GYPSUM DRYWALL IMPACT ON ODOR PRODUCTION AT LANDFILLS: SCIENCE AND CONTROL STRATEGIES

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LIST OF ACRONYMS AND UNITS OF MEASUREMENT

atm	Atmospheric Pressure
BDL	Below Detection Limit
C&D	Construction and Demolition
COD	Chemical Oxygen Demand
DI	Deionized (Water)
DO	Dissolved Oxygen
FDEP	Florida Department of Environmental Protection
GC/MS	Gas Chromatography/Mass Spectrophotometry
mg/L	Milligrams Per Liter
MSW	Municipal Solid Waste
NIOSH	National Institute for Occupational Safety and Health
ORP	Oxidation-Reduction Potential
OSHA	Occupation Safety and Health Administration
ppb	Parts Per Billion
ppm	Parts Per Million
SPLP	Synthetic Precipitation Leaching Procedure
SRB	Sulfate-Reducing Bacteria
US EPA	Environmental Protection Agency
VOC	Volatile Organic Compounds
VSC	Volatile Sulfur Compounds

KEYWORDS

Construction and Demolition (C&D) Debris
Gypsum Drywall
Hydrogen Sulfide
Landfill Gas
Land Application
Odor
Recycling
Volatile Sulfur Compounds
Wallboard

ABSTRACT

Research was conducted to characterize gaseous emissions at Construction and Demolition (C&D) debris landfills and to examine the role of gypsum drywall in the production of odor causing gas compounds. Several reports of odor problems at C&D debris landfills in Florida provided the impetus to conduct this work. Gypsum drywall has been associated with the generation of hydrogen sulfide (H_2S) in environments such as landfills. Researchers conducted two separate studies. First, ambient air at the landfill surface and gas beneath the landfill surface were sampled at ten C&D debris landfills in Florida. The samples were analyzed for hydrogen sulfide as well as other odor-causing volatile sulfur compounds (VSCs). The second experiment involved the simulation of C&D debris landfills in the laboratory with an emphasis on measuring hydrogen sulfide concentrations.

The results of the field research confirmed the presence of hydrogen sulfide at C&D debris landfills. H_2S was detected in landfill gas from all ten sites sampled, occurring at both low (below 10 parts per billion [ppb]) and high concentrations (maximum 12,000 parts per million [ppm]). In most cases, the gas collected from beneath the surface of the landfill was a mixture of gas being emitted from the landfill and air. Unlike municipal waste landfills, C&D debris landfills do not produce large volumes of gas and the flux of gas from the landfill surface should be much less. At least 25% of the subsurface gas samples exceeded the odor threshold level (25 ppb). Two sites exceeded the Occupation Safety and Health Administration (OSHA) personal exposure level of 20 ppm. At one site where relatively undiluted landfill gas was collected, the H_2S concentration averaged 3,016 ppm. H_2S concentration in ambient air at the surface of the landfills ranged from below 3 ppb to over 50 ppm. Ambient hydrogen sulfide concentrations were much lower than soil vapor hydrogen sulfide. No direct correlation was observed between H_2S measured at a point in the cover soil and H_2S measured above the landfill surface. H_2S concentrations varied greatly from site to site and from location to location at a particular site. Some possible reasons for the variability encountered included waste heterogeneity, different weather conditions, and management practices. Several other reduced volatile sulfur gases were also detected.

The laboratory research was conducted to observe H_2S generation when drywall was co-disposed with different C&D waste constituents. Laboratory columns were designed and constructed for two experiments. Experiment 1 researched H_2S generation when drywall was co-disposed with wood and concrete. Experiment 2 researched the impact of concrete on H_2S generation and migration. The results of this study indicated that decaying drywall, even alone, leached enough sulfate ions and organic matter for sulfate-reducing bacteria to generate large H_2S concentrations. This study also showed that H_2S concentrations were lower in the presence of concrete, and initially in the presence of wood. The organic acids leaching from the wood lowered the pH of the leaching solution out of the ideal pH range of sulfate-reducing bacteria. But with time, the strength of the organic acids decreased, allowing a more favorable environment for sulfate-reducing bacteria and thus increasing the production of H_2S. A possible H_2S control mechanism could be to add a solution to C&D debris landfills, which would buffer the pH out of the ideal bacterial pH range. An interaction occurred between the concrete and the H_2S gas that also resulted in lower H_2S concentrations. This raised the

possibility of another control mechanism: the addition of crushed concrete, either with the waste or as a cover layer. Further research is needed to investigate possible control mechanisms.

EXECUTIVE SUMMARY

Hydrogen sulfide (H_2S) gas emitted from construction and demolition (C&D) debris landfills in Florida and other states in the United States is becoming a major environmental and a possible health issue. H_2S is generated as a result of a series of reactions that biologically reduce the sulfate leached from gypsum drywall disposed in C&D debris landfills. H_2S is odorous and a known human irritant at low concentrations (< 50 parts per million [ppm]) and can cause death at concentrations greater than 600 ppm. Currently, there are no restrictions on the disposal of gypsum drywall in Florida and little is known about the factors that govern H_2S generation and transport with respect to C&D debris landfills. The emission of H_2S from C&D debris landfills has been a concern throughout the State of Florida. Residents living near C&D debris landfills have voiced complaints about odors coming from these facilities and have cited the landfills as a source of health problems.

Research was conducted on two fronts. A project was performed to characterize gas at C&D debris landfills in Florida. Ambient air at the landfill surface and gas beneath the landfill surface were sampled at ten C&D debris landfills in the state. The samples were analyzed for H_2S as well as other odor-causing volatile sulfur compounds (VSCs). Typical landfill gas constituents such as methane, carbon dioxide, and oxygen were also measured. Laboratory research was also conducted to observe H_2S generation when drywall was co-disposed with different C&D waste constituents. Laboratory columns were designed and constructed for two experiments. Experiment 1 researched H_2S generation when drywall was co-disposed with wood and concrete. Experiment 2 researched the impact of concrete on H_2S generation and migration. A Synthetic Precipitation Leaching Procedure (SPLP) solution was added weekly to simulate rainfall in both sets of experimental columns. Gas was sampled and analyzed for H_2S, carbon dioxide (CO_2), methane (CH_4), and other VSCs concentrations. Leachate was also collected and the following parameters were analyzed: total sulfide, dissolved oxygen (DO), specific conductivity, pH, oxidation-reduction potential (ORP), sulfate, and chemical oxygen demand (COD).

The results of the field research confirmed the presence of H_2S at C&D debris landfills. Hydrogen sulfide was detected in landfill gas from all ten sites sampled, occurring at both low (below 3 ppb) and high concentrations (maximum 12,000 ppm). The gas was most often a mixture of air and gas being emitted from the landfill. At least 25% of the samples at each site exceeded the odor threshold level (25 ppb). Two sites exceeded the Occupation Safety and Health Administration (OSHA) personal exposure level of 20 ppm. The H_2S concentration averaged 3,016 ppm at one site where relatively undiluted landfill gas was collected.

H_2S concentration in ambient air at the surface of the landfills ranged from below 3 ppb to more than 50 ppm. Ambient H_2S concentrations were much lower than soil vapor H_2S. No direct correlation was observed between H_2S measurement at a point in the cover soil and that above the landfill surface. H_2S concentration was extremely variable from site to site and within each site. Some possible reasons for a variance include waste heterogeneity, different weather conditions, and management practices.

The results of the laboratory study indicated that decaying drywall, even alone, leached enough sulfate ions and organic matter for sulfate-reducing bacteria to generate large H_2S concentrations. This study also showed that H_2S concentrations were lower in the presence of concrete and initially in the presence of wood. The organic acids leaching from the wood lowered the pH of the leaching solution out of the ideal pH range of sulfate-reducing bacteria. The strength of the organic acids decreased with time, thus allowing a more favorable environment for sulfate-reducing bacteria and thus increasing the production of H_2S. A possible H_2S control mechanism could be to add to C&D debris landfills a solution to buffer the pH out of the ideal bacterial pH range. An interaction between the concrete and the H_2S gas also resulted in lower H_2S concentrations. This raised the possibility of another control mechanism—the addition of crushed concrete, either with the waste or as a cover layer. Further research is needed to investigate these possible control mechanisms.

1   INTRODUCTION

Gypsum drywall, also referred to as wallboard, is one of the major components of the construction and demolition (C&D) waste stream. Drywall consists of a gypsum ($CaSO_4 \bullet H2O$) core (90% by weight) with paper facing and backing (10% by weight). It is an excellent material for interior walls in structures because of its superior fire resistant properties and ease in construction. The disposal of gypsum drywall in landfills, however, may result in the production of hydrogen sulfide (H_2S), an odorous and toxic gas (Fairweather and Barlaz, 1998). In Florida, the occurrence of odors at C&D debris landfills has resulted in numerous complaints from local residents and in some cases has required remedial action.

The relationship between the disposal of gypsum drywall in landfills and the production of hydrogen sulfide has been known for years. The City of Vancouver in British Columbia, Canada banned drywall from disposal in landfills in 1990 because of issues associated with H_2S production. While no states in the United States currently ban the landfill disposal of gypsum drywall, odors from landfills in several states have been attributed to its presence. The microbiological and chemical processes that convert sulfate to hydrogen sulfide are well understood, but very little research has been conducted specific to C&D debris landfills. The typical concentrations that occur in the gas at C&D debris landfills have not been documented. Unlike municipal waste landfills, C&D debris landfills are frequently not constructed with gas collection systems and are not considered to produce a very large volume of gas. Other unknowns include the maximum concentrations of H_2S likely to occur, the rate at which H_2S is produced, the production of other reduced sulfur gases, and the impact of co-disposal of other components of the C&D debris stream.

This report documents the work and results of research, which included both fieldwork and laboratory simulations, to gather information on this subject. This report is organized into five chapters. Chapter two presents a review of the relevant literature regarding the mineral gypsum, its occurrence in the waste stream as a result of discarded gypsum drywall, and the properties of hydrogen sulfide and VSCs. Chapter two also presents case studies of landfills that previously had or currently have H_2S odor issues. Chapter three presents the methods, results, and discussion of the field experiments conducted as part of this project. The information was the subject of a Master of Engineering thesis (Lee, 2000). Chapter four presents the methods, results and discussion of the laboratory column experiments conducted as part of this project. The information was also the subject of a Master of Engineering thesis (Yang, 2000). Much of the information in this report was adopted from these sources. Chapter five provides a summary and conclusions.

2   BACKGROUND ON GYPSUM DRYWALL

This chapter provides an overview of construction and demolition (C&D) landfills, gypsum drywall, and the production of hydrogen sulfide (H_2S) from drywall waste.

2.1   C&D Waste

C&D debris results from the fabrication, renovation, or destruction of buildings, bridges, roads, and other structures. C&D debris typically includes wood, concrete, gypsum drywall, asphalt, cardboard, metal, paper, plastic, rocks, and soil. In the Florida Administrative Code (FAC) 62.701.200 the State defines C&D debris as:

> …discarded materials generally considered to be not water soluble and non-hazardous in nature, including but not limited to steel, glass, brick, concrete, asphalt material, pipe, gypsum wallboard, and lumber, from the construction or destruction of a structure as part of a construction or demolition project or from the renovation of a structure, including such debris from construction of structures at a site remote from the construction or demolition project site.

The State's definition of C&D waste also includes "…rocks, soils, tree remains, trees, and other vegetative matter which normally results from land clearing or land development operations for a construction project."

The U.S. Environmental Protection Agency estimated that 136 million tons of building related C&D debris were generated in the U.S. in 1996 (US EPA, 1998). Typically, C&D waste is sent to a landfill or a C&D debris recycling facility. In 1996 an estimated 35 to 45 percent of all building-related C&D waste was disposed in C&D landfills. At the same time, an estimated 20 to 30 percent of the C&D waste stream was recovered for processing and recycling (US EPA, 1998). At C&D debris recycling facilities, constituents of value are separated and removed. The materials most typically recovered include metals, concrete, asphalt, wood, and soil. Drywall is recycled at a few locations in the U.S., but no such facilities currently exist in Florida. For example, full-scale drywall recycling facilities are operated in North Carolina and Ohio. The remaining C&D waste was managed on site, at municipal solid waste (MSW) landfills, or at unpermitted disposal sites (US EPA, 1998). MSW is community-generated waste with the exception of industrial process wastes and agricultural wastes (Tchobanoglous et al., 1993).

The Florida solid waste facility regulations (FAC 62-701) define a number of types of disposal facilities that may receive C&D debris. Class I and II landfills are required to be lined and are permitted to receive most non-hazardous solid waste, including MSW and C&D debris. A Class I landfill receives an average of 20 tons or more of solid waste per day; a Class II landfill receives less than this amount. Although C&D debris may be accepted at these facilities, C&D generators prefer not to because of the tip fees associated with lined landfills. Class III landfills can accept a number of non-putrescible materials, including C&D debris, furniture, and yard waste. C&D debris disposal facilities accept only C&D debris. Liners are not required for Class III or C&D debris facilities

unless conditions warrant. A few Class III landfills in Florida are lined; no C&D facilities are lined. In a recent report (US EPA, 1998), Florida was cited as having more C&D landfills (277) than any other state. This number, however, has dramatically decreased as a result of rule changes. In 2000, there were less than 100 permitted C&D landfills in the state.

The amount of drywall in C&D waste typically ranges from 17 to 27% depending on the source type. The industry standard for residential housing is that one pound of gypsum drywall waste is generated for every square foot of floor area (Musick, 1992; British Columbian Ministry of the Environment, 1991). The National Association of Home Builders (NAHB) Research Center examined the composition of four single-family houses and estimated that drywall composed 27% by weight of residential new construction debris, as shown in Figure 2-1 (NAHB, 1995). In a study of multi-family demolition debris, drywall was 17% by weight. This is shown in Figure 2-2. In this figure, rubble refers to pieces of brick and concrete. These figures are presented to show the typical composition of C&D debris. The composition of any given C&D waste stream will be a function of the specific structure.

2.2   Gypsum Drywall

Drywall consists of a sheet of gypsum covered on both sides with a paper facing and backing (Gypsum Association, 1992). Gypsum is calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$, which is a naturally occurring mineral mined from dried ancient inland sea beds. The mined gypsum is first crushed into 2-inch diameter or smaller pieces (National Gypsum, 1999), dried in a large rotating kiln, and then ground. The grinding is usually performed in a Raymond Mill, which is a roller-type crushing mill. The next step is calcining, in which three-quarters of the chemically combined water in the gypsum is removed by heating. The calcined gypsum is blended with water and other ingredients, which may include starch, sugar, cellulose, and binding agents to make a slurry. The slurry is then spread on a moving belt of cream-colored face paper. A gray back paper is placed on top of the slurry. The drywall travels on a moving belt and roller conveyors for 600 to 800 feet while it hardens. After hardening, the wallboard is cut and dried in a kiln. Once dried, the drywall is trimmed to exact length, bundled, and stacked (National Gypsum, 1999). Drywall sheets come in sizes ranging from 4 feet by 8 feet to 4 feet by 16 feet. The thickness of drywall sheets ranges from ¼-inch to 1-inch. A simplified diagram of the drywall manufacturing process is presented in Figure 2-3. Other common names for gypsum drywall are gypsum board, wallboard, plasterboard, and sheetrock. Drywall is used extensively in the United States for interior walls and ceilings for its fire resistance. In 1995, there were 69 gypsum drywall manufacturing facilities in the United States that produced an estimated 25.1 billion square feet of drywall per year (Balazik, 1996).
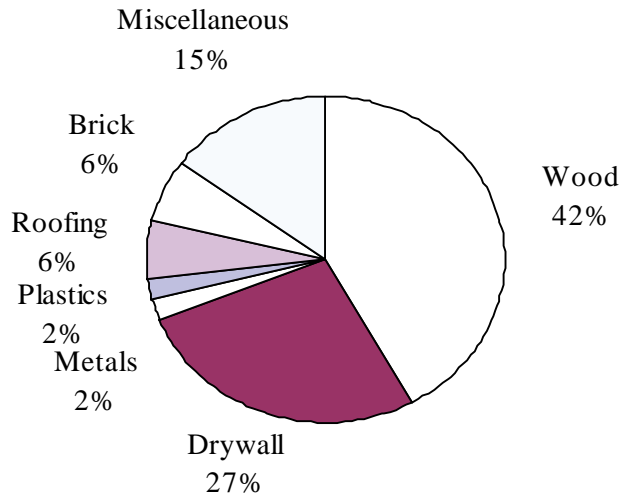
Figure 2-1. Sample Composition of Residential New Construction Debris

(Source: NAHB, 1995)
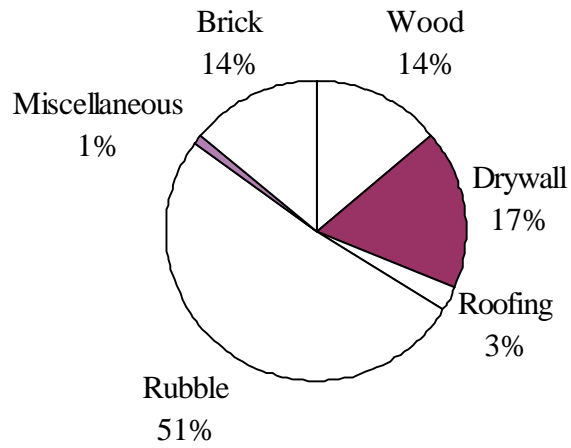
Figure 2-2. Sample Composition of Multi-family Demolition Debris

(Source: NAHB, 1995)

1. Mine

Drilling & Blasting

mined material

2. Fundamental crushing

3. Secondary crushing

4. Calciner

Furnace

7. Plaster additives

6. Tube Mill

5. Raymond Mill

8. Plaster Mixer

10. Board Additives

9. Packer

11. Board Mixer

13 A.

14. Printer

15. Knife

12. Master Roll

13.

17. Drying Kiln

18. Bundled & Piled

20.

16. Inverter

21.

22. Bundled & Piled

23. Distribution
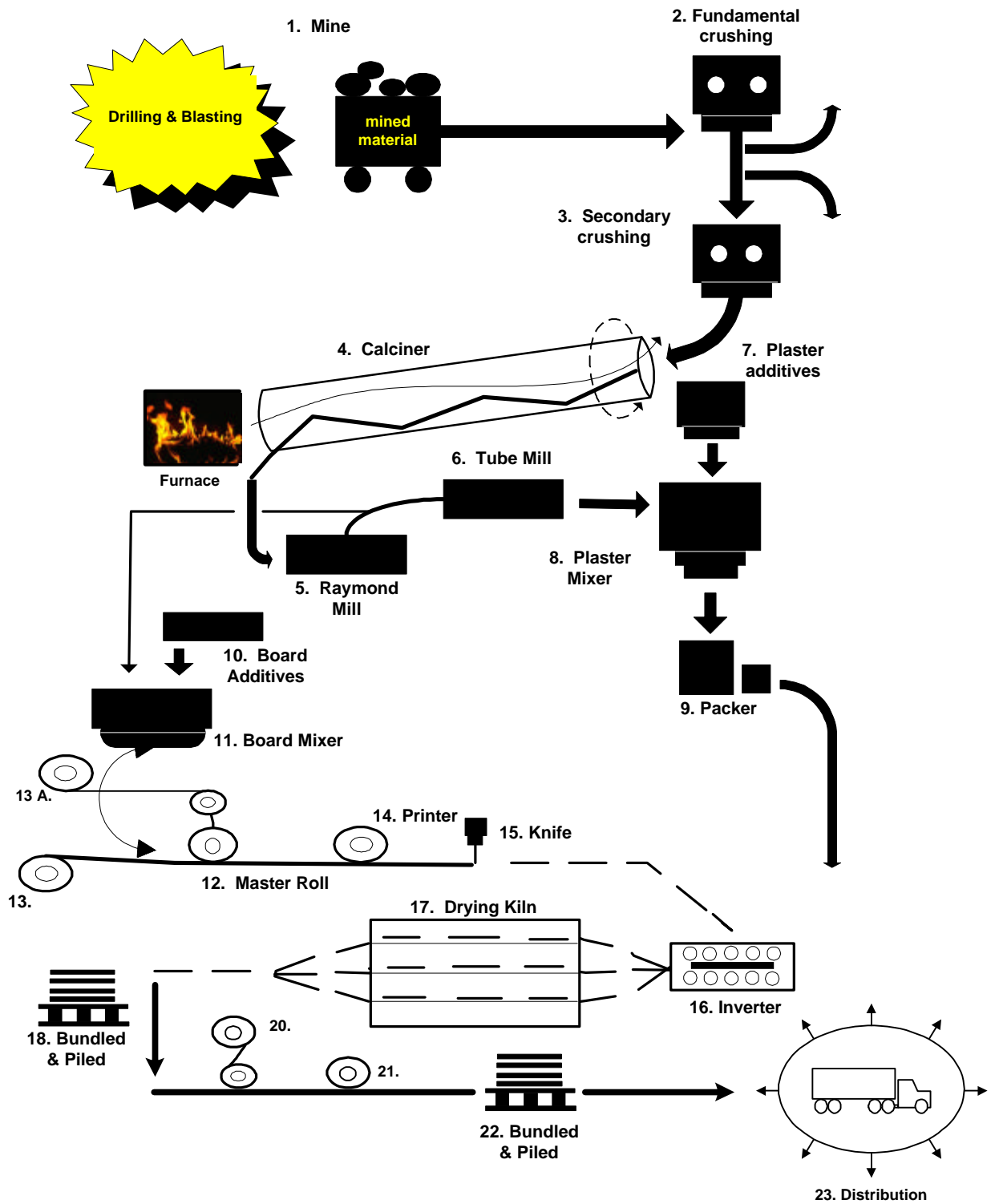
Figure 2-3. The Drywall Manufacturing Process at a Typical Gypsum Plant.
Source: U.S. Gypsum, 1999

2.3   Production of Hydrogen Sulfide

Hydrogen sulfide is produced naturally in various locations including hot sulfur springs, in anoxic sediments and mud, bogs and marshes, and lower water layers of freshwater, marine, and hypersaline environments (Atlas, 1997). Anthropogenic sources of hydrogen sulfide include wastewater treatment and agricultural water as well as the industries of kraft paper manufacturing, oil refining, petroleum coke manufacturing, and tanneries (Vesilind et al., 1994). The source of sulfate in the environment is organic sulfur-containing compounds. In the sulfur cycle, reduction of sulfur compounds occurs in anaerobic environments and oxidation of sulfur compounds occurs in aerobic environments. The sulfur cycle is depicted in Figure 2-4.

Sulfur Oxidation

H_2S Desulfuration S^o

Sulfur Oxidation

Sulfur Respiration

Phototrophic Oxidation

R-SH

Assimilatory Sulfate Reduction

S^o

$SO_4{}^{2-}$

Phototrophic Oxidation
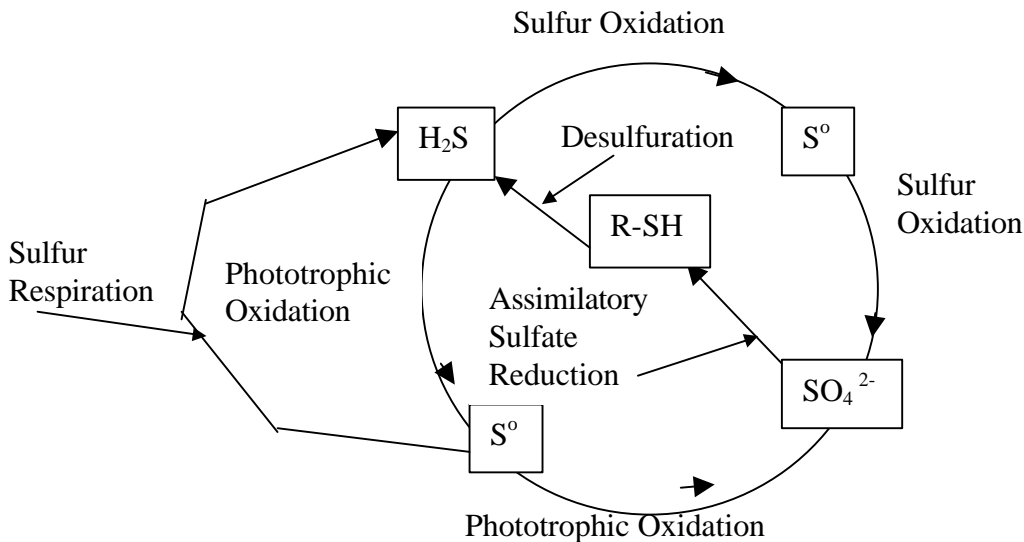
Figure 2-4. The Sulfur Cycle

(Source: Atlas, 1997)

Landfills may contain many of the same microorganisms that inhabit the natural environment where hydrogen sulfide is produced. The microorganisms responsible for generating hydrogen sulfide include sulfate-reducing bacteria and sulfur-reducing bacteria. They are divided into four subgroups. The first subgroup consists of spore-forming sulfate-reducing bacteria. The second subgroup consists of sulfate-reducing bacteria that produce acetate from the incomplete oxidation of organic substrates. The third subgroup consists of sulfate-reducing bacteria that produce carbon dioxide (CO_2) from the complete oxidation of organic substrates. The fourth subgroup consists of sulfur-reducing bacteria. Table 2-1, adapted from Atlas (1997), details the genera of bacteria in each subgroup and their characteristics.

