Technical Assistance Report

Hydrogen Sulfide in Ambient Air near Saufley Construction and Demolition Debris Landfill

Bellview, Escambia County, Florida

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Prepared by: Florida Department of Health, Bureau of Community Environmental Health Under Cooperative Agreement with U. S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry

Background:

- The Saufley Construction and Demolition Debris Landfill is located in Bellview, Escambia County, Florida. Considerable expansion of the landfill has occurred due to large volumes of construction and demolition debris generated during the 2004 and 2005 hurricane seasons. In the fall of 2005, the Escambia County Health Department received numerous health complaints from residents living near the landfill. Concerns due to odors and smoke emitted by the landfill included respiratory problems, mucous membrane irritation, headaches, and nausea. Several area physicians also contacted the health department with concerns that their patients' health was adversely affected by landfill emissions.
- Odors and their corresponding health effects prompted a request for technical assistance to the Agency for Toxic Substances and Disease Registry from the Escambia County Health Department and the Florida Department of Health. A subsequent request for epidemiology aid was made to and granted by the Centers for Disease Control and Prevention. The US Agency for Toxic Substances and Disease Registry and the US Environmental Protection Agency are providing assistance for Escambia County's investigation to determine if community exposures to hydrogen sulfide and particulate air emissions from the Saufley Construction and Demolition Debris landfill could be associated with the health effects being reported. Residents of the community believe that their symptoms are related to chronic hydrogen sulfide exposures, beginning in the fall of 2005. The symptoms they have reported are consistent with chronic exposure to hydrogen sulfide in ambient air.
- Of the many components of construction and demolition debris waste materials present, drywall is of special concern. It is a major component of construction and demolition debris wastes. Drywall is composed of gypsum (CaSO₄ 2H₂O, calcium sulfate molecules bound to two water molecules) covered with a paper facing and backing (Gypsum Association, 1992). When exposed to water, the sulfate in the gypsum becomes dissolved in the landfill leachate (Yang et al., 2006), and hydrogen sulfide gas is produced through an anaerobic bacterial breakdown process. The heat generated from this process results in landfill fires when the concentrations of hydrogen sulfide or methane gas are within the combustible range.

Hydrogen Sulfide:

Hydrogen sulfide is a colorless, flammable gas under normal conditions. In air, people can smell hydrogen sulfide at levels as low as 0.5 parts per billion and the odor is usually characterized as smelling like "rotten eggs" or "sewage." Hydrogen sulfide is ubiquitous in the natural environment, thus low-level exposures are not uncommon. Natural sources account for approximately 90% of the amount of hydrogen sulfide in the atmosphere. Background concentrations of hydrogen sulfide in ambient air are typically less than 1 part per billion (Agency for Toxic Substances and Disease Registry, 2006).

Hydrogen Sulfide Inhalation Health Effects Summary:

Acute Exposure: Short-term exposures to high levels of hydrogen sulfide may cause adverse health effects, including:

- Airway constriction (for example, 2 parts per million for 30 minutes) (Jappinen, Vilkka, Marttila, and Haahtela, 1990);
- Eye irritation (starting at 3.5 ppm) (Keratoconjunctivitis, punctate corneal erosion, blepharospasm, lacrimation, and photophobia) (Ahlborg, 1951; Arnold, Dufresne, and Alleyne, 1985; Chemical Industry Institute of Technology, 1983; Curtis, Anderson, and Simon, 1975; Haider, Hasan, and Islam, 1980; Lopez, Prior, and Yong, 1988; Luck & Kaye, 1989).
- Difficulty breathing (5, 10, and 40 parts per million for short durations) (Bhambini, Burnham, and Snydmillar, et al. 1994; Bhambini, Burnham, and Snydmillar, et al. 1996a, 1996b; Bhambini & Singh, 1991; Spoylar, 1951);
- Inability to smell hydrogen sulfide gas (100 parts per million and higher, short durations, olfactory fatigue) (Reiffenstein, Hulbert, and Roth, 1992); and

The National Institute for Occupational Safety and Health (NIOSH) regulates that the immediately dangerous to life or health (IDLH) guidance concentration is 100 parts per million (NIOSH, 2006).

