Health Consultation

Exposure Investigation Report

AIR SAMPLING FOR SULFUR GASES
WARREN TOWNSHIP, TRUMBALL COUNTY, OHIO

MARCH 13, 2006

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

You May Contact ATSDR TOLL FREE at
1-888-42ATSDR
or
Visit our Home Page at: http://www.atsdr.cdc.gov

HEALTH CONSULTATION

Exposure Investigation Report

AIR SAMPLING FOR SULFUR GASES
WARREN TOWNSHIP, TRUMBALL COUNTY, OHIO

Prepared by:

Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation

Exposure Investigation Report
Warren Township, Trumball County, Ohio
Air Sampling for Sulfur Gases

Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation

Executive Summary

In 2002, the Agency for Toxic Substances and Disease Registry (ATSDR) began a public health evaluation of community odor complaints in Warren, Trumbull County, Ohio. The complaints were associated with the Warren Recycling, Inc. (WRI) construction and demolition debris (C&DD) landfill. Neighboring residents, area workers, and children attending nearby schools reported health concerns from the odors. These concerns included headaches, nausea, fatigue, eye irritation, and difficulty breathing.

ATSDR initiated its first Exposure Investigation (EI) in September 2002. The EI was designed to monitor hydrogen sulfide (H_2S) levels inside and outside homes near the landfill. The results showed H_2S levels as high as 6.1 parts per million in outdoor air at a residence near the landfill.

ATSDR began this, the second, EI in November 2003 to address a specific recommendation from the first EI. ATSDR wanted to determine whether other sulfur gases, in addition to H_2S, were present during odor events. In Warren, there were reported odors described as slightly different from the "rotten egg" odor associated with H_2S. In the second EI, ATSDR attempted to measure other sulfur gases at two locations in Warren.

Air sampling results indicate that several sulfur gases, including H_2S, were found at one indoor and one outdoor location during two separate odor events. However, we do not know how long sulfur gas levels persisted. Although most of the reported levels were near or below occupational exposure or emergency planning guidelines, the level of methyl mercaptan found in outdoor air exceeded the occupational ceiling limit for 15-minute exposure.

Based on the EI findings, only limited conclusions can be drawn about the health effects of airborne exposure to individual sulfur compounds found in Warren. However, exposure to a combination of these compounds, including H_2S, is a potential health hazard. An exposure lasting more than one hour might cause adverse health effects, especially in sensitive people. These effects might include eye and respiratory irritation, nausea, or headache, or exacerbation of existing breathing problems.

Objectives and Rationale

Beginning in 2002, the Agency for Toxic Substances and Disease Registry (ATSDR) responded to a petition requesting a public health evaluation of community odor complaints in Warren, Trumbull County, Ohio [1]. These complaints were associated with the Warren Recycling, Inc. (WRI) construction and demolition debris (C&DD) landfill. Community health concerns were reported for neighboring residents, area workers, and children attending nearby schools.

After evaluating available sampling results for hydrogen sulfide (H_2S) in outdoor air, ATSDR initiated an Exposure Investigation (EI) in September 2002. The EI was designed to provide additional air monitoring for H_2S inside and outside homes near the landfill [2]. In August 2003, ATSDR released results showing H_2S levels as high as 6.1 parts per million (ppm) in outdoor air at a residence near the landfill [3].

ATSDR began a second EI in November 2003 to address a specific recommendation from the first EI. ATSDR had recommended sampling to determine if other sulfur gases, in addition to H_2S, were present during odor events. A University of Florida study shows that construction and demolition debris (C&DD) landfills emit numerous other sulfur gases as well as H_2S. Although typically found in lower amounts, these sulfur gases (including methyl mercaptan and carbon disulfide) are also a potential health hazard [4]. In Warren, there were reported odors described as slightly different from the “rotten egg” odor associated with H_2S. In this EI, we attempted to measure these other sulfur gases at two locations in Warren during the period from November 2003–July 2004.

Background

WRI is located one block south of West Market Street on Martin Luther King Boulevard in Warren, Ohio. The facility property encompasses approximately 200 acres of land and contains the C&DD landfill and a large building formerly used as a transfer station for municipal solid waste. The C&DD landfill has three areas, including a recently active 15-acre tract. The two other areas are filled and covered. The owners had also purchased an adjacent property with plans to expand landfill operations.

The WRI landfill closed on January 1, 2005 when operators voluntarily withdrew their permit application after failure to maintain compliance with environmental guidelines. The U.S. Environmental Protection Agency (USEPA) subsequently began working to reduce hydrogen sulfide emissions as well as the threat of fire and explosion on the landfill.

The WRI property is bordered on all sides by numerous residential and commercial properties, with some homes located within 100 feet of the property boundary. Several schools are also located in the area, including LaBrae High School, Leavitt Elementary School, and Bascom Elementary School. Two of these schools, LaBrae High School and

Leavitt Elementary, are within ½ mile of the landfill property boundary. The third school, Bascom Elementary, is several miles away.

Community Concerns

Community residents, including school children, have identified health concerns such as headaches, nausea, fatigue, eye irritation, and respiratory distress (including difficulty breathing and the exacerbation of asthma and other preexisting respiratory conditions). Most health complaints came from residents living near the most recently active landfill cell. There were also complaints from people who work near the facility. Some people have reported odors strong enough to induce nausea or vomiting. In addition, residents have asked ATSDR to investigate "other odors" that usually occur along with the hydrogen sulfide odor (described as "rotten eggs, but a little different").

Previous Sampling and ATSDR Activities

In 2002, ATSDR responded to a petition requesting a public health evaluation of community odor complaints, community health concerns, and available outdoor air data showing H_2S levels in Warren, Ohio. The petition noted a concern for school children as well as area residents living or working in close proximity to WRI [1]. ATSDR visited the community and reviewed the available information, including H_2S monitoring data collected by an environmental consultant for the LaBrae School District and the Warren Township Board of Trustees in spring 2002. These results showed community outdoor H_2S levels of up to 13 ppm [2].

Based on these findings, ATSDR prepared a Health Consultation concluding that exposures to levels of H_2S in air were a public health hazard. However, because of a lack of quality control information for the air results, ATSDR qualified this conclusion pending verification of the data. ATSDR recommended additional air monitoring, with proper quality assurance, inside and outside homes near the landfill [2]. In late 2002, ATSDR initiated an EI to address this recommendation. ATSDR used tape meters[1] to monitor for H_2S at five locations from November 2002–April 2003. The results indicated the presence of H_2S in outdoor air at levels up to 6.1 ppm in residential areas [3].

Beginning in November 2002, to help ensure student safety, each of the three nearby schools began using a portable electrochemical monitor to survey indoor H_2S levels. These monitors operated during school days, periodically showing elevated readings (1–2 ppm) for periods of 12–72 hours.

During the first EI, from January 4–March 8, 2003, ATSDR placed a tape meter adjacent to the portable instrument used at LaBrae High School to monitor H_2S levels inside the school. A tape meter measures H_2S levels using a tape impregnated with a reagent that

[1] Zellweger Analytics Single Point Monitors (SPMs) equipped with the ChemKey® and Chemcassette® detection systems are commonly referred to as a tape meters.

turns pink or purple in the presence of H_2S. The meter's optical detector measures the reflectance of the tape to determine the H_2S level. A datalogger then continuously records the digital readings.

Although the tape meter at the school never detected H_2S, the school's portable monitor showed periodic readings of up to 2 ppm. The portable monitor uses a different technology than used in tape meters to measure H_2S, and is cross-sensitive to other sulfur compounds. In its report of the first EI, ATSDR could not fully interpret these data, but noted that interference from another sulfur gas might cause the inconsistent readings [3].

