Hydrogen Sulfide, Oil and Gas, and People's Health

Paper submitted for the fulfillment of a Masters Degree, Energy and Resources Group

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Table of Contents

Tables

Figures

1. Introduction

This paper documents impacts on human health caused by exposure to hydrogen sulfide (H_2S) associated with oil and natural gas development. I begin with a brief background on hydrogen sulfide, its presence in oil and natural gas, and possible emission sources from various oil and gas operations. I then present a review of literature[1] from available public health, epidemiology, and industrial health publications, as well as of sources from regulatory and environmental agencies, that addresses human health impacts from exposure to H_2S. The Literature Review section first covers studies of health effects from acute exposure to relatively high concentrations of H_2S. I then review the literature documenting human health effects from chronic exposure to lower ambient H_2S levels. Both kinds of exposure – acute and chronic – can be expected to occur near oil and gas operations. From the available sources, I construct a table of human health effects associated with different levels of hydrogen sulfide and different lengths of exposure. Reviewing studies on the effects of H_2S exposure on laboratory animals is beyond the scope of this study.

Next, I present current federal and state regulations and recommendations pertaining to exposure to hydrogen sulfide. Many recommendations established to protect human health are based on crude exposure estimates or on extrapolation from animal studies. The federal government does not regulate ambient H_2S levels, but many states do. Three states conduct routine monitoring of ambient H_2S levels, and several others have monitored H_2S as part of specific projects. I present the available monitoring

[1] I searched on-line catalogs including Web of Science and Environmental Sciences and Pollution Management, and tracked down relevant references listed within each article.

data, as well as anecdotal evidence about H_2S emissions and human health concerns that I obtained from conversations with staff at state environmental agencies.

The final component of my research consists of informal interviews with people living near oil and gas operations who have been, or believe they have been, exposed to hydrogen sulfide and believe they are experiencing adverse heath effects due to exposure. Enough evidence emerges from literature searches and reviews, environmental health professionals, available monitoring data, and personal stories to warrant more research. Although the evidence is patchy, the potential for health risks is real and the stakes are high. More monitoring and regulation are required to adequately protect human health.

2. Hydrogen Sulfide in the Environment

Approximately 90 percent of the sources that emit hydrogen sulfide into the air are natural.[2] Hydrogen sulfide is released into the air as a product of the decomposition of dead plant and animal material,[3] especially when this occurs in wet conditions with limited oxygen, such as in swamps. Hot springs, volcanoes, and other geothermal sources also emit H_2S.

Anthropogenic releases of H_2S into the air result from industrial processes, primarily from the extraction and refining of oil and natural gas and from paper and pulp

[2] EPA, "Report to Congress on Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Natural Gas." EPA-453/R-93-045, October 1993. " p.III-4.

[3] Decomposition of dead organic matter (DOM) by fungi, actinomycetes, and bacteria releases hydrogen sulfide from sulfur-containing proteins and from the direct reduction of sulfate (SO4+).

manufacturing,[4] but the gas is also present at sewage treatment plants, manure-handling plants, tanneries, and coke oven plants.[5]

3. Hydrogen Sulfide and Oil and Gas

Hydrogen sulfide is a naturally occurring component of crude oil and natural gas. Petroleum oil and natural gas are the products of thermal conversion of decayed organic matter (called kerogen) that is trapped in sedimentary rocks. High-sulfur kerogens release hydrogen sulfide during decomposition, and this H_2S stays trapped in the oil and gas deposits.[6]

Methane (CH_4) is the predominant component of natural gas, comprising 70 to 90 percent, while other gaseous hydrocarbons, butane (C_4H_{10}), propane (C_3H_8), and ethane (C_2H_6), account for up to 20 percent. Contaminants present in natural gas, which have to be removed at natural gas processing facilities, include water vapor, sand, oxygen, carbon dioxide, nitrogen, rare gases such as helium and neon, and hydrogen sulfide.[7] In fact, hydrogen sulfide is the predominant impurity in natural gas.[8] The Environmental Protection Agency (EPA) classifies natural gas as *sour* when H_2S is present "in amounts greater than 5.7 milligrams per normal cubic meters (mg/Nm^3) (0.25 grains per 100 standard cubic feet)."[9]

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[4] New York State Department of Health: available at http://www.health.state.ny.us/nysdoh/environ/btsa/sulfide.htm

[5] "Public Health Statement for Hydrogen Sulfide," Agency for Toxic Substances and Disease, September 2004. Available at http://www.atsdr.cdc.gov/toxprofiles/tp114-c1.pdf

[6] EPA "Report to Congress on Hydrogen Sulfide Emissions", p.II-1.

[7] *Oil and Gas at Your Door? A landowner's guide to oil and gas development*. OGAP 2005. p.I-2.

[8] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.II-i.

[9] Environmental Protection Agency, AP 42, Fifth Edition, Volume I, Chapter 5: The Petroleum Industry, available at http://www.epa.gov/ttn/chief/ap42/ch05/final/c05s03.pdf

Sour gas is routinely 'sweetened' at processing facilities called desulfurization plants. Ninety five percent of the gas sweetening process involves removing the H_2S by absorption in an amine solution, while other methods include carbonate processes, solid bed absorbents, and physical absorption.[10]

Between 15 to 25 percent of natural gas in the U.S. may contain hydrogen sulfide,[11] while worldwide, the figure could be as high as 30 percent. The exact number of sour wells in the United States is not known, though natural gas deposits in Arkansas, southeastern New Mexico, western Texas, and north-central Wyoming have been identified as sour.[12] Hydrogen sulfide occurs naturally in the geologic formations in the Rockies, the Midcontinent, Permian Basin, and Michigan and Illinois Basins.[13] As more natural gas development occurs in these areas, it is likely that the number of sour wells will increase, because new drilling is increasingly focused on deep gas formations that tend to be sour.[14] Although exact statistics on sour wells are not available, the EPA concedes that "the potential for routine H_2S emissions [at oil and gas wells] is significant."[15]

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[10] EPA, "Petroleum Industry." P.5.3-1. For details on these and other technologies for 'sweetening' sour gas, see "Crystasulf Process for Desulfurizing Ultra-deep Natural Gas Near the Wellhead," presented at *Natural Gas Technologies II Conference and Exhibition,* February 2004. Phoenix, AZ. Ref. No. T04135. pp.5-9.

[11] Dalrymple, D.A., Skinner, F.D. and Meserole, N.P. 1991. *Investigation of U.S. Natural Gas Reserve Demographics and Gas Treatment Processes.* Topical Report, GRI-91/0019, Section 3.0, pp. 3-1 to 3-13. Gas Research Institute. And Hugman, R.H., Springer, P.S. and Vidas, E.H. *Chemical Composition of Discovered and Undiscovered Natural Gas in the United States: 1993 update*. Topical Report, GRI-93/0456. p. 1-3. Gas Research Institute. As cited in McIntush, K.E., Dalrymple, D.A. and Rueter, C.O. 2001. "New process fills technology gap in removing H2S from gas," *World Oil*, July, 2001.

[12] EPA, "Report to Congress on Hydrogen Sulfide Emissions". p. I-3.

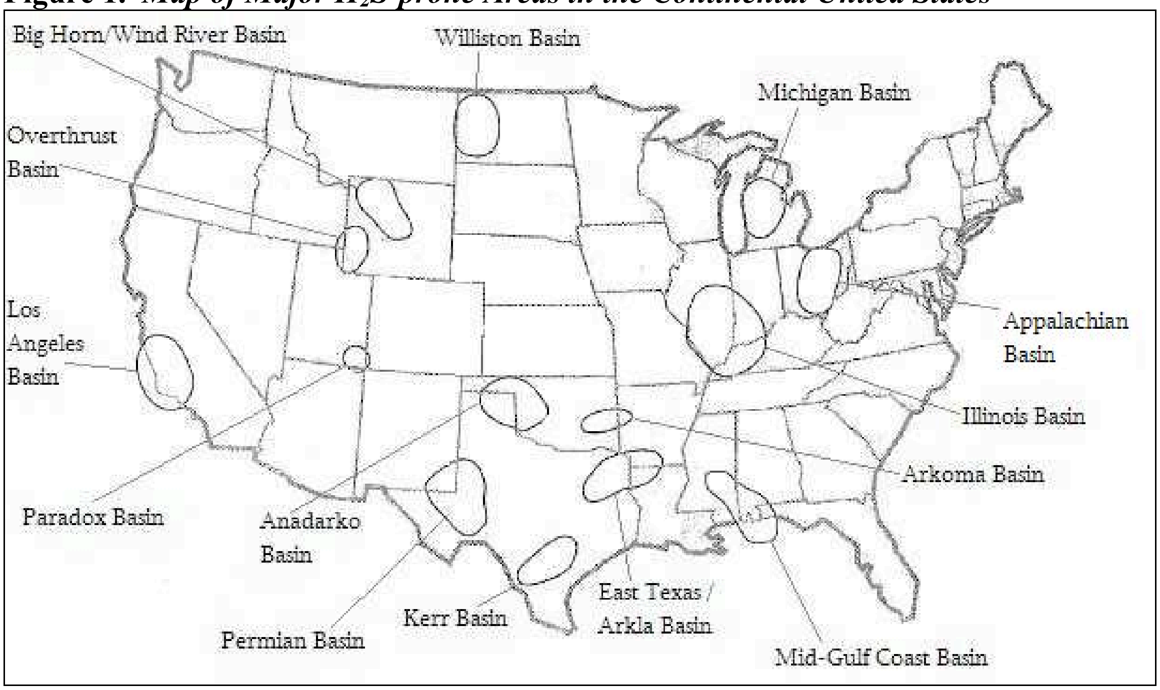
[13] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p. I-3.

