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Control Of Hydrogen Sulfide Emissionsusing Autotrophic Denitrificationlandfill Biocovers

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CONTROL OF HYDROGEN SULFIDE EMISSIONS USING AUTOTROPHIC DENITRIFICATION LANDFILL BIOCOVERS

by

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ABSTRACT

Hydrogen sulfide (H_2S), a major odorous component emitted from construction and demolition debris landfills, has received increasing attention. Besides its unpleasant odor, long-term exposure to a very low concentration of H_2S can cause a public health issue. Although cover materials such as soil and compost are recommended to be used routinely to control an odor problem from the landfills, the problem still remains. Autotrophic denitrification may have environmental applications including treatment of water, groundwater, wastewater or gaseous streams contaminated with sulfur and/or nitrogen compounds. However, there have been no studies reported in the literature on H_2S removal using autotrophic denitrification from landfills. This study, therefore, investigated the application of autotrophic denitrification incorporated into landfill covers in order to evaluate the feasibility of controlling H_2S emissions generated from landfills.

Research was investigated by two techniques, microcosm and laboratory-scale column studies. The microcosm experiments were conducted to evaluate the kinetics of autotrophic denitrification in various cover materials with H_2S-nitrate as electron donor-acceptor couple. Cover materials including soil, compost and sand were tested and nitrate was added. Based on the microcosm study results, the addition of nitrate into soil and compost can stimulate indigenous autotrophic denitrifying bacteria which are capable of H_2S oxidation biologically under anoxic conditions. Results also demonstrated that some amount of H_2S can be removed physically and chemically by soil or compost. There was no H_2S removal observed in sand microcosms. Rapid H_2S oxidation to sulfate was achieved, especially in soil. Zero-order kinetics described the H_2S oxidation rate in soil and compost microcosms. The rates of sulfide oxidation

under autotrophic denitrification in soil and compost were 2.57 mg H_2S/d-g dry soil and 0.17 mg H_2S/d-g dry compost, respectively.

To further explore H_2S removal in a landfill biocover, two sets of column experiments were run. The first set of columns contained seven cm of soil. The autotrophic column was prepared with 1.94 mg KNO_3/g dry soil; an identical control column was prepared without nitrate. A gas stream was introduced to the columns with a H_2S concentration of 930 ppm. The second set contained seven cm of soil, with both an autotrophic (0.499 mg KNO_3/g dry soil) and a control column. Influent H_2S concentration was 140 ppm for the second set. Column studies supported the results of microcosm studies; removal of H_2S was observed in all columns due to the capacity for soil to absorb H_2S, however autotrophic columns removed significantly more. The higher concentration of H_2S resulted in partial oxidation to elemental sulfur, while sulfate was found at levels predicted by stoichiometric relationships at the lower concentration. H_2S oxidation in the column with higher loading was found to follow zero-order kinetics. The rate of H_2S oxidation was 0.46 mg H_2S removed/d-g dry soil.

Economic comparison of cover systems including autotrophic denitrification, soil amended with lime, fine concrete, and compost covers were analyzed. Based on a case-study landfill area of 0.04 km^2, the estimated H_2S emissions of 80,900 kg over the 15-year period and costs of active cover system components (ammonium nitrate fertilizer, lime, concrete and compost), autotrophic denitrification cover was determined to be the most cost-effective method for controlling H_2S emissions from landfills.

To my family

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CHAPTER 1
INTRODUCTION

Background Information

Over the past several years, construction and demolition (C&D) debris landfills and landfills that have been using C&D residuals and fines as daily cover have received a large number of odor complaints from nearby residents (Townsend et al., 2000). These odor complaints are known to be associated with the emissions of hydrogen sulfide (H_2S) by an easily recognized smell of rotten eggs. The emission of H_2S from these facilities results from the biological degradation of gypsum ($CaSO_4 \cdot 2H_2O$) in drywall, a primary component of C&D debris. When the drywall comes in contact with water, sulfate and calcium are released into solution. Under anaerobic landfill conditions, a group of bacteria known as sulfate-reducing bacteria (SRB) utilize sulfate as an electron acceptor and produce H_2S as a byproduct (Reinhart et al., 2004). It has been reported that C&D debris can generate gas with H_2S concentrations as high as 20,000-30,000 ppm (Flynn, 1998). In Florida the concentrations of H_2S produced at C&D debris landfills were found to vary dramatically from landfill to landfill (Lee et al., 2006). H_2S concentrations in ambient air at the surface of the landfills ranged from below 3 ppb to greater than 50 ppm and H_2S concentrations in landfill gas ranged from below 3 ppb to 12,000 ppm.

People can smell H_2S at low levels in the air, ranging in concentrations from 0.0005 to 0.3 ppm (ATSDR, 2006). However, at high concentrations (100 ppm or above) a person may lose their ability to smell H_2S (ATSDR, 2006). Moreover, levels of H_2S above 1000 ppm in a breathing zone can rapidly lead to loss of consciousness and death (Bogner and Heguy, 2004).

These facts can make H_2S generated from landfills a major environmental and public health issue.

Collected gas from sulfur-containing waste can be treated effectively using physicochemical and biological processes such as activated carbon adsorption, chemical and biological scrubbing, ozone oxidation, incineration, air stripping, and biofiltration (Ferguson, 1975; Yang and Allen, 1994; Degorce-Dumas et al., 1997; Nishimura and Yoda, 1997). However, in the case of C&D landfills, where gas collection systems are not normally required, the generated H_2S is typically not controlled and the number of treatment processes to control H_2S emissions in-situ is limited. An attractive alternative may be to use chemically or biologically active landfill covers since landfill cover is usually required at C&D landfills to control litter, odors, and fires. A few studies using various types of cover materials to attenuate H_2S emissions have been done both at the laboratory (Plaza et al., 2006) and field (Xu, 2005) scale. The results demonstrated that H_2S emissions can be effectively reduced using compost, fine concrete, and lime-amended sandy soils as cover materials. The reduction of H_2S emissions was hypothesized to result from the biological oxidation in the compost pilot test or reaction with alkaline components of fine concrete and lime-amended sandy-soil producing sulfide minerals.

Another attractive alternative to control H_2S gas emissions produced from landfills is to incorporate a bioreactive layer into the design of a landfill cover. Under aerobic landfill cover conditions, considerable research has been performed using microbiological methane oxidation to mitigate methane emissions and trace gases from municipal solid waste (MSW) landfills (Hilger and Humer, 2003; Abichou et al., 2004; Barlaz et al., 2004; Huber-Humer and Lechner, 2005; Scheutz et al., 2005). Microbiological sulfur-oxidation under aerobic landfill cover

conditions to reduce H_2S produced from landfills could also be encouraged. Such mechanisms are well understood from the significant amount of research performed on H_2S gas removal using biofiltration (Yang and Allen, 1994; Chung et al., 1996; Degorce-Dumas et al., 1997; Cho et al., 2000; Morgan-Sagastume et al., 2003; Oyarzun et al., 2003).

Recently, autotrophic denitrification has been observed during nitrate removal in wastewaters containing high sulfur concentrations or reduced sulfur sources (Darbi et al., 2002; Oh et al., 2002; Lampe and Zhang, 2005; Wang et al., 2005). With this process, sulfur-oxidizing bacteria (SOB) such as *Thiobacillus denitrificans* and *Thiomicrospira denitrificans* can remove nitrate using an inorganic sulfur source such as H_2S, elemental sulfur (S^0), thiosulfate ($S_2O_3^{2}$) tetrathionate ($S_4O_6^{2-}$), and sulfite (SO_3^{2-}) as the electron donor while reducing nitrate to nitrogen gas. Elemental sulfur or reduced sulfur compounds are oxidized to produce sulfate (Lampe and Zhang, 2005; Onay and Pohland, 2001). In several recent studies, this process has been adopted for odor control in wastewater, oil fields, and the petrochemical industry (Telang et al., 1997; Jenneman et al., 1999; Vaiopoulou et al., 2005; Mathioudakis et al., 2006). The results have proved that the addition of nitrate as a terminal electron acceptor led to preferential autotrophic denitrification with sulfide as an electron donor. Additionally, in some studies (Onay and Pohland, 2001; Vigeron et al., 2006; and Berge et al., 2006) when nitrate was injected into reactors containing stabilized solid waste, autotrophic denitrification was observed, leading to sulfate production. However, there have been no studies reported in the literature on H_2S removal using autotrophic denitrification landfill biocovers. This study, therefore, has applied the concept of autotrophic denitrification in landfill covers in order to explore an alternative approach to control H_2S emissions from landfills.

From previous studies as mentioned above, it is hypothesized that utilizing the autotrophic denitrification process under anoxic landfill cover conditions by adding nitrate as an electron acceptor and using H_2S as an electron donor may create a barrier to minimize H_2S emissions and remove H_2S generated from landfills. This barrier may prove to have cost benefits when compared to other covers. This biocover could be created as simply as providing fertilizer and moisture addition through cover irrigation, therefore, this autotrophic denitrification landfill biocover may offer an attractive alternative to control emission of H_2S generated from landfills.

Research Objectives

The objectives of this research include:

1. Evaluate the capability of sand, soil, and compost as landfill cover materials to control H_2S emissions under autotrophic denitrification conditions and determine the kinetics of autotrophic denitrification with H_2S-nitrate as the electron donor-acceptor couple by using a microcosm technique.
2. Simulate an autotrophic landfill soil biocover and investigate the microbial activity involved in autotrophic denitrification landfill soil biocovers.
3. Evaluate the costs and benefits of an autotrophic denitrification landfill biocover and compare them to other H_2S control methods.

Dissertation Organization

This dissertation is organized in five chapters. Chapter 2 describes microcosm experiments conducted to evaluate the feasibility of using soil, compost and sand as landfill

cover materials for controlling H_2S emissions under autotrophic denitrification. Chapter 3 describes column experiments conducted to simulate an autotrophic denitrification landfill soil cover for controlling gaseous H_2S emitted. Chapter 4 presents cost-benefit comparisons of an autotrotrophic denitrificationn landfill cover to other H_2S control methods. Chapter 5 presents the conclusions and recommendation of this dissertation.

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CHAPTER 2
CONTROL OF H_2S EMISSIONS USING AUTOTROPHIC DENITRIFICATION LANDFILL BIOCOVERS: MICROCOSM STUDIES

Introduction

In recent years, hydrogen sulfide (H_2S) emissions from construction and demolition (C&D) debris landfills have received a high degree of attention due to odor and health complaints from people living near the landfills (Townsend et al., 2000). Among the many compounds emitted from these facilities, H_2S has been identified as a principal odorous component (Flynn, 1998; Lee et al., 2006). The emission of H_2S generated from these facilities has long been known to be a consequence of biological degradation of discarded drywall, a major C&D debris component. Drywall is composed of a core of gypsum ($CaSO_4 \cdot 2H_2O$) covered with paper facing and backing (Gypsum Association, 1992). When the drywall comes in contact with water, sulfate and calcium are released into solution. Under anaerobic landfill conditions, a group of bacteria known as sulfate-reducing bacteria (SRB) utilizes the sulfate as an electron acceptor and produces H_2S as a byproduct (Reinhart et al., 2004). It has been reported that C&D debris can generate gas with H_2S concentrations as high as 20,000-30,000 ppm (Flynn, 1998). Concentrations of H_2S produced at C&D debris landfills were found to vary dramatically from landfill to landfill by Lee et al. (2006) who reported that H_2S concentrations in ambient air at the landfill surface ranged from below 3 ppb to more than 50 ppm and H_2S concentrations in landfill gas ranged from below 3 ppb to 12,000 ppm.

H_2S has the characteristic odor of rotten eggs. People can smell H_2S at low levels in the air, ranging in concentration from 0.5 to 300 ppb. H_2S not only causes odor problems but also, at higher concentrations, may adversely affect human health following chronic and acute exposure. Prolonged exposure to relatively low concentrations of H_2S may affect memory, coordination, eyes and breathing. As concentrations increase beyond 100 ppm, a person may lose their ability to detect H_2S (ATSDR, 2006). Moreover, levels of H_2S above 1,000 ppm in a breathing zone can rapidly lead to loss of consciousness and death (Heguy and Bogner, 2005). These facts make H_2S generation from landfills a major environmental and public health issue.

Collected gas from sulfur-containing waste can be treated effectively using physicochemical and biological processes, e.g. activated carbon adsorption, chemical and biological scrubbing, ozone oxidation, incineration, air stripping, and biofiltration (Ferguson, 1975; Yang and Allen, 1994; Degorce-Dumas et al., 1997; Nishimura and Yoda, 1997). However, in the case of C&D landfills, where gas collection systems are not normally required, the generated H_2S is typically not controlled and the number of treatment processes to control H_2S emissions in-situ is limited. An attractive alternative may be to use chemically or biologically active landfill covers since landfill cover is usually required at C&D landfills to control litter, odors, and fires. A few studies using various types of cover materials to attenuate H_2S emissions have been done both at the laboratory (Plaza et al., 2006) and field (Xu, 2005) scale. The results demonstrated that H_2S emissions can be effectively reduced using compost, fine concrete, and lime-amended sandy soils as cover materials. The reduction of H_2S emissions was hypothesized to result from the biological oxidation in the compost pilot test or reaction with alkaline components of fine concrete and lime-amended sandy-soil producing sulfide minerals.

Another attractive alternative to control H_2S gas emissions produced from landfills is to incorporate a bioreactive layer into the design of a landfill cover. Under aerobic landfill cover conditions, considerable research has been performed using microbiological methane oxidation to mitigate methane emissions and trace gases from municipal solid waste (MSW) landfills (Hilger and Humer, 2003; Abichou et al., 2004; Barlaz et al., 2004; Huber-Humer, 2005; Scheutz et al., 2005). Microbiological sulfur-oxidation under aerobic landfill cover conditions to reduce H_2S produced from landfills could also be encouraged. Such mechanisms are well understood from the significant amount of research performed on H_2S gas removal using biofiltration (Yang and Allen, 1994; Chung et al., 1996; Degorce-Dumas et al., 1997; Cho et al., 2000; Morgan-Sagastume et al., 2003; Oyarzun et al., 2003).

Recently, autotrophic denitrification has been observed during nitrate removal in wastewaters containing high sulfur concentrations or reduced sulfur sources (Darbi et al., 2002; Oh et al., 2002; Lampe and Zhang, 2005; Wang et al., 2005). With this process, sulfur-oxidizing bacteria (SOB) such as *Thiobacillus denitrificans* and *Thiomicrospira denitrificans* can remove nitrate using an inorganic sulfur source such as H_2S, elemental sulfur (S^0), thiosulfate ($S_2O_3^{2}$) tetrathionate ($S_4O_6^{2-}$), and sulfite (SO_3^{2-}) as the electron donor while reducing nitrate to nitrogen gas. Elemental sulfur or reduced sulfur compounds are oxidized to produce sulfate (Lampe and Zhang, 2005; Onay and Pohland, 2001). In several recent studies, this process has been adopted for odor control in wastewater, oil fields, and the petrochemical industry (Telang et al., 1997; Jenneman et al., 1999; Vaiopoulou et al., 2005; Mathioudakis et al., 2006). The results have proven that the addition of nitrate as a terminal electron acceptor led to preferential autotrophic denitrification with sulfide as an electron donor. Additionally, in some studies (Onay and

Pohland, 2001; Vigeron et al., 2006; and Berge et al., 2006) when nitrate was injected into reactors containing stabilized solid waste, autotrophic denitrification was observed, leading to sulfate production. However, there have been no studies reported in the literature on H_2S removal using autotrophic denitrification landfill biocovers. This study, therefore, has applied the concept of autotrophic denitrification in landfill covers in order to offer a promising alternative approach to control H_2S emissions from landfills. Autotrophic denitrification involved with H_2S removal can be described by Equation 2-1:

$$H_2S + 1.6NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} SO_4^{2-} + 0.8N_2 + 0.8H_2O + 0.4H^+ \qquad (2\text{-}1)$$

The objectives of the present study were to evaluate the capability of sand, soil, and compost as landfill cover materials to control H_2S emissions under autotrophic denitrification conditions and determine the kinetics of autotrophic denitrification with H_2S-nitrate as the electron donor-acceptor couple. A microcosm technique was used to prove the concept of autotrophic denitrification in landfill biocovers. Microcosms allowed experimental control of the process even if they did not simulate the normally unsaturated cover system.

Experimental Materials and Methods

Cover Materials Used

Three types of cover materials were investigated in this experiment: sand, soil, and compost. Concrete, sand and topsoil (soil blended with woodchips) were purchased in Orange County, Florida, USA. Compost was obtained from a yard waste composting facility located in

Orange County, Florida, USA. Soil and compost used in this investigation were prepared by passing through a no. 10 sieve (2-mm opening). Sand (particle size less than 2 mm) was used as received.

Microcosm Operation

Three sets of microcosm experiments containing sand, soil, and compost were conducted in 285-mL graduated glass serum bottles (Wheaton®). In order to demonstrate the reproducibility of the data, two replicate tests were conducted in each set of microcosm experiments. Each test was carried out using a series of duplicate microcosm bottles sacrificed each day of the test. Each set of microcosm experiments included autotrophic denitrification microcosms (supplemented with stock KNO_3), abiotic control microcosms (prepared with autoclaved cover material), and biotic control microcosms (without KNO_3).

Microcosms were loaded with each cover material and supplemented with basal mineral nutrients, nitrate (as KNO_3), and sulfide (as $Na_2S{\cdot}9H_2O$), then pH was adjusted to ~ 7.0 using 1M HCl. According to the simplified stoichiometry of anoxic H_2S oxidation (Equation 2-1), the theoretical molar ratio of H_2S to nitrate is 1:1.6. In order to fully oxidize H_2S, nitrate was added in excess to microcosms. The composition of basal mineral nutrients modified from Cardoso (2006) is given in Table 2-1. The trace element solution contained (g/L) EDTA (0.5), $ZnSO_4{\cdot}7H_2O$ (0.04), $CaCl_2$ (0.05), $MnCl_2$ (0.05), $CoCl_2$ (0.02), $CuSO_4$ (0.02), and $(NH_4)_2MoO_4$ (0.01), adjusted to pH ~ 6.0 using 2M NaOH. Detailed composition for each set of microcosms is shown in Table 2-2.

Table 2-1. Composition of basal mineral nutrients used for microcosm studies.

Component	Amount
NH_4Cl (g/L)	0.1
KH_2PO_4 (g/L)	0.05
$NaHCO_3$ (g/L)	2.0
Trace element solution (mL)	0.5

Table 2-2. Microcosm composition.

Parameter	Sand microcosm	Soil microcosm	Compost microcosm
Amount of cover material used (g)	10	3	5
Initial concentration of sulfide (mM)	0.5	1.4	0.7
Initial concentration of NO_3^--N (mM)*	1.4	4	1.9
Volume of stock KNO_3 used (mL)*	20	20	20
Volume of stock $Na_2S{\cdot}9H_2O$ used (mL)	5	8	6
Volume of basal mineral nutrients used (mL)	248	246	246
Volume of 1M HCl used (mL)	2	2	2
Final volume, excluding cover material volume (mL)	275	276	274

* Not used in biotic control

Solutions of stock KNO_3, basal mineral nutrients and 1M HCl were prepared separately and flushed with oxygen-free nitrogen gas for 24 hr. Solutions of basal mineral nutrients, stock KNO_3, and 1M HCl were dispensed into serum bottles containing cover material as stated in Table 2-2. Head-space in bottles was limited to minimize loss of H_2S to volatilization. Prior to capping, the headspace was flushed with oxygen-free nitrogen for two minutes. After flushing, the serum bottles were capped immediately using butyl rubber stoppers and aluminum crimp seals. Prior to the injection of stock $Na_2S{\cdot}9H_2O$ prepared using deaerated reagent water, a needle was inserted through the butyl rubber stopper in order to release pressure while injecting stock $Na_2S{\cdot}9H_2O$. The needle was removed after injecting reagents. The serum bottles were mildly shaken by hand to insure that all components contained in serum bottles were well distributed.

Blank (no cover material) microcosms were also included to correct for compound losses associated with the preparation process. Microcosms were shaken at a speed of 100 rpm in a rotary shaker in an inverted position to minimize H_2S loss. The microcosm experiments were carried out at room temperature (22°C).

In each set of microcosm experiments, abiotic controls were run in parallel under the same environmental conditions as previously described with the exception that the controls contained cover material that had been autoclaved at 120°C for two hours to inhibit biological activity. Controls functioned to evaluate whether the changes in H_2S concentration could be attributed to physical or chemical processes. Biotic controls without stock KNO_3 were also prepared under the same environmental conditions as previously described to evaluate H_2S losses not associated with autotrophic denitrification.

Each set of microcosm experiments consisted of multiple serum bottles operated in a batch mode. Each day serum bottles were sacrificed and liquid samples were withdrawn to monitor the disappearance of sulfide and nitrate and the production of sulfate. Sulfide was analyzed immediately to prevent compound losses by volatilization and/or abiotic oxidation; pH was also determined immediately. Samples for nitrate and sulfate determination were membrane filtered (0.45 μm) and stored without headspace.

Analytical Methods

Physical and chemical characteristics of sand, soil and compost were determined using standard methods for soil analysis (Klute, 1986; Page, 1982). The pH of cover materials was measured in a cover material-water suspension (10 g cover material to 25 mL distilled water) using a Research AR-25 pH/ISE/mV meter (Fisher Scientific, Inc) and combination junction pH gel filled electrode (Fisher Scientific, Inc) with an automatic temperature control probe. Moisture content was determined gravimetrically by oven-drying at 105°C for 24 h and expressed as the mass ratio of water to wet cover material. Organic carbon was determined by measuring weight loss in cover material samples after burning at 450-550°C. Bulk density was determined by oven-drying the cover material sample of known volume at 105°C for 48 hrs then dividing the weight of the dried cover material by the volume. Particle density was determined by measuring the oven-dried weight of cover material and the volume of cover material (excluding pore space) measured by the volume of water displaced by the cover material. These physical and chemical characteristics are summarized in Table 2-3.

Table 2-3. Characteristics of sand, soil and compost used in microcosms.

Physical and chemical characteristics	Unit	Sand (As received)	Soil (< 2-mm)	Compost (< 2-mm)
pH (1:2.5 soil to water ratio)	-	5.35	7.78	8.50
Water content, wet basis	%	0	32.8	56.7
Organic content, dry basis	%	0.133	18.5	29.8
Bulk density	g/mL	1.6	0.51	0.34
Particle density	g/mL	2.6	2.3	2.2

H_2S analysis measured total sulfide as total H_2S and does not differentiate among the sulfide species. The concentration of sulfide was determined using the ion-selective electrode

method found in Standard Methods (1995). Nitrate and sulfate were determined using a DX-120 ion chromatography (IC, Dionex, Inc) equipped with an AS-14 column and a 0.002-M sodium bicarbonate/0.008 M sodium carbonate eluent. The pH was measured immediately after sampling using a Research AR-25 pH/ISE/mV meter (Fisher Scientific, Inc) and combination junction pH gel filled electrode (Fisher Scientific, Inc) with an automatic temperature control probe. Description of quality assurance and quality control (QA/QC) plan is provided in Appendix A.

Results and Discussion

Appendix A provides experimental data for all microcosm experiments. Each set of microcosm experiments included blank (no cover material) microcosms which confirmed that there was no H_2S loss during the preparation process. Described below are results of soil, compost, and sand microcosm experiments.

