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Best Management Practices to Prevent and Control Hydrogen Sulfide and Reduced Sulfur Compound Emissions at Landfills That Dispose of Gypsum Drywall

Office of Research and Development National Risk Management Research Laboratory Land Remediation and Pollution Control Division

Notice

The U.S. Environmental Protection Agency (U.S. EPA) through the Office of Research and Development funded and managed the research described here under contract order number: EP-W-09-004 to RTI International in Research Triangle Park, North Carolina. It has been subject to the Agency's review and has been approved for publication as a U.S. EPA document. Use of the methods or data presented in this manual does not constitute endorsement or recommendation for use. Mention of trade names or commercial products does not constitute endorsement or recommendation.

Foreword

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The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments, and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by U.S. EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Cynthia Sonich-Mullin, Director National Risk Management Research Laboratory

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Abbreviations, Acronyms, and Initialisms

ADC	Alternative Daily Cover
AEGL	Acute Exposure Guideline Level
ATSDR	Agency for Toxic Substances and Disease Registry
BMP	Best Management Practice(s)
°C	Degrees Celsius
C&D	Construction and Demolition
Ca	Calcium
CaSO ₄	Calcium Sulfate
CDC	Centers for Disease Control and Prevention
CH ₂ O	Formaldehyde
CH ₃ SH	Methyl Mercaptan
$(CH_3)_2S$	Dimethyl Sulfur
$(CH_3)_2S_2$	Dimethyl Disulfide
$(CH_3)_2S_3$	Dimethyl Trisulfide
C_3H_8S	Isopropyl Mercaptan
$C_4H_{10}S$	Isobutyl Mercaptan
CH ₄	Methane
$CH_4H_{10}S$	Tert-Butyl Mercaptan
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
COS	Carbonyl Sulfide
CS_2	Carbon Disulfide
GCCS	Gas Collection and Control System
H_2S	Hydrogen Sulfide
LFG	Landfill Gas
MoO ₄ ²⁻	Molybdate
MSW	Municipal Solid Waste
mV	Millivolt
μL/L	Microliters per Liter
N_2	Nitrogen
nL/L	Nanoliters per Liter
RSC	Reduced Sulfur Compound
RSM	Recovered Screen Material
S^0	Elemental Sulfur
SO_2	Sulfur Dioxide
SO_4^{2-}	Sulfate
SRB	Sulfate Reducing Bacteria
U.S.	United States
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization
WWTP	Wastewater Treatment Plant

1. Introduction and Background

1.1 Issue Description and Report Objectives

Hydrogen sulfide (H₂S) gas can be emitted from both construction and demolition (C&D) debris and municipal solid waste (MSW) landfills. H₂S emissions may be problematic at a landfill as they can cause odor, impact surrounding communities, cause wear or damage to landfill gas (LFG) collection and energy utilization components, or contribute to the formation of explosive conditions. H₂S emissions at landfills have often been attributed to the disposal of gypsum drywall, though other sources such as sulfurcontaining industrial wastes and biosolids from municipal wastewater treatment facilities can also contribute to H₂S production. Addressing problems from H₂S emissions at landfills can be costly and time consuming for landfill owners and operators. Several years of operational experience and research efforts have identified several key pieces of information regarding the conditions that can cause H₂S production, factors that result in H₂S production at landfills, and strategies to prevent these conditions from occurring and to minimize the release of H₂S to the surrounding environment when it is produced.

The U.S Environmental Protection Agency (U.S. EPA) Office of Research and Development, in coordination with U.S. EPA Region 5, commissioned the development of a document designed to provide landfill owners and operators with guidance on pertinent subject matter associated with H₂S production, emissions, prevention, and control at landfill sites. A previous effort (U.S. Environmental Protection Agency [U.S. EPA], 2006b) focused on practices to prevent and control H₂S emissions from C&D landfills that accept pulverized gypsum debris in Ohio. This document expands the scope of this previously developed guidance by consolidating additional landfill operational and research information from a broader knowledge base (both C&D and MSW landfills), including additional information regarding the science of H₂S formation and control, the results of case studies with field and laboratory measurement of H₂S, and updated best management practices (BMPs).

1.2 Intended Audience

This report provides regulatory agencies, landfill owners and operators, and other interested parties with information regarding the science of H_2S production and emissions at landfill sites, and information on BMPs to prevent and control these emissions. Emission levels are discussed in the context of published health and safety standards and health-based or nuisance-based thresholds.

1.3 Report Organization

This report is organized into six sections. Section 1 presents the objectives of this report and describes the report organization. Section 2 provides the fundamentals of H_2S generation, related emission or exposure standards, measured levels at C&D and MSW landfills, and information regarding production and emission of other reduced sulfur compounds (RSCs). Section 3 presents a review of measures to prevent and control the formation and/or emission of H_2S from C&D and MSW landfills. Section 4 describes site investigation and monitoring techniques for H_2S . Section 5 includes a framework that landfill owners and operators can use to develop a BMP guide for their facility. Section 6 provides a list of references cited in the report.

2. Fundamentals

2.1 Basics of H₂S

H₂S (CAS #7783-06-4) is a poisonous, irritating, flammable, and colorless gas, with a characteristic rotten-egg-like odor detectable by humans at low concentrations and a sweet odor at higher concentrations. H₂S (also known as hydrosulfuric acid, sewer gas, sulphuretted hydrogen, hepatic gas, sour gas, and stink damp) is naturally occurring and found in crude petroleum, natural gas, volcanic gases, and hot springs. There are also anthropogenic (man-made) sources of H₂S gas, such as food processing, coke ovens, paper manufacturing mills, tanneries, solid waste disposal facilities, petroleum refineries, and waste water treatment plants (WWTPs). H₂S gas is slightly heavier than air (specific gravity of 1.189) and may accumulate in enclosed, poorly ventilated, and low-lying areas. When released into the environment, H₂S has been observed to persist for approximately 18 hours (Agency for Toxic Substances and Disease Registry [ATSDR], 2006a) and up to 42 days, typically persisting longer in cold weather (Bottenheim and Strausz, 1980). In the atmosphere, H₂S transforms into sulfur dioxide (SO₂) and/or sulfuric acid (H₂SO₄).

The explosive limit of H₂S in air ranges from 4.3 to 46% (43,000 μ L/L to 460,000 μ L/L) (Centers for Disease Control and Prevention [CDC], 2000). It has an autoignition temperature of 260 °C, a National Fire Protection Association (NFPA) fire and health rating of 4, and a reactivity rating of 0 (scale 0–4) (CDC, 2000). The water solubility limit of H₂S is relatively high, with an equilibrium concentration of 4,132 mg/L at 20 °C (World Health Organization [WHO], 2003).

2.2 H₂S Regulatory Standards and Health Effects

The lowest detectable concentration of H_2S by humans has been examined by several investigators. Amoore (1985) conducted a literature review of 26 H_2S -related odor studies and found a median odor detection threshold of 0.008 μ L/L (by volume). *Figure 2-1* displays reported odor threshold ranges reported by several different sources; differences in odor detection levels are primarily attributed to differences in individual olfactory systems and sensitivity.

The detectable concentration of H_2S does not necessarily equate to that of a nuisance level, although Amoore (1985) indicated that five of the studies reported a nuisance-level concentration of 0.04 μ L/L, approximately five times the detectable odor threshold. Mean atmospheric (i.e., ambient) H_2S concentrations in the United States reportedly range between 0.00071 μ L/L and 0.066 μ L/L (U.S. EPA, 2010a). Close proximity to a natural or anthropogenic source of H_2S may produce ambient H_2S concentrations greater than the ambient mean.

Humans may not detect H₂S at high concentrations due to olfactory fatigue (which may occur at approximately 100 μ L/L with a 2- to 15-minute exposure) and olfactory paralysis (reported at approximately 150 μ L/L) (Beauchamp, 1984; U.S. EPA, 2010a). Thus, odor is not always a reliable indicator of the presence of H₂S and may not provide adequate warning of hazardous concentrations.

 H_2S affects the body if inhaled or comes in contact with the eyes, skin, nose, and throat (Beauchamp, 1984, ATSDR 2006a, ATSDR 2006b, ATSDR 2006c). Respiratory protection can be used to prevent inhalation if sufficient engineering controls are not available; a self-contained breathing apparatus and supplied airline respirators (both supply a clean source of breathable air rather than purifying ambient air) are considered acceptable protection from H_2S (Kalusche, 2004).

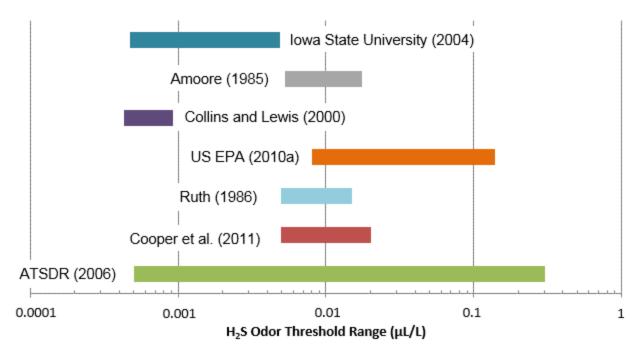


Figure 2-1. Odor Threshold Ranges Reported by Different Sources

Currently, there are no enforceable federal standards for offsite H_2S gas emissions from landfills, or H_2S monitoring requirements specific to landfills. However, health effects due to H_2S exposure have led to the development of H_2S workplace standards, which are typically expressed as a concentration and referenced to an exposure time limit. Nuisance standards and health-based guidelines for human exposure to H_2S in the United States have been developed by numerous agencies and organizations. Individual nuisance or health effects from H_2S exposure vary depending on:

- exposure duration
- exposure concentration
- individual factors (e.g., asthmatics).

 H_2S blocks the oxidative process of tissue cells, reduces the oxygen-carrying capacity of blood, depresses the central nervous system, and causes respiratory failure and asphyxiation in high concentrations (Kalusche, 2004). At acute, lower-level concentrations, nausea, fatigue, loss of appetite, headaches, and irritation can occur (WHO 2003). The reported effect of low-level, long-term H_2S exposure in humans has been mixed in the technical literature. For example, Kalusche (2004) reports effects such as eye irritation, headache, photophobia, and blurred vision from long-term, low-level exposure. However, the WHO (2003) stated that "... effects in human populations exposed for long periods to low levels of (H_2S) cannot serve as a basis for setting tolerable concentrations because of either co-exposure to several substances or insufficient exposure characterization." WHO (2003) states that insufficient data on possible carcinogenicity of H_2S exists, and the compound has not been classified as a carcinogen (ATSDR, 2006b). WHO (2003) summarized human health effects at variable H_2S concentration levels based on acute exposure scenarios, shown in *Table 2-1*.

Table 2-1. Health Effects and Approximate Corresponding H_2S Concentration, as Summarized by
WHO (2003)

Health Effect	H₂S Concentration (µL/L)
No Observed Adverse Effect Level	0.0014
Odor threshold	0.007
Bronchial constriction in asthmatic individuals	2
Eye irritation	4 - 21
Fatigue, loss of appetite, headache, irritability, poor memory, dizziness	20
Olfactory paralysis	>100
Respiratory distress	>400
Death (likely a result of respiratory failure/arrest)	>500

Acute Exposure Guideline Levels (AEGLs) (U.S. EPA, 2010a) for H_2S have been developed and are intended to describe the risk to humans that would result from once-in-a-lifetime, or rare, exposure to airborne chemicals. The AEGLs for H_2S were established based on a three-tiered system (level 1, level 2, and level 3) that acknowledges the severity of expected health effects. Additionally, many other agencies have published their own guidelines, screening levels, or health-based levels for H_2S , which are detailed in *Appendix A* of this report.

Some U.S. EPA regions and states have developed or adopted H_2S air quality standards. Some examples of these standards are included in *Table 2-2*. This list is not exhaustive and is not intended to encompass all regional, state, or local H_2S standards, guidelines, and screening levels. Additionally, the standards may not apply to all areas in the region, state, or municipality.

Standards, Guidelines and Screening Level Description	Concentration (µL/L)
California Ambient Air Quality Standard	0.03 - 1 hour average
Maine Ambient Air Guidelines	0.03 - 30 minute average 0.001 - 1 year average
Minnesota Ambient Air Quality Standards (7009.0080- applies to property boundary, primary standards)	 0.05 - 30 minute average not to be exceeded > 2 times per year 0.03 - 30 minute average not to be exceeded > 2 times in any 5 consecutive days
Montana Ambient Air Quality Standards (17.8.214)	0.05 - 1 hour average not to be exceeded > once per year
New Mexico (20.2.3.110)	0.01 - 1 hour average
New York Ambient Air Quality Standards (257- 10.3)	0.01 - 1 hour
Pennsylvania Ambient Air Quality Standards	0.005 - 24 hour 0.1 - 1 hour
U.S. EPA Region 9 Regional Screening Levels (Also used by U.S. EPA Region 3 and 6 ¹	0.0015 Residential Air 0.0063 Industrial Air

Table 2-2. Examples of State and Regional H₂S Gas Standards, Guidelines, and Screening Levels

Note: ¹ Regional Screening Levels are risk-based target levels developed by guidance from the U.S. EPA Superfund program that are used for Superfund sites. They are generic screening levels considered by U.S. EPA to be protective for humans (including sensitive groups) over a lifetime.