The conclusion in the first EI report (dated November 21, 2003) stated that an urgent public health threat existed based on a combination of elements. These elements included the health hazard of H_2S exposures to people with pre-existing cardiopulmonary disease or respiratory problems, potential for fire and explosion, and physical health hazards. ATSDR made several public health recommendations based on this conclusion. One of these recommendations was to conduct air sampling for other sulfur gases during odor events.

2004–2005 Site-related Activities

In 2004 WRI began construction activities on property it had purchased for expansion. This construction occurred without approval from the Ohio Environmental Protection Agency (OEPA). The uncompleted work allowed leachate from the landfill to pool at the surface. WRI installed a treatment system to remove H_2S from the leachate so that it could be discharged into the sanitary sewer. The system was designed to treat 1000 gallon batches of leachate with hydrogen peroxide for a period of ten minutes [5].

In June 2004, staff from ATSDR and the Ohio Environmental Protection Agency (OEPA) responded to severe odor complaints in the Leavittsburg community. During an inspection of the pre-treatment system, OEPA noted a leachate holding time of only two minutes.

On June 24, 2004, ATSDR measured emissions from a sewer manhole cover on Lover's Lane just south of the Mahoning River. The calibrated, handheld monitor measured H_2S at a concentration of 95 ppm. This level approaches the National Institute for Occupational Safety and Health (NIOSH) IDLH level of 100 ppm. The IDLH level is one considered "immediately dangerous to life or health", but allowing for a 30-minute exposure to escape the contaminated environment.

The USEPA notified WRI that it should stop pumping leachate into the sewer [6]. Thereafter, WRI pumped leachate into tanker trucks for transport to the City of Warren Waste Water Treatment Plant.

In August 2004, WRI completed the installation of a drainage layer on the expansion property. They covered the area of pooling leachate with clay in an unsuccessful attempt

to minimize leachate odors. The OEPA consulted the USEPA to determine whether conditions at the WRI landfill warranted a federal environmental response. After reviewing available data, the USEPA determined that the site met the criteria for a time-critical removal action. From September 9–October 6, 2004, the USEPA conducted air monitoring and sampling in the nearby residential neighborhood to assess existing H_2S exposures. The results showed H_2S levels ranging from <15–120 ppb [6].

The USEPA began emergency response cleanup operations in early 2005. The cleanup plans included installation of a temporary, high capacity leachate treatment system and surface water management system, capping a portion of the landfill, and installing a permanent leachate management system [5]. ATSDR recommended that sulfur gas emissions be monitored during the USEPA removal operations at the landfill. In addition, ATSDR recommended that long-term management of leachate, including collection, treatment, and disposal be implemented. In March 2006, USEPA clean-up activities were completed, including installation of the leachate management system [5].

Methods

The sampling locations of particular interest were: 1) a residential area known to be impacted by H_2S odors, and 2) the LaBrea High School. ATSDR recruited two local participants to collect several indoor and outdoor air samples during odor events and then ship them to a laboratory for analysis. A resident agreed to collect samples at his home. The local fire chief agreed to collect samples at the school during odor events as part of ongoing air monitoring activities there. Samples were collected from November 2003 to July 2004.

Through an Interagency Agreement, ATSDR funded the Division of Federal Occupational Health to provide sampling containers and contract with a laboratory for sulfur compound analyses. ATSDR provided SUMMA® canisters along with sampling and shipping instructions to a local resident as well as the local fire chief. The gases sampled are listed in Table 1.

Target Population

The target population for this EI included the residents of the selected home and the students and staff of LaBrea High School. The potentially affected population included several hundred residents who live within ½ mile of the WRI facility. In addition, 1600 students attend nearby schools, two of which are within ¼ mile of the facility.

Consent Forms

The head of household signed an informed consent form prior to collecting indoor and outdoor air samples at the residential sampling location.

Evaluation Guidelines

Table 1 includes evaluation guidelines for sulfur gases known to be associated with C&DD landfill emissions [4]. These guidelines have been derived by government agencies for occupational exposures and emergency response planning. They provide the only available short-term (1–8 hour) comparison values, since no guidelines exist for residential exposure scenarios.

Occupational Exposure Guidelines

Occupational exposure guidelines can be used to assess community exposure when no other comparison values exist. However, they are intended for workplace exposures and may not be protective of the very young, elderly, and people with pre-existing respiratory problems.

Planning and Emergency Response Guidelines

Planning and emergency response guidelines are based primarily on acute (rather than chronic) toxicology data for airborne exposures. In addition, these values do not normally address effects that could result from repeated exposures.

ERPGs

The American Industrial Hygiene Association (AIHA) Emergency Response Planning Committee has developed thresholds above which there would be an “unacceptable likelihood of observing defined health effects.” These planning and emergency response guidelines, although useful, are not exposure guidelines and do not contain the safety factors normally incorporated into exposure guidelines. These guidance levels are based on available research data, and in cases where the data are limited, the uncertainty may be large [7].

AEGLs

In addition, the USEPA has developed Acute Exposure Guideline Levels (AEGLs) to provide guidance in situations where there can be a rare exposure to a particular chemical involving the general public. AEGLs provide exposure level thresholds for exposure periods ranging from 10 minutes to 8 hours. These values, intended to protect the general public, take into consideration sensitive sub-populations such as children and the elderly.

Table 1. Available occupational exposure and emergency response guidelines for sulfur gases found at C&DD landfills

Sulfur Gas	Source*	Exposure Value† (ppm)	Exposure Period
Hydrogen Sulfide	ACGIH TLV	10	8 hours
	EPA AEGL-1**	0.75	10 minutes
	EPA AEGL-1	0.33	8 hours
Dimethyl disulfide	AIHA ERPG (1) ‡	0.01	1 hr
	AIHA ERPG (2) ‡	50	1 hr
Dimethyl sulfide	AIHA ERPG (1)	0.5	1 hr
	AIHA ERPG (2)	500	1 hr
Carbon Disulfide	NIOSH TWA	1	10 hours
	NIOSH STEL	10	15 minutes
	OSHA TWA	20	10 hours
	OSHA Ceiling	30	***
Methyl Mercaptan	ACGIH TLV	0.5	8 hours
	NIOSH Ceiling	0.5	15 minutes
	OSHA Ceiling	10	***
	EPA AEGL-2** ‡	59	10 minutes
	EPA AEGL-2** ‡	19	8 hours
Diethyl sulfate	NIOSH TWA	0.1	10 hours
	OSHA TWA	1	10 hours
Ethyl Mercaptan	NIOSH Ceiling	0.5	15 minutes
	OSHA Ceiling	10	15 minutes
n-Butyl Mercaptan	ACGIH TLV	0.5	8 hours
	NIOSH Ceiling	0.5	***
	OSHA TWA	10	10 hours

* ACGIH is the American Conference of Governmental Industrial Hygienists;
EPA is the U.S. Environmental Protection Agency;
AIHA is the American Industrial Hygiene Association;
NIOSH is the National Institute for Occupational Safety and Health;
OSHA is the Occupational Safety and Health Administration.

† ppm refers to parts per million (parts sulfur gas per million parts air, by volume)

** AEGL-1 is Acute Exposure Guideline Level 1; AEGL-2 is Acute Exposure Guideline Level 2

‡ Emergency Response Planning Guide (1), ERPG (1), for no more than mild, transient effects for up to 1 hour of exposure;
Emergency Response Planning Guide (2), ERPG (2), without serious, adverse effects for up to 1 hour of exposure

*** At no time should this exposure limit be exceeded.

\# No AEGL-1 is recommended “due to insufficient data”.