H_2S Removal in Soil Microcosms

The disappearance of hydrogen sulfide and nitrate and the formation of sulfate as a function of time for soil microcosms are depicted in Figure 2-1. The soil microcosms had an initial hydrogen sulfide concentration of 1.4 mM. Hydrogen sulfide was removed rapidly in nitrate-added microcosms (Figure 2-1a). Hydrogen sulfide was totally removed by Day 4 while nitrate gradually declined and sulfate gradually formed. At the end of the experiment (Day 10), the sulfate concentration increased by 1.4 and 1.2 mM in series 1 and 2, respectively while the hydrogen sulfide decreased by 1.4 mM, consistent with hydrogen sulfide oxidation. At the time

that hydrogen sulfide was totally consumed (Day 4), the liquid appeared to be cloudy (Figure 2-2), suggesting partial oxidation of hydrogen sulfide to elemental sulfur in colloidal form. This was supported by the observation that stoichiometrically not all of the hydrogen sulfide had been converted to sulfate by the end of Day 4 (Figure 2-1a). The increase in pH (Figure 2-1a) on Day 4 also suggested that partial oxidation of hydrogen sulfide had occurred, since OH^- is released according to Equation 2-2:

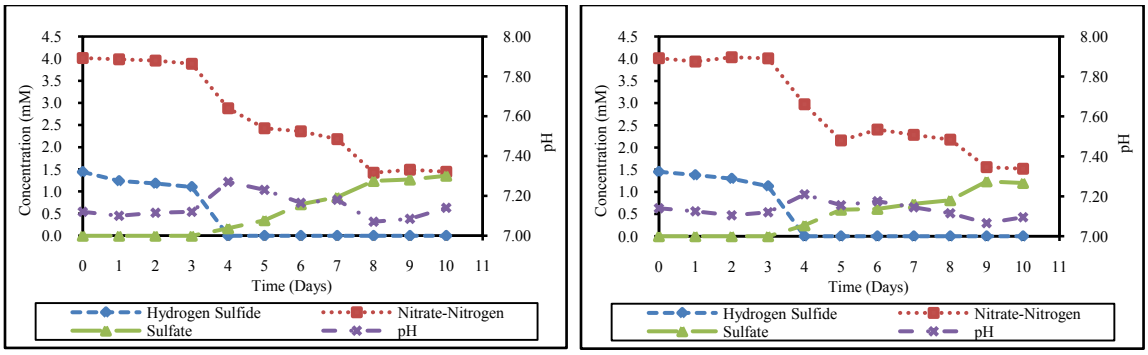
$$H_2S + 0.4NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} S^0 + 0.2N_2 + 0.8H_2O + 0.4OH^- \quad (2\text{-}2)$$

Elemental sulfur was frequently observed as an intermediate product of sulfide oxidation under denitrifying conditions (Krishnakumar and Manilal, 1999; Cardoso et al., 2006; Tang, 2008). It is possible that two steps are involved in H_2S oxidation. First, H_2S is oxidized to sulfur (Equation 2-2). Second, sulfur is oxidized to sulfate if there is excess nitrate (Equation 2-3). The overall biological reaction is described in Equation 2-1.

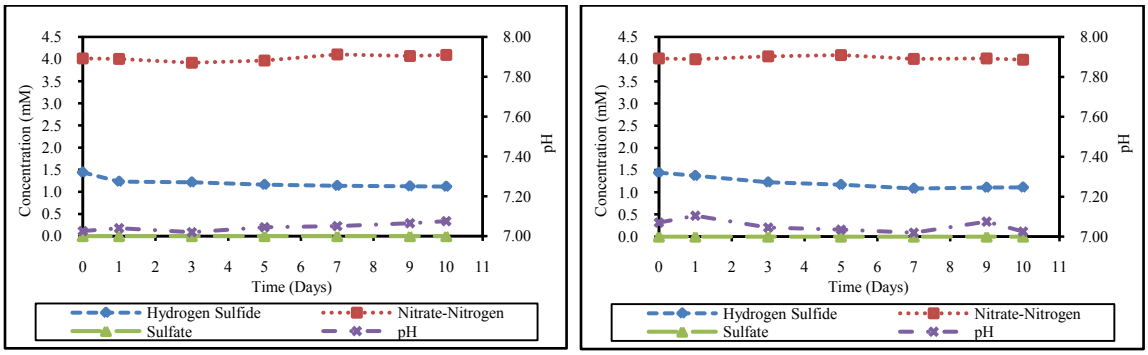
$$S^0 + 1.2NO_3^- + 0.4H_2O \xrightarrow{\text{Autotrophic denitrifiers}} 0.6N_2 + SO_4^{2-} + 0.8H^+ \quad (2\text{-}3)$$

According to the stoichiometric ratios shown in Table 2-4, it is likely that early on H_2S was removed by both sorption and oxidation, however, not completely oxidized to sulfate as suggested by a $\Delta H_2S:\Delta SO_4^{2-}$ ratio greater than 1 and $\Delta NO_3^-:\Delta H_2S$ ratio less than 1.6. By the end of the experiment, the ratios of $\Delta NO_3^-:\Delta H_2S$ and $\Delta NO_3^-:\Delta SO_4^{2-}$ were both greater than 1.6. This may be due to heterotrophic denitrification, since the soil contained organic matter and decomposing biomass which could serve as electron donor for nitrate reduction. The ratio of $\Delta H_2S:\Delta SO_4^{2-}$ in series 1 was near stoichiometry, suggesting complete oxidation of H_2S to sulfate,

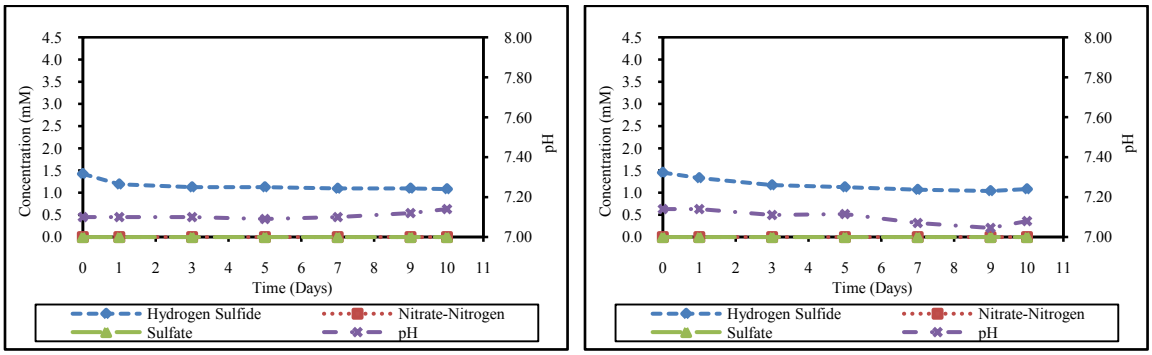
while the ratio of $\Delta H_2S:\Delta SO_4^{2-}$ in series 2 was greater than 1, suggesting incomplete oxidation of H_2S.



a. Autotrophic denitrification microcosms (supplemented with nitrate)



b. Abiotic control microcosms



c. Biotic control microcosms

Figure 2-1. Chemical analyses of soil microcosms (replicate experiments shown, the plotted values are the means obtained from duplicate microcosms).

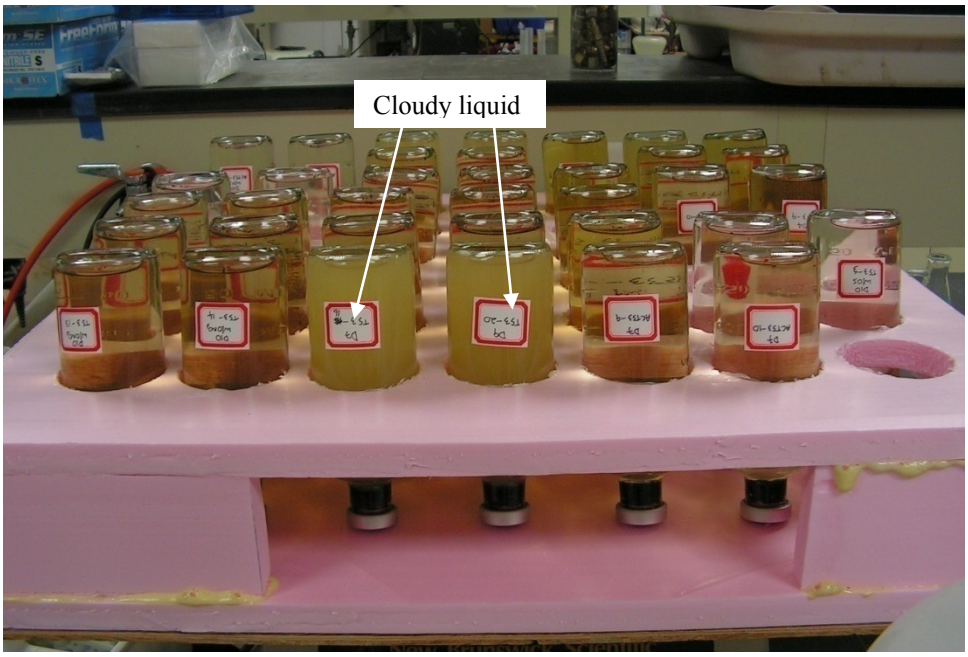


Figure 2-2. Cloudy liquid appeared in soil microcosms treated with nitrate addition.

Table 2-4. Stoichiometry in soil microcosms treated with nitrate addition (mM:mM).

Time (Days)	Series 1			Series 2		
	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$
4	8.58	0.79	6.77	5.91	0.71	4.22
5	4.11	1.10	4.53	2.43	0.28	3.11
6	2.02	1.15	2.33	2.36	1.11	2.61
7	1.65	1.27	2.10	1.98	1.19	2.36
8	1.16	1.80	2.10	1.79	1.26	2.27
9	1.14	1.75	1.99	1.18	1.69	1.99
10	1.06	1.78	1.90	1.21	1.71	2.08
Predicted stoichiometry	1	1.6	1.6	1	1.6	1.6

In abiotic controls (Figure 2-1b) where soil was autoclaved to inhibit microbial activity, a small amount of hydrogen sulfide (1.36 ± 0.03 mg H_2S/g dry soil) was removed. However, nitrate concentrations remained constant and sulfate was not produced. It appears that hydrogen

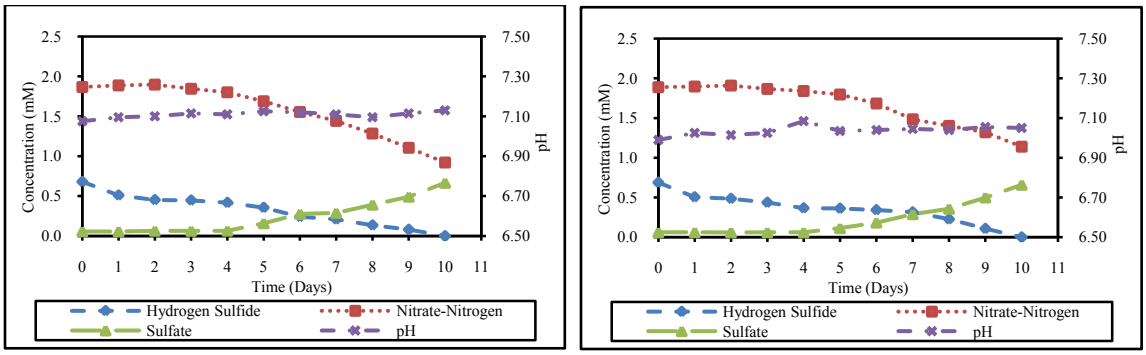
sulfide removed was primarily a physical/chemical reaction such as sorption or ion exchange. Similar results were seen in biotic controls (Figure 2-1c) where there was no nitrate added.

H_2S Removal in Compost Microcosms

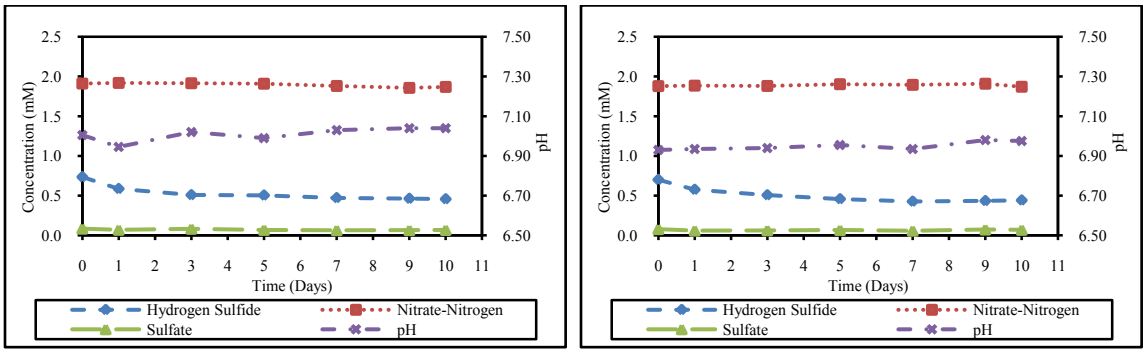
Figure 2-3 illustrates the disappearance of hydrogen sulfide and nitrate, and the formation of sulfate as a function of time for compost microcosms. The compost microcosms had an initial hydrogen sulfide concentration of 0.7 mM. During autotrophic denitrification in compost microcosms (Figure 2-3a), hydrogen sulfide was removed at a slower rate compared to soil and totally disappeared by Day 10. Nitrate was also gradually consumed.

The stoichiometric ratios of ΔNO_3^-:ΔH_2S, ΔH_2S:ΔSO_4^{2-} and ΔNO_3^-:ΔSO_4^{2-} in compost microcosms are presented in Table 2-5. Similar to soil microcosms, H_2S was initially removed by both sorption and oxidation, however, not completely oxidized to sulfate as suggested by ΔH_2S:ΔSO_4^{2-} greater than 1 and ΔNO_3^-:ΔH_2S less than 1.6. By the end of the experiments, the stoichiometric ratios of ΔNO_3^-:ΔH_2S and ΔH_2S:ΔSO_4^{2-} were still less than 1.6 and greater than 1, respectively, suggesting incomplete oxidation of H_2S to sulfate.

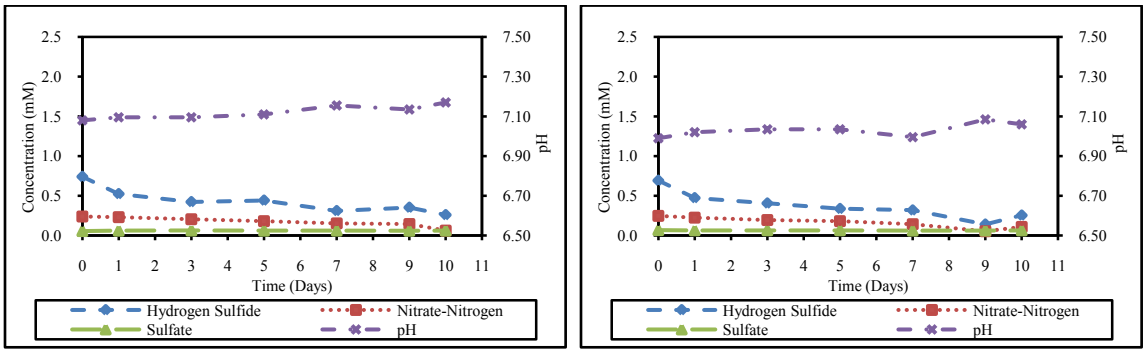
In compost abiotic controls (Figure 2-3b), a pattern similar to that of abiotic soil microcosm controls was observed. Small amounts of hydrogen sulfide (0.78 ± 0.04 mg H_2S/g dry soil) were removed, and there was no nitrate removal or sulfate production.



a. Autotrophic denitrification microcosms (supplemented with nitrate)



b. Abiotic control microcosms



c. Biotic control microcosms

Figure 2-3. Chemical analyses of compost microcosms (replicate experiments shown, the plotted values are the means obtained from duplicate microcosms).

Table 2-5. Stoichiometry in compost microcosms treated with nitrate addition (mM:mM).

Time (Days)	Series 1			Series 2		
	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$
4	*	0.25	*	*	0.15	*
5	3.20	0.55	1.75	6.19	0.29	1.78
6	2.00	0.71	1.42	2.82	0.59	1.68
7	2.03	0.90	1.83	1.64	1.09	1.78
8	1.64	1.07	1.75	1.55	1.06	1.64
9	1.38	1.27	1.75	1.32	0.98	1.30
10	1.12	1.39	1.55	1.15	1.09	1.25
Predicted stoichiometry	1	1.6	1.6	1	1.6	1.6

* No sulfate produced

In biotic controls where there was no nitrate added, compost was found to have a low background concentration of nitrate (~ 0.29 mg NO_3^--N/g dry soil). As seen in Figure 2-3c, hydrogen sulfide and nitrate were removed gradually and no sulfate was produced. The stoichiometric ratios of $\Delta NO_3^-:\Delta H_2S$ as shown in Table 2-6 were below 1.6, which suggests incomplete oxidation of H_2S. The ratios were consistent with denitrification linked to the oxidation of H_2S to elemental sulfur. The increase in pH (Figure 2-3c) at the end of the experiments also supports partial oxidation of hydrogen sulfide. Krishnakumar and Manilal (1999) and Cardoso et al. (2006) observed the same behavior in synthetic wastewater enriched with chemolithotrophic denitrifier; when nitrate was limiting, sulfate was either not detected at all or found at concentration less than predicted.

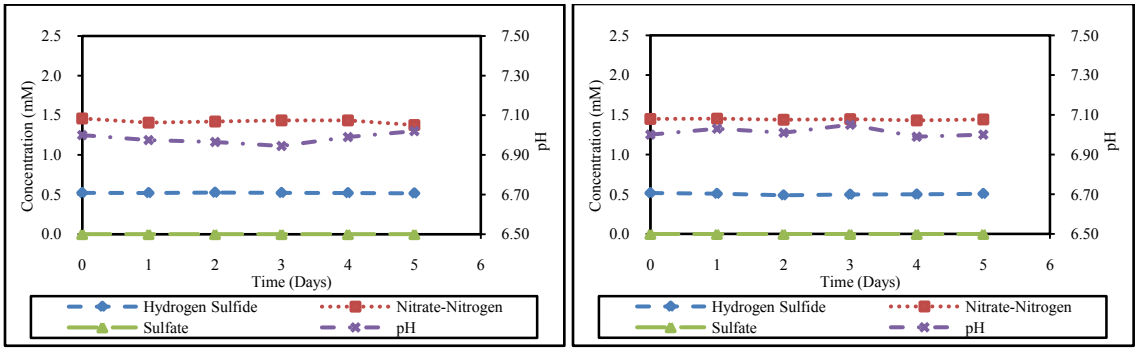
Table 2-6. Stoichiometry of biotic controls in compost microcosms (mM:mM).

Time (Days)	Series 1			Series 2		
	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$	$\Delta H_2S:\Delta SO_4^{2-}$	$\Delta NO_3^-:\Delta H_2S$	$\Delta NO_3^-:\Delta SO_4^{2-}$
1	*	0.03	*	*	0.10	*
3	*	0.11	*	*	0.19	*
5	*	0.20	*	*	0.19	*
7	*	0.20	*	*	0.28	*
9	*	0.24	*	*	0.35	*
10	*	0.37	*	*	0.32	*
Predicted stoichiometry	1	1.6	1.6	1	1.6	1.6

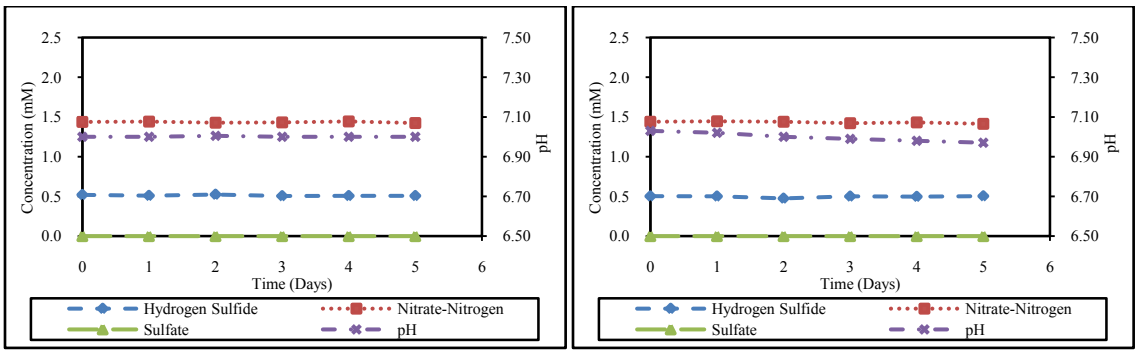
* No sulfate produced

H_2S Removal in Sand Microcosms

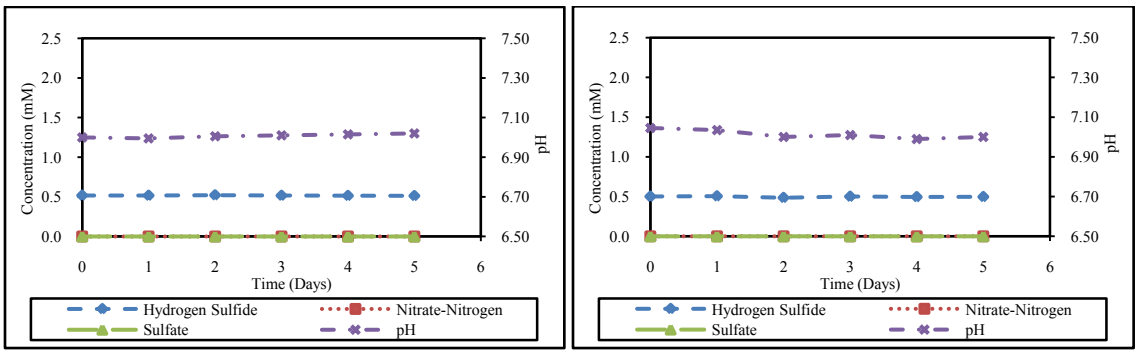
The conversion of hydrogen sulfide and nitrate nitrogen and the production of sulfate for sand microcosms are depicted in Figure 2-4. The sand microcosms had an initial hydrogen sulfide concentration of 0.5 mM. For the nitrate-added microcosms (Figure 2-4a), results showed no change in hydrogen sulfide and nitrate nitrogen concentration, and sulfate was not detected. Similar results were seen for abiotic (Figure 2-4b) and biotic controls (Figure 2-4c).



a. Autotrophic denitrification microcosms (supplemented with nitrate)



b. Abiotic control microcosms



c. Biotic control microcosms

Figure 2-4. Chemical analyses of sand microcosms (replicate experiments shown, the plotted values are the means obtained from duplicate microcosms).