[14] Quinlan, M., 1996. "Evaluation of selected emerging sulfur recovery technologies," *GRI Gas Tips*, 3(1):26-35. In McIntush, K.E., Dalrymple, D.A. and Rueter, C.O. 2001. "New process fills technology gap in removing H2S from gas," *World Oil*, July, 2001.

[15] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-35.

The most comprehensive source on the distribution of sour gas is a report prepared by consultants for the Gas Technology Institute, formerly Gas Research Institute, a research, development, and training organization that serves the natural gas industry.[16] This report states that "Regions with the largest percentage of proven reserves with at least 4 ppm hydrogen sulfide are Eastern Gulf of Mexico (89 percent), Overthrust (77 percent), and Permian Basin (46 percent)."[17] Figure 1 illustrates the major H_2S prone areas in the United States and identifies the basins.

Figure 1. ***Map of Major H_2S-prone Areas in the Continental United States***[18]



4. Hydrogen Sulfide Emissions from Oil and Gas Facilities

There has been some investigation of hydrogen sulfide emissions associated with oil and gas development.[19] In the Literature Review section, I summarize several studies

[16] Energy and Environmental Analysis, Inc. for Gas Research Institute, "Chemical Composition of Discovered and Undiscovered Natural Gas in the Lower-48 United States," GRI 90/0248. November 1990. (mailed to me by librarian for Gas Technology Institute).
[17] Energy and Environmental Analysis, Inc. for Gas Research Institute. pp.2-3.
[18] Energy and Environmental Analysis, Inc. for Gas Research Institute. p.1-13 and p.A-5.

that researched H_2S emissions near oil and gas facilities. Several states' environmental departments have monitored H_2S concentrations near oil and gas operations. My conversations with personnel at these agencies confirm that there are H_2S emissions associated with oil and gas activities. I present the evidence from the state studies and my conversations with staff in the State Regulations section. Finally, the interviews I conducted with people living near oil and gas sites attest to the presence of H_2S in the ambient air. Detailed narratives of the interviews are in Appendix D.

Oil and gas operations may emit hydrogen sulfide, routinely or accidentally, during the extraction, storage, transport, or processing stage.[20] During of extraction, hydrogen sulfide may be released into the atmosphere at wellheads, pumps, piping, separation devices, oil storage tanks, water storage vessels, and during flaring operations.[21] Flares burn gases that cannot be sold as well as gases at points in the system where operating problems may occur, as a safety measure. Because it cannot be sold, hydrogen sulfide is routinely flared. Sulfur dioxide (SO_2) is the product of combusting hydrogen sulfide, but in the event of incomplete combustion, H_2S may be emitted into the atmosphere.

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[19] For example, Environmental Protection Agency, "Report to Congress on Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Natural Gas." EPA-453/R-93-045, October 1993. and Tarver, Gary A. and Purnendu K. Dasgupta. "Oil Field Hydrogen Sulfide in Texas: Emission Estimates and Fate." *Environmental Science and Technology*. **31**: (12) 3669-3676. 1997.

[20] *Schlumberger Oilfield Glossary*, available at http://www.glossary.oilfield.slb.com/default.cfm

[21] EPA "Report on Hydrogen Sulfide Air Emissions," P.II-6. See Section II, pp.3 to 10 for details. A wellhead is the first piece of equipment where the oil leaves the ground. Pumps that extract the oil may leak at the seals. Piping connects the various machinery and storage units at an oil pad. Separation devices separate oil from gas and water, and pipes take the gas to a dehydrator, while other pipes direct water and oil to a heater-treater where the two are separated. The oil is then piped into an oil storage tank, and the water is piped into a produced water storage tank. Wellheads, pipes, and separation devices may leak hydrogen sulfide because of corrosion and embrittlement caused by the reaction of water with metal and H_2S, or due to poor maintenance and poor materials. The heater-treaters may release hydrogen sulfide due to high pressures or pressure changes above design specifications. Oil storage tanks may release hydrogen sulfide as a result of day-night temperature changes, volatilization, and filling operations. Produced water storage vessels may contain hydrogen sulfide dissolved in water that is brought up from the reservoir, or it may be produced by sulfate-reducing bacteria found in water and oil.

Based on reviewing the available literature and the records of agencies to which accidental releases of hydrogen sulfide might be reported,[22] the EPA states that well blowouts, line releases, extinguished flares, collection of sour gas in low-lying areas, line leakage, and leakage from idle or abandoned wells are sources of documented accidental releases that have impacted the public, not just workers at of oil and gas extraction sites.[23] Well blowouts are uncontrolled releases from wells, and can occur during drilling, servicing, or production, as a result of a failed 'blowout preventer' during drilling or a failed subsurface safety valve during production.[24] The release from a well blowout can last for an indefinite period.[25] After all economically recoverable oil and gas has been removed, the well needs to be plugged, or sealed. If a well is improperly sealed, hydrogen sulfide may routinely seep into the atmosphere. One study, discussed below, documented precisely this type of hydrogen sulfide emissions in Whaler's Cove, a community in Long Beach, California, where a townhouse development was built on a 1940s oil field. Additionally, hydrogen sulfide may be routinely or accidentally released into the atmosphere at oil refineries and natural gas processing facilities, including desulfurization plants.

Hydrogen sulfide emissions from oil and gas development may pose a significant human health risk, as the studies discussed below reveal. Workers in the oil and gas industry are trained to recognize and respond to high-concentration accidental releases of H_2S. The American Petroleum Institute (API), an oil and gas industry technical organization, publishes recommendations for practices that help prevent hazardous H_2S

[22] State agencies, emergency response organizations, industry officials. EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-36.
[23] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-38.
[24] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-45.
[25] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-49.

concentrations from occurring in the workplace.[26] People living near oil and gas development sites may be chronically exposed to much lower, but nonetheless dangerous ambient H_2S levels, as well as to accidental high-concentration releases. A 1993 EPA report on the emissions of hydrogen sulfide from oil and gas extraction acknowledges that because of the proximity of oil and gas wells to areas where people live, the affected population may be large.[27]

Additionally, the "Public Health Statement for Hydrogen Sulfide," a public health advisory summarizing the longer H_2S Toxicological Profile issued by the Centers for Disease Control and Prevention's Agency for Toxic Substances and Disease Registry (ATSDR), acknowledges that "As a member of the general public, you might be exposed to higher-than-normal levels of hydrogen sulfide if you live near a waste water treatment plant, a gas and oil drilling operation, a farm with manure storage or livestock confinement facilities, or a landfill. Exposure from these sources is mainly from breathing air that contains hydrogen sulfide."[28] The ATSDR also reports that higher than normal ambient "levels [of hydrogen sulfide] (often exceeding 90 ppb) have been detected in communities living near natural sources of hydrogen sulfide or near industries releasing hydrogen sulfide."[29]

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[26] API Recommended Practice (RP) 54, *Recommended Practice for Occupational Safety for Oil and Gas Well Drilling and Servicing Operations* and API RP 49, *Safe Drilling of Wells Containing Hydrogen Sulfide*.
[27] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-65.
[28] "Public Health Statement for Hydrogen Sulfide," Agency for Toxic Substances and Disease, September 2004. Available at http://www.atsdr.cdc.gov/toxprofiles/tp114-c1.pdf
[29] ATSRD, Ch2, p.1.

5. Human Health Effects from Exposure to Hydrogen Sulfide

Human health effects of exposure to hydrogen sulfide, an irritant and an asphyxiant, depend of the concentration of the gas and the length of exposure. Background ambient levels of H_2S in urban areas range from 0.11 to 0.33 ppb, while in undeveloped areas concentrations can be as low as 0.02 to 0.07 ppb.[30] A rotten egg odor characterizes H_2S at low concentrations, and some people can detect the gas by its odor at concentrations as low as 0.5 ppb.[31] About half of the population can smell H_2S at concentrations as low as 8 ppb, and more than 90% can smell it at levels of 50 ppb.[32] Hydrogen sulfide, however, is odorless at concentrations above 150 ppb, because it quickly impairs the olfactory senses.[33] This effect of disabling the sense of smell at levels that pose serious health risks and possibly are life-threatening is one especially insidious aspect of hydrogen sulfide exposure. Odor is not necessarily a reliable warning signal of the presence of H_2S.

Most effects to humans occur from inhalation, though exposure generally also affects the eyes. Because most organ systems are susceptible to its effects, hydrogen sulfide is considered a broad spectrum toxicant.[34] The organs and tissues with exposed mucous membranes (eyes, nose) and with high oxygen demand (lungs, brain) are the

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[30] Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological profile for hydrogen sulfide (*Draft for Public Comment*). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. Chapter 2, p.1.

[31] New York State Department of Health: available at http://www.health.state.ny.us/nysdoh/environ/btsa/sulfide.htm

[32] Collins, P. and Lewis, L. 2000. *Hydrogen Sulfide: Evaluation of Current California Air Quality Standard with Respect to Protection of Children.* Prepared for California Air Resources Board and California Office of Environmental Health Hazard Assessment. In: Summary of the toxicity assessment of hydrogen sulfide conducted by the Secretary's Scientific Advisory Board on Toxic Air Pollutants. http://daq.state.nc.us/toxics/studies/H2S

[33] Knight, Laura D., MD, and S. Erin Presnell, MD. 2005. "Death by Sewer Gas: Case Report of a Double Fatality and Review of the Literature." *The American Journal of Forensic Medicine and Pathology*. p.183.