AEGLs are derived for 10-minute, 30-minute, 1-hour, 4-hour, and 8-hour exposures. ATSDR considered the two following health effect levels:

- AEGL-1: The airborne concentration of a substance at or above which the general population, including "susceptible" individuals, could experience discomfort, irritation, or certain asymptomatic, non-sensory effects. However, the effects are not disabling, and are transient and reversible when exposure stops.

- AEGL-2: The airborne concentration of a substance above which the general population, including "susceptible" individuals, could experience irreversible or other serious, long-lasting health effects or impaired ability to escape.

Despite the uncertainty factors included to account for variable responses in the population, the AEGL-1 allows some effects, such as mild sensory irritation or asymptomatic, non-sensory effects, to occur at the guidance level. These effects could be considered adverse for some susceptible individuals.

Air Sampling Procedures

The participating resident collected a total of eight 1-minute grab air samples during four separate odor events occurring from December 15, 2003–July 21, 2004. Six samples were collected using SUMMA® canisters; two were collected using tedlar bags. The fire chief collected no air samples.

Of the six SUMMA® samples collected at the resident's home, four were collected outdoors; two were collected indoors. The resident used tedlar bags to collect two outdoor air samples in a nearby field adjacent to a residential area. All samples were shipped to a laboratory and analyzed for sulfur gases using a Gas Chromatograph - Selected Ion Capture Device (GC-SCD).

SUMMA® canisters

A SUMMA® canister is an airtight, stainless-steel container with an inner surface that has been electro-polished and chemically deactivated. The six-liter canisters (also known as SilcoCans) used in this investigation have an interior surface coating designed to eliminate reactivity to sulfur compounds. The laboratory is required to clean each canister and evacuate it to a high vacuum prior to shipping it to the sampling location. A canister can hold the vacuum for up to 30 days. The air being sampled is "drawn" into the canister by the high vacuum, thus eliminating the need for a pump.

ATSDR provided the participating resident and the fire chief with SUMMA® canisters after demonstrating the proper procedures for sample collection and shipment. ATSDR

provided participants with a schedule indicating appropriate sampling and shipping dates to minimize the holding time prior to sample analysis. The schedule was flexible, but designed to avoid sample holding times during weekends.

ATSDR initially provided two sets of SUMMA® canisters to capture odor events at each location of interest (the residence and the school). Each set contained two canisters; one to sample indoor air and one to sample outdoor air during the odor event. ATSDR provided additional sampling supplies as needed.

Tedlar bag samples

After the use of 2 sets of SUMMA® canisters, ATSDR provided the participating resident with several 1-liter tedlar bags. Previous experience in sampling with tedlar bags suggested that they might minimize reactive losses. The residential participant collected 2 tedlar bag samples in a field near Lover's Lane, in an area near the sewer manhole cover mentioned on page 5.

The tedlar bags used during this EI are made with polyvinyl fluoride (tedlar) film and polypropylene fittings. These sample bags are inert (non-reactive) and commonly used with a vacuum pump to collect grab air samples of low-level sulfur gases.

Tedlar bag sampling was not originally included in this investigation. ATSDR eventually provided the bags in an attempt to minimize reactive losses in the sample containers. However, samples were collected without the typically used pump for drawing air into the bag. During the April 28, 2004 odor event, two bags were each manually opened for less than one minute, manually sealed, and then shipped to the lab.

Based on the apparent success of capturing sulfur compounds using tedlar bags, ATSDR provided additional, foiled tedlar bags to the resident. However, these bags were not used during the investigation.

Results

Sulfur gases were found in one indoor and two outdoor air samples.

SUMMA® Results

Table 2 summarizes the results for all SUMMA® samples collected at the residence during the EI. The results for five of the six SUMMA® canisters did not indicate the presence of any sulfur compound. However, two sulfur compounds were detected in one indoor SUMMA® sample.

Table 2. Summary of Results for SUMMA® Samples

Sample Collection Date	Sample Analysis Date	Location	Results	
12/15/2003	12/30/2003	Indoor	28 ppb	Dimethyl disulfide
			12 ppb	Methyl mercaptan
12/15/2003	12/30/2003	Outdoor	ND*	
03/03/2004	03/05/2004	Outdoor	ND	
03/03/2004	03/05/2004	Outdoor	ND	
07/21/2004	07/22/2004	Indoor	ND	
07/21/2004	07/22/2004	Outdoor	ND	

* ND – No sulfur compounds were detected in the sample.

The indoor air sample collected on December 15, 2003 showed 28 ppb dimethyl disulfide and 12 ppb methyl mercaptan. No sulfur compounds were detected in the corresponding outdoor air sample. Additional indoor and outdoor air samples were collected on March 3, 2004 and July 21, 2004. No sulfur compounds were found in any of these samples.

ATSDR had stipulated that the laboratory conduct the analyses no later than one day after sample receipt. However, the lab did not analyze the samples collected on December 15, 2003 until December 30, 2004. Because of concerns about reactive losses of sulfur compounds in the canisters, ATSDR alerted the laboratory when all subsequent samples were shipped so that they could be analyzed promptly. Although the lab analyzed all remaining samples within two days of receipt, no sulfur compounds were detected in any of those samples.

ATSDR provided a summary of the results from the residential (SUMMA®) samples to the participating resident along with an explanation of their significance. The fire chief reported that although several odor events occurred during the EI, they did not appear to impact the area of the school. As a result, he collected no samples at the school.

Tedlar Results

On April 28, 2004, during a reportedly strong odor event, the residential participant collected two tedlar bag samples in an outdoor location near Lover's Lane and West Market Street. This area, located near the WRI facility in an open field, is also within 50 feet of a residence.

Table 3 summarizes the analytical results for these two samples. The first sample showed several sulfur gases at elevated levels. The second sample showed H_2S at a concentration of 60 ppb.

Table 3. Summary of Results from Tedlar Samples

Sample	Sample Collection Date	Sample Analysis Date	Sulfur Gas	Concentration (ppb)
1	04/28/2004	04/30/2004*	Dimethyl sulfide	530
			Dimethyl disulfide	180
			Methyl mercaptan	750
			n-Butyl mercaptan	83
2	04/28/2004	04/30/2004*	Hydrogen sulfide	60

* Amended results issued on 05/17/2004

The initially reported results indicated that no sulfur compounds were detected in either of these samples. ATSDR noted that the detection limits for these initial results (as well as previous non-detect results) were higher than those published for the analytical method. ATSDR and USEPA personnel contacted the lab for guidance about obtainable detection limits and ways to optimize the capture of airborne sulfur compounds. Based on this request, the lab reviewed the results of the laboratory control samples (LCSs). LCS results were used to develop a calibration curve to quantify any sulfur compounds present in the tedlar bag samples. The lab subsequently revised the calibration curve to allow lower estimated detection levels. On May 17, 2004, the lab issued an amended report with the results shown in Table 3. The revised detection limits are 0.8–25 times lower than the detection limits initially reported.

However, the calibration curve is based on LCSs containing five different sulfur compounds at levels ranging from 36–68 ppm. These LCS levels are up to 1000 times greater than the levels ultimately reported for the tedlar bag samples. Because the response at lower levels may be non-linear, the revised levels must be interpreted with caution. These amended results may indicate only that specific sulfur compounds were present at low levels in the sample. The results may not indicate the precise levels actually present.

Discussion

Residents occasionally noted odors that were somewhat different than the typical “rotten egg” odor associated with H_2S. Other sulfur gases found to be associated with C&DD landfills have odors that differ from the characteristic H_2S odor. Table 4 summarizes the levels found for each sulfur gas detected during the EI and shows their typical odor characteristics and odor thresholds. Levels noted in **bold** text exceed the evaluation guideline(s).

