FINAL REPORT

Reactive Gas Process for In Situ Treatment of 1,2,3-Trichloropropane in Vadose Zone Soils

ESTCP Project ER-201632

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14. ABSTRACT
The key objective of the project was to determine whether the application of gaseous ammonia to unsaturated soils could be effective for increasing soil pH and subsequently for treating 1,2,3-trichloropropane (TCP) and other halogenated propanes (HPs) via alkaline hydrolysis. Laboratory microcosm studies showed that soil pH could be increased to >10 using ammonia, effectively promoting hydrolysis of TCP and other HPs. However, flow-through columns with site soils indicated that it would not be possible to independently quantify hydrolysis from volatile losses of the target contaminants at field scale due to the flow rate of ammonia required to increase soil pH. As a result the planned field study was not performed.

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ACRONYMS AND ABBREVIATIONS

%	percent (vol/vol)
µg	microgram
µL	microliter
µm	micrometer
AMO	ammonia monooxygenase
AOA	ammonia oxidizing archaea
APPL	Agriculture & Priority Pollutants Laboratories, Inc.
APTIM	Aptim Federal Services, LLC
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
B&B	Brown and Bryant Superfund Site
bgs	below ground surface
^{o}C	degrees Celsius
$CaCl_2$	calcium chloride
CCL4	Contaminant Candidate List 4
CDPH	California Department of Public Health
cf	cubic foot
Cl^-	chloride ion
cm	centimeter
DBCP	1,2-dibromo-3-chloropropane
1,2-DCP	1,2-dichloropropane
1,3-DCP	1,3-dichloropropane
DI	deionized water
DNA	deoxyribonucleic acid
DNAN	2,4-dinitroanisole
DoD	Department of Defense
DoE	Department of Energy
DPT	direct push technology
ERDC	United States Army Engineer Research & Development Center
ESTCP	Environmental Security Technology Certification Program
ft	feet
ft bgs	feet below ground surface
g	gram
GC/MS	gas chromatography/mass spectrometry
GC/TCD	gas chromatography/thermal conductivity detector

HDPE	high density polyethylene
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
H_2O	water
hr	hour
ID	inside diameter
KCl	potassium chloride
kg	kilogram
L	liter
lb	pound
LEL	lower explosive limit
M	molar
m	meter
MCL	maximum contaminant level
mg	milligram
min	minute
mL	milliliter
mm	millimeter
N_2	nitrogen gas
NB	nitrobenzene
NH_3	ammonia
NH_3-N	ammonia nitrogen
NH_4^+	ammonium ion
NH_2OH	hydroxylamine
NO_3^-	nitrate
NO_2^-	nitrite
NPT	National pipe taper
NTP	National Toxicology Program
OH^-	hydroxide ion
O&M	operation and maintenance
PHG	public health goal
PI	principal investigator
PID	photoionization detector
PQL	practical quantitation limit
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
qPCR	quantitative polymerase chain reaction
RCRA	Resource Conservation and Recovery Act

RDX	Hexahydro-1,3,5-trinitro -1,3,5-triazine
ROI	radius of influence
scc	standard cubic centimeters
sccm	standard cubic centimeters per minute
scfm	standard cubic feet per minute
SERDP	Strategic Environmental Research and Development Program
SU	standard units
SDWA	Safe Drinking Water Act
Tc	Technetium
TCP	1,2,3-trichloropropane
TNT	2,4,6-trinitrotoluene
U	Uranium
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
VOA	volatile organic analysis

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EXECUTIVE SUMMARY

INTRODUCTION

This project was designed to demonstrate the efficacy of a novel, ammonia-based reactive gas process for remediation of vadose zone source areas containing 1,2,3-trichloropropane (TCP). TCP is an emerging contaminant that is present at DoD sites primarily through its application as a solvent for cleaning and maintenance, paint and varnish removal, and degreasing. However, its sources also include chemical manufacturing processes (particularly polysulfone liquid polymers, dichloropropene, hexafluoropropylene, and polysulfides) and production and/or application of pesticides and soil fumigants. Compared to many other halogenated compounds, such as chlorinated ethenes and ethanes, there is relatively little information on effective approaches to treat TCP or other chlorinated propanes in groundwater and virtually no data on treatment in the unsaturated zone. This report describes the results of laboratory column studies conducted to evaluate the potential for applying gaseous ammonia (NH_3) for (1) increasing soil pH and (2) promoting the subsequent alkaline hydrolysis of TCP, 1,2-dichloropropane (1,2-DCP), 1,3-dichloropropane (1,3-DCP) and dibromochloropropane (DBCP) in vadose soils from the Brown and Bryant Superfund Site (B&B) in Alvin, CA. The potential for using this approach to stimulate ammonia monooxygenase (AMO) to enhance biotic degradation of these compounds was also assessed.

OBJECTIVES

The key objective of the project was to determine whether the application of gaseous NH_3 to unsaturated soils can be effective for increasing soil pH and subsequently for treating TCP, 1,2-DCP, 1,3-DCP, DBCP and other priority contaminants subject to alkaline hydrolysis. A secondary objective was to determine if addition of NH_3 to soils promotes a cometabolic polishing effect due to induction of the enzyme AMO within microorganisms present near the treatment zone. If this effect could be documented, it would represent a separate mechanism of contaminant destruction, and possibly a separate treatment approach using lower NH_3 concentrations.

TECHNOLOGY DESCRIPTION

The reactive gas process entails injection of a blend of air and NH_3 in order to raise the pH of soil and promote the destruction of contaminants via alkaline hydrolysis. When NH_3 is added to soil, it combines with H_2O to produce ammonium ion (NH_4^+) and hydroxide ion (OH^-), subsequently increasing soil pH. The pK_a of this reaction is 9.25 at 25°C. The process may also stimulate cometabolic biodegradation reactions mediated by the enzyme AMO as a secondary effect as pH declines or at the edge of the reactive zone. Thus, this approach may have utility for treatment of any contaminant subject to alkaline hydrolysis and may also promote cometabolic treatment as a polishing step.

PERFORMANCE ASSESSMENT

Five column studies were conducted with B&B site soils to evaluate the potential to increase soil pH by adding different concentrations of NH_3 (5 % or 9.5 % in air) to an inlet port under continuous flow. After 8-14 days (depending on the study; 5-6 g total NH_3 added to each column), columns were sectioned, and subsamples were collected to quantify the soil pH and concentration of NH_3-N along the column length. The effect of soil moisture on pH was also evaluated.

In all studies, pH increases from ~ 8.2 to 10 were observed as ammonia levels increased from ~ 1,500 to 2,000 mg NH_3-N/kg (baseline values at B&B Site) to ~ 4,000 mg NH_3-N/kg. The pH increased very little thereafter, with a measured soil pH of < 10.5 at ammonia levels exceeding 10,000 mg-N/kg. The biphasic curve is consistent with the pKa of the NH_3/NH_4^+ reaction. The data suggest that it will be easy to increase soil pH to 10 in the field but difficult to bring soil pH much above this value. Based on the tests, the conditions under which the greatest quantity of soil (at typical field moisture) was impacted by the gaseous ammonia was the addition of 5 % NH_3 at a flow rate of 10 standard cubic centimeters per minute (sccm). These conditions were subsequently selected to evaluate the effectiveness of the NH_3 addition process on treatment of TCP, 1,2-DCP, and 1,3-DCP in B&B soils.

For the contaminated soil studies, B&B core material was spiked with TCP, 1,2-DCP, 1,3-DCP and DBCP. Baseline soil samples showed mean soil concentrations of 5,700 µg/L for TCP, 322,000 µg/L for 1,2-DCP, 1,600 µg/L for 1,3-DCP, and 20,000 µg/L for DBCP. The "Treated Column" then received 5 % NH_3 in air at a flow rate of 10 sccm for 15 days, after which time the soil was stored for ~ 30 days to provide additional time for hydrolysis of chlorinated propanes to occur. A second "Control Column" was constructed with the same design except that it was supplied with nitrogen gas (N_2) (no NH_3) at 10 sccm for 15 days as a means to evaluate volatile rather than destructive losses of the contaminants. The soil was also incubated for an additional 30 days and then sampled as described for the Treated Column. In the NH_3-treated column, the final soil pH was ~ 10.2 over the entire length of the soil column. Conversely, in the N_2-treated soil column, the soil pH was ~ 8.6 in those extracted with deionized (DI) water over the entire length of the soil column.

The data from the Treated Column indicated nearly a complete loss (99.6 % – 100%) of the four different halogenated propanes added to the soil columns compared to the initial concentrations. However, the data from the Control Column showed a similar loss percentage for each of the compounds, ranging from 92.3 % to 99.7%. Thus, the data indicate that the passage of gas (NH_3 or N_2) through the soil columns likely resulted in significant physical stripping/removal from the soil phase. Only a small percentage of the contaminants were trapped by adsorbent tubes placed at the end of the columns, so it was not possible to obtain a reasonable mass balance.

Batch microcosms were prepared to evaluate the potential for cometabolic degradation of chlorinated propanes at the B&B site via ammonia oxidation. The initial objective of this study was to assess whether nitrification could be stimulated in B&B soils with the addition of different quantities of NH_3. However, the exceedingly high NH_3 in the soil during baseline conditions (i.e., ~ 2,500 mg-N/kg soil) prevented the execution of the study as planned. Rather, we evaluated whether nitrification was ongoing in the soils under in situ conditions with the high NH3 present. The initial data, particularly the nitrite data (an intermediate product in nitrification), suggested the potential for activity, but nitrite only increased at the first sample time, and decreased thereafter. Moreover, the high levels of nitrate evident in the soil (which may have resulted from nitrification of ammonia or discharge of nitrate-containing agricultural products) largely prevented an accurate assessment of the occurrence of nitrification via measuring increases in soil nitrate. If appreciable nitrification activity had been observed over the 28-week study in the Live (but not the Killed) microcosms, soil samples were to be collected and reanalyzed for AMO and ammonia oxidizing archaea (AOA) to evaluate increases in the relevant organisms, and then the microcosms were to be spiked with 1,2,3-TCP, 1,2-DCP, and 1,3-DCP to evaluate cometabolic biodegradation of the compounds.

However, the microcosm data did not show definitive nitrification activity (other than the small initial increase in nitrite) when Live and Killed samples were compared, and the contaminated soil column results indicate that the gas addition process is likely to strip the halogenated propanes from the soil matrix, so the study was terminated at 28 weeks.

IMPLEMENTATION ISSUES

The nearly complete loss of the halogenated propanes in the column treated with N_2 gas for 15 days is problematic for the field implementation of this approach because the data suggest that it may not be possible to discern losses of these contaminants to hydrolysis from losses due to simple stripping from the soil phase. Modeling suggests that several months of NH_3 gas addition at 5 % would be required to increase soil pH over a 10 – 15 ft radius from the gas injection wells in the field at relatively high flow rates (~ 10,000 to 30,000 sccm). Extrapolating from the column tests, this addition is likely to increase soil pH to > 10 over the treatment area as desired, but it is also likely to strip a high percentage of the chlorinated propanes in the process. Thus, the technology will most likely be effective at removing most of the contaminants within the treatment radius of influence (ROI), but much of this removal may reflect volatilization rather than hydrolysis. At a minimum, the influence of the two processes would not be independently quantifiable. As a result, the technology was not scaled for field implementation at the B&B site.

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1.0 INTRODUCTION

1.1 BACKGROUND

This project was a joint effort between the Biotechnology Development & Applications Group at Aptim Federal Services LLC (APTIM) and the US Army Corps of Engineers (USACE) Directorate of Environmental and Munitions CX and Engineer Research and Development Center (ERDC). The project objective was to demonstrate a novel reactive gas process for remediation of vadose zone source areas containing 1,2,3-trichloropropane (TCP). This process is also expected to be effective for other compounds that are susceptible to alkaline hydrolysis, such as common munitions constituents (e.g., RDX) and some insensitive munitions components (e.g., DNAN). The focus on vadose zone treatment represents a step forward from the current approach of allowing contaminants to slowly leach into groundwater before initiating treatment (i.e., contaminants that are not amenable to soil vapor extraction or bioventing). Directly attacking vadose-zone source areas, and cutting off leaching pathways, will usually be a more cost-effective course of action than allowing contaminants to move into groundwater before initiating treatment. In addition, vadose zone contamination often represents a long-term source for underlying groundwater. For complex sites, treatment of both vadose zone and groundwater may be required to accelerate the remediation of groundwater, achieve remediation in a reasonable timeframe, and to reduce cost to complete.

TCP is an emerging contaminant that is present at United States Department of Defense (DoD) sites primarily through its application as a solvent for cleaning and maintenance, paint and varnish removal, and degreasing (ATSDR, 1992). However, its sources also include chemical manufacturing processes (particularly polysulfone liquid polymers, dichloropropene, hexafluoropropylene, and polysulfides) and production and/or application of pesticides and soil fumigants (USEPA, 2014; ATSDR, 1992; Konnecker and Schmidt, 2003). Polysulfide polymers, for which TCP was used as a crosslinking agent, were widely used as aircraft tank sealers and, during the 1940s and 1950s as a rocket fuel binder (USEPA, 2006). According to a United States Air Force presentation on emerging contaminants, TCP has been found in groundwater at > 45 DoD bases, with over 1400 wells impacted, resulting in a 17% detection rate (Hunter et al., 2006). At least 27 bases had TCP in soil boreholes, amounting to more than 850 detections (7% detection rate). It is likely that there are more DoD sites where TCP is present, but where testing has yet to be conducted. There are also a large number of industrial and hazardous waste sites with TCP in vadose soils and groundwater, particularly from the aforementioned pesticide and chemical manufacturing applications (USEPA, 2014).

TCP is known to cause gene mutations and deoxyribonucleic acid (DNA) damage in many different species and is listed by United States Environmental Protection Agency (USEPA) as *reasonably expected to be a human carcinogen* (IRIS, 2009; NTP, 2014). Although there is currently no Federal Maximum Contaminant Level (MCL) for TCP in drinking water, it is present on the latest draft version of the USEPA Contaminant Candidate List (CCL4), which specifies compounds that may require regulation under the Safe Drinking Water Act (SDWA) (USEPA, 2015a). 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 1×10^{-6} lifetime excess cancer risk, and CDPH has set a public health goal (PHG) of only 0.0007 µg/L (CDPH, 2010, 2013).

Other states including New Jersey and Minnesota have also established drinking water guidance values ranging from 0.003 to 0.005 µg/L (USEPA, 2014).

Because of its physicochemical characteristics, including a moderate water solubility, (1,750 mg/L), low octanol-water partitioning coefficient (log $K_{ow} \sim 2$) and moderate Henry's law constant ($\sim 3 \times 10^{-4}$), TCP would be expected to be found in both the vapor and aqueous phases in the environment, with moderate sorption to soils or soil organic matter (USEPA, 2014; Konnecker and Schmidt, 2003). For comparison, benzene has very similar physicochemical properties (Dragun, 1998). TCP has been observed to be highly persistent in the environment with little evidence of aerobic or abiotic degradation under typical unsaturated and saturated aquifer conditions (Samin and Janssen, 2012; Sarathy et al., 2010; Konnecker and Schmidt, 2003; USEPA, 2014). Recent research sponsored by the Strategic Environmental Research and Development Program (SERDP, Project ER-1457) has shown that TCP can be abiotically reduced by zero-valent zinc (Sarathy et al., 2010; Tratnyek et al., 2010; Salter-Blanc et al., 2012), and previous bench tests have suggested that some advanced oxidation processes may be effective for its treatment in water (USEPA, 2014; Dombeck and Borg, 2005). There is also evidence that specific *Chloroflexi* sp. can reductively dehalogenate TCP (Yan et al., 2009), and that it can be cometabolized by methanotrophs (Bosma and Janssen, 1998), propanotrophs (Wang and Chu, 2017) and ammonia-oxidizing bacteria, such as *Nitrosomonas europaea* (Hyman et al., 1988; Vanelli et al., 1990), a process that we describe further in **Section 2.0**.

Compared to many other halogenated compounds, such as chlorinated ethenes and ethanes, there is relatively little information on effective approaches to treat TCP or other chlorinated propanes in groundwater and virtually no data on treatment in the unsaturated zone. Ammonia gas (NH_3) addition in the vadose zone for treatment of TCP, and potentially other compounds susceptible to alkaline hydrolysis, represents a novel remedial approach, and one that may include both a rapid abiotic phase, and a slow biological polishing step through cometabolism. The importance of developing cost-effective treatment technologies for TCP is underscored by the stringent cleanup levels that have been proposed, and the fact that the USEPA is considering this compound for further regulation under CCL4 (USEPA, 2015a).

1.2 SITE SELECTION

Based on the site selection criteria rating that was presented in the Site Selection Memorandum (APTIM and USACE, 2017), the Brown and Bryant Superfund Site (B&B) was determined to be the most appropriate location for demonstrating this remedial approach. The site has many characteristics that make it ideal for this demonstration, including site accessibility, the presence of significant TCP contamination in the vadose zone, a reasonable depth and thickness of the target treatment interval, and significant historical contaminant concentration data.

1.3 OBJECTIVES OF THE DEMONSTRATION

The objectives of the demonstration project were as follows:

(1) Demonstrate the effectiveness of the novel reactive gas process for treatment of TCP and possibly other priority contaminants subject to alkaline hydrolysis.

(2) Perform a field demonstration to determine real-world treatment effectiveness and

radius of influence that can be achieved in the field. This demonstration would allow a field determination of the required spacing of injection points, which is a critical cost consideration for large-scale implementation.

(3) Document whether any increase in nitrate in groundwater can be detected as an undesirable side-effect of the vadose zone treatment process.

(4) Determine if the process could be used to exert a cometabolic *polishing* effect, due to induction of ammonia monooxygenase (AMO) enzymes within microorganisms present near the treatment zone. If this effect can be documented, it would represent a separate mechanism of contaminant destruction, and possibly a separate treatment approach using lower NH_3 concentrations.

Performance objectives that were to be used to evaluate this technology during the field demonstration are provided in detail in the Site Selection Memo (APTIM and USACE, 2017) and shown in **Table 1.1** below. The field demonstration was not conducted.

Table 1.1. Performance Objectives for the Field Demonstration.

Performance Objective	Data Requirements	Success Criteria
Quantitative Performance Objectives		
Increasing local soil pH	pH in soil cores at different depths before and after NH_3 addition. pH meter in laboratory	• pH increase in soil cores from natural pH to > 10 SU • Comparisons: ▪ **Pre- and post-NH_3 treatment ▪ ** multiple soil cores and core intervals
Effectiveness of TCP Treatment	• TCP in vapor samples via SUMMA canister or GORE samples with GC/MS analysis via USEPA method TO-15 • TCP in soil core samples via USEPA Method 8260	• Reduction in TCP > 99% in at least one soil core and gas sample • Overall reduction in TCP > 90% in Test Plot • Comparisons: ▪ **Pre- and post-NH_3 treatment ▪ ** multiple soil cores and core intervals ▪ ** soil vapor samples
Qualitative Performance Objectives		
System Operation / Ease of Use	• System operation logs • Feedback from field technician on system O&M and time required	• > 95 % system up time • A single field technician able to effectively collect system and groundwater measurements

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2.0 TECHNOLOGY DESCRIPTION

The process entails injection of a blend of air and NH_3 in order to raise the pH of soil, and to promote destruction of contaminants via alkaline hydrolysis. When NH_3 is added to soil, it combines with water (H_2O) to produce ammonium ion (NH_4^+) and hydroxide ion (OH^-), subsequently increasing soil pH according to Equation 1:

Eq. 1. $$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

The pK_a of this reaction is 9.25 at 25ºC (ATSDR, 2015). Mechanistically, the hydroxide ion is believed to serve as the primary nucleophile, which displaces chlorine during the TCP dechlorination reactions. The process may also stimulate cometabolic biodegradation reactions mediated by the enzyme AMO as a secondary effect as pH declines or at the edge of the reactive zone (e.g., Hyman et al., 1988; Vannelli et al., 1990), as detailed later in this section. Thus, this approach will have utility for treatment of any contaminant subject to alkaline hydrolysis, and may also promote cometabolic treatment as a secondary, polishing step.

Laboratory studies completed by the ERDC have shown that delivery of a dilute mixture of ammonia in air (5% ammonia) is an effective way to raise the soil pH to above 10.0 standard units (**Figure 2.1**), and that the process is effective for destruction of TCP, 1,2-dichloropropane (1,2-DCP) and 2,4,6-trinitrotoluene (TNT) (**Figure 2.2** & **Figure 2.3,** modified form Coyle et al., 2017). The process should also be effective for other contaminants that have been shown to be amenable to alkaline hydrolysis, such as the explosives RDX, HMX, and DNAN among others (Hwang et al., 2006; Davis et al., 2006, Karakaya et al., 2005; Salter-Blanc et al., 2013). In addition, the Department of Energy (DoE) has been evaluating the same general process for immobilization of uranium (U) and Technetium (Tc) at the DoE Hanford Site and has done extensive laboratory testing in support of this effort (Truex et al., 2014 and references therein.