Many microbes are capable of metabolizing sulfates and taking sulfur into their cell structure. The sulfur is assimilated into the organisms' protein or built into co-factors such as panthothenic acid and biotin. These microbes release a small amount of hydrogen sulfide. Sulfate-reducing bacteria are different, however, in that they use the sulfur as

electron acceptors when oxidizing organic matter during sulfate respiration. Sulfate respiration only occurs with sulfate-reducing bacteria. They assimilate a small amount of sulfur, as virtually all of the sulfur they use is released as hydrogen sulfide. Sulfate respiration (dissimilatory sulfate reduction) generates many times the amount of hydrogen sulfide than assimilatory sulfate reduction and subsequent desulfuration (Postgate, 1984). Sulfate-reducing bacteria use electrons to reduce sulfate in the following equation:

$$SO_4^{\ 2-} \rightarrow SO_3^{\ 2-} \rightarrow S_3O_6^{\ 2-} \rightarrow S_2O_3^{\ 2-} \rightarrow S^{2-}$$
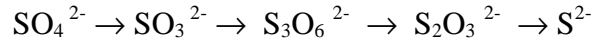
sulfate → sulfite → trithionate → thiosulfate →sulfide

Table 2-1 Sulfate-Reducing Bacteria and Sulfur-Reducing Bacteria

Subgroup	Genera	Sulfur Metabolism	Carbon Metabolism	Electron Donor
1	*Desulfotomaculum*	$SO_4^{\ 2-}$ reduced to H_2S	Organic substrates oxidized to acetate or completely to CO_2	H_2, C_1 – C_{18} monocarboxylic acids, lactate
2	*Desulfobulbus* *Desulfomicrobium* *Desulfomonas* *Desulfovibrio* *Thermodesulfobacterium*	$SO_4^{\ 2-}$ reduced to H_2S; some genera reduce S^o to H_2S	Organic substrates oxidized incompletely to acetate	Propionate, H_2, lactate, malate, ethanol
3	*Desulfobacter* *Desulfobacterium* *Desulfococcus* *Desulfonema* *Desulfosarcina*	$SO_4^{\ 2-}$ reduced to H_2S; some genera reduce S^o to H_2S	Organic substrates oxidized completely to CO_2	Acetate, lactate, pyruvate, ethanol, succinate, fumarate, C_4 – C_{16} monocarboxylic acids
4	*Desulfurella* *Desulfuromonas*	S^o reduced to H_2S	Organic substrates oxidized completely to CO_2	Acetate, propionate, ethanol

(Source: Atlas, 1997)

This dissimilatory sulfate reduction gives adenosine triphosphate (ATP), a major carrier of phosphate and energy, to cells (Atlas, 1997). The sulfate ion may be biochemically

reduced to form hydrogen sulfide by the following bacterial reaction (Dohnalek and FitzPatrick, 1983):

$$2(CH_2O\text{-}R) + SO_4^{2-} \rightarrow 2(HCO_3^-) + H_2S + 2R \qquad (1)$$

$$S^{2-} + H^+ \leftrightarrow HS^- \qquad (2)$$

$$HS^- + H^+ \leftrightarrow H_2S \qquad (3)$$

In reaction 1 $CH_2O\text{-}R$ represents organic matter and SO_4^{2-} is the sulfate ion. The products are bicarbonate (HCO^{3-}), hydrogen sulfide (H_2S), and an undefined radical (R). Reactions 2 and 3 are not related to bacterial action. S^{2-} is sulfide and HS^- is the bisulfide ion.

Sulfate-reducing bacteria require the following to produce hydrogen sulfide: a sulfate source, a carbon source, anaerobic conditions, and moisture. The optimum pH for sulfate-reducing bacteria is approximately 7. Inhibition usually occurs at a pH lower than 6 or higher than 9 (Connell and Patrick, Jr., 1968; Widdel and Pfennig, 1984). The optimum temperatures for most sulfate reducers are in the same range—between 20-39°C—with the exception of *Thermodesulfobacterium commune*, which survives at 70°C (Zeikus et al., 1983). *Desulfobacter* has a temperature optimum of between 28 and 30°C (Widdel and Pfenning, 1984). The *Desulfobulbus* species has a wider temperature optimum, between 28 and 39°C. The *Desulfobacterium* species prefer a lower temperature range, between 20 and 28°C (Widdel and Pfenning, 1984).

2.4   Hydrogen Sulfide Chemistry

Hydrogen sulfide is a soluble gas and may volatilize from its aqueous solution into the gas phase in accordance with Henry's law (Henry's Constant of 550 atm @ 25°C). Table 2-2, adapted from the Toxicological Profile for Hydrogen Sulfide prepared for the U.S. Department of Health and Human Services (1999), summarizes the properties of hydrogen sulfide. The presence of hydrogen sulfide and other reduced sulfur species is dependent on pH. Figure 2-5 illustrates the distribution of hydrogen sulfide at 25°C. At pH levels above 8, most of the sulfur species exist as sulfide (S^{2-}) and bisulfide ion (HS^-). At a pH between 6 and 7, which has been observed in C&D laboratory simulations (Townsend et al., 1999; Jang, 2000) and field studies (Weber, 1999), hydrogen sulfide and bisulfide ion are the predominate species. At a pH of 7.1 and at 25°C, H_2S and HS^- are present in equal concentrations.

Table 2-2. Hydrogen Sulfide Properties

Property	Information
Molecular Weight	34.08
Color	Colorless
Physical state	Gas
Odor Threshold	0.5 parts per billion (ppb)
Characteristic Odor	Rotten egg
Solubility @ 20^oC	4,132.23 mg/ L
Vapor Pressure at 21.9^oC	1929 kPa or 14,469 mmHg
Freezing point	-85.49^oC
Boiling point	-60.33^oC
Auto-ignition temperature	500^oC
Flammability limits	Lower limit, 4.35% by volume
Henry's law constant @ 20^oC	468 atm/mole fraction

(Source: U.S. Department of Health and Human Services, 1999)

The U.S. Department of Health and Human Services reports that H_2S stays in the atmosphere an average of 18 hours. In the United States, the amount of H_2S in ambient air ranges between 0.11 and 0.33 ppb (U.S. Department of Health and Human Services, 1999). In this report, gas concentrations reported in units of ppb or ppm refer to ppbv and ppmv, respectively. In undeveloped areas, background H_2S concentrations are lower, between 0.02 and 0.07 ppb. Hydrogen sulfide concentrations are generally less than 1 ppm in groundwater and range from less than 1 to 5 ppm in surface water and wastewater.

2.5 Hydrogen Sulfide Health Effects

Hydrogen sulfide is a toxic, colorless gas. It has a distinctive rotten egg odor at low concentrations (Vesiland et al., 1994). The odor threshold cited by EPA is 25 ppb. However, the U.S. Department of Health and Human Services reports that humans can smell hydrogen sulfide at concentrations as low as 0.5 ppb. The National Institute for Occupational Safety and Health (NIOSH) set a ceiling limit of 10 ppm over a 10-minute period was set as a recommended guideline. Figure 2-5 presents a diagram of the range of hydrogen sulfide concentrations typically encountered and important odor, health, detection, and regulatory benchmarks. The Occupational Safety and Health Administration (OSHA) established a regulation ceiling hydrogen sulfide concentration of 20 ppm in the workplace. OSHA set a maximum level of 50 ppm allowed for a 10-minute maximum duration. In the range of 20 to 30 ppm, hydrogen sulfide becomes an offensive strong odor (Beauchamp et al., 1984). In the range of 50 to 100 ppm, irritation of the eye and the mucous membranes of the respiratory tract occur. At concentrations greater than 150 ppm, hydrogen sulfide paralyzes the olfactory nerves (Reiffenstein et al., 1992). Prolonged exposure to high concentrations can cause paralysis of the respiratory system. Extended exposure at a concentration of 2,000 ppm can be fatal to humans.
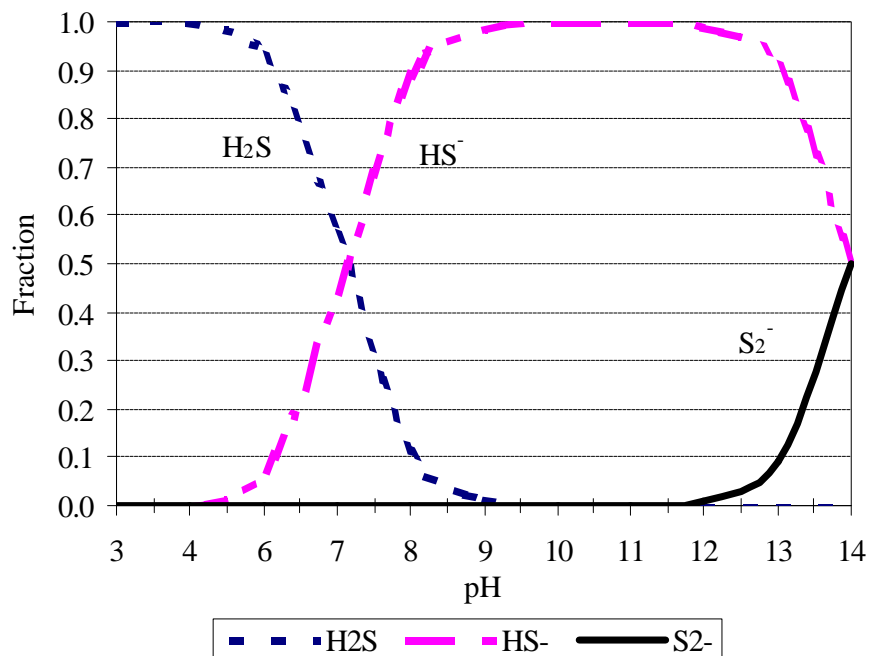
Figure 2-5. Sulfide Species Distribution

(Source: Snoeyink and Jenkins, 1980)

Limited information has been reported regarding the human health impact from low-level exposure to hydrogen sulfide. Some available information on human health effects at lower concentrations of hydrogen sulfide is included as follows. It should be noted, however, that there is no consensus by the scientific or regulatory community on health impacts at these low levels. Kilburn and Warshaw (1995) conducted a study to determine the effect of prolonged exposure of a population exposed to sulfide gases from crude oil processing plants. The exposed population that was examined either worked at or lived downwind of the plants. The study found that these exposed workers and residents complained about nausea, headache, vomiting, breathing abnormalities, nosebleeds, depression, and personality changes. Air monitoring at the street level, near the homes of the exposed population, showed H_2S at 10 ppb with periodic peaks of 100 ppb. Other reduced sulfur species peaks were also detected, including dimethyl sulfide (4 ppb) and mercaptans (2 ppb).

Kilburn (1997) published a second study documenting exposure to sulfur gases and impaired neurobehavioral function. The study tested 16 people months to years after either acute or chronic exposure to various levels of sulfide gases. Mood status and frequency of 35 symptoms of the people were appraised using psychological and neurophysiologic tests. This testing revealed cognitive disability, reduced perceptual motor speed, impaired memory, and abnormal mood status related to H_2S exposure.

A study was performed on sewer workers and water treatment workers to investigate whether exposure to H_2S was associated with reduced lung function (Richardson, 1995). Sewer workers, classified by title, were assumed to have hydrogen sulfide exposure. Water treatment workers were presumed to have no exposure to H_2S. The study found a statistically significant difference in mean ratio of forced expiratory volume in 1 second to forced vital capacity (FEV_1/FVC) values between sewer workers and water treatment workers. It was concluded that chronic low-level exposure to H_2S was associated with reduced lung function.

2.6   Volatile Sulfur Compounds (VSCs)

In addition to H_2S, other VSCs may be the cause of odors. Reduced sulfur compounds have very low odor detection thresholds (Devai and Deluane, 1999). Table 2-3 presents a list of typical VSCs. Natural sources of VSCs include oceans, soil, vegetation, and volcanoes (Ketola et al., 1997). Methyl mercaptan, dimethyl sulfide, carbon disulfide, and carbonyl sulfide are gaseous compounds have been measured at composting facilities (Kuroda et al, 1996) and wastewater treatment plants (Devai and Deluane, 1999) and may also cause odors in C&D landfill gas. Devai and Deluane (1999) found H_2S at a wastewater treatment plant to be the dominant sulfur species, with up to 315 ppm in the air. Other VSCs were found in lower peak concentrations including methanethiol (4.4 ppm), dimethyl sulfide (10.2 ppm), carbon disulfide (1.2 ppm), and carbonyl sulfide (2.9 ppm). Industrial sources of VSCs are from the production of fossil fuels, solvents, and pulp and paper mills.

2.6.1   Carbonyl Sulfide

Carbonyl sulfide, COS, is a colorless, flammable gas (US EPA, 1994). In pure form, it is odorless. When carbonyl sulfide contains impurities, it may have a sulfur odor. Carbonyl sulfide can be found in petroleum crude oil, salt marshes, and volcanic gases and is made in the production of carbon disulfide. Carbonyl sulfide is soluble in water at 1220 mg per liter at $25^{o}C$. Reaction with water produces H_2S. When carbonyl sulfide is released into the air, it can remain for several years before breaking down to other chemicals (US EPA, 1994). The odor threshold has not yet been established. Carbonyl sulfide can cause headaches, giddiness, dizziness, confusion, nausea, diarrhea, weakness, and muscle cramps. Inhalation of large amounts of carbonyl sulfide can cause a person to stop breathing and lose consciousness. Little information exists about chronic effects, reproductive effects, developmental effects, and cancer risk (US EPA, 1994b).

Table 2-3. Volatile Sulfur Compounds

Compound	Chemical Formula
Hydrogen Sulfide	H_2S
Carbonyl Sulfide	COS
Methyl Mercaptan (Methanethiol)	CH_4S
Dimethyl Sulfide	C_2H_6S
Ethyl Mercaptan (Ethanethiol)	C_2H_6S
Carbon Disulfide	CS_2
Isopropyl Mercaptan (2-Propanethiol)	C_3H_8S
Tert-Butyl Mercaptan (2-Methyl-2-Propanethiol)	$C_4H_{10}S$
Ethyl Methyl Sulfide	C_3H_8S
Thiophene	C_4H_4S
Methyl Isopropyl Sulfide	$C_4H_{10}S$
Diethyl Sulfide	$C_4H_{10}S$
Dimethyl Disulfide	$C_2H_6S_2$
2-Methylthiophene	C_5H_6S
3-Methylthiophene	C_5H_6S
Tetrahydrothiophene	C_4H_8S
Sec-Butyl Mercaptan	$C_4H_{10}S$
Diethyl Disulfide	$C_4H_{10}S_2$

2.6.2   Methyl Mercaptan

Methyl mercaptan or methanethiol, CH_4S, is a colorless gas with a rotten cabbage and garlic odor. OSHA has established an exposure-ceiling limit of 10 ppm. The maximum workplace concentration limit in West Germany for methanethiol is 0.5 ppm. Methyl mercaptan inhalation causes respiratory system irritation, vomiting, convulsions, lung congestion, bluish skin color, headache, and nausea (Matheson Tri-Gas, 1999d). Methanethiol has been detected in air streams of wastewater treatment plants (Hwang et al., 1995), hog manure (Al-Kanani et al., 1992), and exhaust gases of soil treatment plants (Park at al., 1993). Many food-processing industries also have methyl mercaptan in their air streams, including processors of meat, coffee brews, cheese flavoring, wine, and beer. The odor threshold is between 0.9 and 8.5 ppbv (Smet and Van Langenhove, 1998).

2.6.3   Dimethyl Sulfide

Dimethyl sulfide, C_2H_6S, is a colorless to yellow gas and liquid. It has an unpleasant odor that can be detected at 0.001 ppm (Matheson Tri-Gas, 1999b). When inhaled, dimethyl sulfide causes irritation, breathing difficulty, and lung congestion and may cause skin and eye irritation. Dimethyl sulfide is heavier than air and is a severe fire

hazard. The vapor form of dimethyl sulfide may cause flash fires. No occupational exposure limits have been established (Matheson Tri-Gas, 1999b).

2.6.4   Ethyl Mercaptan

Ethyl mercaptan, also known as ethanethiol, C_2H_6S, is a flammable liquid and gas (Matheson Tri-Gas, 1999) with a garlic odor with an odor threshold of 1 ppbv. The OSHA general industry exposure limit is 10 ppm. NIOSH has a recommended ceiling limit of 0.5 ppm. Short-term inhalation causes irritation, nausea, breathing difficulty, headache, convulsions, and coma. Ethyl mercaptan also causes skin and eye irritation (Matheson Tri-Gas, 1999).

2.6.5   Carbon Disulfide

Carbon disulfide, CS_2, is a volatile liquid that is very reactive (US EPA, 1994c). Carbon disulfide is listed as a hazardous air pollutant in the 1990 Clean Air Act Amendments. The odor threshold for carbon disulfide is 0.016 ppm (US EPA, 1994c). In the air, carbon disulfide has a 12-day half-life. Oxidation and hydroxylation are the main pathways for carbon disulfide degradation. Inhalation of carbon disulfide can result in pharyngitis and central nervous system effects. The symptoms include dizziness, fatigue, headache, mood changes, lethargy, blurred vision, agitation, delirium, hallucinations, convulsions, and coma. Skin contact can cause pain and erythema. Vesiculation and chemical burns are caused by prolonged skin contact. Eye contact causes severe chemical burns of the cornea. Slight symptoms have been reported at exposure of 320 to 390 ppm for several hours. Definite symptoms are experienced at exposure of 420 to 510 ppm for 30 minutes. Serious symptoms occur during exposure to 1,150 ppm for 30 minutes (US EPA, 1994c).

2.6.6   Isopropyl Mercaptan

Isopropyl mercaptan, C_3H_8S, is a colorless liquid and vapor with a skunk-like odor (Matheson Tri-Gas, 1999c). Short-term exposure causes irritation, lack of sense of smell, nausea, vomiting, diarrhea, difficulty breathing, headache, lung congestion, kidney damage, and coma. No information is available for long-term exposure. The odor threshold is 0.25 ppb (Matheson Tri-Gas, 1999c).

2.6.7   Tert-Butyl Mercaptan

Tert-butyl mercaptan is very similar to isopropyl mercaptan in physical state, color, odor, and health effects (Matheson Tri-Gas, 1999e). It has a skunk-like odor. Short-term inhalation exposure causes irritation, lack of sense of smell, nausea, vomiting, diarrhea, breathing difficulty, headache, symptoms of drunkenness, bluish skin color, lung congestion, kidney damage, convulsions, and coma. However, no odor threshold information is available (Matheson Tri-gas, 1999e).

2.6.8 Ethyl Methyl Sulfide

Ethyl methyl sulfide is a colorless liquid (Sigma-Aldrich, 2000f). The vapor is irritating to the eyes, mucous membranes, and upper respiratory tract. Exposure can cause nausea, vomiting, and headache.

2.6.9 Thiophene

Thiophene is a clear, colorless liquid (Sigma-Aldrich, 1999b). It has a slight odor resembling benzene. Exposure causes eye irritation, headache, and nausea. Hydrogen sulfide and sulfur oxides are decomposition products of thiophene (Sigma-Aldrich, 1999b).

2.6.10 Diethyl Sulfide

Diethyl sulfide (also known as ethyl sulfide) is a highly flammable, colorless liquid (Sigma-Aldrich, 2000g). Decomposition or combustion products of diethyl sulfide include carbon monoxide, carbon dioxide, sulfur oxides, and hydrogen sulfide. Acute effects from inhalation, ingestion, or skin absorption are eye, mucous membrane, and upper respiratory tract irritation. Headache, nausea, and vomiting are other symptoms of exposure (Sigma-Aldrich, 2000g).

2.6.11 Dimethyl Disulfide

Dimethyl disulfide is a flammable, very toxic, colorless to yellow liquid (Sigma-Aldrich, 2000e). The vapor irritates the eyes, mucous membranes, and upper respiratory tract. Inhalation may cause death. Other exposure symptoms include headache, nausea, and vomiting. OSHA has established an eight-hour time weighted average concentration of 0.5 ppm (Sigma-Aldrich, 2000e). Dimethyl disulfide has a foul smell that can be detected in the concentration range of 0.1 to 3.6 ppbv (Smet and Van Langenhove, 1998).

2.6.12 2-Methylthiophene

2-Methylthiophene is a flammable, pale-yellow liquid (Sigma-Aldrich, 2000b). It is harmful if inhaled, swallowed, or absorbed through the skin. Exposure causes nausea, headache, and vomiting. Toxicological properties have not been thoroughly investigated (Sigma-Aldrich, 2000b).

2.6.13 3-Methylthiophene

3-Methylthiophene is a flammable, very pale-yellow liquid (Sigma-Aldrich, 2000c). Exposure causes nausea, headache, and vomiting. It is harmful if inhaled, swallowed, or absorbed through the skin. Toxicological and ecological information have not been thoroughly investigated (Sigma-Aldrich, 2000c).

2.6.14 Tetrahydrothiophene

Tetrahydrothiophene is a highly flammable colorless to light yellow liquid (Sigma-Aldrich, 1999). The exposure limit is 1.1 to 12.3% by volume. Effects on the central nervous system after short-term exposure may occur.

2.6.15 Sec-Butyl Mercaptan

Sec-butyl mercaptan is also known as 1-methyl-1-propanethiol (Sigma-Aldrich, 2000). The vapor mist irritates the eyes, mucous membranes, and upper respiratory track. Exposure can cause skin irritation, nausea, vomiting, and headache.

2.6.16 Diethyl Disulfide

Diethyl disulfide is a flammable, combustible yellow tinted liquid with an objectionable odor (Sigma-Aldrich, 2000d). It may be harmful if inhaled, ingested, or absorbed by the skin. Diethyl disulfide irritates the upper respiratory tract and mucous membranes and may cause nausea, headache, and vomiting.

2.6.17 Butyl Sulfide

Butyl sulfide is a colorless liquid with a mercaptan odor (Baker, 1999). Inhalation of butyl sulfide causes respiratory tract irritation, which may include coughing and shortness of breath. Skin and eye contact causes irritation, redness, itching, and pain (Baker, 1999).

2.7   Occurrence of Odors at Landfills

The occurrence and concentration of H_2S and other VSCs have been measured at landfill sites throughout the United States and overseas. These landfills, however, are all MSW landfills. The occurrence of those compounds in C&D debris landfills gas has not been documented in the referenced literature, although reports of H_2S at C&D debris landfills have appeared in the press. This section presents a literature summary of sulfur gas concentrations reported in MSW landfill gas. Incidents of reported odor problems from sulfur gases at C&D landfill sites in Florida are also presented. This information was gathered from a wide variety of nonreferred sources, including newspaper articles and engineering reports.

2.7.1   MSW Landfill Gas

The US EPA Office of Air Quality Planning and Standards Emission Factor and Inventory Group (EFIG) (2000) compiled a list of air pollutant emission factors for several industries in AP-42. The AP-42 factor is a representative value that relates the activity associated with the release of a pollutant with quantity of a pollutant released. The AP-42 emission factors for H_2S and other reduced sulfur compounds for MSW landfill gas are presented in Table 2-4. In Table 2-4, the symbol – indicates that those specific substances were not analyzed. Capenter and Bidwell (1996) sampled gas at a MSW landfill that was equipped with a series of gas extraction wells, mostly located at the perimeter with an additional

branch extending into the interior. Young and Parker (1983) sampled six landfills using a gas sampling probe at depths between 1.0 and 4.3 meters. The gas-sampling probe was a 19-mm internal diameter galvanized steel pipe perforated for a length of 300 mm with a plated steel tip. The California Waste Management Board sampled gas from 66 landfills.

Table 2-4. Sulfur Compounds in MSW Landfill Gas

Compound	AP-42 (ppm)	Capenter and Bidwell (ppm)	Young and Parker (ppm)	CWMB (ppm)
Hydrogen sulfide	35.5	28.33	-	<1.98 – 14.0
Carbon disulfide	0.58	0.01	-	<0.03 – 0.60
Carbonyl sulfide	0.49	-	-	<0.20 – 8.81
Dimethyl sulfide	7.82	-	1.55	0.62 – 9.46
Dimethyl disulfide	-	-	10.21	0.01 – 3.70
Ethyl mercaptan	2.28	0.62	-	-
Methyl mercaptan	2.49	0.80	43.49	0.05 – 214.96
Thiophene	-	-	-	<0.003 – 0.14

(Source: Capenter and Bidwell, 1996; CWMB, 1987; US EPA, 2000; Young and Parker, 1983)

2.7.2   Odor at Florida Landfills

Several landfills throughout the State of Florida have had odor problems that are believed to be caused by the degradation of gypsum drywall. The landfills with the most public attention have been C&D or Class III facilities, although one MSW landfill received publicity when H_2S odors became a problem as a result of C&D debris disposal.