[34] Legator, Marvin S., et al.. "Health Effects from Chronic Low-Level Exposure to Hydrogen Sulfide." *Archives of Environmental Health*. **56:** (2) 123-131. March/April 2001. p.124.

main targets of hydrogen sulfide.[35] Hydrogen sulfide acts similarly to hydrogen cyanide, interfering with cytochrome oxidase and with aerobic metabolism.[36] Essentially, hydrogen sulfide blocks cellular respiration, resulting in cellular anoxia, a state in which the cells do not receive oxygen and die. The human body detoxifies hydrogen sulfide by oxidizing it into sulfate or thiosulfate by hemoglobin-bound oxygen in the blood or by liver enzymes.[37] Lethal toxicity occurs when H_2S is present in concentrations high enough to overwhelm the body's detoxification capacity.[38]

At levels up to 100 to 150 ppm, hydrogen sulfide is a tissue irritant, causing keratoconjunctivitis (combined inflammation of the cornea and conjunctiva), respiratory irritation with lacrimation (tears) and coughing.[39] Skin irritation is also a common symptom. Instantaneous loss of consciousness, rapid apnea (slowed or temporarily stopped breathing), and death may result from acute exposure to levels above 1,000 ppm.[40] At these higher levels, hydrogen sulfide is an asphyxiant.

The non-lethal effects can be summarized as *neurological* – consisting of symptoms such as dizziness, vertigo, agitation, confusion, headache, somnolence, tremulousness, nausea, vomiting, convulsions, dilated pupils, and unconsciousness, and *pulmonary* – with symptoms including cough, chest tightness, dyspnea (shortness of

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[35] Legator, Marvin S., et al.. p.124.
[36] Knight, Laura D., MD, and S. Erin Presnell, MD. 2005. "Death by Sewer Gas: Case Report of a Double Fatality and Review of the Literature." *The American Journal of Forensic Medicine and Pathology*. p.183.
[37] Knight, 2005. p.184.
[38] Knight, 2005. p.184.
[39] Knight, 2005. p.183.
[40] Knight, 2005. p.183.

breath), cyanosis (turning blue from lack of oxygen), hemoptysis (spitting or coughing up blood), pulmonary edema (fluid in the lungs), and apnea with secondary cardiac effects.[41]

Table 1 lists the health effects associated with H_2S exposures of varying durations. The table reports health effects that toxicological and epidemiological studies have attributed to specific concentrations (or a range of concentrations) of hydrogen sulfide. Table 1 also includes health effects of exposure to known concentrations of H_2S that were self-reported by participants in the studies discussed below.

[41] Snyder, Jack W., MD, PhD. et al.. "Occupational Fatality and Persistent Neurological Sequelae After Mass Exposure to Hydrogen Sulfide." *American Journal of Emergency Medicine*. **13**: (2) 199-203. 1995. p.201.

Table 1: Health Effects Associated with Hydrogen Sulfide

entration ppm)	Length of Exposure	Effect	Source
)3 – 0.02	Immediate	Detectable odor	EPA Report 1993, p.III-5
0.2	Not reported (n.r.)	Detectable odor	Fuller, p.940
0 – 0.300	Prolonged	Nuisance due to odor from prolonged exposure	Milby, p.194
10	10 minutes	Eye irritation, chemical changes in blood and muscle tissue after 10 minutes	New York State Departmer Chart
> 30	Prolonged	Fatigue, paralysis of olfaction from prolonged exposure	Snyder, p.200
50	n.r.	Eye and respiratory irritation	Fuller, p.940
) – 100	Prolonged	Prolonged exposure leads to eye irritation; eye irritation (painful conjunctivitis, sensitivity to light, tearing, clouding of vision) and serious eye injury (permanent scarring of the cornea)	Milby p.194; EPA Report 1
0 - 200	n.r.	Olfactory nerve paralysis	EPA Report 1993, p.III-6
200	n.r.	Respiratory and other mucous membrane irritation	Snyder, p.200
250	n.r.	Damage to organs and nervous system; depression of cellular metabolism	EPA Report 1993, p.III-5
250	Prolonged	Possible pulmonary edema from prolonged exposure	Milby p.193
0 – 530	n.r.	Pulmonary edema with risk of death	Kilburn (1999), p.212
500	30 minutes	systemic symptoms after 30 minutes	Fuller, p.940
) –1000	Immediate	Stimulation of respiratory system, leading to hyperpnoea (rapid breathing); followed by apnea (cessation of breathing)	EPA Report 1993, p.III-5
750	Immediate	Unconsciousness, death	Fuller, p.940
1000	Immediate	Collapse, respiratory paralysis, followed by death	Fuller, p.940, EPA Report
) – 1000	Immediate	Abrupt physical collapse, with possibility of recovery if exposure is terminated; if not terminated, fatal respiratory paralysis	Milby, p.192
0 – 2000	n.r.	Immediate collapse with paralysis of respiration	Kilburn (1999), p.212
5000	Immediate	Death	Fuller, p.940

5.1 Literature Review - Acute Exposure

The following studies focused on short-term exposure to relatively high levels of hydrogen sulfide, the kind of scenario that can be expected from an accidental release. There are many documented instances and peer-reviewed studies of serious health effects and deaths from exposure to relatively high concentrations of hydrogen sulfide.

Fuller and Suruda (2000), who reviewed Occupational Safety and Health Administration (OSHA) investigation records from 1984 to 1994, reported 80 deaths in the United States from occupational exposure to hydrogen sulfide, out of a total 18559 occupational death during this period.[42] Twenty-two of the 80 deaths were in the oil and gas industry.[43] These deaths occurred as a result of workers' exposure to accidental releases of hydrogen sulfide in high concentrations. The authors concluded that portable H_2S meters or alarms could have prevented these deaths.[44]

In their 1997 study, Hessel et al. submitted a questionnaire about health effects from hydrogen sulfide exposure to 175 oil and gas workers in Alberta, Canada, a known region of sour gas. Of the 175 workers, one third reported having been exposed to H_2S, and 14 workers (8%) experienced knockdown,[45] a term for the loss of consciousness due to inhaling high concentrations of hydrogen sulfide. The workers who had experienced knockdown exhibited the respiratory symptoms of shortness of breath, wheezing while hurrying or walking up hill, and random wheezing attacks.[46] The investigators found no

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[42] Fuller, Douglas C., MD, MPH, and Anthony J. Suruda, MD, MPH. "Occupationally Related Hydrogen Sulfide Deaths in the United States From 1984 to 1994." *Journal of Occupational and Environmental Medicine*. **42**:(9) 939-942. September 2000. p.940.
[43] Fuller and Suruda, p.941.
[44] Fuller and Suruda, p.942.
[45] Hessel, Patrick A., PhD. et al.. "Lung Health in Relation to Hydrogen Sulfide Exposure in Oil and Gas Workers in Alberta, Canada." *American Journal of Industrial Medicine*. **31**:554-557. 1997., p.555
[46] Hessel, pp.555-556.

"measurable pulmonary health effects as a result of exposure to H_2S that were intense enough to cause symptoms but not intense enough to cause unconsciousness."[47] In other words, the workers who reported initially experiencing symptoms from H_2S exposure did not report exhibiting any lingering respiratory symptoms at the time of the study. However, other kinds of long term effects could exist; indeed, the study itself acknowledged that long term effects of acute short term exposure have not been studied enough, and finds this lack "noteworthy."[48]

Milby and Baselt (1999) relied on a review of literature about hydrogen sulfide poisoning, and state that "A phenomenon referred to as 'knockdown' has been reported in oil field workers and others to describe sudden, brief loss of consciousness followed by immediate full recovery after short-lived exposure to very high concentrations of hydrogen sulfide (e.g., 750-1000 ppm)."[49] However, other studies have contested this claim of full recovery following a knockdown.

Kaye Kilburn, a medical doctor and professor of medicine at the University of Southern California, has devoted a considerable part of his career to studying and reporting on the adverse health effects of hydrogen sulfide. Refuting Milby and Baselt's (1999) finding that full recovery followed unconsciousness, or 'knockdown,' Kilburn states, "In 1989, for the first time, sensitive testing showed that, although survivors who had been unconscious looked all right, brain functions were impaired. Similar impairments were measured in people exposed to amounts below 50 ppm that had not caused unconsciousness. Next, subtle impairments of brain function were measured from

[47] Hessel, p..556.
[48] Hessel, p.555.
[49] Milby, Thomas H. MD, and Randall C. Baselt, PhD. "Hydrogen Sulfide Poisoning: Clarification of Some Controversial Issues." *American Journal of Industrial Medicine*. **35**: 192-195. 1999. p.192.

exposures to concentrations of less than 5 ppm in air."[50] Kilburn reported examining one oil field worker, Stan, who had experienced 'knockdown' on the job after exposure to 1 percent hydrogen sulfide concentration (or 9,999 ppm as Stan's meter recorded it.) Three years after the incident, while appearing physically healthy, Kilburn's tests of Stan revealed significant brain damage (IQ lowered to 77, though the previous IQ is not reported), severely impaired balance and motor function, and inability to recall stories and visual designs.[51]

Another study by Kilburn (2003)[52] reported long term effects of hydrogen sulfide exposure. Kilburn performed physiologic and psychological measurements on nineteen exposed and 202 unexposed subjects.[53] Ten of the nineteen subjects were exposed at work, including four at oil and gas sites, while the other nine were exposed in their residences, which were near various sources of H_2S.[54] The concentrations to which the subjects were exposed are not known. Exposure times ranged from twenty minutes to nine years, and Kilburn examined the subjects from 1.7 to 22 years after their exposures.[55] The study methods consisted of a questionnaire and a series of neurophysiological and neuropsychological tests. The neurophysiological tests measured simple reaction time, visual two-choice reaction time, balance, color recognition, and hearing, and the neuropsychological tests measured immediate memory recall, mood, and vocabulary.[56] Tension, depression, anger, fatigue, and confusion were all significantly elevated in the