H_2S Removal Rates

The reaction order of H_2S oxidation was determined by plotting experimental data. The linearity of plots of H_2S concentration versus time (zero order), ln[H_2S] versus time (first order), and 1/[H_2S] versus time (second order) was compared. H_2S oxidation followed a zero-order reaction with reasonably good R^2 values (Table 2-7). The zero-order rate data were normalized by the dry mass of cover material in each microcosm test and are presented in Table 2-7. In the study of bacterial oxidation of H_2S under denitrifying conditions by *Thiobacillus denitrificans* in synthetic wastewater (Krishnakumar and Manilal, 1999) sulfide oxidation also followed zero-order reaction. Because of the rapid removal of H_2S in soil, the actual removal rate may be greater than shown in Table 2-7. As can be seen in Table 2-7, autotrophic denitrification (nitrate-added) in soil was at least an order of magnitude greater than in compost, perhaps due to a lower number of autotrophic denitrifiers in compost. This conclusion is supported by polymerase chain reaction results in autotrophically denitrifying columns reported by Sungthong et al. (2010).

Table 2-7. H_2S removal rates in soil and compost.

Type of cover material	H_2S zero-order removal rate,* mg H_2S/d-g dry cover material (R^2)	
	Nitrate-added	Biotic control
Soil	2.57 ± 0.17 (0.82)	0.12 ± 0.04 (0.70)
Compost	0.17 ± 0.01 (0.94)	0.08 ± 0.01 (0.71)

*Average of two sets

Application of Autotrophic Denitrification Landfill Biocovers

Using the flux rates of H_2S measured at five C&D landfills in Florida which ranged from 0.192 to 1.76 mg/m^2-d (Eun et al., 2006), the H_2S removal rate of soil from this study (2.57 mg H_2S/d-g dry soil) and a soil bulk density of 0.46 g dry soil/mL, the theoretical thickness of a soil cover required to remove H_2S would be less than 1 mm. The soil cover thickness to remove H_2S using autotrophic denitrification calculated from this study is significantly less than soil cover usually used in landfills. However, H_2S removal rates in the field may be lower than in the laboratory due to mass transport limitations and lower water content. A minimum of 15 cm of cover material for daily cover is generally required by regulations and is recommended to be used as a bioactive cover material under autotrophic denitrification conditions. Based on the maximum flux rate, the nitrate-nitrogen should be theoretically added at least at a rate of 1.16 mg NO_3^--N/m^2-d. Nitrate-nitrogen should be added in excess to soil in order to fully oxidize H_2S.

Conclusions

The microcosm studies confirm that H_2S can be effectively removed during autotrophic denitrification in soil and compost. Addition of excess nitrate as an electron acceptor under anoxic conditions can stimulate indigenous autotrophic denitrifiers both in soil and compost leading to H_2S removal. In compost microcosms with no nitrate addition, nitrate naturally present also stimulated native autotrophic denitrifiers. Results also demonstrated that small amounts of H_2S can be removed physically/chemically by soil or compost. There was no H_2S removal observed in sand microcosms.

Rapid H_2S oxidation to sulfate with nitrate addition can be achieved, particularly in the soil tested. Zero-order kinetic rates were found to describe H_2S oxidation. The rates of H_2S oxidation under autotrophic denitrification in soil and compost were 2.57 mg H_2S/d-g dry soil, and 0.17 mg H_2S/d-g dry compost, respectively. A lower rate of H_2S oxidation in compost than in soil may be caused by a lower number of autotrophic denitrifiers in compost, as reported by Sungthong et al. (2010). Based on these laboratory studies, a minimum 15-cm soil thick cover is recommended with the addition of a minimum of 0.7 mg NO_3^- per mg H_2S removed.

The addition of nitrate to soil or compost cover material provides a promising method to minimize H_2S emissions from landfills. Further study is needed, however, under conditions more closely simulating landfill cover systems (i.e. unsaturated condition and gaseous H_2S removal).

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CHAPTER 3
CONTROL OF H_2S EMISSIONS USING AUTOTROPHIC DENITRIFICATION LANDFILL BIOCOVERS: LABORATORY COLUMN STUDIES

Introduction

Construction and demolition (C&D) debris landfills that dispose of large amounts of drywall frequently have problems associated with hydrogen sulfide (H_2S) generation. H_2S can be produced when sulfate in gypsum ($CaSO_4 \cdot 2H_2O$), the main component in drywall, decomposes by sulfate-reducing bacteria (SRB) activity under anaerobic conditions in landfills. Due to the low odor threshold of H_2S, C&D debris landfills receive odor complaints from surrounding communities. Prolonged exposure to relatively low concentrations of H_2S gas may affect memory, coordination, eyes and breathing (ATSDR, 2006). Brief exposures to concentrations of H_2S gas greater than 500 ppm can cause loss of consciousness and possibly death. Measurements of H_2S produced at several C&D landfills by Lee et al. (2006) found H_2S concentrations in ambient air at the landfill surface ranging from below 3 ppb to greater than 50 ppm and H_2S concentrations in landfill gas from below 3 ppb to 12,000 ppm.

H_2S gas emissions at C&D landfills can be effectively reduced using active gas collection and treatment such as activated carbon adsorption, chemical oxidation, incineration, and biofiltration. However, due to the high capital, operating, and maintenance costs of gas collection and treatment systems, it may not be feasible to install these systems at all landfills. Studies have demonstrated that the use of chemically or biologically active landfill covers can effectively reduce H_2S gas emissions from C&D landfills (Plaza et al., 2006; Xu, 2005). These studies

concluded that fine concrete, sandy soil amended with lime, and compost in landfill covers can effectively reduce the H_2S emissions from landfills.

The addition of nitrate has been reported to be effective in controlling odors and sulfide production from wastewater and oil reservoirs (Bentzen et al., 1995; Jenneman et al., 1986; Jobbagy et al., 1994; Okabe et al., 2003a, b; Myhr et al., 2002; Nemati et al., 2001a, b). The process of nitrate utilization as an electron acceptor to oxidize inorganic sulfur compounds such as H_2S, sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), tetrathionate ($S_4O_6^{2-}$) and sulfite (SO_3^{2-}) is known as autotrophic denitrification. Promotion of autotrophic denitrification in a bioactive cover can create a barrier to H_2S emissions generated from landfills (Sungthong and Reinhart, 2010). This biocover may prove to have cost and efficiency benefits when compared to other cover systems and therefore may offer an attractive alternative for controlling H_2S emissions from landfills.

Given the successful demonstration of liquid-phase H_2S removal by autotrophic denitrification in soil microcosms presented in Chapter 2, gas-phase H_2S removal simulating a landfill cover system was investigated. The objectives of this study were to (1) simulate an autotrophic denitrification landfill soil biocover, and (2) investigate the microbial communities involved in autotrophic denitrification landfill soil biocovers.

Experimental Materials and Methods

Laboratory-scale columns filled with soil were permeated with gas containing H_2S and monitored for H_2S breakthrough over time. These investigations were aimed to evaluate whether indigenous microorganisms present in soil could be stimulated to reduce H_2S emissions in a simulated autotrophic denitrification landfill cover soil environment. Soil was used as a cover

material since rapid H_2S reduction was observed in autotrophic denitrification microcosms (Chapter 2).

Physicochemical Properties of Soil Used as a Cover Material

Physical and chemical characteristics of soil as received were determined using standard methods for soil analysis (Klute, 1986; Page, 1982). Analytical methods for measurement of pH, water content, organic content, and bulk density can be found in Chapter 2. Particle size distribution was determined by sieve analysis in accordance with the American Standard for Testing and Materials (ASTM) D422-63 Standard Test Method for Particle-Size Analysis of Soil (ASTM D 422-63, 2003). These physicochemical properties are summarized in Table 3-1. Figure 3-1 shows the particle size distribution curve for the soil. According to the coefficients of uniformity, C_u, and curvature, C_c, calculated from effective sizes D_{10}, D_{30}, and D_{60}, the soil is classified as poorly graded sand (ASTM D 422-63, 2003).

Table 3-1. Characteristics of soil - as received.

Physical and chemical characteristics	Units	Soil (As-Received)
Soil added in the columns, dry mass basis	g	86
pH (1:2.5 soil to water mass ratio)	-	7.65
Water content, wet mass basis	%	36.3
Organic content, dry mass basis	%	28.2
Bulk density	g/mL	0.46
Effective size D_{10} D_{30} D_{60}	 mm mm mm	 0.15 0.29 0.52
The coefficient of uniformity, $C_u = D_{60}/D_{10}$	-	3.5
The coefficient of curvature, $C_c = (D_{30})^2/(D_{60} \times D_{10})$	-	1.1

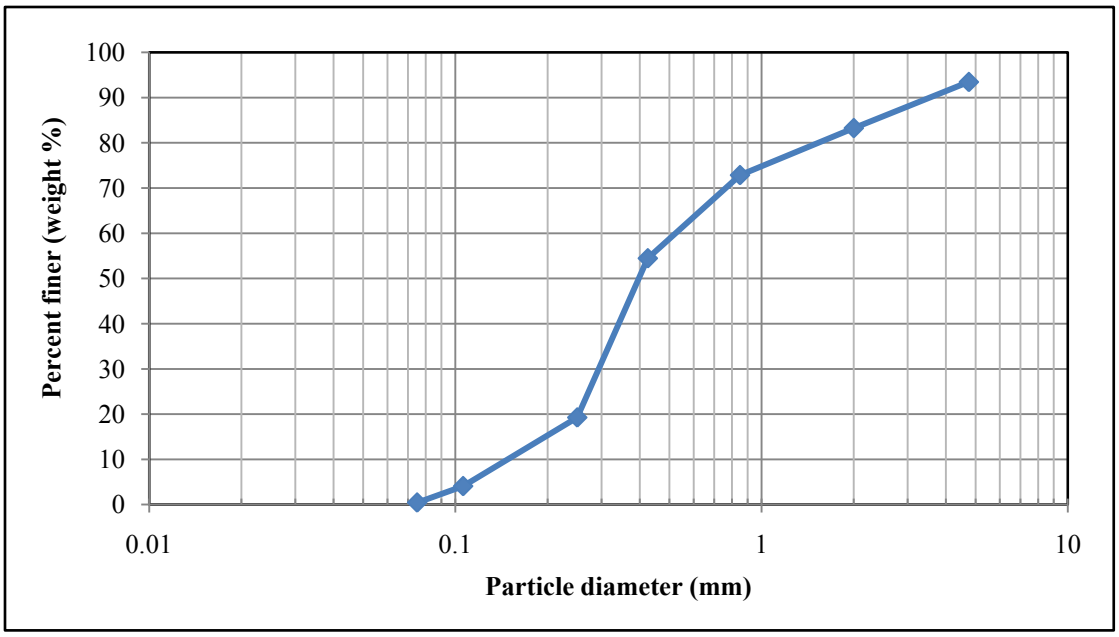


Figure 3-1. Particle size distribution curve for soil obtained by sieve analysis.

Column Design

Two laboratory-scale columns were created using 5-cm inside diameter, schedule-40 clear polyvinyl chloride (PVC) pipe; an autotrophic denitrification column (supplied with KNO3) and a control column (without KNO3 addition). Each column was 20 cm in length with PVC female adapters and male cleanout plugs at each end. The caps were modified to permit gas introduction and exit. A 5-cm layer of gravel was placed at the bottom of each column to ensure homogenous distribution of gas. A layer of geotextile was placed on top of the gravel layer to support the soil. Soil was placed in the columns to a depth of seven cm. Gas containing H2S was introduced at the bottom of the columns. Figure 3-2 provides a schematic drawing of laboratory-scale columns. Prior to the final experimental design, several columns with various thicknesses

of soil were used. It was found that 7-cm soil thickness showed promising results. Appendix B shows results from the different trials.

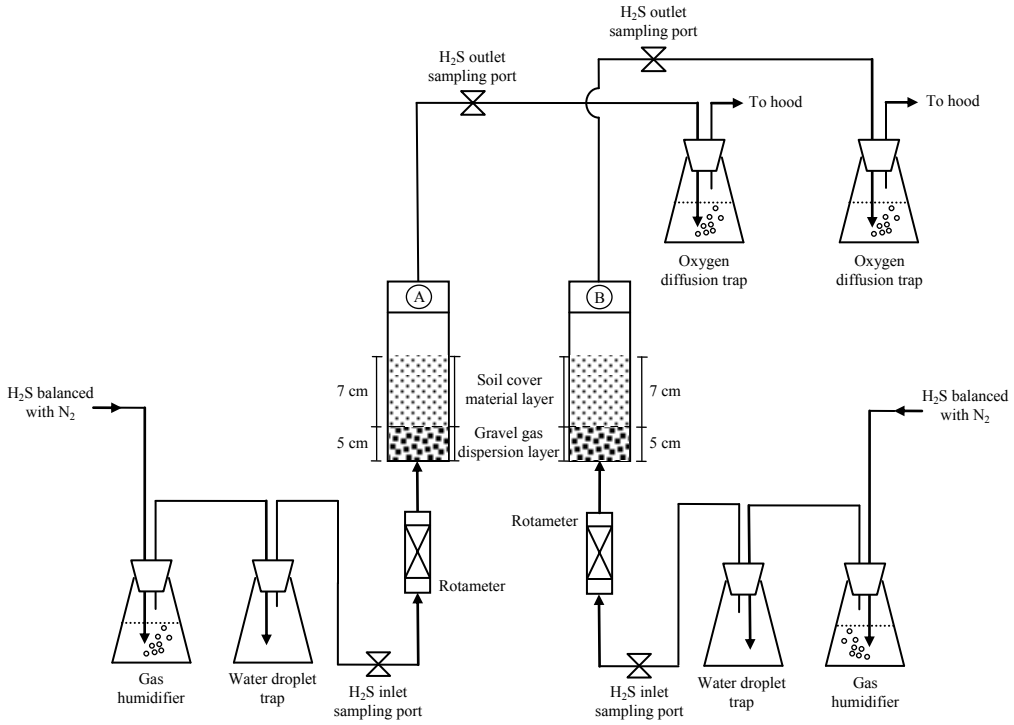


Figure 3-2. A schematic drawing of a laboratory-scale column system simulating autotrophic column (A) and control column (B).

Column Operations

Two sets of laboratory-scale column experiments simulating autotrophic landfill soil covers were carried out. H_2S gas balanced with N_2 (Air Liquide, Houston, TX) was introduced with H_2S concentration of approximately 930 ppm_v to the experimental columns of the first set. The second set tested a H_2S concentration of approximately 140 ppm_v. Each column was loaded with soil containing a moisture content of 47% on a wet weight basis. The autotrophic denitrification column was loaded with soil wetted with a solution containing KNO_3 (1.94 mg

NO_3^--N/g dry soil in the first set and 0.499 mg NO_3^--N/g dry soil in the second set), whereas the control column was loaded with soil wetted with distilled water only.

Prior to introduction to columns, gas was passed through a 500-mL humidification flask containing 300 mL of distilled water to saturate the incoming gas stream. After removing the larger entrained water droplets by passing through an empty flask (250-mL in size), moisture-saturated gas was introduced through the bottom of each column. Gas flow rate through the columns was regulated by rotameters (Cole Parmer, Vernon Hills, IL). The exhaust gas stream from each column passed through 250-mL flask filled with a saturated NaCl solution to create back pressure and prevent oxygen diffusion into the columns.

In order to remove any residual oxygen in the columns, gas containing 99.99% of N_2 (Air Liquide, Houston, TX) was delivered to the columns for two hours prior to introducing H_2S. Subsequently, moisture-saturated H_2S gas balanced with nitrogen at concentrations near 930 ppm_v and 140 ppm_v for the first and second set, respectively was supplied to the columns at gas flow rate of ~30 ml/min, corresponding to H_2S gas flux of 29 and 4.3 g/m^2/day for Set 1 and 2 respectively. The first set of columns was operated individually as shown in Figure 3-2, while the second set of columns was operated in parallel with a split inlet, not shown in Figure 3-2. The H_2S concentrations were measured at the gas inlet and outlet of the columns until H_2S breakthrough occurred. A sheet of aluminum foil was wrapped around each column to prevent exposure to light and the growth of phototrophic microorganisms. Throughout the study, the columns were maintained at room temperature of approximately 22°C.

Analytical Methods

H_2S and related parameters analysis

Gas samples were collected at the inlet and outlet for H_2S concentration determination in Tedlar® bags. H_2S was analyzed using gas detection tubes (RAE Systems, San Jose, CA) at least once per day until H_2S breakthrough was observed. Gas detection tubes of various detections range from 0.2-1000 ppm were used. Flowrate was confirmed twice daily with the use of a hand-held flow meter (ADM 1000, Agilent Technologies, Santa Clara, CA) connected to the end of the outlet tubing.

At the end of the experiment, each column was disassembled and soil samples were collected along its length. Soil pH was measured in a soil/water suspension according to standard methods for soil analysis (Klute, 1986; Page, 1982). Nitrate and sulfate were analyzed by extracting 5-10 g of soil with 200 mL of distilled water for one hour followed by filtration of the extraction solution through a 0.45-µm filter. Nitrate and sulfate concentrations were determined using a DX-120 ion chromatography (IC, Dionex, Inc, Bannockburn, IL) equipped with an AS-14 column and a 0.002-M sodium bicarbonate/0.008 M sodium carbonate eluent.

PCR analysis

Soil samples were collected from the column experiments conducted at 930 ppm and 140 ppm H_2S concentration and also of the raw soil mix which was used in the column experiments. Samples of compost used in column experiments were also collected. These samples were

approximately 80 to 100 mg each, collected in 1.5 mL sterile capped-plastic tubes. Samples were stored at 4ºC immediately after collection. DNA extractions were carried out within 24 hours of collection of samples.

Genomic DNA was extracted from the samples using Soil Master DNA extraction kit. The DNA pellets were suspended in TE buffer (10 mM Tris-HCl and 1 mM EDTA at pH 8.0). DNA was quantified spectrophotometrically at 230, 260, 280 nm. Given the heterogeneous nature of the samples with varying amount of organic contents in each collected sample, the DNA yield was variable. DNA samples with high yield were selected for further experiments.

The reduction of nitrite to nitric oxide by nitrite reductase distinguishes denitrifiers from nitrate-respiring bacteria, which do not reduce nitrite to nitric oxide gas (Prieme et al., 2002). The reduction of NO_2^- to NO is catalysed by either copper nitrite reductase (nirK) or cytochrome cd1 nitrite reductase (nirS) (Zumft, 1997). The primer sets previously reported to amplify these gene fragments were used. Table 3-2 shows the different set of primers used for PCR amplification of nirK and nirS used in this study. The different set of primers were tried in order to make an assessment of the best primer-set that can give maximum positive PCR amplification results for various experimental samples.

Table 3-2. Different sets of primers used for PCR amplification.

Gene fragments	Primer Set	Reference
nirK	nirK1F-nirK3R	Braker et al. (1998)
nirK	nirK1F-nirK5R	Braker et al. (1998)
nirK	F1aCu-R3Cu	Hallin and Lindgren (1999)
nirS	nirS1F-nirS3R	Braker et al. (1998)
nirS	nirS1F-nirS6R	Braker et al. (1998)
nirS	Cd3aF-R3cd	Throback et al. (2004)

PCR amplifications for DNA extracted from experimental samples were performed in a total volume of 30 µl containing 16 ul, 2X PCR buffer (Promega, USA) and 15 pmol of each primer, and DNA (3 to 50 ng). All the primer pairs were run with an initial denaturation step at 94°C for 4 minutes. Touchdown PCR, a technique for improving PCR amplification, was performed which consisted of 30 s at 95°C, a primer-annealing step of 40 s, and an extension of 40s at 72°C. After 40 cycles, a final 7-min incubation at 72°C was performed. During the first 10 cycles, the annealing temperature was decreased by 0.2°C every cycle, starting at 47.5°C until it reached at touchdown at 45.5°C. The additional 30 cycles were performed at an annealing temperature at 45.5°C. The amplification products were analyzed by electrophoresis on 0.9% (wt/vol) agarose gel and UV translumination after staining with ethidium bromide. A positive result for PCR amplification was considered by a presence of band at appropriate location corresponding to the ladder on agarose gels. The relative amounts of PCR products obtained for nirS and nirK in experimental samples were estimated by visual comparison of the band intensities on agarose gels.

Results and Discussion

High H_2S Loaded Columns

H_2S Concentrations

The first column test including a control column and an autotrophic column had an inlet H_2S concentration of ~930 ppm_v for an average mass loading rate of 0.66 mg/g dry soil/d. The

hydrogen sulfide concentrations in control and autotrophic columns measured at the inlet and the outlet during the operating period are shown in Figure 3-3. Control columns were shut down after the outlet concentration stabilized for two weeks. In the autotrophic column, the H_2S concentrations peaked rapidly within 3 to 4 days, following which H_2S was effectively removed for approximately 20 days and thereafter H_2S concentrations gradually increased then stabilized after 35 days. White powder was observed throughout the column as shown in Figure 3-4.

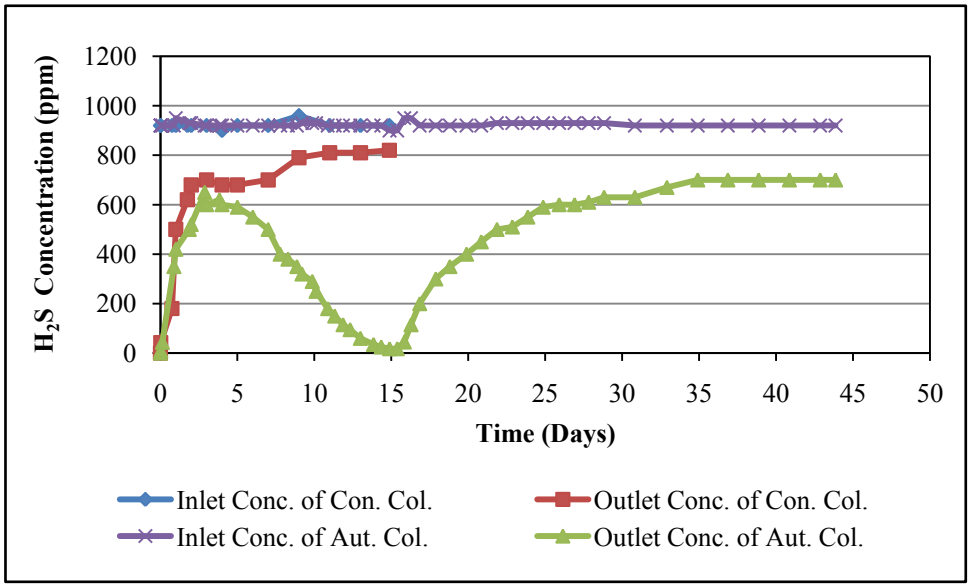


Figure 3-3. Hydrogen sulfide concentrations at the inlet and the outlet of the control and autotrophic denitrification columns.

Figure 3-4. White powder appeared in the autotrophic nitrification column at high H_2S loading.

pH, Nitrate-N and sulfate

After shutting down the columns, soil pH measurements were taken at three levels; bottom (0-1 cm), middle (3-4 cm), and top (6-7 cm). In the control column, pH at the bottom (7.69) was slightly lower than that of the initial soil (7.80) while the pH values at the middle (7.94) and at the top (7.91) were slightly higher than that of the initial soil. In the autotrophic column, pH at all three levels; bottom (8.50), middle (8.77), and top (8.87), were higher than that of the initial soil (7.40), as well as the control column.

In the autotrophic column, to which KNO_3 was initially added, nitrate was undetectable in soil extracts at all three levels. Sulfate concentrations of 0.84, 0.55 and 0.33 mg/g dry soil were found at the top, middle and the bottom of the column, respectively, for a total production of 0.51 mM. In the control column, no sulfate was produced.