2.7.2.1   Sunset Sand Mine and Landfill

The Sunset Sand Mine and Landfill is a 75-acre C&D landfill located in Pasco County, Florida, and was a combination sand mine and C&D debris landfill. The site began operating as a C&D landfill in 1990, and one year later residents started complaining about an odor problem. In January 1995 the landfill was closed due to high concentrations of H_2S. Residents near the landfill were evacuated twice. In February 1995 county officials reported that the H_2S level was 3 ppm at a quarter mile around the landfill (Crosson, 1995). Levels reaching 205 ppm were found on site at ground level. At a height of more than 4 feet off the ground the H_2S concentration decreased to 50 ppm. The landfill owner had a cover layer of soil and clay placed over the exposed waste (Conner, 1995). On May 7, 1995 in the *St. Petersburg Times* reported that neighbors of the Sunset Landfill still experienced problems associated with H_2S (Smith, 1995).

2.7.2.2   Material Exchange Landfill

The Material Exchange Landfill is a C&D debris landfill in Citrus County, Florida. Originally, the site was a sand mine in the 1970s (Florida Department of Health, 2000). The site received 1.25 million tons of fly ash from a coal-fired power plant from 1980 to 1990, and a second C&D cell began receiving waste in 1993. Residents began complaining about odors and respiratory problems in 1994. In April 1999, a resident petitioned for the Agency for Toxic Substances and Disease Registry to evaluate the site's potential health threat (Florida Department of Health, 2000).

2.7.2.3   Pine Ridge Recycling and Disposal Facility

Pine Ridge Recycling and Disposal Facility in Orange County, Florida, received a Class III landfill permit in 1990. The disposal area covers 68.3 acres. A preliminary H_2S monitoring was undertaken in 1995 in response to residents' complaints concerning health and safety issues (Atwood and Tessitore, 1995). Three on-site monitors measured average ambient H_2S concentration over 1-minute intervals. From August through September 1995, the average H_2S concentrations from the three monitors were 0.26 ppm, 0.25 ppm, and 0.48 ppm. The maximum 24-hour average H_2S concentrations were 0.58 ppm, 0.58 ppm, and 1.25 ppm. A portable H_2S meter was used in areas surrounding the landfill. H_2S concentrations ranged from 0.1 to 0.3 ppm. The preliminary H_2S monitoring report concluded that the H_2S concentrations found were well below health and safety standards. In addition, the report concluded that several off-site sources of H_2S were the responsible sources of odor in approximately 74 percent of the complaints reported from August through September of 1995.

2.7.2.4   G.E.L. Corp. C&D Recycling

G.E.L. Corp C&D Recycling is a C&D facility in Volusia County, Florida. The landfill processed materials on site, including wood and concrete. The Class I landfill closed in June 1983 (FDEP, 1983) and was permitted to accept C&D waste. Odor complaints started in 1997 (Burns, 1997), resulting in an air quality assessment performed in March 1998 (Atkins, 1998). Gas from the gas collection system was sampled. The laboratory analysis showed that the H_2S concentration was below the detection limit of 0.015 ppm. The testing also determined that the gas sample contained 0.11-ppm ammonia and 8.9-ppm methane.

2.7.2.5   Municipal solid waste (MSW) landfills

The Naples landfill in Collier County, Florida, is a Class I landfill that used material processed from C&D debris as an alternative daily cover. In 1998, an odor evaluation found H_2S at 15 ppm in areas of no active gas collection (Moore, 1998). In addition, "pockets" of odorous gas were detected in a range of 30 to 250 ppm at gas points of escape identified by yellow residue on the surface. At these points, surface faults with a leachate seep or a crack in the cover were observed. Seven samples were taken in March, and two samples were taken in June for volatile organic compound (VOC) analysis. The

H_2S concentrations in the samples ranged from 12 ppb to 5,600 ppm in all the samples. Five samples had concentrations of carbonyl sulfide ranging from 4.9 ppb to 32 ppm. Methyl mercaptan was detected in two samples, at 4 ppb (Moore, 1998).

The Central Sanitary Landfill and Recycling Center in Broward County, Florida, is an MSW landfill. C&D debris from Hurricane Andrew's aftermath was disposed at the Central Sanitary landfill. A severe odor problem began shortly afterwards. H_2S in the landfill gas was measured up to 5,000 ppm. The H_2S caused odor problems in the surrounding residential area.

2.7.3   Out of State Landfills

Landfills from Florida to New York have had problems with rotten egg odors. In Princetown, New York, residents formed a group called Citizens Against the Dump in protest of a landfill with H_2S odors (Gardinier, 1998). The residents started complaining in 1995 and sent over 300 letters to the state Department of Environmental Conservation. The landfill was a MSW landfill recently turned into a C&D debris landfill. In 1998 a company was hired to monitor H_2S sulfide emissions.

A landfill in Danbury, New York, presented a problem beginning in August 1996. The rotten egg odor caused health problems, decreased property values, and in one extreme case, forced a family out of their home. The 40-acre MSW landfill that used a gas collection and flares, closed in December 1996. Florida Department of Environmental Protection (FDEP) officials say heavy rainfall, 17 inches more than normal in 1996, contributed to the odor problem.

Residents near an odorous landfill in Caroline County, Virginia, filed a $7.5 million lawsuit against county officials (The Washington Post, 1996). The Caroline Landfill Closure Group is seeking damages from "…the release of noxious, unhealthy and toxic emission" from the landfill. The cause of the odor is believed to be from the use of a state-approved landfill cover mixture of drywall material and compost.

2.8   Laboratory Observations

H_2S production from waste has been researched in the laboratory by Fairweather and Barlaz (1998). Four-liter reactors were used to simulated refuse decomposition in 6 months. The test investigated MSW, decomposed refuse, and various mixtures of anaerobically digested polymer-treated sludge, anaerobically digested lime-stabilized sludge, and C&D waste.

The C&D waste was made up of mostly wallboard, tree stumps, and other wood. Well-decomposed refuse material was placed in each reactor to promote decomposition. The reactors were run under conditions to accelerate decomposition, including neutralization, leachate recycle, and incubation at 40°C. More sulfide was produced in the reactors with wallboard than in those without wallboard. The reactor containing C&D waste had a concentration of 34.3 total sulfide as mg S^{-2}/dry gram fresh refuse, whereas

the reactor with refuse only had a concentration of only 0.2 total sulfide as mg S^{-2}/dry gram fresh refuse.

Hydrogen sulfide was also observed in a laboratory study designed to simulate and characterize C&D waste leachate (Jang 2000). Laboratory lysimeters made of 5-feet high, 12-inch diameter polyvinyl chloride (PVC) pipes contained mixed C&D waste including gypsum drywall, concrete, wood, and cardboard. One gallon of synthetic rainwater solution (synthetic precipitation leaching procedure [SPLP] solution) was added to the lysimeters every two days. After one month, the H_2S concentration increased significantly and peaked at 37 milligrams per liter (mg/L) as S^{2-}.

2.9   Summary of Literature Review

C&D debris consists of mostly wood, drywall, and concrete by weight. The materials disposed at C&D debris landfills are usually considered to be nonhazardous. The gas at C&D debris landfills is not typically collected and maintained. However, recent reports of H_2S have appeared in the press. No exploration of C&D landfill gas composition can be found in referenced literature.

Gypsum drywall, which makes up about 17 to 27% of C&D waste by weight, has been noted as the source of odorous H_2S gas (Gypsum Association, 1992). H_2S presents an odor nuisance and a potential health threat and has a characteristic rotten egg odor. National exposure limits exist for hydrogen sulfide. Human health effects include headache, eye irritation, respiratory difficulties, and nausea. Serious impacts are coma and death. Other reduced sulfur compounds present similar problems as H_2S. Reduced sulfur compounds have low odor thresholds and also cause respiratory problems.

C&D debris landfills have had odor problems throughout the State of Florida. Residents and businesses near these facilities have complained about a rotten egg odor and expressed concern for their health. MSW landfills that have accepted C&D waste have also experienced H_2S odor problems.

Two laboratory research experiments have confirmed the production of sulfide from drywall wastes in C&D debris landfill simulators. Fairweather and Barlaz (1998) performed a study in which four-liter reactors were used to simulate refuse decomposition. The reactors with gypsum drywall produced more total sulfide than reactors with no drywall. Jang (2000) conducted research to characterize C&D debris leachate. The leachate from laboratory lysimeters containing drywall was observed to have a strong H_2S odor. Like the Fairweather and Barlaz (1998) study, the lysimeters with drywall contained higher total sulfide concentrations than lysimeters with no drywall.

3 CHARACTERIZATION OF LANDFILL GAS AT FLORIDA C&D DEBRIS LANDFILLS

3.1   Overview

This research consisted of both fieldwork and laboratory simulations. The fieldwork included sampling of both ambient air at the landfill surface and gas collected from within the landfill cover soil at C&D or Class III landfills. Hydrogen sulfide (H_2S); "permanent" gases including methane, carbon dioxide, and oxygen; and VOCs including VSCs were also investigated. Two laboratory experiments were conducted to support the findings in the field. Gas samples were analyzed, however, no microbial measurements were performed to substantiate sulfate reduction to H_2S catalyzed by microbial enzymes.

Laboratory experiments were conducted to determine the H_2S characteristics within a controlled environment. Four laboratory experiments were conducted: a Serum bottle experiment, a Tedlar® bag experiment, a heterogeneous waste column experiment, and a homogenous waste column experiment. The serum bottle experiment was conducted to determine how much H_2S is produced with concrete, paper backing, and another substrate under different conditions. The Tedlar bag experiment determined the amount of H_2S produced from drywall alone.

3.2   Equipment and Instrumentation

Gas sampling instruments were used in the field and laboratory experiments. To obtain gas samples from the various C&D landfills, a soil vapor probe and a bag sampler were used. Gas samples collected were analyzed in the field with the Landtec GEM 500 meter for permanent gases and the Jerome 631-X for H_2S; in the laboratory, a micro-scale purge and trap gas chromatograph with a mass spectrometer (GC/MS) for VOCs was used. Gas samples obtained from the laboratory experiments were analyzed using the Jerome 631-X meter, a micro-scale purge and trap GC/MS, and a gas chromatograph with a thermal conductivity detector (GC/TCD) for permanent gases. The following sections describe the equipment used for gas sampling and analysis.

3.2.1   Soil Vapor Probe

Since most C&D landfills do not use gas collection systems, a soil vapor probe was used to determine the composition of gas inside C&D landfills. A manual soil gas vapor probe (AMS, American Falls, Idaho) was used to sample gas from between 1 feet to 3 feet below the surface of the landfill. The soil vapor probe consisted of a 0.5-inch diameter, 3-feet long hollow stainless steel tube with a hardened stainless steel tip. The tip had vent holes for gas entry. A removable liner rod prevented soil intrusion into the probe.

3.2.2   Gas Sample Collector

Grab samples of landfill gas were obtained with a bag sampler, the Vac-U-Tube Model 231-945 (SKC Inc., Eighty Four, Pennsylvania). The Vac-U-Tube was an acrylic

syringe with a removable faceplate, as shown in Figure 3-2. Samples were collected in 1-liter Tedlar® bags Model 232-01 (SKC Inc., Eighty Four, Pennsylvania). The internal size of the sample bags was 7 inches by 7 inches. The sample bags had a single polypropylene hose/valve and septum fitting. A sample bag was attached to the faceplate, which is then secured onto the syringe. The Teflon tubing, inserted in the soil vapor probe or attached to soil vapor wells, was attached to the faceplate and sample bag. The sample bag was filled by pulling the plunger.

3.2.3 Jerome 631-X Hydrogen Sulfide Meter

The meter used to analyze the concentration of H_2S gas was Arizona Instrument's (Phoenix, Arizona) Jerome 631-X Hydrogen Sulfide Analyzer. The Jerome meter has a detection range from 0.003 ppm to 50 ppm and was used only for gas phase samples. An internal pump pulled the gas sample at a flow rate of 0.15 liters/min over a thin gold film, which underwent an increase in electrical resistance proportional to the mass of H_2S present. The concentration was then displayed in ppm. The gold film sensor requires regeneration before and after sampling and when saturation occurs. The regeneration process was conducted by attaching the meter to an AC power outlet and pushing the regeneration button. During regeneration, the gold film is heated and the H_2S is burned off, thus clearing any accumulation. After regeneration, the meter is zeroed by pushing the zero button and turning the zero adjust potentiometer with a trimmer tool.

3.2.4 GEM 500 Meter

In addition to determining the concentration of H_2S in landfill gas, the concentration of permanent gases, methane, carbon dioxide, and oxygen, were measured. The Landtec (Colton, California) GEM 500 meter was used to measure the permanent gases when attached to the soil vapor probe. An infrared gas analyzer inside the meter determined the concentration of methane and carbon dioxide in percent by volume. Oxygen concentration was determined using the galvanic cell principle. The GEM 500 meter was calibrated with calibration gases from Landtec. One calibration gas tank contained 50.0% methane, 35.0% carbon dioxide, and a balance of nitrogen. Another calibration gas tank contained 4.0% oxygen and a balance of nitrogen. For calibration, a regulator and hose assembly with a water trap filter pack was used. Under the utilities menu option, the GEM 500 can be calibrated using a span menu for each gas type. Calibration involves selecting the gas type, turning the pump on, and waiting approximately 2 minutes for the gas concentration to be steady. When the gas concentration does not change, the actual calibration gas concentration can be entered. Gas concentrations are read using the hose assembly with a water trap filter pack. Under the option to read gas concentrations, the pump can be turned on, and the concentrations for methane, carbon dioxide, oxygen, and balance are displayed. After at least 1 minute, the gas concentrations were recorded.

3.2.5 GC/TCD

In laboratory experiments, permanent gases were analyzed using a HP5890 Gas Chromatograph with a Thermal Conductivity Detector. The concentration range for the

GC/TCD was 1% (10,000 ppmv) to 100%. EPA method 3C (US EPA, 1996) and two GC columns were used. A GSQ column was used for carbon dioxide, and a Molesieve column was used for methane, oxygen, and nitrogen. The GC column was a J&W GS-Q Porous Layer Open Tubular (PLOT) column consisting of a Divinylbenzene Homopolymer, 60 m by 0.53 mm I.D. The temperature program was 35°C to 250°C at 25°C/minute with initial hold at 35°C for 12 minutes. Samples are injected with a syringe onto a heated block. The sample was vaporized and swept with helium carrier gas onto a column. On the column, compounds absorbed and desorbed. Compounds exited the column depending on the preference for the stationary phase. Upon exiting the column, compounds altered the conductivity of a hot filament. A detector sent a signal to a recorder. A calibration curve was prepared by plotting the response (peak height or area) versus a known concentration of standards.

3.2.6   GC/MS

VOCs in the gas samples were analyzed using the Entech 2000 Microscale Purge and Trap Concentrator attached to a HP5890 Gas Chromatograph with a Finnigan INCOS XL Single Quadruploe Mass Spectrometer Detector. Analytes included several classes of VOCs: chlorinated solvents, C3 – C10 hydrocarbons, aromatics, pinenes/terpenes, light ketones and aldehydes, and C1 – C3 sulfides, mercaptans, and thiophenes. The sulfides and mercaptans from the field and laboratory experiments were the VOCs targeted. The concentration range for the GC/MS was from 5 ppbv to 100 ppmv. Lee (2000) provides the detection limits for the target compounds. The GC/MS used US EPA Method TO14. The GC Column used was a J&W DB-1 cross-linked and surface bonded dimethylpolysiloxane non-polar capillary column, 60 m by 0.32 mm I.D., 1-mm film thickness. Samples are processed on the gas chromatograph and then passed to the mass spectrometer detector. In the mass spectrometer, the sample molecules first entered an evacuated chamber and a then a second chamber through a small hole. In the second chamber, 70eV of energy ionized the molecules into positively charged particles. The particles are sent through a series of lenses and are focused onto a mass analyzer. In the mass analyzer, a direct current and two positively charged rods and two negatively charged rods moved fragments in a spiral motion. Lighter fragments exited the rod and are detected by an electrometer, which sent a signal to a recorder. The recorder plotted intensity versus voltage.

3.3   Field Sampling

3.3.1   Sampling Methodology

Sampling for landfill gas varied depending on the layout of the landfill. If a gas collection system was in place, landfill gas was sampled directly from the piping of the system. If not, landfill gas was sampled using a soil vapor probe or repeated measurements from gas wells installed with the permission of landfill managers. Soil vapor wells were installed at three landfills: Sites A, B, and E. The soil vapor wells consisted of ¼' stainless steel tubes, ranging in length from 1 feet to 3 feet. At Site B, 4-feet and 5-feet deep vapor

wells were installed. The soil vapor wells were capped using rubber caps or electrical tape until the next sampling event.

Samples were taken at random points within a landfill. Sampling points were chosen to cover a majority of the landfill area whenever possible. At each sampling location the Jerome 631-X hydrogen sulfide meter was used to determine hydrogen sulfide concentration in the ambient air at the landfill surface. The Jerome meter was laid on the surface of the landfill. The sampling port of the meter was 1.85 inches (4.7 cm) above the surface of the landfill. After ambient hydrogen sulfide was measured, gas from within the landfill was sampled. The soil vapor probe was used to obtain gas beneath the surface of the landfill. The probe was inserted into the landfill surface with a slide hammer, after which the liner rod was removed before gas sampling. Then the GEM meter was attached to a piece of 34" long Teflon tubing in the soil vapor probe to determine concentration of methane, carbon dioxide, and oxygen. The Jerome meter was used to determine hydrogen sulfide concentration. In some instances, when a high hydrogen sulfide concentration was suspected, measurement was performed in the laboratory from a soil vapor grab sample. A grab sample was taken using the Vac-U-Tube and a 1-liter Tedlar bag. In the laboratory, dilutions were made with laboratory air using a glass syringe and a separate clean Tedlar bag. The grab bag sample was also analyzed on the GC/MS for VOCs when the concentration of hydrogen sulfide was 1 ppm or above.

3.3.2   Description of Landfills Sampled

Ambient air and soil vapor were sampled at ten landfill sites in Florida. All the landfills received C&D waste, except for Sites F and H, which received Class III waste. The relative locations of the landfills sampled are shown on Figure 3-5. Sites F and H were Class III and designated with a box. Site B, D, and E, marked with a shaded box, were the sites most visited and sampled. Site maps with sampling locations are included in Appendix A.

Site A is a C&D landfill located in Pasco County. The landfill has 66.5 permitted acres. A closed cell covers approximately 15 acres. The facility receives 700 to 1000 tons/day of waste, mainly from demolition sites. On-site clay is used as cover material, which made sampling with the soil vapor probe difficult. A soil auger or digger was used to penetrate approximately 0.5 foot into the cover soil prior to use of the soil vapor probe. Three sampling wells were installed on the closed cell for a period of two weeks. One well was 1.5-feet deep, and two wells were 1-feet deep. No history of odor complaints from nearby residences exists.

Site B is a C&D 132 acre landfill that receives waste from material recovery facilities (MRFs). The site is located in Citrus County, close to a residential community. According to the 1990 census, about 52,000 people live within a two-mile radius of the landfill. Since 1993, the landfill has received C&D waste from Citrus County and several counties south of it. Soil vapor sampling wells were installed on the closed cell. One set of wells was installed in the middle of the cell. Five wells ranging in depth from 1 foot to 5 feet were installed 1 foot apart from each other. Another set of wells was installed in the

southeast corner of the closed cell. Three wells ranging in depth from 1 foot to 3 feet in depth were installed 1 foot apart from each other. The wells remained on site and were sampled for a period of 5 months. Residents of nearby communities have reported numerous odor complaints to FDEP. In addition, one resident filed a petition to have the Agency for Toxic Substances and Disease Registry evaluate the site's potential health threat.

Site C is a privately owned C&D landfill in southeast Marion County. Nearby residents have shown some concern about the odors generated at the site, but no odor complaints were filed with FDEP.

Site D is a C&D landfill in Volusia County. An existing gas collection system consists of 4 flares and horizontal piping. Large amounts of drywall from construction of a nearby mall were disposed in this landfill. Nearby residents and businesses have filed numerous odor complaints to FDEP. Residents concerned about the landfill odors have formed a group called Citizens Against Landfills in the City of Orange City (CALICO).

Site E is a C&D landfill located a few miles away from Site D in Volusia County. The C&D debris disposal area covers 59 acres. Wood, metals, and concrete are separated. Three sets of soil vapor sampling wells were installed on the perimeter of the landfill. Each set of wells consisted of 1-foot, 2-feet, and 3-feet deep wells. No odor complaints have been filed with the FDEP.

Site F is a Class III landfill in Alachua County. Two cells were receiving waste; one cell closed approximately 10 years ago (1990) and one closed 10 months ago in early 2000. Upon closing, the Class III disposal area was covered with a geomembrane liner and 1-2 feet of cover soil. Passive vent pipes were installed.

Site G is a C&D landfill in Marion County. Every six months the operator placed a six to eight inch sand cover. The disposal area was 38.7 acres. The first phase, cell 1, has a permanent cover of 18 inches to 2 feet deep. Nearby residents have voiced concerns at public meetings about odor problems.

Site H is a facility in Columbia County that has a MSW disposal area and a Class III disposal area. The Class III area has a non-active section that is approximately seven years old. The material received at the Class III landfill is from direct hauls. Large pieces of metal are removed from the loads. The operator places 6 inches of cover on the Class III once a week. In the past, the landfill experienced odor problems and black leachate seeps.

Site I is a small C&D landfill in Highlands County that receives waste from MRFs. The landfill was in the process of closure at the time of sampling. Approximately 2 inches to 1 foot of sand was in place and the 8.2-acre disposal area was filled in 2 years. The landfill is now closed and will have 2 feet of cover. FDEP has observed odor events at this location.

Site J is a small privately owned C&D landfill in Highlands County. The landfill has multiple areas where large amounts of asphalt were placed. The landfill is not active and has not been covered. No odor reports have been filed by the few nearby residents.

Table 3-1 summarizes the main facts about the sampled landfills, including. the scale of odor complaints. A + symbol indicates an odor complaint was reported. More than one + indicates multiple odor complaints from nearby residents and businesses to FDEP.

3.4   Results

Ten landfills were visited, three of which were initially selected for repeated site sampling (B, D, and E). Sites B and D had known odor complaints, and Site E did not have documented odor complaints. Each of these sites was visited at least seven times. The remaining seven sites were visited to expand the database and were each visited at least twice. Table 3-2 summarizes the number of sampling visits and number of samples collected at each site. For each site, the results will be presented in the following order: ambient hydrogen sulfide, soil vapor hydrogen sulfide, and a summary of other constituents. The other constituents are permanent gases (methane, carbon dioxide, and oxygen) and VOCs. VOCs include VSCs, halocarbons, hydrocarbons, aromatics, pinenes, miscellaneous polar compounds, and ketones.

Table 3-1. Some Characteristics of Landfills Sampled in Florida

Site	Type	Location	Active/Closed	Sampling Type	Odor Complaints*
A	C&D	Pasco County	1 active cell, 2 closed cells	Soil vapor probe, Three soil vapor wells	
B	C&D	Citrus County	1 active cell, 1 closed cell	Soil vapor probe, Eight soil vapor wells	+ +
C	C&D	Marion County	1 active cell	Soil vapor probe	+
D	C&D	Volusia County	1 active cell	Soil vapor probe, Four existing gas collection flares	+ +
E	C&D	Volusia County	1 active cell	Soil vapor probe, Soil vapor wells	
F	Class III	Alachua County	2 closed cells	Nineteen existing gas passive vents	
G	C&D	Marion County	1 active cell, 1 closed cell	Soil vapor probe	+
H	Class III	Columbia County	1 active cell, 1 closed cell	Soil vapor probe	
I	C&D	Highlands County	1 closed cell	Soil vapor probe	+ +
J	C&D	Highlands County	1 closed cell	Soil vapor probe	

* + = odor complaint recorded and ++ = multiple odor complaints

Table 3-2. Number of Sampling Visits and Samples a Ten Landfill Sites in Florida

Site	Visits	Ambient H_2S	Soil Vapor H_2S	VOCs	Permanent Gases
A	3	19	21	4	10
B	11	100	116	2	70
C	2	7	8	4	6
D	8	30	26	17	23
E	7	61	72	8	51
F	2	24	24	5	20
G	2	24	24	0	18
H	2	22	22	2	12
I	3	27	23	10	20
J	3	27	26	1	17

Hydrogen sulfide was detected over an extremely large concentration range (e.g., seven orders of magnitude). To illustrate the relative occurrence of hydrogen sulfide in this wide range, hydrogen sulfide concentrations are presented as histograms for both the ambient and soil vapor samples at each site. For the purpose of future comparisons, all histograms include the same concentration range. This range is from below the detection limit (BDL) to greater than 10,000 ppm. The detection limit on the Jerome meter was 0.003 ppm, as detailed in the operation manual. VOCs were analyzed from grab bag samples. Grab bag samples were collected in the field when the hydrogen sulfide concentration was suspected to be high and would require dilution in the laboratory. In a few cases in which the hydrogen sulfide concentration was not high, bag samples were collected and analyzed for VOCs. Fifty-three VOC analyses were performed on samples from nine of the ten sites. For the purpose of calculating mean concentrations, values below the detection limit were assumed to be one half the detection limit. For example, when the reading was below 0.003 ppm on the Jerome Hydrogen Sulfide meter, 0.0015 ppm was used to calculate the average.