Table 4. Summary of results from air samples in which a sulfur gas was detected along with typical odor description and odor threshold

Sulfur Gas	SUMMA® 1 (ppb)	Tedlar 1† (ppb)*	Tedlar 2 (ppb)	Typical Odor Description	Odor Threshold (ppb) [6]
Hydrogen sulfide	ND (<60)	ND (<60)**	60	Rotten egg	4.7
n-Butyl mercaptan	ND (<30)	83	ND (<30)	Garlic	0.1–1
Dimethyl disulfide	**28**	**180**	ND (<2)	Burnt rubber	7.5
Dimethyl sulfide	ND (<20)	**530**	ND (<2)	Boiled cabbage	1
Methyl mercaptan	12	**750**	ND (<20)	Rotten cabbage	2

† Lab analyses were conducted on 4/30/04; data were revised and submitted on 5/17/04.
* ppb is parts per billion
** reported laboratory detection limits

These results (from 1-minute grab samples) do not tell us the duration of exposures that could have occurred for these odor events. However, based on patterns of H_2S exposures found during the first EI, episodic peaks lasting 15 minutes or more occurred at residential locations near the landfill [2]. In evaluating the data for this EI, ATSDR hypothesized a similar exposure pattern.

ATSDR evaluated the sulfur gas levels found based on available occupational exposure or emergency planning guidelines. Table 4 shows the highest level found for each sulfur gas along with the corresponding, most conservative guideline. Results highlighted in **bold** indicate levels exceeding the selected guidelines.

Indoor Air

Dimethyl disulfide was found at 28 ppb and methyl mercaptan was found at 12 ppb in a SUMMA® canister sample collected inside a home located near the WRI facility. Because of a two-week delay in lab analysis, it is possible that the actual levels of sulfur compounds present at the time of sampling were higher.

Table 5. Sulfur gas levels from grab air samples and corresponding evaluation guidelines

Sulfur Gas	Source†	Evaluation Guideline (ppb)††	Exposure Period	Outdoor Level (ppb)	Indoor Level (ppb)
Hydrogen Sulfide	AEGL-1	330	8 hours	60	ND
Dimethyl disulfide (DMDS)	ERPG-1*	10	1 hour	**180**	**28**
	ERPG-2**	50,000	1 hour		
Dimethyl sulfide (DMS)	ERPG-1	500	1 hour*	**530**	ND
Methyl Mercaptan	NIOSH Ceiling	500	15 minutes	**750**	12
n-Butyl Mercaptan	NIOSH Ceiling	500	***	83	ND

† AEGL is Acute Exposure Guideline Level (developed by USEPA); ERPG is Emergency Response Planning Guideline (developed by the American Industrial Hygiene Association); NIOSH is the National Institute for Occupational Safety and Health.
†† ppb is parts per billion (parts sulfur gas per billion parts air, by volume)
* Emergency Response Planning Guide-1, for no more than mild, transient effects for up to 1 hour of exposure
** Emergency Response Planning Guide-2, for no irreversible or other serious health effects that could prevent protective action
*** At no time should this exposure limit be exceeded.
ND Not detected

Dimethyl Disulfide

Dimethyl disulfide (DMDS) occurs naturally in many foods such as onion, garlic, and cabbage. It is released during biodegradation of food and garden waste and can be smelled at about 2 ppb. At 7.5 ppb, it has a recognizable odor.

Very limited data are available to show typical levels of DMDS in residential indoor air. In one Korean study, DMDS was found at 231 ppb inside a refrigerator in which Kimchi, a traditional dish of fermented cabbage, was often stored [8]. While the level of DMDS found indoors during the EI (28 ppb) is 10 times lower, ATSDR has no data to suggest that food items were the source of the DMDS found.

No residential or occupational standards have been developed for airborne exposures to DMDS. However, the AIHA has established an emergency planning guideline (ERPG-1) of 10 ppb. Except for an objectionable odor, exposure to levels below 10 ppb for one hour would be expected to cause no more than mild, transient adverse health effects [7]. The AIHA ERPG-2 of 50,000 ppb indicates that, in an emergency situation, people could be exposed to a level below 50,000 ppb (or 50 ppm) for up to one hour "without experiencing or developing irreversible or other serious health effects that could prevent protective action" [7].

Because workplace exposure data were considered inconclusive, the ERPG-2 level is based on animal studies [7]. In one workplace study, investigators monitored exposures to a mixture of sulfur compounds, including H_2S (0.64–2.0 ppm), SO_2 (3.4–7.4 ppm), methyl mercaptan (0.14–2.8 ppm), dimethyl sulfide (0.14–4.7 ppm, and DMDS (0.05–0.31 ppm) [10]. Workers exposed to the higher concentrations in this mixture (including up to 310 ppb DMDS) had recurrent headaches and took more sick leave [9]. However, these findings were difficult to attribute to DMDS because DMDS levels were relatively low compared to those for the other sulfur compounds present [7]. The ERPG guidance references two animal studies. In one study, rats exposed to DMDS for 20 days at 100 ppm (100,000 ppb) showed no signs of toxicity [10]. In the other study, rats exposed to 520 ppm (520,000 ppb) DMDS in air for four hours showed signs of mild lacrimation [11].

Based on the ERPG levels, the concentration of DMDS found indoors (28 ppb) during the EI would not be expected to pose a health threat for a one-time, short-term (≤ 1-hour) exposure. However, ERPG levels do not address recurring exposures of up to several hours and can only provide perspective on the sampling results from this EI.

Methyl Mercaptan

Methyl mercaptan can be highly irritating to the eyes, skin, and upper respiratory tract, and can induce headache, dizziness, nausea, and vomiting. Very little is known about the long-term health effects of exposure to low levels of methyl mercaptan. It occurs naturally in some foods, including certain nuts and cheeses. Methyl mercaptan was not reported in the Korean study [8].

Methyl mercaptan at 12 ppb is significantly less than the occupational 15-minute ceiling of 500 ppb (or 0.5 ppm) [12]. A short-term exposure to methyl mercaptan at the level found indoors during this EI would not be expected to cause adverse health effects. However, because of the previously mentioned two-week delay in analysis of the sample, it is possible that the actual level of methyl mercaptan present at the time of sampling was higher. As a result, we do not know the level of methyl mercaptan actually present, and we do not know how long that level persisted.

Outdoor Air

A total of five different sulfur compounds were found in two 1-minute grab samples of outdoor air. Three of these compounds were found at levels above guidance levels. Two compounds, n-butyl mercaptan and hydrogen sulfide, however, were below the guidance levels.

Dimethyl Disulfide

Dimethyl disulfide (DMDS) was found at 180 ppb in one sample. Although this level exceeds the ERPG-1 level of 10 ppb, it is well below the ERPG-2 of 50,000 ppb [14]. As in the previous discussion of indoor sampling results, it must be noted that ERPG levels do not address recurring exposures of up to several hours. They cannot be used in conjunction with sampling results from the 1-minute grab samples from this EI to fully determine whether or not there is an exposure threat.

Dimethyl Sulfide

Dimethyl sulfide (DMS) is also an eye and upper respiratory tract irritant, and can cause headache and lowered concentration. DMS was found at 530 ppb, a level that approximates the ERPG-1 level (500 ppb) [14]. The ERPG-1 level is the maximum concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing health effects more severe than mild odor perception or irritation [14].

