated vapors. Lastly, the  $\text{NH}_3$  gas treatment processes can be applied to intermediate and deep levels within the vadose zone; and is generally less prone to being limited by obstacles such as UXO, foundations, and paved surfaces.

The primary objective of this laboratory study was to evaluate the potential application of  $\text{NH}_3$  gas to increase soil pH and stimulate AH of various DoD contaminants, including TCP, RDX, and TNT.

## 2. Materials and methods

### 2.1. Materials

A pre-blended mixture of 5%  $\text{NH}_3$  in air, was purchased from Airgas, Inc. The following chemicals were obtained from Sigma Aldrich: 1,2,3-trichloropropane (99%), 1,2-dichloropropane (99%), 1,3-dichloropropane (99%), 1,2-dibromo-3-chloropropane (97%), and chloroform (99%). All chemicals were reagent grade or higher. A

solution of  $\text{NH}_3$ -in-methanol (7 N, from Sigma Aldrich) was used for the  $\text{NH}_3$  biotransformation study.

The vadose zone soil used for the halogenated propane studies was obtained from a former pesticide mixing facility near Bakersfield, CA. The soil cuttings, originated from a depth of ~6–7.5 m below ground surface, and were obtained during drilling operations. Soils were sieved (1 mm sieve), and then homogenized using a tumbling, ceramic ball mixer (20 rpm for 5 days). Explosives-contaminated soils consisted of a mixture, obtained from two sources. The mixture included of 92 g from the former Sioux Army Depot (SAD) in Nebraska and 1000 g from the former Plum Brook Ordnance Works (PBO) in Ohio. The soils were homogenized by tumbling in a ceramic ball mixer (20 rpm for 5 days).

### 2.2. Experimental setup and procedures

#### 2.2.1. Soil column pH study

Glass columns were 2.5 cm diam. x 20 cm long with air-tight, Luer-lock fittings (Sigma-Adrich, C4794). Gas flow into the columns was regulated by a gas mass flow controller and confirmed at the outlet by a gas mass flow meter and totalizer. The flow rate of the gas mixture (5%  $\text{NH}_3$  in air) through the columns was maintained at 1 standard cubic centimeter per minute (sccm) for a set time period to meet target total gas volumes (15, 25, 75, 250, and 1150 standard cubic centimeters [scc]). After the desired treatment time, the columns were disassembled and the soil was segregated into two batches, the bottom (influent) and top (effluent); and the pH of each soil batch was measured.

#### 2.2.2. Batch reactor study for halogenated propanes

Prior to spiking, the soil was added to a 6 L ceramic mixing drum. The mixture of contaminants was withdrawn from the source vial and distributed across the soil via a syringe. The contaminant mixture included the components shown in Table 1. Soil concentrations were less than total mass spiked because of partitioning into the headspace within the drum.

The mixing drum was sealed and placed on a drum roller for a minimum of three days. The soil was taken directly from the drum, weighed, and placed into a set of 250 ml amber screw-cap jars. Test 1 was performed prior to Test 2, and the spiking procedures were also performed separately. However, the same source soil was used for both Test 1 and Test 2. For Test 1, no sample splits were collected from the drum at the time that the spiked soil was transferred into the batch test jars. For Test 2, sample splits were collected directly from the drum, for contaminant analysis, at the time that the spiked soil was transferred into the batch test jars.

Spiked soil was added to each jar before closing. A 40 mL volatile organic analysis (VOA) vial was prepared with 6.7 g  $\text{NH}_4\text{Cl}$  and 5.0 g  $\text{NaOH}$ . A needle was used to puncture the septa on the VOA vial and a drop of water was added to start the chemical reaction which generated  $\text{NH}_3$ . The screw-cap jar used for the batch test was opened, one of the VOA vials was placed inside, and the lids were tightly sealed. The setup was designed to provide gaseous  $\text{NH}_3$  to

**Table 1**  
Contaminant spike mixture for batch reactor studies.

Contaminant	Source Concentration (%)	Test 1 Volume (ml)	Test 2 Volume (ml)
chloroform <sup>a</sup>	99	6.20	0
1,2,3-TCP	99	0.150	0.17
1,2-DCP	99	1.50	1.6
1,3-DCP	99	0.670	0.7
DBCP	97	0.075	0.1

<sup>a</sup> Chloroform was not included in Test 2.

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