3.5   Summary of Hydrogen Sulfide in C&D Debris Landfills

The results of this research confirm that hydrogen sulfide is indeed a common component in C&D debris landfill gas. The following explores the range of hydrogen sulfide concentrations encountered, the role of gypsum drywall, and the conditions that promote the formation of hydrogen sulfide.

3.6   Occurrence

Hydrogen sulfide was detected at all ten sampled landfills. The occurrence and concentration of hydrogen sulfide found in the gas beneath the surface of the landfills will be discussed. The relationship between ambient and soil vapor hydrogen sulfide concentrations will be evaluated. A comparison and contrast between C&D debris landfill gas from this study and MSW landfill gas from other studies will be presented.

3.6.1   Soil Vapor Hydrogen Sulfide

The detected soil vapor hydrogen sulfide concentrations are summarized in Table 3-3. As a reminder, the term *soil vapor* in this report refers to gas collected from some point within the landfill. Most of these points were collected at the cover soil-waste interface (321 of 362 measurements), but some were collected from gas wells (41). Soil vapor hydrogen sulfide concentrations were measured over a wide range of concentrations (seven orders of magnitude). The range of concentrations was from below the detection limit (0.003 ppm) up to 12,000 ppm. In most cases (6 of 10 sites) the average concentrations were high (greater than 5 ppm), whereas the median concentrations were low (less than 0.5 ppm). This resulted from the occurrence of a few very high concentration measurements. The occurrence of predominantly low concentrations and a few high concentrations was illustrated in the histograms presented in the previous chapter.

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Table 3-3 Soil Vapor Hydrogen Sulfide

Site	Soil Vapor Hydrogen Sulfide (ppm)					
	Number of	Number	Minimum	Maximum	Average	Median
A	21	19	<0.003	470	26.32	0.013
B	116	77	<0.003	920	8.07	0.007
C	8	8	0.013	12000	30.19	24.74
D	26	25	<0.003	7000	2110	1800
E	72	62	<0.003	2500	35.64	0.02
F	24	16	<0.003	49	5.85	0.004
G	24	19	<0.003	0.64	0.0068	0.005
H	22	20	<0.003	3300	150.7	0.025
I	23	22	<0.003	11000	1186	22.5
J	26	26	<0.003	530	26.16	0.35
Total	362	294	<0.003	12000	656.8	0.023

Site C, D, and I have high median values (i.e., all greater than 20 ppm), as shown in Table 3-3. The hydrogen sulfide concentrations detected at these sites were among the highest of all sites sampled. At Site D, with a median value of 1,800 ppm, the gas samples were collected from gas collection wells installed within the waste. Methane was also detected in these wells, indicating that methane displacement was providing a driving force for gas to leave the landfill. The Site D measurements are unique in that they represent true landfill gas being emitted from the landfilled waste. Most other measurements with the soil vapor probe were most likely mixtures of landfill gas and air. Site F also had gas wells, but it was a capped Class III landfill and the gas contained oxygen (0.3% – 19.2%), indicating that this gas was also a mixture of landfill gas and air. Site I and J had the unique characteristic of accepting residuals from C&D debris recycling facilities. These recycling facilities remove large recoverable materials with established markets (e.g., wood, concrete, metal). Drywall is not typically recycled; thus the residuals stream contains greater than normal concentrations of drywall. This fact, combined with the size reduction of material occurring with the processing system, creates conditions conducive to hydrogen sulfide formation.

The concentration of hydrogen sulfide varied from site to site and among samples at each site. One explanation for the variance is that the C&D debris in the landfill was heterogeneous; drywall was not present in all levels of waste. Other waste components may also impact hydrogen sulfide production. Research conducted by Yang (2000) to investigate the impact of waste components on hydrogen sulfide production in simulated C&D debris landfills found that lysimeters containing concrete have much lower hydrogen sulfide concentrations. Other factors creating variability include compaction rates and weather.

3.6.2   Changes With Respect to Time

At the sites where an existing gas collection system or soil vapor wells were sampled repeatedly, variation from visit to visit occurred. This was seen at Sites B, D, and E, the initial sites chosen to research. Site B and Site D were chosen because of a history of odor complaints from nearby residents and businesses. Site E was then chosen as a site to sample for background comparison. FDEP had not received odor complaints for Site E. The site is a few miles away from Site D.

At Site B hydrogen sulfide was measured at 1 ppm or below except for four samples. The concentrations detected at Site B were lower than expected, considering the extent of odor complaints in the surrounding area. At Site D the concentrations ranged from below the detection limit up to 7,000 ppm. The hydrogen sulfide concentrations at Site D were high, as expected from the history of odor complaints and that gas collection wells were used. Although Site E was not associated with odor complaints, hydrogen sulfide concentrations above the odor threshold and at higher concentrations up to 2,500 ppm were used.

Hydrogen sulfide concentration at Site B was fairly constant from the end of October through the beginning of February. However, on February 18, 2000, higher concentrations were detected in all the wells. One month later, the hydrogen sulfide concentration declined. The amount of decline was different for each soil vapor well. At Site D the hydrogen sulfide concentration at the gas collection wells averaged approximately 3,400 ppm. The concentrations had one notable decrease (average 900 ppm) on January 18, 2000. One month later the hydrogen sulfide concentration returned to an average of 4,200 ppm and climbed to 5,300 ppm the following month. The hydrogen sulfide concentration at Site E followed a different trend, decreasing over the sampling time period. The first measurements recorded in November averaged 5.8 ppm, with the highest hydrogen sulfide at 17 ppm. In December the concentration dropped to an average of 1.2 ppm. Then the following months, the hydrogen sulfide concentration leveled out and averaged 0.047 ppm. In addition, the concentrations were less variable from January through March.

The hydrogen sulfide concentrations at Site D were more constant than those at Site B and E. One explanation for this is that the gas system wells at Site D were much deeper wells than those installed manually at Site B and E. The small 0.25-inch diameter wells were installed at depths of 1 foot to 5 feet. Details of the soil vapor wells installed at Sites B and D are presented in Appendix A. The gas from the gas collection system at Site D is more representative because little mixing with ambient air and is thus landfill gas occurs.

3.6.3   Ambient Versus Soil Vapor Hydrogen Sulfide

Ambient air and soil vapor hydrogen sulfide concentration were compared. As shown in Figure 3-1, no obvious correlation between ambient and soil vapor hydrogen sulfide exists. In fact, high hydrogen sulfide in the ambient air was detected in areas where soil

vapor hydrogen sulfide concentration was low and where soil vapor hydrogen sulfide concentration was high. Low ambient hydrogen sulfide concentrations were measured where soil vapor hydrogen sulfide was both low and high. Clearly, the ambient hydrogen sulfide concentration measured at any one point on the surface of the landfill was not a function of the gas in the soil vapor one foot or more below it. Rather, it was a function of the aggregate emissions from the entire surface of the landfill. As hydrogen sulfide migrates out of the landfill, wind carries the gas away from its point of origin.
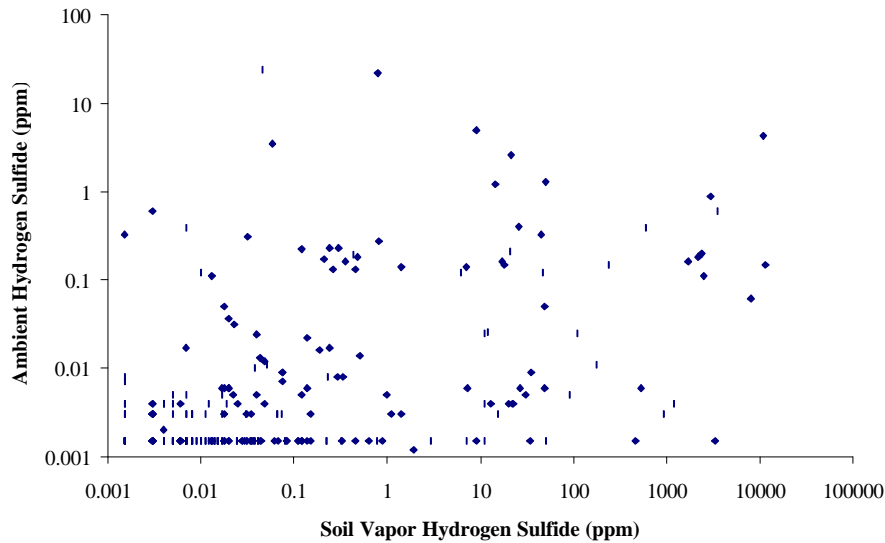
Figure 3-1. Ambient versus Soil Vapor Hydrogen Sulfide

Ambient hydrogen sulfide was difficult to detect due its variable nature. Hydrogen sulfide odor could be detected by observation one minute and not the next. Instances in which strong hydrogen sulfide in the ambient air could be smelled occurred, but the soil vapor hydrogen sulfide directly beneath where the odor was detected would be extremely low.

3.6.4   Comparison Between C&D Gas and MSW Gas

The concentrations of soil vapor hydrogen sulfide measured at the ten C&D debris landfills were compared to those typically found in MSW landfill gas. Table 3-4 presents the average hydrogen sulfide concentration found in the field, drywall bottle experiment, drywall Tedlar bag experiment, and from the literature. The field data are an average of measurements at all the sites and the Site D gas collection system measurements. Site D is included because the samples collected better represent C&D debris landfill gas rather than gas mixed with ambient air. The drywall bottle experiment concentration shown in Table 3-4 is the average of all the bottles. The drywall Tedlar bag experiment concentration is the average of all the bags. The hydrogen sulfide concentration (35.5 ppm) listed in AP-42

is a representative value for MSW landfill gas (US EPA, 2000). Capenter and Bidwell (1996) performed a study at a MSW landfill in Connecticut by sampling from wells. The California Waste Management Board sampled gas from 66 landfills, finding hydrogen sulfide concentrations up to 14 ppm (CWMB, 1997).

The average hydrogen sulfide of the C&D debris landfills is much greater than that of the typical MSW landfill. The hydrogen sulfide concentration measured at Site D was much greater than that of a typical MSW landfill. The average hydrogen sulfide at Site D was much greater by two orders of magnitude than that of the AP-42 emission factor and the other MSW landfill gas literature.

Table 3-4. C&D Debris Landfill Gas and MSW Landfill Gas Hydrogen Sulfide

Source	Average Hydrogen Sulfide (ppm)
Total C&D Sites	656
Site D	3016
Bottle Experiment	16700
Tedlar Bag Experiment	1170
AP-42	35.5
Capenter and Bidwell	28.3
Young and Parker	-
CWMB	<1.98 – 14

(Source: Capenter and Bidwell, 1996; CWMB, 1987; US EPA, 2000)

3.7   Role of Gypsum Drywall

Many of the operators and managers at the visited landfills cited gypsum drywall as the source of odors. Operators noted that after receiving large amounts of drywall either from a storm or construction of a large building, hydrogen sulfide odors were more prevalent. For example, after a large storm in 1995, Site B received large amounts of wet gypsum drywall and noticed odors developing afterward. Site D received large amounts of drywall from the construction of a nearby mall and noted subsequent odors in 1995.

3.8   Conditions for Hydrogen Sulfide Formation

The literature review clearly showed that the following conditions are factors contributing to hydrogen sulfide production: anaerobic conditions, pH, moisture, organic matter content, and the presence of sulfate as an electron acceptor (Gypsum Association, 1992; Postgate, 1984; Widdel and Pfenning, 1984). The conditions required for sulfate-reducing bacteria to survive and produce hydrogen sulfide and the conditions observed in the field are compared and discussed.

3.8.1   Anaerobic conditions

Sulfate-reducing bacteria (SRB) are strict anaerobes and thus require the absence of oxygen (Atlas, 1997; Gypsum Association, 1992). However, oxygen was present in the C&D debris landfills. Oxygen ranging from BDL (0.1%) to 21% was detected in 97% of all the samples analyzed with the GEM 500 meter in the field. The presence of oxygen in the samples does not, however, imply that conditions were not adequate for the formation of hydrogen sulfide gas. Methane was also detected in 45% of the field samples, ranging from below the detection limit (0.1%) to 47.5%. The detection of methane, which is also produced by anaerobic bacteria (methanogens) in the field samples, suggests the possibility of anaerobic pockets or areas in the landfills. Anaerobic conditions can be produced within C&D debris landfills when large amounts of waste are placed together and compacted.

Jang (2000) observed hydrogen sulfide production concurrent with measurable DO (2 mg/L and less) in leachate of lysimeters simulating a C&D debris landfill.

3.8.2 pH

The optimum pH for SRB is approximately 7, with inhibition occurring above 9 and below 6. In the field, pH was not measured. However, previous studies indicate that the pH of leachate from C&D debris is acceptable for SRB survival. Leachate from C&D debris landfills has a pH range of 6.1 to 7.9 (NADC, 1994; WMI, 1993, Weber, 1999).

3.8.3 Moisture Content

Although the moisture content of the waste in the landfills was not measured, water is a factor in hydrogen sulfide production. SRB require moisture for survival (Atlas, 1997; Gypsum Association, 1992). In nature, SRB thrive in marine environments, bog, marshes, and hot sulfur springs. Two of the landfill odor cases cited in Chapter 2 (D'Orio, 1997; Nagl and Cantrall, 1996) and landfill operators at Sites A, B, D, E, F, and H link the occurrence of odors with rainfall events. Landfill operators observed rotten egg odors a few days to a few weeks after rainfall events. Also, unusually high amounts of rain have been cited as a contributor to odor problems. The role of rain in C&D landfill odor problems can be attributed to several possible mechanisms including displacement of hydrogen sulfide gas, solubility of sulfate, and pressure changes associated with a rain event.

3.8.4 Organic Substrate

SRB require an organic substrate for growth. The literature states that SRB use low molecular weight organic molecules as carbon sources (Atlas, 1997).

3.9 Volatile Sulfur Compounds (VSCs)

The results of this research confirm the finding of VSCs in C&D debris gas. The following discussion details the occurrence of VSCs and the source of VSCs.

3.9.1 Occurrence

VSCs were detected in seven of the nine landfills in which grab bag samples were collected for analysis on the GC/MS. The VSCs detected and the frequency at which they were detected are presented in Table 3-5. Hydrogen sulfide was detected the most frequently (81%), followed by methyl mercaptan (51%) and carbonyl sulfide (45%). Hydrogen sulfide was detected at much higher concentration ranges (up to 12,000 ppm) than other VSCs (up to 1,727 ppm). Table 3-6 details the average hydrogen sulfide and VSCs found at the ten sites and in MSW landfill literature.

In comparison to MSW landfill gas, the VSCs in C&D landfill gases are similar. Sites C, D, H, and I had more VSCs than what was analyzed in MSW landfill gas research. Carbonyl sulfide and carbon carbon disulfide were within the range of MSW gas concentrations, except for Site C, which had a high of 61 ppm and 91 ppm respectively.

Methyl mercaptan, dimethyl sulfide, ethyl mercaptan, and thiophene in C&D debris landfill gas and MSW were in the same range. Dimethyl disulfide was two orders of magnitude lower than at Site I, the only site in which it was detected, than in literature. The VSCs found in the drywall Tedlar bag experiment were similar to the VSCs at the sites.

3.10   Other Gases

In addition to hydrogen sulfide, other components such as VSCs and permanent gases were detected at the C&D landfills. The grab bag samples collected were analyzed by GC/MS for toxic air pollutants. Table 3-7 presents the classes of VOCs detected in the soil vapor. Hydrocarbons were the class of VOCs detected the most frequently, followed by halocarbons and pinenes. Potential contributors to hydrocarbons are roofing tiles, pavement, asphalt cement, waste oil and greases, and petroleum distillates in paint thinner. Tree stump, wood framing, and wood pallets are the most likely sources of pinenes. Other potential sources of VOCs include paint containers, solvent containers, varnishes, and stains.

3.11   Implications for Odor and Health Impacts

Hydrogen sulfide in the soil vapor and in the ambient air and possible hydrogen sulfide control measures are discussed.

3.11.1 Soil Vapor

The characterization of gas produced at C&D debris landfills indicates that it serves as a source of odor and may in some cases be a health threat. Gas beneath the surface of the landfill, the soil vapor, contains hydrogen sulfide concentrations in excess of the odor threshold and regulatory guidelines. Table 3-8 details the percent of the samples at each site that were above the 25 ppb odor threshold, NIOSH's 10 ppm recommended exposure limit, and OSHA's 20 ppm acceptable ceiling concentration. At all the sites, 25% or more of the samples exceeded the odor threshold level. At Sites C, D, and I 50% or more of the soil vapor hydrogen sulfide samples exceeded OSHA's regulation exposure limit. In the range of 50 to 100 ppm, human health effects include irritation of the respiratory system and eye irritation. At least one soil vapor sample at each site, except Sites F and G, was above 50 ppm. This presents a health concern for landfill workers who install gas wells or work near gas wells. For residents or businesses near C&D debris landfills, however, the soil vapor concentrations are not the most appropriate values to use for regulatory limit comparison. Ambient air concentrations, which are much lower than soil vapor concentrations, would be more appropriate to use. The same sites with at least one soil vapor hydrogen sulfide sample above 50 ppm also had a sample that exceeded 150 ppm. An exceedance of 150 ppm paralyzes the olfactory nerves and presents a health threat. When a person is exposed at high levels, they will not sense the immediate danger of the situation without a sense of smell.

Table 3-5. Soil Vapor VSC Detection Frequency

Constituent	Number of Samples	Number of Samples Detected	%
Hydrogen Sulfide	362	294	81.2
Methyl Mercaptan	51	26	51.0
Carbonyl Sulfide	51	23	45.1
Carbon Disulfide	51	22	43.1
Isopropyl Mercaptan	51	14	27.5
Dimethyl Sulfide	51	13	25.5
Thiophene	51	8	15.7
2-Methylthiophene	51	6	11.8
Tert-Butyl Mercaptan	51	3	5.9
Ethyl Mercaptan	51	4	7.8
Sec-Butyl Mercaptan	51	3	5.9
Methyl Isopropyl Sulfide	51	1	2.0
Dimethyl Disulfide	51	1	2.0
Ethyl Methyl Sulfide	51	1	2.0
3-Methylthiophene	51	1	2.0
Tetrahydrothiophene	51	0	0
Diethyl Sulfide	51	0	0
Diethyl Disulfide	51	0	0
Butyl Sulfide	51	0	0

Table 3-6. Soil Vapor Hydrogen Sulfide and VSCs at Ten Florida C&D Landfills

Constituent	A	B	C	D	E	F	G	H	I	J	AP-42	Capenter and Bidwell	Young and Parker	CWMB
Hydrogen Sulfide (ppm)	26	8.1	3020	2100	36	5.9	0.64	151	1200	26.2	35.5	28.3	--	<1.98 - 14
Carbonyl Sulfide (ppm)	0.04	-	61	0.71	2.5	22	-	0.16	0.35	-	0.49	--	--	<0.20 - 8.81
Methyl Mercaptan (ppm)	0.04	-	30	164	14	85	-	4.4	1.9	-	2.49	0.8	43.49	0.05 - 214.96
Dimethyl Sulfide (ppm)	-	-	2.1	1.7	0.07	0.53	-	0.02	0.04	-	7.82	--	1.55	0.62 - 9.46
Ethyl Mercaptan (ppm)	-	-	0.19	-	-	-	-	-	0.03	-	2.28	0.62	--	--
Carbon Disulfide (ppm)	-	-	91	0.06	0.03	1.7	-	0.04	0.03	-	0.58	--	0.01	<0.03 - 0.6
Isopropyl Mercaptan (ppm)	-	-	0.14	2.8	0.03	-	-	0.11	0.15	-	--	--	--	--
Tert-Butyl Mercaptan (ppm)	-	-	-	0.13	-	-	-	0.01	-	-	--	--	--	--
Ethyl Methyl Sulfide (ppm)	-	-	-	-	-	-	-	0.01	-	-	--	--	--	--
Thiophene (ppm)	-	-	0.14	0.06	-	-	-	0.02	0.01	-	--	--	--	0.14
Methyl Isopropyl Sulfide (ppm)	-	-	-	-	-	-	-	-	0.01	-	--	--	--	--
Dimethyl Disulfide (ppm)	-	-	-	-	-	-	-	-	0.01	-	--	--	10.21	--
2-Methylthiophene (ppm)	-	-	0.19	0.13	-	-	-	-	-	-	--	--	--	--
3-Methylthiophene (ppm)	-	-	0.24	-	-	-	-	-	-	-	--	--	--	--
Sec-Butyl Mercaptan (ppm)	-	-	0.06	0.05	-	-	-	-	-	-	--	--	--	--

- = in this study constituent BDL

-- = in literature not analyzed

Table 3-7. Soil Vapor VOC Detection Frequency

Constituent	Number of Samples	Number of Samples Detected	%
Hydrocarbons	51	48	94.1
Halocarbons	51	34	66.7
Pinenes	51	34	66.7
Ketones	51	33	64.7
Aromatics	51	30	58.8
Misc. Polars	51	20	39.2

Table 3-8 Soil Vapor Hydrogen Sulfide Concentration Exceedances

Site	%>25 ppb	%>10 ppm	%>20 ppm
A	47.6	19.0	9.5
B	28.4	0.9	0.9
C	75.0	50.0	50.0
D	88.5	80.8	73.1
E	37.5	5.6	2.8
F	25.0	16.7	12.5
G	25.0	0	0
H	50.0	9.1	4.5
I	91.3	60.9	56.5
J	92.3	26.9	19.2

3.11.2 Ambient Air

Ambient air at C&D landfills is the issue of concern for neighbors of these facilities. Ambient hydrogen sulfide readings were measured with the Jerome meter at the surface of the landfill. Hydrogen sulfide concentrations in the ambient air were much lower than in the soil vapor. This was most likely a result of dilution and mixing with ambient air. Ambient hydrogen sulfide concentrations at landfill surfaces were variable, fluctuating with time, wind speed, and wind direction. The range of ambient hydrogen sulfide readings was from below the lower detection limit of the meter, 3 ppb, up to and above the upper detection limit, 50 ppm. The minimum, maximum, and average ambient hydrogen sulfide readings taken at each site are summarized in Table 3-9. All the median values were 0.61 ppm and below.

As presented for the soil vapor hydrogen sulfide concentrations, Table 3-10 details the percentage of samples at each site that exceeded the odor threshold, the NIOSH recommended guideline, and the OSHA regulation values. Samples at all landfills exceeded the odor threshold. Two sites exceeded both the NIOSH and OSHA values.

Ambient hydrogen sulfide was present above the odor threshold level at times at all the landfills. Since the concentration measured at the surface of the landfill would likely be even more diluted by the time it traveled off site, the occasional measurement of high concentration in the ambient air coupled with the documented odor complaints suggests that these facilities will present a source of odors for surrounding neighborhoods and businesses. The hydrogen sulfide concentration in ambient air should in most cases be below acceptable OSHA worker safety guidelines, but the potential impact of low concentrations is somewhat unknown. Additional work needs to be conducted in this area.