The ERPG-2 level of 500,000 ppb (500 ppm) is a maximum concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible adverse health effects or symptoms that could prevent protective action [14]. It is based primarily on animal data combined with limited human data, and recognizes the limited toxicological data available. A 14-week oral intubation study in rats showed no apparent effects at 250 mg/kg/day. This dose approximates a no-observable-adverse-effect-level (NOAEL) of 688 ppm for an 8-hour exposure [15].

Methyl Mercaptan

The Occupational Safety and Health Administration (OSHA) set a permissible exposure limit of 10 ppm for an 8-hour workday in a 40-hour workweek. The American Conference of Governmental and Industrial Hygienists (ACGIH) and the National Institute for Occupational Safety and Health (NIOSH) recommend an occupational exposure limit ceiling of 0.5 ppm (500 ppb) for 15-minute exposures to methyl mercaptan.

The USEPA established an AEGL-2 of 19,000 ppb (or 19 ppm) for an 8-hour exposure to methyl mercaptan. This level is one above which the general population, including susceptible individuals, could experience notable discomfort and irritation. However, the effects are not disabling, and are temporary as well as reversible after the exposure stops [13].

Methyl mercaptan at 750 ppb is above the 15-minute occupational ceiling limit (500 ppb). Therefore, a relatively brief (≥15 minute) exposure to methyl mercaptan at this level might cause transient health effects such as respiratory and eye irritation or headache. However, even an 8-hour exposure would not be expected to cause permanent adverse effects.

Effects of multiple sulfur gases

Exposures to sulfur gases typically involve more than one reduced sulfur compound. As a result, few epidemiological studies address the health effects of individual sulfur gases. Each sulfur gas has similar toxic effects (eye, nose, and respiratory irritation and headaches), so we would expect them to have additive toxicity.

Studies have been conducted on the human health effects of exposures to reduced sulfur gases emitted from paper pulp mills. In particular, a series of studies conducted in southeastern Finland show that exposures to TRS (total reduced sulfur) concentrations at low levels (<100 ppb) are associated with respiratory symptoms and other health effects [16,17,18,19,20,21].

Limitations

There are two key limitations associated with this EI. First, all samples were collected as 1-minute grab samples and primarily provided a snapshot of the sulfur compounds present during odor events. While useful for meeting the purpose of this EI, the results do not provide a complete exposure profile for fully assessing potential health threats from exposure to these compounds.

Secondly, in some cases, the laboratory was unable to achieve the lowest detection limits published for the analytical method used. As a result, sulfur compounds may have been present at levels that could be smelled, but below levels that could be measured. Also, on at least one occasion, reactive losses probably occurred as a result of a delay in sample analysis.

Conclusions

These air sampling results indicate that several sulfur gases, including H_2S, were found at one indoor and one outdoor location during two separate odor events. However, we do

not know how long sulfur gas levels persisted. Although most of the reported levels were near or below occupational exposure or emergency planning guidelines, the level of methyl mercaptan found in outdoor air exceeded the occupational ceiling limit for 15-minute exposure.

Based on the EI findings, only limited conclusions can be drawn about the health effects of airborne exposure to individual sulfur compounds found in Warren. However, exposure to a combination of these compounds, including H_2S, is a potential health hazard. An exposure lasting more than one hour might cause adverse health effects, especially in sensitive people. These effects might include eye and respiratory irritation, nausea, or headache, or exacerbation of existing breathing problems.

Recommendations

None.

Author, Reviewers

Author

Gail E. Scogin, MS

Environmental Health Scientist
Exposure Investigations Team
Exposure Investigations and Consultations Branch
Division of Health Assessment and Consultation

Reviewers:

Michael Patterson, MD
Exposure Investigations Team
Exposure Investigations and Consultations Branch
Division of Health Assessment and Consultation

Lynn Wilder, MS, CIH
Environmental Health Scientist
Division of Health Science

Michelle Colledge, MS
Regional Representative
Division of Regional Operations

References

1. Letter from Petitioner to the Agency for Toxic Substances and Disease Registry, Atlanta, Georgia: U.S. Department of Health and Human Services; April 2002.

2. ATSDR. Agency for Toxic Substances and Disease Registry, Health Consultation: Hydrogen Sulfide Exposure, Warren Township, Trumbull County, Ohio. September 12, 2002.

3. ATSDR. Agency for Toxic Substances and Disease Registry, Exposure Investigation: Warren Township Hydrogen Sulfide Air Sampling, Warren Township, Trumbull County, Ohio. November 21, 2003.

4. State University System of Florida, Florida Center for Solid and Hazardous Waste Management. Gypsum drywall impact on odor production at landfills: Science and control strategies. December 2000 (updated January 2002). Report #00-09.

5. USEPA. U.S. Environmental Protection Agency, Warren Recycling, Warren, Ohio, EPA Region V On-Scene Coordinator website. [Accessed on March 8, 2006.] http://www.epaosc.net/polrep_profile.asp?site_id=1622&counter=2747

6. USEPA. U.S. Environmental Protection Agency, Site Assessment Report: Warren Recycling Incorporated Site, Warren, Trumbull County, Ohio. December 2, 2004.

7. AIHA. American Industrial Hygiene Association, Emergency Response Planning Guideline for Dimethyl Disulfide. Fairfax, VA, 1996.

8. Yang, S.B., Application of odour measurements in Korea. University of Ulsan, Korea, School of Chemistry and Biological Sciences.

9. Kangas, J., P. Jappinen, and H Savolainen: Exposure to Hydrogen Sulfide, Mercaptans and Sulfur Dioxide in Pulp Industry. Am. Ind. Hyg. Assoc. J. 45 (12):787-790 (1984).

10. Gage, J.C.: The Subacute Inhalation Toxicity of 109 Industrial Chemicals. Br. J. Ind. Med. 27:1-18 (1970).

11. Industrial BIO-TEST Laboratories: “Report to Crown Zellerbach Corporation on Acute Toxicity Studies on Dimithyl Disulfide:” (IBT No. A4595). 1966. [Unpublished Information.] Industrial Bio-Test Laboratories, Inc., 1810 Frontage Road, Northbrook, IL 60062.

12. NIOSH. National Institute of Occupation Safety and Health. NIOSH Pocket Guide to Chemical Hazards. http://www.cdc.gov/niosh/npg/npg.html [Accessed on September 19, 2005].

13. USEPA. U.S. Environmental Protection Agency, Acute Exposure Guideline Levels (AEGLs) website: http://www.epa.gov/oppt/aegl [Accessed on September 28, 2005].

14. AIHA. American Industrial Hygiene Association, Emergency Response Planning Guideline for Dimethyl Sulfide. Fairfax, VA, 1995.

15. Butterworth, K.R., F.M.B. Carpanini, I.F. Gaunt, J. Hardy, I.S. Kiss, and S.D. Gangolli: Short-Term Toxicity of Dimethyl Sulphide in the Rat. Fd. Cosmet. Toxicol. 13:15-22 (1975).

16. Jaakkola JJ, Vilkka V, Marttila O, et al. 1990. The South Karelia air pollution study: The effects of malodorous sulfur compounds from pulp mills on respiratory and other symptoms. Am Rev Respir Dis 142:1344-1350.

17. Haahtela T, Marttila O, Vilkka V, et al. 1992. . The South Karelia air pollution study: Acute health effects of malodorous sulfur air pollutants released by a pulp mill. Am J Public Health 82:603-605.

18. Marttila O, Haahtela T, Silakoski I, et al. 1994. The South Karelia air pollution study: Relationship of outdoor and indoor concentrations of malodorous sulfur compounds released by pulp mills. J Air Waste Manag Assoc 44:1093-1096.