H_2S removal

The cumulative H_2S removed from control and autotrophic columns were calculated from the inlet and outlet concentrations and flow measurements during the course of the experiment. The H_2S removal in the control column was attributed to physical/chemical reactions such as ion exchange and/or adsorption because of the absence of an electron acceptor and the lack of sulfate production. The removal in the autotrophic column was assumed to be a combination of biological (autotrophic denitrification) and physical/chemical processes. The complete oxidation of H_2S results in the production of sulfate as shown in Equation 3-1. Partial oxidation can also occur at high H_2S loading which results in the production of elemental sulfur (Equation 3-2) and other byproducts such as polysulfides (Cardoso et al., 2006).

$$H_2S + 1.6NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} SO_4^{2-} + 0.8N_2 + 0.8H_2O + 0.4H^+ \quad (3\text{-}1)$$

$$H_2S + 0.4NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} S^0 + 0.2N_2 + 0.8H_2O + 0.4OH^- \quad (3\text{-}2)$$

Biological removal of H_2S in the autotrophic column was assumed to occur until nitrate was consumed, around Day 35, after which continued removal of ~ 230 ppm_v was due to physical/chemical reactions. Biological H_2S removal over time was calculated by subtracting the amount of H_2S removed by physical/chemical reactions (230 ppm_v) from the total H_2S removed, assuming that physical/chemical removal occurred at the same rate during the entire column operation. Figure 3-5 shows the cumulative H_2S mass removed by the different mechanisms.

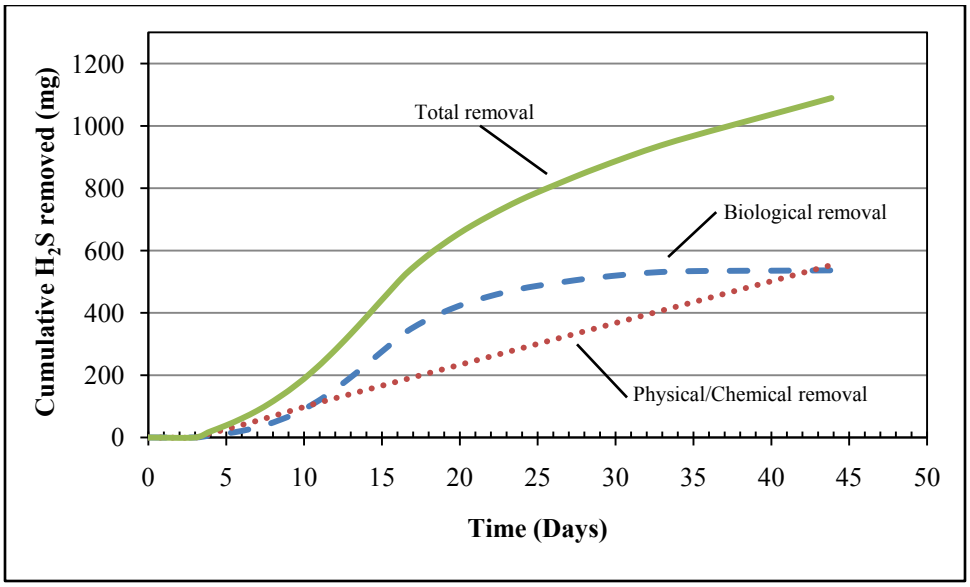


Figure 3-5. Cumulative H_2S removed by biological and physical/chemical processes in the autotrophic column.

During the course of the experiment (44 Day), it is estimated that a total of 553 mg of H_2S (51% of total) was physically/chemically removed and a total of 536 mg of H_2S (49%) was removed biologically, or 6.43 mg H_2S/per g dry soil and 6.24 mg H_2S/g, respectively. According to the amount of nitrate added to the autotrophic column and the amount of H_2S removed, the molar ratio of nitrate consumed to H_2S removed was 0.75, as shown in Table 3-3. This value was lower than 1.6, the theoretical requirement of nitrate for complete oxidation of H_2S to sulfate, suggesting incomplete oxidation of H_2S, a conclusion supported by the high H_2S removed to sulfate produced ratio reported in Table 3-3. The ΔNO_3^-:ΔH_2S ratio was nearer to the value of 0.4 which is the stoichiometric requirement of nitrate for oxidation of H_2S to sulfur. Partial oxidation of H_2S was also supported by the observation of white powder (assumed to be elemental sulfur)

along the column and the increase in soil pH due to the production of hydroxide during the oxidation of H_2S to sulfur, according to Equation 3-2.

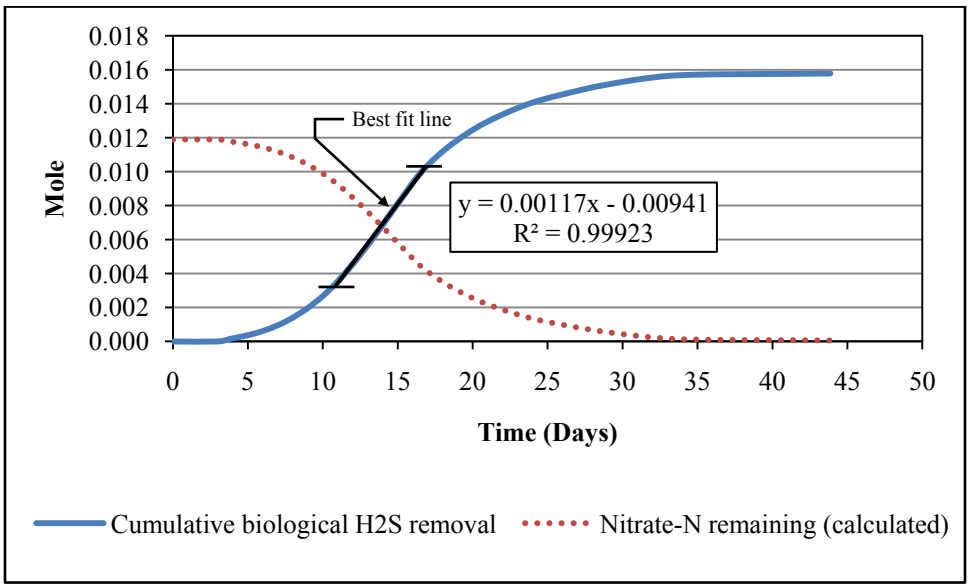
Table 3-3. Removal ratios for autotrophic denitrifying column at high H_2S loading (M:M).

Ratio	Experimental	Stoichiometry (Equation 3-1)	Stoichiometry (Equation 3-2)
$\Delta H_2S:\Delta SO_4^{2-}$	30.7	1	NA
$\Delta NO_3^-:\Delta H_2S$	0.75	1.6	0.4
$\Delta NO_3^-:\Delta SO_4^{2-}$	23.2	1.6	NA

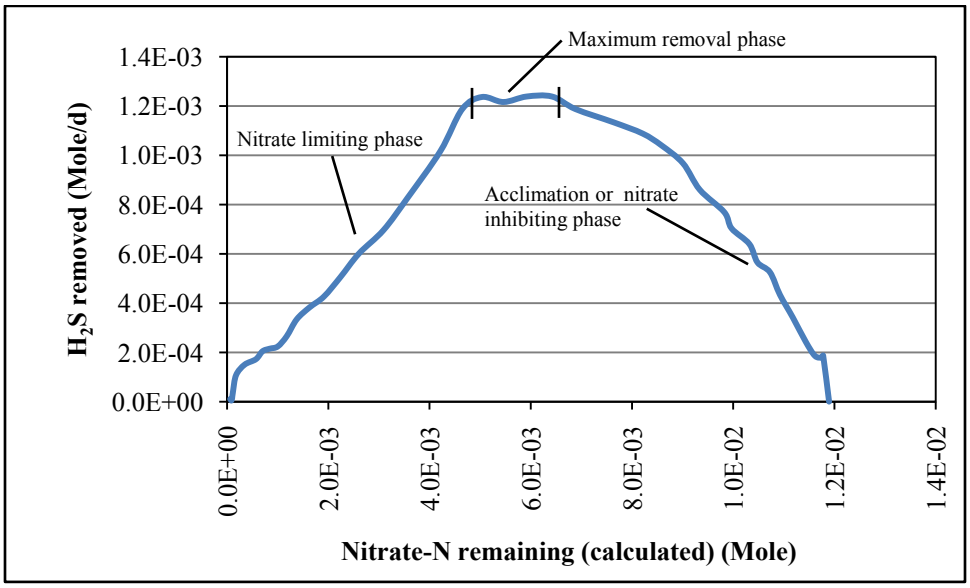
H_2S removal rates

Figure 3-6 presents calculated nitrate nitrogen consumption and biologically H_2S removal in the autotrophic column. The remaining nitrate nitrogen was calculated by assuming a ratio of 0.75 moles of NO_3^--N consumed per mole of H_2S removed obtained as described above. Initially, 12 mmoles of nitrate nitrogen were present. As seen in Figure 3-6, biological H_2S removal followed three phases over time including a lag or acclimation phase, maximum removal phase, and a diminishing removal phase. During the initial lag or acclimation phase, the H_2S removal rate was relatively low (approximately 0.348 mmole/day) then gradually increased which is typical of microbially-mediated processes (Reynolds and Richards, 1995). During the next phase, where nitrate and bacterial growth were not limited, H_2S was removed at a faster rate. During this removal phase, H_2S oxidation was found to follow zero-order kinetics (R^2 of 0.999 - Figure 3-6) with a zero-order rate constant of 1.17 mmol/day. The zero-order rate constant was normalized by the dry soil mass used in the column and was found to be 0.46 mg H_2S removed/d-g dry soil. During the third phase, where nitrate presumably became limited,

microbial growth was inhibited, and H_2S was removed at a diminishing rate (approximately 0.30 mmole/day).



a) Biological H_2S removal and nitrate nitrogen remaining over time



b) Biological H_2S removal related to the amount of nitrate remaining

Figure 3-6. Nitrate nitrogen consumption corresponding to biological H_2S removal.

Regeneration test for adsorbed H_2S

The remaining soil from the autotrophic column was placed back into the column and tested for reappearance of H_2S in the gas phase (mediated by sulfate-reducing organisms) by introducing 99.99% pure N_2 through the bottom of the column at a flow rate of 4-6 mL/min for 75 days. The effluent gas was monitored for H_2S. Initially, H_2S concentrations as high as 220 ppm were detected. It is likely that H_2S sorbed by soil particles or dissolved in soil-water was released. After Day 5, H_2S concentration declined, falling to 0.5 ppm or less during the remaining 70 days.

Low H_2S Loaded Columns

H_2S concentrations

Another set of column experiments was performed with column inlet concentration of 140 ppm_v H_2S in the gas phase, for an average mass loading rate of 0.10 mg/g dry soil/d. The hydrogen sulfide concentrations in control and autotrophic columns measured at the inlet and the outlet during the operating period are shown in Figure 3-7. In the autotrophic column the H_2S concentrations peaked rapidly and then gradually declined after Day 2. By Day 6, the outlet concentration was 0.2 ppm and gradually increased thereafter. This behavior was similar to that of the autotrophic column operated at high H_2S concentration. The concentration in the control column initially increased until Day 3 and eventually stabilized at a value similar to autotrophic column. In the control column the highest H_2S outlet concentration detected was 50 ppm, while in the autotrophic column the outlet concentration never exceeded 22 ppm over a period of 23

days. After operating for about two weeks both columns reached steady state and showed nearly identical H_2S removal, therefore the columns were shut down.

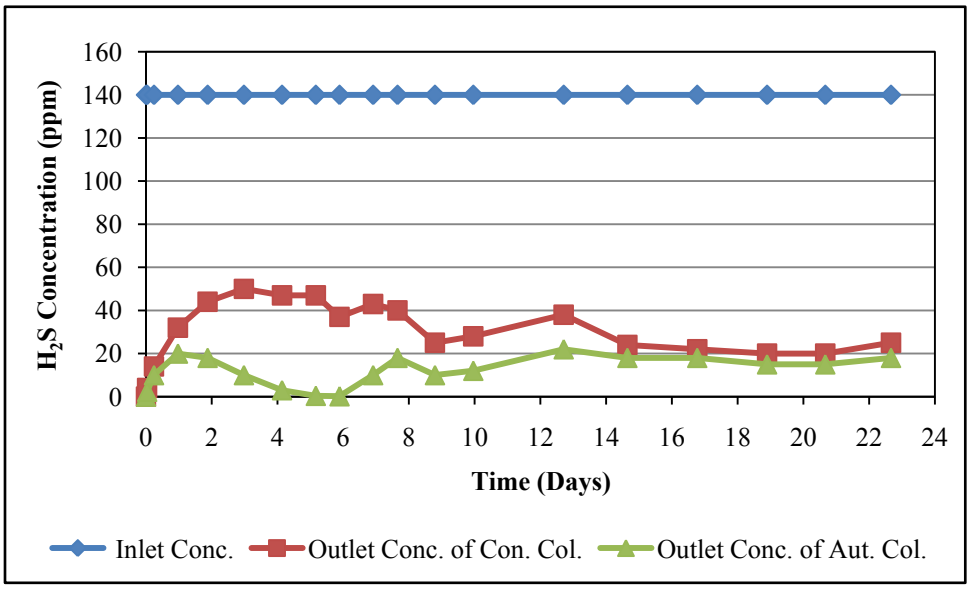


Figure 3-7. Hydrogen sulfide concentrations at the inlet and the outlet of the control and autotrophic denitrification columns.

pH, Nitrate-N and sulfate

After shutting down the columns soil pH, Nitrate-N, and sulfate were analyzed. Soil pH measurements were taken at three levels, bottom (0-1 cm), middle (3-4 cm), and top (6-7 cm) from both columns. In the control column, pH at all three levels, bottom (7.58), middle (7.56), and top (7.53) was found to be higher than that of the initial soil (7.18). In the autotrophic column, pH at all three levels, bottom (7.46), middle (7.23), and top (7.20), was found to be lower than that of the initial soil (7.68).

KNO_3 was added to the autotrophic column at 0.499 mg NO^-_3-N/g dry soil. Soil samples were analyzed for nitrate and sulfate at the end of the experiment. Similar to the previous experiment with higher H_2S concentration, all nitrate nitrogen was consumed, suggesting autotrophic denitrification had occurred. Sulfate concentrations of 2.45, 2.28 and 2.05 mg/g dry soil were found at the top, middle and the bottom of the column, respectively. The ΔNO_3^-:ΔSO_4^{2-} ratio was 1.5, near to that predicted by the stoichiometric relationship of Equation 3-1, indicating complete oxidation of H_2S to sulfate. This finding was supported by the decrease in pH, resulting from hydrogen ion production as seen in Equation 3-1. It is likely that under the lower H_2S loading, sulfate was the preferred end product of autotrophic denitrification.

H_2S removal

The cumulative H_2S removed from control and autotrophic columns was calculated from inlet and outlet concentrations and flow measurements taken during the course of the experiment. Total removal by the autotrophic and control columns was 173 and 167 mg H_2S, respectively. From Figure 3-7, it appears that biological H_2S removal ceased after Day 14, presumably due to the exhaustion of nitrate. The removal was due to physical/chemical processes thereafter, which explains nearly identical outlet H_2S concentrations from both columns from Day 15 to 23.

The total biological H_2S removal over time, calculated as described previously, was 5.2 mg, yielding a H_2S:SO_4 ratio of 0.1 M/M and a NO_3:H_2S ratio of 0.6, considerably deviating from the stoichiometric ratios. These results suggest that the assumption that physical/chemical removal was at equilibrium during the entire column operation is erroneous at the lower H_2S

loading. Therefore it can be assumed that biological removal was occurring rapidly enough to limit physical/chemical removal until biological removal ceased after Day 14. Based on the nitrate removed and sulfate produced, and stoichiometry described by Equation 3-1, the H_2S removal would total 65 - 69 mg (or ~39% of the total H_2S removed). Assuming biological removal of 69 mg of H_2S over 14 days, the average removal rate was 0.058 mg/g dry soil-day.

PCR on Soil and Compost Columns

PCR amplification reactions were performed as per the methods described earlier. Initial reactions were performed in a reaction volume of 30 µl containing about 50 ng DNA extracted from experiment samples. Successful amplification results were obtained by reducing the quantity of DNA to between 3 to 5 ng. This could be due to the presence of certain inhibitors of PCR which were diluted by using lower quantity of DNA in the PCR reaction.

Most samples from the column experiment with inlet H_2S concentration of 930 ppm produced positive PCR results. Therefore the comparison of different primer sets was done using the DNA obtained from the 930 ppm inlet H_2S concentration column experiment. Out of 16 samples collected from this experiment, 14 yielded positive results for both primer sets F1aCu-R3Cu and F1aCu-R3Cu. The K1F-K3R, S1F-S3R, K1F-K5R, and S1F-S6R showed 11, 8, 6, and 6 positive PCR amplifications respectively with low intensity UV translumination on agarose gel. Figure 3-8 shows the agarose gel of the PCR products of nirS fragments using K1F-K3R and Cd3aF-R3cd primer sets that corresponds to approximately 374 bp of nirK and 406 bp of nirS respectively.

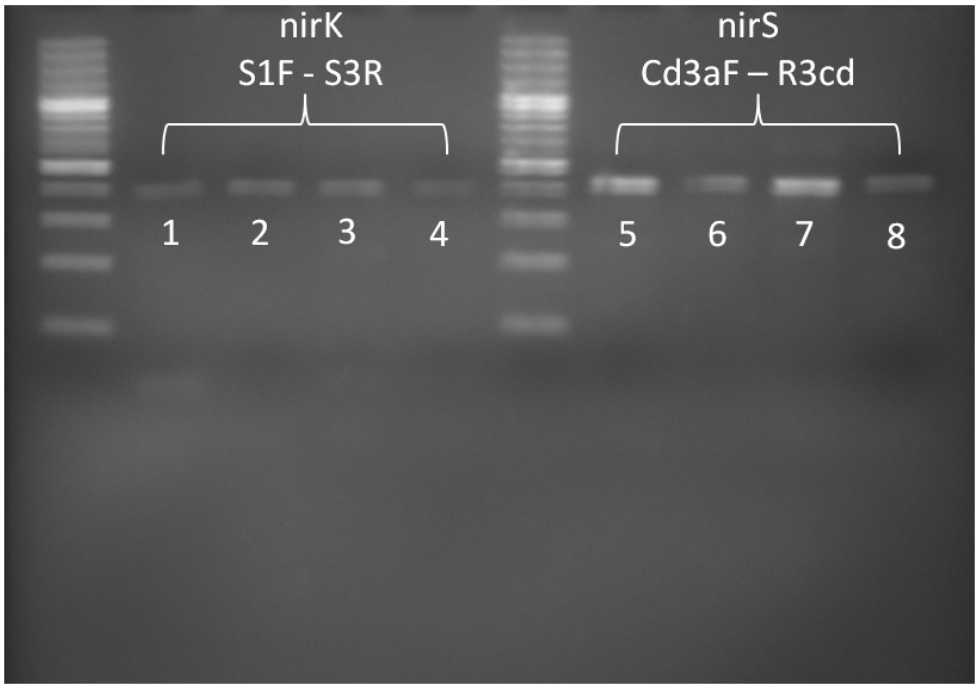


Figure 3-8. Agarose gel of PCR products of nirK and nirS fragments using S1F-S3R and Cd3aF-R3cd primer sets respectively.

The DNA samples from the column study with 140 ppm inlet H_2S concentration also showed positive results for nirK and nirS fragments using the F1aCu-R3Cu and Cd3aF-R3cd. Similarly the raw soil sample used in the column experiments showed positive PCR amplications for nirK and nirS but produced a low intensity on the agarose gel.

PCR amplification was also performed on the samples from a column experiment containing compost as media with inlet H_2S concentration of 930 ppm (results not reported). Primer pairs F1aCu-R3Cu and Cd3aF-R3cd were used for detecting nirK and nirS respectively. PCR reactions were run by varying the quantity of DNA from 3 to 50 ng. All eight samples failed to produce positive results, indicating absence or undetectable denitrification activity which also corresponding to the low H_2S removal rates for the compost (Sungthong and

Reinhart, 2010). Figure 3-9 shows the agarose gel of PCR products of nirK and nirS fragments using S1F-S3R and Cd3aF-R3cd primer sets that corresponds to approximately 455 bp of nirK and 406 bp of nirS respectively.

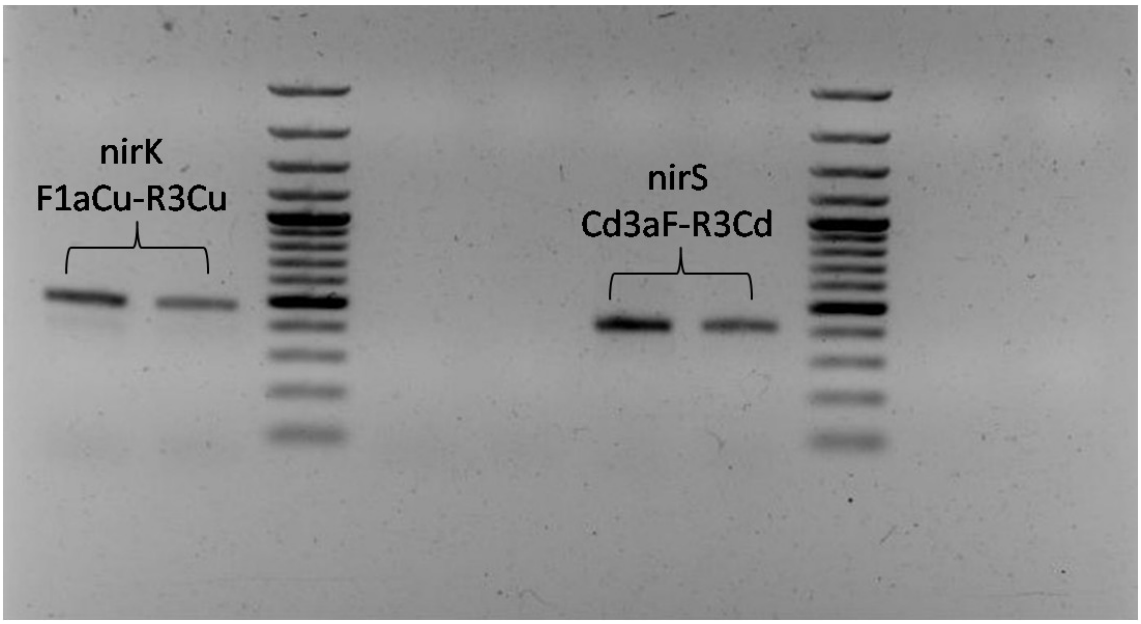


Figure 3-9. Agarose gel of PCR products of nirK and nirS fragments using F1aCu-R2Cu and Cd3aF-R3cd primer sets respectively.

Based on the results from the PCR experiments it can be concluded that the soil column experiments which showed positive results for PCR may help remove H_2S from gas phase better than compost. The fragments of nirK and nirS amplified using F1aCu-R2Cu and Cd3aF-R3cd primer sets respectively, were cloned and sequenced to identify the microorganisms carrying out the denitrification process in the column. This work falls outside the scope of this dissertation and therefore is not included here.