2.3 H₂S Formation in Landfills

 H_2S is generally formed in a landfill environment through the reduction of sulfate (SO₄²⁻). Sulfatereducing bacteria (SRB) causing SO₄²⁻ reduction to H_2S are commonly observed in groundwater, wastewater treatment plants, and sewers. Additionally, H_2S production is attributed to hydrolysis of sulfur-containing minerals (e.g., FeS₂) in natural sources such as volcanoes and hot springs (ATSDR, 2006b). The reduction of SO_4^{2-} represents the primary generation mechanism in landfills; SO_4^{2-} may be present from gypsum or other waste sources in the landfill (e.g., WWTP sludge), though the mass of reducible sulfur minerals in drywall far exceeds that typically present in WWTP sludge. Gypsum is hydrated calcium sulfate (CaSO₄ •2H₂O) and is the major component of gypsum drywall panels, which normally consists of 90% (by weight) gypsum and 10% backing paper. Gypsum drywall is also known as plasterboard, gypsum board, gyproc, gib board, sheetrock, and wallboard, and hereafter referred to in this report as *gypsum drywall*.

Gypsum drywall is a component of C&D waste and can be disposed of in C&D landfills or MSW landfills, where it can arrive in bulk form or in size-reduced (pulverized or fine) form. Gypsum may also be present in landfills (particularly MSW landfills) that accept screened, fine-grained material from C&D recycling operations, which is typically referred to as recovered screen material (RSM). RSM is typically sized from 3/8" to 2" or more and can contain a varying amount of size-reduced gypsum (the degree of gypsum is largely dependent on the practices of the C&D recycler to remove gypsum prior to processing the C&D at its facility). There are several contributing factors that may result in the production of H₂S in landfills. These factors are summarized in *Table 2-3*.

H₂S Formation Factor	Discussion		
SO4 ^{2.} Source	Sources of reducible sulfur in landfills may include gypsum drywall, WWTP sludges, or other residential, commercial, or industrial wastes (e.g., auto shredder fluff impacted by lead-acid batteries). Gypsum may be present in larger pieces of drywall or size-reduced drywall, and may be present in fine particles contained in RSM.		
Moisture provides a medium for SRB growth and chemical reactions to occur. Infiltration stormwater into the waste, lack of leachate collection and removal, and moisture inhere deposed waste can all act to contribute to moisture within landfills.			
Organic MatterProduction of H2S requires organic matter as a substrate for SRB utilization. Several studies (Hardy Associates, 1978; Townsend et al., 2002, New Hampshire Departme Environmental Services 2004) have indicated organic matter presence in C&D landfil not limiting, and that the paper backing on drywall is sufficient to sustain a viable corr of SRB that can produce H2S. MSW landfills have substantially more organic matter 			
		Temperature Conditions	SRB can thrive over a wide range of temperatures – investigators have observed SRB in the thermophilic range at temperatures up to 80 °C (Elsgaard et al., 1994) and at cryophilic ranges as low as -1.8 °C (Knoblauch and Jorgensen, 1999).

Table 2-3. Summary of Factors that Contribute to the Production of H₂S in Landfills

SRB produce H_2S gas from the SO_4^{2-} present in gypsum and organic carbon waste materials, as demonstrated by using formaldehyde (CH₂O) as an example (Townsend et al., 2002; Bogner and Heguy, 2004):

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S$$

Based on stoichiometry, one hundred tons of SO_4^{2-} have the potential to produce 35 tons of H_2S gas (Bogner and Heguy, 2004).

Laboratory studies have examined H_2S production potential in batch reactors or in simulated landfill columns. Yang et al. (2006) measured H_2S concentrations as high as 65,000 µL/L in a reactor containing only drywall that was flushed with a synthetic precipitation leaching procedure solution, which is a simulated rainfall used in standard laboratory leaching tests. Additionally, Yang et al. (2006) tested a simulated column with mixed C&D debris (wood and drywall) and flushed in a similar fashion as the drywall-only experiment, and the results showed an H_2S concentration of approximately 40,000 µL/L.

2.4 Factors Impacting Emission of LFG

The emission of landfill gas (LFG) from landfills depends on the different transport mechanisms associated with the LFG and the factors that influence the transport mechanisms. The mechanisms and influencing factors are presented in *Table 2-4*.

LFG Transport Mechanism	Factors that Impact Emission
Diffusion Through the Waste or Cover Soils	 Soil porosity Concentration gradient Diffusivity of the LFG Thickness of cover soil
Diffusion Through the Air Boundary Layer	 Wind speed, which is related to atmospheric stability Concentration gradient Diffusivity of the LFG
Convection	 Pressure gradient (which is influenced by LFG production rates). A larger pressure gradient between the landfill and the atmosphere results in greater emissions.
Displacement	 Compaction or size reduction of waste Settlement of waste Water table fluctuations (unlined sites) Changes in atmospheric pressure

Table 2-4. Transport Mechanisms and the Factors That Impact LFG Emission (U.S. EPA 1997)

H₂S migrates with LFG through pore space and soil cover in landfills to escape to the atmosphere. H₂S is heavier than air and thus tends to settle in low-lying areas, including outside of the landfill boundary. Pressure changes (causing convection) in the landfill are influenced by nutrient availability, refuse composition, moisture content, landfill age, temperature, pH, oxygen availability, the presence of a LFG collection system, and wastes that may inhibit biological activity (industrial waste, or waste containing large quantities of metals). Landfill settling and compaction can also cause displacement of LFG and force the gas to migrate out of the landfill. The displacement can occur also through water table fluctuations, which are affected by the presence of a liner, evaporation, precipitation, and variations between horizontal and vertical permeability. If the landfill is unlined, the ground water table and surrounding water bodies may have an impact. Xu et al. (2014) developed a model to predict emitted concentrations of H₂S based on conditions that may be present at a specific site (e.g., cover soil thickness, cover soil compaction, and moisture content of the cover soil).

H₂S has a relatively high solubility, thus the gas tends to dissolve in landfill leachate and serve as an emissions source in leachate collection areas or areas on a landfill where leachate is exposed to the atmosphere (Profumo et al., 1992; Reinhart et al., 2004).

Evaluation of where H_2S concentrations are measured at landfills is an important consideration, as the implications measured inside of the landfill differ from those measured at the property boundary. *Figure 2-2* presents an illustration of a landfill and the locations where LFG samples including H_2S may be collected. Additional discussion regarding these potential sampling locations is presented below.

- LFG Header Pipe, LFG Well, or Soil Vapor Probe. Concentrations measured at these locations would be expected to be the highest measured H₂S levels at a landfill, as limited dilution with atmospheric air would have occurred. Normally, measurements are conducted by directly connecting the monitoring instrument to the pipe or probe. Monitoring H₂S at these points may help to identify areas of high concentrations in the landfill or allow the operator to evaluate overall collected H₂S concentration, which has importance particularly at sites with energy conversion systems.
- Landfill Surface. Measurements conducted at the landfill surface can identify areas of high concentration and assess concentrations to which landfill workers or site visitors may be exposed. Measurements at the surface are typically conducted anywhere from just above the surface to the normal breathing zone, depending on the goals of monitoring and the instrument used.
- Ambient Air. Measurements in ambient air are typically conducted to measure the concentration of H₂S that may be present at the landfill's perimeter, property boundary, or even offsite. Measurements can be conducted with fixed instruments (which analyze H₂S levels at a single point) or using a roving instrument to capture a larger area.

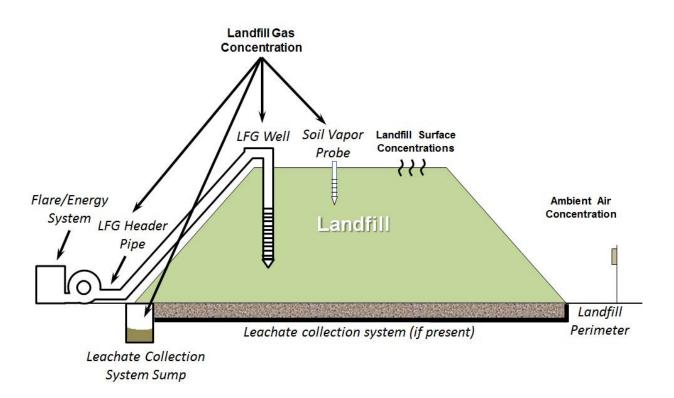


Figure 2-2. Illustration Indicating Common Landfill Processes and Examples of Areas Where H₂S May Be Sampled

Sections 2.6 and 2.7 discuss H_2S production and measured concentrations at C&D landfills and MSW landfills, respectively. Information in each section is grouped to acknowledge measurements of H_2S inside of landfills, on the surface of landfills, and in ambient air on or off of the landfill property. The concentrations measured at each of these points have different implications with respect to operational impacts, environmental impacts, and human health impacts.

It is noted that the monitoring or measurement of H_2S is not necessarily a standard practice at C&D or MSW landfills, and that some data in Section 2.6 and 2.7 were gathered based on published information at sites where an actual or suspected problem with H_2S production or emissions was present. Therefore, the concentrations presented in this report should not necessarily be viewed as "typical" or "average" for C&D landfills or MSW landfills, but simply examples of concentrations that may be encountered. As discussed previously, numerous site-specific factors (waste types and quantities, weather conditions, topographic conditions, distance to receptors) play a role when considering whether a landfill has H_2S production or emissions at problematic levels.

2.5 Composition of Waste Disposed of in C&D and MSW Landfills

Assessing the composition of waste disposed of in C&D debris and MSW landfills is important to understand the potential for the formation of H₂S in these facilities. Gypsum drywall is one of the major components of the C&D debris waste stream. Staley and Barlaz (2009) summarized several statewide studies that estimated the composition of C&D debris discarded at landfills. The mean weight-based composition was calculated and is presented in *Figure 2-3*. Based on composition data reported by seven states in the United States, the average weight-based composition of discarded gypsum in C&D debris was calculated to be approximately 10%.

U.S. EPA (1998a) and (2009) presented estimates of building-related C&D debris generation in the United States based on an assumed waste weight per unit construction activity area and Census Bureau data on construction industry project activity. These studies estimated a building-related C&D debris generation rate estimate of 136 and 170 million tons for years 1996 and 2003, respectively. The estimated recycling rate of C&D reported by U.S. EPA (1998a) ranged from 20 to 30%; the most commonly recycled components included concrete, asphalt, metal, and wood. Assuming that the drywall recycling rate based on the 1996 data was minimal, the amount of disposed gypsum drywall may be on the order of 10 million tons annually in the United States.

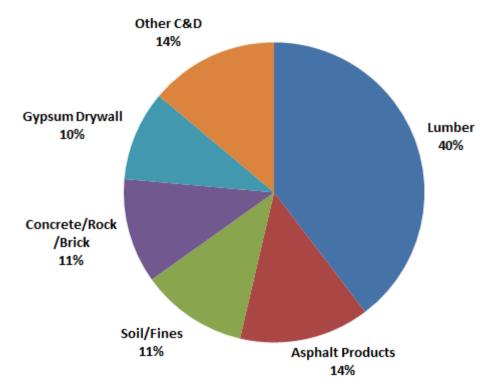


Figure 2-3. Mass-Based Discarded C&D Debris Composition Based on Reported Data From Seven States (adapted from Staley and Barlaz, 2009)

The generation of MSW in the United States is estimated annually by the U.S. EPA. In 2010, total MSW generation was estimated to be 250 million tons, with an approximately 34% recycling rate and 54% discard rate (U.S. EPA, 2011). Staley and Barlaz (2009) summarized reported statewide waste composition data for discarded MSW, as shown in *Figure 2-4*. It is important to note that many MSW landfills accept waste other than MSW (e.g., C&D debris, industrial wastes, and ash). C&D debris may be disposed of at an MSW landfill for a variety of reasons, including (but not limited to) lack of recycling markets, lack of permitted C&D debris-only facilities, and disposal costs.