The rate of hydrolysis of TCP in aqueous solution is a direct function of both pH and temperature, with rates increasing as both variables increase (Sarathy et al., 2010). It is presumed that this general relationship also holds in an unsaturated matrix, although rates may be very different than in solution due to surface interactions between TCP and soil mineral particles. The studies conducted at ERDC showed estimated half-lives of TCP, 1,2-DCP, and 1,3-dichloropropane (1,3-DCP) on the order of days at 23ºC and 62ºC (although very little data are available for this calculation; **Figure 2.2**). Assuming a soil pH of ~10 (**Figure 2.1**), the half-life is somewhat shorter than would be expected in aqueous solution at this temperature (~500 days), whereas the half-life at 62ºC in the same soil study appears longer than would be predicted from aqueous studies (< 1 day) (Sarathy et al., 2010). Experiments were completed with samples from the demonstration site to quantify TCP degradation under field conditions.

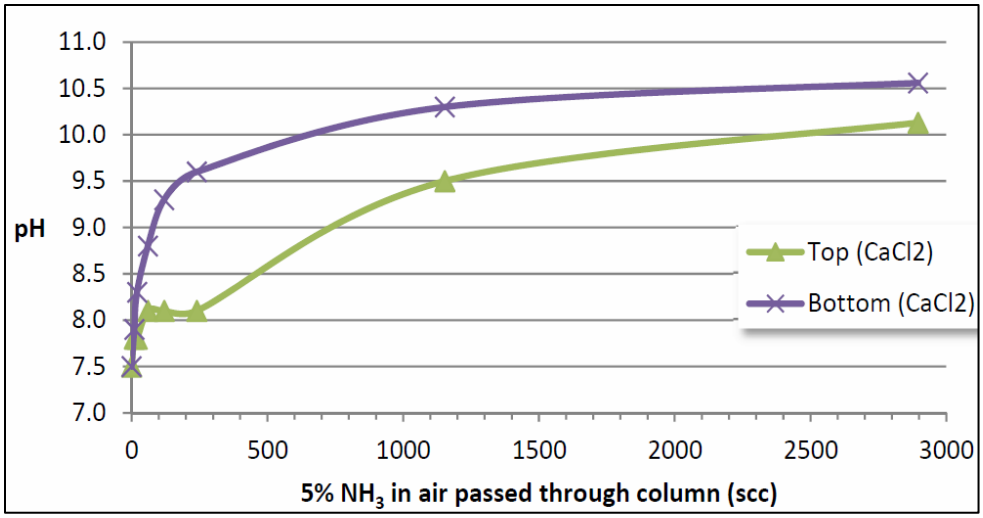

Figure 2.1. Effect of Gaseous Ammonia on Soil pH in a Laboratory Column Study.

Data are from a laboratory column study in which an ammonia-in-air mixture (5% ammonia, by volume) was injected into a soil column. The x-axis shows the cumulative volume of gas injected, and the y-axis shows the soil pH. Data are presented for both the inlet end of the column (bottom) and the outlet end of the column (top).

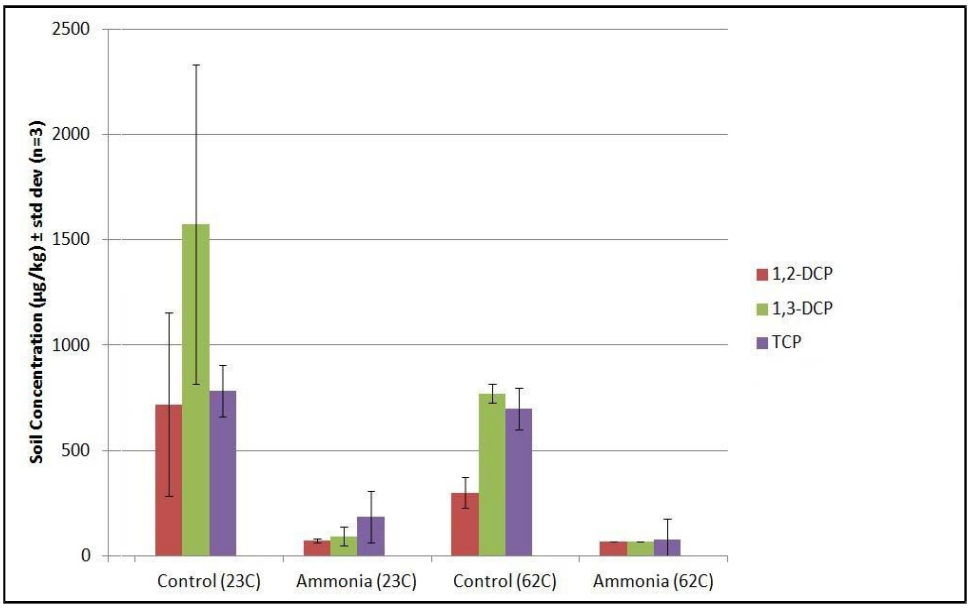

Figure 2.2. Results of a Batch Reactor Study with Gaseous Ammonia and Contaminated Soil.

Gaseous ammonia was generated in sealed glass vessels containing contaminated soil. The soil was spiked with 1,2,3-TCP, 1,2-DCP, 1,3-DCP prior to exposure to gaseous ammonia. Tests were run at both room temperature (23°C), and at 62°C. The length of the exposure period was approximately 5 days. It is unclear why error bars for 1,2-DCP and 1,3-DCP in the Control at 23°C were higher than for all other treatments. This may reflect nonuniform initial distribution or volatile losses during preparation. Figure modified from Coyle et al., 2017.

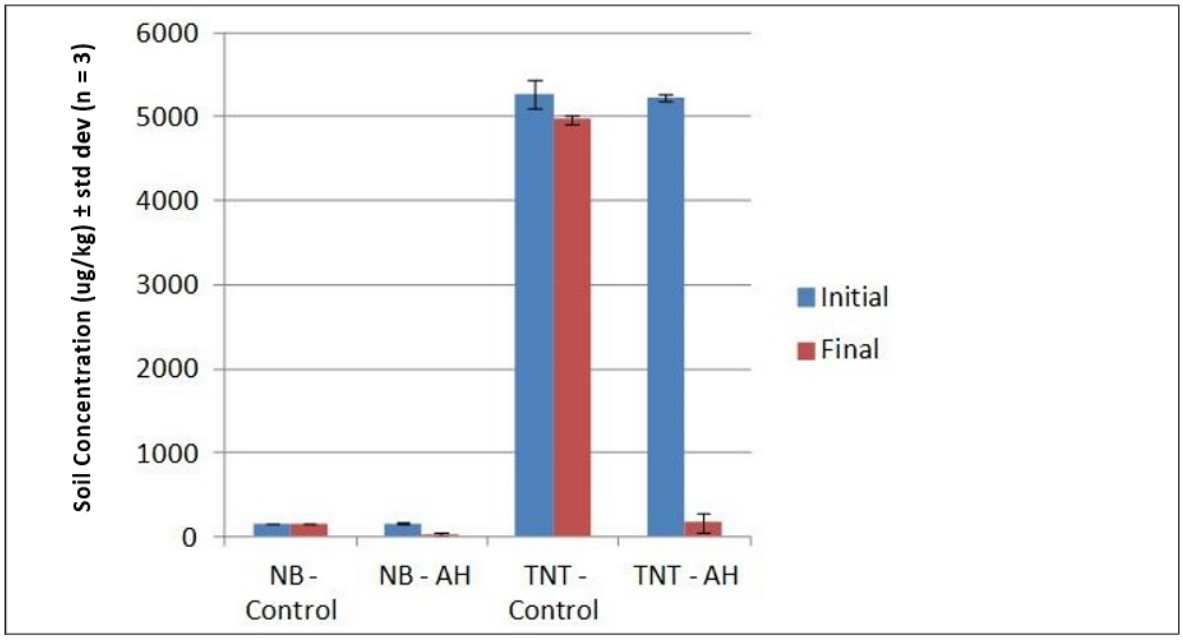

Figure 2.3. Results of a Batch Reactor Study with Gaseous Ammonia and Contaminated Soil.

For this study, gaseous ammonia was generated in sealed glass vessels containing explosives-contaminated soil. Data are shown for nitrobenzene (NB) and 2,4,6-trinitrotoluene (TNT). The tests were run at room temperature, and the length of the exposure period was approximately 14 days. Figure modified from Coyle et al., 2017.

Alkaline hydrolysis of TCP is expected to result in the production of 2-chloro-2-propen-1-ol and/or 3-chloro-2-propene-1-ol (also called 2-chloroallylalcohol and 3-chloroallylalcohol, respectively) as the major transformation product(s) (i.e., 2 Cl^- removed) (Sarathy et al., 2010; Pagan et al., 1998). It is expected that 2,3-dichloro-1-propene would be generated, as a transient intermediate, along the pathway for production of these products. The potential abiotic reaction pathways of TCP are presented in **Figure 2.4** (from Sarathy et al., 2010). Previous studies have shown that both 2-chloroallylalcohol and 3-chloroallylalcohol are subject to aerobic biodegradation, and bacteria have been isolated that can use these compounds as growth substrates (Belser and Castro, 1971; van der Waarde et al., 1993; van Agteren et al., 2013). Thus, the alkaline hydrolysis products of TCP are expected to be readily biodegradable as vadose zone pH naturally declines after the NH_3 treatment.

Although remediation technology development has been primarily focused on groundwater treatment, in recent years the importance of treating vadose zone contamination has been gaining attention (Wellman, et al., 2012; Evans, et al., 2009; Newell, et al., 2013). Characterization of the vadose zone is often overlooked during remedial investigations. However, vadose zone source areas are often shown to be present at sites where proper vadose zone investigations are undertaken. A long-term trend of aquifer drawdown, and its direct impact on increasing the thickness of the vadose zone, has also been recognized in parts of the United States (McGuire, 2009). Going forward, if groundwater levels continue to recede, new vadose-zone source areas will likely emerge (i.e., capillary fringe smear zones, and shallow, saturated-zone source areas will turn into vadose-zone source areas as the level of the water table recedes).

For the purposes of remediation, gases are easier to distribute in unsaturated soils to achieve contact with site contaminants than liquid amendments in saturated aquifers. In an unsaturated matrix, the zone of influence that can be achieved using gaseous amendments is generally much greater than what can be achieved via liquid amendments in a saturated matrix, all things being equal. Thus, on a volumetric basis (i.e., dollars per cubic yard), gaseous remediation methods for vadose-zone soils will likely be more cost-effective than remediation of groundwater. Directly attacking vadose-zone source areas, and cutting off leaching pathways, will often be a more cost-effective course of action than allowing contaminants to leach into groundwater before initiating treatment. Moreover, once such contaminants have reached the saturated zone, removing the vadose zone source is generally necessary for effective long-term groundwater remediation to prevent contaminant rebound in groundwater due to leaching.

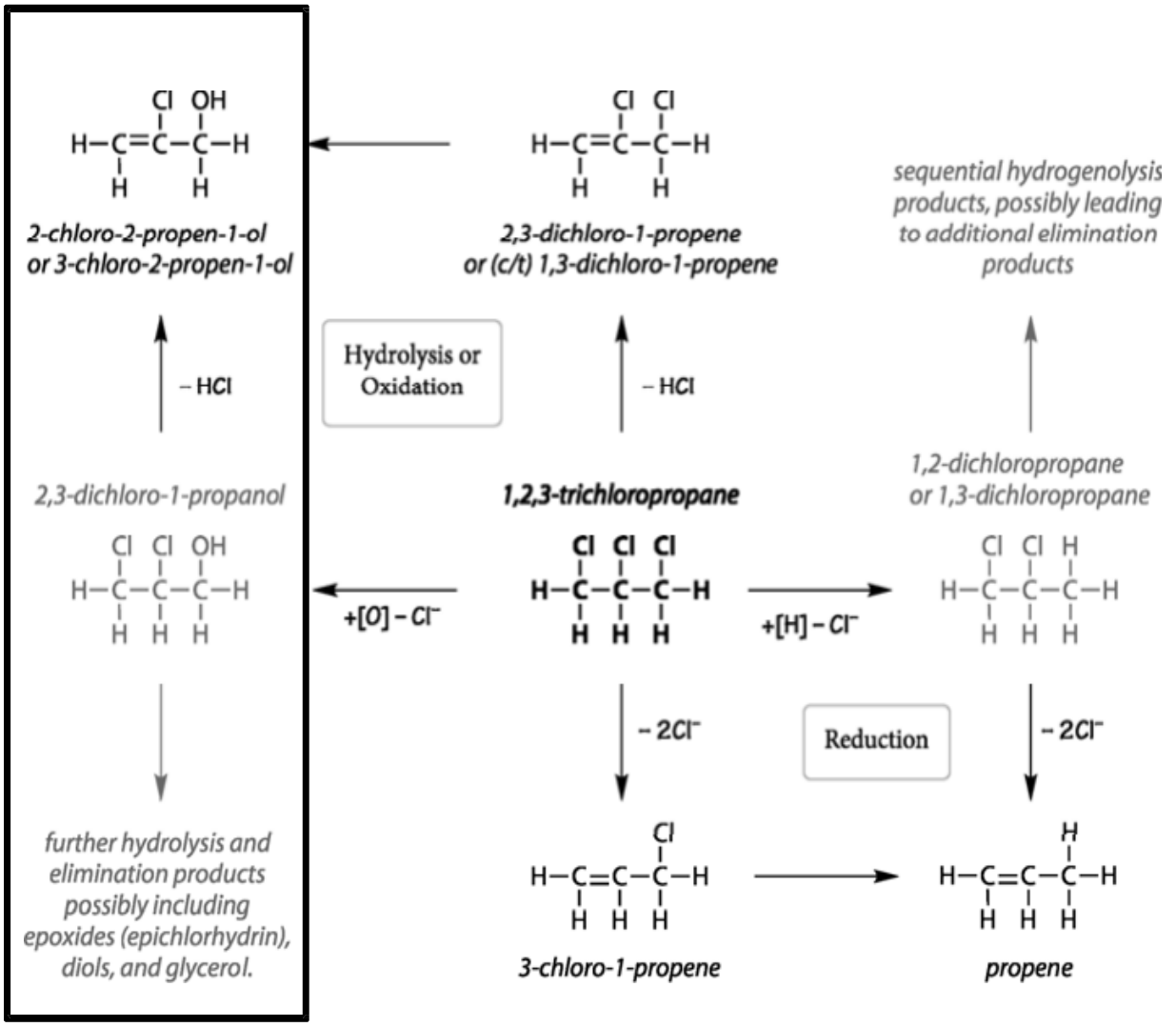

Figure 2.4. Anticipated Reaction Pathways for 1,2-3-trichloropropane.

Anticipated reaction pathways for TCP during oxidation, hydrolysis and hydrogenolysis (from Sarathy et al., 2010). The potential hydrolysis/oxidation products are shown in the box on the left.

Beyond alkaline hydrolysis, the introduction of ammonia to the vadose zone may also stimulate ammonia oxidizing microorganisms. These organisms, which are nitrifying bacteria, use the enzyme AMO to convert NH_3 to hydroxylamine (NH_2OH). AMO is also capable of degrading a wide range of chlorinated hydrocarbons 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; Vanelli et al., 1990). Peripheral distribution of ammonia around the outer area of influence of the injection wells (where the pH levels do not become too elevated to inhibit microbial activity), may promote cometabolic biodegradation of contaminants. Also, after the pH reverts back toward ambient levels (due to the buffering capacity of the soil), residual ammonia may stimulate a prolonged, cometabolic "polishing" effect and possibly serve as a slow-release substrate for driving cometabolic activity. This secondary, cometabolic effect could continue to contribute to degradation of contaminants, after the alkaline hydrolysis reactions have subsided. One of the significant advantages of cometabolic treatment of trace contaminants is the potential to achieve exceedingly low remedial levels (e.g., ng/L; Fournier et al., 2009, Hatzinger et al., 2011, 2015, 2017; Webster et al., 2013).

The application of gases to the vadose zone for bioremediation (e.g., aerobic bioventing; USEPA, 2015b) and other applications have been demonstrated at large scale (e.g., Evans and Trute, 2006). Additional testing is needed to determine if higher concentrations of ammonia (i.e., up to 10%) are more effective than the concentration tested previously by ERDC. Higher concentrations are desirable because this may enable treatment using lower volumes of gas, which will reduce the potential for displacement of volatile and semi-volatile contaminants during treatment. The potential to stimulate cometabolic degradation of TCP by NH_3 addition is also an intriguing process that requires further evaluation.

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3.0 LABORATORY STUDY DESIGN AND IMPLEMENTATION

3.1 STUDY OBJECTIVES

Laboratory column studies were conducted at ERDC with vadose-zone core materials obtained from the B&B demonstration site by APTIM (**Section 3.2.1**). The studies were designed to determine if the key Performance Objectives in Table 1.1 - *increase of soil pH* under different regimens and the hydrolytic *treatment of TCP* in site soils were going to be achievable in the field and to evaluate the most effective approach to meet these objectives. Two different types of column studies were conducted: (1) uncontaminated soil columns designed to assess the movement of the ammonia front in the B&B soils under varying soil moisture levels and ammonia concentrations and (2) TCP/DCP-contaminated soil columns in which hydrolysis of the chlorinated propanes was evaluated under optimized ammonia addition (determined from the initial column studies).

During the first set of column studies, soil pH was used as a surrogate indicator of the effectiveness of the reactive gas process, and to track the zone of influence of the ammonia (e.g., Truex et al., 2014). A pH increase of the soil to >10 standard units (SU) indicates that conditions have been made favorable for alkaline hydrolysis reactions. The reaction of gaseous ammonia with moisture in soil is exothermic. A temporary increase in soil temperature is expected to occur as the ammonia gas moves through the soil column. Temperature monitoring was also performed in one study, as a rapid and non-destructive means of tracking the ammonia front, as it proceeds through the soil column. During the second set of columns, relevant concentrations of halogenated propanes were added to the soils, and the fate of these contaminants was evaluated throughout the length of two soil columns that received either ammonia (using optimized concentrations/flow from the first set of studies) or air (control) at similar flow rates.

Additional microcosm testing was performed at APTIM to examine possible cometabolic degradation of TCP by nitrifying bacteria expressing AMO. This treatability task was also used to evaluate the potential for this biological process to contribute to the *treatment of TCP* in site soils, a key Performance Objective in **Table 1.1.**

3.2 MATERIALS AND METHODS

3.2.1 Sample Collection

As discussed in Section 1.2, the B&B Site was selected as the location for the field demonstration. Collection of site soil for laboratory treatability testing was performed during pre-design site characterization activities. The samples were collected from the proposed demonstration area, which is located within an area of elevated TCP concentrations in vadose zone soils (see the red-shaded area on **Figure 3.1**).

During site investigation, continuous cores were collected from four locations (SB-30, SB-31, SB-32, SB-33) using a Geoprobe® 8040DT direct-push technology (DPT) drilling rig (blue highlighted locations presented on **Figure 3.2**). Prior to sampling, a hand auger was utilized to clear utilities to 5 feet below ground surface (ft bgs). As shown on **Figure 3.2**, the four borings were located off the RCRA cap, as per USEPA instructions, to avoid the penetration and subsequent repair of the cap.

A 152-cm long, 8.3-cm outer diameter dual-tube soil sampling tool fitted with an approximate 5.1-cm inner diameter liner was advanced to the target saturated depth interval(s) to collect sections of continuous intact soil core. Borings were generally advanced to 45 ft bgs (13.7 m bgs). Upon retrieval, the acetate core sleeves were sliced open for logging and screening with a photoionization detector (PID) by an Aptim geologist. The boring logs are provided in **Appendix B**, as are photos of the drilling and core collection field activities.

Once the soil cores were logged and screened, the soil from some locations (primarily zones designated to have relatively elevated PID readings and/or permeable materials) was transferred to Ziploc-type bags (shipping of intact, sealed cores was not required, as laboratory treatability testing was performed under aerobic conditions and relevant chlorinated propanes were added in the laboratory at known concentrations). Each sample was double bagged, to minimize the potential for sample loss due to tearing of the bags, and clearly marked with the location, depth interval, and date. The soil sample quantity (number of bags collected) and depth intervals from which they were obtained are provided in **Table 3.1.** Soils from select intervals were subsampled and placed in 40 mL VOA vials containing methanol for analysis of TCP and other contaminants, and in 8oz soil jars for analysis of ammonia and anions.