19. Marttila O, Jaakkola JJK, Vilkka V, et al. 1994. The South Karelia air pollution study: The effects of malodorous sulfur compounds from pulp mills on respiratory and other symptoms in children. Environ Res 66:152-159.

20. Marttila O, Jaakkola JJK, Partti-Pellinen K, et al. 1995. South Karelia air pollution study: Daily symptom intensity in relation to exposure levels of malodorous sulfur compounds from pulp mills. Environ Res 71:122-127.

21. Partti-Pellinen K, Martilla O, Vilkka V, et al. 1996. The South Karelia air pollution study: Effects of low-level exposure to malodorous sulfur compounds on symptoms. Arch Environ Health 51:315-320.

Appendix A:

Table 1. Soil Gas Detection Ranges for Other Sulfur Gases at C&DD Landfills

Sulfur Gas	**Range Detected (ppm)**
Carbonyl Sulfide	BDL[+] to 61 ppm
Methyl Mercaptan	BDL to 164 ppm
Dimethyl Sulfide	BDL to 2.1 ppm
Ethyl Mercaptan	BDL to 0.2 ppm
Carbon Disulfide	BDL to 91 ppm
Isopropyl Mercaptan	BDL to 2.8 ppm
Butyl Mercaptans	BDL to 0.2 ppm
Thiophene	BDL to 0.1 ppm
2- and 3-Methylthiophene	BDL to 0.4 ppm

[+] BDL means Below the Detection Limit

Source: State University System of Florida, Florida Center for Solid and Hazardous Waste Management. Gypsum drywall impact on odor production at landfills: Science and control strategies. December 2000 (updated January 2002). Report #00-09.

Appendix B: ERPG Definitions and Background Information

The Emergency Response Planning Guideline (ERPG) values are intended to provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects as described in the definitions for ERPG-1, ERPG-2, and ERPG-3 as a consequence of exposure to the specific substance.

- The 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.
- The 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.
- The ERPG-3 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 life-threatening health effects.

It is recognized by the committee (and should be remembered by all who make use of these values) that human responses do not occur at precise exposure levels but can extend over a wide range of concentrations. The values derived for ERPGs should not be expected to protect everyone but should be applicable to most individuals in the general population. In all populations there are hypersensitive individuals who will show adverse responses at exposure concentrations far below levels where most individuals normally would respond. Furthermore, since these values have been derived as planning and emergency response guidelines, not exposure guidelines, they do not contain the safety factors normally incorporated into exposure guidelines. Instead, they are estimates, by the committee, of the thresholds above which there would be unacceptable likelihood of observing the defined effects. The estimates are based on the available data that are summarized in the documentation. In some cases where the data are limited, the uncertainty of these estimates is large. Users of the ERPG values are encouraged strongly to review carefully the documentation before applying these values.

In developing these ERPGs, human experience has been emphasized to the extent data are available. Since this type of information, however, is rarely available, and when available is only for low level exposures, animal exposure data most frequently forms the basis for these values. The most pertinent information is derived from acute inhalation toxicity studies that have included clinical observations and histopathology. The focus is on the highest levels not showing the effects described by the definitions of the ERPG levels. Next, data from repeat inhalation exposure studies with clinical observations and histopathology are considered. Following these in importance are the basic, typically acute studies where mortality is the major focus. When inhalation toxicity data are either unavailable or limited, data from studies involving other routes of exposure will be considered. More value is given to the more rigorously conducted studies, and data from short-term studies are considered to be more useful in estimating possible effects from a single 1-hr exposure. Finally, if mechanistic or dose-response data are available, these are applied, on a case by case basis, as appears appropriate.

It is recognized that there is a range of times that one might consider for these guidelines; however, it was the committee's decision to focus its efforts on only one time period. This decision was based on the availability to toxicology information and a reasonable estimate for an exposure scenario. Users who may choose to extrapolate these values to other time periods are cautioned to review the documentation fully since such extrapolations tend to hold only over very limited time frames, it at all.

Source - http://www.orau.gov/emi/scapa/erpgdefinitions.htm Accessed on September 19, 2005.

Appendix C: EI Protocol

Exposure Investigation Protocol
Warren Township, Trumball County, Ohio
Air Sampling for Sulfur Gases

November 2003

Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation

Background and Purpose

Warren Recycling Incorporated [WRI] is located one block south of West Market Street on Martin Luther King Boulevard in Warren, Trumball County, Ohio. The facility property encompasses approximately 200 acres of land and contains a construction and demolition debris (C&DD) landfill and a large building that serves as a transfer station for municipal solid waste. The C&DD landfill currently has three areas: two areas have been filled and covered and one 15-acre area is currently active. The landfill owners have purchased an adjacent property and plan to expand landfill operations.

Access to the facility is not adequately restricted. Residential and commercial properties surround the WRI site. Some homes are within 100 feet of the WRI property, and many yards abut facility boundaries. Several schools are located in the area: LaBrae High School, Leavitt Elementary School, and Bascom Elementary School. LaBrae High School and Leavitt Elementary School are each within one half mile of the landfill property boundary, while Bascom Elementary is several miles away.

In August 2003, the Agency for Toxic Substances and Disease Registry (ATSDR) presented the results of an Exposure Investigation (EI) involving hydrogen sulfide (H_2S) monitoring in Warren. In October 2003, ATSDR accepted a second EI proposal to follow up on findings from the first investigation. The purpose of the second EI is to determine if there are other sulfur gases present in indoor and ambient air. The presence of these gases may explain the differences found in instrument readings at the school as well as odors reported as having a slightly different smell than “rotten eggs”.

Previous sampling and ATSDR Activities

In mid-2002, ATSDR responded to a petition requesting a public health evaluation of community odor complaints, community health concerns, and available outdoor air hydrogen sulfide (H_2S) sampling results for Warren, Ohio. The petition noted special concern for school children as well as area residents living in close proximity to WRI [1]. ATSDR visited the community and reviewed the available information, including H_2S monitoring data collected in Spring 2002.

From May 7 through June 3, 2002, an environmental consultant hired by the LaBrae School District and the Warren Township Board of Trustees monitored air for H_2S. The consultant monitored five locations in the community including LaBrae High School and Leavitt Elementary School. Air sampling results showed H_2S levels reaching up to approximately 13 parts per million (ppm).

ATSDR subsequently prepared a Health Consultation concluding that exposures to levels of H_2S found in air were a public health hazard. However, because quality control information was lacking for the air results, ATSDR qualified this conclusion pending verification of the data. ATSDR recommended additional air monitoring, with proper quality assurance, inside and outside homes near the landfill [2]. In September 2002, the

ATSDR accepted an EI proposal to address this recommendation. ATSDR completed sampling activities for the first EI in April 2003 and documented levels of H_2S in ambient air at levels up to 6.1 ppm in the community.

In November 2002, each of the three schools purchased a portable electrochemical monitor/alarm to survey gas levels and to help ensure student safety. These monitors have been operating during school days since then. The school monitors have periodically indicated elevated readings (1-2 ppm) for extended durations of time (12-72 hours). For a three week period during the first EI, monitoring for H_2S was conducted at LaBrea High School. However, the monitoring results were not consistent with readings from the school's electrochemical monitor. This inconsistency may have occurred as a result of interference from other sulfur gases.

In the first EI, ATSDR concluded that an urgent public health threat exists based on a combination of elements. These elements include risks to people with pre-existing cardiopulmonary disease or respiratory problems, potential for fire and explosion, and physical health hazards. One of several recommendations was to conduct air sampling for other sulfur gases during odor events.