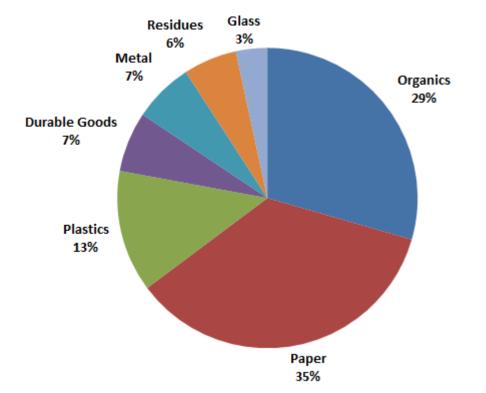


Figure 2-4. Discarded MSW Composition by Mass (adapted from Staley and Barlaz, 2009)

Accurate nationwide estimates of the fraction of waste received at MSW landfills that is composed of C&D debris are not available. However, statewide characterization studies can provide relevant data. For example, a statewide waste characterization study conducted in Delaware that examined the waste composition of six facilities owned by the Delaware Solid Waste Authority found that approximately 23% (weight basis) of materials handled at these facilities was C&D debris (Delaware Solid Waste Authority, 2007). So while accurate nationwide estimates of the fraction of waste disposed of in MSW landfills that consists of C&D debris are not available, the data from Delaware show that the amount of C&D debris disposed of in MSW landfills can be substantial.

2.6 H₂S at C&D Debris Landfills

2.6.1 Factors Contributing to H₂S Formation and Emission at C&D Landfills

The data presented in Section 2.5 show that potentially large quantities of SO_4^{2-} from gypsum drywall disposal are available at C&D landfills. Coupling this with the fact that these landfills harbor the broad conditions that need to exist at landfills for H₂S formation to occur, the potential exists for appreciable quantities of H₂S to form at C&D landfills. Additional conditions that may promote H₂S production at C&D landfills are summarized in *Table 2-5*.

Condition or Factor	Discussion
Cover Soil Requirements	Cover soil requirements at C&D landfills (which can reduce the amount of stormwater that infiltrates into the waste and can also serve to reduce quantities of H ₂ S emitted as described later) are limited in some states. A review of state-mandated cover soil requirements indicated that 12 states require daily cover, 14 require weekly cover at a minimum, and 24 states have no operational cover requirements or a cover placement requirement less frequent than weekly (U.S. EPA, 2012b). The lack of a cover soil requirement may tend to increase the production of H ₂ S by promoting conditions that cause its formation.
Bulky Nature of C&D Debris	The bulky nature of C&D debris may allow moisture to more readily infiltrate into the waste or percolate through the waste when compared to another waste stream such as MSW.
Liquids management	As of 2012, 17 states in the US have a minimum requirement for C&D landfills to collect and remove leachate (U.S. EPA, 2012b). Depending on local geology (e.g., presence of a low permeability layer underlying the waste or presence of groundwater at or near the waste bottom), conditions may form that allow for the build-up of moisture or the contact of groundwater with the waste mass. This could increase moisture content of waste and result in greater H ₂ S formation, but could also result in greater leaching of SO ₄ ²⁻ into solution, thus representing a potential source for H ₂ S off-gassing within or beyond the landfill footprint. Also, recirculation of leachate into the waste and poor surface water management can lead to an increase in waste moisture content.
Placement of Size- Reduced Gypsum Drywall in the Landfill	Some C&D landfills accept or have accepted size-reduced C&D debris, which can include ground-up pieces of gypsum drywall. The reduced size creates an increased specific surface area which can lead to greater rates of H ₂ S gas production compared to larger, bulkier pieces of drywall. Size-reduced gypsum drywall may be in the form of processed C&D debris or in RSM.

Table 2-5. Conditions That May Promote H₂S Production at C&D Landfills

2.6.2 H₂S Concentrations Measured at C&D Landfills

This section summarizes measured H_2S concentrations at C&D landfills, focusing on the three major data types presented in *Figure 2-2*. This includes data collected in the waste or LFG extracted from the waste, at the landfill surface, and in ambient air at or near C&D landfills. The data indicate levels of H_2S that may be encountered at a C&D landfill based on what has been reported in the technical literature and other sources.

H₂S Measurements in LFG at C&D Landfills

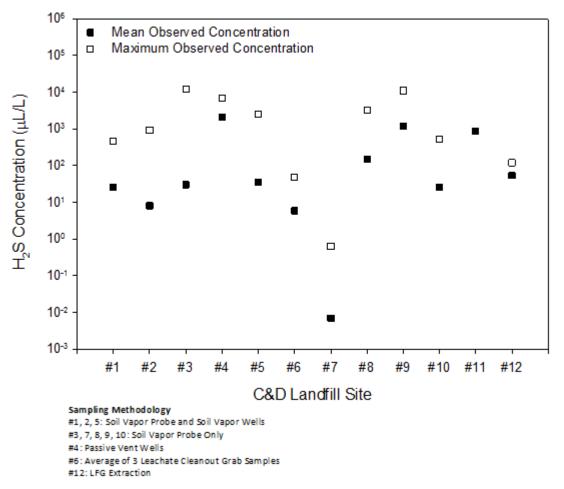
Although most C&D landfills do not have active LFG collection, data from a limited number of sources were examined to assess concentrations of H₂S that have been measured at C&D landfills. Lee et al. (2006) sampled in-situ LFG using soil vapor probes installed 0.3 m below the landfill surface and from existing passive gas collection vent wells at 10 C&D landfills. The results showed highly variable H₂S concentrations, ranging from <0.03 μ L/L to 12,000 μ L/L. Collected samples from the C&D landfill with the highest observed H₂S concentrations, which showed a mean concentration of 2,110 μ L/L and a median of 1,800 μ L/L, were collected from passive gas collection vent wells.

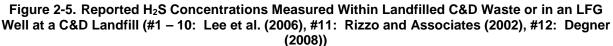
Sampling from two leachate cleanout lines at a C&D landfill in Ohio showed H₂S concentrations as high as 1,995 μ L/L and 600 μ L/L (Rizzo and Associates, 2002). A 74-acre C&D landfill in Kansas experienced H₂S odor problems attributed to the collection and buildup of stormwater within the waste footprint because of a low-permeability shale layer underlying the site and lack of a mechanism to remove the liquid. The landfill contains 25 onsite wells that serve as the LFG collection system. Degner (2008)

reported an average collected LFG H₂S concentration of 54 μ L/L, with a range of 4 to 120 μ L/L at a facility in Kansas.

 H_2S concentrations were measured at a New York landfill with two phases devoted to C&D disposal. Phase 1 consisted of processed C&D debris and Phase 2 consisted of bulk C&D debris (McCarron and DiMaria, 2007). H_2S measurements conducted in 2000 in Phase 1 reached 9,000 µL/L. Investigations conducted between 2001 and 2006 in Phase 1 measured concentrations as high as 12,000 µL/L and Phase 2 concentrations as high as 18,000 µL/L.

Figure 2-5 summarizes the measured concentrations of H₂S within C&D landfills reported in the investigations described above.





H₂S Concentration Measurements at the Landfill Surface of C&D Landfills

Lee et al. (2006) measured H₂S concentrations on the surface of 10 C&D landfill sites in Florida to measure concentrations near soil vapor probes. The results indicated readings between <0.003 μ L/L and >50 μ L/L; detections of H₂S at the landfill surface occurred in 48% of measurements. The two sites with

the highest observed H₂S concentrations (maximum concentrations of >50 μ L/L at the surface) were sites known to accept processed C&D debris.

The ATSDR (2007) reported on H₂S concentrations measured using personal badge monitors affixed to landfill workers during the work day at a C&D site. The maximum observed concentration from this evaluation was 130 μ L/L. *Figure 2-6* summarizes the reported H₂S surface concentration measurements from these studies. The figure shows that three of the landfills had a maximum H₂S concentration greater than 10 μ L/L, which exceeds the AEGL-1 standard presented in *Appendix A*, and other guideline levels.

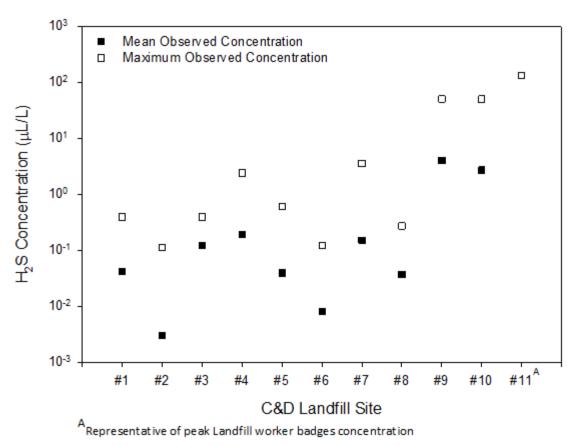


Figure 2-6. Reported H₂S Concentrations Measured at the Surface of 11 C&D Landfill Sites in Florida (#1 – 10: Lee et al. (2006), #11: ATSDR (2007))

Eun et al. (2007) measured the H₂S flux from five C&D landfills (n = 20 measurements per site) in central Florida during the summer using a dynamic flux chamber. Measured flux rates ranged from 0.192 - 1.76 mg/m²-day. These flux rates are less than those reported for LFG flux rates reported by Amini and Reinhart (2012) at MSW landfills, which was approximately 20 to 120 g/m²-day. The H₂S measured by Eun et al. (2007) was detected at frequencies ranging from 10% to 55% of measurements, indicating that emissions through the cover of C&D landfills were variable.

Ambient H₂S Concentrations Measured Near C&D Landfills

Residents living near a C&D landfill in Florida with documented odor nuisance problems wore H_2S personal badge monitors for one month. The results showed 15 positive detections of H_2S , ranging from 0.015 to 0.123 μ L/L. Additionally, stationary ambient air monitors detected H_2S concentrations up to 0.224 μ L/L (ATSDR, 2007).

Cooper et al. (2011) utilized techniques to assess H_2S emission rates from C&D landfills to calculate an odor buffer distance beyond which nuisance odors would not be detected. The study measured H_2S concentrations near a C&D landfill in Florida and subsequently used the measured results in a model that used a problematic odor threshold (0.015 μ L/L, which was established based on a literature review of six studies) to delineate the odor buffer distance from the landfill. H_2S readings were measured in the morning, where higher concentrations were more likely because of lower atmospheric turbulence. On the first site visit, H_2S concentrations from 0.2 μ L/L to 0.4 μ L/L were observed at two corners of the landfill, at a maximum of approximately 40 m from the edge of the landfill. H_2S concentration declined to 0.015 μ L/L at approximately 70 to 200 m from the landfill edge. On the second site visit, H_2S measurements surrounding the landfill was >0.8 μ L/L.

Table 2-6 shows the modeled buffer distances with their corresponding predicted H_2S concentration ranges. The calculated buffer distance varied substantially between the two visits (which was a reflection of the difference in measured concentrations at the landfill). This demonstrates a couple of important phenomena: 1) that the concentration of H_2S produced from landfills has the potential to be highly variable, even when measured at a similar time of day at the same location; and 2) based on the results of site-specific atmospheric modeling, the impact that the source H_2S concentration has on the area surrounding the landfill that may experience problematic H_2S concentrations is dramatic.

Table 2-6. Calculated Modeled Minimum Nuisance Odor Buffer Distances Based on H₂S Measurements Collected at a Florida C&D Landfill (adapted from Cooper et al., 2011)

Measured H ₂ S Concentration Near Landfill (µL/L)	Site Visit #1: Buffer Distance (m)	Site Visit #2: Buffer Distance (m)
0.0 – 0.015	600	2,800
0.015 – 0.030	400	2,400
0.03 - 0.10	200	2,000
>0.10	100	1,600

A C&D landfill site with reported odor issues in Ohio reported monitoring data from three ambient monitoring locations (bordering the landfill perimeter) of 60-minute rolling average H₂S concentrations of 0.154 μ L/L, 0.043 μ L/L, and 0.071 μ L/L during September 2004 (Tetra Tech, 2004).

Figure 2-7 displays ambient air H₂S data collected from three different sites as reported by ATSDR (2007), Tetra Tech (2004), and Cooper et al. (2011).

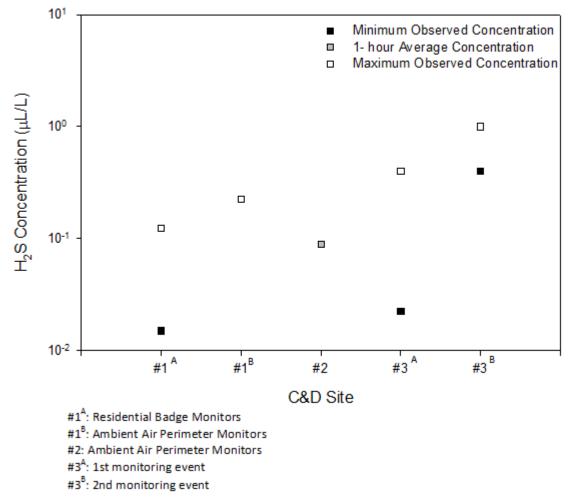


Figure 2-7. Compilation of Ambient Air H₂S Measurements Near C&D Landfills (#1: ATSDR (2007), #2: Tetra Tech (2004), and #3: Cooper et al. (2011))

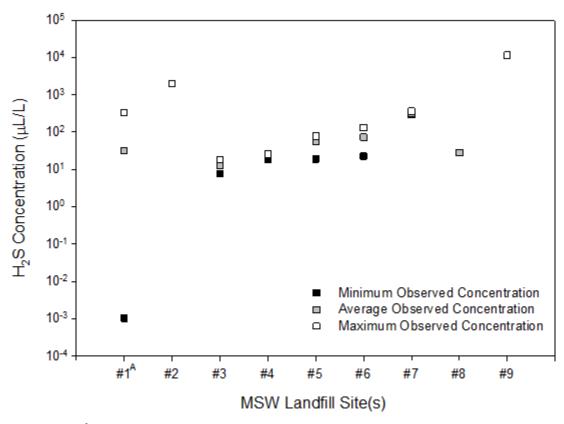
Summary

The results show that measured concentrations within C&D landfills, and in some cases at the landfill surface, are high enough to fall within the range where acute exposure symptoms may occur. Data from the measurements in the waste mass or collected LFG showed H₂S concentrations above the level that could cause death in a short-term exposure scenario. Thus, operators at C&D debris landfills that accept gypsum drywall should be made aware of the potentially high concentrations of H₂S that may be encountered.