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[50] Kaye H. Kilburn. "Killer Molecules in Natural Gas." Chapter 7 in *Endangered Brains: How Chemicals Threaten Our Future*. Birmingham, AL: Princeton Scientific Publishers Company, Inc. 2004. p.78.
[51] Kilburn, (2004) p.79.
[52] Kilburn, Kaye H. "Effects of Hydrogen Sulfide on Neurobehavioral Function." *Southern Medical Journal*. **96**: (7) 639-646. 2003.
[53] Kilburn, (2003), p.640.
[54] Kilburn, (2003), p.640, see Table 1, p.641.
[55] Kilburn, (2003), p.640.
[56] Kilburn, (2003), pp.640-641.

exposed subjects compared to the control group. In addition, respiratory symptoms were more prevalent among the exposed subjects.[57] Even subjects who did not experience unconsciousness at the time of their exposure exhibited permanent neurobehavioral damage.[58]

The studies mentioned thus far focused on occupational exposure. They document the dangerous properties of hydrogen sulfide, as well as highlight the fact that more research is needed on the long term effects of even short duration exposures. There have been some studies of non-occupational exposure to relatively high H_2S levels. The proximity of oil refineries, gas treatment and processing plants, and oil and gas wells to residences constitutes a likely source of H_2S emissions and potentially poses a risk to people in a non-occupational setting.

Kilburn has studied the health effects of a series of explosions at an oil refinery in Wilmington, California, which occurred in October 1992. The explosions released unknown amounts of hydrogen sulfide into the air, making people ill in Wilmington, Torrance, Carson, Long Beach, and South Los Angeles.[59] Some street monitors recorded H_2S concentrations as high as 24 ppm, and since no one died, Kilburn concluded that concentrations probably did not exceed 200 ppm. Seven thousand people who had been exposed and sickened filed a consolidated lawsuit against the refinery, and a random sample were examined three and a half years after the explosion for court proceedings.[60]

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[57] Kilburn, (2003), p.643.
[58] Kilburn, (2003), p.644.
[59] Kilburn, (2004) p.77.
[60] 400 people were selected to represent the 7000 filing suit, and 120 were selected at random to be examined by a general practitioner. Then, 68 of the 120 were examined using sensitive neurobehavioral tests. Kilburn, (2004) p.81.

Persistent symptoms included impaired balance, delayed recall memory, elevated depression and confusion scores, and abnormally slow reaction times.[61]

As background to their 1987 study, which focused on methods of improving the prediction and management of public health risks associated with the development of sour gas wells, Layton and Cederwall[62] summarized studies of two incidents during which people were exposed to hydrogen sulfide released from gas operations. One occurred in 1950 in Mexico, where 320 people were hospitalized and 22 died as a result of a major hydrogen sulfide release from a gas purification plant.[63] The second incident, known as the Lodgepole blowout, was a sour gas blowout in Alberta, Canada, in 1982. In this case, the hydrogen sulfide releases lasted for 67 days, and the affected people reported headaches, eye irritation, and various respiratory and gastrointestinal symptoms.[64] In both instances, there were no reliable measurements of H_2S concentrations. In Alberta, maximum reported hourly concentrations were 15 ppm, and concentrations 100 kilometers away from the source were below 100 ppb, but residents there filed over a thousand complaints.[65] This study concluded that the hazard zone for sublethal effects around sour gas wells encompasses from less than 400 meters up to 6500 meters, while lethal exposure to hydrogen sulfide could occur as far as 2000 meters from the source.[66] Among the proposed recommendations for improving public safety is "preemptive land ownership,"[67] an issue which I revisit in the Concluding Remarks section. This study also stressed that

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[61] Kilburn, (2004) p.81.
[62] Layton, David W. and Richard T. Cederwall. 1987. "Predicting and Managing the Health Risks of Sour-Gas Wells." *Journal of the Air Pollution Control Association.* **37**: 1185-1190.
[63] Layton and Cederwall, 1987. pp.1185-1186.
[64] Layton and Cederwall, 1987. p 1186.
[65] Layton and Cederwall, 1987. p 1186.
[66] Layton and Cederwall, 1987. p 1188.
[67] Layton and Cederwall, 1987. p 1187.

sublethal effects of hydrogen sulfide are not well studied and that the dose-response relationship at lower levels is not well characterized.[68]

5.2 Literature Review - Chronic Exposure

Literature is also available on the human health impacts of chronic exposure to relatively low concentrations of hydrogen sulfide. Generally, chronic exposure to low-level concentrations of hydrogen sulfide is associated with neurological symptoms that include fatigue, loss of appetite, irritability, impaired memory, altered moods, headaches, and dizziness.[69] At persistent concentrations of 0.250 to 0.300 ppm (250 to 300 ppb), the rotten egg odor of H_2S creates a nuisance to communities, and exposure to such concentrations has been documented to affect quality of life by causing headaches, nausea, and sleep disturbances.[70]

Schiffman et al. (1995) evaluated the effect of odors emanating from swine operations on mood.[71] Although the source of odors were swine operations rather than oil and gas sites, the study is relevant because hydrogen sulfide caused the persistent odors, much as is the case near oil refineries and natural gas processing plants. This study concluded that continuously smelling odors is associated with "significantly more tension, more depression, less vigor, more fatigue, and more confusion."[72]

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[68] Layton and Cederwall, 1987. p 1185.
[69] McGavran, Pat. "Literature Review of the Health Effects Associated with the Inhalation of Hydrogen Sulfide." Idaho Department of Environmental Quality, Boise, Idaho. June 19, 2001. p.3.
[70] Milby, 1999, p.194.
[71] Schiffman, Susan S., Elizabeth A. Sattely, et al.. "The Effect of Environmental Odors Emanating From Commercial Swine Operations on the Mood of Nearby Residents." *Brain Research Bulletin*. 37:4 369-375. 1995
[72] Schiffman et al., p.371.

One frequently cited study, by Partti-Pellinen et al. (1996), examined the health effects of chronic, low-level exposure to sulfur compounds, including hydrogen sulfide, near a paper and pulp mill in Finland.[73] They found that the exposed people experienced eye and nasal symptoms, coughs, and headaches or migraines much more frequently than the people in the control group, while acute respiratory infections also occurred more frequently in the study group.[74] Once again, the study acknowledged the lack of data on long term effects of low-dose, chronic exposure, and concluded that, at the very least, the exposure and odor make "everyday life uncomfortable."[75]

Legator et al. (2001) investigated the effects of chronic, low levels of hydrogen sulfide by surveying two exposed communities, Odessa, Texas, and Puna, Hawaii, and comparing the health findings with several control communities.[76] Due to emissions from industrial wastewater, ambient concentrations of H_2S in Odessa, Texas, registered at 335 to 503 ppb over 8 hours, 101 to 201 ppb over 24 hours, with an annual average of 7 to 27 ppb.[77] Puna, Hawaii, is situated in a volcanically active area.[78] There were no reliable measurements of H_2S levels at Puna—they ranged from less than 1 ppb to periodic highs of 200 to 500 ppb. The study relied on a multi-symptom health survey and found various adverse health effects associated with hydrogen sulfide exposure in the study populations. The health symptoms included central nervous system impacts (fatigue, restlessness,

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[73] Partti-Pellinen, Kirsi, Marttila Olli, Vilkka Vesa, et al.. "The South Karelia Air Pollution Study: effects of low-level exposure to malodorous sulfur compounds on symptoms." *Archives of Environmental Health.* **51**. (4) 315-320 1996. The study looked at the main components of total reduced sulfur (TRS) compounds—hydrogen sulfide H_2S, methyl mercaptan, CH_3SH, dimethyl sulfide $[CH_3]_2S$, and dimethyl disulfide $[CH_3]_2S_2$.

[74] Partti-Pellinen et al.. Acute respiratory infections occurred 1.6 times per year in the study group as compared to 1.1 times per year in the control group.

[75] Partti-Pellinen, et al., p.320.

[76] Legator, Marvin S., et al.. "Health Effects from Chronic Low-Level Exposure to Hydrogen Sulfide." *Archives of Environmental Health*. **56:** (2) 123-131. March/April 2001.

[77] Legator, p.124.

