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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Exhibit 4

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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.

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.

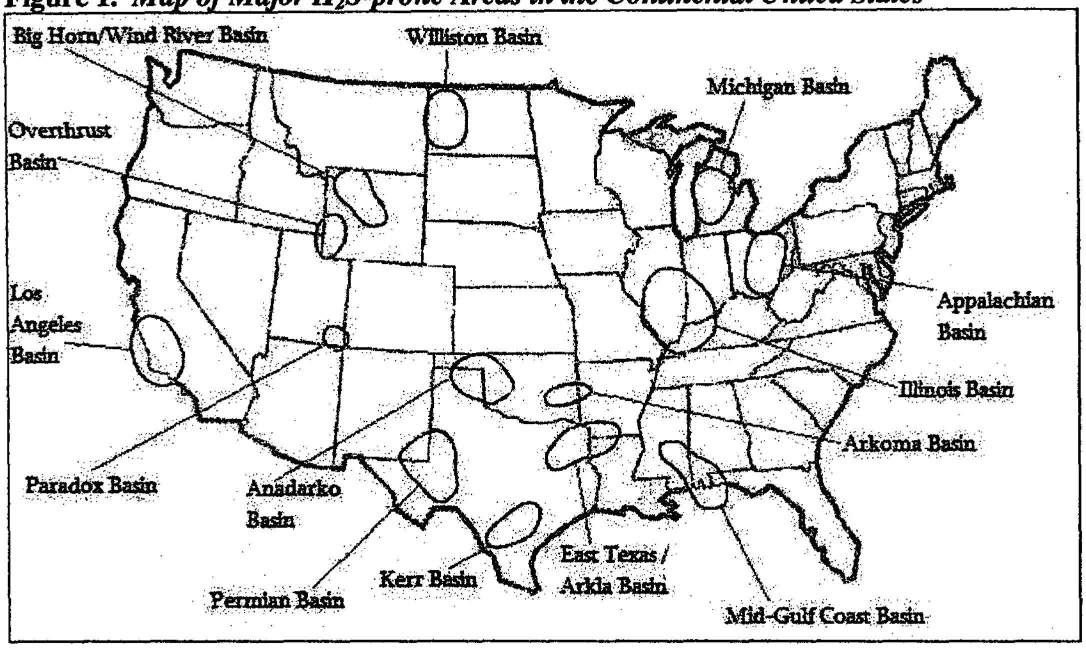
[13] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p. I-3.

[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.

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 the minerals under the surface, is partly responsible for the proximity of oil and gas facilities to residences. Another factor are low setbacks, the minimum distance required between an energy facility and a specific type of development.[151] For example, in Colorado, where some of the interviewees live, the residential setback requirement for oil and gas wells is 150 feet.[152] In Texas, the setback is also 150 feet,[153] while the New Mexico residential setback is just 100 feet.[154] In Alberta, Canada, the residential setback requirement for sour gas wells areas is 100 m (approximately 330 feet).[155] While greater than Colorado's and Texas's required setback, this distance may not be sufficient, as some of the interviewees were exposed to hydrogen sulfide in Alberta. To truly provide a margin of safety and protection to people who live in areas of oil and gas development, whether the facilities are on their surface property or not, greater setback distances need to be established. The siting of oil refineries and gas processing plants near residences, and conversely, building homes near existing refineries and gas plants, exposes people to a host of pollutants, including hydrogen sulfide. This is often an issue with the dimension of social and environmental justice added to protecting public health.

Some technological options exist that may help mitigate the effects of hydrogen sulfide on the health of people who live near emission sources. One advanced technology for odor control, consisting of a dry scrubbing system with multiple beds of engineered media (made by soaking, or on a rotating agglomeration disk), removed hydrogen sulfide at a wastewater

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[151] http://www.eub.ca/portal/server.pt/gateway/PTARGS_0_0_257_229_0_43/http%3B/extContent/publishedcontent/publish/eub_home/public_zone/eub_process/enerfaqs/EnerFAQs5.aspx#1
[152] Colorado Oil and Gas Conservation Commission, Rule 603. Available at http://oil-gas.state.co.us/RR_Asps/600Series.pdf
[153] Texas Administrative Code, Title 16, Part I, Chapter 3, Rule 3.21 (a) and (i). Available at http://info.sos.state.tx.us/pls/pub/readtac$ext.ViewTAC?tac_view=4&ti=16&pt=1&ch=3&rl=Y
[154] Personal communication, Denny Foust, New Mexico Environment Department, April 12, 2006.
[155] Alberta Energy and Utilities Board, Directive 056, Energy Development Applications and Schedules. Available at http://www.eub.ca/docs/documents/directives/directive056.pdf, pp.54-55.