The measured landfill surface H₂S concentrations in the studies evaluated were somewhat variable, but several cases indicated concentrations that may be of concern. For example, one site reported an H₂S concentration measured by a personal badge worn by a landfill worker during the work day of greater than 100 μ L/L, which exceeds the Occupational Safety and Health Administration's Immediately Dangerous to Life and Health level of 100 μ L/L (refer to *Appendix A* for details on additional H₂S guidance and standards). In the 10-landfill study conducted by Lee et al. (2006), the mean surface H₂S

concentration was less than 10 μ L/L for each site, but two sites had measured concentrations greater than the 10-minute AEGL-1 (which corresponds to nuisance and irritation in a short-term exposure scenario) and five of the sites examined by Lee et al. (2006) had a measured concentration that exceeded the ATSDR's acute maximum risk level.

The H_2S concentrations reported in ambient air near three C&D landfills (two of which were sites that had reported H_2S emission problems) indicate that the potential exists for the detection of H_2S concentrations above nuisance odor thresholds at or beyond the landfill property boundary, but the results varied and demonstrated that the presence of problematic or nuisance-level H_2S concentrations is not necessarily constant. The effect that H_2S source concentration at the landfill on the migration of H_2S offsite can be dramatic, as demonstrated by Cooper et al. (2011), which underscores the importance of mitigating H_2S at the landfill site.



#1^A: Compilation of data from multiple sites for AP-42 defaults

2.7 H₂S at MSW Landfills

2.7.1 Factors Contributing to H₂S Formation and Emission at MSW Landfills

The conditions that cause H_2S formation in MSW landfills are similar to C&D landfills, in that a SO_4^{2-} source, carbon source, anaerobic conditions, moisture, and appropriate pH and temperature must be present. Gypsum drywall may be disposed of in MSW landfills through bulk C&D disposal, processed C&D disposal, or the use of C&D fines (also referred to as RSM) for initial cover or for grading and shaping of side slopes.

The presence of gypsum drywall in MSW landfills is a large contributor to H_2S formation at these sites. Fairweather and Barlaz (1998) conducted laboratory experiments comparing SO_4^{2-} reduction in reactors containing fresh MSW with and without gypsum drywall. The results indicated that the reduction of SO_4^{2-} to H_2S occurred concurrently with the production of methane (CH₄) from the MSW, and the reactors containing gypsum drywall produced sulfur emissions that were 10 times greater compared to the reactors without added gypsum drywall.

In contrast to C&D landfills, MSW landfills are required per federal regulations (40 CFR Part 258) to apply a soil cover (or equivalent) at least daily to control moisture and reduce odors and disease vectors. Thus, the presence of a daily cover is expected to reduce the infiltration of stormwater relative to a C&D landfill that does not have a soil cover requirement; however, it is expected that the higher moisture content inherent in MSW supplies enough moisture to contribute to H_2S production.

Several factors exist at MSW landfills that may contribute to the production or emission of H_2S beyond the basic conditions that must be met for H_2S to form. These factors are presented in *Table 2-7*.

Condition or Factor	Discussion
SO4 ²⁻ Source	Larger sources of SO_4^{2-} from gypsum drywall may be present, in addition to other potential sources such as sludges. The amount of the SO_4^{2-} is a function of the amount of SO_4^{2-} containing wastes accepted by the facility, which can vary widely. For example, a statewide characterization of waste at disposal facilities in Georgia indicated a weighted average of approximately 12% C&D debris (out of the total waste disposed in MSW landfills in the state), with a range of 0 % to 50% (Georgia Department of Community Affairs, 2005).
Waste Moisture ContentThe nature of MSW differs from C&D debris in several ways, including the inherent m content of the waste as delivered to the disposal facility. Reported weight-based mois contents range from 15% to 40% (Tchobanoglous et al., 1993), although multiple inver- 	
LFG Production Rate The content of highly and moderately degradable organic waste normally found is landfills results in the production of large volumes of LFG (particularly relative to landfills), which may lead to greater transport of H ₂ S into LFG collection systems the landfill surface.	
RSM Use in Cover Soil	MSW landfills have more stringent cover application requirements compared to C&D landfills, and as a result several MSW landfills have evaluated sources of material to use as cover, including RSM. Several states (e.g., Massachusetts) have C&D recycling mandates, thus the expansion in availability of RSM has led to an increase in the delivery of this material to facilities that beneficially use (as an alternative daily cover [ADC]) or dispose of the RSM. Several states have granted approvals for using RSM as an ADC. The presence of fine gypsum particles in RSM, which can be dramatic (Musson et al. (2008) measured the gypsum content of RSM from several facilities in the U.S. and the results ranged from 1% to 25% by weight gypsum) can lead to the production of H_2S .
Leachate Recirculation Leachate recirculation is a common practice at MSW landfills. This process attempts the moisture content of MSW in order to promote decomposition of the waste. Subsecting gas production is increased, thus increasing the production of H ₂ S.	

Table 2-7. Conditions That May Promote H₂S Production at MSW Landfills

2.7.2 H₂S Concentrations at MSW Landfills

H₂S Measured in MSW LFG

 H_2S in MSW LFG can pose additional issues beyond potential worker health and safety and nuisance conditions—specifically, sites that have active gas collection and control systems (GCCS) may be at risk of triggering emission thresholds for sulfur oxides (SO_x) if mass flow rates of H_2S are high enough (H_2S is converted into SO_x following combustion in typical LFG destruction devices). SO₂ is one of the six priority pollutants that are subject to the National Ambient Air Quality Standards (U.S. EPA, 2012a).

Landfills with Title V air permits and/or stationary source permits typically have an upper allowable limit of SO₂ emissions. Additionally, high H₂S concentrations can be problematic at MSW landfills that collect and beneficially use LFG to produce energy because a performance standard related to H_2S concentrations must usually be met (these performance standards vary depending on the type of energy conversion system, as discussed in Section 3.2.5); the requirement to reduce H₂S concentrations to meet these levels represents a cost that can impact energy project economics.

U.S. EPA (1998b) reported a default H₂S concentration of 35.5 µL/L for MSW LFG in the compilation of air pollutant emission factors (AP-42), which was developed based on the average of 37 test reports analyzed. The AP-42 develops emission factors, which facilitate the estimation of emissions from various sources of air pollution. The emission factors are typically averages of available data of acceptable quality. In recent years, U.S. EPA (2008) began to update the AP-42 default concentrations based on more recent measurements, and a draft background document presented updated H₂S monitoring data collected from active GCCS. Table 2-8 presents summary statistics of the H₂S concentrations reported in U.S. EPA (2008). Note that the majority of data points were collected from MSW landfills in California.

Table 2-8. Summary of H₂S Concentration Data in MSW LFG Reported in the Draft Compilation of Air Pollutant Emission Factors for MSW Landfills (U.S. EPA, 2008)

Metric	Value (µL/L)
Minimum Concentration	0.001
Maximum Concentration	330
Mean Concentration	32.0
Standard Deviation	55.7
95% Upper Confidence Level	18.2

H₂S was measured in the field from active GCCS wells at an MSW landfill in Virginia that had been the subject of odor complaints. The results showed that approximately 15% of wells (approximately 22 out of 129) exhibited an H₂S concentration greater than 2,000 μ L/L (Tennant, 2012). Note that these concentrations were measured prior to a destruction device. The U.S. EPA (2007) conducted a study of five MSW landfills (two in the Northeast and three in the Midwest) with active GCCS. LFG samples were collected from the GCCS from a main header pipe (which represents the cumulative volume of LFG collected from each site). The results of the sampling events are presented in *Table 2-9*.

Table 2-9.	Reported H_2S Measurement Data From Five MSW Landfills (U.S. EPA, 2007)

Landfill	Range of H₂S Measured in Raw LFG (µL/L)	Average H₂S Concentration in Raw LFG (µL/L)
Α	7.6 – 18.4	13.0
В	18.7 – 25.6	22.9
С	19.0 – 78.0	55.5
D	22.7 – 132	72.7
E	291 – 366 ^A	322 ^A
	A. Estimated Value	

A: Estimated Value

Capenter and Bidwell (1996) reported an H₂S concentration (determined by a chemiluminescence detector) in MSW LFG of 28.33 µL/L from a 60-acre landfill in Connecticut from a GCCS header pipe.

A regional MSW landfill in New Jersey accepted C&D screenings from 1998 to 2004 for use as an ADC (Carlton et al., 2005). The site began to receive odor complaints in 2002 (and reportedly had not received any odor complaints prior to this time) and an active GCCS was installed in early 2003 and expanded in

early 2004. LFG sampling in 2004 revealed H₂S concentrations up to 11,600 μ L/L. Prior to acceptance of C&D screenings, a target SO₄²⁻ level in the screenings was established at 3% (by weight). Monthly testing reportedly indicated the target SO₄²⁻ level was met (Carlton et al., 2005). *Figure 2-8* presents a summary of reported H₂S measurements in MSW LFG presented by U.S. EPA (1998b), Tennant (2012), U.S. EPA (2007), Capenter and Bidwell (1996), and Carlton et al. (2005).

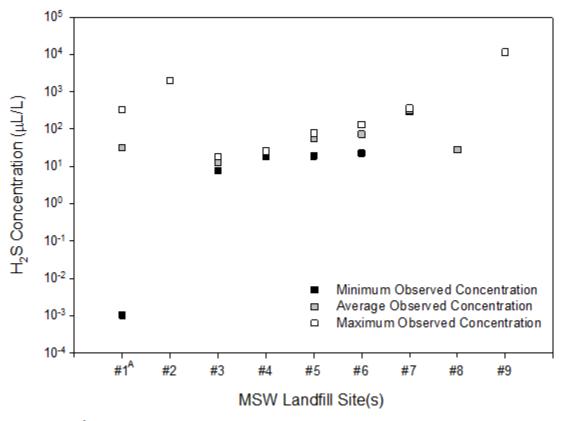




Figure 2-8. H₂S Concentrations Measured in LFG at MSW Landfills (#1: U.S. EPA (1998b), #2: Tennant (2012), #3 – 7: U.S. EPA (2007), #8: Capenter and Bidwell (1996), and #9: Carlton et al. (2005))

Anderson et al. (2010) conducted a study to estimate the H_2S production potential and kinetics based on the acceptance of C&D screenings at MSW landfills using SO_4^{2-} content measurement data from the C&D screenings and field-measured H_2S concentrations. The range of field-measured H_2S concentrations was from approximately 100 μ L/L to 14,000 μ L/L. Models were developed to predict H_2S production amounts based on data collected from six different landfills. The average production potential was calculated to be 4,310 ft³ of H_2S per ton of sulfur in C&D fines. Anderson et al. (2010) also suggested that H_2S from the production of C&D screenings in MSW is expected to peak and decline more rapidly compared to CH₄ production.

The data provided in this section indicate that the concentrations of H₂S that can be formed in MSW landfills can be significant and comparable to levels measured in C&D landfills.

H₂S Concentrations Measured on the Surface of MSW Landfills

Gowing (2001) measured the flux of several gases, including H₂S through the landfill surface using a flux chamber at an MSW landfill in Waterloo, Canada. A total of 20 sampling locations that consisted of a 30-cm thick interim cover comprised of clay. The landfill site had an active GCCS in place on the side slopes, and measurements were taken in areas that were and were not under the influence of the GCCS. The results ranged from below the detection limit to approximately 7.7 μ L/L. Measurements in the areas of highest H₂S flux ranged from approximately 4.2 μ L/L to 7.7 μ L/L.

Capenter and Bidwell (1996) measured ambient air samples 10 to 13 cm above the landfill surface, collected in a grid pattern, at a regional MSW landfill in Connecticut that had been subject to offsite odor complaints. At the time of the study, an active GCCS and enclosed flare had been operational for 2 years and intermediate or daily cover soil was in place at the site. Five grids on the landfill surface encompassing 4,650 m² were sampled over 9 days in locations considered to be "worst-case scenario" (e.g., odors noted previously, visible leachate or residue). H₂S in ambient surface air was measured to be 0.00095 μ L/L. As a point of reference, the measured concentration of H₂S during the study collected from an active GCCS header was approximately 27 μ L/L.