Conclusions

Column studies supported the results of microcosm studies. The studies confirm that gaseous H_2S can be effectively removed using an autotrophic denitrification landfill cover. Removal of H_2S was observed in all columns due to the capacity for soil to absorb H_2S; however autotrophic columns removed significantly more. The higher inlet concentration of H_2S resulted in partial oxidation to elemental sulfur, while sulfate was found at levels predicted by stoichiometric relationships at the lower inlet concentration. H_2S oxidation in column with higher loading was found to follow zero-order kinetics. The rate of H_2S oxidation was 0.46 mg H_2S removed/d-g dry soil. PCR amplifications of soil samples from columns with both higher and lower inlet concentration of H_2S indicate the presence of denitrifying organisms.

References

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CHAPTER 4
CONTROL OF H_2S EMISSIONS USING AUTOTROPHIC DENITRIFICATION LANDFILL BIOCOVERS: ENGINEERING APPLICATIONS

Introduction

Construction and demolition (C&D) waste landfills were once considered to be environmentally benign as they are used for disposing of stable waste materials such as wood, wallboard, concrete, bricks, and paving materials. Because of the low organic matter disposed, C&D landfills would result in little or no leachate contamination or methane production. Consequently, C&D landfills have less stringent requirements compared to other landfills accepting municipal or industrial solid waste. C&D landfills are classified as Class III landfills in Florida, where the regulations for Class III landfills do not require liners, leachate management systems, gas extraction and treatment systems, or air or water quality monitoring (FDEP, 2010).

However, C&D debris landfills have experienced problems with hydrogen sulfide (H_2S) emissions. The generation of H_2S in these landfills results from the decomposition of gypsum ($CaSO_4 \cdot 2H_2O$) in wallboard, a primary component of C&D debris. Under optimal conditions in the landfills including absence of air, presence of moisture, pH around 7, temperature range between 30°C and 37°C, and the presence of a carbon source, sulfate-reducing bacteria (SRB) utilize sulfate in gypsum as an electron acceptor when oxidizing carbon to produce H_2S during the respiration process (O'Connell, 2005; Hao et al., 1996; Widdel, 1986). Because of the heterogeneous mixtures of C&D wastes and the differences in landfill management practices, the locations of landfills, landfill ages, and climate, H_2S generation at C&D debris landfills varies

from one landfill to another. In ambient air, levels of H_2S were found to range from below 3 ppb to greater than 50 ppm. In landfill gas, H_2S was encountered at concentrations ranging from below 3 ppb to 12,000 ppm (Lee et al., 2006).

Due to the distinctive rotten-egg odor and extremely low odor threshold (0.5 ppb) of H_2S (ATSDR, 2006), C&D landfill owners often face numerous complaints from the surrounding communities. Residents complain not only about the odor but also of health problems including loss of sense of taste, difficulty in breathing, coughing, and eye irritation (Brat, 2007). Human health effects of exposure to H_2S depend on the concentration of the gas and the length of the exposure (Lewis et al, 2008; ATSDR, 2006; Glass, 1990). Long-term exposure to relatively low concentrations of H_2S (ppb range) may cause irritation to the eyes, nose, or throat; memory loss; loss of the sense of the smell; loss of balance; and difficulty in breathing. Exposure to levels of H_2S between 50 and 100 ppm after one hour can cause conjunctivitis and respiratory irritation. Exposure for more than 30 minutes at concentrations above 500 ppm results in loss of consciousness and death. It is clear that H_2S emissions from C&D landfills may pose a significant risk to health and the environment.

In response to increasing odor and health complaints linked to the generation of H_2S, C&D landfill operators have developed a set of best management practices (BMPs) to control H_2S emissions (U.S.EPA, 2006). Basically, the BMPs include (but are not limited to) diversion or recycling of drywall, controlling the pH of the C&D waste at an alkaline level ($pH > 9$) using lime addition, controlling moisture by diversion of stormwater and surface water, using various alternative cover materials including fine concrete, compost or a mixture of soil, ash, and lime as passive treatment systems, and installing gas collection and recovery systems.

Although active gas collection systems can collect the gas for subsequent treatment and effectively reduce H_2S emissions at C&D landfills, the systems have high capital, operating and maintenance costs. Therefore, interest in using alternative cover materials to control H_2S emissions at less cost has been increasing. As shown in Chapters 2 and 3, an autotrophic denitrification landfill biocover has proved to be an effective alternative for controlling H_2S emissions. The objectives of this study are to provide an overview of available H_2S control technologies and to evaluate the costs and benefits of H_2S cover systems.

Hydrogen Sulfide Control

This section provides an overview of approaches to control or minimize H_2S emissions from landfills. It describes landfill cover materials and active extraction and treatment systems used to control gaseous emissions in landfills. It also provides information on masking or neutralizing agents used to control odor caused by H_2S production. Table 4-1 provides an overview of these control processes and lists advantages and disadvantages of each.

Table 4-1. Advantages and disadvantages of H_2S prevention/control measures.

Measure	Advantages	Disadvantages
Autotrophic denitrification landfill biocover (Cover soil + nitrate addition)	• Simple and effective operation • Minimal operation & maintenance • Nitrate requirement function of H_2S emissions	• The product, SO_4^{2-}, may be converted back to H_2S over time • Requires absence of oxygen • Multiple additions required
Cover soil + lime	• Simple and effective operation • Minimal operation & maintenance	• H_2S is not eliminated • H_2S is reformed if pH drops • Finite capacity • Lime requirement function of cover area • Handling of lime is dangerous

Measure	Advantages	Disadvantages
Fine concrete cover	• Simple and effective operation • Minimal operation & maintenance	• H_2S is not eliminated • H_2S is reformed if pH drops • Finite capacity • Fine concrete requirement function of cover area
Compost cover	• Simple and effective operation • Minimal operation & maintenance	• The product, SO_4^{2-}, may be converted back to H_2S • Requires availability of oxygen • Limited availability of compost • Compost requirement function of cover area
Gas extraction + flare	• Highly effective operation	• Limited capacity for H_2S oxidation • High capital, operation, and maintenance costs • SO_2 emissions
Gas extraction + incinerator	• Highly effective operation • Applicable for wide range of H_2S concentrations • Energy recovery if enough methane is produced	• High capital, operating, and maintenance costs • SO_2 emissions
Gas extraction + biofiltration	• Effective operation • Low capital and operating costs on biofiltration	• High capital, operating, and maintenance costs on gas extraction installation
Gas extraction + iron sponge	• Highly effective operation	• High capital, operating and maintenance cost • Difficult to remove byproduct • Byproduct needs to be properly disposed
Gas extraction + SulfaTreat®	• Highly effective operation	• High capital, operating, and maintenance costs • High chemical cost
Gas extraction + Sulfur-Rite®	• Highly effective operation	• High capital, operating and maintenance costs • Byproduct needs to be properly disposed
Gas extraction + The Elimiator®	• Highly effective operation	• High capital, operating, and maintenance costs • Byproduct needs to be properly disposed
Gas extraction + LO-CAT®	• Highly effective operation	• High capital, operating, and maintenance costs
Gas extraction + MINI-CAT®	• Highly effective operation	• High capital, operating, and maintenance costs
Masking and neutralizing agents	• Low capital and operating costs	• H_2S is not eliminated • Odors are temporarily masked providing short-term control

Cover Materials

Generally, there are three types of covers that are used in a landfill, daily, intermediate, and final covers (Tchobanoglous et al., 1993). The daily cover is a layer that is placed on top of the landfilled waste at the end of each day. It is used to reduce vector attraction, fires, odors, and precipitation infiltration. The intermediate cover is used on top of any landfill area that will not be used for a long period of time (typically one year or more). Covering the parts of a landfill that are not used will minimize the amount of precipitation infiltration. The final cover is a multilayered system of various materials that is placed at the completion of landfilling operations in order to reduce precipitation infiltration and landfill gas emissions.

Typically soil is used in cover systems, however, alternative cover materials including sandy soil amended with lime, clayey soil, fine concrete, coarse concrete, and compost have been evaluated as alternative control measures for H_2S emissions at both laboratory and field scales. At laboratory scale (Plaza et al., 2007), the cover materials studied consisted of sandy soil, sandy soil amended with 5% hydrated lime ($Ca(OH)_2$), clayey soil, fine concrete (particle size less than 2.5 cm), and coarse concrete (particle size greater than 2.5). The study demonstrated that sandy soil amended with 5% hydrated lime and fine concrete were most effective for the control of hydrogen sulfide. Both materials exhibited reduction efficiencies greater than 99%. The clayey and sandy soil had lower reduction with average efficiencies of 65% and 30%, respectively. The coarse concrete was the least efficient material. At field scale (Xu et al., 2010), the cover materials studied were sandy soil, compost, fine concrete, sandy soil amended with both 1% and 3% hydrated lime, and sandy soil amended with 10% agricultural lime ($CaCO_3$). With an average emission rate of 0.403 mg $H_2S/m^2/d$ over a 10-month period, the field results indicated that cover

materials including compost, fine concrete, and sandy soil amended with both types of lime effectively attenuated H_2S emissions. The H_2S emissions were only detected from the test plot using sandy soil as cover.

As described in Plaza et al. (2007) and Xu et al. (2010), the possible H_2S attenuation mechanisms by these cover materials included physical adsorption, chemical reaction, and biological degradation. When H_2S gas diffused through the cover materials, some of the gas molecules were physically adsorbed on the surface of the cover materials or dissolved into the interstitial cover material pore water. Absorbed or dissolved H_2S can then be neutralized or biologically removed. In concrete and lime-amended sandy soil covers, calcium in lime and concrete can react with H_2S and ultimately be converted to sulfide minerals through reactions shown in 4-1 through 4-3 (Borgwardt et al., 1984 and Laurent et al., 1994):

$$H_2S + CaO \rightarrow CaS + H_2O \quad (4\text{-}1)$$

$$H_2S + Ca(OH)_2 \rightarrow CaS + 2H_2O \quad (4\text{-}2)$$

$$H_2S + CaCO_3 \rightarrow CaS + H_2O + CO_2 \quad (4\text{-}3)$$

The use of lime and concrete can increase the pH of cover material to levels greater than 9, which may inhibit SRB growth, limiting H_2S production (Widdel and Pfennig, 1984). Under alkaline conditions, the equilibrium of H_2S can also be driven toward HS^- (Equation 4-4), therefore, gaseous H_2S emission is avoided. However, if the pH is allowed to drop, H_2S can be easily reformed.

$$H_2S_{(g)} \leftrightarrow H_2S_{(aq)} \leftrightarrow H^+_{(aq)} + HS^-_{(aq)} \quad (4\text{-}4)$$

The observation of black material at the bottom of the cover materials (Xu et al., 2010) suggests an alternative pathway for H_2S removed. A reaction between H_2S and trace metal oxides (MO_x) naturally contained in cover materials (e.g. ferrous, zinc, copper, nickel, and manganese) may occur to form metal sulfide compounds (MS_x), as shown in Equation 4-5 (Xu, 2005), leading to H_2S removal.

$$MO_x + xH_2S \rightarrow MS_x + xH_2O \quad (4\text{-}5)$$

In compost cover, it was hypothesized that H_2S removal was mainly due to aerobic biological oxidation (Xu et al., 2010). Because of the pH reduction found in compost, it is likely that H_2S was biologically oxidized to sulfate with H^+ production, as shown in Equation 4-6, resulting in the acidification of compost. Naturally found *Thiobacillus* species may be involved in this process (Syed et al., 2006).

$$H_2S + 2O_2 \xrightarrow{Microorganisms} SO_4^{2-} + 2H^+ \quad (4\text{-}6)$$

Xu (2005) conducted column experiments to investigate migration of H_2S through landfill cover materials. The study also provided a possible method for designing the alternative cover system. Based on parameters derived from the experiments as shown in Table 4-2 and Equation 4-7, the required depth of cover material can be calculated.

Table 4-2. Values of D, v, and μ of different cover materials (Xu, 2005).

Parameters	Sandy soil	Fine concrete	Coarse concrete	Lime-amended sandy soil
D (m^2/s)	6.09 x 10^{-6}	6.53 x 10^{-6}	1.09 x 10^{-5}	6.16 x 10^{-6}
v (m/s)	4.23 x 10^{-5}	4.42 x 10^{-5}	3.10 x 10^{-5}	4.21 x 10^{-5}
μ (1/s)	1.65 x 10^{-3}	1.00 x 10^{-2}	1.23 x 10^{-3}	9.86 x 10^{-3}

$$Z = \frac{2D}{\sqrt{v^2+4\mu D}-v}(lnC_0 - lnC_z) \quad (4\text{-}7)$$

where Z is depth of cover soil (m), D is H_2S effective diffusion coefficient (m^2/s), v is advection velocity of H_2S (m/s), μ is H_2S adsorption coefficient of cover soil (1/s), C_z is acceptable H_2S concentration on the surface of the cover soils (ppm), and C_0 is H_2S concentration underneath the cover soils (ppm).

The thickness of alternative landfill cover to reduce 1,000 ppm of H_2S in landfill gas to an acceptable level of 3 ppb was calculated to be 0.35 m for fine concrete and lime-amended soil, 0.95 m for sandy soil, and 1.37 m for coarse concrete.

Recently, autotrophic denitrification, an alternative biological denitrification process, has been observed during nitrate removal in wastewaters containing high sulfur concentrations or reduced sulfur sources (Darbi et al., 2002; Oh et al., 2002; Lampe and Zhang, 2005; Wang et al., 2005). With this process, sulfur denitrifying bacteria use a reduced inorganic sulfur source (i.e. H_2S, S, $S_2O_3^{2-}$, $S_4O_6^{2-}$, SO_3^{2-}) as the electron donor when reducing nitrate to nitrogen gas and oxidizing sulfur compounds to sulfate (Lampe and Zhang, 2005; Onay and Pohland, 2001). The process has been applied for controlling odors caused by the generation of H_2S in wastewater treatment plants, oil fields, and petrochemical industries (Telang et al, 1997; Jenneman et al., 1999; Vaiopoulou et al., 2005; Mathioudakis et al., 2006). The results of these studies have

proved that the addition of nitrate as a terminal electron acceptor resulted in autotrophic denitrification and led to sulfate production.

The autotrophic denitrification process may also have potential for controlling H_2S emissions from landfills. Promoting autotrophic denitrification under anoxic landfill cover conditions by adding nitrate as an electron acceptor and using H_2S as an electron donor creates a barrier to minimize gaseous H_2S emissions. When applied to landfills, the concept is described as shown in Figure 4-1.

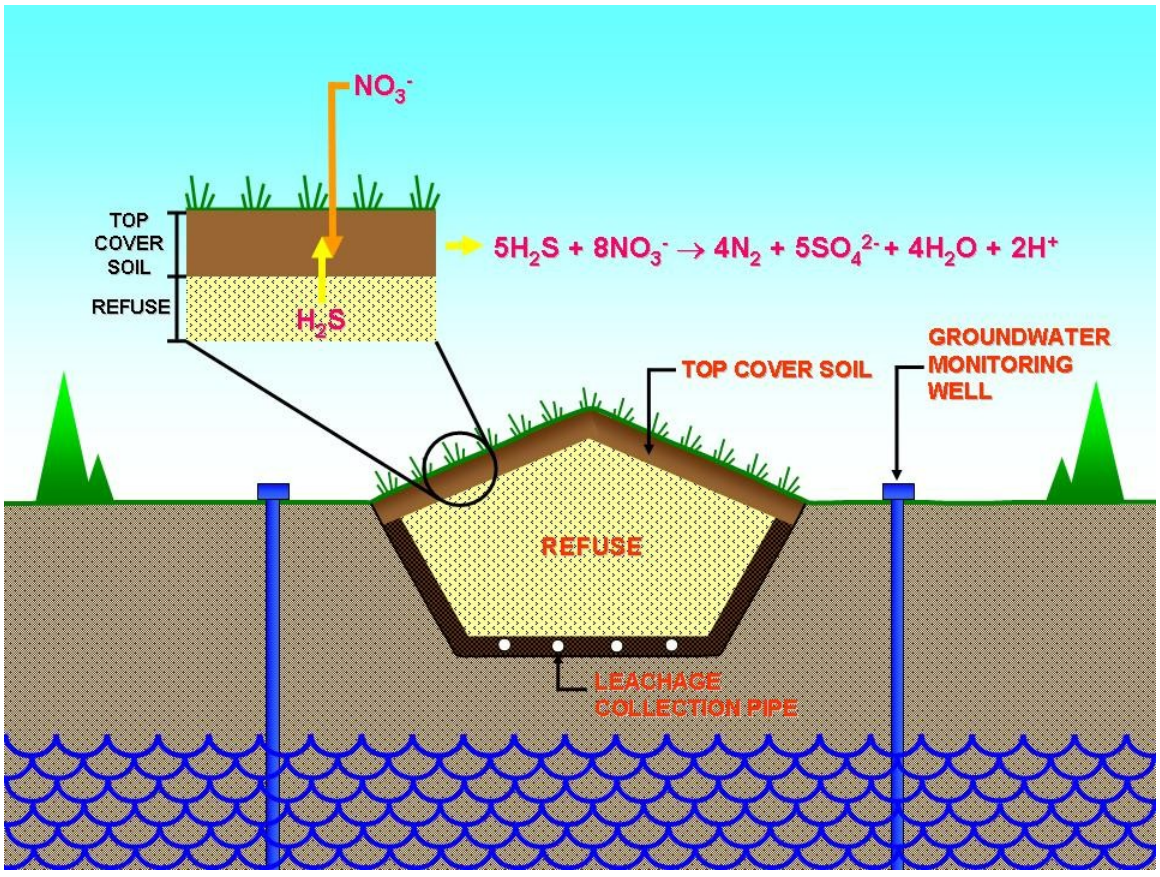

Figure 4-1. Autotrophic denitrification landfill biocover.

Autotrophic denitrification was investigated using microcosm and laboratory-scale column studies. The microcosm studies were conducted in order to evaluate the ability of sand, compost, and soil as landfill cover materials to remove H_2S under autotrophic denitrification conditions (Chapter 2). The microcosm studies demonstrated that H_2S can be effectively removed using autotrophic denitrification in compost and soil. Addition of nitrate as an electron acceptor under anoxic conditions stimulated indigenous autotrophic denitrifiers both in compost and soil leading to H_2S removal, although soil removal rates (2.57 mg H_2S/d-g dry soil) were significantly higher than compost (0.17 mg H_2S/d-g dry compost). No removal of H_2S was observed in sand microcosms.

Further investigation of gas-phase H_2S removal in a system simulating a landfill cover was undertaken using column experiments (Chapter 3). Soil was used as cover material since rapid H_2S reduction was observed in autotrophic denitrification microcosms. Two sets of column experiments were run. Each column was constructed of clear polyvinyl chloride (PVC) and was five cm in diameter. The first set of columns contained seven cm of soil. The autotrophic column was prepared with 1.94 mg NO_3^--N/g dry soil and a moisture content of 47% by weight, wet basis; an identical control column was prepared without nitrate. A gas stream was introduced to the columns with a H_2S loading rate of 0.66 mg/g dry soil/d. The second set contained seven cm of soil, again with both an autotrophic (0.499 mg NO_3^--N/g dry soil) and control column; H_2S loading rate was 0.10 mg/g dry soil/d for the second set. Column studies supported the results of microcosm studies. Removal of H_2S was observed in all columns due to the capacity for soil to absorb H_2S; however, autotrophic columns removed significantly more. The higher loading of

H_2S resulted in partial oxidation to elemental sulfur as shown in Equation 4-8, while sulfate was found (Equation 4-9) at levels predicted by stoichiometric relationships at the lower loading.

$$H_2S + 0.4NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} S^0 + 0.2N_2 + 0.8H_2O + 0.4OH^- \quad (4\text{-}8)$$

$$H_2S + 1.6NO_3^- \xrightarrow{\text{Autotrophic denitrifiers}} SO_4^{2-} + 0.8N_2 + 0.8H_2O + 0.4H^+ \quad (4\text{-}9)$$

Active Gas Collection and Treatment Systems

C&D debris landfills are typically constructed without gas collection and recovery systems. Due to the high capital, operating, and maintenance costs associated with them, gas collection and treatment systems may be one of the last control options to be implemented. However, these systems are frequently installed at landfills with serious H_2S odor problems.

Active gas collection systems include vertical and horizontal gas collection wells, piping, and vacuums or pumps to move gas out of the landfill and into a treatment system. Once collected, gas can be treated by combustion, biofiltration, or chemical oxidation. However, combustion of H_2S may lead to sulfur dioxide (SO_2) emissions, which requires additional treatment to prevent potential harm to the environment by acid rain (Thichy et al, 1998). Venting collected malodorous gas through a biofilter is another technology used to reduce odor. The biofilter is made of a filter bed that has high porosity, high buffer capacity, high nutrient availability and high moisture retention capacity to support microbial growth (Syed et al., 2006). The fundamental principal of biofiltration is that malodorous emissions are utilized by microorganisms as a food or energy source, and are destroyed in the process, being converted into carbon dioxide (CO_2), water, biomass, and other benign byproducts such as chloride and

sulfate (Cooper and Alley, 2002). Biofiltration has been particularly successful in the removal of hydrogen sulfide from gas streams produced by a number of different processes including agricultural practices (Nicolai and Janni, 2001), sewage treatment systems (Brennan et al., 1996), and MSW transfer stations (O'Malley, 2003).

Collected H_2S can also be removed via commercial treatment processes using technologies which include adsorption on a solid media (dry H_2S removal process) and absorption into a liquid (liquid H_2S removal process). Dry H_2S removal processes include an iron sponge, SulfaTreat®, and Sulfur-Rite®. Liquid H_2S removal processes include the Eliminator®, and LO-CAT® or MINI-CAT®.

The iron sponge is the oldest commercial process for removing H_2S, consisting of hydrated iron oxide (Fe_2O_3) impregnated onto wood chips. The basic chemistry of the process can be represented by equations 4-10 to 4-12 (Kohl and Nielsen, 1997):

$$2Fe_2O_3 + 6H_2S \rightarrow 2Fe_2S_3 + 6H_2O \quad (4\text{-}10)$$

$$2Fe_2S_3 + 3O_2 \rightarrow 2Fe_2O_3 + 6S \quad (4\text{-}11)$$

Combining equations 4-10 and 4-11,

$$6H_2S + 3O_2 \rightarrow 6H_2O + 6S \quad (4\text{-}12)$$

After operation for several months, the spent iron sponge material is very hard to remove from the vessel. During the removal of spent material, the highly reactive iron sulfide can generate enough heat to ignite the wood chips. It also has other disadvantages, it is relatively expensive to install, produces materials requiring disposal, and causes a high pressure drop in the gas collection system. For these reasons, most iron sponges have been replaced by other solid or liquid scavenger systems.

The SulfaTreat® process uses a proprietary granular material to remove H_2S. The iron oxide in SulfaTreat® is reportedly present in two forms, Fe_2O_3 and Fe_3O_4. Hydrogen sulfide reacts with both to produce a mixture of iron sulfides. Conversion efficiency in commercial systems is in the range of 0.55 - 0.72 kg H_2S/kg iron oxide, which is slightly higher than the value of 0.42 kg H_2S/kg iron oxide recommended for the iron sponge bed design (Kohl and Neilsen, 1997). SulfaTreat® is reportedly easier to handle than spent iron sponge media because the material does not become cemented, thus reducing operating costs, labor for change-out, and pressure drops in the bed. Drawbacks associated with this product are similar to the iron sponge; the process is non-regenerable, chemically intensive, and spent product can be problematic or expensive to dispose of properly.