Soil sample bags were shipped (overnight delivery) to the USACE ERDC laboratory (Vicksburg, MS) in coolers, while the subsample bottles were packed in coolers and transported to Agriculture & Priority Pollutants Laboratories, Inc. (APPL) via local laboratory courier. Completed chain of custody forms were shipped with all Site materials specifying the sampling location, depths from which the samples were taken, the date and time samples were obtained, and the samplers' names/initials. TCP and 1,2-DCP concentrations at the four boring locations are presented on **Figure 3.2**.

Table 3.1. Soil Samples Collected and Shipped to USACE ERDC.

Depth (ft bgs)	Soil Boring Number and Quantity of Bags			
	SB-30	SB-31	SB-32	SB-33
0-5	6	6	6	6
5-10	1	1	1	1
10-15	1	1	1	1
15-18		1		
15-20	1		1	1
16-18		1		
20-25	1		1	1
25-30	1			1
30-35	1	1	1	1
35-40	1		1	
40-45	1	1	2	1

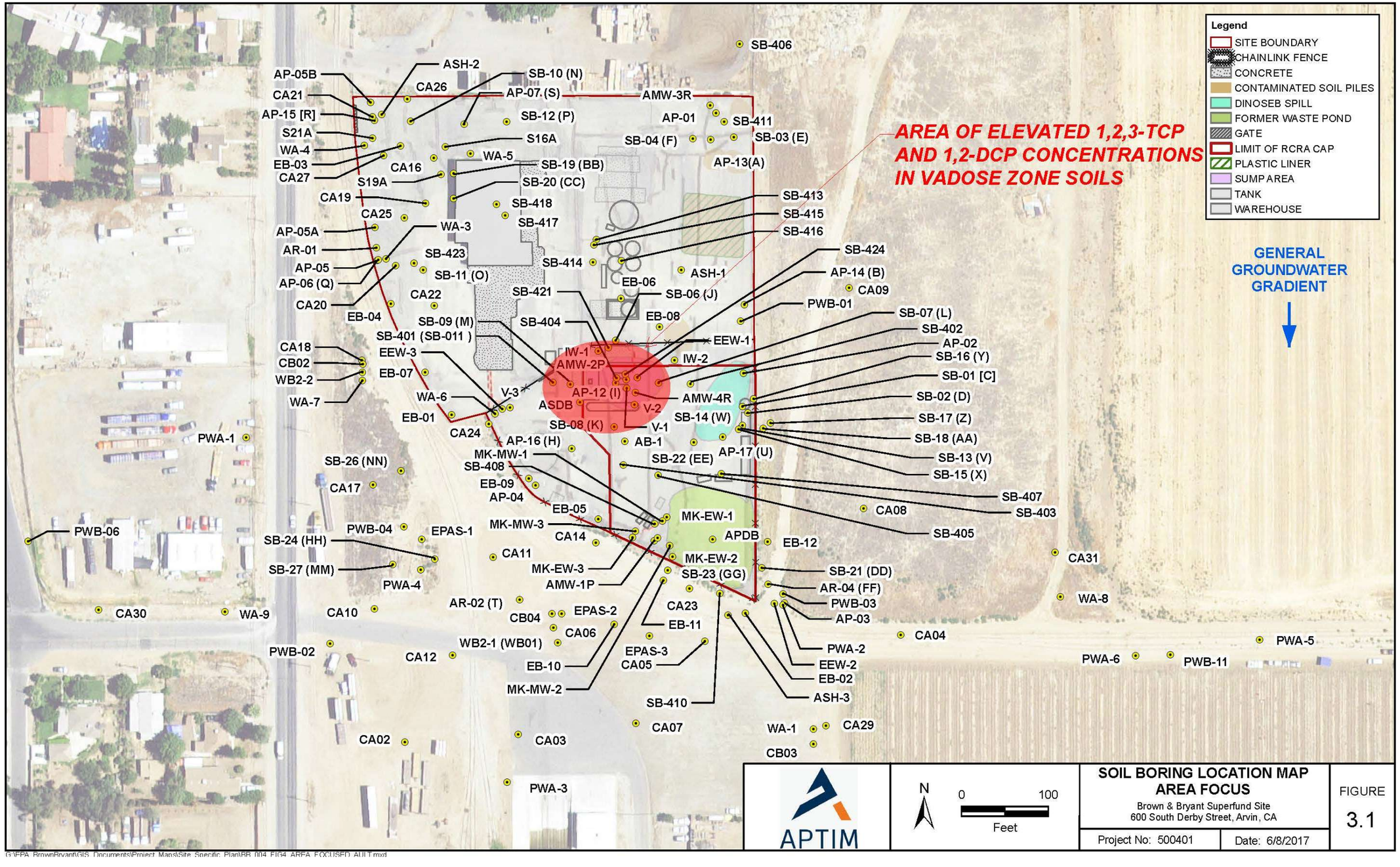

Figure 3.1. Soil Boring Location Map Area Focus

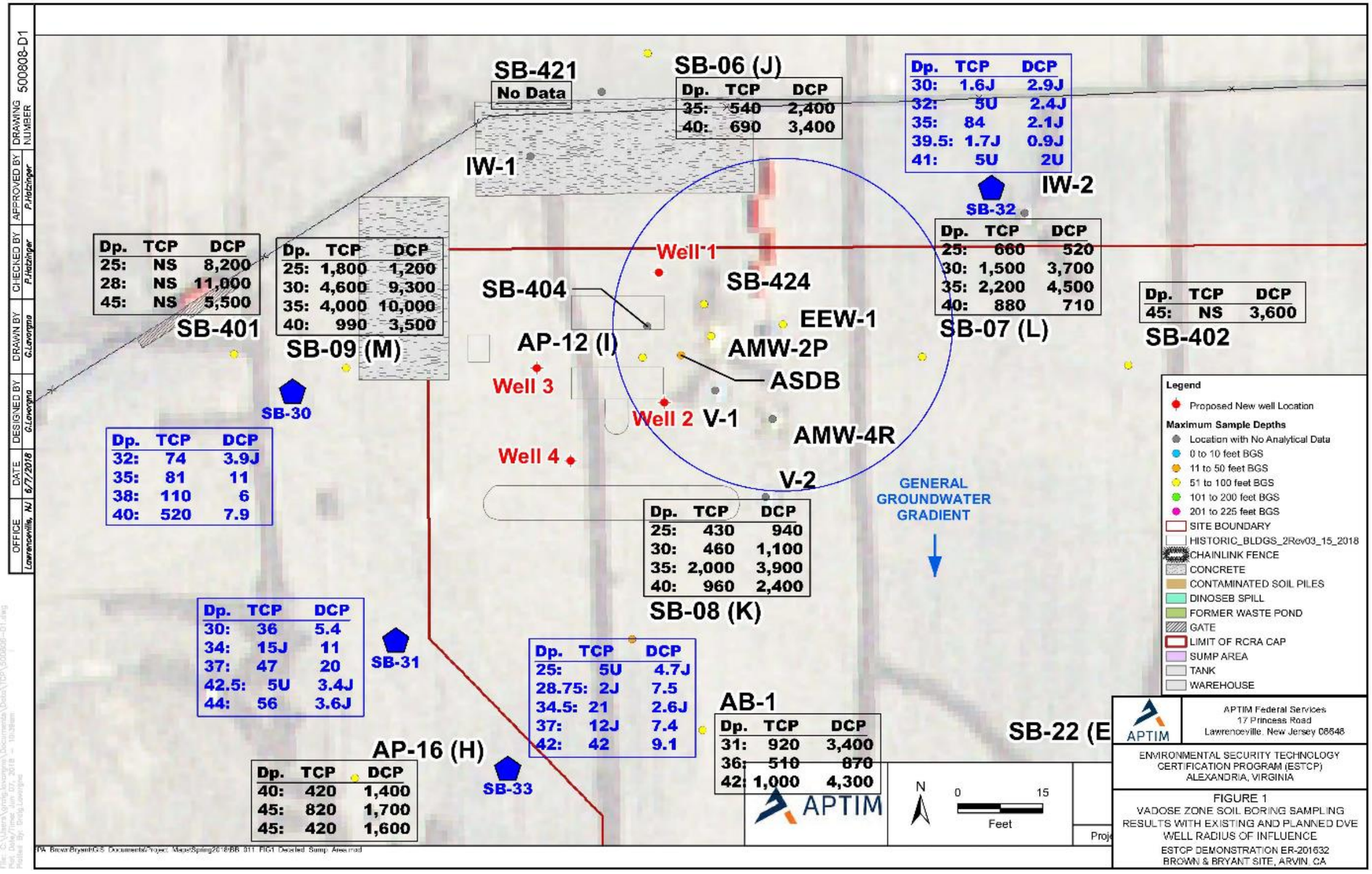

Figure 3.2. Location of Site Assessment Soil Borings and Treatability Study Sample Collection.

Locations are indicated as SB-30 to SB-33 and concentrations of DCP and TCP at depth (ft bgs) are provided.

Upon receipt of the soil sample bags by ERDC laboratory personnel, soil samples were logged in and stored at approximately 4°C until initiation of the study. Subsamples were collected from some of the bagged samples and analyzed for any residual chlorinated propanes (see **Section 3.2.3.6**), which were below detection. In order to create a large enough batch of homogenous soil for column studies, all samples from a depth of 30 to 40 ft bgs were combined into one batch (see **Table 3.1**). The soil was mixed by hand with a garden cultivator hand tool and a Collomix Xo 55 duo mixer. In an effort to remove the majority of the cohesive clay, solid cores of soil that would not crumble when squeezed by hand were removed. A subsample of the homogenized material was sent from ERDC to APTIM's Biotechnology Laboratory in Lawrenceville, NJ for microcosm testing as described in **Section 3.2.6**.

3.2.2 Column Studies

Two different types of soil column studies were conducted as described previously in **Section 3.1**. The materials and methods used in these studies are provided in the subsequent sections.

3.2.2.1 Materials and Design

Two types of soil test columns were used in treatability testing. Column Test 1 and Test 2 (see Results **Section 3.3.1**) were conducted in columns constructed from clear PVC pipe (**Figure 3.3**). All other tests were conducted in Kimble Flex-Columns (420400-2520), which have a glass barrel.

The columns were constructed from 61-cm long sections of clear schedule 80 polyvinyl chloride (PVC) pipe with an inside diameter (ID) of 2.38 cm. A column bed was glued to one end of the pipe, and 2.5-cm schedule 40 PVC male adapters were glued onto each end of the pipe. The column bed was cut from 0.32-cm thick porous high-density polyethylene (HDPE) with a nominal pore size of 100 microns. Threaded PVC caps were tapped and fitted with male Luer-lock adapters. Thermocouples were added to the columns for Study #1 to measure soil temperature. This technique was not used thereafter due to high variability in the ambient room temperature, which limited the ability to detect small changes in soil temperature. A finished column with thermocouples is shown in **Figure 3.3** (top panel).

The Kimble Flex-Columns (**Figure 3.3**; bottom panel) are composed of a borosilicate glass barrel of 20-cm length and 2.5-cm ID, and an HDPE bed support with 20-micron porosity. Column end adapters and cap are made of polypropylene with Luer-lock male ports.

Three gases were used in the column tests. The first was air from the laboratory building's dried compressed air system. The second and third gases were compressed gas cylinders of specialty gas blends of ammonia in air provided by Airgas Specialty Gases. These tanks of gas contained 5.0 % and 9.5 % ammonia on a molar basis.

3.2.2.2 Column Packing and Preparation

Packing of soil in columns was accomplished by scooping 5 to 10 g amounts of soil with disposable plastic spatulas and gently adding the soil to the soil columns. Soil was added in approximately 6-cm layers and compacted between layers by tapping the bottom of the column on the counter until no further settling was observed. A short section of PVC pipe placed on the counter was used to prevent damage to fittings on the bottom of the column during compaction. After each column was filled with soil, the cap was screwed on the top of the column, and two-way valves were attached to each end of the column and closed.

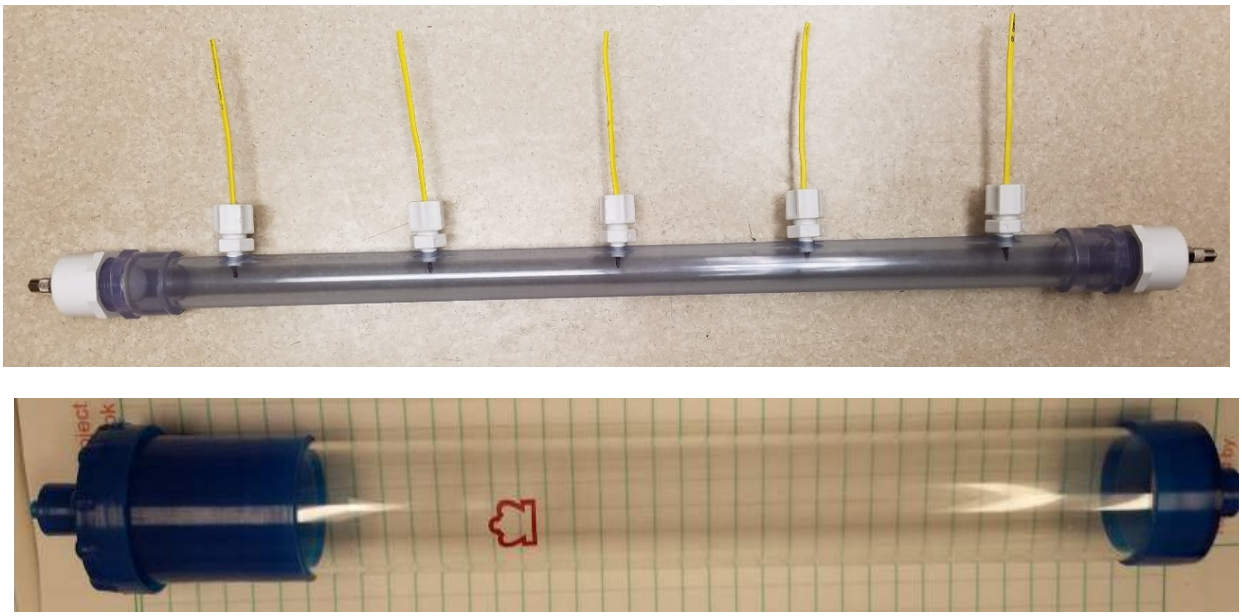

Figure 3.3. PVC Column with Thermocouples (top panel) and Borosilicate Glass Kimble Flex-column (bottom panel).

3.2.2.3 Soil Moisture Adjustment

When necessary based upon the experimental conditions, soil moisture was increased by spreading soil in a container, spraying the soil with deionized (DI) water utilizing a plant mister, and homogenizing the soil with a hand cultivator. This process was repeated over several days until the desired soil moisture content was achieved. Drying soil was produced by spreading the soil in a shallow pan, allowing it to air dry on the lab counter, and homogenizing the soil with a hand cultivator. This process was repeated over several days until the desired moisture content was achieved.

3.2.2.4 Spiking Soil with Chlorinated Propanes

Contaminated soil for tests was created by spiking the soil with four contaminants. The source solutions used for spiking were as follows:

- 1,2-Dichloropropane 99%, Sigma-Aldrich D72182-100G, Lot # 01113DOV
- 1,3-Dichloropropane 99%, Sigma-Aldrich D72204-25G, Lot # BCBG2162V
- 1,2,3-Trichloropropane 99%, Sigma-Aldrich 110124-100G, Lot # BCBH8722V
- 1,2-Dibromo-3-chloropropane (DBCP) 97%, Sigma-Aldrich 676713-5G, Lot # MKBG6103V

Spiking of soil and loading of columns were conducted in a disposable glove bag (Glas-Col 108D X-27-17HG), which is made of 2.5-mm thick polyethylene. Approximately 2.8 kg of wet soil in a pan and all materials necessary to spike and mix soil and to load the columns were added to the glove bag before sealing the bag (**Figure 3.4**).

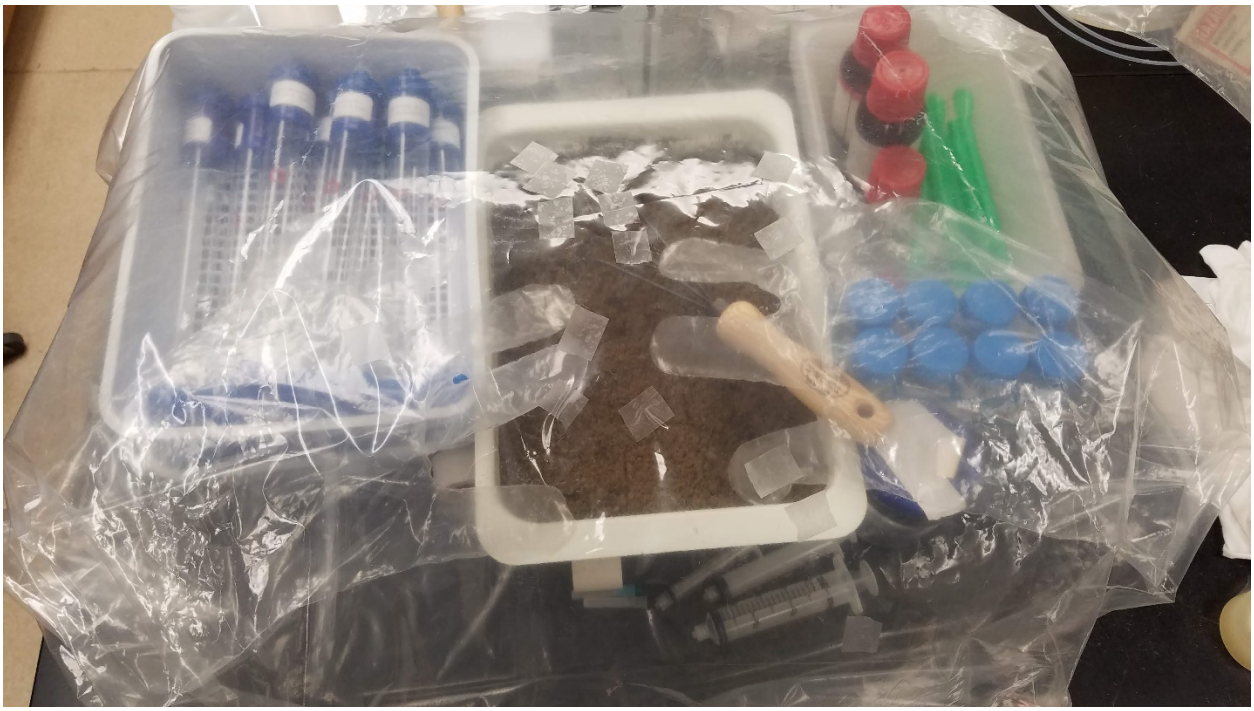

Figure 3.4. Glove Bag and Materials Used for Soil Spiking.

Spike solutions were withdrawn from vials and distributed on the surface of the soil utilizing smallest size syringe and needle required for the volume to be withdrawn from each vial. The soil was then mixed with a hand cultivator three days a week for the next three weeks to distribute the contaminants in the batch of soil. A second spike event occurred approximately six weeks after the first spike event. In the second spike event, additional 1,2-DCP was added to the soil using the same volume of spike solution as in the first event. This was done over concerns of possible losses of 1,2-DCP due to its high volatility and concerns that it may have been permeating through the glove bag. In the first spike event the approximate volumes used for each spike solution are listed in **Table 3.2**.

Table 3.2. Volumes of Spike Solutions Applied to Soil.

Solution	Volume (mL)
1,2-DCP	12.8
1,3-DCP	5.7
1,2,3-TCP	1.2
DBCP	0.6

3.2.2.5 Soil Column Test Trains

Soil columns were connected in series to simulate a long soil column. This allowed for effective packing and sampling of the soil columns. In Column Test 1 and Test 2, five PVC columns were connected in series to simulate a 3-m long column. The experimental setup is pictured in Error! Reference source not found..**5**. The columns were wrapped with closed-cell polyurethane pipe insulation to reduce the influence of ambient air temperature on soil temperature. A similar design was used for the glass columns in later studies (**Figure 3.6**).