Ambient H₂S Concentrations Measured Near MSW Landfills

An ATSDR (2009) public health assessment of an MSW landfill in New York found offsite migration of H_2S resulting from poor operational practices exceeding 1 μ L/L (daily maximum levels exceeding 3 μ L/L) at the landfill perimeter for a period of 2 months (December 1990 and January 1991) before control measures were put in place and concentrations decreased to approximately 0.5 μ L/L in downwind samples.

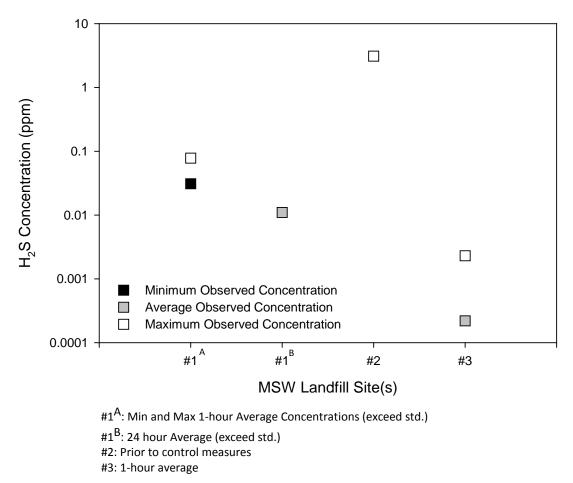
An MSW landfill that also included a C&D landfill in Ohio accepted a large amount of size-reduced C&D debris that resulted in odor problems (Ohio Environmental Protection Agency [OEPA], 2006). Roving monitoring data near the perimeter of the facility in 2005 exhibited 1-hour average H₂S concentrations ranging from 0.031 μ L/L to 0.078 μ L/L. During the same time frame, a 24-hour average of 0.011 μ L/L was measured.

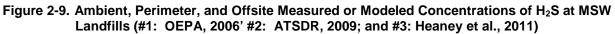
As part of an effort to address H_2S odors emanating from an MSW landfill in Illinois, which was attributed to the acceptance of pulverized C&D debris, a year-long monitoring effort was conducted to establish ambient H_2S concentrations around the site perimeter and define fluctuations in concentration that could be related back to weather data and landfill operations by the Lake County Health Department and Community Health Center (LCHDCHC; 2011a, 2011b). Three high-sensitivity, Honeywell low-level H_2S single-point monitors were installed around the perimeter of the site (one at a location upwind [#1] and two located downwind [#2 and #3]) from April 2010 through March 2011; the monitors had a lower detection limit of 1 nL/L (0.001 μ L/L) and an upper detection limit of 90 nL/L (0.09 μ L/L).

The monitoring results showed that a measured H_2S concentration greater than 0.005 μ L/L was observed at monitor #2 at least once on 82 different days, whereas monitor #1 and #3 had a measured concentration exceeding 0.005 μ L/L on 28 and 21 different days, respectively. Measured H_2S concentrations of greater than 0.09 μ L/L were observed once at monitor #1 and #3 and on seven different days at monitor #2. The location of monitor #2 was most proximate to an area of the landfill where pulverized C&D was disposed. In general, peaks in H_2S concentration occurred during the late evening and early morning hours, when wind activity was minimal.

Heaney et al. (2011) evaluated H₂S concentrations measured between an MSW landfill and a neighboring community that was located within 0.75 miles of the site. Measurements using two different fixed H₂S monitors were conducted. One monitor conducted measurements at 15-minute intervals for 47 days, and one analyzer conducted measurements at 5-minute intervals for 58 days. The H₂S 1-hour average concentration during the study period was 0.00022 μ L/L, with a range of below detection limit to 0.0023 μ L/L. The H₂S monitoring results were compared with reports from nearby residents that maintained a

log of observed odor. The results were mixed to some degree in that resident observations of odor did not always correlate with an observed detection of H₂S. For example, 76% of reported "no odor" observations corresponded with H₂S detections less than 1 nL/L, and 72% of reported "no odor" observations corresponded with H₂S detections greater than 1 nL/L. Conversely, 8% of "strong" odor observations by residents corresponded to instances of H₂S less than 1 nL/L, but 6% of "strong" odor observations corresponded to instances of H₂S greater than 1 nL/L. The results of the study underscore some of the challenges associated with correlating a subjective observation (i.e., the presence of odor) with quantitative measurement data. *Figure 2-9* presents a summary of ambient concentrations reported by OEPA (2006), ATSDR (2009), and Heaney et al. (2011).





Summary of H₂S Measured at MSW Landfills

The H₂S measurement data from LFG at MSW landfills suggest that high concentrations of H₂S may be produced at levels comparable to that measured within C&D landfills. In many of the cases presented, the measurements were taken from a GCCS (either individual collection wells or header pipes). The results indicate the importance of routine monitoring of H₂S for systems that have active GCCS, particularly larger sites that may accept gypsum drywall or RSM, as potentially high H₂S concentrations may impact LFG to energy systems and in some cases could have implications on SO_x limits in a landfill's Title V permit. The results of landfill surface concentration sampling of H_2S were somewhat variable, with one case indicating low measured concentrations that were generally less than the nuisance level for H_2S presented by Amoore (1985) and comparable to U.S. EPA (2010a) reported atmospheric concentrations of H_2S . Another case indicated measured concentrations greater than 1 µL/L, exceeding irritation levels summarized by WHO (2003), and some of the exposure guideline levels presented in *Appendix A*. The results indicate different factors such as operation of a GCCS, cover soil type and quality, and H_2S source concentration can have an impact on measured concentrations at the landfill surface.

Ambient H₂S concentration data, similar to surface concentration measurements, were variable. Data from the sites in Ohio and Illinois both indicated ambient concentrations beyond the landfill footprint greater than the H₂S nuisance level of 0.015 μ L/L reported by Cooper et al. (2011), and in the case of Ohio, measured concentrations exceeded the acute minimum risk level of 0.07 μ L/L established by ATSDR. Conversely, monitoring data near a landfill in North Carolina indicated H₂S concentrations below nuisance levels and most of the reported human odor detection limits as well. Regardless of the low H₂S levels, the evaluation by Heaney et al. (2011) concluded that observations and log books maintained by nearby residents during the study still indicated effects such as irritation and behavioral changes.

2.8 Considerations for Other Reduced Sulfur Compounds

Although H_2S is the most-studied RSC with respect to landfill emissions, other RSCs have been investigated in LFG; most are malodorous, with low odor thresholds, and considered undesirable contaminants in LFG (Moreau-Le Golvan, 2003). Other RSCs that may be detected in LFG include methyl mercaptan (CH₃SH), isopropyl mercaptan (C₃H₈S), isobutyl mercaptan (C₄H₁₀S), dimethyl sulfur ((CH₃)₂S), dimethyl disulfide ((CH₃)₂S₂), dimethyl trisulfide ((CH₃)₂S₃), carbonyl sulfide (COS), carbon disulfide (CS₂), and tert-butyl mercaptan (CH₄H₁₀S). These compounds generally are malodorous, and some have odor thresholds at similar concentrations to H₂S. Christensen et al. (1996) reports that RSCs such as mercaptans are formed from highly degradable materials and are usually only found during the initial operational phase of the landfill, whereas H₂S is normally generated in all phases of a landfill's life.

As with H₂S, the odor detection threshold of other RSCs occurs at different concentrations based on the individual. ATSDR (n.d.) reports odor thresholds for CH₃SH of 0.002 μ L/L, Cameo Chemicals (1999) reports 0.00025 μ L/L as an odor threshold for C₃H₈S, and ATSDR (2011) reports CS₂ can be detected by most humans from 0.02 to 0.1 μ L/L. C₄H₁₀S has a reported odor threshold of <0.001 μ L/L (Chevron Phillips, n.d.). (CH₃)₂S has an odor threshold of approximately 0.001 μ L/L (Bayou Engineering, 2004); (CH₃)₂S₂ has an odor threshold of 0.008 μ L/L (Bayou Engineering, 2007).

U.S. EPA (2008) reported uncontrolled LFG data on several RSCs, in addition to H_2S . *Table 2-10* summarizes the data from U.S. EPA (2008) for several RSCs. Samples of LFG were collected from MSW landfills, and the sample collection point was from the main GCCS header pipe.

Compound	Minimum (µL/L)	Maximum (µL/L)	Mean (µL/L)	Standard Deviation (µL/L)
CH₃SH	9.8 x 10 ⁻⁴	4.05	1.37	0.955
C ₃ H ₈ S	3.75 x 10⁻⁵	1.22	0.175	0.26
COS	1.04 x 10 ⁻⁴	0.275	0.122	7.12 x 10 ⁻²
CS ₂	2.92 x 10 ⁻⁴	0.353	0.147	8.74 x 10 ⁻²
(CH₃)₂S	7.51 x 10 ⁻³	14.7	5.66	0.383
(CH ₃) ₂ S ₂	2.29 x 10 ⁻⁴	0.435	0.137	0.103

 Table 2-10. Summary of Measured RSC Concentrations From MSW LFG (U.S. EPA, 2008)

Lee et al. (2006) measured RSCs at 10 C&D landfill sites in Florida. Samples were collected above the landfill surface, and from gas collection pipes and subsurface vapor probes. H₂S was typically found in significantly greater concentrations than the other RSCs. However, at one site where samples were drawn from LFG wells, concentrations of COS (22 μ L/L) and CH₃SH (85 μ L/L) exceeded that of H₂S (average of 5.9 μ L/L).

While the presence of all RSCs can create potential odor and operational issues (with respect to gas collection and energy utilization) at landfills, the relative and persistent dominance of H_2S indicates that in most cases the measurement of H_2S will likely provide appropriate information to site operators regarding the presence and magnitude of potential odor or other issues related to RSCs at a landfill.

3. Methods to Prevent and Control H₂S Emissions

Knowledge of the factors that contribute to H_2S formation is essential to preventing its formation, and strategies to actively reduce emitted H_2S concentrations are detailed in this section. Formation of H_2S in landfills may not be avoidable due to varying constraints; thus it is critical to discuss strategies to control H_2S emissions once the gas is formed. There are several strategies to prevent and control H_2S that have been explored at the research level and in practical application. Given the differences in site characteristics and regulatory schemes that landfill sites may be subject to, an integrated approach that employs one or more of the strategies in this section, coupled with effective site-specific BMPs, may yield effective results.

3.1 Methods to Prevent H₂S Formation

3.1.1 Diversion of Drywall and Limiting SO₄²⁻ Content of RSM

The diversion of drywall from disposal has been recommended as a measure to prevent H_2S formation in landfills (CalRecycle, 2007; FDEP, 2011). In some cases, landfills have instituted bans on the disposal of drywall except for small amounts. For example, a landfill in Vancouver, Canada is subject to a bylaw created by the Greater Vancouver Sewerage and Drainage District Act (GVSDDA) of 2012, which states, in part:

No person shall dispose of any Gypsum at a Disposal Site: (a) except at a Recycling Area designated for Gypsum; and (b) unless the Load of Gypsum weighs one-half (1/2) tonne or less.

Metro Vancouver uses two elements in addition to the disposal ban to facilitate compliance and appropriate management of gypsum drywall. First, an economic disincentive for delivering gypsum drywall to the landfill was established. Generators that bring prohibited gypsum drywall to the landfill are assessed a minimum surcharge of \$50, plus the cost of removal, cleanup, or remediation. Loads that contain banned materials are assessed a 50% tipping fee surcharge. Second, Metro Vancouver provides generators with information on a drywall recycling facility where scrap drywall can be delivered (provided the material does not contain asbestos) (Metro Vancouver, 2012).

A variety of recycling markets have been developed for gypsum drywall, including for purposes such as agricultural soil amendments and manufacture of new drywall, so the increase in the diversion of drywall for recycling would be expected to reduce the amount of drywall that is deposited into landfills. As with any recycled product, the ability to effectively recycle a waste component depends on market demand, the cost of virgin materials or materials being replaced by the recycled product, disposal costs, transport costs, and other factors.

Another practice that may reduce H_2S emissions at disposal facilities that accept RSM is to limit the SO_4^{2-} content of the RSM delivered to the facility. Musson et al. (2008) developed a method to establish SO_4^{2-} content in RSM, which can be used by C&D recyclers to track performance related to gypsum drywall removal and provides receiving facilities with important data to understand the SO_4^{2-} content (and

therefore potential to produce H_2S) in RSM that is accepted. In some states (e.g., Massachusetts and New Hampshire), the removal of gypsum drywall at the front end of the C&D recycling process is required where feasible. Landfills may also develop specifications for RSM that include sampling procedures and sampling personnel training requirements, and chemical limits of the RSM, which may include SO_4^{2-} .