[78] Since 1976, Puna is a site of geothermal energy production, and supplies about 30% of Hawaii's electricity. US Department of Energy.

depression, short term memory loss, balance, sleep problems, anxiety, lethargy, headaches, dizziness, tremors), respiratory system impacts (wheezing, shortness of breath, coughing), and various ear, nose, and throat symptoms.[79] This study also concluded with a call for more research:

> The findings in our study, taken together with previously reported data concerning adverse responses to H_2S, strongly mandate the need for continued research on the possible detrimental effects of chronic exposure to the toxic agent. This is of decided public health significance, given the relatively large segment of the population that is regularly exposed to low levels of H_2S.[80]

Kilburn has also studied health impacts from chronic exposure to lower concentrations of hydrogen sulfide. He examined a preacher and eighteen congregation members in Odessa, Texas, who lived downwind from an oil refinery and often smelled the characteristic rotten egg odor of H_2S, occasionally experiencing nausea and vomiting.[81] Kilburn observed impaired balance, delayed verbal recall for stories, and difficulty distinguishing colors among the people he studied in Odessa.[82] Workers and people living downwind of another oil refinery, in Nipoma Mesa near San Luis Obispo, California, also exhibited impaired reaction time, impaired balance, depression, and impaired recall memory.[83]

As a result of poorly plugged wells of an abandoned oil and gas field in Long Beach, California, people living in a community built on this location were exposed to hydrogen sulfide that collected under concrete foundations and crawl spaces of homes,

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[79] Legator, pp.126-129.
[80] Legator, p.130.
[81] Kilburn, (2004) p.79.
[82] Kilburn, (2004) p.80.
[83] Kilburn, (2004) p.80.

and in a low lying area around a communal swimming pool.[84] The H_2S measurements ranged from 0.1 ppm to 1 ppm, with several peaks up to 5 ppm.[85] Kilburn examined 24 people from this community, and recorded abnormal balance with closed eyes, delayed verbal recall, and impaired color discrimination and grip strength, as compared to a control group.[86]

As reported by the EPA,[87] two notable occasions of increased ambient concentrations of hydrogen sulfide occurred in Great Kanawha River Valley, West Virginia, in 1950, and in Terre Haute, Indiana, in 1964. In Terre Haute, ambient H_2S concentrations ranged from 2 to 8 ppm, emanating from a lagoon. In West Virginia, the highest concentration was 293 ppb, but there is no information on other levels. In both cases, symptoms included malaise, irritability, headaches, insomnia, and nausea, while the people exposed in Terre Haute also reported, among other effects, throat irritation, shortness of breath, eye irritation, diarrhea, and weight loss.[88] These incidents provide some evidence of health impacts from chronic exposure to ambient levels of hydrogen sulfide in the range that may be expected to occur near oil and gas sites.

Tarver and Dasgupta (1997) measured hydrogen sulfide concentrations near several oil fields in western Texas.[89] Although the researchers were studying the effects of increased anthropogenic sources of sulfur emissions on the sulfur cycle, the authors nevertheless gathered data that is pertinent to my research. The study found nighttime

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[84] Kilburn, Kaye H. "Evaluating health effects from exposure to hydrogen sulfide: central nervous system dysfunction." *Environmental Epidemiology and Toxicology*. **1**:207-216. 1999. p.208.
[85] Kilburn (1999), p.208.
[86] Kilburn, (1999), p.210.
[87] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-32. For the entire paragraph.
[88] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-32
[89] Tarver, Gary A. and Purnendu K. Dasgupta. "Oil Field Hydrogen Sulfide in Texas: Emission Estimates and Fate." *Environmental Science and Technology*. **31**: (12) 3669-3676. 1997.

maximum H_2S concentrations between 1 and 5 ppb.[90] While this concentration of hydrogen sulfide is only enough to produce an odor, a persistent odor can be a nuisance, and has been associated with increased tension, depression, fatigue, confusion, and decreased vigor.[91]

Some evidence exists on the effects of hydrogen sulfide on the reproductive system. Xu et al. (1998) conducted a retrospective epidemiological study to assess the association between spontaneous abortion and exposure to petrochemicals.[92] By reviewing the plant employment records, which also contain medical information, the researchers identified over 3000 women from the Beijing Yanshan Petrochemical Corporation who had been pregnant. Trained interviewers administered a questionnaire to gather information on the subjects' reproductive history, pregnancy outcomes, employment history, occupational exposure, smoking habits, alcohol consumption, indoor air pollution, diet, and demographic variables.[93] The study found that "exposure to petrochemicals, specifically benzene, gasoline, and hydrogen sulphide is significantly associated with increased frequency of spontaneous abortion."[94] Each chemical was individually found to have a statistically significant effect on the frequency of spontaneous abortion. Although the exposures mainly occurred in maintenance operations or due to accidental leaks and spillages,[95] rather than being chronic low level exposures,[96] this study is nevertheless important for the link it established between hydrogen sulfide

[90] Tarver and Dasgupta, p.3673.
[91] Schiffman et al. Discussed above on p.18.
[92] Xu, Xiping, Sung-Il Cho, et al.. "Association of petrochemical exposure with spontaneous abortion." *Occupational and Environmental Medicine*. 55: 31-36. 1998.
[93] Xu et al., p.31.
[94] Xu et al., p.34.
[95] Xu et al., p.35.
[96] The study acknowledged that "at lower exposures, the reproductive effects of hydrogen sulphide have not been determined, although it has been shown to enhance the fetal toxicity of carbon disulphide." Xu et al., pp.34-35.

and effects on the reproductive system. According to one personal account recounted below, hydrogen sulfide exposure is associated with spontaneous abortions in cattle as well as other reproductive effects in animals.

Most studies acknowledge that there is a need for more research on the health impacts of chronic exposure to lower concentrations of H_2S. Although the health effects are not well documented,[97] many studies recognize the potential for harm. In 1993, the EPA prepared an in-depth report on hydrogen sulfide emissions associated with oil and gas extraction.[98] The report matched available routine emissions data from oil and gas sites with studies documenting health effects of these levels, and assessed the risk of accidental releases, to determine whether these warrant a national control strategy.[99] Although the report acknowledged that oil refineries and gas processing plants are a major possible source of H_2S, these were not included in the analysis because they fall outside the definition of the term 'extraction.'[100] The report also excluded exploration and well development activities. Each of these areas of oil and gas operations is a potential source of hydrogen sulfide emissions.

The report concluded that "the potential for human and environmental exposures from routine emissions of H_2S from oil and gas wells exists, but insufficient evidence exists to suggest that these exposures present any significant threat,"[101] and that "there appears to be no evidence that a significant threat to public health or the environment exists from routine H_2S emissions from oil and gas extraction."[102] The EPA reached this

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[97] New York State Department of Health, http://www.health.state.ny.us/nysdoh/environ/btsa/sulfide.htm
[98] EPA, "Report to Congress on Hydrogen Sulfide Emissions."
[99] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-1.
[100] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.I-4.
[101] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.iii.
[102] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.V-1.

conclusion "from the limited data available."[103] However, because, as the report itself acknowledged, there is not enough information on ambient air quality around well sites,[104] the conclusion that there are no health risks is ill founded. A call for further research would have been more appropriate, but strikingly, the "Research and Further Studies" section of the last chapter does not recommend additional research of routine hydrogen sulfide emissions and health effects.

[103] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.V-1.
[104] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-1.

and Suruda)	Medicine	To determine the number of occupational deaths related to hydro sulfide; review of OSHA records; acute exposure
and Baselt)	Medicine / Toxicology	Review of literature on hydrogen sulfide; focusing on neurotoxi acute exposure, effects on the lungs, diagnosis of poisoning, and community exposure issues.
l et al. (1997)	Public Health	To assess pulmonary health effects of oil and gas workers in Alb Canada; administered questionnaire to 175 workers
r et al. (1995)	Medicine	To assess neurological problems from exposure to hydrogen sul review of case reports from an incident of mass exposure to H2S Jersey; calls for annual neurological and neuropsychological tes exposed subjects to enhance knowledge of long term effects
Pellinen et al.)	Medicine / Public Health	Examined health effects chronic, low-level exposure to sulfur co including H2S, near a paper and pulp mill; administered cross-se questionnaire to 336 subjects and to a reference community; inc frequency of eye and nasal symptoms, coughs, and headaches or migraines, and acute respiratory infections.
or et al. (2001)	Medicine / Toxicology / Public Health	Investigate effects of chronic exposure to low levels of hydroger multi-symptom health survey submitted to two exposed commu Odessa, Texas and Puna, Hawaii, and to control communities; f central nervous system impacts: fatigue, restlessness, depression term memory loss, balance and sleep problems, anxiety, letharg headaches, dizziness, tremors; respiratory system impacts: whee shortness of breath, coughing; and various ear, nose, and throat s
r and Dasgupta)	Chemistry	To determine hydrogen sulfide concentrations near oil fields in Texas
al. (1998)	Medicine / Epidemiology	To determine effects of exposure to hydrogen sulfide on the rep system; conducted a retrospective epidemiological study to asse association between spontaneous abortion and exposure to petro in Beijing, China; found an association.
rn (1999)	Epidemiology	To determine long-term effects of exposure to hydrogen sulfide; and submitted a questionnaire to four groups of people that were to hydrogen sulfide (from boreholes in the ground, downwind o refinery, due to an oil refinery explosion, and a group of people odors); found abnormal balance, delayed verbal recall, impaired discrimination and grip strength.
man et al. (1995)	Psychiatry	To determine the effect of persistent environmental odors on the people living near the source of odors; submitted a questionnair subjects and 44 controls; found more tension, depression, fatigu confusion, and less vigor among the exposed subjects.
rn (2003)	Epidemiology	To measure long term effects of hydrogen sulfide exposure – va lengths of exposure and various concentrations; submitted a que and performed neuropsychological and neurophysiological tests exposed subjects and 202 unexposed subjects; found elevated te depression, anger, fatigue, and confusion, and more prevalent re symptoms among exposed subjects.
n and Cederwall)	Engineering / Public Health	Methods for improving the prediction and management of publi risks associated with development of sour gas wells
t and Presnell)	Medicine / pathology	Review of literature on H2S toxicology; case study of two fatali occupational exposure to H2S

6. Regulations and Recommendations for Exposure to Hydrogen Sulfide

6.1 Federal Recommendations and Regulations

At the federal level, some regulations and recommendations exist to protect humans from the health effects of exposure to hydrogen sulfide. Regulations are laws that can be enforced by agencies such as the Environmental Protection Agency (EPA), the Food and Drug Administration (FDA), and the Occupational Safety and Health Administration (OSHA). Recommendations, on the other hand, do not carry the force of law, and are determined by agencies such as the National Institute for Occupational Safety and Health (NIOSH) and the Agency for Toxic Substances and Disease Registry (ATSDR), both part of the federal Centers for Disease Control and Prevention (CDC).