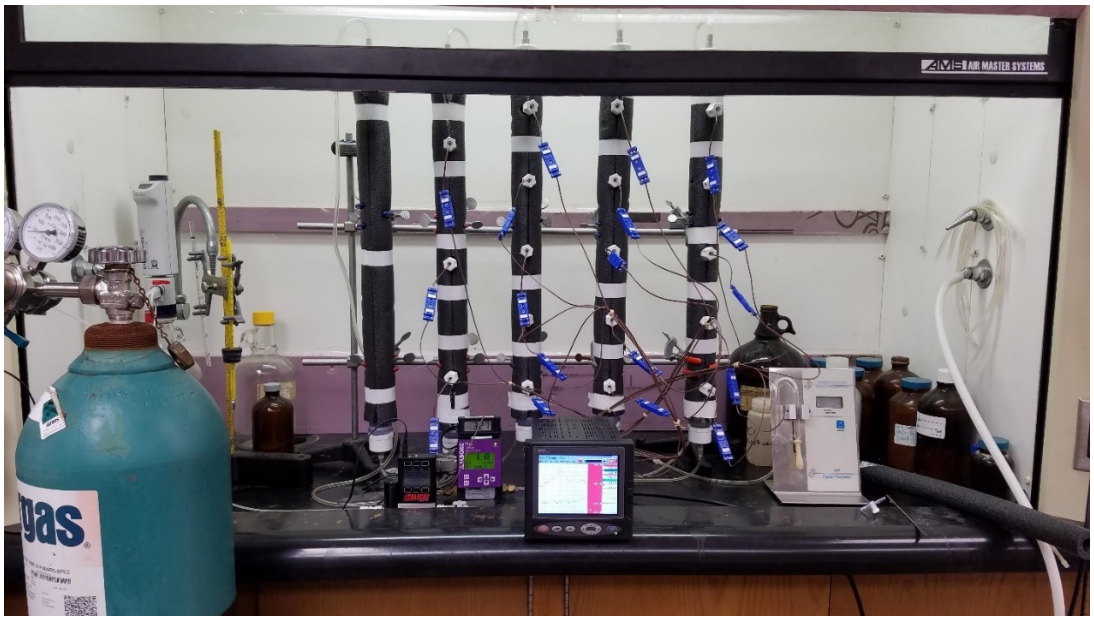

Figure 3.5. PVC Column Train with Thermocouples.

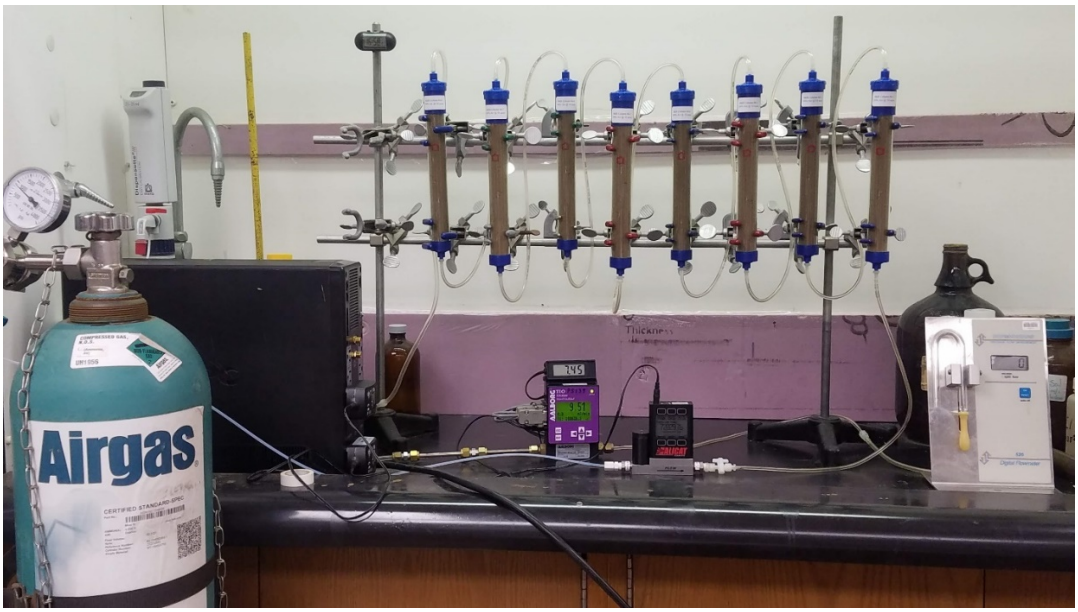

Figure 3.6. Glass Column Train.

3.2.3 Measurements and Analytical

3.2.3.1 Gas Flow Measurement

Three gas flow meters were used during testing. Gas flow into the column train was measured and controlled by an AliCat gas-mass flow controller and totalizer (MC-10SCCM-D) with a flow range from 0 to 10 standard cubic centimeters per minute (sccm). Gas flow out of the column train was measured by an Aalborg gas mass flow meter (GFM17) with a flow range from 0 to 10 sccm and totalizer (TIO-LAA2). Gas flow rates from the meters were confirmed with a Humonics 520 Digital (bubble) Flowmeter.

3.2.3.2 Soil Temperature Measurement and Logging

Soil temperatures were measured using Type T thermocouples in two tests conducted in the soil columns constructed from PVC pipe. Thermocouples were added along the length of four of the PVC columns. Five were added to each of three columns, and three were added to a fourth column. The thermocouples were created from Type T thermocouple wire. The wire was passed through ¼-inch (0.64 cm) tubing compression fitting with a 1/8-inch (0.32 cm) National Pipe Taper (NPT) threaded end. The wire was sealed in the fitting by passing the wire through four septa cut to size on the compression end of the fitting, and by filling the NPT end with dielectric sealant. The sidewall of the columns was tapped with 1/8-inch (0.32 cm) NPT holes through which the fittings were inserted. The tips of the thermocouple extended to the center of the columns. Temperature measurements from the thermocouples were recorded using a Fuji Paperless Recorder PHL (Fuji Electric Co.) with 18 data acquisition channels. Soil temperatures were not recorded after the initial two column studies.

3.2.3.3 Soil Moisture

The moisture content of soil was determined following American Society for Testing and Materials (ASTM) Method D4859-00. Approximately 10 g of wet soil was weighed into a pre-weighed aluminum pan and dried in a 105 ± 2 °C oven overnight. The moisture was determined by the difference in weight between the wet and dry soil.

3.2.3.4 Soil pH

Determination of soil pH followed ASTM D 4972-01 Method A with the following modification. Two subsamples were taken of each soil sample. Each subsample was weighed to 5 ± 0.05 g of wet soil and added to a 50-mL plastic centrifuge tube. 20 mL of DI water was added to one sample tube, and 20 mL of 0.01-M calcium chloride ($CaCl_2$) was added to the other sample tube. The tube was sealed and placed on a laboratory rotator for approximately 2 hours (hr). The tube was removed from the rotator and allowed to settle for at least 30 minutes (min). The pH of the supernatant was then measured by a combination pH electrode.

3.2.3.5 Ammonia and Inorganic Nitrogen in Soil

Determination of free and exchangeable ammonia and inorganic nitrogen in soil samples was determined following guidance in Chapter 38 of *Methods of Soil Analysis, Part 3 – Chemical Methods* (Mulvaney 1996). Two subsamples were taken from each soil sample. Extraction was accomplished by adding 3 ± 0.05 g of wet soil to a plastic 50 mL centrifuge tube. 30 mL of extract solution was added to the tube. The tube was sealed and placed on a laboratory rotator for approximately 2 hours or more. The tube was removed from the rotator and allowed to settle for at least 30 min. The clear extract was then withdrawn and passed through a 0.45 µm glass-fiber syringe filter.

For ammonia determination, a 2-M potassium chloride (KCl) extract solution was used. Ammonia content was then determined using Hach Method 10031 for determination of nitrogen ammonia using high range (0.4 to 50.0 mg/L NH_3-N) Test 'N Tube™ Vials. This is a salicylate-based method. For inorganic nitrogen determination, a 0.01-M KCl extract solution was used. Nitrogen and nitrate content were then determined via ion chromatography (USEPA Method 300).

3.2.3.6 Chlorinated Propanes in Soil

Analyses of soil for chlorinated propanes was conducted by Air Water & Gas Laboratories, Inc. (Richmond, Virginia). Analyses were conducted according to USEPA SW-846 Method 8011, which is microextraction and gas chromatography. Soil samples were collected in 30-mL glass jars with Teflon lined caps and frozen overnight. They were packed in coolers with dry ice the following day and shipped to the analytical laboratory via overnight delivery.

3.2.3.7 Chlorinated Propanes Captured from Air

Analyses of chlorinated propanes captured from air were conducted by Beacon Environmental Services, Inc. (Forest Hill, Maryland). Air samples were passed through two adsorbent tubes attached in series to the end of the train of test columns. At the completion of the test the tubes were removed, the ends were sealed, and the tubes were placed in individual resealable plastic bags and frozen overnight. The samples were packed in a cooler with ice the following day and shipped to the analytical laboratory via overnight delivery.

3.2.4 Soil pH Column Studies

Packing of soil into and extraction of soil from the test columns was conducted inside a glove bag. The total weight of soil packed into each column was determined as was the soil moisture at the time of each test. Five different column studies were conducted to assess the propagation distance of ammonia in the columns and the subsequent increase in soil pH. These column studies compared the soil pH response after addition of 5% or 9.5% ammonia-in-air. Other variables examined included the impact of soil moisture on the movement of ammonia and subsequent pH increase in the soil and the impact to ammonia gas flow rate on these same parameters. The propagation distance of the pH effect, reactive gas flow rate, and volume of gas pushed thru the columns over the time course of the study were measured.

3.2.5 Contaminated Soil Column Studies

The soil core samples were spiked with relevant field concentrations of chlorinated propanes present at B&B, including 1,2,3-TCP, 1,2-DCP, 1,3-DCP, and DBCP (target concentrations of 1-10 mg/kg) as previously described. Baseline soil samples were collected for analysis after spiking, and soils were quickly packed into the basic columns to avoid extensive volatile losses. Reactive gas was then added for a period of up to 15 days. The reactive gas injection conditions were based upon from the results generated in the tests described in **Section 3.2.4** and are further described in the Results (**Section 3.3**). At the conclusion of each study, the soil columns were disassembled, and samples were collected along the length of each column. Samples were analyzed for halogenated propanes, NH_4^+ and pH. A control column, with addition of N_2 rather than NH_3 gas, was also prepared and run as a control for volatile losses.

For these tests, two adsorbent tubes (Chromosorb 102) were placed in series at the end of the columns to quantify volatile losses of the chlorinated propanes. At the completion of the test, the adsorbent tubes were capped, taped, sealed in vials, and shipped for analysis of halogenated propanes as described in **Section 3.3.3**.

3.2.6 3.2.6 Microcosms to Evaluate Cometabolism

Microcosm studies were conducted to evaluate whether nitrification was occurring in the NH_3-amended soils and whether this process could contribute to cometabolic activity in zones where lower NH_3 concentrations occur. The key enzyme initiating nitrification, AMO, has also been observed to oxidize TCP, in addition to a host of other chlorinated solvents, via aerobic cometabolism as previously noted. To conduct these studies, homogenized soil was shipped from ERDC to APTIM's Biotechnology Laboratory in Lawrenceville, NJ and stored at 4°C until use.

Microcosms were prepared in sterile borosilicate glass wide mouth soil jars (approximate volume, 125 mL) using approximately 30 g of homogenized solids at ambient soil moisture leaving approximately 100 mL of room air in the headspace. The jars were sealed with polytetrafluoroethylene (PTFE)-faced silicone-lined screw caps. Initial soil moisture content was assessed by ASTM Method D4959 removing soil moisture by oven-drying a soil sample until the weight remains constant. The moisture content (%) was calculated from the sample weight before and after drying (~15.1%). In addition, 2.5 g of homogenized soil was taken in duplicate for an initial ammonia analysis (Turrion et al. 1999). Results from the ammonia analysis showed there was 2,075 mg NH_3-N per kg of wet soil. The original experimental design was to add differing quantities of ammonia to the soil to evaluate the influence of ammonia concentration on nitrification, but that plan was altered due to the exceedingly high ammonia concentration in the site soils. Duplicate 10 g soil samples were sent out to Microbial Insights, Inc (Knoxville, TN) for quantitative polymerase chain reaction (qPCR) analysis of AMO-containing microorganisms to provide a baseline level for the presence of organisms with the genes for this enzyme.

The microcosms were prepared in two treatments in quadruplet. These treatments consisted of live samples with no amendments and killed samples that received 1% formaldehyde by weight (~0.8 g). Microcosms were incubated in the dark at room temperature. At various times, microcosms were opened in a laboratory fume hood and 2.5 g samples were removed for analysis of N species (NH_3, NO_2^-, NO_3^-) and pH. The analyses were conducted at time zero, and monthly thereafter for a total of 5 sampling time points. After the initial time zero sampling point, it was discovered that the formaldehyde in the killed controls interfered with the ammonia analysis. Two jars from the quadruplet live treatments were then placed into the refrigerator (4ºC) to inhibit further reaction, and these served a second set of controls. Two of the killed control treatment jars were also placed in the refrigerator to monitor any other anion changes. In addition, headspace oxygen levels (100 µL sample) were taken through the septa after one week and measured on a gas chromatography/thermal conductivity detector (GC-TCD) to ensure that anoxic conditions did not develop. The jars were then sealed with new sterile PTFE-faced silicone-lined screw caps. Photos of the microcosms are provided in **Figure 3.7.**

Figure 3.7. Photograph of Soil Microcosms Used for Nitrification Studies.

3.3 RESULTS

3.3.1 Soil pH Column Results

3.3.1.1 Soil pH Column Test 1

During the initial column test, a gas flow of 1 sccm containing 10% NH_3 was passed through a ~3 m column constructed of PVC and fitted with thermocouples to measure temperature along the column length (See **Figure 3.5**). A total of 10,181 scc of the gas mixture was passed through the soil column over 7 days of continuous operation. At the conclusion of this time, the column was disassembled, sectioned, and soil subsamples were collected and analyzed for percent solids, ammonia, soil moisture and pH by the methods described in **Section 3.2**. Temperature was measured along the length of the column as well to evaluate whether the NH_3 front correlated with temperature increases along the length of the column.

The soil moisture across the column after the gas addition ranged from ~ 15% to 19% with a slight increase with distance from the gas inlet port (**Figure 3.8**). The percent solids in the soil column remained reasonably constant at ~ 87% showing that the soil was well homogenized during the initial preparation. The pH in the soils varied somewhat based on the extraction method, with a higher pH being recorded with DI water than with 0.01M $CaCl_2$ (~ 0.5 pH unit difference; **Figure 3.9**). A significant increase in soil pH in the column extended ~ 1 ft from the inlet port (pH > 9 by both methods compared to 7.8 to 8.4 in bulk soil depending on method), and a pH increase to > 10 was observed at the first sample point only ~ 0.08 m from the inlet.

One of the significant observations from this study was that indigenous levels of ammonia in the soil exceeded 1500 mg/kg as N (**Figure 3.9**). This high concentration indicates that a previous process or event at the B&B facility released large quantities of ammonia into the vadose soils. This supports field reports that the odor of ammonia was detected while drilling at some locations.

During this study, 18 thermocouples were placed in the columns along the 3 m length in order to determine if temperature changes in the soil could be used as a means to track the front of ammonia as it moved through the soil in that the reaction of NH_3 with water is exothermic. The temperature data collected during the study indicated that, despite insulating the soil column to the extent possible, the variation in external temperature in the laboratory fume hood was too great to allow differences in soil temperature to be detected. This temperature variation is shown in **Figure 3.10**.

If the ammonia front was detected, a significant temperature difference would be expected from the front of the column (e.g., CH01) where ammonia accumulated and pH increased to the later thermocouples, where ammonia concentrations did not increase. Rather, the temperature at all of the thermocouples tracked each other closely, apparently varying primarily with ambient temperature. An attempt was made to normalize the temperature data, but no discernable difference trend was observed between the thermocouple locations.

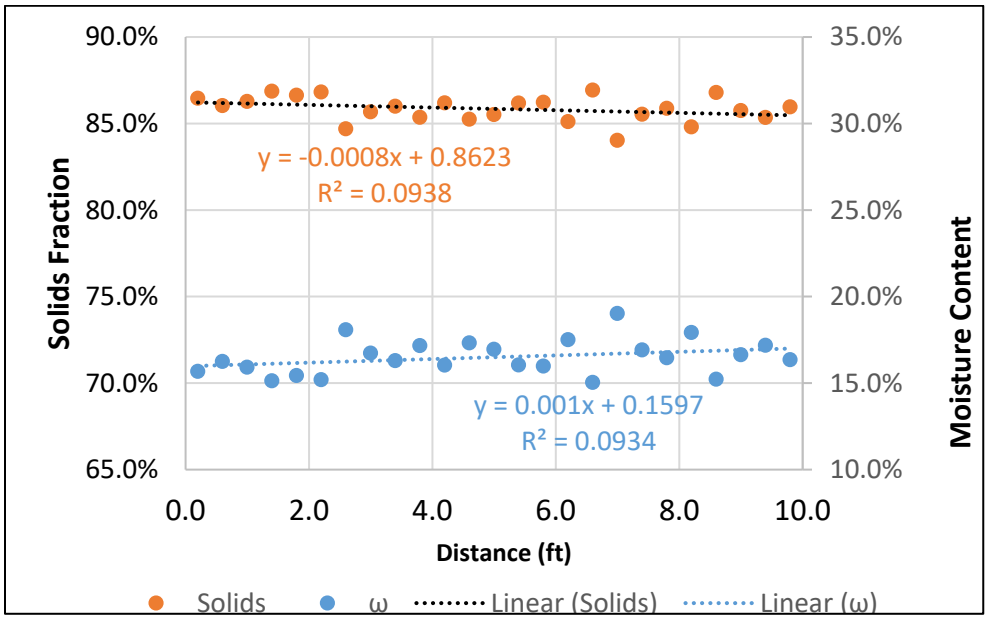

Figure 3.8. Soil Solids (Orange Marker) and Soil Moisture Content (Blue Marker) in Column #1 after Treatment with 10% Ammonia Gas for 7 days at 1 sccm.

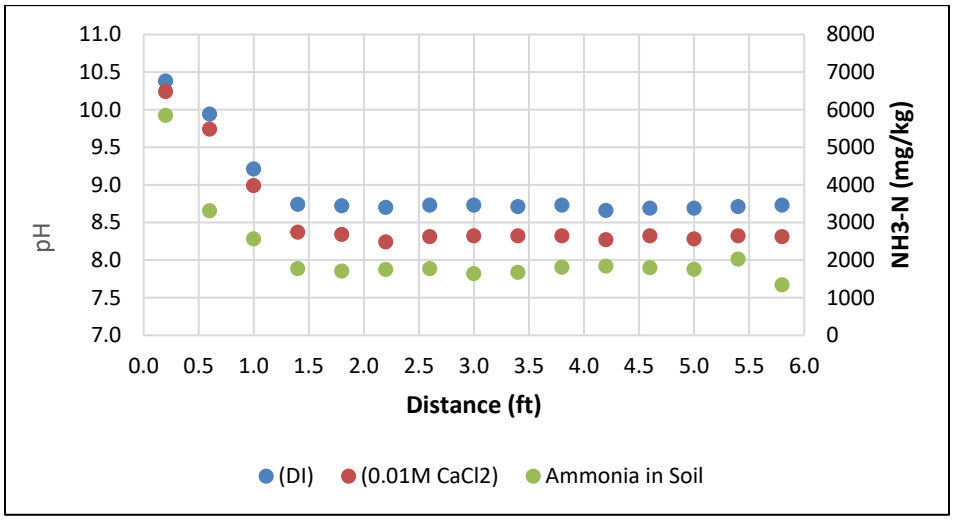

Figure 3.9. Soil pH in DI (Blue Marker) and $CaCl_2$ (Red Marker) and Soil NH_3-N (Green Marker) in Column #1 after Treatment with 10% Ammonia Gas for 7 Days at 1 sccm.

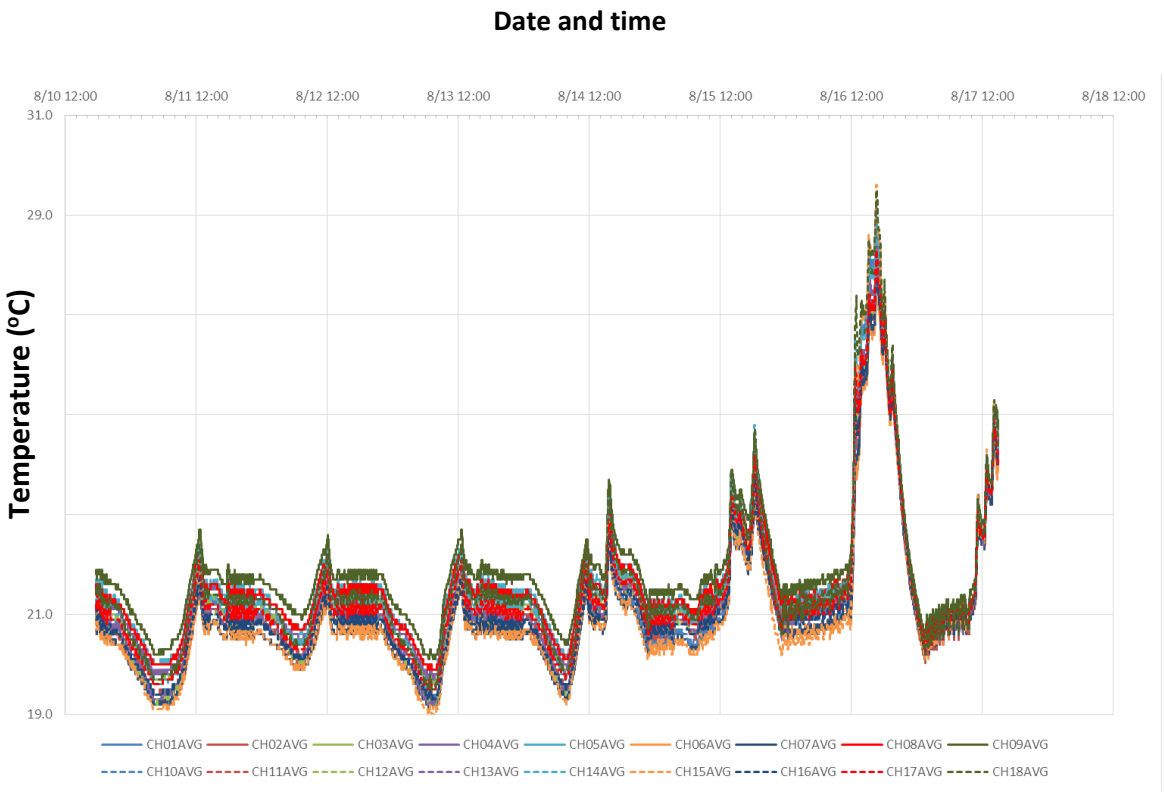

Figure 3.10. Temperature Measured in Thermocouples Along the Length of Column #1 Over Time During Treatment with 10% Ammonia Gas for 7 days at 1 sccm.