While the practice of separating drywall and limiting the SO_4^{2-} content of RSM produced by C&D recycling facilities should decrease the amount of reducible sulfur entering a landfill, the specification of maximum SO_4^{2-} limits at a landfill that uses RSM may not necessarily prevent all H₂S emission problems. For example, Carlton et al. (2005) reported that an MSW landfill that accepted C&D fines specified and routinely met a SO_4^{2-} limit of 3%, but odor problems at the facility persisted anyway. Another consideration for operators that specify SO_4^{2-} limits in RSM is that the results can be somewhat variable between C&D recyclers and even at the same recycling facility. For instance, Anderson et al. (2010) summarized SO_4^{2-} content data from eight C&D recyclers in Massachusetts and found the mean SO_4^{2-} content of C&D fines to range from 1.6% to 8.7%. Data presented by Anderson et al. (2010) for one C&D recycling facility over a 2-year sampling period showed a SO_4^{2-} content range from approximately 0% to 15%. Anderson et al. (2010) also noted data from a landfill that monofilled C&D fines and layered the fines with material to reduce odors, which suggested some effectiveness, but further study was needed to more closely evaluate this technique.

3.1.2 Moisture Control

Minimization of moisture contact with gypsum-containing waste is a key to minimizing H₂S generation; thus, practices to reduce the infiltration of moisture into the waste are expected to reduce the production and emissions of H_2S – note that many of these practices can help to reduce the emission of other gases that are not in the form of a reduced sulfur compound. These practices, which are summarized in *Table 3-1*, are expected to apply to both C&D and MSW landfills. It is noted that some of the practices (such as minimizing the size of the working face) are more commonly required in MSW landfill permits.

Landfilling Practice	Discussion			
Minimizing the Landfill Working Face	Reducing the size of the working face reduces the potential for surface water to contact and percolate through the waste mass. A smaller working face also reduces the amount of cover soil needed, thus the quantity of soil needed would be less, which would be a benefit at sites that use RSM as daily cover. A smaller working face would also reduce the area of waste open to the atmosphere, which would be expected to reduce odorous gas emissions compared to a facility with a larger working face.			
Working Face Grading	Grading the active face for drainage helps to avoid ponding of water on the landfill surface and thus encourages runoff.			
Landfill Phasing	The use of intermediate cover, particularly on side slopes as a landfill is built up, would be expected to encourage surface water runoff and reduce the amount of moisture that infiltrates into the waste mass.			
Using Daily or Weekly Cover	Many states do not have a regulatory minimum requirement to apply cover soil at C&D landfills. The use of cover soil can help reduce the migration of liquid into and through the waste, and can act as a barrier and removal mechanism for H ₂ S, depending on the cover material used. Soil has the potential to absorb released H ₂ S that passes through the cover,			

Table 3-1. Summary of and Discussion of Moisture Control and Cover Soil Use Techniques toMinimize the Production and Emissions of H2S

(continued)

Table 3-1. Summary of and Discussion of Moisture Control and Cover Soil Use Techniques to Minimize the Production and Emissions of H₂S (continued)

Landfilling Practice	Discussion
Disposal Practices with Drywall	 Instituting unique practices at landfills that accept gypsum drywall may help to mitigate issues that can occur when the materials are exposed to moisture. Options may include: Placing loads of material containing drywall in areas of the active landfill face that are at a higher elevation, which would decrease the potential of moisture contact compared with placement in a low-lying area on the active face. Immediately placing additional waste or a cover (e.g., temporary tarp or soil cover) on top of newly-placed loads that contain gypsum drywall to reduce the likelihood of contact with stormwater. Segregating received drywall to distinct areas and perhaps making note in operations records of areas where larger amounts of drywall were placed (similar to how landfills that accept asbestos make note of incoming quantities and disposal location). This practice would be expected to consolidate locations where H₂S may be formed and facilitate future H₂S mitigation, if needed.
Run-On and Run-	The use of run-on controls will prevent stormwater from encroaching onto or into the
Off Controls for Stormwater	landfill, while run-off controls help to divert stormwater to appropriate stormwater management areas.
Use and Proper Operation of Leachate Removal and Treatment Systems	Leachate build-up on the bottom of landfills can occur if there is naturally-occurring low permeability material beneath the waste, and can occur with an improperly functioning leachate collection system. As an example of the impact that liquid levels can have on H ₂ S production, Bergersen and Haarstad (2008) observed in the laboratory an approximately 8-fold difference in H ₂ S off-gassing from effluent from submerged MSW mixtures containing crushed gypsum board compared to MSW mixtures with crushed gypsum board with a low water content.

3.1.3 Bacterial Inhibition

The use of bacterial inhibitors to reduce the proliferation of SRBs has been evaluated at the laboratory scale. Isa and Anderson (2005) evaluated the use of molybdate (MoO_4^{2-}) as an SRB inhibitor in a continuous feed anaerobic digestion process. The findings showed that SRB and CH₄-producing bacteria were inhibited; thus, such a solution may not be appropriate for MSW landfills that are recovering LFG for energy. Xu et al. (2011) evaluated the use of different chemical inhibitors at the laboratory scale, including sodium molybdate on the production of H₂S from gypsum drywall. The results showed that a three orders of magnitude decrease in H₂S concentration was observed when the inhibitor was used, which was attributed to the development of pH conditions unfavorable to biological growth. Overall, the use of bacterial inhibitors has not been examined on a field scale and further evaluation is needed to assess the effectiveness of a bacterial inhibitor on H₂S production and potential environmental impacts (such as resultant leachate concentrations and subsequent potential impact to groundwater).

3.2 Methods to Control H₂S Emission

3.2.1 Leachate Management

Once leachate is generated in a landfill, it is either collected in a leachate drainage system or infiltrates into the groundwater (in the case of unlined landfills). H_2S contained in leachate volatilizes in accordance with Henry's law due to new concentration and pressure gradients outside of the landfill. Profumo et al. (1992) demonstrated that leachate can be a significant source of H_2S . Thus, the identification and control of leachate (e.g., seeps at side slopes, at the landfill surface, or at the toe of the landfill) may help to limit exposure of raw leachate to the atmosphere and thus reduce the potential for H_2S to volatilize into the atmosphere. An additional consideration is acknowledging the potential hazardous atmospheres that can form in areas where leachate may accumulate, including gas wells, leachate sumps and cleanout lines, and tanks, and ensuring that landfill personnel are aware of these areas and the potential for H_2S to be present. Oxidation of H_2S inside of leachate containment areas such as sumps can prevent the eventual off-gassing of H_2S ; an oxidizing agent (e.g., hydrogen peroxide) oxidizes H_2S to elemental sulfur or SO_4^{2-} , depending on pH. Also, aerated leachate ponds (e.g., using floating aerators) are commonly used to lower BOD and COD levels in leachate, which can oxidize RSCs as well.

3.2.2 Cover Soil Amendments

Research regarding various landfill cover amendments to reduce H_2S through precipitation, adsorption, or oxidation has been conducted at the laboratory and field scale. Prior to consideration of a soil amendment, it should be noted that the use of natural soils has shown the ability to decrease the concentration gradient (one of the main driving forces behind H_2S emissions, as described in Section 2) and thus provide time for H_2S to be adsorbed or removed. For example, Xu et al. (2010) observed up to a 60% removal capacity of H_2S by natural soils in a set of field experiments in Florida.

In some cases, the use of natural soils may require supplementation to further enhance the removal or mitigation of H_2S . Below is a summary of cover soil amendments that have been used at the laboratory or field scale and shown to decrease H_2S emissions. Note that the effectiveness (short-term and long-term) depends on the amendment blend that is used and specific site characteristics such as source H_2S concentration, atmospheric characteristics, and landfill characteristics. The materials list provided in this section represents examples of amendments listed could potentially be used at landfills other than those that accept C&D debris and MSW (such as an industrial waste facility that accepts paper mill sludge); however, factors such as waste mass stability should be considered when applying cover amendments to industrial waste facilities. The selection and use of a cover soil amendment must be made with consideration of numerous factors, including economics, site permit conditions, and other relevant site characteristics.

- Ammonium nitrate fertilizer. Sungthong (2010) and Sungthong and Reinhart (2011) evaluated the removal of H₂S at the lab scale by ammonium nitrate fertilizer, which proceeded under the autotrophic denitrification process. An analysis of an example 10-acre MSW landfill (modeled after an actual operating facility) using measured H₂S concentrations (which had H₂S concentrations in collected LFG ranging from 480 to 2,800 µL/L) suggested that the application of 157,000 kg of 34% nitrogen fertilizer could sufficiently remove the anticipated 15-year emission amount of 80,900 kg of H₂S.
- *Coal ash*. CMRA (n.d.) reported that a mixture of 30% coal ash and 70% RSM helped to control H₂S emissions by an order of magnitude in a C&D cell. New Hampshire evaluated the use of a 50% coal ash and 50% RSM blend that indicated H₂S reduction (NHDES, 2004). In most cases, the use of coal ash would likely only be allowable at an MSW landfill because of restrictions on using/disposing ash in many C&D landfills based on a review of state regulations (U.S. EPA, 2012b).
- Compost/biocover soil. Xu et al. (2010a) showed that a yard waste-derived compost in a field study at a C&D landfill attenuated H₂S more effectively than sandy soil. Materials similar to composted yard waste such as chipped waste wood or bark may also be effective. Bergersen and Haarstad (2008) used organic filter materials and observed H₂S removal capacities of 215 and 387 mg S/kg for spruce bark and wood chips, respectively.
- Concrete fines. Plaza et al. (2007) showed that concrete fines (those smaller than 2.5 cm) reduced H₂S concentrations by 99% in a laboratory column study. At the field scale, Xu et al. (2010a) covered plots at a C&D debris landfill and observed a 90% reduction in H₂S levels, which was attributed to a pH shift caused by the high-pH concrete fines and adsorption of H₂S onto the fines.

- *Fuller's earth*. This material is a clay-like substance that has been used as an absorbent in numerous applications (e.g., cat litter). Commercial products and patents have been developed that are Fuller's earth-based. Lab-scale test results presented in USPTO (2005) indicate approximately 0.2 mg of H₂S could be removed (to levels at a normal human odor threshold) per g of a blend comprised mostly of Fuller's earth, or approximately 65 to 75 tons per acre of landfill surface for a 2-cm thick layer.
- *Lime*. Plaza et al. (2007) showed that lime-amended soil (5% by weight mixture) removed H₂S substantially in a laboratory column study. Xu et al. (2010a) conducted a field study that evaluated a 1% and 3% by weight lime-soil mixture on the surface of a C&D landfill. In both cases, the lime-amended soils were shown to attenuate H₂S, which was attributed to changing of pH conditions and physical removal. Sungthong (2010) calculated that approximately 176,000 kg of hydrated lime would be needed to create a 1% (wt) blend with a 2-ft thick cover soil to attenuate expected H₂S emissions from an example 10-acre landfill (described in the ammonium nitrate fertilizer section above) with a 15-year H₂S emissions amount of 80,900 kg.
- Steel tire shreds. Anunsen (2007) showed that M1 steel from a tire shredder placed near passive LFG vents at an MSW landfill showed the attenuation of H₂S over a range of flow rates. Xu et al. (2010b) showed substantial attenuation of H₂S (from 100 μL/L to 1 μL/L) using tire-derived steel in a simulated landfill cover.
- Metallic filter materials. Metallic filter materials removed H₂S (600–1,200 µL/L) in laboratory experiments where H₂S was generated from submerged waste materials with and without gypsum drywall in column reactors (Bergersen and Haarstad, 2008). Iron oxide, iron-rich sewage sludge compost, and a 3:1 mixture of bottom ash and iron oxide removed 983 mg S/kg, 762 mg S/kg, and 3,345 mg S/kg, respectively.

3.2.3 Capping Systems

Capping a landfill with a low-permeability layer can help to remediate H₂S emission by both curbing production and preventing emissions from entering the atmosphere. Landfill capping systems limit or prevent infiltration of stormwater (and thus the production of leachate) into the waste. Once H₂S has been generated in a landfill, the cap systems provide a barrier to uncontrolled venting of LFG. The use of a capping system in combination with a GCCS minimizes escape of H₂S gas. The deployment of capping systems in combination with an active GCCS has been recommended as a BMP for H₂S control at both MSW and C&D landfills (Waste Management, 2005; Massachusetts DEP, 2007). Capping systems are often part of a final or intermediate cover at landfills, and both will be discussed in this section. Discussion regarding the integration of a capping system with an active GCCS is presented in Section 3.2.5.