Table 3-9 Ambient Hydrogen Sulfide Concentrations at 10 C&D Landfills sites in Florida

			Ambient Hydrogen Sulfide (ppm)			
Site	Number of Samples	Number of Samples Detected	Minimum	Maximum	Average	Median
A	19	5	<0.003	0.39	0.042	<0.003
B	100	18	<0.003	0.11	0.003	<0.003
C	7	5	<0.003	0.39	0.115	0.05
D	30	24	<0.003	2.40	0.193	0.007
E	61	41	<0.003	0.60	0.039	0.004
F	24	17	<0.003	0.12	0.008	0.004
G	24	2	<0.003	3.50	0.147	<0.003
H	22	6	<0.003	0.27	0.037	<0.003
I	27	23	<0.003	>50	4.02	0.610
J	27	21	<0.003	>50	2.74	0.008

Table 3-10 Ambient Hydrogen Sulfide Concentration Exceedances

Site	%>25 ppb	%>10 ppm	%>20 ppm
A	21.1	0	0
B	1.0	0	0
C	71.4	0	0
D	33.3	0	0
E	16.4	0	0
F	4.2	0	0
G	4.2	0	0
H	18.2	0	0
I	59.3	7.4	7.4
H	40.7	7.4	7.4

4 PRODUCTION AND MIGRATION OF HYDROGEN SULFIDE IN C&D DEBRIS LANDFILL SIMULATORS

Additional research was conducted in laboratory columns to simulate the chemical and biological activity occurring within C&D debris landfills. The columns were subjected to an artificial rainfall, and the resulting leachate and gas were collected and analyzed. The waste components loaded into the columns consisted of major constituents found in C&D debris landfills. Two separate column experiments were conducted. Experiment 1 investigated the impact of three different C&D debris components—drywall, wood, and concrete—mixed in different combinations. Experiment 2 was conducted as a follow-up to Experiment 1. In Experiment 2, only two components were used: concrete and drywall. The components were not mixed but were instead placed one layer on top of the other layer. This chapter describes the methods used, the results, and a discussion. Complete details of this work including all data are presented in Yang (2000).

4.1 Experimental Methods

As described in previous chapters, the emission of hydrogen sulfide (H_2S) gas is a major environmental issue at many C&D debris landfills (Lee, 2000). H_2S generation in C&D debris landfills has been concluded to result from the biological reduction of sulfate present in gypsum drywall (Jang, 2000). Two laboratory experiments were designed to simulate the environment within C&D debris landfills and to measure H_2S concentrations resulting from different compositions of C&D debris. The following experiments differ from previous C&D debris landfill simulations (Thurn, 1997; Jang, 2000) in that gaseous H_2S composition, not leachate quality, was the primary target of the research. This section describes the selection and preparation of the C&D components, the design and construction of the columns, and the method used to simulate rainfall.

4.1.1 Experiment 1

4.1.1.1 Waste components

In Experiment 1, the waste loaded into the columns consisted of mixtures of three different C&D debris components, drywall, wood, and concrete, in a two-foot thick layer. The different combinations were selected to observe H_2S production from decaying drywall co-disposed with other waste constituents. The constituents included in each column are presented in Table 4-1.

Table 4-1. Waste Components in Column Experiment 1

	Drywall	Pea Gravel	Wood	Concrete
Column C – Control		Included	Included	Included
Column 1D	Included	Included		
Column 2D	Included	Included		
Column 3DW	Included	Included	Included	
Column 4DW	Included	Included	Included	
Column 5A	Included		Included	Included
Column 6A	Included		Included	Included
Column 7A	Included		Included	Included

Eight columns were constructed. Column C served as a control representing a C&D debris landfill that does not contain gypsum drywall. Column C contained wood, concrete, and pea gravel. Columns 1D and 2D contained drywall and pea gravel. The only organic matter present in these columns was the paper backing on the drywall itself. Columns 3DW and 4DW contained drywall, wood, and pea gravel. Wood and drywall are the primary waste components generated during the construction of a wood frame house (see Chapter 2). One objective of these columns was to observe the impact of wood serving as an additional carbon source. Columns 5A, 6A, and 7A contained drywall, wood, and concrete and was believed to most resemble the environment within a C&D debris landfill.

4.1.1.2   Waste preparation

The waste constituents required preparation—size reduction and screening—in order to be loaded into the columns. Untreated 1-inch by 4-inch southern yellow pine wood purchased from a local home improvement store was chipped using a MTD Yard Machine (SHP Chipper/Shredder model 135212). The chipped wood was then sieved using a 0.64 cm (0.25 inch) sieve to separate the wood chips from the finer material. The larger chips were used in the experiment. Crushed concrete was obtained from a local concrete recycling facility. It was also separated using a 0.64-cm (0.25-inch) sieve. The concrete that did not pass through the sieve was rinsed with water to remove dirt and impurities and allowed to dry. A 4-foot by 8-foot sheet of gypsum drywall was purchased from a local home improvement store and cut into 2.5-cm by 2.5-cm (1-inch by 1-inch) squares. Parker's Brand pea gravel was washed with water to remove soil and other debris. After the pea gravel was washed and allowed to dry, a few pieces were placed in a beaker with deionized (DI) water. The pH was determined to be approximately 7.6. This observation was important because a non-reactive material (i.e., a material that did not change the pH of the solution as limestone could) was required. Table 4-2 presents the sources and sizes of the column components.

Table 4-2. Sources and Sizes of C&D Debris Components

C&D Components	Sources	Sizes
Drywall	Lowe's hardware store	2.5 by 2.5-cm
Wood	Lowe's hardware store	> 0.64-cm
Concrete	Florida Concrete Recycling	> 0.64-cm
Pea Gravel	Lowe's hardware store	> 0.64-cm

4.1.1.3 Waste loading

The desired total waste depth in each column was two feet. Columns were loaded so that each component would represent one third of the total waste layer volume. Component bulk densities were determined in order to calculate the respective masses required to maintain equal volume distribution in each column. Table 4-3 provides the respective bulk densities determined for each column component. Bulk density calculations are included in Jang (2000).

The mass of each material required was calculated using the bulk density values in Table 4-3. The mass loaded in each column is presented in Table 4-4. To maintain constant waste volumes, pea gravel was used as a filler material when a component was not included in certain columns. Pea gravel was selected because of its non-reactive properties.

Table 4-3. Bulk Density of Materials used in Column Experiments

Material	Bulk Density	
	ρ_b (g/cm^3)	ρ_b (lb/ft^3)
Drywall	0.24	15.24
Concrete	1.07	66.89
Wood	0.19	11.68
Pea Gravel	1.39	86.92
Sand	1.30	81.23

Table 4-4 also presents the total depth of waste in each column that was measured after the column was loaded. The actual waste layer depth ranged from 20.5 inches to 22.25 inches. The method slightly underestimated the required component masses but remained within 15% of the total two-foot depth.

Table 4-4. Experiment 1 – Mass Required and Final Depth

	Components	Volume of Each (cm³)	Mass (g)				Total Volume (cm³)	Final Depth of Waste (inch)
			Drywall	Concrete	Wood	Gravel		
C	Wood & Concrete	2,471	—	1,766	308	2,297	4,942	22.3
1D	Drywall	4,942	402	—	—	4,590	4,942	20.5
2D	Drywall	4,942	402	—	—	4,590	4,942	20.5
3DW	Drywall & Wood	2,471	402	—	308	2,298	4,942	21.3
4DW	Drywall & Wood	2,471	402	—	308	2,298	4,942	20.5
5A	All	1,647	402	1,766	308	—	4,942	21.0
6A	All	1,647	402	1,766	308	—	4,942	21.5
7A	All	1,647	402	1,766	308	—	4,942	21.0

4.1.1.4 Column construction

Eight PVC columns were constructed. The column schematic for Experiment 1 is presented in Figure 4-1. The pipe length was approximately 90 cm (3 feet) with a diameter of 10 cm (4 inches). Ten-cm (4-inch) slip caps were glued to the ends of the PVC columns. The slip caps were drilled and threaded for valve installation. The valves were used for liquid addition at the top of the columns and leachate removal from the bottom of the columns. Stainless steel Swagelok® valves (model SS-4P4T4) were used and connected to the slip end caps with CPVC ¼-inch nation pipe tread (NPT) male hex nipple fittings.

Before the bottom slip caps were glued to the columns, they were threaded and the bottom valves were attached. Then, sieved gravel (2.5 cm [1 inch]) was placed in the bottom slip caps. Next, stainless steel screen circles were used as layer dividers and placed over the gravel. The gravel was used so that the screen dividers would not deform under the weight of the contents and allow sand to flow out of the bottom of the columns. Once the screen dividers were in place, the columns and bottom slip caps were cleaned using Oatey's PVC clear cleaner (No. 30795) and then glued together using Oatey's PVC clear cement (No. 31015). After the bottom caps had been held in place to allow the glue to set, a 15-cm (6-inch) sand layer was loaded from the top of the columns. Five hundred milliliters of DI water were added to check for leaks around the bottom valve attachments and then drained to ensure that the bottom valves would not clog with any sand that went through the screen dividers.

The waste was loaded in two lifts. Each column was designed to have one gas extraction port located in the middle of the waste layer. These gas extraction ports were drilled after the first lift was loaded. Whitney gas valves (model SS-1RS4, 5000 PSI) were used as a means to extract gas. A 2.5-inch stainless steel extension was attached to the gas valve so that gas samples could be extracted from the center of the column. If the extensions were not used, the gas sample would have been obtained from inside the column wall and not considered to be a representative sample of the waste layer. Red Devil adhesive sealant caulk (No. 0866) was used to provide an airtight seal around the extension.

Once the gas extraction ports were in place, the second lift of the waste was loaded. Then, stainless steel screen dividers were placed over the second lift to ensure that the top sand layer, loaded next, would not fill the pore spaces of the waste layer. Next, the 15-cm (6-inch) sand layer was loaded. The top slip caps were threaded, and valves were attached. Stainless steel Swagelok® valves were attached to the top slip caps using CPVC ¼-inch NPT male hex nipple fittings. Next, the caps were cleaned with PVC cleaner and glued to the tops of the columns.
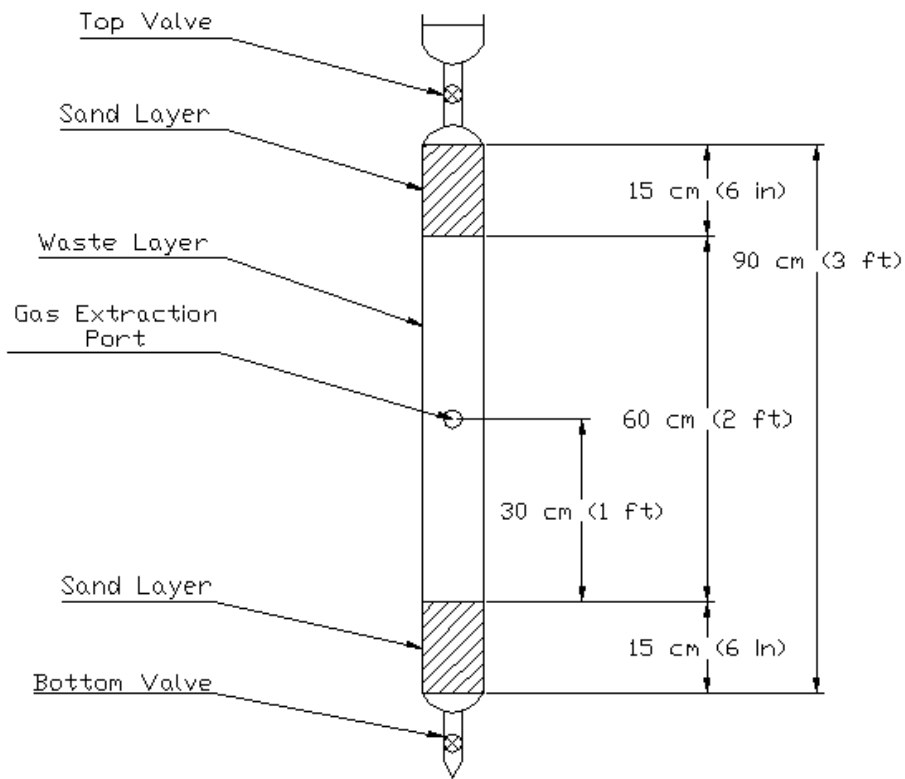
Figure 4-1. Column Schematic for Experiment 1

An anaerobic environment was required for sulfate-reducing bacteria activity. To ensure that the columns remained anaerobic during the addition of the SPLP solution, slip

caps were used as funnels (see Figure 4-1). By using these slip caps, the Swagelok® valves were closed before the columns were exposed to the atmosphere. The slip caps also permitted better control of the SPLP solution flow rate into the columns. Eight more slip caps were threaded and attached to the valves already attached to the top slip caps.

After construction was completed, cleaner and glue fumes were allowed to dissipate for two weeks. Nitrogen gas was flushed (in approximately five-minute durations) through the columns every other day for two weeks for decontamination purposes.

4.1.1.5   Simulated rainfall application

A synthetic rainfall was added to the columns to simulate the process of rainfall infiltration into landfills and the subsequent formation of leachate. No standardized methodology exists for this type of experiment, which was not conducted to research leaching processes but rather to simulate an environment conducive to the production of H_2S. For a discussion of leachate from C&D debris landfills, the reader is referred to Jang (2000) and Townsend *et al.* (1999). The experiment was not designed to evaluate the impact of different moisture addition rates.

Four hundred milliliters of SPLP solution were added to the columns weekly. The SPLP solution was made following the EPA SW-8461312 (US EPA, 1994) measured at a pH of 4.22 ± 0.05. The SPLP solution was not deaerated and was made using 60/40 by weight percent mixture of sulfuric and nitric acid. The primary objective of selecting the amount of rainfall to be added was to maintain the waste in the columns at field capacity. The addition of a periodic rainfall event also permitted the sampling and analysis of leachate, which provided some additional information regarding activities within the columns. Four hundred milliliters corresponds to 2 inches of infiltration at one time.

4.1.2   Experiment 2

Experiment 2 was performed using laboratory columns designed to simulate a C&D debris landfill in which a layer of concrete was placed above a layer of drywall and vise versa. The presence of concrete was observed to have a definite impact on H_2S concentrations within the column in Experiment 1. To verify this observation, four columns were constructed. Two columns (1DC and 2DC) were loaded with a drywall layer above a concrete layer. The other two columns (3CD and 4CD) were loaded with a concrete layer above a drywall layer. Table 4-5 presents the waste-layering scheme.

Table 4-5. Column Constituents in Experiment 2

Column	Description
1DC	Concrete layer above drywall layer
2DC	Concrete layer above drywall layer
3CD	Drywall layer above concrete layer
4CD	Drywall layer above concrete layer

4.1.2.1 <u>Waste preparation</u>

The waste constituents required preparation—size reduction and screening—in order to be loaded into the columns. The waste constituent preparation in Experiment 2 was the same as in Experiment 1 (see 4.1.1.2, Waste Preparation).

4.1.2.2 <u>Column loading</u>

The loading procedure and the component sizes for Experiment 2 was the same as Experiment 1. Also like Experiment 1, a total waste layer thickness of two feet was selected with two distinct layers: one foot of drywall and one foot of concrete. Waste layers were loaded in lifts. Once each lift was loaded, a gas extraction valve was installed. Thus, constituent masses for the different lifts were calculated from the material bulk densities. See Table 4-3 for bulk densities. Table 4-6 shows the masses per lift.

4.1.2.3 <u>Column construction</u>

Four PVC columns were constructed. The pipe length was approximately 100-cm (3.5 feet) with a diameter of 8 cm (3 inches). Eight-cm (3 inches) slip caps were fitted on the ends of the PVC pipes. PVC cleaner and glue were not used because of contamination concerns and the long period of fumigation time required. Stainless steel Swagelok valves (model SS-4P4T4) were connected to the slip caps using CPVC ¼-inch NPT male hex nipple fittings. Asahi/America ¼-inch MPT X hose labcock valves were used for gas extraction and leachate drainage.

Table 4-6. Experiment 2 – Mass Required

| Description	Volume of Each Component (cm^3)	Mass (g) Drywall	Concrete	Total Volume (cm^3)
3 Inch Layer	347	85	372	695
8 inch Layer	927	226	993	1853
1 Inch Layer	116	28	124	232
Total	*1,390*	*339*	*1,490*	*2,780*

Before the bottom slip caps and valves were attached to the columns, the bottom slip caps were filled with sieved, 2.5-cm (1-inch) gravel. Stainless steel screen dividers were then placed over the gravel so that sand would not be flushed out of the bottom valve. The gravel was used to ensure that the stainless steel screen dividers would not deform under the weight of the contents and allow sand to escape out of the bottom valves. Next, a plastic mallet was used to hammer the bottom slip caps onto the pipe. Once the bottom slip caps were attached, a 15-cm (6-inch) sand layer was loaded into the top of the column. Three hundred milliliters of DI water were added to check for leaks at the bottom seals. After the DI water was drained, the columns were loaded by lifts.

Five gas extraction valves were placed along the length of the column to determine H_2S generation profiles. Table 4-7 presents the locations of the various gas extraction ports.

Table 4-7. Gas Sampling Port Locations

Gas Sampling Port	Columns 1DC & 2DC	Columns 3CD & 4CD
First (Top)	Above top sand layer	Above top sand layer
Second	3" below bottom of top	3" below bottom of top
Third	1" above bottom of	1" above bottom of
Fourth	1" below top of concrete	1" below top of drywall
Fifth (Bottom)	3" above top of bottom	3" above top of bottom

The columns were drilled and tapped to allow each gas extraction valve to be attached. A plastic extension tube was placed inside each gas extraction valve to obtain a gas sample from the center of the column, which was thought to be a more representative sample. Without this plastic extension tube, a gas sample would have been obtained from inside the column wall. The first lift was 3 inches, which corresponded to the location of the fifth (bottom) gas extraction port. Next, 8 inches of waste were loaded, and the fourth gas extraction valve was attached. Then, 1 inch of the bottom waste layer was loaded. A screen divider was placed above this layer before the top waste layer (either concrete or drywall) was loaded. One inch of the top waste layer was added, and the third gas extraction valve was attached. Eight inches of the top waste layer was loaded, and the second gas extraction valve attached. The remaining 3 inches of the top waste layer were loaded next. Once the top waste layer was completely loaded, a screen divider was placed over it to ensure that the top sand layer, loaded next, would not fill the pore spaces of the waste layer. A 15-cm (6-inch) sand layer was placed above the waste layer. The first gas extraction port located above the top sand layer was then attached. Figure 4-2 is the column schematic.
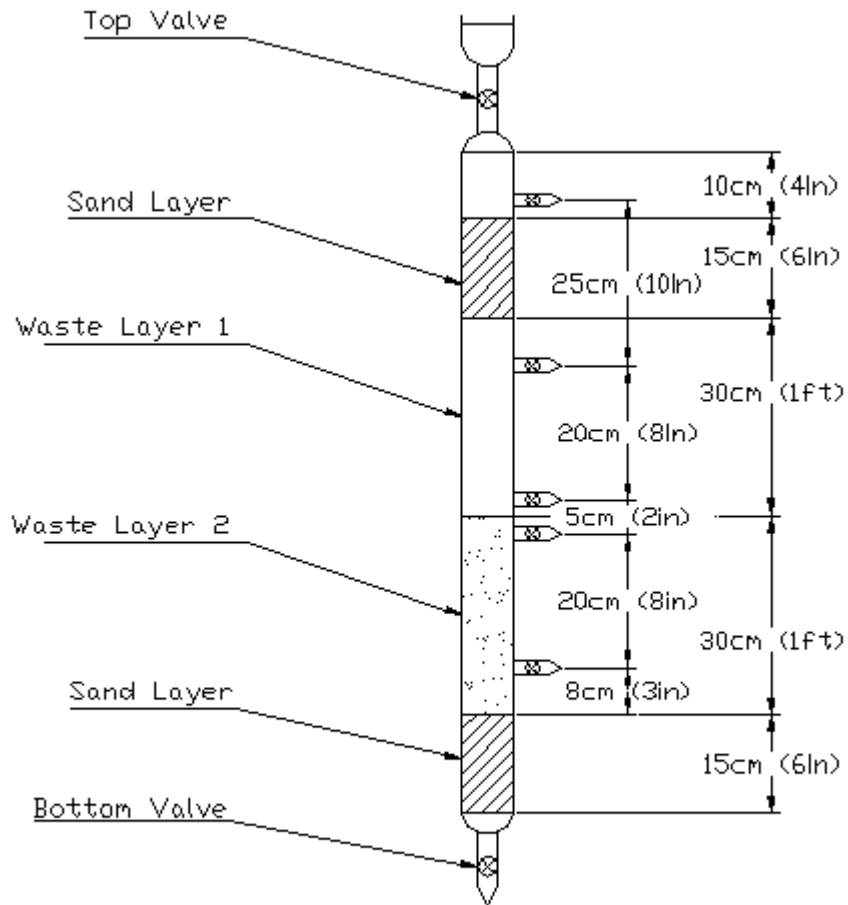
Figure 4-2. Column Schematic for Experiment 2

Swagelok® valves and slip caps were used for SPLP addition. The methodology was the same as in Experiment 1 (see 4.1.1.4, Column construction). After the top configurations were hammered into place, a bubble leak test was conducted around the valves. Red Devil adhesive sealant caulk (No. 0866) was used where any leaks were found. Caulking was also used around the top and bottom slip caps to prevent leaks. Nitrogen gas was added for 15 minutes to flush oxygen out of the columns. Nitrogen gas was not added for the same duration as in Experiment 1, because Experiment 2 did not use PVC cleaner or glue.

4.1.2.4 <u>Simulated rainfall application</u>

The SPLP leaching solution was also added to the columns to simulate the process of moisture infiltration into C&D debris landfills. Two hundred and twenty-five milliliters of SPLP solution was added to the columns weekly. This volume was calculated applying the rainfall addition rate used in Experiment 1 to the smaller diameter columns in

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Experiment 2 (i.e., 3-inch versus 4-inch diameter). The void volume in the bottom drainage layer was sufficient to hold the entire volume of leachate added.

4.1.3 Sampling Collection and Analysis

Once the columns were constructed and loaded, sample collection and analysis began. Experiment 1 gas samples were collected from the middle of the waste layer from the bottom and the top of the columns. The following section includes the sampling schedule, gas sampling methodology, leachate sampling methodology, and gas and leachate analysis.

4.1.3.1 Experiment 1-Sampling Schedule

Gas samples were analyzed for H_2S, CH_4 and CO_2, and VSCs, as presented in Table 4-8. Toward the completion of this study, the frequency of CH_4, CO_2, and VSCs sampling was decreased. From December 1, 1999, to February 10, 2000, the Jerome meter gas intake was observed to be decreasing. Then in early February, a 2.2-ppm H_2S standard was used to check the operation of the Jerome meter, which measured the standard at a concentration of 0.2 ppm. The H_2S data when the Jerome meter was out of calibration are included in Jang (2000) B but is not included in subsequent sections.

Table 4-8. Gas Sampling for Experiment 1

Parameters	Instrument Used	Frequency
H_2S	Arizona Instrument Jerome 631-X Hydrogen Sulfide Analyzer	Intermittent, or whenever another analysis was being performed
CH_4 and CO_2	Gas Chromatography – Thermal Conductivity Detector (GC – TCD)	Once every two weeks
Other Sulfur Compounds	Gas Chromatography – Mass Spectrometry (GC – MS)	Once every two weeks

A yearly recalibration of the Jerome meter by their technicians is the standard procedure recommended by Arizona Instruments; the meter does not have owner calibration ability. Therefore, the Jerome meter was sent promptly back to Arizona Instruments for recalibration. H_2S sampling resumed when a replacement Jerome meter arrived on February 16, 2000. After March 2, 2000, Air Liquide America Corp. (Lot 60416) H_2S 25-ppm standard was used to verify the calibration of the Jerome meter. The standard checks are included in Jang (2000).

Leachate was collected and sampled from the bottom of the columns while the SPLP solution was added. The leachate was analyzed for sulfide, DO, conductivity, pH, ORP, sulfate, and COD, as presented in Table 4-9.

Table 4-9. Leachate Sampling for Experiment 1

Parameters	Instrument Used	Frequency
Sulfide	HACH DR/4000U Spectrophotometer	Weekly
DO	YSI Incorporated DO Meter Model 55/12 FT	Weekly
Conductivity	Hanna Instruments HI9033 Multi-range Conductivity Meter	Weekly
pH	Fisher Scientific Accumet® – pH / Conductivity Meter Model 20	Weekly
ORP	Fisher Scientific Accumet® – pH / Conductivity Meter Model 20	Weekly
Sulfate	Ion Chromatograph (IC)	Once every two weeks
COD	HACH DR/4000U Spectrophotometer	Once every two weeks

4.1.3.2   Experiment 2 - Sampling Schedule

Experiment 2 gas samples were collected from various gas extraction ports and from the bottom of the column. Gas sampling for Experiment 2 was conducted weekly before the rain event and limited to H_2S analysis (see Table 4-8 for instrument used). Leachate was collected and analyzed for sulfide and pH while time the SPLP solution was added (see Table 4-9 for instruments used).

4.1.3.3   Gas Sampling and Analysis

Gas samples from Experiment 1 were collected from the middle of the waste layer and from the top and the bottom of the columns. These gas samples were then analyzed for H_2S, CH_4 and CO_2, and VSCs using various analytical instruments. Gas samples from Experiment 2 were collected from the various gas extraction ports and from the bottom of the columns and were analyzed for H_2S only.