Community Concerns

On August 6, 2002, ATSDR held an availability session inviting residents to meet with local, state, and federal officials to express their health concerns. Staff members of ATSDR, ODH, and Ohio EPA interviewed approximately 150 residents. The health concerns voiced by residents consistently included the following: headaches, nausea, fatigue, eye irritation, and respiratory distress (including difficulty breathing and the exacerbation of asthma and other preexisting respiratory conditions). Many residents expressed that their children were exposed to odorous gases in school and reported that these odors have caused children to come home with headaches and nausea. Many residents further reported that children have been sent home from school repeatedly with "pink eye" (also called *conjunctivitis*). Residents living outside the area stated that when their children are sent home from school from nausea or headaches, they recover rapidly.

Most health complaints came from the residential areas closest to the active landfill cell, particularly from residents living off South Leavitt Road. People not residing in the area, but who work near the facility report that they do not notice the smell until they "come in to town for work", or "pass the landfill". The odor has been reported to be strong enough at times to induce vomiting or immediate nausea. In addition, residents have repeatedly asked ATSDR to investigate "other odors" that usually occur with the hydrogen sulfide odor (described as "rotten eggs, but a little different").

Rationale

On October 2, 2003, the ATSDR Exposure Investigation (EI) Section accepted a second EI proposal for the Warren community. This second EI will address a recommendation from the first EI to *conduct sampling for other sulfur gases during odor events.* At least one study indicates that, in addition to hydrogen sulfide, C&DD landfills emit several sulfur gases. The University of Florida tested ambient air and soil gas for H_2S and other sulfur gases at ten C&DD landfills. The following table summarizes the results for soil gases other than H_2S that were found at the C&DD landfills studied [3].

Table 1. Soil Gas Detection Ranges for Other Sulfur Gases at C&DD Landfills

Sulfur Gas	Range Detected (ppm)
Carbonyl Sulfide	BDL[+] to 61 ppm
Methyl Mercaptan	BDL to 164 ppm
Dimethyl Sulfide	BDL to 2.1 ppm
Ethyl Mercaptan	BDL to 0.2 ppm
Carbon Disulfide	BDL to 91 ppm
Isopropyl Mercaptan	BDL to 2.8 ppm
Butyl Mercaptans	BDL to 0.2 ppm
Thiophene	BDL to 0.1 ppm
2- and 3-Methylthiophene	BDL to 0.4 ppm

[+] BDL means Below the Detection Limit

During the initial EI, ATSDR co-located a tape meter with a portable monitor used at LaBrae High School to monitor H_2S levels. The tape meter measured H_2S levels using a tape impregnated with a reagent that turns pink or purple in the presence of H_2S. An optical detector measured the reflectance of the tape to determine the H_2S level. The tape meter provided a digital reading that was continuously recorded on a datalogger.

Although the tape meter never detected H_2S at the school, the portable monitor showed periodic readings of up to 2 ppm. The portable monitor uses a different technology to measure H_2S and is cross-sensitive to other sulfur compounds. As a result, it was not possible to fully interpret the data. Interference from another sulfur gas may have caused the different readings in the portable monitor and the tape meter.

By collecting several indoor and outdoor air samples during odor events, ATSDR can determine if exposures to other sulfur gases occur and if there are potential health implications from this exposure. Locations of interest include LaBrea High School and a residential area known to be impacted by hydrogen sulfide.

The exposure guidelines shown in Table 2 have been derived by government agencies for exposures to sulfur gases (other than hydrogen sulfide). Note that occupational exposure values are not used for community exposure/health outcome assessments. Occupational

values are provided for informational purposes and for short-term (10 to 15-minute ceiling values) comparisons that do not exist for environmental exposure scenarios.

Table 2. Available Exposure Guidelines for Other Sulfur Gases

Sulfur Gas	Agency*	Exposure Value **	Exposure Period†
Carbon Disulfide	NIOSH	1 ppm (3 mg/m^3) 10 ppm (30 mg/m^3)	TWA STEL
	OSHA	20 ppm 30 ppm 100 ppm	TWA Ceiling 30-minute max. peak
Methyl Mercaptan	NIOSH	0.5 ppm (1 mg/m^3)	Ceiling (15-minute)
	OSHA	10 ppm (20 mg/m^3)	Ceiling
Diethyl sulfate	NIOSH	0.1 ppm (0.5 mg/m^3)	TWA
	OSHA	1 ppm (5 mg/m^3)	TWA
Ethyl Mercaptan	NIOSH	0.5 ppm (1.3 mg/m^3)	Ceiling
	OSHA	10 ppm (25 mg/m^3)	Ceiling
m-Butyl Mercaptan	NIOSH	0.5 ppm (1.8 mg/m^3)	Ceiling
	OSHA	10 ppm (35 mg/m^3)	TWA

* NIOSH is the National Institute for Occupational Safety and Health; OSHA is the Occupational Safety and Health Administration.
** ppm is parts per million (part sulfur gas per million parts air, by volume); mg/m^3 is milligrams per cubic meter.
† TWA is time-weighted average; STEL is short-term exposure limit.

Investigators/Collaborators

Through an Interagency Agreement, ATSDR has provided funding to the Division of Federal Occupational Health to provide assistance in conducting air sampling in Warren. ATSDR will coordinate these sampling activities with the Mahoning/Trumball County Air Division, the Ohio Department of Health, the Ohio Environmental Protection Agency, and the U.S. EPA Region V.

ATSDR has recruited a resident who participated in the previous EI and whose home is located in an area where previous monitoring showed elevated H_2S levels. ATSDR will meet with the selected resident, obtain consent, provide the sampling canisters, and explain and demonstrate how to collect the samples as well as ship them to the laboratory.

ATSDR will work with the LaBrea District School Superintendent to arrange for air sampling at the school. The local fire chief has agreed to collect the samples at the school as part of his air monitoring activities there. ATSDR will notify the community

about the school air sampling activities. All efforts will continue to be coordinated through the ATSDR Regional Office and the Ohio Department of Health.

The Warren Health Department, the Trumball County Health Department, the U.S. EPA Region V, the Ohio EPA, and various other city and community representatives will be kept informed of ATSDR exposure investigation activities. ATSDR will evaluate the air sampling results and prepare an individual report for the school and residential participant as well as prepare the final report.

Target Population

The target population for this EI includes the residents of the selected home and the students and staff of LaBrea High School. The potentially affected population includes several hundred residents who live within ½ mile of the WRI facility. In addition, 1600 students attend nearby schools, two of which are within 0.25 mile of the facility.

Consent Forms

For the residential location, the adult who is currently the head of household (or their partner) will be required to sign an informed consent form (Attachment 1) in order to collect indoor and outdoor air samples.

Air Sampling Procedures

Grab air samples will be collected in SUMMA® canisters during two separate odor events. These samples will be analyzed for sulfur gases using a Gas Chromatograph - Selected Ion Capture Device (GC-SCD). Sample collection will involve opening a valve and drawing air into an evacuated chamber (the SUMMA® canister) for a 1-minute interval. ATSDR will demonstrate to the participants how to open and close the valve and have them to practice the procedure on a demonstration canister.

ATSDR will also provide instructions to each participant about proper procedures for sample handling and shipping. These instructions will include information about proper chain of custody and storage procedures. ATSDR will provide the necessary chain of custody and shipping documents and will fill them out as completely as possible ahead of time. The participants will need to fill out the time and date of sampling, sampling location, and collector's signature. For best results, the air samples must be analyzed within 48 hours of collection. Therefore, ATSDR will also provide a schedule of the best sampling and shipping dates.