3.3.1.2 Soil pH Column Tests 2-5

Four additional column tests were conducted to evaluate the influence of ammonia gas concentration, soil moisture and ammonia gas flow rate on the extent of pH increase in the B&B soil. These variables were selected for evaluation as a basis for optimizing the field application of this technology and estimating the impact of soil moisture on ammonia transport and pH increase in site soils. The PVC column was used in Column 2 and the Kimble glass columns were used in the remaining tests (**Figure 3.6**). The conditions in the columns were as follows: Column 2 – 9.5% ammonia gas at 5 sccm with 16.9% soil moisture; Column 3 – 5.0% ammonia gas at 10 sccm with 16.3% soil moisture; Column 4 - 9.5% ammonia gas at 10 sccm with 15.9% soil moisture; and Column 5 - 5.0% ammonia gas at 10 sccm with 5.5% soil moisture. The treatment conditions and the results from this study are summarized in **Table 3.3.,** and individual graphs showing soil pH and soil ammonia as a function of distance in the column are provided in **Figures 3.11** to **3.14**.

For Column 2 (9.5% ammonia at 5 sccm), soil pH reached > 10 for a distance of ~ 1.8 ft (0.55 m) from the column inlet, with a total estimated treated mass of 400 g of soil (**Figure 3.11**). These data are similar to those from Column 4, where 9.5% ammonia was added at 10 sccm, and a similar soil moisture (**Figure 3.13**). In this case pH reached > 10 for a distance of ~ 2.0 ft (0.61 m) from the inlet and 438 g of soil was treated, but the quantity of total mass of ammonia added to Column 4 was also slightly greater (~ 23%) than that added to Column 2. The data suggest that the ammonia flow rate makes little difference in terms of the extent of soil treatment.

The primary difference between Column 3 (**Figure 3.12**) and Column 4 was the percent of NH_3 in the gas stream (5.0% vs 9.5%, respectively). The total mass of ammonia added was similar between the columns (5.9 vs 6.2 g, respectively). The pH reached > 10 for a distance of ~ 3 ft (0.92 m) from the inlet in Column 3 with a total of 721 g soil treated vs 2 ft (0.61 m) and 438 g soil in Column 4. Thus, more soil reached the desired pH in Column 3 when the percent NH_3 in the applied gas was lower. It should also be noted that the NH_4^+ detected in the soil ("saturation" in **Table 3.3**) in the columns was appreciably lower in the column that received 5% ammonia compared to that receiving 9.5% ammonia.

The final important comparison for the column tests is between Column 4 and Column 5, in which the only difference was the percent soil moisture. For both columns, NH_3 was added at 9.5% at a flow rate of 10 sccm, but the percent soil moisture in Column 5 was 5.5% compared to 15.9% in Column 4. As can be observed in **Figure 3.14**, more than 5 ft (1.5 m) of the soil in Column 5 was at pH >10 at the end of the ammonia addition time (1129 g treated), compared to 2 ft (0.61 m) and 438 g treated in Column 4. This observation is consistent with the fact that much less water is present in Column 5, and thus ammonia more readily saturates the water phase and increases soil pH.

3.3.2 Soil pH Column Test Summary and Conclusions

The data from the 5 previous tests designed to evaluate the potential to increase soil pH by adding different concentrations of NH_3 in the gaseous phase to soil columns indicate that this approach can readily be used to increase pH to > 10. The combined data comparing soil ammonia levels and soil pH from the 5 columns is provided in **Figure 3.15.** The figure shows that soil pH rapidly increases from ~ 8.2 to 10 as ammonia levels increase from ~ 1,500 to 2,000 mg NH_3-N/kg (baseline) to ~ 4,000 mg NH_3-N/kg. The pH increases very slowly thereafter, with a measured soil pH of < 10.5 at ammonia levels exceeding 10,000 mg-N/kg. The biphasic curve is consistent with the pKa of the NH_3/NH_4^+ reaction (shown in **Figure 3.15**) being ~ 9.25. The data suggest that it will be easy to increase soil pH to 10 in a field setting but difficult to bring soil pH much above this value. One factor that contributes to this is the high initial starting NH_4^+-N concentration in the soil.

Based on the 5 column tests conducted, the conditions under which the greatest quantity of soil (at typical field moisture) was impacted by the gaseous ammonia was the addition of 5 % NH_3 at a flow rate of 10 sccm (Column 3). These conditions were subsequently selected to evaluate the effectiveness of the NH_3 addition process on treatment of TCP and DCP in B&B soils. Prior to this work, a modeling exercise was conducted with the data to evaluate the expected radius of influence (ROI) of the ammonia (in terms of pH enhancement) from a single gaseous injection well (**Figure 3.16**). The model makes the following assumptions the gas injected flows radially in a uniform horizontal direction through a 1-ft (0.305 m) thick formation bounded on the top and bottom. The level of ammonia demand by the soil was estimated by results from Column Test 3 for 5 % ammonia in air and an average of the results from Column Tests 2 and 4 for 9.5 % ammonia in air. The bulk density of the soil was estimated to be 108 lb/cf (1.73 kg/L), which was determined during the packing of the soil test columns. The model indicates that the ROI increases with increasing NH_3 flow rate, which is expected. At a flow rate of 0.35 standard cubic feet per minute (scfm) which is ~ 10,000 sccm, a ROI of 10 ft could be achieved after ~ 10 months of gas addition. The same ROI could be achieved after ~ 3 months at a flow rate of 1.06 scfm (~ 30,000 sccm). These estimated ROI values allow this process to be practical at the field scale, so the final column study was conducted to assess treatment efficacy of the ammonia injection process.

Table 3.3. Treatment Conditions and Results from Soil Column Tests 2-5.

	Conditions					Saturation pH		Ammonia			Soil Treated (g $soil_{dry}$)
Column Test	Ammonia (%)	Flow (sccm)	Total gas (L)	Total Days Treated	Moisture Content (ω)	DI	0.01M $CaCl_2$	Saturation (g NH_3-N/ kg $soil_{dry}$)	Soil Demand (g NH_3-N/kg $soil_{dry}$)	Total Injected (g NH_3-N)	
2	9.5	5	91	13	16.9%	10.4	10.2	8.0	12.5	5.0	400
3	5.0	10	205	14	16.3%	10.3	10.1	5.0	8.2	5.9	721
4	9.5	10	112	8	15.9%	10.6	10.4	9.9	14.1	6.2	438
5	9.5	10	112	8	5.5%	10.3	10.0	4.4	5.4	6.1	1129

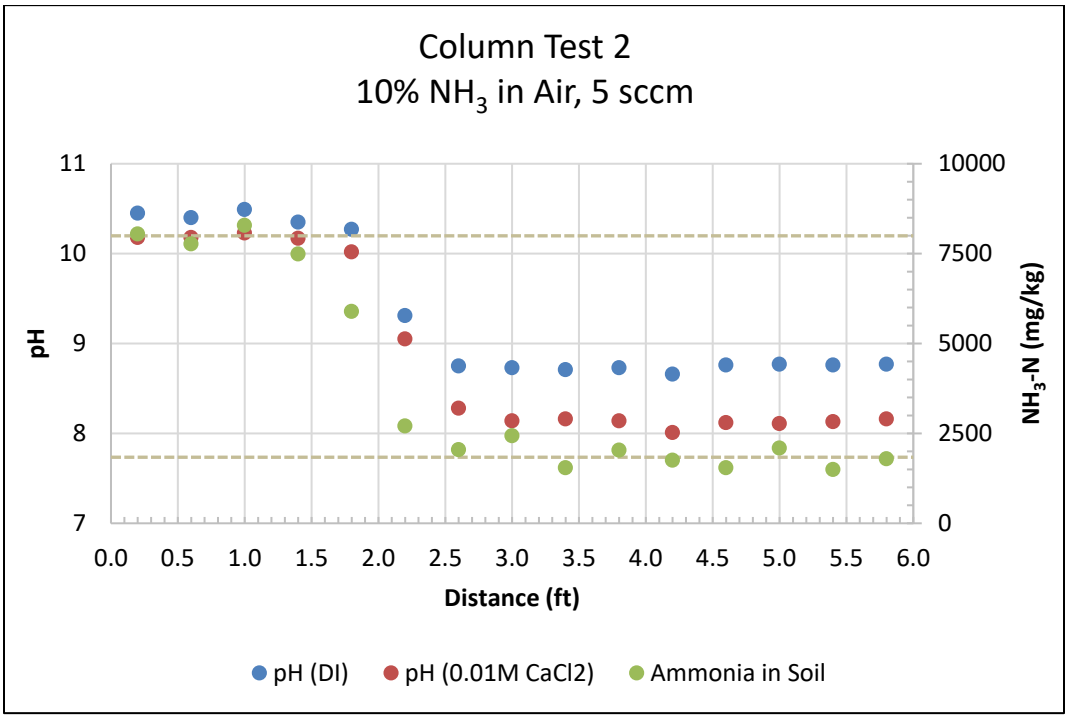

Figure 3.11. Soil pH in DI (Blue Marker) and CaCl2 (red marker) and soil NH3-N (Green Marker) in Column 2 after Treatment with 10% Ammonia Gas for 13 Days at 5 sccm.

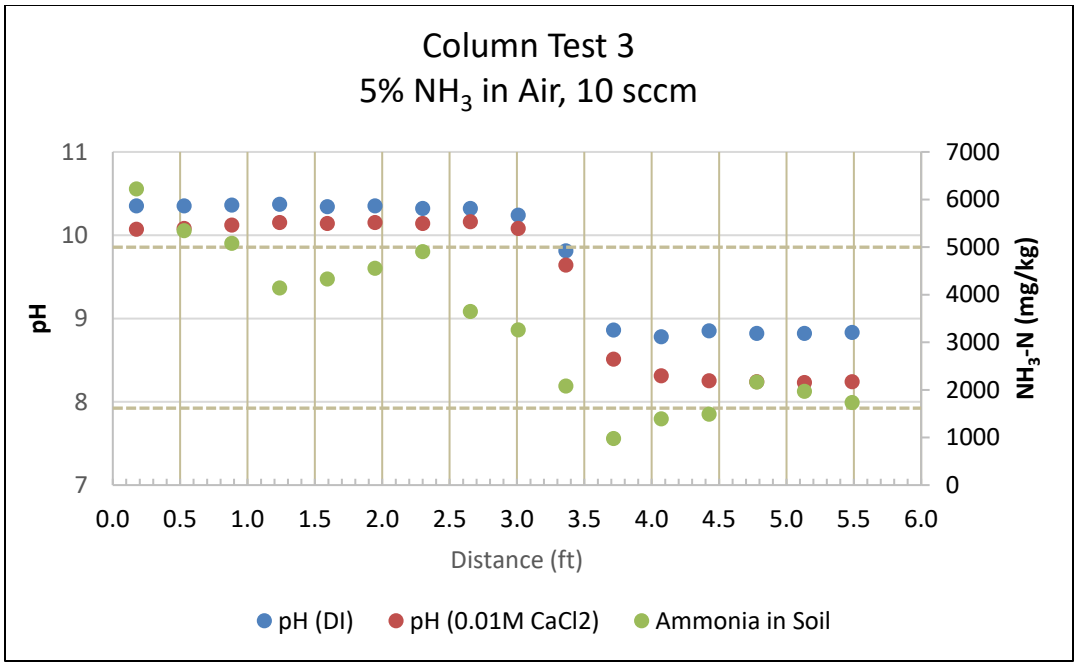

Figure 3.12. Soil pH in DI (Blue Marker) and $CaCl_2$ (Red Marker) and Soil NH_3-N (Green Marker) in Column 3 After Treatment with 10% Ammonia Gas for 14 Days at 5 sccm.

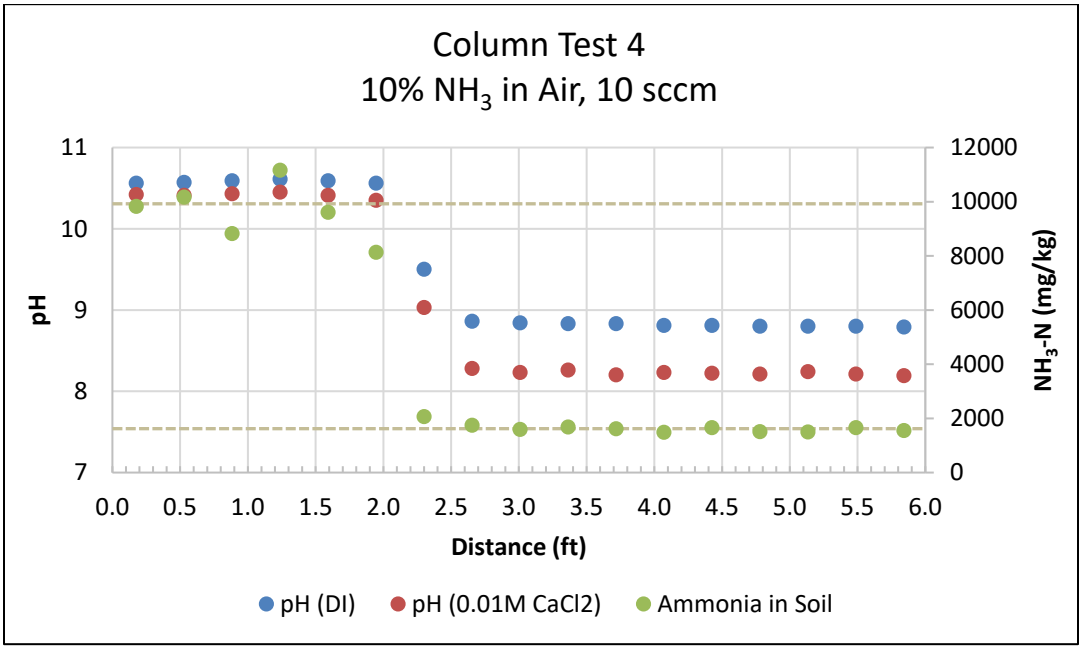

Figure 3.13. Soil pH in DI (Blue Marker) and $CaCl_2$ (Red Marker) and Soil NH_3-N (Green Marker) in Column 4 After Treatment with 10% Ammonia Gas for 8 Days at 10 sccm.

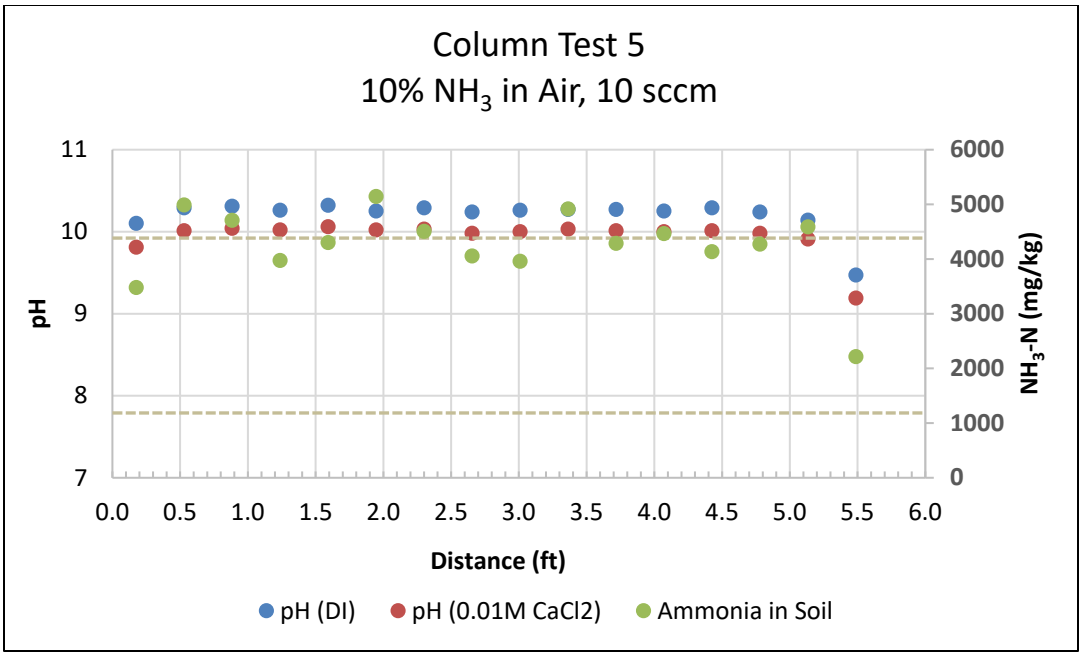

Figure 3.14. Soil pH in DI (Blue Marker) and CaCl2 (Red Marker) and Soil NH3-N (Green Marker) in Column 5 After Treatment with 10 % Ammonia Gas for 8 Days at 10 sccm.

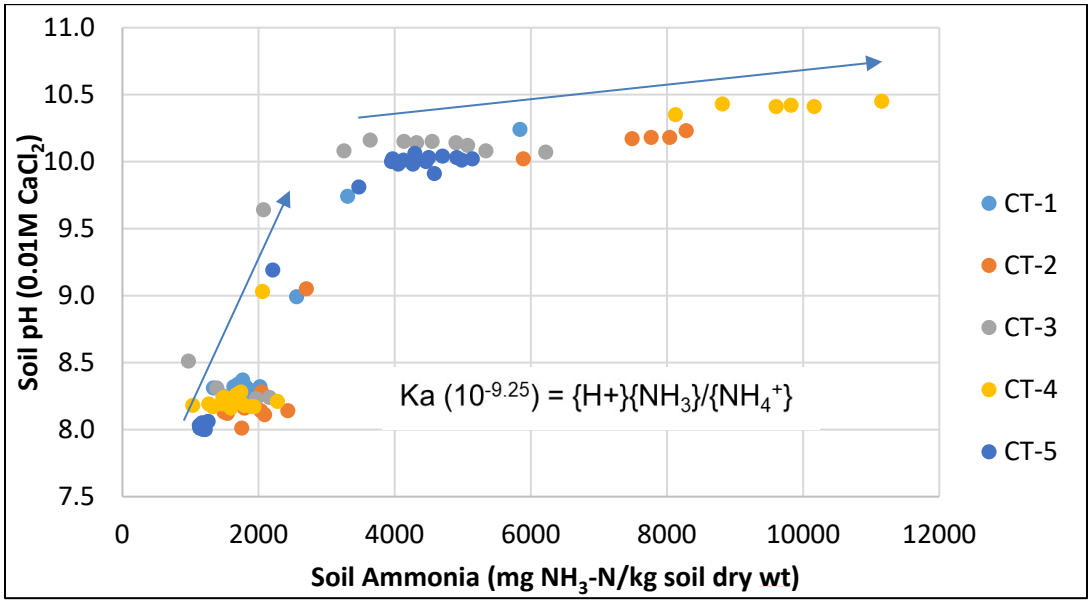

Figure 3.15. Comparison of Ammonia and pH in Soil Samples Collected from the Different Column Studies.