Gas samples were collected using various sized glass syringes connected to the appropriate sampling ports via a neoprene nipple. Pure nitrogen (99.999%) was used to replace the volume of gas extracted for the various sampling parameters.

4.1.3.4   Leachate Sampling and Analysis

Leachate samples were collected from Tedlar® bags connected to the bottom valves via connector hoses while the SPLP solution was added. Tedlar® bags were used to ensure that oxygen could not infiltrate into the columns as leachate was drained. The leachate samples from Experiment 1 columns were analyzed for sulfide, DO, conductivity, pH, ORP, sulfate, and COD. Leachate samples from Experiment 2 columns were analyzed for sulfide and pH. See Yang (2000) for complete details of the leachate analysis.

4.2 Experiment 1 Results

4.2.1 Hydrogen Sulfide Results

H_2S was measured from three different locations along the length of the Experiment 1 columns. The majority of H_2S measurements were performed on samples collected using the gas extraction valves located in the middle of the waste. Measurements were also performed on gas samples obtained from the top and bottom of the columns. The H_2S results are presented as follows: concentrations from within the waste obtained using the gas extraction valves, then concentrations in the bottom of the columns, and concentrations in the top of the columns.

4.2.2 Concentrations within the waste

The minimum, maximum, and average H_2S concentrations for each column are presented in Table 4-10. At times, some measurements were below the detection limit of the analytical instrument. Averages were calculated using the detected sample concentrations and 50% of the detection limit when the sample concentrations were BDL for H_2S concentrations and many of the following gaseous parameters.

Table 4-10. Minimum, Maximum, and Average H_2S Concentrations (ppm)

Column	# of Samples	# Detected	Minimum	Maximum	Average[a]
C	74	37	< 0.003	1.500	0.127
1D	74	73	< 0.003	47,000	21,636
2D	74	73	< 0.003	50,000	24,389
3DW	74	73	< 0.003	63,000	14,075
4DW	74	74	0.003	48,000	11,155
5A	74	56	< 0.003	1.600	0.277
6A	74	62	< 0.003	1.030	0.203
7A	74	64	< 0.003	0.670	0.149

a. Averages are calculated from detected samples and 50% of the detection limit for BDL samples.

The H_2S concentrations reported above were measured from gas samples obtained using the gas extraction valves. Seventy-four samples were analyzed, some BDL, from each column over a 192-day period. The maximum H_2S concentration measured was 63,000 ppm from Column 3DW. Figure 4-3 presents H_2S concentrations over the 192-day period. As previously described, the Jerome meter was out of calibration from December 1, 1999 (day 53), to February 10, 2000 (day 124). The data from this period were eliminated as shown in Figure 4-3. Sulfide data were used in an attempt to calculate H_2S concentrations in the range of the missing data. This calculation is discussed in subsequent sections.

The H_2S concentration in the columns with drywall increased rapidly. The H_2S concentrations in the drywall and wood columns lagged behind the H_2S concentrations in

the drywall only columns but reached similar H_2S concentration levels (38,000 ppm) at day 145. The control column and the columns with drywall, wood, and concrete remained at relatively low H_2S concentrations (< 0.003 to 1.6 ppm) for the experimental period.
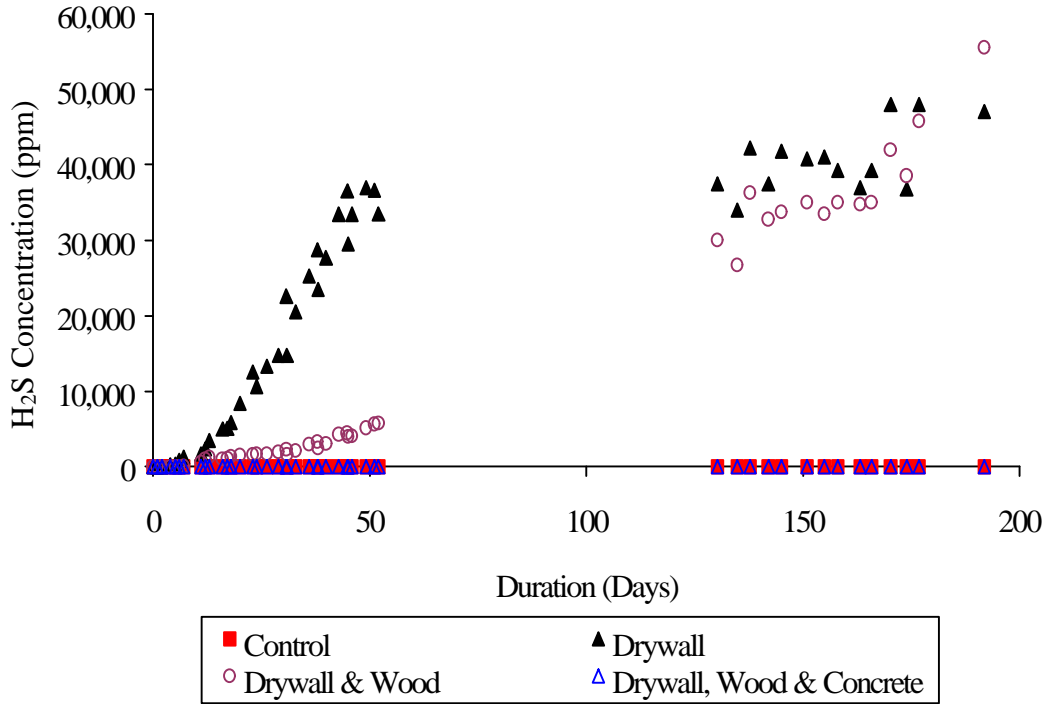
Figure 4-3. H_2S Concentrations

4.2.2.1   Concentrations in the bottom of the columns

Gas would also collect in the Tedlar® bags when the columns were drained. This gas was measured and represents H_2S concentrations in the bottom of the columns. Even though a strong H_2S smell emanated from the bottom of the drywall, wood, and concrete columns, H_2S concentrations in the middle of the waste in these columns were low relative to the other columns. The purpose of measuring H_2S at the bottom of the columns was to investigate this difference. Table 4-11 presents a comparison between the concentrations in the middle of the waste layer and in the bottom of the columns.

Table 4-11. Comparison of H_2S Concentrations (ppm) in the Middle of Waste and in the Bottom of Columns

	Columns							
Day 31	C	1D	2D	3DW	4DW	5A	6A	7A
Middle of Waste	0	18,700	26,500	3,000	1,500	0.017	0.032	0.022

Bottom of Column	3	10,100	16,000	2,000	3,800	4,500	5,300	3,200
Day 38								
Middle of Waste	0	29,000	28,500	3,800	2,800	0.41	0.044	0.15
Bottom of Column	30	17,000	15,000	2,400	2,300	3,900	3,100	3,800
Day 45								
Middle of Waste	0	36,500	36,500	5,200	3,700	0.002	0.006	0.017
Bottom of Column	25	23,000	20,000	5,100	2,350	5,300	3,000	2,700
Day 138								
Middle of Waste	1.5	41,500	43,000	42,000	30,500	1.6	1.03	0.67
Bottom of Column	52.5	26,000	22,000	26,000	24,000	39.5	32	36

Table 4-11 shows that columns 1D, 2D, 3DW, and 4DW contained H_2S concentrations on the same order of magnitude in the middle of the waste layer and the bottom of the column. However, in columns 5A, 6A, and 7A, the bottom of the column H_2S concentrations were as much as seven orders of magnitude larger than the middle of the waste layer H_2S concentrations. On day 138, H_2S concentrations in the bottom of the drywall, wood, and concrete columns were all less than 40 ppm as compared to concentrations in the thousands on day 45.

4.2.2.2   Concentrations in the top of the columns

Although H_2S measurements were performed in the top of the columns five times, only one day of results is presented because the four other sampling dates occurred when the Jerome meter was miscalibrated. Table 4-12 presents the magnitudes in the middle of the waste and in the top of the columns as of the same order; thus, uniformity existed from the middle of the waste to the top of all the columns.

Table 4-12. Comparison of H_2S Concentrations (ppm) in the Middle of the Waste and in the Top of Column (Day 142)

Columns	Middle of Waste	Top of Column
C	0.15	0.15
1D	39,000	40,000
2D	36,000	40,500
3DW	36,500	39,000
4DW	29,000	28,500

5A	0.68	0.7
6A	0.51	0.71
7A	0.4	0.46

4.2.3   Methane and Carbon Dioxide Results

CH_4 and CO_2 concentrations in the gas were measured in Experiment 1 from October 14, 1999 (day 5), to March 24, 2000 (day 166). The frequency of sampling was weekly until November 11, 1999 (day 33), once every two weeks until January 4, 2000 (day 87), and bimonthly until March 24, 2000 (day 166). CH_4 and CO_2 minimum, maximum, and average percent concentrations for each column are presented in Table 4-13. The raw data for CH_4 and CO_2 are included in Jang (2000).

Table 4-13. Minimum, Maximum, and Average CH_4 and CO_2 Concentrations (%)

	Column							
	C	**1D**	**2D**	**3DW**	**4DW**	**5A**	**6A**	**7A**
CH₄								
# of Samples	12	12	12	12	12	12	12	12
# Detected	12	0	0	0	5	5	3	0
Min	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Max	< 0.1	< 0.1	< 0.1	5.49	3.41	1.14	< 0.1	< 0.1
Avg[a]	0.05	0.05	0.05	1.42	0.74	0.21	0.05	0.05
CO₂								
# of Samples	9	9	9	9	9	9	9	9
# Detected	3	8	9	9	9	4	2	2
Min	< 0.1	< 0.1	1.35	1.85	0.95	< 0.1	< 0.1	< 0.1
Max	0.45	10.64	12.20	18.10	16.50	0.72	0.34	0.22
Avg[a]	0.16	6.67	6.24	6.74	6.62	0.26	0.09	0.07

a. Averages are calculated from detected samples and 50% of the detection limit for BDL samples.

CH_4 was found only in the drywall and wood columns, with 5,000-ppm (0.5%) concentrations starting approximately day 53. CH_4 concentrations continued to rise to approximately 50,000 ppm (5%), measured on day 122 but dropped to approximately 30,000 ppm (3%) at day 166. CO_2 was present in all the columns but in higher average concentrations (62,000 to 67,000 ppm) in the drywall only and the drywall and wood columns. Figure 4-4 presents CO_2 concentrations as a function of time.

Figure 4-4. CO$_2$ Concentrations
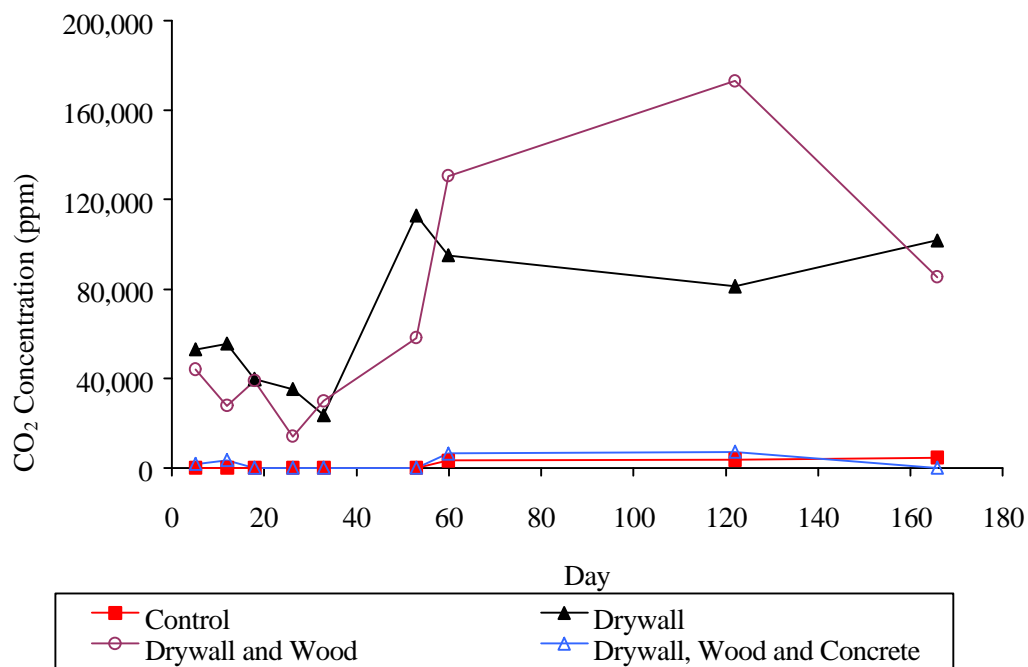
4.2.4 Other Volatile Sulfur Compounds (VSCs) Results

VSCs were analyzed from October 14, 1999 (day 5), to March 28, 2000 (day 170). The frequency of sampling was weekly until November 4, 1999 (day 26), once every two weeks until January 7, 2000 (day 90), and bimonthly until March 28, 2000 (day 170). The minimum, maximum, and average VSCs concentrations are presented in Table 4-14.

Table 4-14. Minimum, Maximum, and Average VSCs Concentrations (ppm)

	Column							
	C	**1D**	**2D**	**3DW**	**4DW**	**5A**	**6A**	**7A**
Carbon Disulfide								
Number of Samples	11	11	11	10	9	11	11	10
Number Detected	1	5	6	4	5	2	2	2
Min	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Max	0.1	2.9	1.7	1.1	0.8	0.2	0.2	0.1
Avg[a]	0.1	0.5	0.3	0.2	0.3	0.1	0.1	0.1
Carbonyl Sulfide								
Number of Samples	9	11	10	9	10	11	10	7
Number Detected	3	7	6	6	6	5	4	2
Min	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Max	0.4	32.1	122.9	119.8	151.6	25.6	3.7	0.5
Avg[a]	0.1	4.5	14.9	20.1	22.6	5.4	0.8	0.1
Dimethyl Sulfide								
Number of Samples	10	11	11	10	10	11	11	10
Number Detected	6	10	9	8	7	10	10	8
Min	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Max	0.3	3.6	3.3	2.2	3.9	11.4	11.1	5.2
Avg[a]	0.1	1.1	1.0	0.9	1.3	3.8	2.7	1.5
Methyl Mercaptan								
Number of Samples	9	11	11	10	10	9	9	7
Number Detected	0	11	11	9	7	0	0	0
Min	< 0.1	0.6	0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Max	0.0	243.2	254.9	221.9	175.4	0.0	0.0	0.0
Avg[a]	0.1	48.8	44.9	26.3	20.9	0.1	0.1	0.1
Sec-Butyl Mercaptan								
Number of Samples	0	4	4	0	0	0	0	0
Number Detected	0	4	4	0	0	0	0	0
Min	0.0	5.7	5.9	0.0	0.0	0.0	0.0	0.0
Max	0.0	85.4	29.5	0.0	0.0	0.0	0.0	0.0
Avg[a]	--	37.9	14.4	--	--	--	--	--

a. Averages are calculated from detected samples and 50% of the detection limit for BDL samples.

Carbon disulfide was found in all the columns, with a maximum concentration of 2.9 ppm from Column 1D. Carbonyl sulfide was also found in all the columns, with a maximum concentration of 151.6 ppm from Column 4DW. Dimethyl sulfide was the last compound detected in all the columns with a maximum concentration of 11.4 ppm from Column 5A. Methyl mercaptan concentrations were present only in the drywall column and the drywall and wood column, with a maximum concentration of 254.9 ppm from Column 2D. Sec-butyl mercaptan concentrations were present only in the drywall columns, with a maximum concentration of 85.4 ppm from Column 1D. All samples were analyzed for the following compounds were at BDL (< 0.1 ppm): tert-butyl mercaptan, ethyl methyl sulfide, ethyl mercaptan, 2-methylthiophene, isopropyl mercaptan, and 3-methylthiophene.

4.2.5   Leachate Results

4.2.5.1   Sulfide

The total sulfide minimum, maximum, and average concentrations in mg/L for each column are presented in Table 4-15. These sulfide concentrations were measured from October 19, 1999 (day 10), to March 23, 2000 (day 166). The maximum sulfide concentrations measured were 171 mg/L in Column 2D. Figure 4-3 presents the total sulfide concentrations as a function of time.

Figure 4-5 indicates that the drywall columns increased rapidly and continued to have high sulfide concentrations (>100 mg/L) beyond the last sampling date. The sulfide concentrations in the drywall and wood columns lagged behind those in the drywall columns but reached the same range of sulfide concentrations at day 125. This trend was similar to the H_2S gas concentration trend observed in the middle of the waste.

Table 4-15. Leachate Analysis -- Min, Max, and Avg Sulfide Concentrations (mg/L)

Column	Minimum	Maximum	Average
C	0.08	9.60	1.15
1D	19.58	159	112
2D	10.63	171	107
3DW	3.53	137	65.5
4DW	1.80	120	51.6
5A	0.69	52.5	21.9
6A	0.53	51.8	19.1
7A	0.13	41.0	13.6
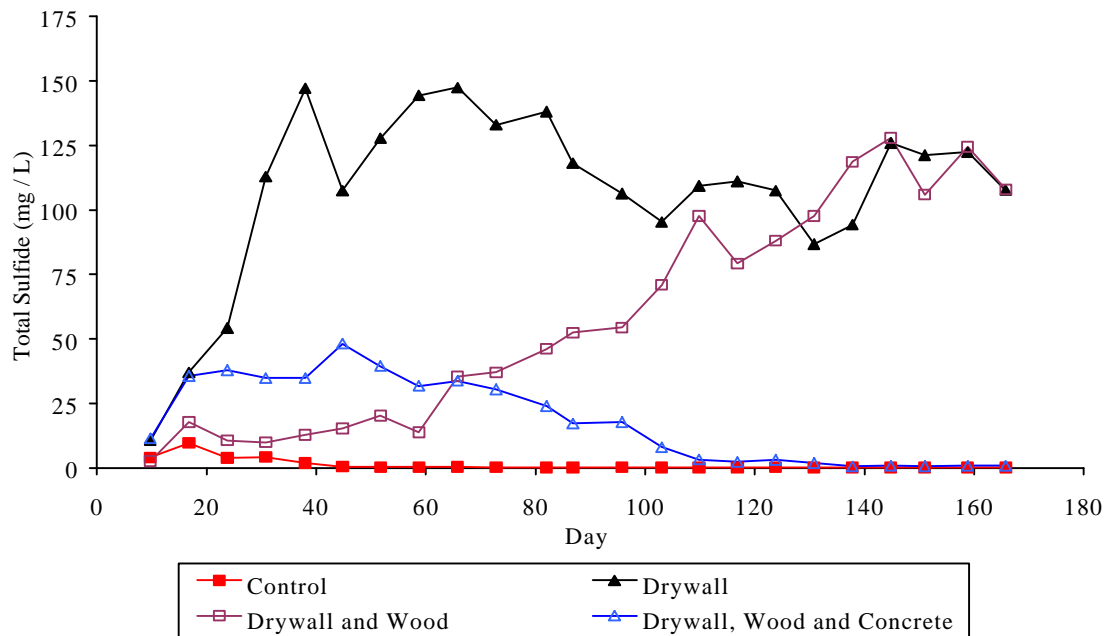
Figure 4-5. Total Sulfide Concentrations

4.2.5.2 Dissolved oxygen (DO)

DO minimum, maximum, and average concentrations in mg/L for each column are presented in Table 4-7 for analysis conducted from October 19, 1999 (day 10), to March 30, 2000 (day 173). A maximum DO concentration of 5.99 mg/L was measured in the control column.

Table 4-16. Leachate Analysis -- Min, Max and Avg DO (mg/L)

Column	Minimum	Maximum	Average
C	1.06	5.99	3.02
1D	1.22	3.32	1.92
2D	0.68	3.17	1.81
3DW	1.02	2.04	1.51
4DW	1.17	2.61	1.70
5A	0.91	3.36	1.82
6A	0.94	4.69	2.05
7A	1.25	5.60	2.54

4.2.5.3   Specific Conductivity

The minimum, maximum, and average specific conductivity readings in millisiemens per centimeter for each column are presented in Table 4-17. Specific conductivity measurements were taken from October 19, 1999 (day 10), to March 30, 2000 (day 173). The maximum specific conductance reading was 2.90 mS/cm from Column 4DW. No trend over time was observed; most column samples remained within 20% of their respective averages.

4.2.5.4   pH

The pH of the Experiment 1 leachate was measured from October 19, 1999 (day 10), to March 30, 2000 (day 173). Maximum, minimum, and average pH for each column are presented in Table 4-18. Figure 4-6 presents the pH trends as a function of time.

Table 4-17. Leachate Analysis -- Min, Max, and Avg Specific Conductivity (mS/cm)

Column	Minimum	Maximum	Average
C	0.77	1.09	0.94
1D	1.54	2.60	1.97
2D	1.42	2.52	1.81
3DW	2.05	2.89	2.53
4DW	1.89	2.90	2.34
5A	1.18	2.52	1.81
6A	1.59	2.55	2.02
7A	1.43	2.56	2.04

Table 4-18. Leachate Analysis -- Min, Max, and Avg pH

Column	Minimum	Maximum	Average
C	6.01	11.70	10.49
1D	6.28	6.96	6.73
2D	6.50	7.04	6.74
3DW	5.53	6.81	6.40
4DW	5.45	6.82	6.28
5A	5.96	11.17	8.46
6A	5.89	10.84	8.73
7A	5.85	11.29	9.39

Per Table 4-18, columns with concrete—C, 5A, 6A, and 7A—all exhibited an average pH range from 8.5 to 10.7. Per Figure 4-6, the columns with concrete started at a pH around 6.5 but eventually became basic (pH 11). The pH of concrete (9.5 to 11) was affecting the overall pH of the leachate. The pH in the drywall only columns started at 6.3 but increased to the ideal pH range for sulfate-reducing bacteria (6.5 to 7.5). The drywall and wood columns reached the same pH levels as measured in the drywall only columns around day 100.
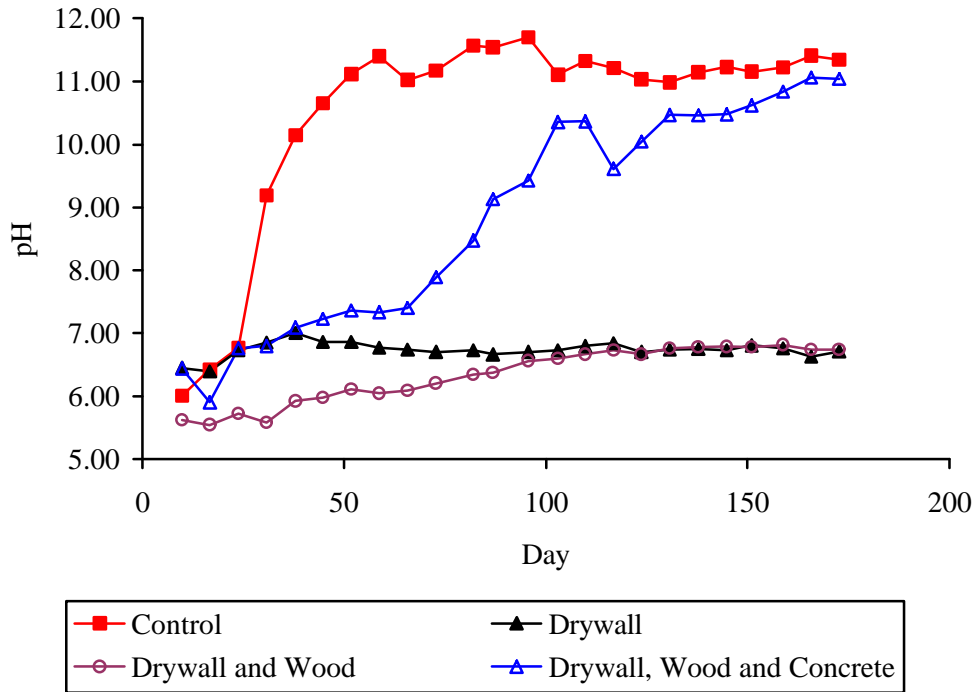

Figure 4-6. pH of Lysimeter Leachate

4.2.5.5   Oxidation-reduction potential (ORP)

ORP minimum, maximum, and average readings are presented in Table 4-19. ORP data, measured from October 19, 1999 (day 10), to March 30, 2000 (day 173), remained relatively in the same range per column for the duration of the experiment.

4.2.5.6   Sulfate

The sulfate minimum, maximum, and average concentrations in mg/L are presented in Table 4-20. Sulfate concentrations were analyzed bimonthly and were taken from October 20, 1999 (day 11) to February 10, 2000 (day 124). The maximum sulfate concentration measured was 1,319 mg/L from Column 4DW. The majority of sulfate concentrations remained near the average sulfate concentrations shown in Table 4-20.