The American Conference of Governmental Industrial Hygienists (ACGIH), a longstanding member-based organization committed to promoting worker health and safety, also recommends exposure limits for various substances. The current ACGIH hydrogen sulfide standards are 10 ppm for the Threshold-Limit Value-Time Weighted Average (TLV-TWA), and 15 ppm for the TLV short term exposure limit (TLV-STEL). The TVL-TWA is the time-weighted average concentration to which workers can be routinely and consistently exposed over an 8-hour workday and 40-hour workweek without adverse effect. The TVL-STEL is the concentration to which workers can be exposed for short periods of time without suffering adverse health effects. The ACGIH updates its standards annually, and can relatively quickly modify its standards in response to new research.[105]

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[105] EPA "Report to Congress on Hydrogen Sulfide Emissions," p.III-10.

OSHA began setting standards for workers' exposure to hazardous substances in the 1970s, and initially adopted the ACGIH values.[106] The current OSHA workplace standard for H_2S exposure is 10 parts per million (ppm), while the exposure times are longer than the ACGIH recommends. In more detail, according to OSHA, "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."[107] The OSHA regulations do not specify an 8-hour time weighted average (TWA) for H_2S. Exposure to these concentrations even for the seemingly short duration of 10 minutes can nevertheless result in eye and respiratory irritation, according to several sources. The NIOSH recommended exposure limit to the OSHA 10 ppm standard is 10 minutes, and its Immediately Dangerous to Life or Health (IDLH) H_2S concentration is 100 ppm.[108] OSHA standards have the force of law, while ACGIH's and NIOSH's levels are only recommendations.

It is important to note that OSHA standards apply only to workplaces and not to domestic situations or residences. The human data on which the standards are based are from uncontrolled exposure incidents, so the levels of exposure are crudely estimated.[109] In general, the controlled exposure data is derived from animal studies and then extrapolated to humans. As one study discussed above summed up, "a precise ratio with which to predict human effects on the basis of the ratio of rat-to-human effects is

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[106] EPA "Report to Congress on Hydrogen Sulfide Emissions," p.III-10.
[107] Occupational Safety and Health Administration, 29 CFR 1910.1000, available at http://www.osha.gov/dts/chemicalsampling/data/CH_246800.html
[108] NIOSH is a department within the Centers for Disease Control and Prevention. See http://www.cdc.gov/niosh/npg/npgd0337.html for NIOSH's H_2S exposure recommendations.
[109] Guidotti, Tee L. 1994. "Occupational exposure to hydrogen sulfide in the sour gas industry: some unresolved issues." *International Archives of Occupational and Environmental Health*. p.157.

lacking."[110] Further, the standards are based on the expected effects of hydrogen sulfide on healthy adult males, so people who are young, old, or have compromised immune systems may be at risk at considerably lower concentrations of H_2S. Additionally, exposure to hydrogen sulfide may affect the human reproductive system, as determined in the study by Xu et al. and reported above, so standards based on males may not protect women's reproductive health.

In addition to general standards for workplace inhalation exposure, OSHA specifically sets standards for industries in which hydrogen sulfide occurs in quantities exceeding 1500 pounds, in their Process Safety Management of Highly Hazardous Chemicals Standard (1910-119). Significantly, the oil and gas industry is exempt from this standard.[111] According to the 1993 EPA report, the reason OSHA gave for this exemption is that OSHA "continues to believe that oil and gas well drilling and servicing operations should be covered in a standard designed to address the uniqueness of the industry."[112] OSHA also proposed a monitoring program for hydrogen sulfide for drilling and service operations that occur in areas where H_2S exposure is a potential risk.[113] Neither of these exists at the time of writing.

The 1990 Clean Air Act is the primary federal law that regulates air pollution. The EPA sets the levels of various air pollutants, including the National Ambient Air Quality Standards (NAAQS) for six criteria pollutants and the National Emissions Standards for Hazardous Air Pollutants (NESHAPs) for another 188 substances commonly referred to as

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110 Kilburn, Kaye H. "Effects of Hydrogen Sulfide on Neurobehavioral Function." 2003. p.639.
111 OSHA, http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9760
112 As quoted in EPA "Report to Congress on Hydrogen Sulfide Emissions," p.IV-28.
113 EPA "Report to Congress on Hydrogen Sulfide Emissions," p.IV-30.

HAPs.[114] The EPA does not regulate hydrogen sulfide as one of its criteria pollutants nor as one of the HAPs under the 1990 Clean Air Act. When George Bush, Sr. signed the Clean Air Act in 1990, H_2S was not among the 188 chemicals on the final HAPs list to be regulated, despite the calls of public interest groups and government scientists, some even within the EPA, for its inclusion. Hydrogen sulfide had been on the proposed original list of hazardous substances,[115] and was removed from this list as a result of successful efforts by the oil and gas, chemical, and paper industries.[116] For instance, the American Petroleum Institute, representing the interests of the oil and gas industry, argued that H_2S emissions are an "accidental-release issue" rather than a routine one,[117] and that H_2S therefore should not be regulated as one of the Clean Air Act's Hazardous Air Pollutants. This lack of an EPA standard has prompted one newspaper to label hydrogen sulfide "the least regulated common poison."[118]

Hydrogen sulfide is on the EPA's list of Extremely Hazardous Substances,[119] another category under the Clean Air Act, which regulates substances "known or may be anticipated to cause death, injury, or serious adverse effects to human health or the

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[114] According to the EPA, "Hazardous air pollutants, also known as toxic air pollutants or air toxics, are those pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects." http://www.epa.gov/ttn/atw/pollsour.html

[114] Interestingly, hydrogen sulfide remained on the list as a result of "administrative error" until it was removed by a Senate Joint Resolution on August 1, 1991. See http://www.epa.gov/ttn/atw/pollutants/atwsmod.html for details.

[115] Interestingly, hydrogen sulfide remained on the list as a result of "administrative error" until it was removed by a Senate Joint Resolution on August 1, 1991. See http://www.epa.gov/ttn/atw/pollutants/atwsmod.html for details.

[116] Jim Morris. "Lost Opportunity: EPA had its chance to regulate hydrogen sulfide." November 8, 1997. *The Houston Chronicle.*

[117] As quoted in *The Houston Chronicle.*

[118] Jim Morris, *The Houston Chronicle.*

[119] Environmental Protection Agency, Chemical Emergency Preparedness and Prevention. Look for H_2S on the list at http://yosemite.epa.gov/oswer/ceppoehs.nsf/Alphabetical_Results!OpenView&Start=146

environment upon accidental release."[120] This classification requires companies that produce the substance to develop plans to prevent and respond to accidental releases. Importantly, however, this classification does not require regular emission controls of the substance.[121] Additionally, H_2S is not on the list of toxic substances whose releases companies are required to report under the EPA's Toxic Release Inventory (TRI).[122] This exclusion is due to an administrative stay put in place on August 22, 1994, as a result of lobbying by a paper, forest, and wood products industry association.[123] The administrative stay will remain in effect until the EPA decides to lift it.

At the time of writing, the EPA is considering whether to re-evaluate including hydrogen sulfide on the HAPs list of the Clean Air Act.[124] The EPA is motivated by some concerns regarding chronic and acute exposure to hydrogen sulfide.[125] Further, if they proceed with research, the EPA's findings may inform action on the current administrative stay that is responsible for exempting H_2S from TRI reporting requirements.[126]

The EPA does, however, have an inhalation reference concentration (RfC) for hydrogen sulfide, which is "an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure of the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a

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[120] Section 112(r) of the Clean Air Act, as cited in EPA, "Report to Congress on Hydrogen Sulfide Air Emissions," p.i.
[121] Jim Morris, *The Houston Chronicle*.
[122] EPA's Toxic Release Inventory list of chemicals for Reporting Year 2004. Available at http://www.epa.gov/tri/chemical/RY2004ChemicalLists.pdf
[123] See http://www.epa.gov/tri/guide_docs/2001/brochure2000.pdf, footnote on p.18.
[124] Personal communication with Jim Hirtz, February 24, 2006. US EPA, Health and Environmental Impacts Division, Research Triangle, North Carolina. The EPA undertook this action in response to a request by an environmental organization from Texas.
[125] Personal communication with Jim Hirtz, February 24, 2006. US EPA, Health and Environmental Impacts Division, Research Triangle, North Carolina.
[126] Personal communication with Jim Hirtz, March 2, 2006. US EPA, Health and Environmental Impacts Division, Research Triangle, North Carolina.

lifetime."[127] The RfC is one important standard for chronic exposure. According to the EPA's on-line Integrated Risk Information System (IRIS) database, the current inhalation RfC for hydrogen sulfide is $2x10^{-3}$ mg/m^3 (1.4 ppb). Applying the RfC definition, this means that it is possible that inhaling more than this concentration on a daily basis over a lifetime poses "an appreciable risk of deleterious effects." The RfC is well below any occupational standards set by OSHA or recommended by NIOSH and the ACGIH

The EPA also recommends levels of hydrogen sulfide for their Acute Exposure Guideline Levels (AEGL) for various exposure periods. These threshold exposure limits apply to the general public for emergency exposures ranging from 10 minutes to 8 hours, and are "intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals."[128] Appendix A includes definitions of the AEGL categories, and the recommended H_2S levels for each exposure period and AEGL category.

Other guidelines also exist for exposure to hydrogen sulfide in emergency situations. To protect the health of the general public in the event of an emergency release, the American Industrial Hygiene Association (AIHA) establishes Emergency Response Planning Guidelines (ERPGs), which specify one-hour exposure limits. These limits are also included in the table in Appendix A.