Sulfur-Rite® is also a dry-based iron-oxide product. The Sulfur-Rite® manufacturer claims that insoluble iron pyrite is the final end product (Gas Technology Products, 2010). The Sulfur-Rite® systems come in prepackaged cylindrical units that are recommended for removing low levels of H_2S, about 25 to 150 kg/day. Company literature claims spent product is non-pyrophoric and landfillable and has 3-5 times the effectiveness of the iron sponge (Graubard et al., 2007; Zicari, 2003).

The Eliminator® uses a liquid scavenger technology for treating very low levels of H_2S, typically less than 150 kg/day (Gas Technology Products, 2010; Graubard and Bogner, 2010). The Eliminator® contains an amine-based material which is reportedly superior to materials in other scrubbing systems. Company literature claims that the Eliminator® does not form salts that can lead to H_2S release upon heating or acidification. Conversion efficiency in commercial

systems is 0.2 kg H_2S/kg Eliminator®. This technology results in a liquid waste stream that requires disposal.

The LO-CAT® or MINI-CAT® uses a liquid oxidation catalytic process to remove higher levels of H_2S, from 150 kg to several tons per day (Graubard and Bogner, 2010). MINI-CAT® is a smaller version of LO-CAT® with the same chemistry but reduced capital cost. It has been developed for treating 150 kg to 2 tons of H_2S per day. The LO-CAT® and the smaller scale MINI-CAT® use an aqueous solution of ferric ion, held in solution by organic chelating agents, to oxidize hydrogen sulfide ions absorbed in the solution, converting them to elemental sulfur while the ferric iron is reduced to the ferrous state. The spent ferrous solution is then circulated to an oxidizer where it is regenerated with air. The basic chemistry of the process can be represented by Equations 4-13 to 4-15:

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S + H^+ \quad (4\text{-}13)$$

$$4Fe^{2+} + O_2 + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \quad (4\text{-}14)$$

Combining equations 4-13 and 4-14,

$$2H_2S + O_2 \rightarrow 2H_2O + 2S \quad (4\text{-}15)$$

The LO-CAT® process operates at ambient temperature and requires no heating or cooling of the solution. It is also very efficient in removing H_2S (Kohl and Nielsen, 1997). The solid sulfur product can be recovered for agricultural or other productive uses (Graubard and Bogner, 2010).

Masking and Neutralizing Agents

Masking and neutralizing agents involve the addition of a substance to an odor source to reduce the odor intensity or to change the odor characteristic to one that is less objectionable. Generally, masking agents are mixtures of essential oils (limonene, pinene, terpene, etc.) and esters that have a strong scent and are designed to cover up the objectionable odor with a more acceptable odor. Masking agents do not actually react with the odor-causing compound or alter the odorous molecules but decrease the perception of the odor by overpowering it (Meyer, 2003). Neutralizing agents also are mixtures of aromatic oils that are used to cancel or neutralize offensive odors. Rather than overpowering an offensive odor with the more pleasing one of a masking agent, the aim of using neutralizing agent is to produce a net zero odor. In the process of neutralization, there is no chemical interaction between the odor-causing chemical and the neutralizing agent (Meyer, 2003). A wide variety of masking and neutralizing agents are sold to control odor emissions associated with H_2S generation. Few vendors of these chemicals have data documenting their effectiveness for odor reduction. Otieno and Magagula (2001) studied the effectiveness of synthetic organic oils, Ecosorb®, Ecolo®, and Lavender® in reducing the odor intensity of H_2S gas. Both Ecosorb® and Ecolo® are neutralizing agents, while Lavender® is a masking agent. The results showed that Ecosorb® and Ecolo® consistently reduced the odor intensity, whereas Lavender® showed no effect. In addition, a further study on possible negative effects of these oils on test microorganisms, *Bacillus megaterium, Clostridium spp., and Staphylooccus aureus* was undertaken. Ecosorb® showed non-toxic activity against the tested microbes, while both Ecolo® and Lavender were toxic to the tested microbes.

Currently, masking and neutralizing agents are used at many landfills to mitigate odor problem caused by H_2S generation. These chemical can be sprayed along the landfill perimeter, around areas where fugitive H_2S is present, during waste excavations for gas pipe placement, or near the waste offloading area. They are not considered as a permanent odor control system but may provide a temporary solution while a permanent system is installed.

Economic Comparison of Landfill Cover Materials

The focus of this economic analysis is on cover systems. Installation of gas collection and treatment systems and use of masking or neutralizing agent will not have cost-benefits over using alternative covers designed to control H_2S, therefore their costs and benefits are not considered in this study. As demonstrated in previous studies, utilization of compost, soil amended with lime, fine concrete, and autotrophic denitrification covers can effectively mitigate H_2S emissions. Assuming systems have similar application costs, costs of active cover system components (NO_3^--N fertilizer, lime, fine concrete, and compost) only are compared.

The economic comparison of cover systems is based on a case-study landfill described by Anderson et al. (2009). The case-study landfill is a closed and capped municipal solid waste (MSW) landfill containing approximately 2.3 million metric tons of waste. The landfill consists of two phases of operation and development, the original landfill area and an expansion area. The original landfill area is a 0.12-km^2 unlined facility operated from 1940 to 1999 and was then closed with geomembrane cap system in 2001. The landfill accepted MSW and unprocessed C&D waste. The expansion area is a 0.04-km^2 facility constructed over a portion of the original landfill with a RCRA composite liner and leachate collection system. The landfill expansion cell

was operated from 2000 to 2005 and was then closed with a geomembrane cap system in 2006. The landfill expansion cell accepted approximately 360,000 metric tons of MSW, 18,000 metric tons of unprocessed C&D waste, and 79,000 metric tons of C&D fines used as alternative cover material.

Prior to 2003, landfill gas in the original area was managed via passive vent flared. In 2003, an active landfill gas collection and flare system was first installed in the original area. The system was then expanded into the expansion area in 2004. Collection of H_2S concentration data at the landfill gas collection system started in late 2004. Between October 2004 and April 2009, H_2S concentrations were measured in collected gas and H_2S emissions were estimated as shown in Figure 4-2. Concentrations of H_2S in the collected gas ranged from 480 to 2,800 ppm. The total amount of collected H_2S emissions during this period of time was estimated to be 64,500 kg. A summary of the monthly values of H_2S emissions shown in Figure 4-2 is listed in Appendix D. An exponential trendline was fitted to the amount of H_2S produced over time (Equation 4-16). Using Equation 4-16 H_2S emissions were estimated over a 15-year period. Total amount of H_2S collected over a 15-year period was projected to be 80,900 kg.

$$Q_{H_2S} = 3810e^{-0.046t} \quad (4\text{-}16)$$

where Q_{H_2S} is H_2S production (kg/month) and t is time (month).

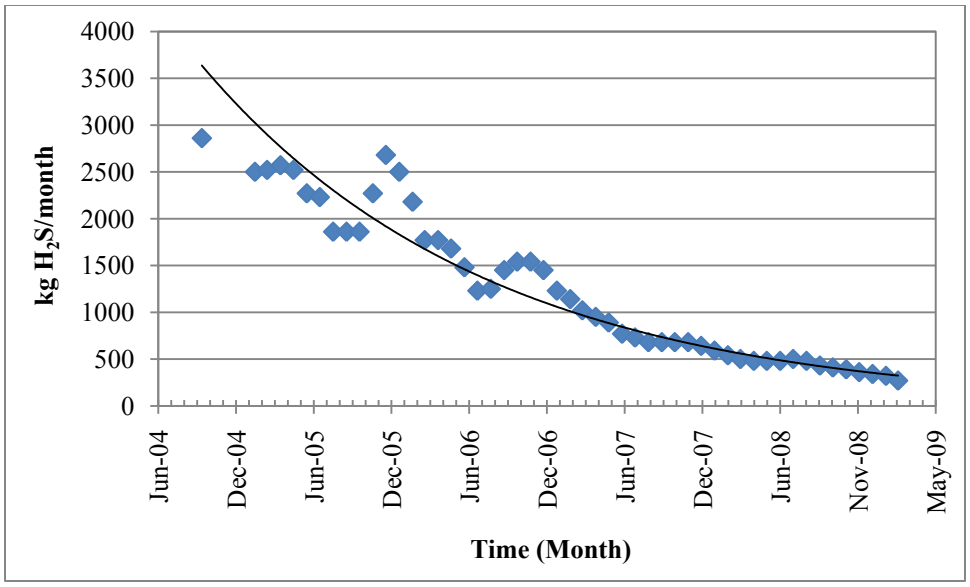

Figure 4-2. Collected H_2S emissions from case-study landfill over time.

Based on the amount of H_2S emitted over 15 years (Table 4-3) and the total landfill area of 0.16 km^2, the emission flux rates would range from 1.71 to 587 $mg/m^2/d$ and the average emission flux rate would be 92.4 $mg/m^2/d$. The emission flux rates obtained from the case-study landfill are quite high compared to 0.179 to 1.94 $mg/m^2/d$ reported as H_2S emission flux rates from C&D landfills by Eun et al. (2007) perhaps due to the large amount of C&D fines disposed. For the purpose of this economic analysis, it is assumed that all generated H_2S is emitted through the cover in the expansion area only (0.04 km^2) and gas collection is not practiced.

Ammonium Nitrate Fertilizer

In order to create an autotrophic denitrification landfill cover system, nitrate-nitrogen must be provided and diffusion of oxygen must be prevented. According to the stoichiometry shown in Equation 4-9 and the total amount of H_2S produced over 15 years (80,900 kg), the total

amount of nitrate-nitrogen required was calculated to be 53,300 kg. Nitrate-nitrogen would be applied to a final cover soil having thickness of 60 cm, typically required at for C&D landfills (FDEP, 2010).

Atmospheric diffusion into a soil cover is limited by soil compaction which reduces porosity. In addition, infiltration of liquid leads to partial or complete cover saturation. Oxygen concentration generally declines with increasing depth of soil cover. Studies have shown that oxygen may be present down to a depth of 40 cm below the soil surface (Christophersen and Kjeldsen, 2001). For typical soil the aerobic zone, where oxygen is available, may be present at the top 15 to 30 cm (Kinsey, 2007; Natural Environmental Systems, LLC, 2010). Therefore, the 60-cm soil cover will ensure sufficient anoxic region to support autotrophic denitrification cover.

In order to create the most economical autotrophic denitrification landfill cover and meet the demand of H_2S emissions, annual addition of granular ammonium nitrate fertilizer (34% N) is proposed. The amount of fertilizer required each year was determined according to the amount of H_2S produced, shown in Table 4-3. The total amount of ammonium nitrate fertilizer needed for the case-study landfill was approximately 157,000 kg. Fertilizer can be applied using a tractor-hauled granular fertilizer spreader.

Table 4-3. Amounts of ammonium nitrate fertilizer to be used each year.

Year	H_2S emissions (kg)	Fertilizer, 34% N (kg)
1	34,300	66,500
2	19,800	38,300
3	11,400	22,100
4	6,600	12,700
5	3,800	7,300
6	2,200	4,200
7	1,300	2,400
8	700	1,400
9	400	800
10	200	500
11	100	300
12	100	200
13	<100	100
14	<100	100
15	<100	100
Total	80,900	157,000

Cover Soil Plus Lime

Cover soil amended with 1% lime was considered because the material effectively attenuated H_2S emissions in pilot tests (Xu et al., 2010). Hydrated lime is proposed because it is more effective in removing H_2S than agricultural lime (Xu, 2005). A 60-cm cover is recommended in order to meet requirements at C&D landfills. Based on the expansion area of the case-study landfill of 0.04 km^2, the volume of the cover soil is calculated to be 24,000 m^3. Assuming a cover soil bulk density of 1,100 kg/m^3 (Xu, 2005), the weight of cover soil is calculated to be 26,400 metric tons. The amount of hydrated lime needed is then 260 metric tons which exceeds the stoichiometric amount needed (176 metric tons) to react with 80.9 metric tons

of H_2S. The addition of hydrated lime to soil will result in an increase of pH to as high as 12 (Plaza, 2003), therefore emitted H_2S should be neutralized, leading to control of H_2S emissions.

Fine Concrete

Because of the availability of fine concrete at many C&D landfills and its reported effectiveness in removing H_2S, fine concrete is also considered in this analysis. Based on the volume of final cover (24,000 m^3) calculated from the expansion area of the case-study landfill (0.04 km^2), the required thickness (60 cm), and an estimated bulk density of 1,300 kg/m^3 (Xu, 2005), the amount of fine concrete needed to provide landfill over is determined to be 31,200 metric tons, which contains approximatly 2,808 metric tons of CaO. The amount of CaO in fine concrete exceeds the stoichiometric amount needed (133 metric tonns) to react with 80.9 metric tons of H_2S. Similar to using soil amended with hydrated lime as a cover, emitted H_2S is neutralized within the fine concrete layer, leading to the reduction of H_2S emissions.

Yard Waste Compost

Yard waste consists of leaves, grass, clippings, brush, and tree prunings. Through the process of composting, these organic wastes can be treated to produce a material that can be used as a soil amendment. Compost can also be used as a final cover for landfills serving as a biofilter to remove H_2S and volatile organic compounds. Based on the calculated volume of 24,000 m^3 for the final cover with bulk density of 740 kg/m^3 (Hurst et al., 2005), the amount of yard waste compost needed is 17,800 metric tons.

Cover System Cost Comparison

Costs of ammonium nitrate fertilizer, hydrated lime, fine concrete and compost converted to 2010 dollars are presented in Table 4-4. The cost of transportation is estimated at $17/metric ton based on a 22-metric ton truck load and a 100-mile delivery (Sonny Glasbrenner Inc., 2010). Cost of ammonium nitrate fertilizer was obtained from USDA (2010) as an average U.S. farm price of $483/metric ton in 2009. The cost of fertilizer in 2009 dollars was then converted to 2010 dollars using an inflation conversion factor of 1.015 (Sahr, 2010). Cost of compost was obtained from U.S. EPA (1992). This cost represents processing costs of yard waste compost using windrow technique. In 1992 the processing cost was estimated to be $33/metric ton and was converted to 2010 dollars using inflation conversion factor of 1.547 (Sahr, 2010).

Table 4-4. Chemical and material costs in year 2010.

Chemical/material	Unit chemical/material cost (2010$/metric ton)
Ammonium nitrate fertilizer, 34% N (purchased and delivered[a])	507[b]
Hydrated lime (purchase and delivered[a])	370[c]
Fine concrete (on-site process)	17[d]
Fine concrete (purchased and delivered[a])	34[d]
Compost (on-site process)	51[e]
Compost (purchased and delivered[a])	68[e]

[a]Delivery cost of $17/metric ton based on verbal quote provided by Sonny Glasbrenner Inc. (2010)
[b] USDA (2010)
[c] Republic Mills Inc. (2010)
[d] Cost based on verbal quote provided by Sonny Glasbrenner Inc. (2010)
[e] U.S.EPA (1992)

Based on the amount of chemicals or materials required, the chemical/material unit cost, and the emission rate of H_2S; chemical/material cost per kg of H_2S treated was determined as shown in Table 4-5. Due to the need for yearly application, present worth (PW) costs of fertilizer were determined assuming an average interest rate of 5% (USTREAS, 2010). Ammonium nitrate fertilizer is the most cost effective, followed by hydrated lime, fine concrete, and yard waste compost, when only the chemical/material costs are considered. Fine concrete and yard waste compost covers are expensive measures to control H_2S emissions because of the large amount of materials needed to create a cover. Controlling H_2S emissions using fine concrete and compost is less expensive at landfills that provide on-site concrete recovery and composting facilities; however, ammonium nitrate fertilizer or hydrated lime would still be more cost effective applications.

Table 4-5. Chemical/material costs to treat case-study landfill.

Chemical/Material	Amount used (metric ton)	Total PW cost (2010 $)	Cost ($/kg H_2S removed)
NH_4NO_3 Fertilizer	157	76,200[1]	0.94
Hydrated lime	260	96,200	1.19
Fine concrete (on-site process)	31,200	530,400	6.6
Fine concrete (purchased)	31,200	1,060,800	13.1
Compost (on-site process)	17,800	905,800	11.2
Compost (purchased)	17,800	1,210,400	14.7

[1] PW of annual application

In addition to cost benefits, an autotrophic denitrification landfill cover system provides advantages associated with simple construction and effective control. The products resulting from biological conversion of H_2S, sulfate and sulfur, could be the concerns because infiltrating precipitation could lead to leaching of these oxidized materials back into the landfill.

Consequently, H_2S may be regenerated from the sulfate and sulfur under anaerobic conditions within the landfill. Therefore, multiple additions of fertilizer may be required for long-term H_2S control.

Lime-amemded soil cover system also provides advantages similar to autotrophic denitrification landfill cover system including cost benefits, simple construction and effective operation. However, lime dust can be created while mixing lime and soil, which may pose health concerns such as skin, eye, and respiratory irritation to workers (MSDS, 2008). Addition of lime would create an alkaline environment in the soil cover system, resulting in an incrase of pH. Diffusing H_2S from landfill is then neutralized within the cover soil. When the capacity for neutralization is exhausted, H_2S may be released. Consequently, additional lime may be need.

Even though construction of a fine concrete cover system is simple, there are some drawbacks associated with it. Because of the considerable amount required, fine concrete may not be available in sufficient quantities. Working with fine concrete may create health concerns similar to working with lime. Similar to using soil amended with hydrated lime as a cover, the H_2S neutralization capacity is limited and additional fine concrete may be needed.

Construction of compost landfill cover system is less complicated. However, the cover system requires a considerable amount of compost, which may not be available in sufficient quantities to create a 60-cm cover. Sulfate and sulfur, which are the products of biological oxidation of H_2S, may be leached back by infiltrating precipication and H_2S may be reproduced. In the long run, the compost cover may become clogged by particulate matter and/or biomass growth, preventing oxygen diffusion. The system would be less effective and the cover need to be replaced.

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CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Autotrophic denitrification has been adopted in environmental applications including treatment of water, groundwater, wastewater or gaseous streams contaminated with sulfur and/or nitrogen compounds. However, there have been no studies reported in the literature on hydrogen sulfide removal using autotrophic denitrification from landfills. In this study, a proof-of-concept of autotrophic denitrification landfill biocover was investigated using microcosm followed by laboratory-scale column experiments. Based on the results of this study the conclusions for the microcosm and column experiments can be drawn as followings.

Microcosm experiments were conducted in order to prove the concept of autotrophic denitrification in a landfill cover. Although microcosms did not simulate the normally unsaturated cover system, they allowed experimental control of the process. Soil, compost, and sand were tested as landfill cover materials under saturated autotrophic denitrification conditions with aqueous hydrogen sulfide-nitrate as the electron donor-acceptor couple. Microcosm results demonstrated that autotrophic denitrification in landfill covers composed of soil or compost proved is possible, as hydrogen sulfide and nitrate were removed and sulfate was produced. Hydrogen sulfide was also removed physically/chemically by soil and compost. Results indicated that the addition of nitrate into soil and compost can stimulate indigenous autotrophic denitrifying bacteria which are capable of hydrogen sulfide oxidation biologically under anoxic conditions. The presence of autotrophic denitrification bacteria was confirmed by PCR analyses of soil and compost samples taken from autotrophic column experiments. Additionally,

microcosm results demonstrated that two steps are involved in hydrogen sulfide oxidation under anoxic condition. Firstly, hydrogen sulfide is oxidized to sulfur; then, sulfur is oxidized to sulfate if there is excess nitrate. Zero-order kinetics described the hydrogen sulfide oxidation. The rates of hydrogen sulfide oxidation under autotrophic denitrification in soil and compost were 2.57 mg H_2S/d-g dry soil and 0.17 mg H_2S/d-g dry compost, respectively. Because of the rapid removal of hydrogen sulfide in soil, the actual removal rate in soil may be greater than the calculated rate.

Given the successful results of hydrogen sulfide removal under saturated condition of soil, further study was conducted under conditions more closely simulating the landfill soil cover system (i.e. unsaturated condition and gaseous H_2S removal). Two sets of laboratory-scale column studies containing seven cm of soil were carried out. Each set consisted of an autotrophic column (prepared with nitrate addition) and a control column (prepared without nitrate). The first set was exposed to high concentration of H_2S in a gas stream, while the second set had a lower concentration of H_2S. Results demonstrated that gaseous H_2S can be effectively removed using an autotrophic denitrification landfill soil cover. At the higher loading of H_2S, partial oxidation of H_2S to elemental sulfur was observed. Conversely, complete oxidation of H_2S to sulfate was found at the lower loading of H_2S. H_2S oxidation in the column with higher loading was found to follow zero-order kinetics. The rate of H_2S oxidation was 0.46 mg H_2S removed/d-g dry soil.

Due to these very promising experimental results, an economic comparison of cover systems including autotrophic denitrification, soil amended with lime, fine concrete, and compost covers was conducted. Based on the case-study landfill area of 0.04 km^2 and the estimated H_2S emissions of 80,900 kg over the 15-year period, costs of active cover system components were estimated to be \$0.94/kg H_2S removed for NH_4NO_3 fertilizer, \$1.19/kg H_2S

removed for hydrated lime, \$6.6/kg H_2S removed for fine concrete produced on-site, \$13.1/kg H_2S removed for fine concrete purchased and delivered, \$11.2/kg H_2S removed for compost produced on-site, and \$14.7/kg H_2S removed for compost purchased and delivered. Results showed that ammonium nitrate fertilizer was the most cost effective, followed by hydrated lime, fine concrete, and yard waste compost. Based on laboratory results and cost effectiveness of fertilizer, the autotrophic denitrificaiton landfill biocover offers an attractive alternative to control emission of H_2S generated from landfills.

Recommendations

This work is effective as a proof-of-concept, indicating that the addition of nitrate directly to landfill covers under anoxic conditions can be utilized to control H_2S emissions effectively and economically. However, future work should be conducted to better determine and quantify the reactions taking place under autotrophic denitrification landfill covers. The following investigations should be performed.

- Larger scale column studies should be performed to explore scaling effects on H_2S removal kinetics.
- A biological assessment of the major active microbial communities in autotrophic denitrification landfill cover should be performed.
- The intermediate products during sulfide oxidation and nitrate reduction should be determined to better understand the autotrophic denitrification landfill cover.
- Large-scale field studies on autotrophic denitrification landfill cover should be performed to assess the removal performance at full scale.

APPENDIX A
QA/QC DATA OF MICROCOSM EXPERIMENTS

A quality assurance and quality control (QA/QC) plan was followed in order to ensure the reliability of the results, as well as to minimize errors while collecting and analyzing the samples. This section describes the activities used for sampling and analysis of microcosm samples.

Cleaning of Classware

Glassware utilized while analyzing liquid samples from microcosm experiments was thoroughly cleaned with soap water. Afterwards, glassware was triple washed with distilled water.

Sample Collection

Liquid samples from microcosm experiments were withdrawn to monitor the disappearance of sulfide and nitrate, and the production of sulfate. Sulfide was analyzed immediately to prevent compound losses by volatilization and/or abiotic oxidation, pH was also determined immediately. Samples for nitrate and sulfate determination were membrane filtered (0.45 μm) and stored without headspace.