Chronic Exposure: Long-term exposures to hydrogen sulfide may also result in adverse health effects. These include:

- Neurological effects (for example fatigue, loss of appetite, nausea, headache, vomiting, irritability, poor memory, depression, loss of motor skills, and dizziness) (Ahlborg, 1951; Kilburn, 1997; Kilburn and Warshaw, 1995), and
- Respiratory effects (for example nosebleeds and breathing abnormalities)
 (Agency for Toxic Substances and Disease Registry, 2002b; Campagna,
 Kathman, Pierson, Inserra, Phifer, Middleton, Zarus, and White, 2004; Kilburn and Warshaw, 1995).

The magnitude of hydrogen sulfide exposure in these studies ranged from low parts per billion to low parts per million. The following table outlines current regulatory and guidance values for hydrogen sulfide exposures.

Hydrogen Sulfide Concentration	Exposure Period	Source	Health Basis
1.4 parts per billion	Lifetime	Environmental Protection Agency (EPA, 1994b) Reference Concentration (RfC)	Nasal mucosa inflammation (mice)
20 parts per billion	15-365 days	Agency for Toxic Substances and Disease Registry (ATSDR, 2006) Intermediate Minimum Risk Level (MRL)	Olfactory neuron loss and basal cell hyperplasia (mice)
70 parts per billion	14 days	Agency for Toxic Substances and Disease Registry (ATSDR, 2006)Acute Minimum Risk Level (MRL)	Changes in airway resistance and specific airway conductance in asthmatics

Hydrogen Sulfide Concentration	Exposure Period	Source	Health Basis
100 parts per billion	1 hour	America Industrial Hygiene Association (AIHA, 1991) emergency response planning guideline (ERPG-1) [†]	Odor
10 parts per million	10 minutes	National Institute for Occupational Safety and Health (NIOSH, 2005) 10- minute exposure ceiling	Acute eye irritation, neurological affects
30 parts per million	1 hour	America Industrial Hygiene Association (AIHA, 1991) emergency response planning guideline (ERPG-2) [†]	No deaths occurred
100 parts per million	Immediate	National Institute for Occupational Safety and Health (NIOSH, 2005) Immediately dangerous to life or health	Acute systemic toxicity; central nervous system effects, eye-irritation, conjunctivitis, lungs Affected organs: respiratory system, eyes

Saufley Landfill residential ambient air and personal badge hydrogen sulfide results:

Residential ambient air monitoring for hydrogen sulfide began the week of October 22, 2006. Some study volunteers began wearing personal hydrogen sulfide badges at the same time. The ambient air monitors can detect hydrogen sulfide ranging from 2 to 15,000 parts per billion. The personal badges can detect hydrogen sulfide as low as 17 parts per billion if worn for 24 hours.

To date, residential ambient air monitors have detected hydrogen sulfide concentrations up to 224 parts per billion in residential ambient air. During the 1-month study period, there were 15 detections of hydrogen sulfide on personal badges that range from 15 to 123 parts per billion. Badges were worn for periods ranging from 2 to 24 hours.

Saufley Landfill residential ambient air particulate monitoring results:

Residential ambient air monitoring for fine particulate matter (particles 2.5 micrometers in diameter and smaller) began on November 11, 2006. The US Environmental Protection Agency has a National Ambient Air Quality Standard for fine particles:

- The annual standard is 15 micrograms per cubic meter based on the 3year average of annual mean fine particle concentrations.
 - The 24-hour standard is 65 micrograms per cubic meter, based on the 3year average of the 98the percentile of 24-hour concentrations.

[†] see Appendix for explanation of ERPG levels

To date, residential ambient fine particle monitors have detected fine particle concentrations above 15 micrograms per cubic meter at all four monitoring locations, on four different dates for the following durations:

- 32 hours (approximately) on November 18th and 19th with a peak value of 17.5 micrograms per cubic meter,
- 88 hours (approximately) from November 23rd to November 26th with a peak value of nearly 24 micrograms per cubic meter,
- 72 hours (approximately) from December 5th to December 7th with a peak value of nearly 21 micrograms per cubic meter,
- 120 hours (approximately) from December 14th to December 18th with a peak value of 19 micrograms per cubic meter.