Table 4-19. Leachate Analysis -- Min, Max and Avg ORP (mV)

Column	Minimum	Maximum	Average
C	-332.30	-47.20	-146.85
1D	-382.60	-271.40	-338.69
2D	-394.10	-281.20	-343.55
3DW	-363.60	-216.90	-304.47
4DW	-376.30	-174.40	-284.83
5A	-365.80	-246.60	-315.18
6A	-366.20	-194.00	-300.69
7A	-347.60	-115.40	-279.04

Table 4-20. Leachate Analysis -- Min, Max and Avg Sulfate (mg/L)

Column	Minimum	Maximum	Average
C	4	81	19
1D	348	867	646
2D	512	807	638
3DW	870	1,217	1,096
4DW	668	1,319	1,050
5A	392	591	493
6A	429	910	639
7A	348	845	612

4.2.5.7   Chemical oxygen demand (COD)

The minimum, maximum, and average COD concentrations (mg/L) are presented in Table 4-21 and COD trends over time are presented in Figure 4-7. COD was analyzed bimonthly from November 16, 1999 (day 38), to March 30, 2000 (day 173), with a maximum concentration of 2,378 mg/L from Column 7A.

Table 4-21. Leachate Analysis -- Min, Max, and Avg COD (mg/L)

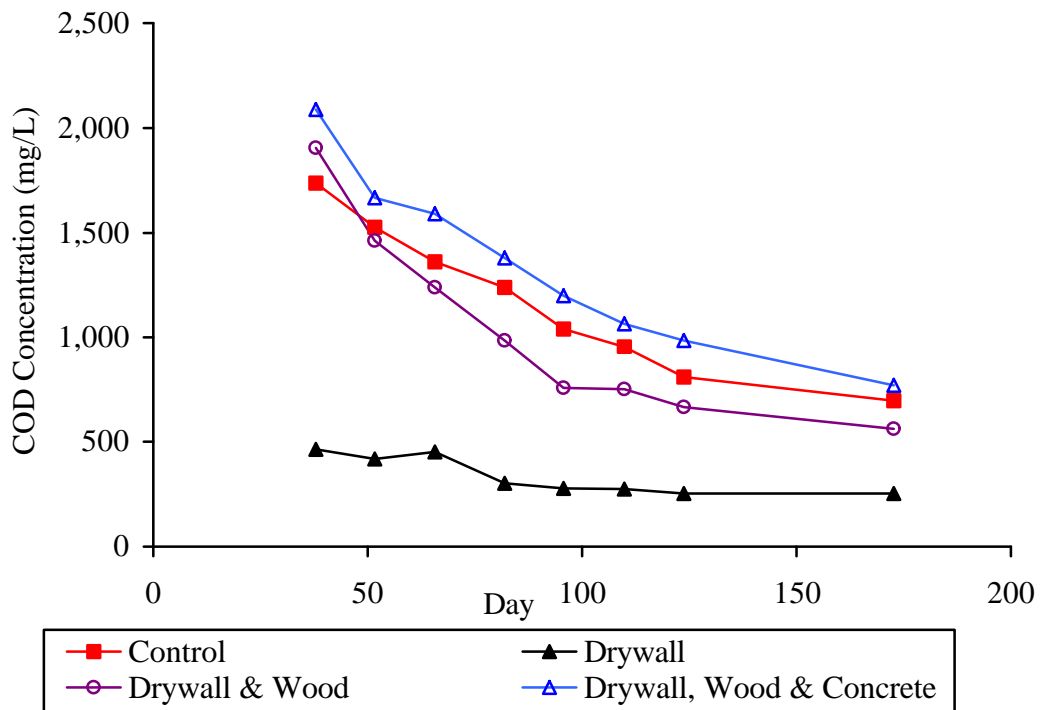| Column	Minimum	Maximum	Average
C	696	1,736	1,170
1D	234	472	338
2D	270	495	337
3DW	511	1,672	941
4DW	610	2,136	1,139
5A	860	2,194	1,364
6A	722	1,726	1,287
7A	730	2,378	1,379

Figure 4-7. COD Concentrations

4.3   Experiment 2 Results

Experiment 2 was designed to examine the effect of concrete on H_2S. As stated previously, Experiment 1 revealed that the H_2S concentrations were different in the middle of the waste than in the bottom of some columns. The drywall, wood, and concrete columns had low concentrations of H_2S gas in the middle of the waste layer but high H_2S

gas concentrations in the bottom of the columns. Experiment 2 was designed to examine the cause of this difference and was conducted from February 17, 2000, to March 14, 2000. Experiment 2 results include H_2S gas, sulfide, and pH data.

4.3.1 Hydrogen Sulfide Gas Concentrations

The H_2S gas profiles are presented in Figure 4-8. The drywall layer was above the concrete layer in columns 1DC and 2DC. Large concentrations of H_2S were measured in the top drywall layer, whereas the bottom concrete layer had minimal H_2S concentrations. The concrete layer was above the drywall layer in columns 3CD and 4CD. Large concentrations of H_2S were generated in the lower drywall layer, but no H_2S migration into the concrete layer above.

4.3.2 Sulfide Concentrations in Leachate

The sulfide concentrations in mg/L for each column are presented in Table 4-22. The maximum sulfide was 1.5 mg/L in 1DC and 2DC and 82.3 mg/L in 3CD and 4CD. The sulfide data correlate with the bottom layers in the respective columns (i.e., sulfide concentrations were higher when the bottom layer was drywall) and like the H_2S gas profiles verifies sulfate-reducing bacteria activity.

4.3.3 pH of Leachate

Table 4-23 presents the five pH measurements. As with H_2S gas and sulfide, pH was representative of the bottom layer and is discussed further in the next section.

4.4 Discussion of Results

The following chapter discusses Experiment 1 and 2 results that were presented in Chapter 4. Evidence of sulfate-reducing bacteria activity (i.e., subsequent H_2S and CO_2 production and leachate characteristics from Experiment 1) is discussed. The impact of wood when co-disposed with drywall on H_2S production is discussed, and the impact of concrete on H_2S production from both experiments is presented. Finally, a discussion on the results relative to actual C&D debris landfills and possible control mechanisms are presented.
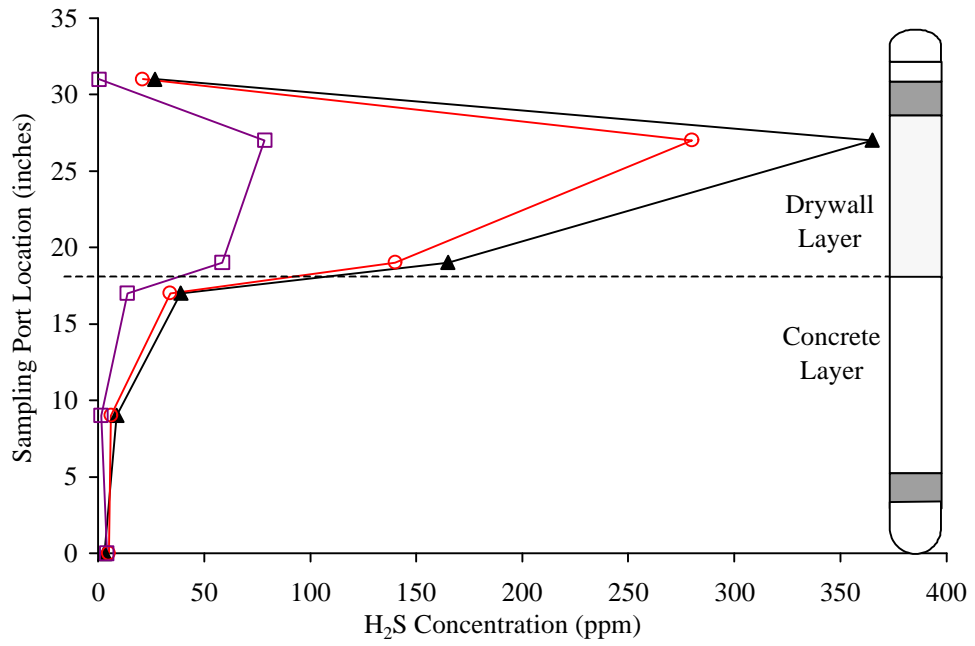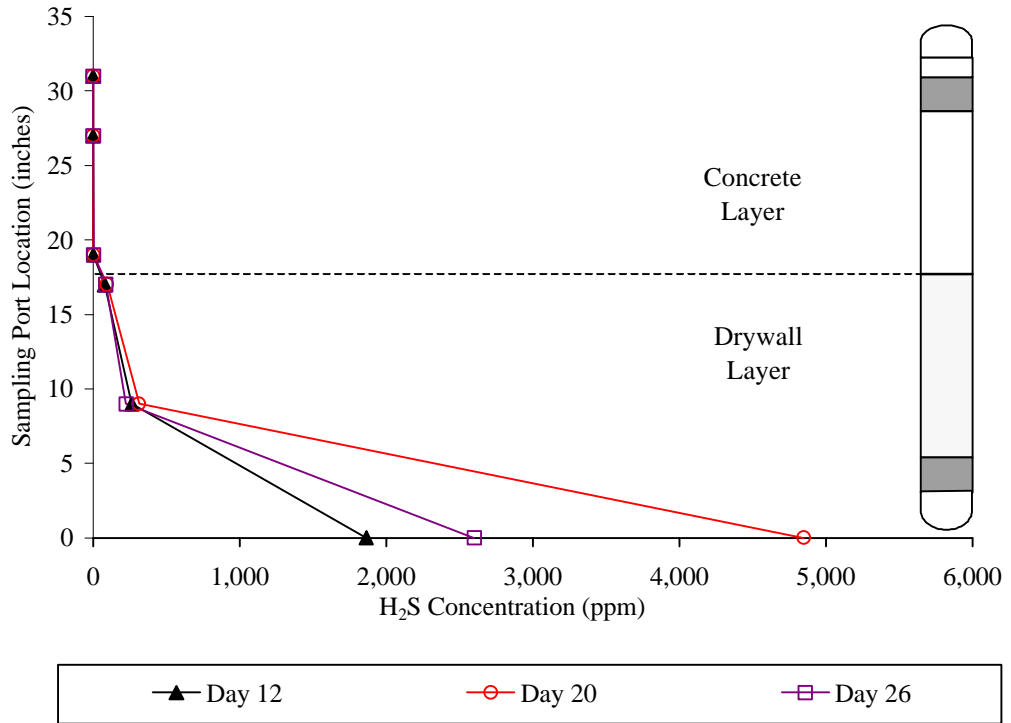
Figure 4-8. Experiment 2 – H₂S Gas Concentration Profiles

Table 4-22. Leachate Analysis -- Sulfide (mg/L)

Day	Column			
	1DC	2DC	3CD	4CD
0[a]	--	0.05	2.38	--
5	0.33	0.36	3.25	1.33
12	1.03	0.55	14.33	21.75
20	0.49	1.48	33.65	77.25
26	0.34	0.95	12.49	82.25

a. No leachate from 1DC and 4CD

Table 4-23. Leachate Analysis -- pH

Day	Column			
	1DC	2DC	3CD	4CD
0[a]	--	7.90	7.76	--
5	9.05	11.02	7.08	6.78
12	9.31	10.69	7.70	6.89
20	10.34	11.48	7.63	7.24
26	10.77	11.61	7.88	7.71

a. No leachate from 1DC and 4CD

4.4.1 Sulfate-reducing Bacteria Activity

Experiment 1 results provided evidence of sulfate-reducing bacteria activity. H_2S production, when bacteria reduce decaying drywall in specific conditions, was once again confirmed as it was in previous studies (Fairweather and Barlaz, 1998; Jang, 2000). Experiment 1 proved that drywall alone leaches enough sulfate ions for the production of high H_2S concentrations (> 40,000 ppm), as observed in Figure 4-9. Even though the leaching solution had an acidic pH (4.22 ± 0.05), the dissolution of impurities (possibly carbonate) present in gypsum buffered the solution to the ideal sulfate-reducing bacteria pH range of 6.5 to 7.5. To confirm this observation, drywall placed in DI water yielded a solution pH ranging from 6 to 7. Experiment 2 also proved that decaying drywall had ample sulfate for bacterial growth. This observation also demonstrated that the paper backing on the drywall from Experiment 1 drywall only columns was an ample carbon source for sulfate-reducing bacteria. However, the quantity of organic matter may have been insufficient for methanogens only because of the absence of methane. Sulfate-reducing bacteria out-compete methanogens for carbon substrate because of their generally higher maximum growth rates and higher affinity for substrates, and methane is a product of methanogensis (Bitton, 1999). The drywall and wood columns did have enough carbon because methane was present at up to 5.5% in these columns.

4.4.1.1   Sulfide Generation

Two of Experiment 1 parameters were sulfide in the leachate and H_2S in the gas. Figure 4-10 presents both of these and shows their similar trends and the change in pH over time, which is discussed later in this chapter.

The trends for the drywall only and the drywall and wood columns are the same for sulfide and H_2S in Figure 4-10. For the drywall only columns, sulfide increased rapidly and reached steady state at day 110. H_2S concentrations also increased rapidly but, based upon available data, reached steady state at approximately day 125. As mentioned previously, the Jerome meter was out of calibration from December 1, 1999, to February 10, 2000. The data from this time period were thus omitted. Calculations were performed to determine if the existing sulfide data could be converted to fill in the missing H_2S data (see Yang 2000). Sulfide concentrations in leachate were converted to H_2S in the aqueous phase and then to gaseous H_2S following Henry's Law. This calculation was performed using the drywall only and drywall and wood column data. As seen in Figure 4-10, the measured H_2S and the calculated H_2S followed the same trend until day 38 in the drywall only columns; then the calculated H_2S became approximately half of the measured H_2S. This trend continued when the analysis resumed on day 124. As seen in Figure 4-10, the measured H_2S and the calculated H_2S followed the same trend until day 51 in the drywall and wood columns. When sampling continued, the calculated H_2S was approximately half of the measured H_2S. The other four columns were not included because sulfide and H_2S concentrations decreased over time and therefore did not show the same difference in measured and calculated H_2S concentrations.

The differences between predicted (based on leachate sulfide analysis) and measured H_2S concentrations in both the drywall only and the drywall and wood columns may be attributed to experimental error during the sulfide analysis. Sulfide volatizes rapidly when exposed to the atmosphere. Some sulfides may have volatized or oxidized during the analysis, thus lowering the total sulfide concentration. A 1:250 dilution was performed for the majority of the drywall only and the drywall and wood leachate samples. A high dilution magnifies the error, especially when the sample size decreases. Before day 38 for the drywall only columns and day 51 for the drywall and wood columns, the majority of the dilutions were 1:25, which would reduce the error and may explain why similar trends exist for the measured and calculated concentrations. Methods of minimizing this error should be investigated if future research is to be conducted.

Figure 4-9. Sulfide, H$_2$S from the Middle of the Waste, and pH Trends
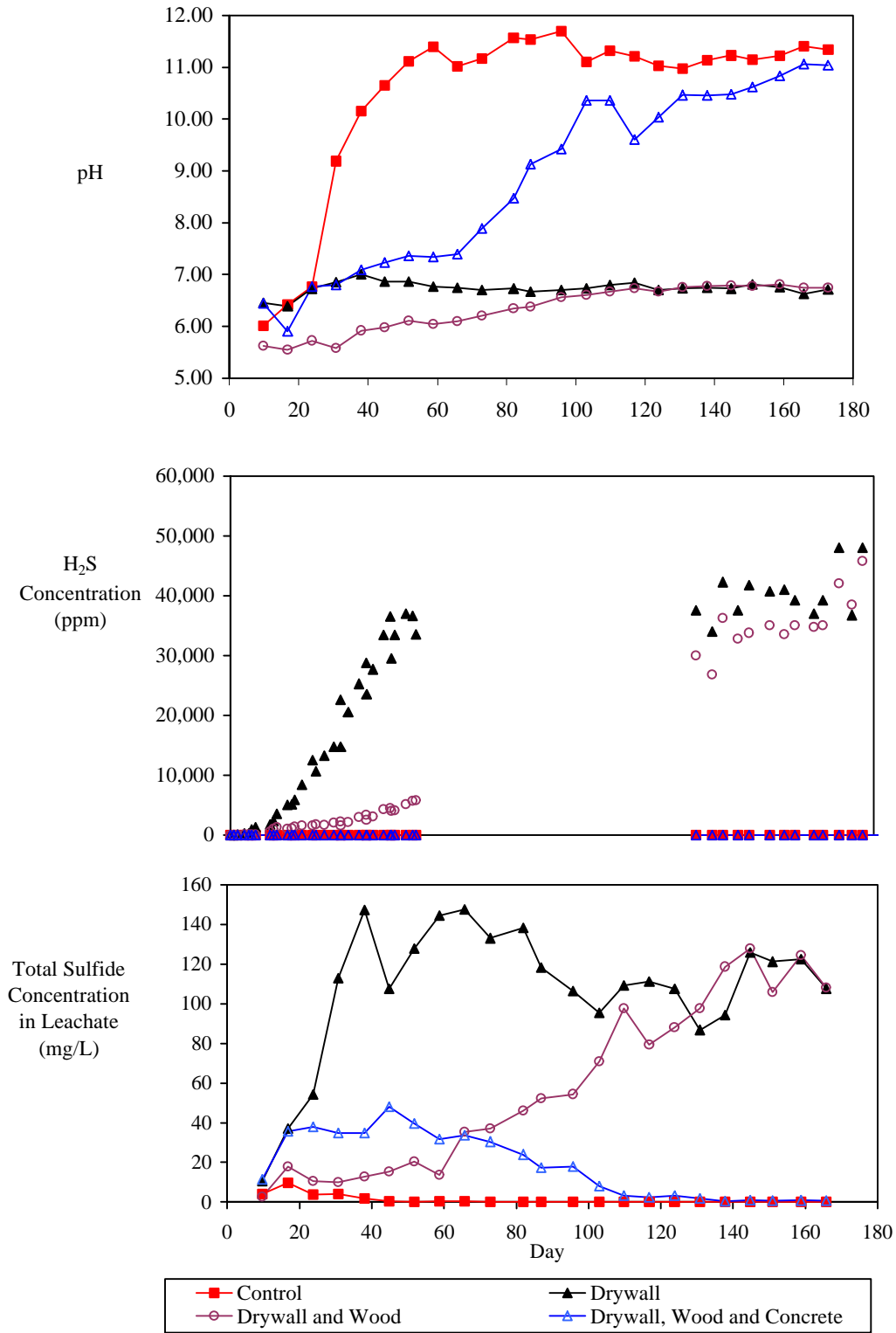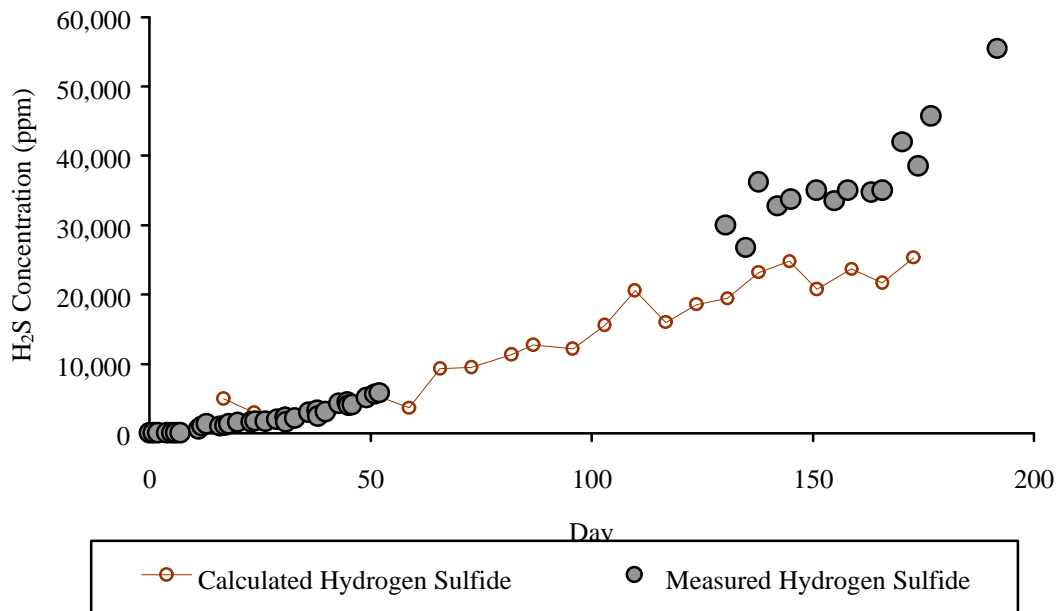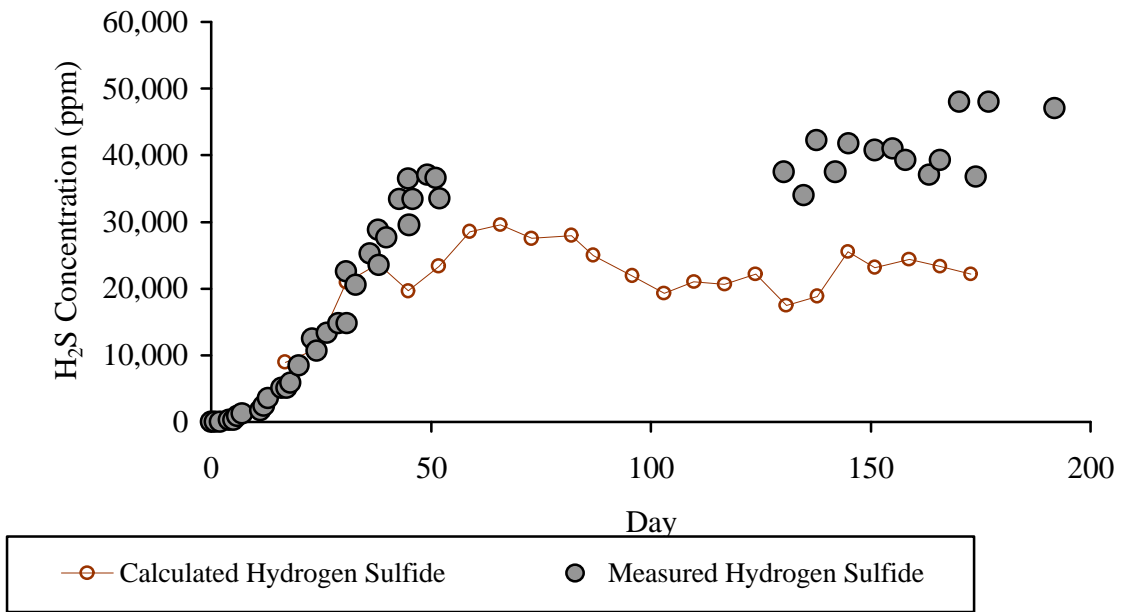
Figure 4-10. Comparison of Calculated H₂S and Measured H₂S in the Drywall and Wood Columns

4.4.1.2   Maximum Hydrogen Sulfide Concentration

The maximum H_2S concentration measured in Experiment 1 was 63,000 ppm (Table 4-10). Another study conducted by Lee (2000) encountered H_2S concentrations up to 50,000 ppm in serum bottles loaded with drywall and C&D debris leachate. The trend for the serum bottle H_2S concentrations is similar to Experiment 1 column H_2S concentration trends in that they both increased and remained at a concentration for some time. These trends are comparable even though the serum bottles were exposed to different conditions (i.e., no weekly SPLP solution addition).

The increasing and then steady state concentration trend in relation to H_2S production rate, or more specifically the decrease in this H_2S production rate, raises an interesting point. As seen in Figure 4-11, the H_2S production rate increased rapidly resulting in an increase in H_2S concentrations. Once the H_2S production rate was linear (i.e. steady state was reached), H_2S concentrations increased linearly. But once the H_2S production rate decreased, H_2S concentrations remained constant indicating accumulation of H_2S gas.