Sample Analysis

Analytical procedures for sulfide, nitrate, sulfate, and pH followed minimum quality assurance and quality control requirements to assess precision and accuracy of the method utilized. Duplicate samples were taken for precision by calculation of relative percent difference (RPD). RPD is calculated by taking the absolute value of the difference between the two measurements, and dividing it by the average of the two, and multiplying the quotient by 100. A relative percent difference value of less than 10 is typically good. The accuracy of the analysis

was also assessed by preparation of spikes. A known quantity of standard material was added to a known volume of sample. The yield of a spike is determined by taking the difference between the spiked and unspiked samples, and dividing by the amount that was spiked with, and multiply the quotient by 100. An acceptable percent yield is between 80 and 120%. QA/QC data for H_2S, nitrate, sulfate, and pH measurements are provided as follows.

Table A - 1. Concentrations of H_2S, nitrate and sulfate, and pH values from sand microcosms (with nitrate addition): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.521	97	0.8	1.459	116	1.3	BD	98	0.0	7.00	0.0
1	0.520	102	0.0	1.406	116	2.6	BD	98	0.0	6.98	0.0
2	0.525	100	0.0	1.420	116	2.3	BD	98	0.0	6.97	0.0
3	0.521	99	0.8	1.435	112	2.0	BD	100	0.0	6.95	0.0
4	0.519	101	0.0	1.436	112	1.3	BD	100	0.0	6.99	0.0
5	0.516	100	0.8	1.377	112	2.6	BD	100	0.0	7.02	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 2. Concentration of H_2S, nitrate and sulfate, and pH values from sand microcosms (Abiotic control): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.519	97	0.0	1.438	116	0.6	BD	98	0.0	7.00	0.0
1	0.508	98	0.0	1.443	116	1.9	BD	98	0.0	7.00	0.0
2	0.523	99	0.8	1.427	116	2.0	BD	98	0.0	7.01	0.0
3	0.504	97	1.5	1.432	112	0.3	BD	100	0.0	7.00	0.0
4	0.506	98	0.8	1.445	112	1.4	BD	100	0.0	7.00	0.0
5	0.506	97	0.0	1.425	112	0.1	BD	100	0.0	7.00	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 3. Concentration of H_2S, nitrate and sulfate, and pH values from sand microcosms (Biotic control): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.518	97	0.8	BD	116	0.0	BD	98	0.0	7.00	0.0
1	0.516	101	1.5	BD	116	0.0	BD	98	0.0	7.00	0.0
2	0.521	100	0.0	BD	116	0.0	BD	98	0.0	7.01	0.0
3	0.516	99	0.0	BD	112	0.0	BD	100	0.0	7.01	0.0
4	0.514	99	0.8	BD	112	0.0	BD	100	0.0	7.02	0.0
5	0.512	99	0.8	BD	112	0.0	BD	100	0.0	7.02	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 4. Concentration of H_2S, nitrate and sulfate, and pH values from sand microcosms (with nitrate addition): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.516	98	0.0	1.447	94	0.0	BD	109	0.0	7.00	0.0
1	0.506	99	0.8	1.452	94	0.3	BD	109	0.0	7.03	0.0
2	0.487	99	0.8	1.438	94	0.8	BD	109	0.0	7.01	0.0
3	0.496	101	0.0	1.447	92	0.1	BD	98	0.0	7.05	0.0
4	0.498	97	0.0	1.430	92	0.4	BD	98	0.0	6.99	0.0
5	0.505	98	0.0	1.441	92	0.5	BD	98	0.0	7.00	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 5. Concentration of H_2S, nitrate and sulfate, and pH values from sand microcosms (Abiotic control): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.502	95	0.8	1.441	94	0.8	BD	109	0.0	7.03	0.0
1	0.501	98	1.5	1.447	94	0.6	BD	109	0.0	7.02	0.0
2	0.474	95	1.6	1.439	94	0.6	BD	109	0.0	7.00	0.0
3	0.500	100	0.0	1.421	92	0.5	BD	98	0.0	6.99	0.0
4	0.496	95	0.0	1.431	92	2.4	BD	98	0.0	6.98	0.0
5	0.503	96	0.7	1.413	92	0.6	BD	98	0.0	6.97	0.0

BD = below detection limit
R = percent recovery
RPD = relative percent difference

Table A - 6. Concentration of H_2S, nitrate and sulfate, and pH values from sand microcosms (Biotic control): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.500	93	0.0	BD	94	0.0	BD	109	0.0	7.05	0.0
1	0.504	98	0.0	BD	94	0.0	BD	109	0.0	7.04	0.0
2	0.485	98	1.6	BD	94	0.0	BD	109	0.0	7.00	0.0
3	0.500	100	0.0	BD	92	0.0	BD	98	0.0	7.01	0.0
4	0.495	96	0.8	BD	92	0.0	BD	98	0.0	6.99	0.0
5	0.496	97	2.2	BD	92	0.0	BD	98	0.0	7.00	0.0

BD = below detection limit
R = percent recovery
RPD = relative percent difference

Table A - 7. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (with nitrate addition): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.441	99	1.6	4.015	94	0.0	BD	98	0.0	7.12	0.0
1	1.236	99	0.0	3.986	94	0.0	BD	98	0.0	7.10	0.3
2	1.179	96	3.9	3.957	94	0.0	BD	98	0.0	7.12	0.1
3	1.102	97	6.3	3.883	94	0.0	BD	98	0.0	7.12	0.3
4	BD	103	4.7	2.877	94	0.1	0.168	98	0.5	7.27	0.3
5	BD	102	0.0	2.426	102	0.0	0.350	96	0.1	7.23	0.0
6	BD	105	0.0	2.358	102	0.1	0.712	96	0.3	7.17	0.1
7	BD	104	0.0	2.183	102	0.0	0.873	96	0.1	7.18	0.3
8	BD	99	0.0	1.422	102	0.1	1.237	96	0.1	7.07	0.3
9	BD	100	0.0	1.492	102	0.1	1.269	96	0.0	7.09	0.1
10	BD	110	0.0	1.445	102	0.2	1.355	96	0.0	7.14	0.3

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 8. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (Abiotic control): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.44	99	0.0	4.014	107	0.0	BD	99	0.0	7.03	0.1
1	1.23	98	3.9	4.005	107	0.0	BD	99	0.0	7.04	0.0
3	1.22	101	0.8	3.918	107	0.0	BD	99	0.0	7.02	0.0
5	1.16	96	0.0	3.968	107	0.0	BD	99	0.0	7.05	0.1
7	1.14	102	0.0	4.105	107	0.0	BD	99	0.0	7.05	0.0
9	1.13	98	5.5	4.067	107	0.0	BD	99	0.0	7.07	0.1
10	1.12	97	3.0	4.093	107	0.0	BD	99	0.0	7.08	0.1

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 9. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (Biotic control): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.424	99	0.0	BD	99	0.0	BD	98	0.0	7.10	0.0
1	1.189	98	0.0	BD	99	0.0	BD	98	0.0	7.10	0.3
3	1.124	96	3.9	BD	99	0.0	BD	98	0.0	7.10	0.0
5	1.125	100	1.6	BD	99	0.0	BD	98	0.0	7.09	0.0
7	1.094	101	1.6	BD	99	0.0	BD	98	0.0	7.10	0.0
9	1.095	97	1.6	BD	99	0.0	BD	98	0.0	7.12	0.3
10	1.082	97	0.7	BD	99	0.0	BD	98	0.0	7.14	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 10. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (with nitrate addition): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.453	91	0.0	4.013	106	3.9	BD	99	0.0	7.14	0.0
1	1.378	92	0.5	3.937	106	0.8	BD	99	0.0	7.13	0.1
2	1.297	103	0.8	4.033	106	1.1	BD	99	0.0	7.11	0.1
3	1.129	101	0.8	4.010	106	2.7	BD	99	0.0	7.12	0.8
4	BD	105	0.0	2.976	106	6.4	0.246	99	2.7	7.21	0.8
5	BD	104	0.0	2.158	106	8.8	0.597	99	1.6	7.16	0.4
6	BD	102	0.0	2.405	106	7.2	0.616	99	2.6	7.18	0.1
7	BD	100	0.0	2.285	106	2.2	0.732	99	5.2	7.15	0.1
8	BD	101	0.0	2.175	106	1.5	0.811	99	6.4	7.12	0.4
9	BD	101	0.0	1.555	106	4.6	1.236	99	9.6	7.07	0.1
10	BD	104	0.0	1.521	106	8.8	1.200	99	3.4	7.10	0.4

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 11. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (Abiotic control): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.442	94	0.0	4.016	96	0.7	BD	106	0.0	7.07	0.6
1	1.371	96	0.5	3.997	96	1.2	BD	106	0.0	7.11	0.1
3	1.226	98	0.0	4.062	96	1.8	BD	106	0.0	7.05	0.1
5	1.170	98	0.8	4.093	96	0.3	BD	106	0.0	7.04	0.1
7	1.085	90	0.8	4.007	96	1.1	BD	106	0.0	7.02	0.3
9	1.106	96	3.9	4.016	96	1.2	BD	106	0.0	7.08	0.1
10	1.111	98	2.4	3.989	96	0.1	BD	106	0.0	7.03	0.1

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 12. Concentration of H_2S, nitrate and sulfate, and pH values from soil microcosms (Biotic control): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	1.453	92	0.8	BD	105	0.0	BD	109	0.0	7.14	0.3
1	1.331	94	0.5	BD	105	0.0	BD	109	0.0	7.14	0.3
3	1.169	98	1.6	BD	105	0.0	BD	109	0.0	7.11	0.0
5	1.125	99	4.0	BD	105	0.0	BD	109	0.0	7.12	0.4
7	1.068	92	3.9	BD	105	0.0	BD	109	0.0	7.07	0.3
9	1.038	100	0.8	BD	105	0.0	BD	109	0.0	7.05	0.1
10	1.080	101	1.6	BD	105	0.0	BD	109	0.0	7.08	0.3

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 13. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (with nitrate addition): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.679	98	0.8	1.867	110	1.0	0.057	103	4.3	7.08	0.1
1	0.510	92	5.6	1.887	110	2.1	0.056	103	9.0	7.10	0.4
2	0.452	98	2.4	1.897	110	2.7	0.064	103	6.4	7.10	0.0
3	0.446	101	0.8	1.846	110	0.5	0.064	103	4.6	7.12	0.1
4	0.417	101	2.3	1.801	110	1.2	0.065	103	2.0	7.11	0.0
5	0.355	104	2.1	1.690	110	8.8	0.159	103	5.6	7.13	0.4
6	0.242	101	1.4	1.556	110	5.3	0.276	103	7.4	7.12	0.6
7	0.209	105	3.1	1.442	110	1.1	0.289	103	4.7	7.11	1.1
8	0.134	106	3.1	1.284	110	7.0	0.391	103	6.3	7.10	0.7
9	0.081	107	0.0	1.106	110	3.2	0.491	103	5.6	7.12	0.1
10	BD	106	0.0	0.922	110	2.2	0.665	103	4.4	7.13	0.0

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 14. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (Abiotic microcosm): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.734	99	96	1.911	104	0.1	0.084	108	4.1	7.01	0.1
1	0.586	91	93	1.919	104	0.3	0.069	108	4.4	6.95	0.1
3	0.508	101	103	1.915	104	1.4	0.082	108	4.9	7.02	0.3
5	0.503	102	104	1.909	104	1.9	0.069	108	3.2	6.99	1.1
7	0.471	105	104	1.882	104	2.0	0.064	108	2.1	7.03	0.0
9	0.462	105	102	1.858	104	0.2	0.065	108	1.2	7.04	0.3
10	0.457	105	104	1.868	104	0.2	0.068	108	3.6	7.04	0.3

PR = percent recovery
RPD = relative percent difference

Table A - 15. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (Biotic control): Series 1.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.740	98	99	0.239	107	1.5	0.056	105	4.6	7.08	0.3
1	0.523	93	91	0.232	107	4.9	0.061	105	3.2	7.10	0.1
3	0.423	103	101	0.204	107	5.1	0.063	105	2.8	7.10	0.4
5	0.441	104	102	0.181	107	3.7	0.061	105	4.1	7.11	0.0
7	0.310	104	105	0.153	107	4.6	0.062	105	2.5	7.16	0.1
9	0.352	102	105	0.145	107	3.9	0.060	105	3.1	7.14	0.1
10	0.259	105	105	0.062	107	4.4	0.062	105	4.6	7.17	0.3

PR = percent recovery
RPD = relative percent difference

Table A - 16. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (with nitrate addition): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.687	96	2.2	1.890	104	0.2	0.061	103	0.4	6.99	0.0
1	0.505	96	1.5	1.897	104	0.0	0.063	103	0.1	7.03	0.4
2	0.485	103	3.0	1.910	104	0.7	0.060	103	0.0	7.02	0.7
3	0.437	93	2.2	1.867	104	2.2	0.062	103	0.1	7.03	0.1
4	0.365	97	1.5	1.841	104	1.5	0.061	103	0.2	7.09	0.7
5	0.361	100	2.6	1.796	104	1.5	0.114	103	1.1	7.04	0.4
6	0.342	102	1.5	1.684	104	0.2	0.183	103	3.7	7.04	0.6
7	0.315	98	3.0	1.484	104	2.2	0.289	103	3.4	7.05	0.1
8	0.226	103	4.4	1.402	104	2.4	0.358	103	1.0	7.04	0.9
9	0.108	100	3.4	1.321	104	4.4	0.499	103	4.2	7.06	0.4
10	BD	108	0.0	1.140	104	0.9	0.659	103	1.6	7.05	0.3

BD = below detection limit
PR = percent recovery
RPD = relative percent difference

Table A - 17. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (Abiotic microcosm): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.700	102	0.0	1.879	102	0.1	0.078	99	0.9	6.93	0.0
1	0.576	95	2.3	1.886	102	0.5	0.060	99	2.8	6.94	0.1
3	0.506	96	3.7	1.882	102	0.7	0.063	99	3.9	6.94	0.3
5	0.457	111	3.7	1.903	102	0.6	0.067	99	2.0	6.96	0.4
7	0.426	99	2.8	1.895	102	5.3	0.058	99	3.6	6.94	0.7
9	0.434	97	3.5	1.910	102	0.4	0.073	99	0.7	6.98	0.3
10	0.441	100	2.3	1.871	102	1.6	0.070	99	4.9	6.98	0.1

PR = percent recovery
RPD = relative percent difference

Table A - 18. Concentration of H_2S, nitrate and sulfate, and pH values from compost microcosms (Biotic control): Series 2.

Time (Days)	Concentration									pH	
	Hydrogen Sulfide			Nitrate-Nitrogen			Sulfate				
	mM	PR	RPD	mM	PR	RPD	mM	PR	RPD	Value	RPD
0	0.693	96	0.7	0.248	107	4.8	0.067	99	4.8	6.99	0.0
1	0.473	96	0.8	0.225	107	3.2	0.064	99	2.5	7.02	0.0
3	0.406	92	3.3	0.194	107	3.4	0.065	99	0.5	7.04	0.1
5	0.337	110	0.7	0.180	107	4.1	0.064	99	5.3	7.04	0.1
7	0.319	115	3.7	0.143	107	3.8	0.061	99	0.5	7.00	0.1
9	0.141	97	2.8	0.053	107	4.5	0.062	99	3.2	7.09	0.1
10	0.254	100	3.5	0.107	107	3.2	0.063	99	1.0	7.06	0.0

PR = percent recovery
RPD = relative percent difference

APPENDIX B
UNSUCCESSFUL COLUMN EXPERIMENTS

Prior to the final experimental design with 7-cm thickness of soil as received, several columns with various thicknesses of soil were used as concluded in Table B - 1. Detail explanations are shown below.

Table B - 1. Unsuccessful column experiments.

Experiment	Soil packed	Observations
1	20 cm in height/15 cm in diameter Soil as received tested	Oxygen intrusion, no H_2S detected at the outlet
2	5 cm in height/15 cm in diameter Soil as received tested	Oxygen intrusion, no H_2S detected at the outlet
3	15 cm in height/5 cm in diameter Soil as received tested	No H_2S detected at the outlet
4	3 cm in height/5 cm in diameter Sieved soil and sieved soil acid tested	Early breakthrough of H_2S
5	7 cm in height/5 cm in diameter Sieved soil tested	Early breakthrough of H_2S

Experiment 1:

Two laboratory-scale columns were created using 0.15 m ID, schedule-40 clear polyvinyl chloride (PVC) pipe, an autotrophic denitrification column, and a control column. Each column is 0.5 m in length with PVC caps at the bottom end, and female adapters and male cleanout plug at the top end. A 10-cm layer of gravel was placed at the bottom of each column to ensure homogenous gas distribution. A layer of geotextile was placed on top of the gravel layer to prevent penetration of soil. Each column contained 20 cm of soil. The autotrophic column was prepared with KNO3 addition; an identical control column was prepared without nitrate. A gas stream was introduced to the columns with a H_2S concentration of 930 ppm. See Figure B - 1 for a schematic drawing of a laboratory-scale biocover column used in this experiment.

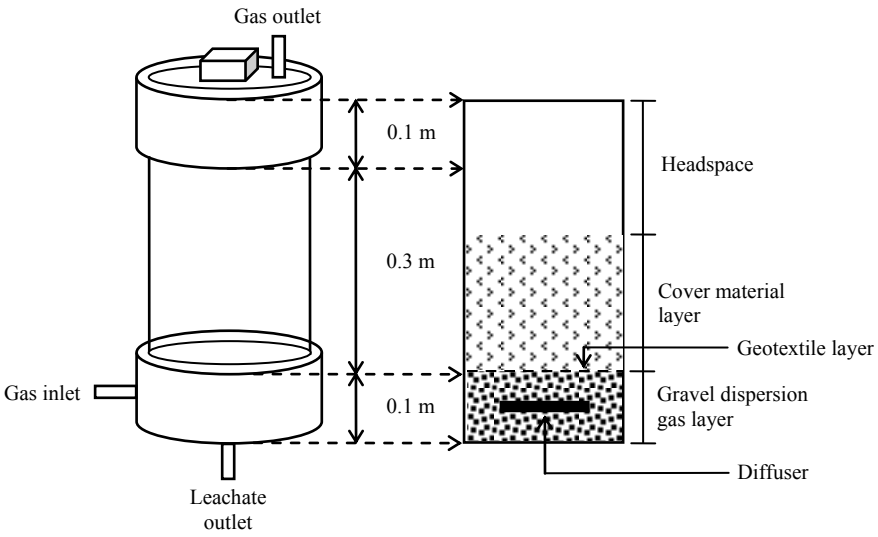

Figure B - 1. A schematic drawing of a laboratory-scale column.

During seven days of operating period, there was no H_2S detected at the outlets (Figure B - 2), suggesting that H_2S is absorbed by a large amount of soil. Columns were then shut down and some amount of soil from both columns was taken out until five centimeters in depth of soil were left.

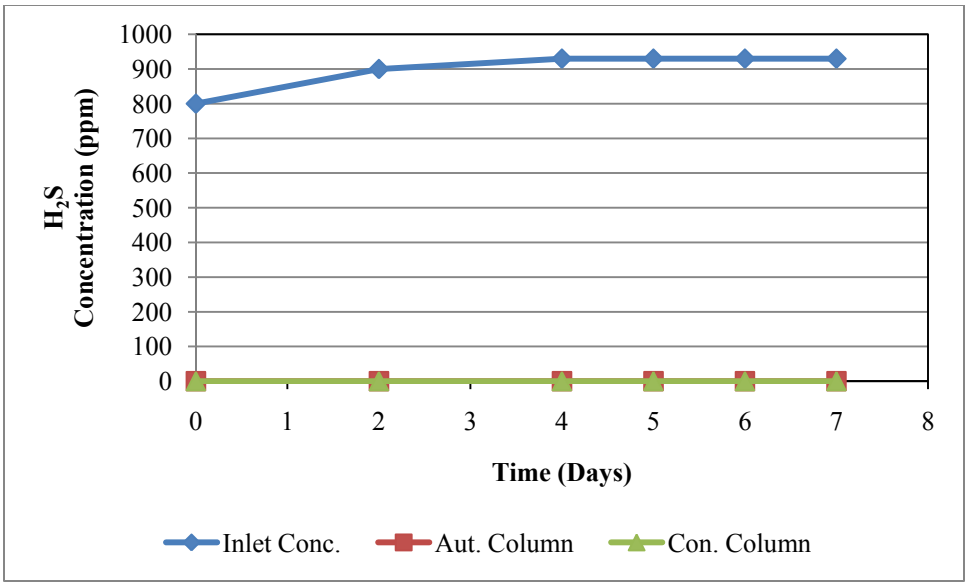

Figure B - 2. H_2S inlet and outlet concentrations from both autotrophic and control columns of experiment 1.

Experiment 2:

Autotrophic and control columns contained five centimeters of soil from Experiment 1 were continued to monitor for H_2S concentrations. The H_2S concentrations in control and autotrophic columns measured at the inlet and the outlet during the operating period are shown in Figure B - 3. In control column, breakthrough was seen after operating for 2 weeks. In autotrophic column, the H_2S concentrations peaked within 4 days, following which H_2S was effectively removed and remained undetected. Both columns were then shut down. After columns were dismantled, white powder was observed at the bottom of both columns, suggesting incomplete oxidation of H_2S to sulfur caused by oxygen intrusion, resulting in undetectable concentrations of H_2S at the outlets.

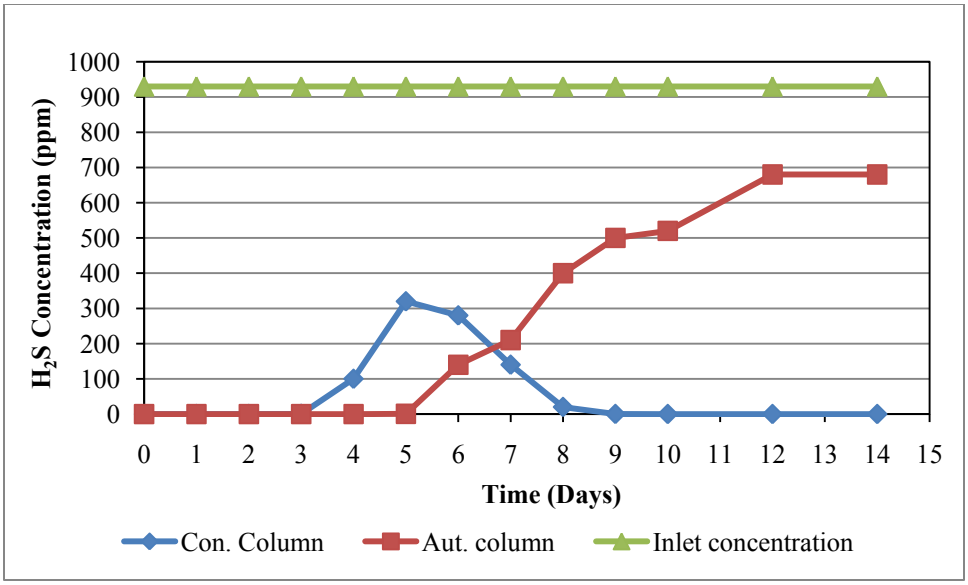

Figure B - 3. H_2S inlet and outlet concentrations from both autotrophic and control columns of experiment 2.