Because the concentrations measured are generally lower than EPA's annual standard, and they did not exceed the 24-hour standard they are unlikely to affect healthy persons. However fine particles aggravate respiratory disease (as indicated by increased hospital admissions, emergency room visits, absences from school or work, and restricted activity days), lung disease, asthma attacks, and certain cardiovascular problems, and so may affect sensitive persons. Persons with existing disease who might also be affected by hydrogen sulfide emissions are likely to be the most affected by fine particulates.

Conclusions

Hydrogen sulfide gas from landfill decay and smoke from landfill fires are a public health hazard for nearby residents. Experts at the federal Agency for Toxic Substances and Disease Registry expect the highest hydrogen sulfide levels measured in outdoor air at nearby homes and on monitors worn by individual residents will cause headaches and breathing difficulty in people with asthma. They also expect these hydrogen sulfide levels will increase the number of hospital visits by children with asthma.

Recommendations

We recommend the following actions:

- 1) Stop community members' airborne exposure to hydrogen sulfide as soon as possible.
- 2) Reduce the threat of fire and explosion that exists on the landfill and/or from landfill operations.
- 3) Develop contingency plans with emergency response personnel to either shelter in place or evacuate community members based on hydrogen sulfide readings (based on (4), below).
- 4) Begin real-time hydrogen sulfide monitoring to determine if/when immediate health decisions should be made (e.g., shelter in place, evacuation).
- 5) Continue to restrict community access to the landfill.

Landfill workers:

Levels of hydrogen sulfide recently measured on the landfill by an outside company and reported to and Escambia County Health Department employee by landfill staff (up to 130 parts per million) exceeded the National Institute for Occupational Safety and Health 10-minute exposure ceiling value of 10 parts per million[†]. The National Institute for Occupational Safety and Health immediately dangerous to life or health (IDLH) concentration is 100 parts per million (NIOSH, 2006).

We recommend the following actions for landfill workers as well as other personnel who access the landfill:

- 1) Utilize personal air monitors for hydrogen sulfide, Lower Explosive Level/Oxygen (LEL/02), and carbon monoxide. Monitors with alarms are preferable.
- 2) Train workers on the use of appropriate personnel protective equipment (for example supplied-air full face respirators or full-face cartridge respirators).

3) Actively integrate landfill status into the community response plan.

The landfill owner/operator can request a National Institute for Occupational Safety and Health, Health Hazard Evaluation (HHE) for assistance in identifying and mitigating occupational hazards.

[†] These levels were verified with the site owner by Stephen C. Metzler, REHS, Environmental Supervisor II, Environmental Health Division, Escambia County Health Department.

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General Description

Synonyms: Sulfuretted hydrogen; Hydrosulfuric acid; Hepatic gas; H2S

OSHA IMIS Code Number: 1480

Chemical Abstracts Service (CAS) Registry Number: 7783-06-4

NIOSH, Registry of Toxic Effects (RTECS) Identification Number: MX1225000

Department of Transportation Regulation Number (49 CFR 172.101) and Guide: 1053 <u>117</u>

NIOSH Pocket Guide to Chemical Hazards, <u>Hydrogen Sulfide</u>: chemical description, physical properties, potentially hazardous incompatibilities, and more

Exposure Limits

OSHA Permissible Exposure Limit (PEL) for General Industry: <u>29 CFR 1910.1000 Z-2</u> <u>Table</u> -- Exposures shall not exceed 20 ppm (ceiling) with the following exception: if no other measurable exposure occurs during the 8-hour work shift, exposures may exceed 20 ppm, but not more than 50 ppm (peak), for a single time period up to 10 minutes.

OSHA Permissible Exposure Limit (PEL) for Construction Industry: <u>29 CFR 1926.55</u> <u>Appendix A</u> -- 10 ppm, 15 mg/m³ TWA

OSHA Permissible Exposure Limit (PEL) for Maritime: <u>29 CFR 1915.1000 Table Z-Shipyards</u> -- 10 ppm, 15 mg/m³ TWA

American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV): 10 ppm, 14 mg/m³ TWA; 15 ppm, 21 mg/m³ STEL

National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL): 10 ppm, 15 mg/m³ Ceiling (10 Minutes)