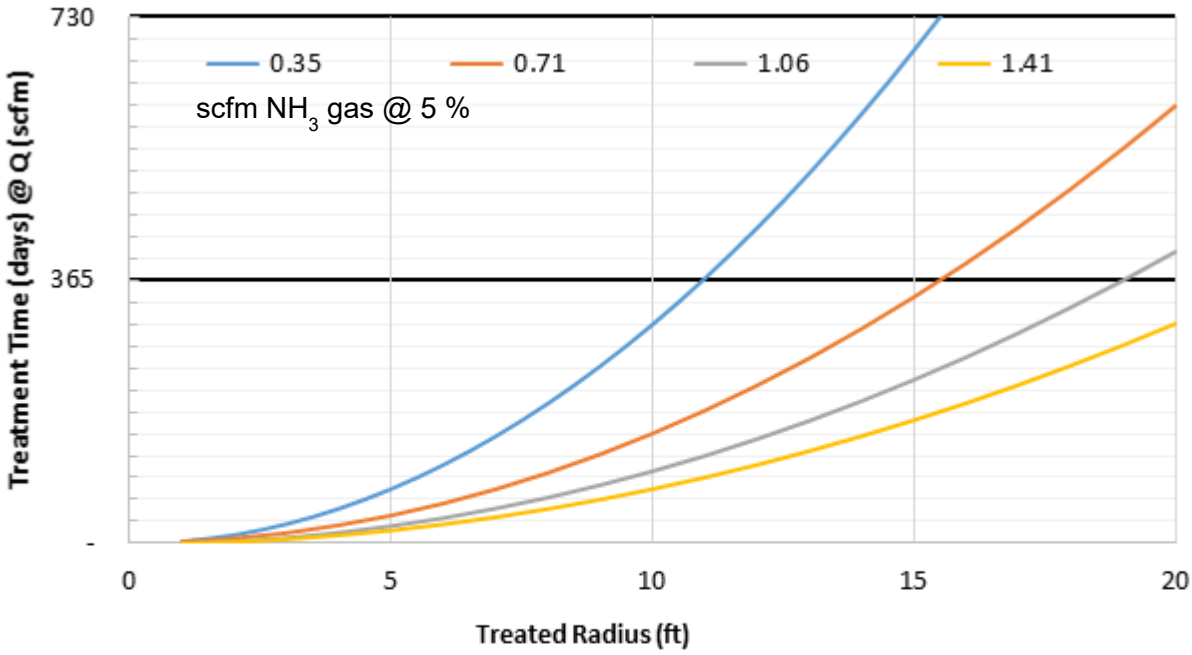

Figure 3.16. Modeled Treatment Time (y Axis) and Radius (x Axis) of B&B Soil Using 5% Ammonia Gas Applied at Different Flow Rates from 0.35 to 1.4 scfm.

3.3.3 Contaminated Soil Column Results

The homogenized soil core material was spiked with TCP, 1,2-DCP, 1,3-DCP and DBCP in a glove bag as described in **Section 3.2.2**. Baseline soil samples were collected for analysis after spiking and showed mean soil concentrations of 5,700 µg/L for TCP, 322,000 µg/L for 1,2-DCP, 1,600 µg/L for 1,3-DCP, and 20,000 µg/L for DBCP (**Figure 3.17**). Soil was rapidly packed into the same Kimble glass soil columns used for Column Tests 2-5 to minimize volatile losses. The "Treated Column" then received 5% NH_3 in air at a flow rate of 10 sccm for 15 days, after which time the soil was stored for ~30 days to provide additional time for hydrolysis of chlorinated propanes to occur. After this incubation period, samples were collected for analysis of chlorinated propanes, pH and total ammonia-N in the soil. A second "Control Column" was constructed with the same design except that it was supplied with nitrogen gas (N_2) (no NH_3) at 10 sccm for 15 days as a means to evaluate volatile rather than destructive losses of the contaminants. The soil was also incubated for an additional 30 days and then sampled as described for the Treated Column. Two adsorbent tubes were placed in series at the end of the Treated and Control Columns to quantify volatile losses of the contaminants. At the completion of the test, the adsorbent tubes were capped, taped, sealed in vials, and shipped for analysis of halogenated propanes as previously described.

The final pH and ammonia levels in the Treated Column and the Control Column as a function of distance in the column are provided in **Figure 3.18** and **Figure 3.19**, respectively. In the NH_3-treated column, the final soil pH was ~9.9 in samples extracted with $CaCl_2$ and 10.2 in those extracted with DI over the entire length of the soil column. Thus, the desired pH was achieved. Conversely, in the N_2-treated soil column, the soil pH was ~ 8.0 in samples extracted with $CaCl_2$ and 8.6 in those extracted with DI over the entire length of the soil column.

The concentrations of chlorinated propane contaminants along the length of the Treated and Control Columns are provided in **Figure 3.20**. Mass balances of the initial vs the final halogenated propanes detected in the Treated and Control Columns are provided in **Figures 3.21-3.24.** The data from the Treated Column indicated nearly a complete loss (99.6% – 100%) of the four different halogenated propanes added to the soil columns compared to the initial concentrations. However, the data from the Control Column shows a similar loss percentage for each of the compounds, ranging from 92.3% to 99.7%. Thus, the data indicate that the passage of gas (NH_3 or N_2) through the soil columns likely resulted in significant physical stripping/removal from the soil phase. Only a small percentage of the contaminants were trapped by the adsorbent tubes, so it was not possible to obtain a reasonable mass balance for any of the contaminants.

The nearly complete loss of the halogenated propanes in the column treated with N_2 gas for 15 days is problematic for the field implementation of this approach because the data suggest that it may not be possible to discern losses of these contaminants to hydrolysis from losses due to simple stripping from the soil phase. Modeling suggests that several months of NH_3 gas addition at 5% will be required to increase soil pH over a 10 – 15 ft radius from the gas injection wells in the field at relatively high flow rates (~ 10,000 to 30,000 sccm). Extrapolating from the column tests, this addition is likely to increase soil pH to > 10 over the treatment area as desired, but it is also likely to strip a high percentage of the chlorinated propanes in the process. Thus, the technology will most likely be effective at removing most of the contaminants from the ROI, but much of this removal may reflect volatilization rather than hydrolysis. At a minimum, the influence of the two processes would not be independently quantifiable.

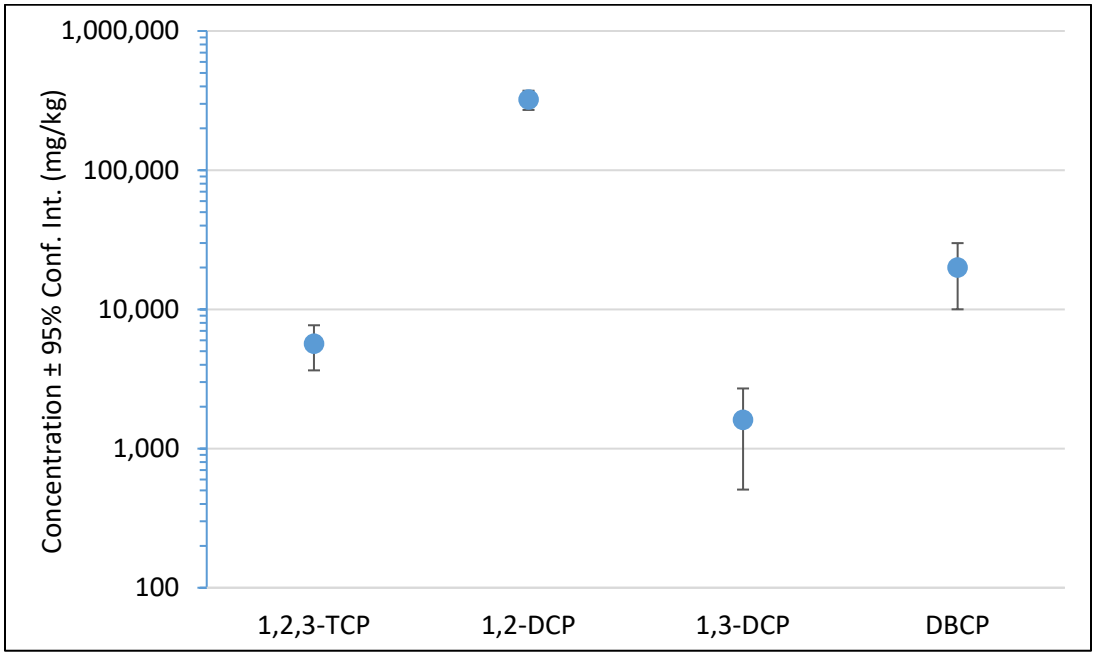

Figure 3.17. Starting Concentrations of Contaminants in the B&B Soil Used for the Contaminated Soil Column Studies.

Values reflect the mean ± 95% confidence interval from 6 samples collected during packing of columns.

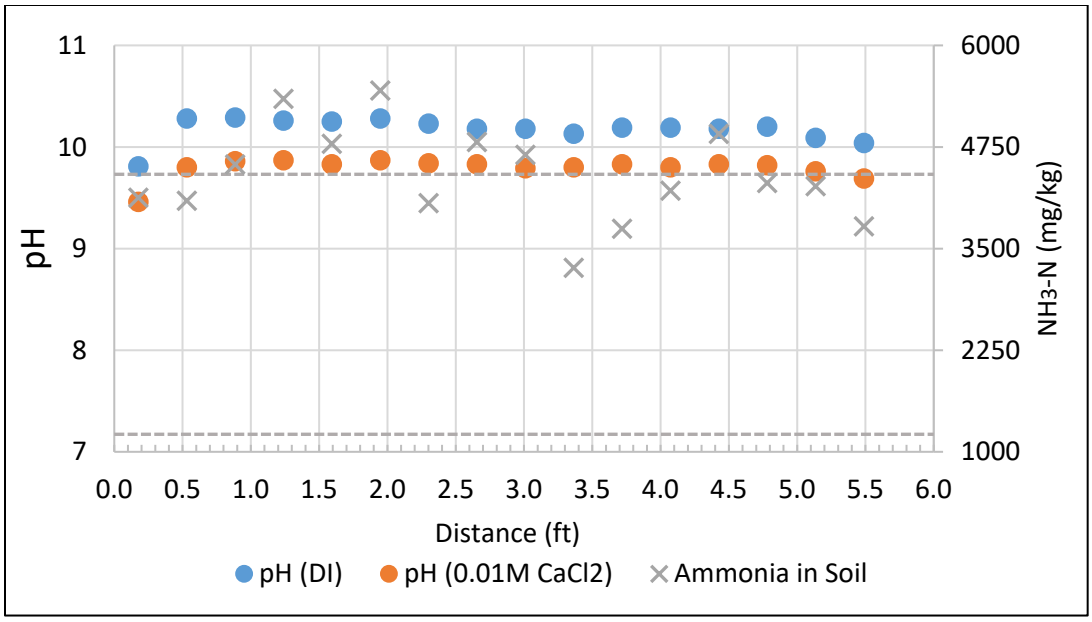

Figure 3.18. Soil pH in DI (Blue Marker), $CaCl_2$ (Red Marker) and Soil NH_3-N (Grey x) in the Treated Column After Application of 5% Ammonia Gas in Air for 15 Days at 10 sccm.

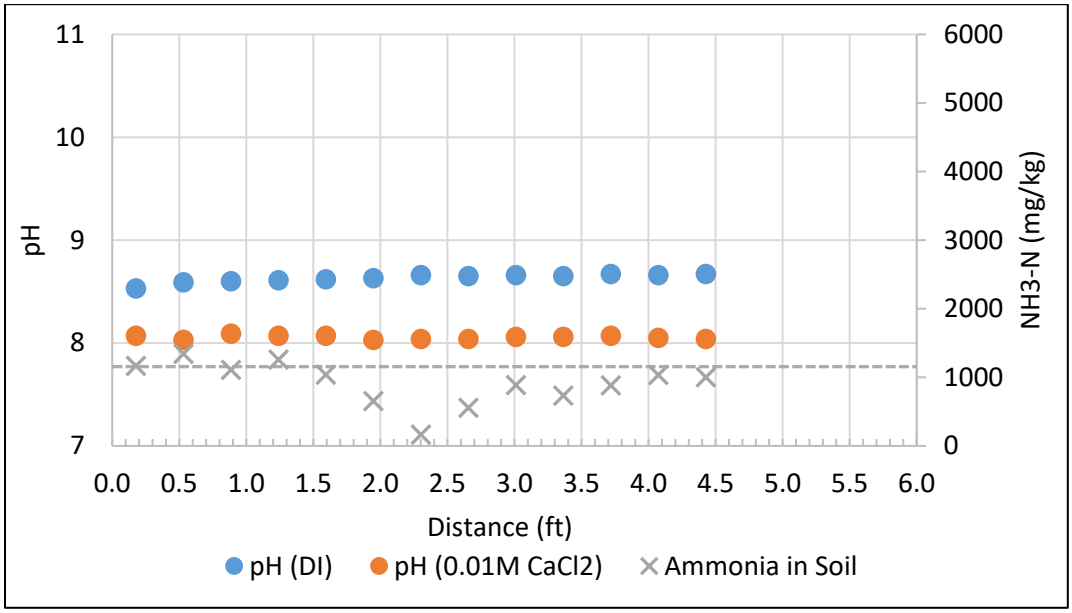

Figure 3.19. Soil pH in DI (Blue Marker), $CaCl_2$ (Red Marker) and Soil NH_3-N (Grey x) in the Created Column After Application of 100% Nitrogen Gas for 15 Days at 10 sccm.

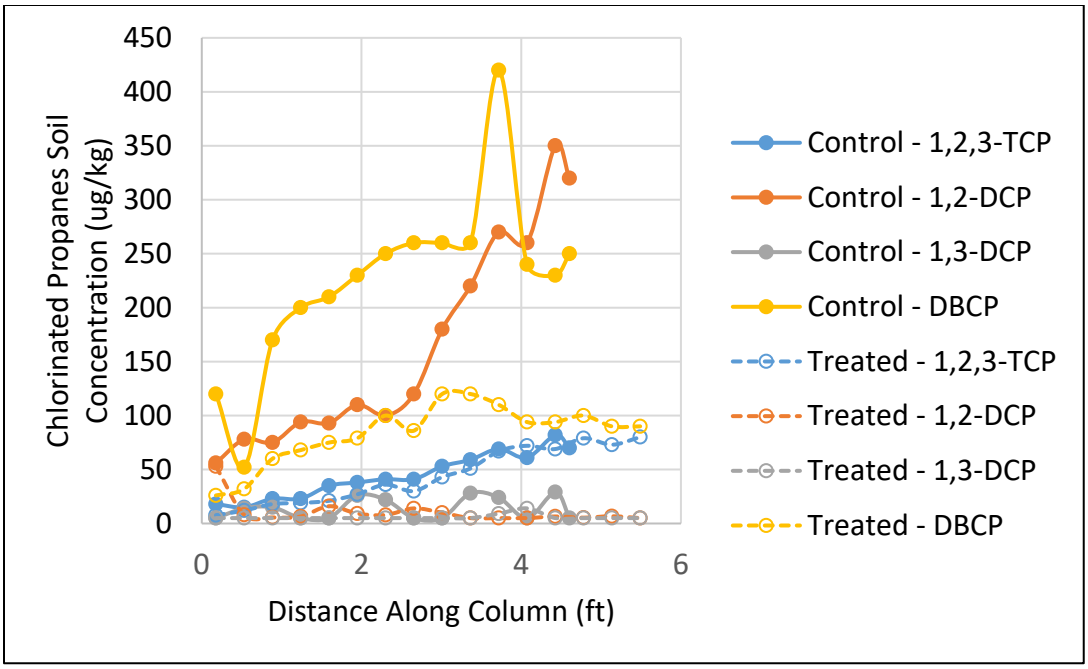

Figure 3.20. Final Concentrations of Halogenated Propane Contaminants in the Treated and Control Columns as a Function of Distance from the Inlet Port.

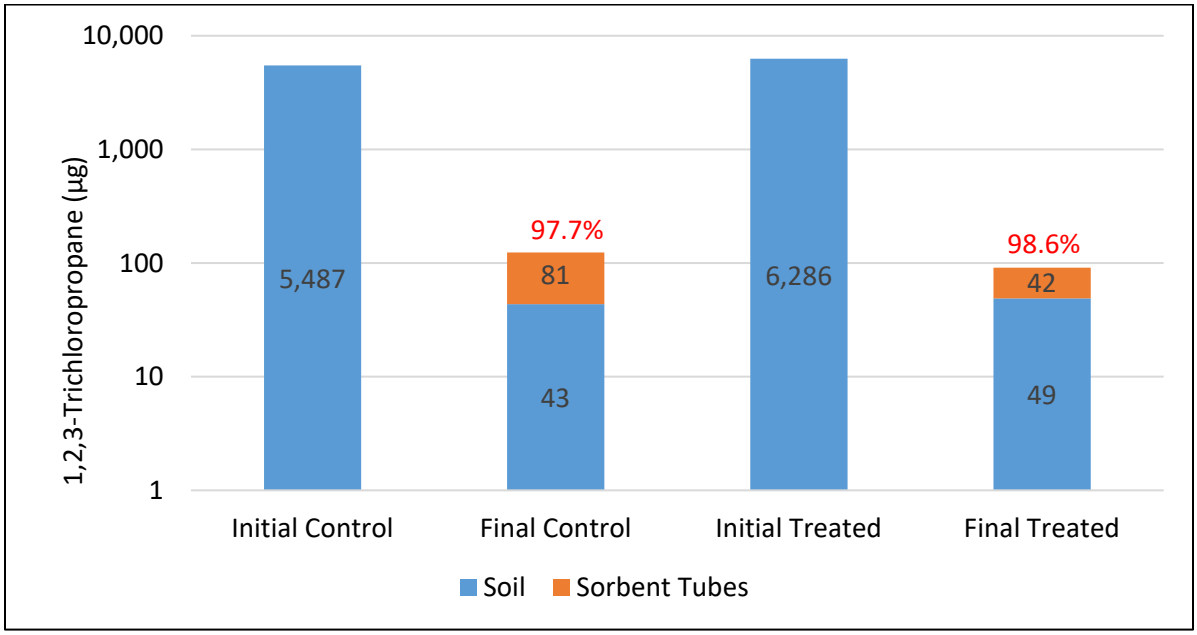

Figure 3.21. Initial and Final Quantities of TCP Measured in the Treated and Control Column Soils (Blue) and Quantity Detected in the Sorbent Tubes (Orange).

The number in red represents the percent reduction in the TCP from the pre-treatment (initial) to the post treatment (final) sample collection.

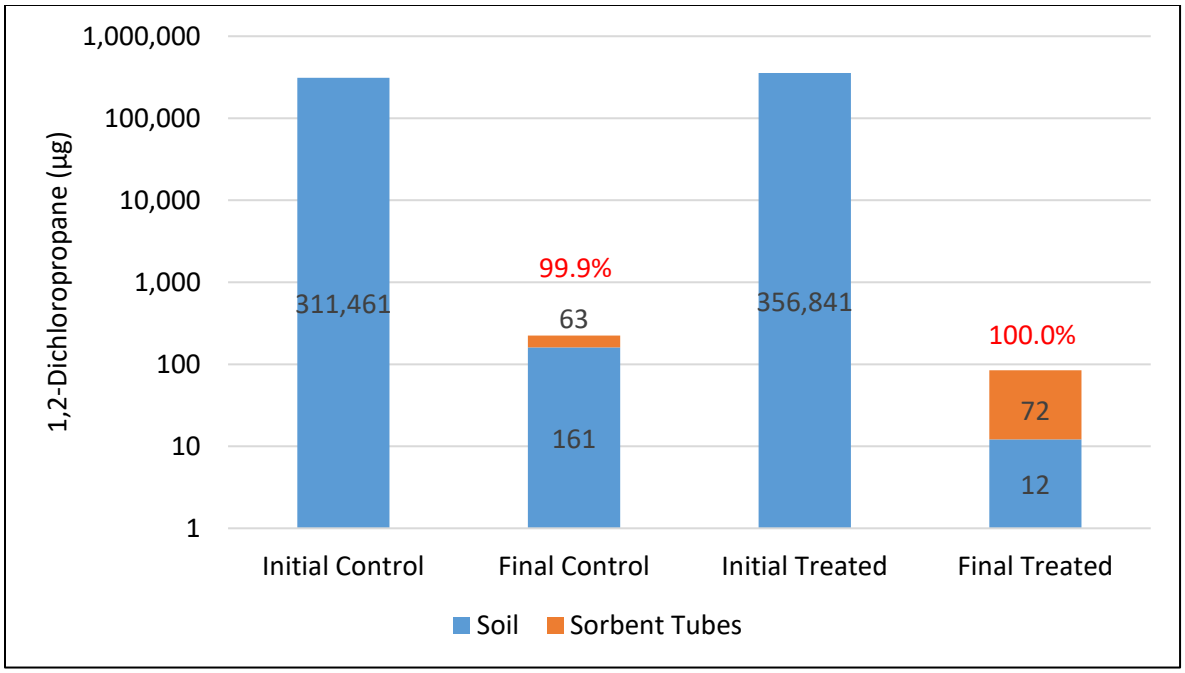

Figure 3.22. Initial and Final Quantities of 1,2-DCP Measured in the Treated and Control Column Soils (Blue) and Quantity Detected in the Sorbent Tubes (Orange).