Future work can be conducted to determine the cause of the decrease in H_2S production rate. One possible explanation for this decrease in H_2S production rate could be that the bacteria were limited in their growth potential, possibly by a limiting agent (e.g., carbon source). One way to determine if the carbon was limiting would be to add a carbon source (e.g., lactic acid) and observe H_2S concentrations. If the concentrations remain the same, carbon was not limiting. Another possible explanation for this decrease in H_2S production rate could be that a toxicity limit for the bacteria could have been reached. One way to test this is to purge Experiment 1 columns with nitrogen and measure H_2S gas. If H_2S concentrations increase to the level previously observed, then a toxicity concentration range could be determined.
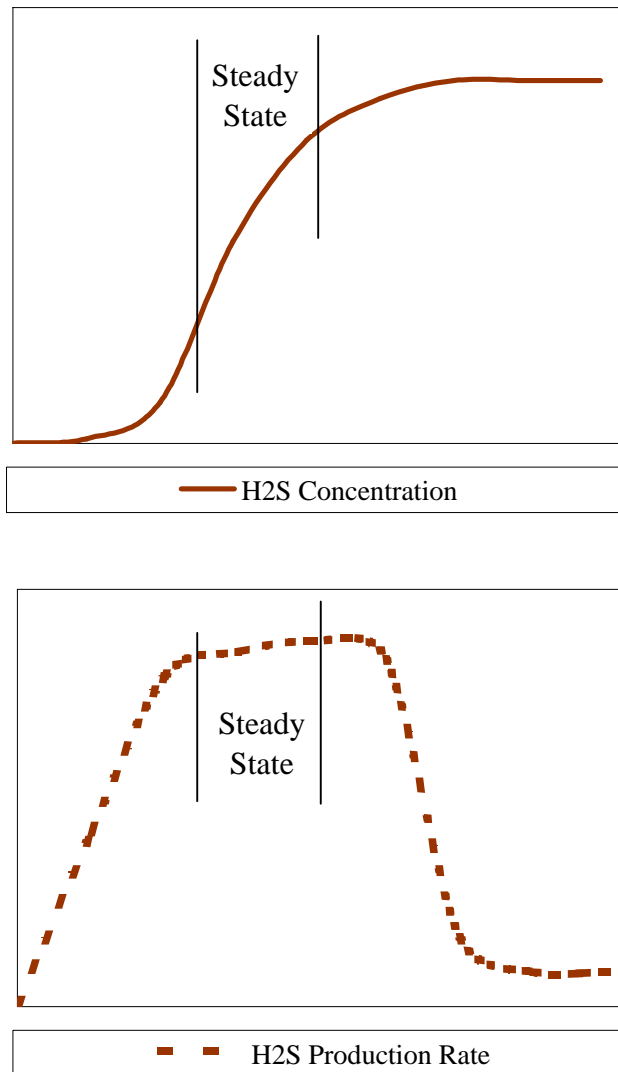
Figure 4-11. Hydrogen Sulfide Production Rate

4.4.1.3   Hydrogen Sulfide Uniformity

As seen in Tables 4-11 and 4-12, H_2S was distributed evenly throughout the drywall, the drywall and wood, and the control columns. Table 4-12 shows that H_2S was uniform from the middle of the waste layer to the top of the drywall, wood, and concrete columns. Table 4-2 shows a difference in H_2S concentrations in the middle of the waste layer to the bottom of the aforementioned columns. Also, by day 38, the H_2S concentrations in the bottom of the drywall, wood, and concrete columns were lower (35 ppm) than on day 45 (concentrations in the thousands ppm). This decrease in H_2S concentrations could have resulted from conditions in the bottom of those columns becoming unfavorable for sulfate-reducing bacteria. Figure 4-11 illustrates that the pH in those columns increased out of the optimal sulfate-reducing bacteria pH range. The decreasing H_2S concentration trend was also observed in the sulfide trend (Figure 4-9).

Sulfide concentrations existed in the drywall, wood, and concrete columns in the beginning of the experiment but decreased below 1 mg/L by day 110. The presence of concrete was responsible for this difference and is discussed later in this chapter.

4.4.1.4 Carbon Dioxide Generation

CO_2 is another product of dissimilatory sulfate reduction (Bitton, 1999). The following equation presents this reduction of sulfate into CO_2:

$$Lactate + SO_4^{2-} \rightarrow Acetate + S^{2-} + 2H_2O + 2CO_2$$

(Source: Tchobanoglous *et al.* 1993)

From this equation, 2 moles of CO_2 are produced to 1 mole of H_2S production, or 2 ppm of CO_2 to 1 ppm of H_2S. Figure 4-4 showed CO_2 in greater concentrations than expected from this equation in the drywall and the drywall and wood columns because of the presence of mercaptans (methyl and sec-butyl) concentrations, which produce CO_2 as a byproduct.

4.4.1.5 Leachate Characteristics

Figure 4-10 illustrates that the pH of the drywall columns was in the ideal range for sulfate-reducing bacteria (6.5 to 7.5) for the duration of the experiment. This pH was conducive for the production of high H_2S concentrations and was similar to the pH trends observed by Jang (2000) in the drywall lysimeters. This trend is not comparable to the drywall and wood columns in which the pH started at 5.6 and increased to 6.5. The difference in pH can be explained by the presence of wood and is discussed in the following section. According to Jang (2000), the pH resulting from a lysimeter loaded with concrete for the duration of the experiment ranged from 11.5 to 12, which conflicts with the control column in Experiment 1 in which the pH started at 6 and increased to 11 by day 50. This can also be explained by the presence of wood and is discussed in the next section. The Jang study measured pH levels, which did not agree with the drywall, wood, and concrete columns where pH started at 6.5 and increased to 10 by day 115. This can be explained by the presence of both concrete and wood and is discussed in the following sections.

Table 4-16 shows that DO concentrations remained near 2 mg/L, thus supporting the fact that the columns that were producing H_2S were predominantly anaerobic. This was similar to Jang's experiment 1 DO results in which DO remained near 1 mg/L in lysimeters loaded with drywall, wood, concrete, and mixture. The ORP results indicated that many of the constituents in the leachate existed in reduced forms, and biological activities were occurring within the columns (Table 4-19).

Table 4-20 shows that the drywall and wood columns had the highest average sulfate concentrations, followed by the drywall only columns, the drywall, wood, and concrete columns, and the control column. These trends are indicative of sulfate-reducing

bacteria activity and subsequent H_2S generation. The drywall and wood columns had the highest average sulfate concentrations because the H_2S generation lagged; hence more sulfate ions were present in the leachate. When comparing the drywall, wood, and concrete columns to the drywall and wood columns, the drywall, wood, and concrete columns would be assumed to have higher average sulfate concentrations because of the lower H_2S generation; however, the sulfate concentrations were lower. This indicated that some other sulfate removal mechanism, possibly dealing with concrete, was active in those columns. The control column sulfate concentrations were indicative of trace amounts of gypsum present in concrete and also the absence of drywall.

Table 4-17 shows that the specific conductivity was the highest in the drywall and wood columns, followed by the drywall, wood, and concrete columns, the drywall only columns, and the control column. Specific conductance is an indicator of dissolved solid content and is dependent on the presence of ions (Snoeyink and Jenkins, 1980) and also measures the ability of a solution to carry an electrical current. Drywall and wood columns were the highest because of the available sulfate ions. Sulfate-reducing bacteria were not as active in these columns until later in the experiment, so sulfate was not being removed or utilized as much as in the drywall only columns. Although small H_2S concentrations were produced and thus sulfate ions readily available in solution, the specific conductance levels of the drywall, wood, and concrete columns were lower than the drywall and wood columns. This supports the previous statement that some interaction was occurring with the concrete that was removing sulfate ions.

From Table 4-21, the average COD concentrations were highest in the drywall, wood, and concrete columns, followed by the drywall and wood columns, the control columns, and the drywall columns. COD is the measure of the organic strength of a solution or specifically the measurement of a waste in terms of the total quantity of oxygen required for oxidation to CO_2 and H_2O (Snoeyink and Jenkins, 1980). The low average COD concentrations in the drywall only columns correspond to bacterial activity and the absence of wood. The more H_2S production means the more organic matter utilized, thus lower COD concentrations. Hence, the drywall, wood, and concrete columns have the highest COD concentrations because of the paper backing on the drywall and the presence of wood, but also because of low sulfate-reducing bacteria activity. Even though the drywall, wood, and concrete columns had little organic substrate utilization, the average COD concentrations decreased over time (see Figure 4-7) because earlier in the experiment smaller organic particles were washed from the surface of the wood. As time progressed, less organic matter was available and the wood began to degrade.

4.4.2   The Impact of Wood

The presence of wood in the drywall and wood columns had an effect on H_2S generation. Figure 4-4 illustrates that sulfide concentrations were similar in the drywall and the drywall and wood columns when the pH in those columns reached similar ranges. When comparing the H_2S concentrations and the pH, H_2S concentrations in the drywall and wood columns were lower than the drywall only columns when the pH of the drywall and wood columns was lower than 6. But when the pH increased to approximately 6.7,

the H_2S concentrations in the drywall and wood columns reached similar concentrations as seen in the drywall only columns. The only difference between the columns was the presence of wood.

The presence of wood explained the H_2S lag in the drywall and wood columns. When wood is placed in DI water, the pH of the solution ranged from 4.8 to 5.0. Even though the impurities in the drywall were buffering the SPLP solution (pH 4.22 ± 0.05), the organic acids (i.e., fulvic and humic) in the wood lowered the leaching solution out of the ideal pH range for sulfate-reducing bacteria activity. But after 80 days, the organic acids in the wood became diluted as the wood became saturated. The overall pH increased to the ideal sulfate-reducing bacteria pH range, while impurities in the drywall continued to buffer the SPLP solution. This buffering capacity was proven by the fact that the drywall columns in Experiment 1 generated H_2S.

Since the pH dictates sulfate-reducing bacteria activity, future work could examine the effect of adding a buffering solution to C&D debris landfills. In the laboratory, a buffering solution could be added to a column after H_2S concentrations reached steady state. If the H_2S concentrations decrease, a pH buffering solution could be used at C&D debris landfills to reduce H_2S generation by moving the pH out of the ideal range for sulfate-reducing bacteria.

4.4.3 The Impact of Concrete

The presence of concrete in the columns affected H_2S concentrations in the columns. It was observed that even though the drywall, wood, and concrete columns had low H_2S concentrations present in the middle of the waste layer, the bottom of these columns had a strong H_2S odor. Accordingly, H_2S was measured from the bottom of the columns (see Table 4.2). A difference of H_2S concentration was measured between the middle of the waste layer and the bottom of the columns. Figure 4-12 compares the average H_2S concentrations between the two sample locations on day 38 (Note: y-axis is log scale).

Columns with drywall and drywall and wood had similar H_2S concentrations in the middle of the waste layer and in the bottom of the column. But in the drywall, wood, and concrete columns, the H_2S concentrations in the bottom of the columns were as much as seven orders of magnitude higher than in the middle of the waste layer. This indicated that some microbial activity and resulting H_2S generation was occurring but not in the middle of the waste layer. Sulfide concentrations also support this observation because concentrations (>25 mg/L until day 80) were present in the drywall, wood, and concrete columns leachate indicating bacterial activity (see Figure 4-12). Experiment 2 was designed and operated to determine if this effect could be reproduced and to identify possible theories explaining why H_2S concentrations were reduced in the presence of concrete.

Figure 4-12. H₂S Concentration Comparison of Middle of Waste and Bottom of

The chart shows H₂S Concentration (ppm) on a logarithmic y-axis (1.E-02 to 1.E+05) for four column categories: Control, Drywall, Drywall and Wood, and Drywall, Wood and Concrete. White bars represent Middle of Waste and dark (maroon) bars represent Bottom of Column.
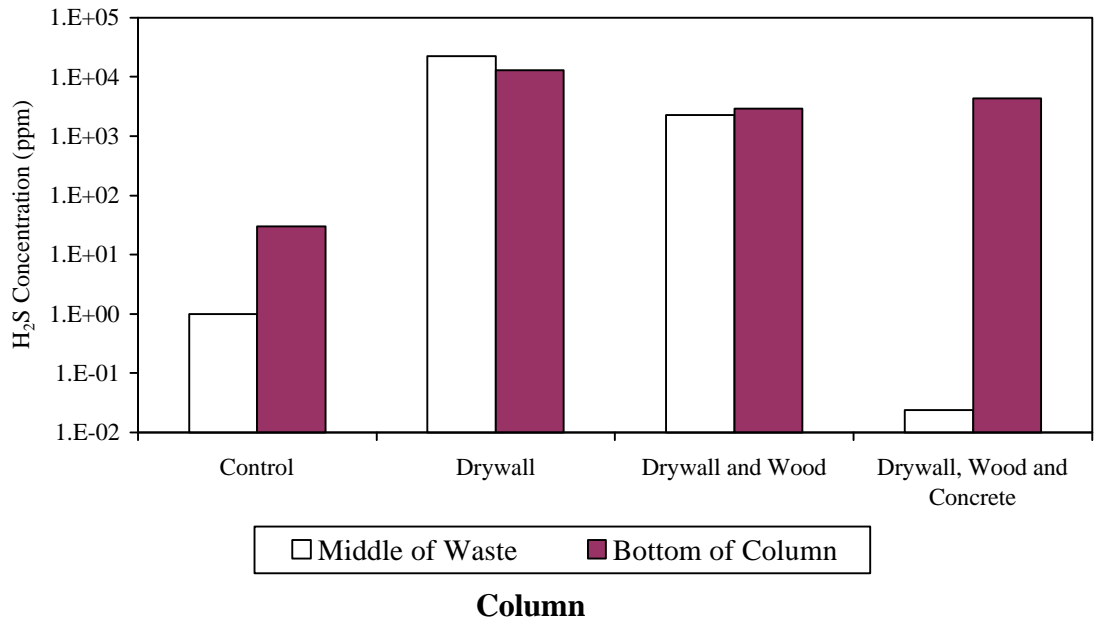
Column

Figure 4-12 shows for H₂S concentration profiles. In columns 1DC and 2DC, the drywall layer was above the concrete layer. Large concentrations of H₂S were measured in this top drywall layer, but lower H₂S concentrations were observed in the bottom concrete layer. One possible explanation was that the pH of the concrete (9.5 - 11.0) was out of the range for sulfate-reducing bacteria growth.

Columns 3CD and 4CD served as the positive control where the concrete layer was above the drywall layer. Large concentrations of H₂S were generated in the bottom drywall layer, yet little H₂S migration occurred into the above concrete layer. One possible theory was that the H₂S interacted with the concrete; the concrete could have acted like a sink.

A follow-up experiment tested the previous interaction theory using 1-liter Tedlar® bags. The same size components and same masses of drywall and concrete were used as in the previous column experiments. Drywall was placed into one Tedlar® bag and concrete into another. The Tedlar® bags were placed under a vacuum to eliminate all air remaining in the bags, and then the 25-ppm H₂S standard was used to fill the bags to capacity. Measurements were taken every two minutes, and the experiment was performed twice. As show in Table 4-24, the H₂S concentrations in the concrete bag were reduced in a matter of minutes. This reinforced the theory of an interaction between concrete and H₂S gas.

The two theories, the high pH of concrete making the environment unfavorable for sulfate-reducing bacteria activity and the physical or chemical interaction between H₂S gas and concrete, are only possible explanations. The scope of Experiment 2 was to determine if this effect would occur again, not to identify the removal mechanism of concrete. Many

other mechanisms could be involved in this reduction of H_2S gas, and only after specific experimentation can they be identified.

Table 4-24. H_2S Concentrations from Tedlar Bag Experiment

Time Elapsed (min)	Run One		Run Two	
	Concrete Bag (ppm)	Drywall Bag (ppm)	Concrete Bag (ppm)	Drywall Bag (ppm)
0	15	23	15	23
2	10.2	21	7	21
4	4.7	22	4.3	21
6	2.1	24	1.5	23
8	1.1	21	0.59	22
10	0.47	21	0.062	20
25-ppm Standard	25		25	

Further experimentation needs to be conducted on the physical properties of concrete that could improve its removal mechanisms. The specific size of concrete required to reduce H_2S emissions remains unknown. A comparison experiment between different concrete particle sizes should be performed to clarify sizing and H_2S removal relationships. Also, the thickness of the concrete layer relation to H_2S emissions remains unknown. Columns could be loaded with different concrete layer thicknesses above a drywall layer. H_2S can be measured above the concrete layer to determine the thickness to concentration relationship. Other columns could further provide explanations by loading sand or soil to determine if large (>2 feet) thicknesses can reduce H_2S emissions.

4.4.4 Relevance of Findings to C&D Debris Landfills

The results indicate that C&D debris landfills that accept drywall should expect H_2S concentrations even without the presence of a carbon source (i.e., yard waste). The presence of yard waste at C&D debris landfills is neither harmful nor helpful in H_2S production, because under ideal conditions the paper backing provides enough carbon for bacterial activity. Under long-terms conditions, yard waste could provide addition carbon source besides the paper backing, but sulfate sources could be depleted by then.

From the experimental results, the presence of concrete at C&D debris landfills could reduce H_2S concentrations. But Lee (2000) found that C&D debris landfill H_2S concentrations varied greatly, regardless of the presence of concrete. This variability cannot be explained by the presence of concrete.

4.4.5 Possible Control Mechanisms

From the experimental results, the pH of the landfill, and the presence of concrete could be possible H_2S control mechanisms. As discussed earlier, organic acids present in the wood affected sulfate-reducing bacteria activity. The addition of a pH buffering solution could be used to effect bacterial activity. As discussed earlier, the presence of concrete reduced H_2S concentrations following a physical or chemical interaction. Concrete could be used as a cover layer or be included in the waste to reduce concentrations. These possible H_2S control mechanisms can only be implemented after larger scale experiments are conducted.

5 SUMMARY AND CONCLUSIONS

5.1 Field Experiments

Minimal scientific research has been conducted characterizing gas, specifically hydrogen sulfide (H_2S), generated by C&D debris landfills. Research is available regarding the generation of H_2S in other environments such as sewer mains, wastewater treatment plants, and compost facilities (Devai and DeLaune, 1999). Research was conducted to chemically characterize the gases produced at C&D debris landfills. Recent concerns about the health and safety of people living or working near these facilities have caused some landfills to evaluate emissions and take remedial action. The primary issue is hydrogen sulfide gas emissions. Hydrogen sulfide is a gas with a characteristic rotten egg odor and is toxic at high concentrations (150 ppm and above). The issue of concern at most of the landfills sampled is odor nuisance. Some residents living near C&D debris landfills complain about headaches, nausea, vomiting, and eye irritation.

In this research, ambient air and soil vapor samples were collected at ten C&D debris and Class III landfills. The samples were analyzed for hydrogen sulfide, methane, carbon dioxide, oxygen, and VOCs, including VSCs. In addition, two supporting laboratory experiments were performed. One experiment, conducted in 10-liter Tedlar bags, was designed to investigate the production of hydrogen sulfide and other VSCs from gypsum drywall. The second experiment was performed to investigate the production of hydrogen sulfide under various conditions, including the presence of gypsum, the presence of organic substrate, moisture content, and the presence of concrete.

The research confirms the presence of hydrogen sulfide at C&D landfills. All ten landfills sampled had a detectable hydrogen sulfide concentration. The hydrogen sulfide in the soil vapor ranged from below the detection limit, 3 ppb to 12,000 ppm. Nine of the ten landfills sampled exceeded national regulations and guidelines for hydrogen sulfide exposure limits. This indicates that workers exposed to undiluted C&D landfill gas, perhaps during excavation or work near gas wells, should take precaution. The concentrations were extremely variable. Hydrogen sulfide was variable from site to site and within each site.

The ambient hydrogen sulfide levels were also extremely variable. Ambient hydrogen sulfide concentrations ranged from below the detection limit to greater than 50 ppm. Ambient hydrogen sulfide levels were much lower than soil vapor hydrogen sulfide, most likely due to dilution with the ambient oxygen and nitrogen. At two of the landfills, ambient air samples at times exceeded OSHA and NIOSH hydrogen sulfide exposure values, representing a definite concern for employees working directly on the landfill site. For local residents, the concern is less clear. The toxicity of low-level hydrogen sulfide exposure requires additional research.

In the laboratory experiments, the role of drywall in the production hydrogen sulfide was confirmed. The serum bottles with gypsum produced higher concentrations of hydrogen sulfide than the bottles with no gypsum. The bottles with leachate only produced

no hydrogen sulfide. However, the bottles containing drywall paper backing and leachate still produced hydrogen sulfide concentrations up to 8,500 ppm. The most likely explanation for the production of hydrogen sulfide from paper backing is that small amounts of gypsum present on the paper-backing surface were sufficient for SRB activity. The hydrogen sulfide concentration reached a maximum of 66,000 ppm in the bottle containing gypsum, paper backing, and leachate. The same observation was made in the drywall Tedlar bag experiment. Both laboratory experiments produced higher hydrogen sulfide concentrations than those measured in the field.

VSCs were also detected, although at much lower concentrations than hydrogen sulfide. The VSCs detected the most were methyl mercaptan, carbonyl sulfide, and carbon disulfide. VSCs were also detected in the laboratory Tedlar bag experiment. The bags containing gypsum drywall and leachate produced higher total VSCs than the control bags containing leachate only.

This research is the first major study of C&D debris landfill gas. While MSW landfill gas has been studied and characterized, the components of C&D landfill gas were unpublished before. The implications of this research are that drywall will produce hydrogen sulfide in C&D debris landfills when disposed under certain conditions. The results of this research identify more possible areas of research about C&D debris landfill gas. This research identified and determined the concentration of hydrogen sulfide and other compounds but did not address the rate of production. The flux of hydrogen sulfide exiting a C&D debris landfill should be investigated. The rate of hydrogen sulfide production during different times of the day should be researched. An improved method to associate soil vapor measurements to ambient air or complaints should be studied. Continuous monitoring of hydrogen sulfide in the ambient air at the site and in the vicinity of neighboring homes and businesses could be an area of future study. Another area of future research is investigating the preventive and control measures to reduce hydrogen sulfide and other odorous gases at C&D debris landfills. The impact of separating and removing drywall out of the waste stream and the effects of different covers should also be studied.

5.2   Laboratory Experiments

No previous measurement of gaseous H_2S concentrations in simulated C&D debris laboratory columns have been reported in the open literature. Questions remain about the generation of H_2S in a laboratory environment, H_2S generation dependence on different waste constituents, and the maximum H_2S concentrations possible. This study was designed to provide information about H_2S production as a result of C&D waste and to attempt to answer the aforementioned questions.

Two experiments were conducted using simulated landfill columns. Experiment 1 consisted of different combinations of drywall, wood, and concrete mixed together and was designed to determine if H_2S could be generated in a controlled environment and to determine the impact of different waste constituents on H_2S generation. Experiment 2 contained two separate layers of concrete and drywall and was designed to reproduce the

effect concrete exhibited in Experiment 1 columns and further clarify the role of concrete in H_2S production and transport. A synthetic rainwater solution was added weekly to both Experiment 1 and 2 columns and the resulting gases and leachates were analyzed.

A major observation from Experiment 1 was the relationship between H_2S generation and the presence of drywall. In many of the columns, large H_2S concentrations were measured when drywall was present. This demonstrated that H_2S could be produced in a laboratory environment and that drywall provided the sulfate ions and the organic matter required for sulfate-reducing bacteria activity. Although this was expected, more important was the observation that the paper backing on the drywall was a sufficient carbon source for the sulfate-reducing bacteria to produce such large amounts of H_2S.

Another major observation was that H_2S concentrations in columns containing wood along with drywall lagged behind those columns containing only drywall, but eventually reached similar levels. The organic acids present in the wood lowered the pH out of the ideal pH range for sulfate-reducing bacteria (pH 6.5 to 7.5). Sulfate-reducing bacteria activity increased once these acids no longer influenced the overall pH.

A difference in measured H_2S concentrations between the middle of the waste layer and the bottom of the columns in the columns containing drywall, wood, and concrete was observed. The only difference was the presence of concrete, which apparently affects H_2S generation and transport. Experiment 2 was designed to answer questions regarding if the concrete effect could be reproduced and to test possible theories that would explain the lower H_2S concentration.

From Experiment 2 results, concrete played a role in the reduction of H_2S production and transport. Possible explanations for this reduction of H_2S concentrations focused on H_2S interaction with concrete and the pH of the concrete. The interaction explanation was examined further with the Tedlar® bag experiment, in which H_2S concentrations were observed to be reduced in a matter of minutes. As the SPLP solution was leached through the concrete, the pH changed because of compounds (e.g., calcium hydroxide) found in concrete. This moved the leachate out of the ideal pH range for sulfate-reducing bacteria. In some manner, H_2S produced in other areas of the columns was removed from the gaseous phase in the vicinity of the concrete. The actual mechanism of H_2S removal was not determined, but the H_2S reduction effect was reproduced. Further experimentation is required to identify the interaction mechanisms between H_2S gas and concrete.

The results of this study have implications regarding the understanding of H_2S generation at C&D debris landfills and possible control mechanisms. C&D debris landfills that accept drywall can expect H_2S generation even without additional carbon sources. This was proven when the drywall only columns generated large concentrations of H_2S with the paper backing as the only carbon source. The results of the concrete interaction with H_2S raise questions in terms of use as a control mechanism, either with the waste or as a cover layer.

Work should be conducted to determine the ability of concrete to control H_2S surface emissions as a function of concrete particle size and cover layer thickness. Other work should investigate the effect of the addition of a buffering solution (e.g., lime) to C&D debris landfills to determine if a pH buffering solution could be used at C&D debris landfills to reduce H_2S generation by moving the pH out of the ideal sulfate-reducing bacteria range.

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