Health Factors

NIOSH Immediately Dangerous To Life or Health Concentration (IDLH): 100 ppm

Potential symptoms: Apnea; coma; convulsions; irritated eyes, conjunctivitis pain, lacrimation, photophobia, corneal vesiculation; respiratory system irritation; dizziness; headaches; fatigue; insomnia; GI disturbances

Health Effects: Acute systemic toxicity (HE4); CNS effects (HE7) Irritation-Eye, (Conjunctivitis), Lungs---Moderate (HE15)

Affected organs: Respiratory system, eyes

Monitoring Methods used by OSHA Laboratory Sampling/Analytical Method:

• sampling media: Zefluor Filter (0.5 um) in series with coconut shell charcoal tube

(400/200 mg)

maximum volume: 40 Liters maximum flow rate: 1.5 L/min current analytical method: Ion CHromatography; IC/Cond method reference: NIOSH Analytical Method (NIOSH 6013) method classification: Fully Validated note: Sulfur Dioxide (SO2) is a positive interference.

On-Site Sampling Techniques/Methods:

- device: Detector Tube
 manufacturer: Dräger
 model/type: Hydrogen Sulphide 1/d, order no. 81 01831
 sampling information: 1/10 strokes
 upper measurement limit: 200 ppm
 detection limit: approximately 0.5 ppm
 overall uncertainty: approximately 25%
 method reference: on-site air secondary (SEI Certified)
- device: Detector Tube manufacturer: Gastec model/type: 4LL sampling information: 0.5 to 10 strokes upper measurement limit: 120 ppm detection limit: 0.1 ppm overall uncertainty: 8% for 2.5 to 60 ppm method reference: on-site air secondary (SEI Certified)
- device: Detector Tube
 manufacturer: Matheson-Kitagawa
 model/type: 8014-120SD
 sampling information: 0.5/1 strokes
 upper measurement limit: 60 ppm
 detection limit: approximately 0.5 ppm
 overall uncertainty: unknown
 method reference: on-site air secondary (SEI Certified)

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From: <u>http://www.osha-slc.gov/dts/chemicalsampling/data/CH_246800.html</u> accessed 2/7/07.

Revised IDLH: 100 ppm

Basis for revised IDLH: The revised IDLH for hydrogen sulfide is 100 ppm based on acute inhalation toxicity data in humans [Henderson and Haggard 1943; Poda 1966; Yant 1930] and animals [Back et al. 1972; MacEwen and Vernot 1972; Tansey et al. 1981].

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From: http://www.cdc.gov/NIOSH/IDLH/7783064.html, accessed 2/2/07.

ERPGs

The Emergency Response Planning Guidelines (ERPGs) were developed by the ERPG committee of the American Industrial Hygiene Association. The ERPGs were developed as planning guidelines, to anticipate human adverse health effects caused by exposure to toxic chemicals. The ERPGs are three-tiered guidelines with one common denominator: a 1-hour contact duration (Figure 1). Each guideline identifies the substance, its chemical

and structural properties, animal toxicology data, human experience, existing exposure guidelines, the rationale behind the selected value, and a list of references.



From: http://archive.orr.noaa.gov/cameo/locs/expguide.html accessed 2/6/2007.

Reference Concentration (RfC)

The RfC is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups which include children, asthmatics and the elderly) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from various types of human or animal data, with uncertainty factors generally applied to reflect limitations of the data used.

From: http://www.epa.gov/ttn/atw/nata/gloss.html accessed 2/7/07

Minimum Risk Level (MRL)

Minimal Risk Levels (MRLs) for Hazardous Substances

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) [42 U.S.C. 9604 et seq.], as amended by the Superfund Amendments and Reauthorization Act (SARA) [Pub. L. 99 499], requires that the Agency for Toxic Substances and Disease Registry (ATSDR) develop jointly with the U.S. Environmental Protection Agency (EPA), in order of priority, a list of hazardous substances most commonly found at facilities on the CERCLA National Priorities List (NPL) (42 U.S.C. 9604(i)(2)); prepare toxicological profiles for each substance included on the priority list of hazardous substances, and to ascertain significant human exposure levels (SHELs) for hazardous substances in the environment, and the associated acute, subacute, and chronic health effects (42 U.S.C. 9604(i)(3)); and assure the initiation of a research program to fill identified data needs associated with the substances (42 U.S.C. 9604(i)(5)).