Intermediate cover is intended to provide a greater barrier between the waste and the atmosphere than daily cover and in addition provide cover to an area that will not to be filled over for an extended period of time and may need to be driven over in order to fill the landfill sequentially. While daily cover typically consists of a six-inch layer of soil (or approved equivalent), intermediate cover is typically thicker (e.g., 1 ft) and is normally compacted to allow ease of access. Thus, intermediate cover with a greater thickness than a typical daily cover is expected to provide the benefits described in Section 3.2.2 for soil covers, but also potentially facilitate LFG collection as well. Temporary membranes (synthetic materials) can also be utilized as an intermediate cap prior to the installation of a final permitted capping system. In cases where intermediate covers cannot be constructed at a slope to allow for positive drainage, supplemental piping and drainage infrastructure may be needed to prevent ponding of stormwater on the landfill surface.

The components of final cover systems vary depending on the type of landfill and the specific conditions of a disposal facility's permit. Low-permeability final cover normally consists of the following layers (from top to bottom): soil layer capable of supporting vegetation, drainage layer (e.g., geonet overlain by geotextile to prevent clogging), barrier layer, grading layer (this is sometimes overlain by a high-permeability layer, such as coarse sand, to allow the transmission of LFG to collection points). The barrier layer can consist of either synthetic (e.g., HDPE) or natural materials (e.g., low-permeability compacted clay). For facilities that do not require a low-permeability final cover, the final cover configuration typically consists of (from top to bottom) a soil layer capable of supporting vegetation and a soil layer to provide a buffer distance between the top of the final cover and the top of the waste mass (e.g., 2-ft thick).

At facilities where H_2S emissions are problematic, the installation of final cover as soon as final waste filling grades are reached can aid in controlling H_2S when coupled with some form of LFG controls. This practice may or may not be accelerated based on permit requirements, and the decision to deploy a final cap earlier than a facility's permit requires may be necessary for practically handling H_2S emission problems in some cases.

3.2.4 Odor Neutralizers

Odor neutralizers can be utilized to mask or mitigate odors from H_2S . Odor neutralizers are chemicals that react with H_2S to form a nonodorous compound, or may simply act to mask odors. Other odor-neutralizing agents work to encapsulate materials and thus block odors from escaping. Odor neutralizers are often misted in a spray, which is then applied at landfills to the working face, near the working face, or near or at the site perimeter, depending on where odor concerns are present.

Examples of chemicals that act as H₂S odor neutralizers include bleach, sodium bicarbonate, ammonium bicarbonate, magnesium bicarbonate, caustic soda, amines, and other proprietary chemicals. Neutralizers are often sold in concentrated form and are diluted upon deployment; in some cases, dilution ratios can be controlled, depending on the severity of odor issues or the area being managed.

Odor neutralizing chemicals in aqueous form can be applied via conventional agricultural sprayers, vapor diffusion systems that use heat to vaporize chemicals (essential oils) and then blow them through a perforated pipe, water trucks that employ spray bars and hoses for heavy working face product application, and fogging or industrial misting systems. Passive odor neutralizers (such as deodorizing sleeves that can be hung at different areas at a site) may be used as well, where a solid granule or powder neutralizes the odor.

In general, odor neutralizers are considered temporary measures as the products typically do not prevent the production of odorous compounds.

3.2.5 LFG Collection and Treatment

LFG collection involves the installation of collection devices (e.g., wells) into the waste to control the flow of LFG, although LFG controls may also include collectors located beyond the perimeter of the waste. LFG can be passively vented or actively controlled. No federal standards for active LFG control exist for C&D landfills, but federal standards (e.g., those found in the New Source Performance Standards for MSW Landfills, 40 CFR Part 63 Subpart WWW) mandate active gas controls once an MSW landfill reaches a certain size or emission rate of nonmethane organic compounds (NMOC). H₂S generated in landfills is considered a trace component of LFG, and the installation of an active GCCS solely to control H₂S is not very common because of the extensive design, permitting, and construction needs associated with an active GCCS.

Collected LFG can be vented to the atmosphere (and typically routed through treatment media or individual destruction devices), routed to a temporary or permanent flare station to combust the collected LFG, or utilized for energy production. Passive vents within the waste could be embedded within a

treatment medium as well (e.g., wood chips), which could provide an added opportunity to remove odorcausing compounds before the gas is vented to the atmosphere or routed for further treatment. Active GCCS systems use compressors or vacuums to create a pressure gradient to route LFG to a collection point. The number and spacing of collection wells depends on waste density, pressure gradients required, and LFG production expected (which depends on the composition of the waste). The U.S. EPA Landfill Methane Outreach Program reports that more than 500 MSW landfills have an LFG to energy project and more than 500 landfills are candidates for an energy project.

Active LFG control at C&D landfills may be complicated by the fact that substantial quantities of other gases such as CH₄ are not produced, which is a reflection of the types of waste normally deposited in C&D landfills (refer to Section 2.5 for discussion of waste composition at C&D landfills). In cases where active LFG controls are used at C&D landfills, supplemental fuel may be required to provide enough BTU content to combust the gas (e.g., an active GCCS at a landfill in New York used natural gas as a supplemental fuel (McCarron, 2007)). Solar spark flares have been used in cases where lower LFG flow rates or CH₄ concentrations are present (e.g., at C&D landfills, in areas of MSW landfills that do not yet require active control, or at areas of landfills where LFG may build up such as leachate lines).

As mentioned previously, high levels of H_2S in LFG can be problematic in LFG to energy projects—for example, Lopez (2012) indicates that the frequency of maintenance and engine overhauls at energy projects that convert collected LFG to electricity is greater when H_2S concentrations are greater because of wear and corrosion of engine parts. High H_2S concentrations in LFG may also void or limit manufacturer warranty (General Electric, 2009). Rasi et al. (2011) reported that a recommended maximum H_2S concentration for biogas (including LFG) used in boilers and internal combustion engines is 1,000 µL/L. GE Jenbacher recommends H_2S limits of 700 mg/10 kWh and 1,200 mg/10 kWh for LFG engines with and without catalytic converters, which equate to 245 µL/L and 419 µL/L, respectively (General Electric, 2009). In cases where LFG is cleaned up to remove CO₂ and other constituents for use as a vehicle fuel or for delivery to natural gas pipelines, H_2S concentrations of less than 4 µL/L are normally required (Wentworth, 2009).

Collected LFG with a high concentration of H_2S can result in the emission of SO_2 following combustion at a LFG destruction device. SO_2 is a primary pollutant subject to national ambient air quality standards in the United States, and Title V operating air permits at MSW landfills may have limits on the emissions of SO_2 . In cases where high LFG collection rates and high concentrations of H_2S are present, the permitspecified SO_2 emission limits could be reached, thus potentially requiring the implementation of a system to reduce H_2S concentrations prior to combustion of the LFG. For example, a study at a large MSW landfill in Virginia estimated that the facility's Title V SO_2 emission limit of 240 tons per year could be exceeded with a LFG collection rate of 8,000 standard cubic feet per minute and an H_2S concentration of 770 µL/L (Tennant, 2012).

A variety of treatment technologies are available to reduce the concentration of H_2S in collected LFG. *Table 3-2* presents a summary of LFG treatment technologies specific to H_2S removal or reduction.

Treatment Technology	Further Classification	Specific Chemicals, Mechanisms, Results		
Liquid Treatment (Scrubbers to treat gas flow) Alkaline Solutions Alkaline Solutions Caustic Soda (NaOH) NaHS or Na ₂ S solid salts are formed (Siem Other hydroxides (KOH, KI)		 NaHS or Na₂S solid salts are formed (Siemak, 1985) Other hydroxides (KOH, KI) 		
	Amine Solutions	Carbonate Solutions (Na ₂ CO ₃ , MgCO ₃) Sulfaclear®, Almont 6,6B, 6F® Methyl Di-ethanol Amine (MDEA) (Pandey 2005)		
	Nitrite Solutions	$3H_2S + NaNO_2 \rightarrow NH_3 + 3S + NaOH$		
Liquid Treatment (Scrubbers to treat gas flow)	Metal Solutions	 Metal SO₄²⁻ Solutions CuSO₄, ZnSO₄, FeSO₄ examined by ter Maat et al. (2005) in laboratory Precipitates metal sulfide, metal carbonate, or metal hydroxide (pH dependent) CuSO₄ purified biogas in a pilot scale project (85% removal of influent H₂S at 170 µL/L) SulFerox® H₂S reacts with aqueous ferric iron, forms S⁰ 		
Solid Advantion	Activated Carbon	 Norit ROZ3® Steam activated carbon, designed for H₂S and mercaptan removal Can be diluted with less selective, less costly AC species (Norit RB4W) for similar H₂S removal (up to 70% dilution) (Mescia et al. 2011) Field scale experiments showed H₂S (245 µL/L) removal to 1 µL/L; removal of 71.99 gH₂S/kg AC (30% ROZ3) (Mescia et al. 2011) 		
Solid Adsorption Treatment	Ash	 MSW bottom ash Removed H₂S (100 μL/L), CH₃SH (4 μL/L), and (CH₃)₂S (30 μL/L) from field LFG; mass removals of 3 g, 44 mg, and 86 mg per kg ash, respectively. Contact time played a large role (Ducom et al. 2009). 		
	Metal Oxides/Catalysts	Iron sponges Produces metal sulfides • Pyrite (FeS ₂), phalerite (ZnS), Molybdenite (MoS ₂) SulfaTreat®		
Chemical Process	Oxidizing Agents	 Hydrogen Peroxide (H₂O₂) Can form elemental sulfur or SO₄²⁻ (pH dependent) 		
Biological Processes	Sulfur Oxidation	 ThioPaq® Biologically mediated HS⁻ to elemental sulfur (S⁰) after alkaline scrubbing Regenerates caustic soda for reuse (Tennant 2012) Bio-Scrubber® 		

Table 3-2. Summary of Treatment Technologies to Reduce H₂S Concentrations in Collected LFG

4. Site Investigation and Monitoring Techniques

4.1 Site Inspection Procedure Considerations

Site investigations may occur as part of routine operations or in response to an odor complaint. If odor complaints are received at a landfill, pertinent information about the complaint (e.g., location of complaint, time of day, weather conditions at the time of complaint, assessment of site conditions at the time of the complaint) should be recorded.

Multiple states have developed BMP or guidance for the evaluation of odor that may be emanating from a landfill and/or require that landfills maintain their own odor management plan to address odor. The practices from several BMP guides were evaluated and the key elements related to site inspection considerations for landfill personnel are summarized below.

- Identify any potential sources of odor from accepted wastes (e.g., dead animals, gypsum drywall (bulk or size-reduced), processing of yard waste, biosolids, other industrial wastes).
- If a GCCS is present, evaluate areas where elevated temperatures are present, as these may be areas of higher decomposition and potential areas of H₂S production and emissions.
- Perform site inspections during early morning or late evening, when odors are most likely to be observed.
- Use monitoring instruments that are properly calibrated to the range of H₂S concentrations expected, and use such equipment consistently with manufacturer specifications.
- Inspect and monitor for H₂S along the site perimeter, particularly paying attention to site topography as H₂S may settle in low-lying areas.
- Monitor for H₂S near and downwind of the working face.
- Record all measured H₂S concentrations and the locations where they were measured.
- Inspect for any leachate seeps or ponded leachate, document and address on- and off-site structures where leachate may migrate and emit H₂S gas, causing exposure to workers and nearby residents.
- Document information regarding weather conditions and area(s) of the site inspection, including (but not limited to):
 - o Date and time
 - Weather conditions
 - Temperature
 - Wind speed and direction
 - Cloud cover
 - Ongoing or recent precipitation events
 - Name of person conducting inspection
 - Areas inspected (written description and/or map)
 - \circ Locations or observations from other potential nearby sources of odor or H₂S (e.g., wastewater treatment plant)
- Maintain documented site inspection records on site.

Another important consideration related to site monitoring is awareness of confined spaces. Confined spaces are generally defined as areas with limited entry or exit that are not designed or intended for

continuous human occupancy. Confined spaces have the potential for hazardous atmospheres, including explosive gas concentrations, concentrations of gases that are toxic to humans, and low oxygen. Examples of confined spaces at C&D and/or MSW landfills include vaults, tanks, pipes, storage bins, sumps, and trenches.

Many landfills are required to have confined space entry plans intended to prevent someone from entering a toxic/oxygen-deficient environment with the potential for asphyxiation. These plans emphasize the buddy system, where if one is entering a confined space, another person stands by ready to aid an escape from the confined space; in some cases a harness or other safety equipment may be required (Bolton, 1995). At a minimum, site personnel should be trained to understand how to identify a confined space and know to not enter a confined space unless in accordance with a confined space entry plan.

4.2 H₂S Monitoring Techniques

Because of the low odor threshold associated with H₂S, the detection of odors by site personnel may serve as an initial indication of H₂S emissions at a site. However, as discussed previously, H₂S present at higher concentrations may not be detectable because of the olfactory paralysis that can occur. OSHA (2005) recommends that workers not rely on the sense of smell to indicate the continuing presence of H₂S or to warn of hazardous concentrations. Monitoring of H₂S concentrations can be part of an odor or H₂S evaluation plan. A variety of instruments have been developed that detect H₂S over a range of concentrations for a variety of purposes (e.g., assessing human exposure levels, measuring concentrations in confined spaces or gas collection wells, measuring concentrations in ambient air).