ATSDR will provide two SUMMA® canisters for each odor event at each location (the residence and the school). At each sampling event, one sample will be collected indoors and one outdoors. ATSDR will provide the participating resident and the fire chief with

the SUMMA® canisters as well as a demonstration and information describing the procedures for use. In addition, ATSDR will provide a contact name and phone number where they can call for any needed assistance.

Quality Assurance/Quality Control

ATSDR will evaluate the analytical accuracy of the results provided by the laboratory using the documented quality control results for chemical recovery data and instrument calibration. In addition, ATSDR will use chain-of-custody forms to document sample collection, storage, and the description of requested analyses. The original forms will be sent along with the samples to the laboratory and ATSDR will maintain copies of the forms.

Reporting Results

Individual sampling results and an explanation of their significance will be provided in writing to the resident and school superintendent. Recommendations for follow-up actions will be made if warranted. A draft write-up of the results for each participant is included in Attachment 2.

Along with the school results, the residential sampling results will be made available to the public. However, ATSDR will not identify the specific participant and confidentiality will be protected according to federal and state laws. All records and computer files will be locked and password protected, respectively. At the conclusion of the EI, ATSDR will prepare a report that summarizes the findings of the investigation. The health guidelines displayed on page 5 of this protocol will be used to help evaluate the results and determine the level of public health hazard (if any). Note that occupational exposure values are not used directly in assessing community exposure and health outcomes. However, occupational values can provide guidelines in those cases where no comparison values exist for environmental exposure scenarios.

ATSDR will evaluate the results to determine if other sulfur gases are present during odor events. The results may also help determine whether sulfur gases are present at levels with potential public health implications. Levels of sulfur gases near or above those levels shown in Table 2 may indicate exposures of public health concern. However, lower levels of sulfur gases may be more difficult to interpret. If the data review indicates that a public health hazard or an urgent public health hazard exists, the resident and school superintendent will be notified by telephone and mail. If no hazard exists, the resident and superintendent will be notified of the results at the end of the investigation. At the end of the EI, all of the data will be evaluated and presented to the participants and community.

References

22. Letter from Petitioner to ATSDR. Atlanta: U.S. Department of Health and Human Services; April 2002.

23. ATSDR Health Consultation: Hydrogen Sulfide Exposure, Warren Township, Trumball County, Ohio; September 12, 2002.

24. State University System of Florida, Florida Center for Solid and Hazardous Waste Management. Gypsum drywall impact on odor production at landfills: Science and control strategies. December 2000 (updated January 2002). Report #00-09.

Attachment 1
Consent Form for Residential Environmental Sampling
Warren Township, Ohio
Exposure Investigation for Sulfur Gases

We are from the Agency for Toxic Substances and Disease Registry (ATSDR). We are inviting you to be part of an Exposure Investigation (EI) to learn if there are sulfur gases in and near your home. We are asking you because you live in an area where high levels of hydrogen sulfide were found. We want samples of indoor and outdoor air from one home and one school near the landfill. We will give you tools to collect air samples during two separate times when the air smells of rotten eggs. Your participation will help us see if levels of sulfur gases found inside or outside your home may pose a health problem to you or your family.

Procedure
We will give you two air sampling canisters. Each canister is about the size of a basketball. We will also show you how to use the canisters. When you smell sulfur, we want you to collect one sample inside and one sample outside your home. After collecting the samples, we want you to package both canisters with the packing supplies we've provided. Then you must promptly ship the package to a laboratory using Federal Express. ATSDR will give you all the forms and information about where the canisters must be shipped. You will need to sign chain of custody forms saying that you are sending the canisters to the lab. If possible, you should ship canisters the same day (Monday through Thursday) that you collect the samples. We will give you a list of the best sampling and shipping days. You can call Gail Scogin at 1-888-422-8737 if you have problems with the canisters or need more instructions. After you ship the first set of samples, ATSDR will send you two more canisters. You can use these canisters to collect another indoor and outdoor sample when you smell a sulfur odor.

Risks
It may be inconvenient to store air canisters in your home for a few days. It may also be inconvenient to collect air samples and ship the canisters to the laboratory. If people find out that your home has high amounts of sulfur gases, it could make it hard for you to sell your home until the source of the odor is removed. There are no other known risks from participating in this EI.

Benefits
You will learn if you are being exposed to sulfur gases other than hydrogen sulfide. You will also learn what the gases are and how high their levels are. You will also learn if these levels are high enough to pose a health problem for you or your family.

Participation
You can choose to be part of this project or not. If you change your mind you can stop being part of this project at any time without penalty. Even if you choose not to be part of this project, you can still get the results of the EI. You must sign this form to participate.

Results
Every effort will be made to send your results in writing within 3 months after the testing is finished. If we find out that there is something that needs to be dealt with right away we will tell you as soon as we find out.

Confidentiality
We will protect your privacy as much as the law allows. We will not use your name in any report from this EI. But because we will only be collecting air samples from one home, people may find out that your home is involved. If you choose to participate, any forms with your name will be kept in locked cabinets at ATSDR. The results will be stored in a computer that is protected by a password. Test results may be released only to other federal, state, and local public health and environmental agencies. These agencies must also protect this confidential information.

Contact
If you have any additional questions or feel that you have been harmed by this investigation, please contact Gail Scogin at ATSDR toll-free at 1 (888) 422-8737, or Michelle Colledge at ATSDR's Chicago Regional Office at (312) 886-0840.

Consent

The risks and benefits of this exposure investigation have been explained to me. All of my questions have been satisfactorily answered. Of my own free will, I agree to be part of the sampling described above.

I, (print) _____, agree to sample for sulfur gases at my home.

Signature: _____ Date: _____

Address: _____
Street

_____
City State Zip Code

Phone #: _____

Witness: _____ _____
(print name) (signature)

Attachment 2
Draft Letter for Providing Participant's EI Results

Date

Name
Address

Dear Participant:

During November and December 2003, you assisted the Agency for Toxic Substances and Disease Registry (ATSDR) by collecting indoor and outdoor air samples at your home. A laboratory tested each of those samples for sulfur gases. The results show that sulfur gases were found in __ of __ the samples you collected inside your home. Also, sulfur gases were found in __ of __ samples you collected outside your home.

Enclosed with this letter is a list of each sulfur gas found along with the amount found. The following table shows the highest level found for each sulfur gas in the indoor/outdoor air at your home.

Sulfur Gas	**Highest Level Found in Indoor/Outdoor Air at Your Home**	**Reference Level**	**Qualitative Level of Concern** **(low, moderate, high)**
n-Butyl mercaptan			
t-Butyl mercaptan			
Carbon disulfide			
Carbonyl sulfide			
Diethyl sulfide			
Dimethyl sulfide			
Dimethyl disulfide			
Ethyl mercaptan			
Hydrogen sulfide			
Isopropyl mercaptan			
Methyl mercaptan			
n-Propyl mercaptan			
Tetrahydrothiophene			
Thiophene			

We used your sample results to determine what sulfur gases are present when there is a sulfur smell at your home. The levels found may not be the same each time you smell sulfur. The sulfur gases found at your home are above/below levels of health concern for sulfur gases in air. [As appropriate, specific gases will be listed along with their respective potential health effects and any exposure-related recommendations.]

ATSDR will prepare a final report about all the investigation results. The report will not include your name or any information that identifies you. We plan to issue the report in _____. We will come back to Warren when the report is ready to present the findings and any recommendations to the community.

Thank you for your participation in the investigation. If you have any questions or concerns, you can call Gail Scogin at ATSDR toll-free at 1 (888) 422-8737, or Michelle Colledge at ATSDR's Chicago Regional Office at (312) 886-0840.

Sincerely Yours,

Gail Scogin
Agency for Toxic Substances and Disease Registry