The National Research Council's Committee on Toxicology recommended Emergency Exposure Guidance Level (EEGL) to the Department of Defense for

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[127] EPA Integrated Risk Information System, Hydrogen sulfide (CASRN 7783-06-4), http://www.epa.gov/iris/subst/0061.htm.

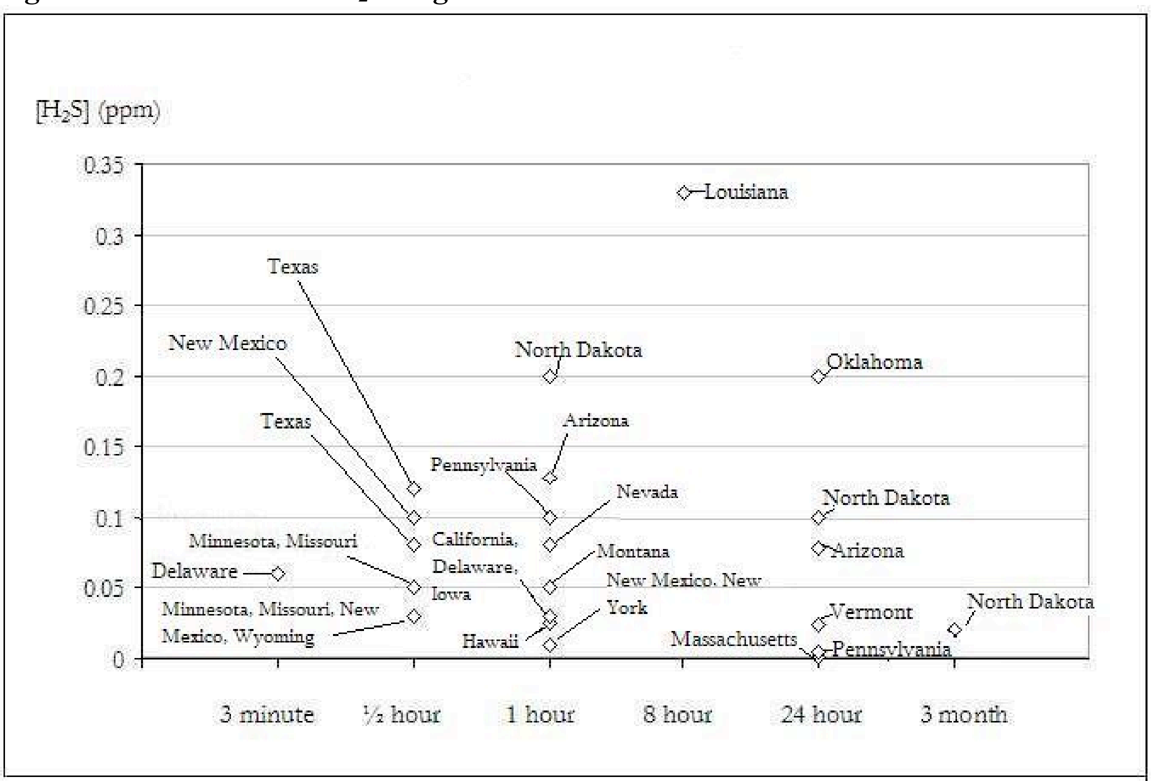
[128] EPA, The Development of Acute Exposure Guideline Levels (AEGLs), http://www.epa.gov/oppt/aegl/index.htm

maximum concentrations acceptable in rare situations such as spills and fires.[129] The EEGLs apply to young and healthy military personnel, and exist for 41 substances, of which hydrogen sulfide is one. The 10 minute EEGL for H_2S is 50 ppm, and the 24 hour H_2S EEGL is 10 ppm.[130]

6.2 State Regulations

In the absence of federal standards for ambient levels of hydrogen sulfide, many states have passed their own laws to regulate H_2S emissions. Figure 2 is a snapshot of state ambient hydrogen sulfide regulations. It illustrates the wide range of existing state standards.

Figure 2: State Ambient H_2S Regulations



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[129] National Oceanic and Atmospheric Administration, Office of Response and Restoration, "Public Exposure Guidelines" at http://archive.orr.noaa.gov/cameo/locs/expguide.html

[130] As cited in the EPA "Report to Congress on Hydrogen Sulfide Emissions," p.III-14.

A detailed table listing the states with ambient H_2S standards can be found in Appendix B. States set their standards based on a variety of justifications, and if available, these are also listed in Appendix B. I compiled this data by reviewing information available on each state environmental department's website, and by speaking with appropriate staff. Some states have based their ambient standard for hydrogen sulfide on odor thresholds, while others have based their standard on health considerations, either adopting the EPA's RfC inhalation guideline, modifying the OSHA safety standard to apply to continuous exposure, or basing their standard on other health studies. The fact that these states have taken the initiative to regulate ambient H_2S indicates that there is concern for human health even at these relatively low levels.

Many states' health/environmental departments routinely receive odor complaints about hydrogen sulfide. Specifically, staff at agencies in Colorado, Idaho, Iowa, Kansas, Michigan, Montana, Nevada, New Mexico, Ohio, Oregon, Texas, and Wyoming reported receiving many H_2S odor complaints. In Kansas and Ohio, people have also complained about health effects from hydrogen sulfide. In Colorado, there have been some cattle deaths attributed to exposure to hydrogen sulfide, which had collected in low-lying areas.

In addition to inquiring about ambient hydrogen sulfide standards, I collected information about any monitoring of H_2S – routine or otherwise – that the state agency conducts. The most frequently cited reason for the lack of routine monitoring, even in states with ambient H_2S standards, are budget constraints. A number of people said that monitoring and more information in general would be desirable. Some states have conducted periodic, project-based monitoring of hydrogen sulfide. Studies of hydrogen sulfide emissions from Arkansas, Colorado, Louisiana, New Mexico, and North Dakota are available. These studies are of varying quality and scope, but each sheds some light on the topic of hydrogen sulfide emissions and oil and gas operations.

6.2.1 Special H_2S Monitoring Studies

6.2.1.1 Arkansas

The Arkansas Department of Environmental Quality conducted two hydrogen sulfide monitoring studies in response to numerous health and welfare related concerns of Texarkana residents about emissions from gas processing plants in the area.[131] The first study, spanning 1995 to 1997, was a scoping study to determine whether hydrogen sulfide was indeed present in ambient air and to determine whether the facilities that were emitting H_2S were in compliance with their emissions permits. After this study established that H_2S was present in the air, a second, more rigorous study was conducted from March 1998 through March 1999. The state does not have an ambient hydrogen sulfide standard.

The monitoring data from the latter study has been reported to the EPA's Air Quality System (AQS) database. The AQS database contains measurements of air pollutants – criteria pollutants, hazardous air pollutants, and other monitored substances – and this data is publicly available.[132] The Arkansas Department of Environmental Quality itself did not provide any monitoring data or comments. Data from the AQS site[133] is available for two monitoring locations, which are classified as rural residential. At the first monitoring location, the mean concentrations for the monitoring periods from May to

[131] Pleasant Hills H_2S Study, obtained February 2006 by mail from Jay Justice, Senior Epidemiologist with the Arkansas DEQ.
[132] http://www.epa.gov/air/data/aqsdb.html
[133] http://oaspub.epa.gov/aqspub1/aqs_query.psite The code for hydrogen sulfide is 42402.

July 1998, and October to December 1998, were 2.4 ppb and 3.4 ppb, respectively, and the maximum hydrogen sulfide concentrations were 35 ppb and 24 ppb, respectively. The levels of H_2S recorded at the second monitoring location for which data is available on the AQS site were slightly higher than at the first. The mean concentration in December 1998 was 4 ppb, and in January 1999, 5.5 ppb. The maximum concentration recorded in those months were 55 ppb and 127 ppb, respectively. These levels of hydrogen sulfide, while not very high, are nevertheless higher than normal urban background levels of up to 0.33 ppb.[134] The levels measured in this study may be expected to produce a persistent odor, which has been shown in one study (Schiffman et al., 1995) to have a negative effect on the mood of nearby residents. Based on the literature reviewed above, there is little evidence of more serious health effects attributable to these levels of H_2S.

6.2.1.2 Colorado

In 1997, the Colorado Department of Public Health and Environment (CDPHE), Air Pollution Control Division, conducted a monitoring study of H_2S concentrations near several known sources, and of urban and rural background ambient levels.[135] The CDPHE initially considered monitoring at oil and gas sites because of the information in the 1993 EPA report on emissions of H_2S at points of oil and gas extraction. Ultimately, the Colorado study excluded oil and gas operations, because of assurances from the Colorado Oil and Gas Conservation Commission (COGCC) that elevated H_2S levels are not

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[134] Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological profile for hydrogen sulfide (*Draft for Public Comment*). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. Chapter 2, p.1.

[135] "Hydrogen Sulfide Concentrations in Colorado; Results from a Screening Survey." Prepared by The Technical Services Program, Air Pollution Control Division, Colorado Department of Public Health and the Environment, 1997. Obtained February 2006 by mail from Ray Mohr, CDPHE.

common in deposits in Colorado.[136] However, interviews with people living near oil and gas sites in Colorado, presented below, suggest that hydrogen sulfide is present near these facilities. The COGCC itself has not conducted any monitoring of H_2S at oil and gas sites. Thus, the question of what concentrations of hydrogen sulfide are present near oil and gas operations in the state is still unanswered. Colorado does not have an ambient hydrogen sulfide standard.