The ATSDR Minimal Risk Levels (MRLs) were developed as an initial response to the mandate.

Following discussions with scientists within the Department of Health and Human Services (HHS) and the EPA, ATSDR chose to adopt a practice similar to that of the EPA's Reference Dose (RfD) and Reference Concentration (RfC) for deriving substance specific health guidance levels for non neoplastic endpoints. An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse noncancer health effects over a specified duration of exposure. These substance specific estimates, which are intended to serve as screening levels, are used by ATSDR health assessors and other responders to identify contaminants and potential health effects that may be of concern at hazardous waste sites. It is important to note that MRLs are not intended to define clean up or action levels for ATSDR or other Agencies.

The toxicological profiles include an examination, summary, and interpretation of available toxicological information and epidemiologic evaluations of a hazardous substance. During the development of toxicological profiles, MRLs are derived when ATSDR determines that reliable and sufficient data exist to identify the target organ(s) of effect or the most sensitive health effect(s) for a specific duration for a given route of exposure to the substance. MRLs are based on noncancer health effects only and are not based on a consideration of cancer effects. Inhalation MRLs are exposure concentrations expressed in units of parts per million (ppm) for gases and volatiles, or milligrams per cubic meter (mg/m3) for particles. Oral MRLs are expressed as daily human doses in units of milligrams per kilogram per day (mg/kg/day). Radiation MRLs are expressed as external exposures in units of millisieverts.

ATSDR uses the no observed adverse effect level/uncertainty factor (NOAEL/UF) approach to derive MRLs for hazardous substances. They are set below levels that, based on current information, might cause adverse health effects in the people most sensitive to such substance induced effects. MRLs are derived for acute (1 14 days), intermediate (>14 364 days), and chronic (365 days and longer) exposure durations, and for the oral and inhalation routes of exposure. Currently MRLs for the dermal route of exposure are not derived because ATSDR has not yet identified a method suitable for this route of exposure. MRLs are generally based on the most sensitive substance-induced end point considered to be of relevance to humans. ATSDR does not use serious health effects (such as irreparable damage to the liver or kidneys, or birth defects) as a basis for establishing MRLs. Exposure to a level above the MRL does not mean that adverse health effects will occur.

MRLs are intended to serve as a screening tool to help public health professionals decide where to look more closely. They may also be viewed as a mechanism to identify those hazardous waste sites that are not expected to cause adverse health effects. Most MRLs contain some degree of uncertainty because of the lack of precise toxicological information on the people who might be most sensitive (e.g., infants, elderly, and nutritionally or immunologically compromised) to effects of hazardous substances. ATSDR uses a conservative (i.e., protective) approach to address these uncertainties consistent with the public health principle of prevention. Although human data are preferred, MRLs often must be based on animal studies because relevant human studies are lacking. In the absence of evidence to the contrary, ATSDR assumes that humans are more sensitive than animals to the effects of hazardous substances that certain persons may be particularly sensitive. Thus the resulting MRL may be as much as a hundredfold below levels shown to be nontoxic in laboratory animals. When adequate information is available, physiologically based pharmacokinetic (PBPK) modeling and benchmark dose (BMD) modeling have also been used as an adjunct to the NOAEL/UF approach in deriving MRLs. Proposed MRLs undergo a rigorous review process. They are reviewed by the Health Effects/MRL Workgroup within the Division of Toxicology and Environmental Medicine; and expert panel of external peer reviewers; the agency wide MRL Workgroup, with participation from other federal agencies, including EPA; and are submitted for public comment through the toxicological profile public comment period. Each MRL is subject to change as new information becomes available concomitant with updating the toxicological profile of the substance. MRLs in the most recent toxicological profiles supersede previously published levels. To date, 130 inhalation MRLs, 219 oral MRLs and 8 external radiation MRLs have been derived. A listing of the current published MRLs by route and duration of exposure is provided as follows.

ATSDR Contact Person for MRLs:

Dr. Selene Chou Division of Toxicology and Environmental Medicine Agency for Toxic Substances and Disease Registry 1600 Clifton Road, Mailstop F32 Atlanta, Georgia 30333 Telephone: 770-488-3357 E-Mail: cjc3@cdc.gov

From: http://www.atsdr.cdc.gov/mrls.html accessed 2/7/07