The number in red represents the percent reduction in the TCP from the pre-treatment (initial) to the post treatment (final) sample collection.

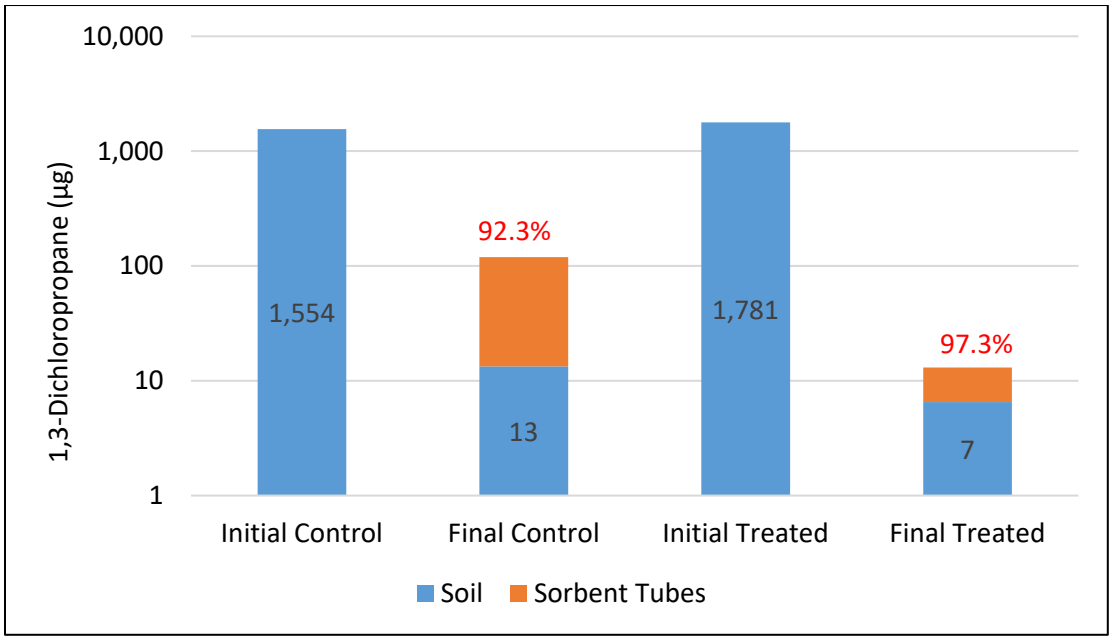

Figure 3.23. Initial and Final Quantities of 1,3-DCP Measured in the Treated and Control Column Soils (Blue) and Quantity Detected in the Sorbent Tubes (Orange).

The number in red represents the percent reduction in the TCP from the pre-treatment (initial) to the post treatment (final) sample collection.

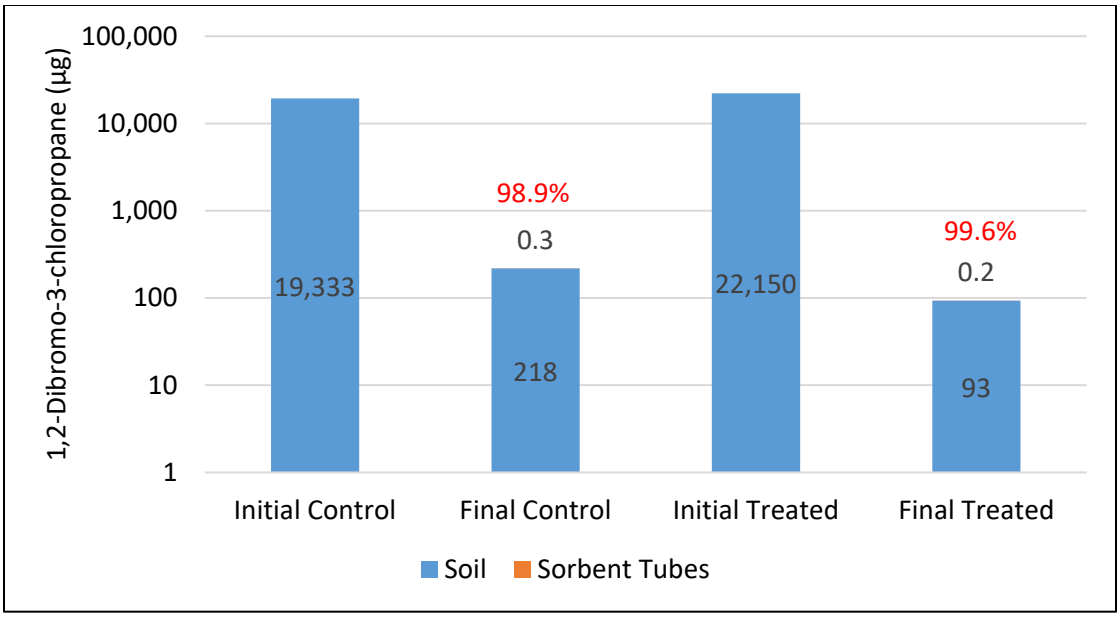

Figure 3.24. Initial and Final Quantities of DBCP Measured in the Treated and Control Column Soils (Blue) and Quantity Detected in the Sorbent Tubes (Orange).

The number in red represents the percent reduction in the TCP from the pre-treatment (initial) to the post treatment (final) sample collection.

3.3.4 Nitrification Microcosm Results

There was an initial increase in nitrite (from ~1 mg-N/kg to 10-12 mg-N/kg) in the soil microcosms that was not detected in the killed control samples (**Figure 3.25**). However, additional nitrite was not detected after this time, and concentrations actually decreased slightly over the 28-week study. Nitrate concentrations were between ~ 350 and 420 mg-N/kg soil in the B&B soils at the time of collection, which is exceedingly high (**Figure 3.26**). These concentrations increased in both the Live and Killed samples as well as the refrigerated Live samples over the course of the 28-week study to between 465 and 565 mg-N/kg soil, suggesting that either the production does not reflect biological nitrification or that the Killed samples were not adequately sterilized using formaldehyde. It is also possible that this increase merely reflects analytical error because the samples require very high dilution to measure the anions within the upper detection limit of the ion chromatograph.

Ammonia levels in the soil were initially ~2,500 mg-N/kg dry soil, and they initially dropped and then increased slightly over the 28-week study. The changes over time, which were similar in the samples incubated at 22ºC (room temperature) and those at 4ºC, and associated variability (see error bars in **Figure 3.27**) probably reflect analytical error, again due to the exceedingly high soil concentrations. The soil pH did not vary appreciably in the different treatments over the course of the study (**Figure 3.28**). The Live soils had an initial pH of ~ 8.7 (in DI water), and the formaldehyde-treated Killed samples were slightly lower at pH of ~ 7.1 to 7.2.

The initial objective of this study was to assess whether nitrification could be stimulated in B&B soils with the addition of different quantities of NH_3. The exceedingly high ammonia in the soil during baseline conditions (i.e., ~ 2,500 mg-N/kg soil) prevented the execution of the initial study as planned. Rather, we evaluated whether nitrification was ongoing in the soils under in situ conditions with the high ammonia present. The initial data, particularly the nitrite data (an intermediate product in nitrification), suggested the potential for activity, but nitrite only increased at the first sample time, and decreased thereafter. The high levels of nitrate evident in the soil (which may have resulted from nitrification of ammonia or discharge of nitrate-containing agricultural products) largely prevented an accurate assessment of the occurrence of nitrification.

Soil samples from the B&B Site were analyzed for AMO and ammonia oxidizing archaea (AOA) by Microbial Insights (Knoxville, TN). Samples from the microcosms as well as samples from other select soils from the B&B site were submitted for analysis (6 total). In general, both target genes/cells were below detection (PQL = 2×10^4 cells/g) in the site samples, with two samples showing "J" values for AMO at 6×10^2 cells/g and 4×10^3 cells/g – meaning that cells with AMO were detectable but below the practical quantitation limit (PQL). Thus, the data suggest that nitrifying bacteria are naturally present at very low densities in the B&B soils.

If appreciable nitrification activity had been observed over the 28-week study in the Live (but not the Killed) microcosms, soil samples were to be collected and reanalyzed for AMO and AOA to evaluate increases in the relevant organisms, and then the microcosms were to be spiked with TCP, 1,2-DCP, and 1,3-DCP to evaluate cometabolic biodegradation of the compounds. However, the microcosm data did not show definitive nitrification activity (other than the small initial increase in nitrite) when Live and Killed samples were compared, and the contaminated soil column results indicate that the gas addition process is likely to strip the halogenated propanes from the soil matrix, so the study was terminated at 28 weeks.

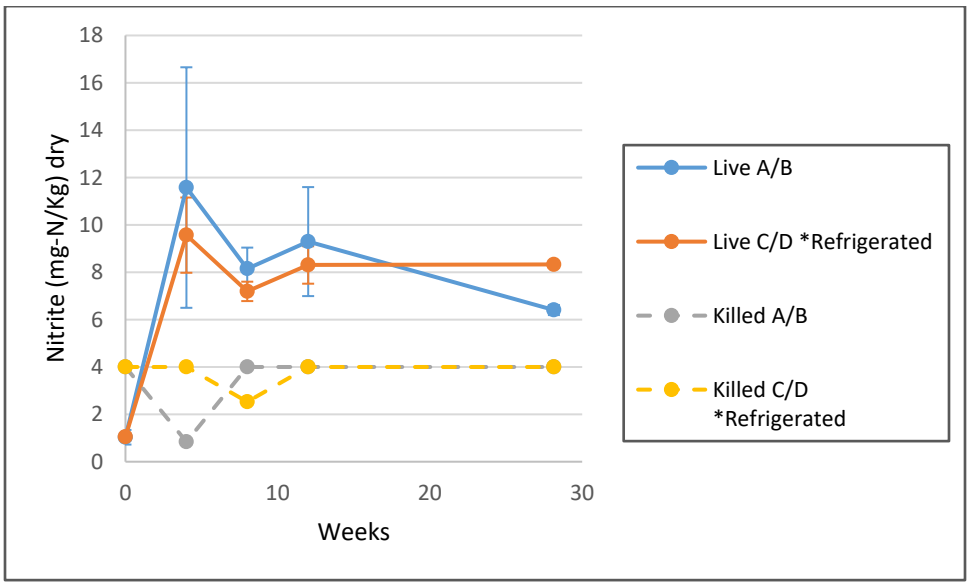

Figure 3.25. Nitrite (mg-N/kg soil) in Live and Killed soil microcosms from the B&B Site.

A subset of the Live microcosms were refrigerated at 4°C because it was determined that formaldehyde interfered with the analysis of ammonia in the soils.

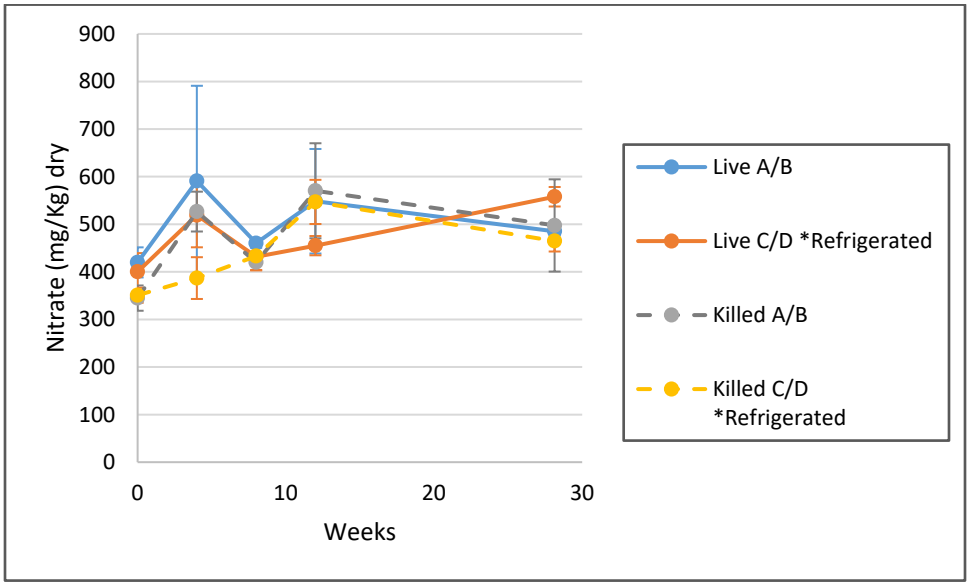

Figure 3.26. Nitrate (mg-N/kg Soil) in Live and Killed Soil Microcosms from the B&B Site.

A subset of the Live microcosms were refrigerated at 4°C because it was determined that formaldehyde interfered with the analysis of ammonia in the soils.

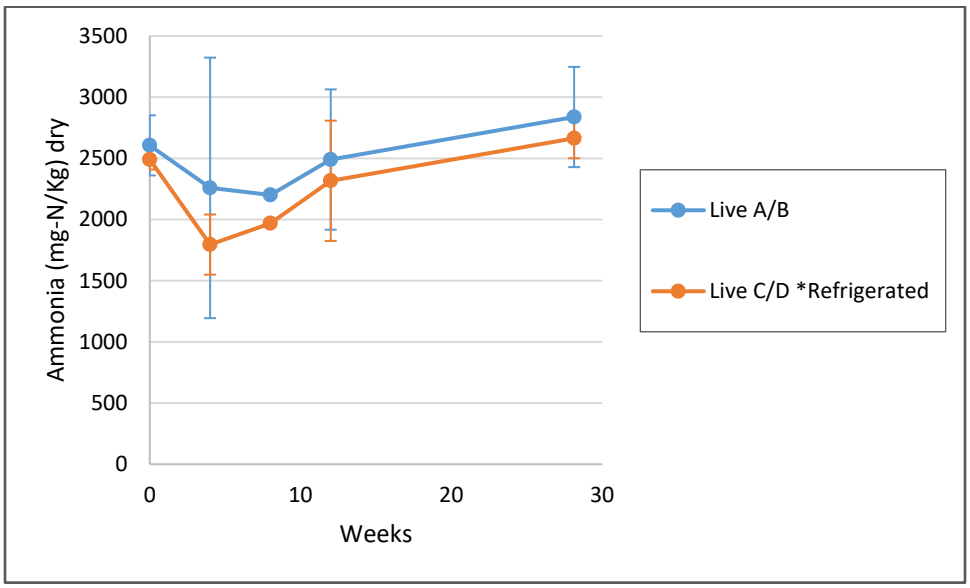

Figure 3.27. Ammonia (mg-N/kg soil) in Live Soil Microcosms from the B&B Site.

A subset of the Live microcosms were refrigerated at 4°C because it was determined that formaldehyde interfered with the analysis of ammonia in the soils

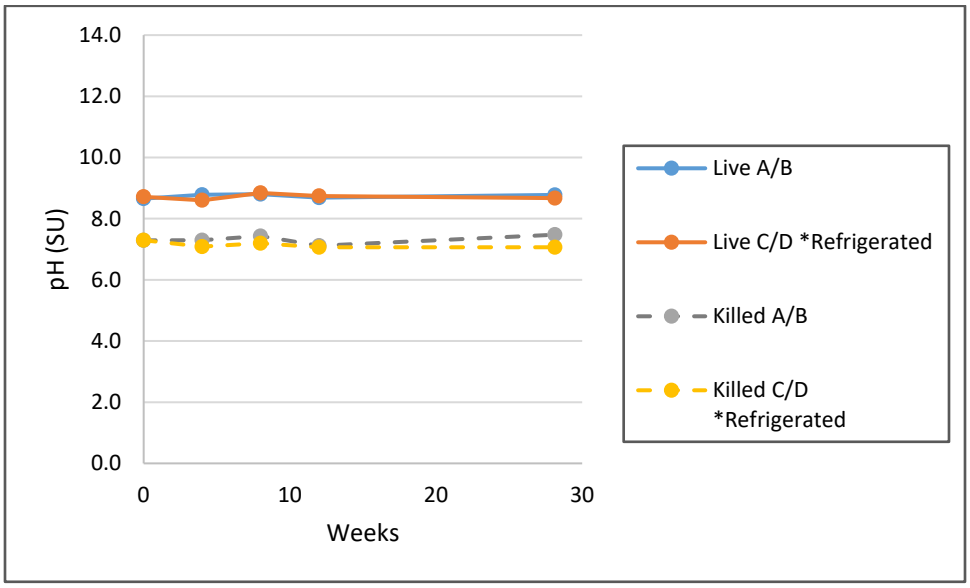

Figure 3.28. Soil pH in Microcosms from the B&B Site.

A subset of the Live microcosms were refrigerated at 4°C because it was determined that formaldehyde interfered with the analysis of ammonia in the soils

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4.0 GO/NO-GO DECISION

The treatability study data served as a basis for a Go-No/Go decision for the field implementation of this project. The key results influencing the Go-No/Go decision are as follows (1) ability to achieve a minimum pH of 10.0 in the soils during **Section 3.3.2** studies; (2) ability to achieve a 10 ft ROI of pH increase based upon **Section 3.3.2** studies at different gas flows and NH_4 concentrations combined with simulation of field scale application; and (3) ability to document at least 25% hydrolytic treatment of TCP in **Section 3.3.3** columns, with the understanding that the column studies will not be operated long enough to achieve the low percentages expected in the field, due to cost and scaling issues.

The initial two objectives determining the Go/No Go decision (achieving a soil pH of ≥10 and a predicted ROI or 10 ft in the field) were met based upon laboratory data and subsequent modeling. However, the third objective of documenting at least 25% hydrolytic treatment of TCP in soil columns was not achieved. The soil column studies showed a nearly complete removal of TCP and other relevant chlorinated propanes in the column that received NH_3 as well as that receiving an equivalent flow of N_2 only (non-reactive gas). As a result of the extensive apparent stripping of the contaminants from the soil, hydrolytic treatment of TCP or the other contaminants at 25% could not be documented. More importantly, the research team believes that the same issue would have occurred during field implementation of the technology at the B&B site. Thus, while the technology may be effective, it is unlikely that hydrolysis and stripping of the chlorinated propanes would be independently quantifiable in a field setting. Alternative methods for adding ammonia to the vadose soils at B&B were evaluated (e.g., passively adding higher concentrations of NH_3 to avoid stripping the chlorinated propanes), but because of the relatively low lower explosive limit (LEL) of ammonia gas, this could not be implemented because of safety concerns. As a result, the data from the treatability study suggest a No-Go decision is warranted for field implementation of this technology at the B&B Site. The entire project team at USACE and APTIM concurred on this decision.

It is feasible that the reactive gas approach could be very effective for promoting the alkaline hydrolysis of less volatile contaminants in the vadose zone, including many different traditional explosives (e.g., RDX and TNT) and newer insensitive munitions constituents (e.g., DNAN). In the absence of the high ammonia concentrations already present in the B&B vadose soils, it is also possible that this this approach could have been successfully implemented and validated because far less ammonia would theoretically be required to raise soil pH into the alkaline range required to catalyze hydrolysis of the chlorinated propanes. In this case, the effects of hydrolysis vs air-stripping of the contaminants may have been independently quantifiable. Thus, we believe that this novel treatment approach has merit, but that the conditions at the B&B Site were not ultimately conducive to its field testing and validation.

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5.0 MANAGEMENT AND STAFFING

Dr. Paul Hatzinger and Mr. Charles Coyle were the principal investigators (PIs) for this project and were responsible for the overall management of the laboratory studies, including analysis of data and preparation the Treatability Study Report at their conclusion. Mr. Scott Waisner directed the design and execution of the column studies at the ERDC laboratory, while Dr. Paul Koster van Groos oversaw the performance of the microcosm studies in APTIM's laboratory. Sample collection and soil core logging at the site were conducted by Mr. Graig Lavorgna from APTIM. The laboratory microcosm studies examining AMO activity were conducted by Ms. Rachael Rezes at APTIM.

A contact list for personnel working on this demonstration project is included as **Appendix A**.

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APPENDIX A POINTS OF CONTACT

POINT OF CONTACT Name	ORGANIZATION Name Address	CONTACT INFORMATION Phone E-mail	ROLE IN PROJECT
Paul B. Hatzinger, Ph.D.	Aptim Federal Services 17 Princess Road Lawrenceville, NJ 08648	609-895-5356 direct 267-337-4003 cell paul.hatzinger@aptim.com	Principal Investigator
Graig Lavorgna	Aptim Federal Services 17 Princess Road Lawrenceville, NJ 08648	609-895-5343 direct 908-309-7651 cell graig.lavorgna@aptim.com	Project Manager Project Engineer
Charles Coyle, P.E.	USACE - Huntsville Engineering and Support Center Environmental & Munitions CX 1616 Capitol Ave Suite 9200 Omaha, NE 68102-9200	402-697-2578 direct Charles.G.Coyle@usace.army.mil	Co-Principal Investigator
Scott Waisner, M.S.	USACE – ERDC 3909 Halls Ferry Road Vicksburg, MS 39180	601-634-2286 direct Scott.A.Waisner@usace.army.mil	Laboratory Study Design & Execution
Mandy Michalsen, Ph.D., P.E.	USACE – ERDC 3909 Halls Ferry Road Vicksburg, MS 39180	206-764-3324 direct mandy.m.michalsen@usace.army.mil	Project Oversight
Andrea Leeson, Ph.D.	SERDP/ESTCP 4800 Mark Center Drive, Suite 17D03 Alexandria, VA 22350-3605	703-696-2118 direct 703-696-2114 fax andrea.leeson@gmail.com	ESTCP Environmental Restoration Program Manager
Rose Marie Caraway, B.S., M.B.A	USEPA Region 9 Mail Code SFD 75 Hawthorne Street San Francisco, CA 94105	415-972-3158 direct Caraway.RoseMarie@epa.gov	USEPA Lead – Brown and Bryant Superfund Site

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APPENDIX B BORING LOGS AND SITE PHOTOGRAPHS

BORING LOG

Boring/Well ID: SB-30
Sheet: 1 **of** 3

Project No.: 500808
Client: USACE-ESTCP
Location: Brown & Bryant Superfund Site
Started: 5/15/2018
Ended: 5/15/2018

Drilling Co.: Cascade Drilling
Drill Rig Model: Geoprobe 8040DT
Driller: David Quezada
Drlling Method: Direct Push
Hole Diameter: 3.25 **(inches)**

Logged By: Carl J. Lind
Edited By: Carl J. Lind
Checked By:
Number:

▽ First Water: ft bgs on at hrs
▼ Static Water: ft bgs on at hrs

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
		0.0							Surface is 4-inch thick layer of asphaltic concrete.	
								SM	**SILTY SAND** ; brown (10YR 4/3); moist; mostly (60%) fine grained sand; some silty (40%) fines.	Cascade hand-augered from below the asphalt layer to 5-feet bgs to clear the boring location for utilities. Soil cuttings were collected in ZipLock bags for transport to USACE lab.
0915		0.0			5			SM	As above ; very dark grayish brown (10YR 3/2); moist.	
								SM	**SILTY SAND** ; dark brown (10YR 3/3); moist; mostly (75%) fine to medium grained sand; little silty (25%) fines; micaceous.	
		0.0			10			SW SM	Interbedded Silty Sand (SM) with Well Graded Sand with Silt (SW). Silty sand layers are 4 to 6-inches thick with mostly (60%) fine grained sand and some (40%) silty fines. Well graded sand layers are 1 to 2-inches thick of subangular to subrounded sand comprised of primarily quartz with some feldspar and few (10%) silty fines.	
		0.0			15			SW- SM	**WELL-GRADED SAND WITH SILT** ; light gray (10YR 7/2); dry; mostly (85 - 90%) fine to coarse grained sand; few silty (10 - 15%) fines; sand is primarily quartz with some feldspar.	
								SM	**SILTY SAND** ; yellowish brown (10YR 5/4); moist; mostly (55%) fine grained sand; few (45%) fines; micaceous.	Soil collected during the DPT drilling was removed from the borehole in 5-foot long 2-inch diameter acetate liners.
					20					

BORING LOG

Boring/Well ID: SB-30
Sheet: 2 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
0945		0.0						ML	**SILT** ; yellowish brown (10YR 5/4); moist; hard; mostly fines with low plasticity, low toughness, rapid dilatancy.	
								SP	**POORLY GRADED SAND** ; brown (10YR 5/3); dry; mostly (95%) medium grained sand; trace fines; sand is micaceous (biotite and muscovite?) with quartz, feldspar, and horneblend or biotite.	Soil not shipped to APPL was removed from the acetate liners and placed in ZipLock bags for shipment to USACE labs.
					25					
1000		7.8						SM CL	Yellowish brown (10YR 5/4); interbedded Silty Sand (SM) and Lean Clay (CL). Silty Sand (SM) is mostly (60%) fine grained micaceous sand with some (40%) silty fines. Clay (CL) has high toughness, medium plasticity, slow to no dilatancy, and thin (<1/2-inch thick) layers of reddish brown material (organics?).	
					30				As above ; at 30 to 35-feet bgs as at 25 to 30-feet bgs.	
		0.0								Samples of the soil were collected at discrete intervals by Terra-Core methods for analysis by APPL.
1020	SB-30-01 (32')	0.0								
					35					
1033	SB-30-02 (35')	0.0							As above ; at 35 to 39-feet bgs as at 25 to 30-feet bgs.	
1045	SB-30-03 (38')	0.0								
					40			SM CL	Grayish brown (2.5Y 5/2); dry to moist; hard; interbedded layers (3 to 4-inches thick) of Silty Sand (SM) and Lean Clay (CL). Silty sand as described above at 25 feet bgs. Clay has mottles of lighter gray.	Very hard drilling (pushing).
1123	SB-30-04 (40')	0.0								

BORING LOG

Boring/Well ID: SB-30
Sheet: 3 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL	RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
						45			CL	**LEAN CLAY** ; grayish brown (2.5Y 5/2); very hard; very hard clay, may be Lean Clay or Fat Clay. Layer has been described (by others) as being a 'caliche' layer, but no evidence of caliche was found. The layer is hard dense clay..	
										Boring was terminated at approximately 45 feet bgs.	
						50					
						55					
						60					
						65					

Project No.: 500808
Location: Brown & Bryant Superfund Site, Arvin, CA

Boring/Well ID: SB-30
Sheet: 3 **of** 3

APTIM SHORT LOG EPA_9.GPJ SHAWEI.GDT 5/23/18

BORING LOG

Boring/Well ID: SB-31
Sheet: 1 **of** 3

Project No.: 500808
Client: USACE-ESTCP
Location: Brown & Bryant Superfund Site
Started: 5/15/2018
Ended: 5/16/2018

Drilling Co.: Cascade Drilling
Drill Rig Model: Geoprobe 8040DT
Driller: David Quezada
Drlling Method: Direct Push
Hole Diameter: 3.25 **(inches)**

Logged By: Carl J. Lind
Edited By: Carl J. Lind
Checked By:
Number:

First Water: ft bgs on at hrs
Static Water: ft bgs on at hrs

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
1445		0.0							Asphaltic concrete.	Surface is 4-inch thick layer of asphaltic concrete.
								SM	**SILTY SAND**.	Cascade hand-augered from below the asphalt layer to 5-feet bgs to clear the boring location for utilities. Soil cuttings were collected in ZipLock bags for transport to USACE lab.
		0.0			5			SM	**SILTY SAND** ; dark yellowish brown (10YR 4/4); moist; mostly (60%) subangular to subrounded, fine to coarse grained sand; some silty (40%) fines.	Soft, or easy, drilling.
					10			SM		
1514		0.0						SW-SM	Interbedded Silty Sand (SM) with Well Graded Sand with Silt (SW-SM), dark yellowish brown (10YR 4/4). SIlty sand layers are 4 to 6-inches thick with mostly (60%) fine grained micaceous sand and some (40%) silty fines. Well graded sand with silt layers are 2 to 4-inches thick, mostly (85 to 90%) fine to coarse grained sand, with trace fine, sub-rounded gravel and few (10 to 15%) silty fines.	
					15					
1525		0.0						SW	**WELL-GRADED SAND** ; dark grayish brown (10YR 4/2); dry; loose; mostly (95%) fine to coarse grained sand.	
								SM	**SILTY SAND** ; grayish brown (10YR 5/2); medium dense; mostly (60%) fine grained sand; some silty (40%) fines; trace medium grained sand.	Soil collected during the DPT drilling was removed from the borehole in 5-foot long 2-inch diameter acetate liners.
					20					

BORING LOG

Boring/Well ID: SB-31
Sheet: 2 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
1530		0.0								
								SW-SM	**WELL-GRADED SAND WITH SILT** ; grades from Silty Sand (SM) at 20-feet bgs to Well Graded Sand with Silt (SW-SM) at about 22-feet bgs.	
								SP	**POORLY GRADED SAND** ; medium grained sand; grades from Well Graded Sand with Silt (SW-SM) at about 22-feet bgs to Poorly Graded Sand (SP) at 24-feet bgs.	Soil not shipped to APPL was removed from the acetate liners and placed in ZipLock bags for shipment to USACE labs.
					25					
1536		0.0						SM	**SILTY SAND** ; grayish brown (10YR 5/2); moist; medium dense; mostly (75 to 55%) fine grained sand; some silty (25 to 45%) fines. Grades from SIlty Sand (SM) with greater percentage of sand at 25.5 feet bgs to Silt with Sand (ML) at about 27 feet bgs.	
								ML	**SILT WITH SAND** ; brown (10YR 5/3); moist; hard; some (30%) fine grained sand; mostly (70%) fines; faint ammonia odor.	
								SM	**SILTY SAND** ; brown (10YR 5/3); moist; mostly (60%) fine grained sand; some silty (40%) fines.	
								ML	**SILT** ; brown (10YR 5/3); moist; hard; thin sand layers are Poorly Graded Sand (SP).	
					30					
1545	SB-31-01 (30')	0.0						SP	**POORLY GRADED SAND**.	
								ML	**SILT**.	Samples of the soil were collected at discrete intervals by Terra-Core methods for analysis by APPL.
								SP	**POORLY GRADED SAND**.	
								ML	**SILT**.	
1555	SB-31-02 (34')	0.0						SP	**POORLY GRADED SAND**.	
					35			ML	**SILT**.	
		0.0						SP-SM	**POORLY GRADED SAND WITH SILT** ; dark grayish brown (10YR 4/2); moist; medium dense; mostly (85 to 90%) fine grained sand; few silty (10 to 15%) fines; sand is predominately quartz, feldspar, biotite/hornblende.	
1610	SB-31-03 (37')	0.0						ML	**SANDY SILT** ; yellowish brown (10YR 5/4); moist; hard; little (20 to 30%) fine grained sand; mostly (70 to 80%) fines with no plasticity, low toughness, rapid dilatancy; micaeous.	
					40					
		0.0							As above.	
1650	SB-31-04 (42.5')							SW-	**WELL-GRADED SAND WITH SILT**.	

Project No.: 500808
Location: Brown & Bryant Superfund Site, Arvin, CA

Boring/Well ID: SB-31
Sheet: 2 **of** 3

BORING LOG

Boring/Well ID: SB-31
Sheet: 3 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL	RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
		0.0							SM	**SILT**.	
									ML		
									SM	**SILTY SAND**.	
1653	SB-31-05 (44')	0.0				45					Very hard drilling (pushing).
										Boring was terminated at approximately 45 feet bgs.	
						50					
						55					
						60					
						65					

Project No.: 500808
Location: Brown & Bryant Superfund Site, Arvin, CA

Boring/Well ID: SB-31
Sheet: 3 **of** 3

BORING LOG

Boring/Well ID: SB-32
Sheet: 1 **of** 3

Project No.: 500808
Client: USACE-ESTCP
Location: Brown & Bryant Superfund Site
Started: 5/16/2018
Ended: 5/16/2018

Drilling Co.: Cascade Drilling
Drill Rig Model: Geoprobe 8040DT
Driller: David Quezada
Drlling Method: Direct Push
Hole Diameter: 3.25 **(inches)**

Logged By: Carl J. Lind
Edited By: Carl J. Lind
Checked By:
Number:

First Water: ft bgs on at hrs
Static Water: ft bgs on at hrs

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
0915		0.0						SM	Aphaltic concrete.	
								SM	**SILTY SAND**.	Surface is 4-inch thick layer of asphaltic concrete.
					5					Cascade hand-augered from below the asphalt layer to 5-feet bgs to clear the boring location for utilities. Soil cuttings were collected in ZipLock bags for transport to USACE lab.
0940		0.0						SM	**SILTY SAND** ; dark yellowish brown (10YR 4/4); moist; mostly (60%) subrounded, fine to coarse grained sand; some silty (40%) fines.	
					10					
0947		0.0							As above ; with occasional 2 to 3-inch thick layers of Silty Sand (SM) that are mostly (70%) fine grained sand with some (30%) silty fines.	
								SW	**WELL-GRADED SAND** ; grayish brown (10YR 5/2); dry; loose; mostly (95%+) subrounded, fine to coarse grained sand; trace fines; sand is micaceous, sand grains are mostly medium grained, composition is primarily quartz, feldspar, and biotite or hornblende.	
					15					
0955		0.0						SM	**SILTY SAND** ; brown (10YR 4/3); moist; medium dense; mostly (60%) fine grained sand; some silty (40%) fines; ratio of sand to fines varies from 60:40% to 75:25%.	Soil collected during the DPT drilling was removed from the borehole in 5-foot long 2-inch diameter acetate liners.
					20					

BORING LOG

Boring/Well ID: SB-32
Sheet: 2 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
1000		0.0						SM	As above.	
					25			SP-SM	**POORLY GRADED SAND WITH SILT** ; dark grayish brown (10YR 4/2); dry; loose; mostly (85 to 90%) fine grained sand; few silty (10 to 15%) fines; micaceous.	Soil not shipped to APPL was removed from the acetate liners and placed in ZipLock bags for shipment to USACE labs.
1008		0.0						SM	**SILTY SAND** ; brown (10YR 4/3); moist; medium dense; mostly (60%) fine grained sand; some silty (40%) fines.	
								ML	**SILT** ; brown (10YR 4/3); moist; hard; no sand; mostly (100%) fines with low plasticity, low toughness, rapid dilatancy.	
					30			SP-SM	**POORLY GRADED SAND WITH SILT** ; dark grayish brown (10YR 4/2); mostly (85 to 90%) fine grained sand; few silty (10 to 15%) fines; micaceous.	
1018	SB-32-01 (30')	0.0						SP	Brown (10YR 4/3); moist; interbedded Poorly Graded Sand (SP) and Silty Sand (SM). Poorly graded sand is mostly (85 to 90%) fine grained micaceous sand, and few (10 to 15%) silty fines. Silty sand is mostly (60%) fine grained sand with some (40%) silty fines. Beds are 3 to 6-inches thick.	Samples of the soil were collected at discrete intervals by Terra-Core methods for analysis by APPL.
1031	SB-32-02 (32')	0.0						CL	**LEAN CLAY** ; brown (10YR 5/3); moist to wet; no sand; mostly (100%) fines with high plasticity, medium toughness, no to slow dilatancy; may have thin layers of sand.	
1034	SB-32-03 (35')	0.0			35					
1050	SB-32-04 (39.5')	0.0			40			SP	**POORLY GRADED SAND**.	
1058	SB-32-05 (45')	0.0						CL	**LEAN CLAY**.	
								SP	**POORLY GRADED SAND**.	
1104		0.0						ML	**SILT** ; olive brown (2.5Y 4/3) with light brownish gray (2.5Y 6/2); with low plasticity, low toughness, rapid dilatancy; lighter gray is mottled on darker (olive) gray at relative surface area percentages of about 25% light gray to 75% dark gray, micaceous.	

Project No.: 500808
Location: Brown & Bryant Superfund Site, Arvin, CA

Boring/Well ID: SB-32
Sheet: 2 **of** 3

BORING LOG

Boring/Well ID: SB-32
Sheet: 3 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL	RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
						45				**Boring was terminated at approximately 45 feet bgs.**	
						50					
						55					
						60					
						65					

Project No.: 500808
Location: Brown & Bryant Superfund Site, Arvin, CA

Boring/Well ID: SB-32
Sheet: 3 **of** 3

APTIM SHORT LOG EPA_9.GPJ SHAWEI.GDT 5/23/18

BORING LOG

Boring/Well ID: SB-33
Sheet: 1 **of** 3

Project No.: 500808
Client: USACE-ESTCP
Location: Brown & Bryant Superfund Site
Started: 5/16/2018
Ended: 5/17/2018

Drilling Co.: Cascade Drilling
Drill Rig Model: Geoprobe 8040DT
Driller: David Quezada
Drlling Method: Direct Push
Hole Diameter: 3.25 **(inches)**

Logged By: Carl J. Lind
Edited By: Carl J. Lind
Checked By:
Number:

First Water: ft bgs on at hrs
Static Water: ft bgs on at hrs

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
		0.0							Asphaltic concrete.	
								SM	**SILTY SAND** ; moist; mostly (60%) sand; some silty (40%) fines.	Surface is 4-inch thick layer of asphaltic concrete.
					5					Cascade hand-augered from below the asphalt layer to 5-feet bgs to clear the boring location for utilities. Soil cuttings were collected in ZipLock bags for transport to USACE lab.
1600		0.0						SM	**SILTY SAND** ; dark yellowish brown (10YR 4/6); dry to moist; medium dense; mostly (55%) fine to medium grained sand; some silty (45%) fines.	
					10					
1610		0.0						SM	**SILTY SAND** ; brown (10YR 5/3); dry; medium dense; mostly (65%) fine to coarse grained sand; some silty (35%) fines; interbedded with Well Graded Sand with Silt (SW-SM) light yellowish brown (10YR 6/4), dry, loose, mostly (85 to 90%) fine to coarse grained sand, few (10 to 15%) silty fines. Beds are approximately 6 to 8-inches thick.	
					15					
1615		0.0						SM	As above ; at 15 feet bgs as at 10 feet bgs.	
								SM	**SILTY SAND** ; brown (10YR 5/3); dry to moist; medium dense; mostly (65%) fine grained sand; some silty (35%) fines.	Soil collected during the DPT drilling was removed from the borehole in 5-foot long 2-inch diameter acetate liners.
					20					

BORING LOG

Boring/Well ID: SB-33
Sheet: 2 **of** 3

TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
1618		0.0						SM	As above ; at 20 feet bgs as at 17 feet bgs.	
								SP	**POORLY GRADED SAND** ; light gray (10YR 7/2); dry; loose; mostly (90 to 95%) medium grained sand; trace fines; trace coarse grained sand.	
					25			ML	**SILT**.	
1625	SB-33-01 (25')	0.0						SM	**SILTY SAND** ; light gray (10YR 7/2); dry; loose; mostly (65%) fine grained sand; some silty (35%) fines; micaceous.	Soil not shipped to APPL was removed from the acetate liners and placed in ZipLock bags for shipment to USACE labs.
	SB-33-02 (28.75')	0.0						ML	**SILT** ; yellowish brown (10YR 5/4); moist; hard; no sand; mostly (100%) fines with low plasticity, low toughness; laminated.	
					30			SW-SM	**WELL-GRADED SAND WITH SILT** ; light gray (10YR 7/2); dry; medium dense; mostly (85 to 90%) fine to coarse grained sand; few silty (10 to 15%) fines.	Samples of the soil were collected at discrete intervals by Terra-Core methods for analysis by APPL.
		0.0								
		1.9						CL	**LEAN CLAY** ; light olive brown (2.5Y 5/3) with light gray (2.5Y 7/2); no sand; mostly (100%) fines with medium to high plasticity, medium to high toughness, no to slow dilatancy; color is mottled with about 20% of surface area being light gray.	
								ML	**SILT** ; with low plasticity, low toughness; clay (CL) at 32 feet bgs grades to silt (ML) at about 33 feet bgs.	
	SB-33-03 (34.5')	1.7						SP	**POORLY GRADED SAND** ; light gray (10YR 7/2); mostly (90 to 95%) fine grained sand; few silty (5 to 10%) fines; micaceous.	
1700		1.9			35					
		1.2						ML	**SILT** ; yellowish brown (10YR 5/4); moist; hard; few (10%) fine grained sand; mostly (90%) fines with low plasticity, low toughness, rapid dilatancy.	
1715	SB-33-04 (37')	1.7								
		0.9		NR	40			ML	**SILT** ; grayish brown (2.5Y 5/2); dry; very hard; few (10 to 15%) medium to coarse grained sand; mostly (85 to 90%) fines with low plasticity, low toughness, rapid dilatancy; mottled with light gray being about 10 to 20% of surface area.	
1123										
								SM	**SILTY SAND**.	
1720	SB-33-05 (42')	1.1						ML	**SILT** ; grayish brown (2.5Y 5/2); dry; very hard; few (10 to 15%) medium to coarse grained sand; mostly (85 to 90%) fines with low	

BORING LOG

Boring/Well ID: SB-33
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TIME	SAMPLE NUMBER	PID (ppm) FID (ppm)	BLOWS (per 6 inch)	INTERVAL	RECOVERY	DEPTH (feet)	ELEVATION (feet msl)	GRAPHIC LOG	SOIL/ROCK SYMBOL	SOIL / ROCK DESCRIPTION	COMMENTS OR NOTES
										plasticity, low toughness, rapid dilatancy.	
						45				As above ; at 44 and 45 feet bgs vertical channels or grooves of clasts or gravel observed in cores.	
										Boring was terminated at approximately 45 feet bgs.	
						50					
						55					
						60					
						65					

Photo 1
Drilling crew setting up at a soil boring location.

Photo 2
APTIM geologist logging soil cores.

Photos 3&4
Typical soil cores collected at the B&B Site.