6.2.1.3 Louisiana

The Louisiana Department of Environmental Quality, motivated by numerous odor complaints from nearby residents, monitored hydrogen sulfide and sulfur dioxide concentrations downwind of the Calumet Refinery in Shreveport.[137] The hourly average concentration for hydrogen sulfide, for the monitoring period from October 2002 to April 2005, was 2.56 ppb, with a maximum of 50.15 ppb and a median of 1.92 ppb.[138] These measurements correspond to the range of the monitoring data from Arkansas, and the same analysis of potential health effects applies.

6.2.1.4 New Mexico

In February 2002, the Air Quality Bureau of the New Mexico Environment Department monitored hydrogen sulfide levels to determine if ambient concentrations near certain facilities are in compliance with the state's ambient standards.[139] Air samples

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[136] "Hydrogen Sulfide Concentrations in Colorado," p.2.
[137] James M. Hazlett, "Report for the Calumet Air Monitoring Project," Louisiana Department of Environmental Quality, Office of Environmental Assessment. June 8, 2005. (obtained from the author and used with permission.)
[138] Hazlett, p.4.
[139] New Mexico Environment Department (NMED), Air Quality Bureau. "Trip Report: H_2S Survey, March 18-22, 2002." By Steve Dubyk and Sufi Mustafa. Obtained from the author.

were collected near a sewage treatment plant, four dairy operations, a poultry operation, one liquid septage facility, one sewage sludge disposal facility, and several oil and gas facilities.[140] Table 3 presents the data from the monitors near the oil and gas facilities, and a discussion of the results follows.

Table 3: Summary of Monitoring Data from New Mexico Study

Facility type	**H_2S concentration measured at monitoring site (ppb)[141]**	
	Range	**Average**
Indian Basin Hilltop, no facility	5 – 8	7
Indian Basin Compressor Station	3 – 9	6
Indian Basin Active Well Drilling Site	7 – 190	114
Indian Basin Flaring, Production, and Tank Storage Site	4 – 1,200	203
Marathon Indian Basin Refining and Tank Storage Site	2 – 370	16
Carlsbad City Limits, near 8 to 10 wells and tank storage sites	5 –7	6
Carlsbad City Limits, Tracy-A	5 – 8	7
Compressor station, dehydrators – Location A	4 –5	4
Compressor station, dehydrators – Location B	2 – 15,000	1372
Huber Flare/Dehydrating Facility [a]	4 – 12	77
Snyder Oil Well Field	2 – 5	4
Empire Abo Gas Processing Plant	1 – 1,600	300
Navajo Oil Refinery	3 – 14	7 - 8

[a] Strong winds, flare not operating correctly at time of sampling may have caused lower readings than expected, according to study, p.8.

The New Mexico data indicates that ambient concentrations of hydrogen sulfide at the sampling locations, which included both oil and gas facilities and sites without oil and gas facilities, are at least an order of magnitude greater than 0.11 to 0.33 ppb, which are the ambient levels of H_2S that can normally be expected in urban areas.[142] The ambient levels recorded at the two sites without expected sources of H_2S – Indian Basin Hilltop, no facility and Carlsbad City Limits, Tracy-A – both averaged 7 ppb, indicating that usual

[140] NMED Trip Report, p.1.
[141] The monitor that the NMED used recorded hydrogen sulfide concentrations every 30 seconds for 3 minutes. The averages reported in this table are averages of 3-minute mean concentrations.
[142] Agency for Toxic Substances and Disease Registry (ATSDR). 2004. Toxicological profile for hydrogen sulfide (*Draft for Public Comment*). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. Chapter 2, p.1.

H_2S concentrations in this part of New Mexico are higher than normal urban background levels.

Hydrogen sulfide levels sampled at flaring, tank storage, and well drilling sites, averaging from approximately 100 to 200 ppb, are significantly elevated compared to normal background levels, and compared to usual background H_2S concentrations in this area of New Mexico. While these concentrations generally produce a nuisance due to odors which may translate into headaches, nausea and sleep disturbances if exposure is constant, one study discussed above (Legator et al., 2001) found central nervous system, respiratory system, and ear, nose and throat symptoms associated with annual average hydrogen sulfide levels ranging from 7 to 27 ppb. Overall, the data shows that concentrations of H_2S vary widely, even at similar facilities: at one compressor / dehydrator, the average concentration over the course of monitoring was 4 ppb, while at another, the average was 1372 ppb. The data further demonstrates that H_2S is present, often at quite elevated levels, at oil and gas facilities. A staff person at the NMED indicated that there is need for more monitoring and a better-designed study, but that budget constraints prevent them from routine monitoring. The department had rented a hydrogen sulfide monitor for this study.

6.2.1.5 North Dakota

The North Dakota State Department of Health and Consolidated Laboratories monitored hydrogen sulfide emissions from oil and gas wells at several locations, from 1980 until 1992. Each location was near at least one oil or gas well. At one location, the Lostwood Wildlife Refuge monitoring station, the highest one hour average concentration recorded was 88 ppb, in 1990.[143] At Lone Butte, 6 miles north of the Theodore Roosevelt National Park, one hour average hydrogen sulfide concentrations frequently exceeded 200 ppb.[144] At another site, in a valley with several wells within one mile from the monitor, recorded concentrations were as high as 250 ppb.[145] These findings highlight the fact that hydrogen sulfide is routinely emitted near oil and gas wells.

These monitoring studies reveal that hydrogen sulfide is present at oil and gas facilities, including oil refineries, gas processing plants, oil and gas wells, flares, and compressor stations. These types of facilities are commonly situated near residences, where people can be routinely exposed to hydrogen sulfide. The levels of H_2S range from relatively low concentrations of 2 ppb recorded in Louisiana to the much higher concentrations observed in New Mexico and North Dakota.

6.2.2 Routine Monitoring

Of the twenty states that have an ambient hydrogen sulfide standard, only three – California, Oklahoma, and Texas – conduct routine monitoring of ambient H_2S concentrations. The other eighteen states do not monitor ambient H_2S levels. Rather, the standard is generally used in permitting facilities that emit hydrogen sulfide. Typically, the health/environmental departments model emissions and permit a facility if the model reports that the emissions would not raise ambient levels above the standard.

6.2.2.1 California

The California Air Resources Board (CARB), which manages air quality and pollution in the state, has authority to enforce the state ambient hydrogen sulfide standard

[143] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-22.
[144] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-26.
[145] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-30.

of 30 ppb, averaged over one hour. CARB also delegates management to the state's 35 Air Pollution Control Districts (APCDs) or Air Quality Management Districts (AQMDs), each with authority to adopt its own rules and regulations to control and monitor emissions of hydrogen sulfide. A map of the state air districts is in Appendix C. The local districts defer to the state ambient standard, but they are in charge of conducting monitoring of ambient H_2S.

The twelve sites in California where hydrogen sulfide is routinely monitored were chosen because of nearby emission sources. Table 4 summarizes the monitoring sites and the sources of H_2S. I discuss the data for 2005 from Contra Costa and Santa Barbara Counties, where the H_2S sources are due to oil and gas facilities. Daily averages of hourly hydrogen sulfide readings at the three monitoring sites in Contra Costa County range from 0.000 to 0.003 ppm, with one reading of 0.007 ppm at one monitoring site. Similarly, the daily averages of hourly H_2S concentrations recorded during 2005 at all three sites in Santa Barbara range from 0.000 to 0.001 ppm.[146] These levels are most likely of no health concern.

Table 4: California H_2S Monitoring Sites

District	County	Sites	Source(s)
Great Basin Unified APCD	Inyo	2	Geothermal Power Plant
Lake County AQMD	Lake	3	Geothermal Power Plants
Mojave Desert AQMD	San Bernardino	1	Chemical Processing Facility
San Francisco Bay Area AQMD	Contra Costa	3	Chevron Oil Refinery
Santa Barbara County APCD	Santa Barbara	3	Oil and Gas Processing Facilities

[146] Data is available at http://www.arb.ca.gov/adam/cgi-bin/db2www/adamweeklyc.d2w/start. In Step 3, select desired county, and on the next page, in Step 1, select "Daily Average of Hourly Measurements." Use arrows on the right to select different time periods.

6.2.2.2 Oklahoma

The Air Quality Monitoring division of the Oklahoma Department of Environmental Quality (DEQ) continuously monitors ambient levels of hydrogen sulfide at sites downwind of two large oil refineries in Tulsa. The DEQ initiated the monitoring because complaints about foul odors numbered as many as 5 or 6 per day.[147] According to staff at the Oklahoma DEQ, the DEQ installed three monitors in Tulsa, and continuous hourly average data for two of the three monitors is available on-line.

Figure 3 summarizes the data on ambient H_2S levels recorded at these two sites in Tulsa. Monitor 235 is in a park right next to residences an eighth to a quarter of a mile downwind and across the river from a refinery. Monitor 501 is on a hill, two to three miles downwind of another refinery. The hill elevation approximately lines up with the height of the refinery stacks. The majority of the odor complaints mentioned above came from residents of this neighborhood. Now, the DEQ receives about 3 or 4 complaints a week. The levels of hydrogen sulfide in both neighborhoods, although not very high, are nevertheless above the EPA's RfC of 1.4 ppb, and are well elevated above normal background levels of 0.11 to 0.33 ppb. It is possible that continuous exposure to these levels poses health risks. While the Oklahoma DEQ is monitoring hydrogen sulfide levels, there is no concurrent community health or exposure study investigating the health effects of chronic exposure to these levels of H_2S.

[147] Personal communication, Rhonda Jeffries, Oklahoma Department of Environmental Quality. February 10, 2006.