Experiment 3:

Two smaller laboratory-scale columns were recreated using 5-cm inside diameter, schedule-40 clear polyvinyl chloride (PVC) pipe for an autotrophic denitrification column (prepared with KNO_3 addition) and a control column (prepared without KNO_3). Each column was 20 cm in length with PVC female adapters and male cleanout plugs at each end. The caps were modified to permit gas introduction and exit. A 5-cm layer of gravel was placed at the bottom of each column to ensure homogenous distribution of gas. A layer of geotextile was placed on top of the gravel layer to support the soil. Soil was placed in the columns to a depth of seven centimeters. Gas containing H_2S was introduced at the bottom of the columns. Prior to introducing with H_2S, columns were tested for leaking and no leaks were found. After operated for 11 days, there is no H_2S detected at the outlets (Figure B - 4), suggesting that H_2S is absorbed by a large amount of soil

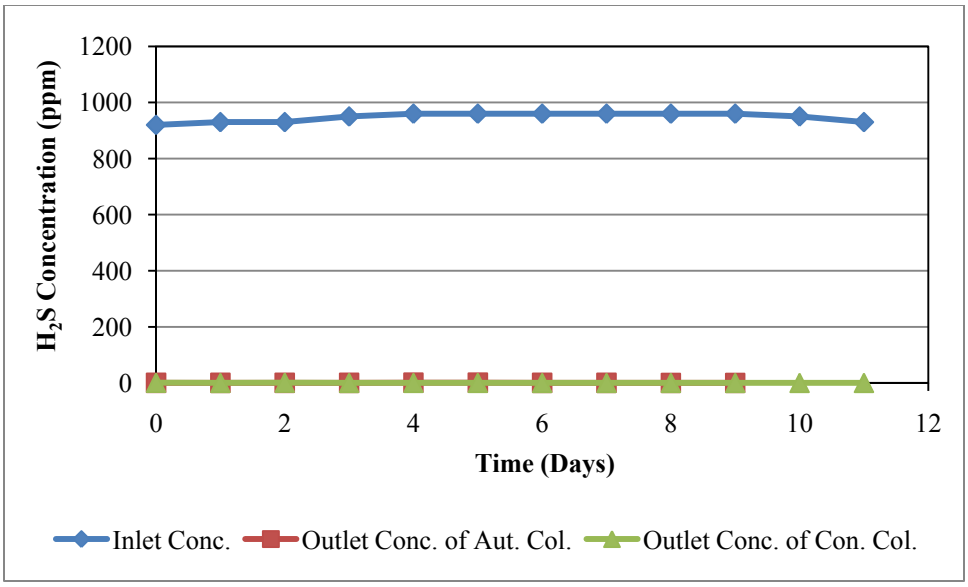

Figure B - 4. H_2S inlet and outlet concentrations from both autotrophic and control columns of experiment 3.

Expreiment 4:

Columns using normal soil and acidic soil with packing height of 3 cm were operated for 24 hrs. H_2S outlet concentrations were monitored during the operation as shown in Figure B - 5. In both columns, the breakthrough was seen early as expected. After 24 hrs of operation, outlet concentration of acidic soil column almost reached the inlet concentration (930 ppm). Considering the early breakthrough it might be because of the preferential flow due to the thinner of soil packing (3 cm of packing). For the next experiment the thicker soil packing height (7-10 cm) was applied.

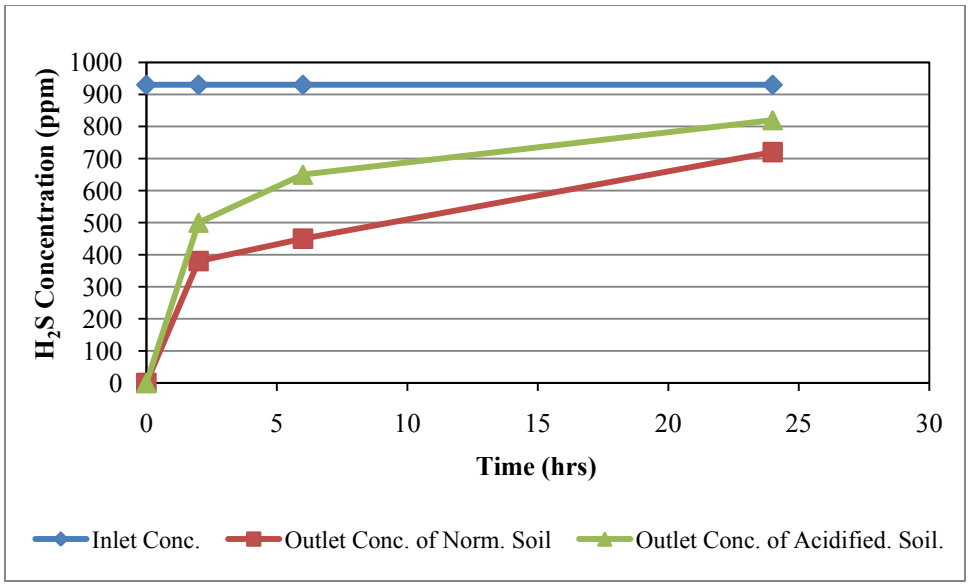

Figure B - 5 H_2S inlet and outlet concentrations from normal soil column and acidic soil column of experiment 4.

Experiment 5:

Columns using sieved soil with packing height of 7 cm were operated for 24 hrs. H_2S outlet concentrations were monitored during the operation shown in Figure B - 6. In both columns the breakthrough are seen early. After 24 hrs of operation, outlet concentrations from both columns almost reached the inlet concentration (930 ppm). Considering the early breakthrough it might be because of the shortcircuiting along the inside wall caused by dense soil.

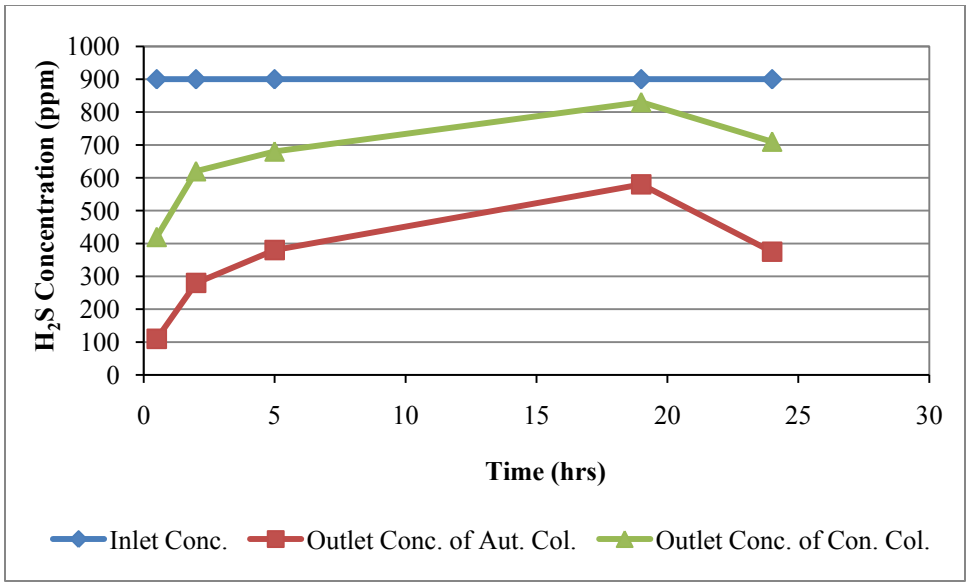

Figure B - 6. H_2S inlet and outlet concentrations from both autotrophic and control columns of experiment 5.

APPENDIX C
QA/QC DATA OF COLUMN EXPERIMENTS

The following activities were used as part of a quality assurance and quality control (QA/QC) plan for sampling and analysis of hydrogen sulfide gas.

Container and Equipment Cleaning

The Tedlar® bags utilized for sampling gas were cleaned three times before and after sampling. The bags were cleaned by opening the bag's valve and remove all the gas out of the bags. Afterwards, the laboratory air was pumped into the bags and was released out of the bags.

Sample Collection

Gas samples were collected at the inlet and outlet for H_2S concentration determination in Tedlar® bags. H_2S was analyzed using gas detection tubes (RAE Systems, San Jose, CA) at least once per day until H_2S breakthrough was observed.

Sample Analysis

Gas detection tubes employing various chemical reactions were used for H_2S measurement. A model LP-1200 piston-type hand pump (RAE Systems, San Jose, CA) was used to draw known volumes of sample through the detector tubes. Hydrogen sulfide detector-tubes of various detections range from 0.2-1000 ppm were used. The detector-tube is pre-calibrated with relative standard deviation of ±12%. Duplicate samples were taken for precision by calculation of relative percent difference (RPD). QA/QC data for H_2S gas measurements are provided as follows.

Table C - 1. Hydrogen sulfide concentrations of control column at high loading H_2S

Day	Flowrate		H_2S Inlet Concentration		H_2S outlet Concentration	
	mL/min	RPD	ppm	RPD	ppm	RPD
0	30.2	2.6	920	0.0	0	0.0
0.02	30.9	3.6	920	0.0	42	0.0
0.75	30.3	2.3	920	0.0	180	0.0
1	30.6	2.3	920	0.0	500	0.0
1.8	30.4	1.0	920	0.0	620	0.0
2	30.5	1.0	920	0.0	680	0.0
3	31.3	0.6	920	0.0	700	0.0
4	30.9	1.3	900	0.0	680	0.0
5	31.1	1.1	920	0.0	680	0.0
7	30.4	2.3	920	0.0	700	0.0
9	30.3	2.6	960	0.0	790	0.0
11	30.1	1.8	920	0.0	810	0.0
13	30.2	2.1	920	0.0	810	0.0
15	30.1	1.8	920	0.0	820	0.0

RPD = relative percent difference

Table C - 2. Hydrogen sulfide concentrations of autotrophic column at high loading H_2S

Day	Flowrate		H_2S Inlet Concentration		H_2S outlet Concentration	
	mL/min	RPD	ppm	RPD	ppm	RPD
0	30.4	3.0	920	0.0	0	0.0
0.02	29.7	3.4	920	0.0	10	0.0
0.13	30.3	2.6	920	0.0	44	0.0
0.88	31.1	1.6	920	0.0	350	0.0
1.00	30.3	1.5	950	0.0	420	0.0
1.88	31.1	2.6	930	0.0	500	0.0
2.00	31.0	2.4	930	0.0	520	0.0
2.88	30.7	9.0	920	0.0	650	0.0
3.00	30.4	1.0	920	0.0	600	0.0
3.83	32.0	1.7	920	0.0	620	0.0
4.00	29.5	1.2	920	0.0	600	0.0
5	29.8	1.3	920	0.0	590	0.0
6	32.2	1.7	920	0.0	550	0.0
7	31.1	2.3	920	0.0	500	0.0
7.8	30.9	1.5	920	0.0	400	0.0
8.3	29.9	1.7	920	0.0	380	0.0
8.9	30.6	1.3	920	0.0	350	0.0

Day	Flowrate		H_2S Inlet Concentration		H_2S outlet Concentration	
	mL/min	RPD	ppm	RPD	ppm	RPD
9.2	30.5	1.8	930	0.0	320	0.0
9.9	30.5	2.6	930	0.0	290	0.0
10.1	30.7	2.3	930	0.0	250	0.0
10.9	30.5	2.3	920	0.0	180	0.0
11.3	30.7	2.3	920	0.0	150	0.0
11.9	30.6	1.3	920	0.0	115	0.0
12.3	30.6	1.8	920	0.0	95	0.0
13.0	30.4	2.6	920	0.0	60	0.0
13.8	30.6	3.1	920	0.0	35	0.0
14.3	31.1	1.8	920	0.0	25	0.0
14.9	30.7	1.5	900	0.0	18	0.0
15.4	30.7	1.5	900	0.0	18	0.0
15.8	30.7	2.6	950	0.0	45	0.0
16.3	30.5	1.5	950	0.0	115	0.0
16.8	30.6	0.8	920	0.0	200	0.0
17.9	30.8	2.4	920	0.0	300	0.0
18.8	30.9	2.6	920	0.0	350	0.0
19.9	30.5	2.8	920	0.0	400	0.0
20.8	30.6	2.6	920	0.0	450	0.0
21.9	30.7	1.8	930	0.0	500	0.0
22.9	30.7	2.0	930	0.0	510	0.0
23.9	30.5	1.8	930	0.0	550	0.0
24.9	31.1	1.4	930	0.0	590	0.0
25.9	31.0	1.6	930	0.0	600	0.0
26.9	31.1	1.4	930	0.0	600	0.0
27.8	30.9	2.1	930	0.0	610	0.0
28.8	30.6	2.6	930	0.0	630	0.0
30.8	31.5	1.3	920	0.0	630	0.0
32.9	31.1	2.1	920	0.0	670	0.0
34.9	31.2	1.4	920	0.0	700	0.0
36.9	31.0	1.6	920	0.0	700	0.0
38.9	30.3	1.8	920	0.0	700	0.0
40.9	30.6	1.1	920	0.0	700	0.0
42.9	31.0	1.8	920	0.0	700	0.0
43.9	30.9	1.5	920	0.0	700	0.0

RPD = relative percent difference

Table C - 3. Hydrogen sulfide concentrations of control column at low loading H_2S

Day	Flowrate		H_2S Inlet Concentration		H_2S outlet Concentration	
	mL/min	RPD	ppm	RPD	ppm	RPD
0.00	30.9	1.6	140	0.0	0	0.0
0.03	31.0	2.1	140	0.0	4	0.0
0.24	31.2	1.4	140	0.0	14	0.0
0.97	30.5	2.1	140	0.0	32	0.0
1.88	31.7	2.4	140	0.0	44	0.0
2.98	32.2	1.1	140	0.0	50	0.0
4.14	32.0	1.9	140	0.0	47	0.0
5.17	32.5	0.8	140	0.0	47	0.0
5.89	30.4	2.0	140	0.0	37	0.0
6.91	31.4	1.6	140	0.0	43	0.0
7.65	30.0	2.2	140	0.0	40	0.0
8.79	29.7	5.7	140	0.0	25	0.0
9.96	30.7	3.6	140	0.0	28	0.0
12.71	34.4	2.0	140	0.0	38	0.0
14.65	31.4	1.7	140	0.0	24	0.0
16.77	31.4	2.0	140	0.0	22	0.0
18.90	31.6	1.8	140	0.0	20	0.0
20.67	31.1	1.6	140	0.0	20	0.0
22.67	31.5	2.0	140	0.0	25	0.0

RPD = relative percent difference

Table C - 4. Hydrogen sulfide concentrations of autotrophic denitrification at low loading H_2S

Day	Flowrate		H_2S Inlet Concentration		H_2S outlet Concentration	
	mL/min	RPD	ppm	RPD	ppm	RPD
0.00	30.9	6.2	140	0.0	0	0.0
0.03	31.2	1.9	140	0.0	2.3	0.0
0.24	29.7	2.9	140	0.0	10	0.0
0.97	30.6	2.1	140	0.0	20	0.0
1.88	30.7	1.6	140	0.0	18	0.0
2.98	31.0	1.6	140	0.0	10	0.0
4.14	30.4	1.5	140	0.0	3	0.0
5.17	28.1	1.2	140	0.0	0.4	0.0
5.89	30.5	1.5	140	0.0	0.2	0.0
6.91	30.1	2.7	140	0.0	10	0.0
7.65	30.6	1.8	140	0.0	18	0.0
8.79	30.6	3.1	140	0.0	10	0.0
9.96	30.8	2.6	140	0.0	12	0.0
12.71	34.3	0.9	140	0.0	22	0.0
14.65	31.5	3.1	140	0.0	18	0.0
16.77	32.4	2.4	140	0.0	18	0.0
18.90	31.4	1.9	140	0.0	15	0.0
20.67	31.0	2.7	140	0.0	15	0.0
22.67	30.9	2.9	140	0.0	18	0.0

RPD = relative percent difference

APPENDIX D
DATA USED FOR COST ANALYSIS

Table D - 1. Monthly amounts of H_2S produced between October 2004 and April 2009.

Time	H_2S produced* (kg)
Oct-04	2860
Nov-04	No available data
Dec-04	No available data
Jan-05	No available data
Feb-05	2500
Mar-05	2520
Apr-05	2570
May-05	2520
Jun-05	2270
Jul-05	2230
Aug-05	1860
Sep-05	1860
Oct-05	1860
Nov-05	2270
Dec-05	2680
Jan-06	2500
Feb-06	2180
Mar-06	1770
Apr-06	1770
May-06	1680
Jun-06	1480
Jul-06	1230
Aug-06	1250
Sep-06	1450
Oct-06	1540
Nov-06	1540
Dec-06	1450
Jan-07	1230
Feb-07	1140
Mar-07	1020
Apr-07	950
May-07	890
Jun-07	770
Jul-07	730
Aug-07	680
Sep-07	680
Oct-07	680

Time	H_2S produced* (kg)
Nov-07	680
Dec-07	640
Jan-08	590
Feb-08	540
Mar-08	500
Apr-08	480
May-08	480
Jun-08	480
Jul-08	500
Aug-08	480
Sep-08	430
Oct-08	410
Nov-08	390
Dec-08	360
Jan-09	340
Feb-09	320
Mar-09	270
Total	**64,500**

* Monthly amounts of H_2S produced were measured by Jambeck et al. (2009).

Table D - 2. Amounts of H_2S produced, NO_3^--N required by stoichiometry, and ammonium nitrate fertilizer required.

Month	H_2S produced* (kg)	Stoichiometry of NO_3^--N** (kg)	NH_4NO_3, 34%N (kg)
1	3,639	2,397	7,051
2	3,475	2,289	6,734
3	3,319	2,187	6,431
4	3,170	2,088	6,142
5	3,027	1,994	5,866
6	2,891	1,905	5,602
7	2,761	1,819	5,350
8	2,637	1,737	5,110
9	2,518	1,659	4,880
10	2,405	1,585	4,661
11	2,297	1,513	4,451
12	2,194	1,445	4,251
13	2,095	1,380	4,060
14	2,001	1,318	3,877
15	1,911	1,259	3,703
16	1,825	1,202	3,537
17	1,743	1,148	3,378
18	1,665	1,097	3,226
19	1,590	1,047	3,081
20	1,518	1,000	2,942
21	1,450	955	2,810
22	1,385	912	2,684
23	1,323	871	2,563
24	1,263	832	2,448
25	1,206	795	2,338
26	1,152	759	2,233
27	1,100	725	2,132
28	1,051	692	2,036
29	1,004	661	1,945
30	959	631	1,857
31	915	603	1,774
32	874	576	1,694
33	835	550	1,618
34	797	525	1,545
35	762	502	1,476
36	727	479	1,409

Month	H_2S produced* (kg)	Stoichiometry of NO_3^--N** (kg)	NH_4NO_3, 34%N (kg)
37	695	458	1,346
38	663	437	1,285
39	634	417	1,228
40	605	399	1,173
41	578	381	1,120
42	552	364	1,069
43	527	347	1,021
44	503	332	975
45	481	317	932
46	459	303	890
47	439	289	850
48	419	276	812
49	400	264	775
50	382	252	740
51	365	240	707
52	348	230	675
53	333	219	645
54	318	209	616
55	304	200	588
56	290	191	562
57	277	182	536
58	264	174	512
59	252	166	489
60	241	159	467
61	230	152	446
62	220	145	426
63	210	138	407
64	201	132	389
65	192	126	371
66	183	121	355
67	175	115	339
68	167	110	323
69	159	105	309
70	152	100	295
71	145	96	282
72	139	91	269
73	133	87	257
74	127	83	245

Month	H_2S produced* (kg)	Stoichiometry of NO_3^--N** (kg)	NH_4NO_3, 34%N (kg)
75	121	80	234
76	116	76	224
77	110	73	214
78	105	69	204
79	101	66	195
80	96	63	186
81	92	60	178
82	88	58	170
83	84	55	162
84	80	53	155
85	76	50	148
86	73	48	141
87	70	46	135
88	67	44	129
89	64	42	123
90	61	40	118
91	58	38	112
92	55	36	107
93	53	35	102
94	50	33	98
95	48	32	93
96	46	30	89
97	44	29	85
98	42	28	81
99	40	26	78
100	38	25	74
101	37	24	71
102	35	23	68
103	33	22	65
104	32	21	62
105	30	20	59
106	29	19	56
107	28	18	54
108	27	17	51
109	25	17	49
110	24	16	47
111	23	15	45
112	22	15	43

Month	H_2S produced* (kg)	Stoichiometry of NO_3^--N** (kg)	NH_4NO_3, 34%N (kg)
113	21	14	41
114	20	13	39
115	19	13	37
116	18	12	36
117	18	12	34
118	17	11	32
119	16	11	31
120	15	10	30
121	15	10	28
122	14	9	27
123	13	9	26
124	13	8	25
125	12	8	23
126	12	8	22
127	11	7	21
128	11	7	20
129	10	7	20
130	10	6	19
131	9	6	18
132	9	6	17
133	8	6	16
134	8	5	16
135	8	5	15
136	7	5	14
137	7	5	14
138	7	4	13
139	6	4	12
140	6	4	12
141	6	4	11
142	6	4	11
143	5	3	10
144	5	3	10
145	5	3	9
146	5	3	9
147	4	3	9
148	4	3	8
149	4	3	8
150	4	3	7

Month	H_2S produced* (kg)	Stoichiometry of NO_3^--N** (kg)	NH_4NO_3, 34%N (kg)
151	4	2	7
152	4	2	7
153	3	2	6
154	3	2	6
155	3	2	6
156	3	2	6
157	3	2	5
158	3	2	5
159	3	2	5
160	2	2	5
161	2	2	4
162	2	1	4
163	2	1	4
164	2	1	4
165	2	1	4
166	2	1	4
167	2	1	3
168	2	1	3
169	2	1	3
170	2	1	3
171	1	1	3
172	1	1	3
173	1	1	3
174	1	1	2
175	1	1	2
176	1	1	2
177	1	1	2
178	1	1	2
179	1	1	2
180	1	1	2
Total	**80,915**	**53,309**	**156,791**

*Amounts of H_2S produced were projected using Equation 4-16.

**Amounts of NO_3^--N required by stoichiometry were calculated using Equation 4-9.

Table D - 3. Calculations of present worth for fertilizer.

Year #	Year	Fertilizer, 34% N (kg)	Inflation Conversion factor* (base year 2009)	Future cost ($)	Equivalent cost (2010 $)	Present worth (2010 $)
1	2010	66,500	1.015	33,715	33,715	33,715
2	2011	38,300	1.030	19,705	19,418	18,766
3	2012	22,100	1.047	11,558	11,205	10,483
4	2013	12,700	1.064	6,750	6,439	5,831
5	2014	7,300	1.082	3,945	3,701	3,246
6	2015	4,200	1.100	2,308	2,129	1,808
7	2016	2,400	1.118	1,340	1,217	1,000
8	2017	1,400	1.136	794	710	565
9	2018	800	1.155	462	406	312
10	2019	500	1.174	293	253	189
11	2020	300	1.190	178	152	109
12	2021	200	1.208	121	101	71
13	2022	100	1.226	61	51	34
14	2023	100	1.244	62	51	33
15	2024	100	1.261	63	51	32
Total		157,000			79,598	76,194

* Sahr (2010)

Future costs of fertilizer from year 2010 to 2024 were determined using various conversion factors based on the unit price of fertilizer in the year 2009 ($500/metric ton). A series of future payments was converted to the present worth of year 2010 using a constant annual interest of 5 percent following the Equation below:

$$PW_{2010} = \frac{F}{(1+i)^n}$$

where PW_{2010} is the present worth in dollars of year 2010, F is future value ($), i is interest rate, and n is number of years.