It is important when selecting a device that the purpose of the monitoring is clear and that the appropriate limitations (e.g., detection limits, potential interferences) of a given instrument are understood so that the data gathered meet the H_2S monitoring program's objectives. A presentation and discussion of common types of H_2S monitoring devices is presented in *Table 4-1*.

Sampler Type	Applications and Limitations/Interforences						
	Applications and Limitations/Interferences						
Personal badges	Disposable devices normally used for detecting acute H ₂ S exposure. Clips on clothing or fits in a pocket near the wearer's breathing zone. Can produce visual, vibratory, or audible alarm upon exceedance of a set standard (10 μ L/L is common) or simply produce a color change. H ₂ S reacts with an indicator layer (e.g., lead acetate). Visual color comparison to exposure dose color (in μ L/L*hr) is used to calculate average concentration by dividing this value (in μ L/L*hr) by exposure time. Some can detect other gases in addition to H ₂ S. Temperature limitations may be an issue (one sampler reported in the 16 °C – 36 °C range). They can also be used as stationary monitors over limited periods of time simply by affixing to a pole with the detector facing the emission source. Typical H ₂ S range: 1–240 μ L/L*hr						
	Example products: Industrial Scientific Gas Badge Pro and Gas Badge Plus, Chromair Gas Monitoring Badge, Safeair Gas Monitoring Badge, BW Honeywell Gas Alert Clip Extreme H ₂ S Monitor						
Multi-gas meters	Standard multi-gas samplers typically use an active sample pump to draw gas into the inlet orifice. Used when monitoring of other gases is necessary (e.g., CH ₄ , CO ₂ , O ₂ , CO). Because standards often exist for CH ₄ or CO concentrations on site and at the perimeter boundary (i.e., a certain percentage of the LEL) monitoring of H ₂ S can be conducted in conjunction with these gases. Meters are typically battery-operated and use a microprocessor to display concentrations on a display and can often store data via a data logger; some have alarms that sound at significant concentration levels. Regular calibration is necessary. More elaborate systems are available that operate using an analyzer with a near-infrared laser that quantifies spectral features of molecules in a sample gas passed through an optical measurement cavity. This technology also allows for vehicle mounting and simultaneous gas measurement and mapping of H ₂ S and CH ₄ concentrations.						
	Typical H ₂ S range: 0–100 μ L/L, although other ranges are available						
	Example standard multi-gas samplers: Gas Alert Mac XTII, MSA Altair 4X Multigas Detector, MultiRAE Plus 4 Gas Meter, RKI GX-2003 Multi Gas Monitor, RKI Eagle 2,						
Electrochemical cells/pods	Example near-infrared laser gas analyzer with mapping capability: Picarro Model G2204 Sensors designed for a specific gas measurement. Operate through diffusion of H ₂ S (or other gas of interest) into measurement cell where an oxidation (in the case of H ₂ S) or reduction reaction at the working electrode occurs. Working electrode is typically contained in an acidic solution. A measureable voltage is produced upon oxidation; the measured gas concentration is linearly proportional to the electrical output of the gas sensor.						
	Other gases (NO, H ₂ , etc.) can cause some interference. Can also utilize a reference electrode that eliminates interference from side reactions. Low temperatures (<freezing) and="" cannot="" cell="" chemical="" current.="" environments="" for="" function.="" h<sub="" is="" low="" necessary="" not="" oxygen="" reactions="" reactions;="" stop="" sustain="" the="" will="">2S is a gas that will oxidize; the presence of a reducible gas may interfere.</freezing)>						
	Typical H ₂ S range: 1–500 μ L/L						
	Example products: CES Landtec GEM 2000/5000 (add-on pod or built-in cell), Delphian Electrochemical Sensor 755, Kimessa AG GSE 627						

Table 4-1. Examples of H₂S Monitoring Devices, Applications, and Limitations

(continued)

Sampler Type	Applications and Limitations/Interferences						
Dedicated H ₂ S meters	Specialty meters that can detect H ₂ S over a range of low and intermediate concentrations. Technology used includes gold film sensors that work via selective adsorption and desorption. Interference may be caused by some constituents (e.g., chlorine, ammonia, NO ₂ , and mercaptans) but filters are available to reduce interference. Detection limits on several of the meters were reported as 0.003 µL/L. Meters can be set for either a single sample or survey mode; survey mode provides quicker source detection. Another technology includes the Honeywell Chemcassette system, which uses an optical scanning system to detect a gas via color change. Other technologies include pulsed fluorescence, which converts H ₂ S to SO ₂ and measures the SO ₂ , thus the measurement of H ₂ S is indirect. Typical H ₂ S Range: 0.003–50 µL/L Example products: Arizona Instruments Jerome J605, Jerome 631-X, Jerome 631-XE, Honeywell Single Point Monitor, Thermo Scientific 451i						
Remote systems	These systems utilize detectors that can be placed in an area where continuous, remote monitoring is desired (i.e., site perimeter boundary, confined spaces onsite). Remote sensor units are either wired or wirelessly connected to a controller. Detectors can be self-powered (e.g., solar, battery) and selected based on the desired range of H ₂ S concentrations to be measured. Systems can be changed or expanded to include many monitoring points. Electrochemical sensors are sometimes used for the sensor components. Visual and audible alarms can be produced upon exceedance of a given gas concentration. It is recommended that fixed monitors be placed in low spots due to the H ₂ S-specific gravity. These dedicated meters are typically expensive as they require infrastructure installation.						
Colorimetric detector tubes	 One-time use tubes (with printed H₂S scales on the tube) specific to a certain gas and concentration range is opened (tips broken) and inserted into a pump. Ambient air or gas (e.g., collected in a nonreactive sample container) to measure H₂S is pumped through the tube. Measurements are indicated by the length of the color change in relation to the scale printed on the tube; adjustment factors for sample volume, temperature, and humidity can be applied using manufacturer datasheets. Tubes do not require calibration and may be subject to some interferants, depending on product; range-specific tubes are sold (e.g., low, high, ultra-high). Standard range of 25–250 μL/L. Passive colorimetric detection tubes can also be used for longer-term time-weighted average measurements. Example products: Dräger Detector Tubes, RAE Systems H₂S Colorimetric Gas Detection Tubes 						
Electronic noses	These devices contain an array of sensors that quickly analyze multiple molecules at once; they are utilized in the food, beverage, and perfume industry extensively. They generally consist of a wide array of technologies, including conducting polymer sensors, sintered metal oxide semi-conductors, catalytic metals, organic semi-conductors, surface wave gas sensors, quartz crystal microbalance, electrochemical, smell-seeing, and field effect transistors (Otles 2008).						

Table 4-1.	Examples of H ₂ S Monitoring Devices, Applications, and Limitations (continued)
	Examples of fige monitoring bettees, Applications, and Emitations (continued)

5. BMP Framework to Manage H₂S Emissions from Disposal of Gypsum Drywall

Most permitted landfills are required to develop and maintain operations plans that cover a wide range of issues and considerations. Normally, odor management is addressed in broad landfill operations plans, but often do not require the background and detail needed to address the potentially severe issues caused by elevated H₂S emissions. Thus, in some cases the development of a site-specific BMP guide may be necessary to allow landfill owners and operators to understand the specific issues and challenges associated with H₂S, provide the landfill operators with valuable documentation that can be used to demonstrate the procedures used to address H₂S emissions, and provide direction to landfill staff so that issues encountered with H₂S emissions can be observed and managed more rapidly. *Figure 5-1* presents a simplified flow chart that can be used by landfill owners and operators as a starting point to develop a site-specific BMP guide for H₂S emissions management. Each step presented in Figure 5-1 is described in more detail below.

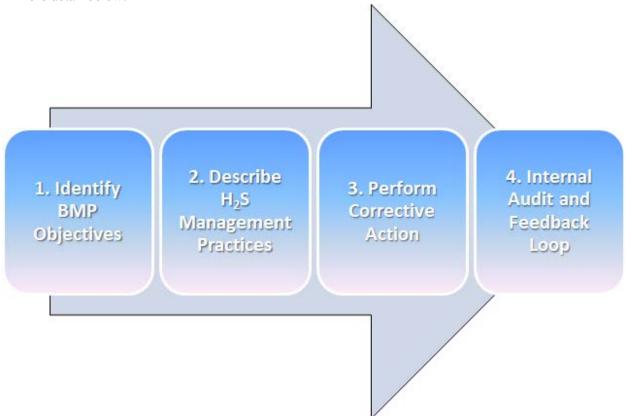


Figure 5-1. Framework for Developing a BMP Guide for Managing H₂S at C&D or MSW Landfills

A discussion of each of the framework elements is provided below.

1. Identify the BMP guide objectives. Each landfill's site-specific considerations should be accounted for when the BMP guide is developed. For example, a landfill that accepts large amounts of drywall but has never had odor issues or H₂S emission issues may structure the BMP guide in a way that includes measures to help prevent H₂S emissions. This would be in contrast to the structure of a BMP guide for an MSW landfill that beneficially uses collected LFG and has not had odor issues but has high H₂S levels in the collected LFG. In this case, the guide may be focused on monitoring and maintenance associated with an H₂S treatment system.

- 2. Describe the management practices to be employed. The BMP guide would identify key information, such as responsible parties and lines of communication for maintenance, monitoring, and inspections; types of equipment to use for monitoring; frequency and location(s) of H₂S monitoring (including documentation requirements); and an enumeration of practices that the site adopts based on site-specific conditions to mitigate or otherwise manage H₂S emissions. The conditions and ultimately the management practices employed should consider the variety of sources and conditions that may lead to H₂S production and emission (as described in Section 2) and the procedures that can be used to reduce emissions (as described in Section 3). The description of management practices should also identify action levels that are tailored to the facility's needs, which will be used in conjunction with corrective actions (Step 3 below).
- **3. Perform corrective action.** The BMP guide should discuss actions that should be taken if H₂S emissions or concentrations are greater than target levels established for the facility. The corrective action steps may include equipment or monitoring instrument evaluation or calibration, assessment and modification of operating practices, or other activities to mitigate H₂S emissions.
- **4. Internal audit and feedback loop.** The efficacy of the BMP guide should be periodically evaluated or audited to ensure that the guide matches up with the needs of the site, as operating needs and conditions at landfills may change frequently. The BMP guide should include a mechanism to provide an effective feedback loop so that gaps or limitations in the procedures for monitoring and addressing H₂S emissions can be quickly identified and remedied.

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APPENDIX A

		2010	va) (all uni					
Guideline	Exposure Duration							
	10 min	30 min	1 hr	4 hr	8 hr	Other		
AEGL-1	0.75	0.60	0.51	0.36	0.33			
AEGL-2	41	32	27	20	17			
AEGL-3	76	59	50	37	31			
ERPG-1			0.1					
ERPG-2			30					
ERPG-3			100					
Acute MRL						0.07 (0 – 14		
						days)		
Intermediate						0.02 (14 – 365		
MRL						days)		
EEGL	50					10 (24 hr)		
IDLH (NIOSH)		100						
TLV-TWA (ACGIH)					1			
PEL (OSHA)	50					20 (peak)		
TLV-STEL (ACGIH)						15 (15 min)		

Table A-1. Summary of Standards and Guideline Values for Airborne H2S (adapted from US EPA2010a) (all units in ppm)

Notes and definitions of terms:

<u>AEGL</u>. Acute Exposure Guideline Levels. **AEGL-1** is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure. **AEGL-2** is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape. **AEGL-3** is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

<u>ERPG</u>. Emergency Response Planning Guideline. **ERPG-1** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor. **ERPG-2** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hr without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. **ERPG-3** is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 hour without experiencing or developing or developing life-threatening health effects.

<u>Acute/Intermediate Minimum Risk Level (MRL)</u>. MRLs are developed by ATSDR and are set below levels that, based on current information, might cause adverse health effects in the people most sensitive to such substance-induced effects. Acute is 1-14 days exposure and intermediate is >14-364 days.

EEGL. National Research Council Emergency Exposure Guidance Levels (EEGLs).

<u>IDLH.</u> Immediately Dangerous to Life and Health. An atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.

<u>TLV-TWA.</u> Threshold Limit Value – Time-Weighted Average. The TWA concentration for a conventional 8-hour work day and 40-hour work week, to which it is believed nearly all workers may be repeatedly exposed each day without adverse effect.

PEL. Permissible Exposure Limit. An exposure limit that is published and enforced by OSHA as a legal standard.

<u>TLV-STEL</u>. As defined by ACGIH, <u>concentration</u> to which it is believed that workers can be <u>exposed</u> continuously for a short period of time without suffering from 1) irritation, 2) <u>chronic</u> or irreversible tissue damage, or 3) <u>narcosis</u> of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded.