Report on Air Sampling
Monroe, Conecuh and Escambia Counties, Alabama
(August 1-5, 2005)

DRAFT – not for distribution

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1.0 Background

In 2004, Wilma Subra, an environmental chemist from Louisiana, was contact by Audrey Silcox and Thomas McKenzie. At the time, Silcox and McKenzie were living in the same rural-residential area of Monroe County, Alabama. Both Silcox and McKenzie had been experiencing health problems, but their doctors had not been able to determine the cause of their symptoms. Other members of the Silcox and McKenzie families, as well as neighbors and other residents in Monroe and nearby Conecuh county, had also been experiencing similar health issues.

Subra, who has worked for decades on environmental pollution and community health issues, visited with Silcox and McKenzie to try to determine if there might be a connection between environmental pollution and their health problems. During Subra's visit, and based on her research, it occurred to her that the oil and gas facilities located throughout the county were possible sources of air contamination that could be affecting residents' health.

There are both sweet and sour oil and gas wells in Monroe and nearby counties – sour gas contains high concentrations of hydrogen sulfide (H_2S). Subra, who is familiar with oil and gas air emissions, was able to smell H_2S and volatile organic compounds (VOCs) during her tour of the area.

During a subsequent visit to Monroe County, efforts were made by Subra to encourage various federal and state agencies to examine the potential problems with air emissions in Monroe County. Silcox and McKenzie also asked state agencies to monitor the air quality in the county (Appendix 1). Unfortunately, the requests from Subra, Silcox and McKenzie were unsuccessful, and to-date no agency has seriously undertaken an investigation of air emissions from oil and gas or other facilities in the county.

In August, 2005, Wilma Subra and the Oil and Gas Accountability Project spent five days in Monroe, Conecuh and Escambia counties. The purpose of the visit was to measure concentrations of hydrogen sulfide and volatile organic compounds in the vicinity of known sources of air emissions, and to measure ambient concentrations of H_2S and VOCs in residential neighborhoods. The goal of the project was not to identify facilities that have been breaking air quality laws, but rather, to determine if there is a potential air pollution problem that needs to be investigated and addressed in order to protect the health of the citizens of Monroe County, Alabama.

2.0 Methods

Hydrogen sulfide was measured using a Jerome 631-X hydrogen sulfide analyzer, which has a detection level of 0.001 ppm.

Volatile Organic Compounds (VOCs) were measured using a "ppb-Rae" portable photo-ionization detector (PID). The ppb-RAE is a broad-spectrum monitor that measures the total concentration of VOCs that have a carbon range from one to ten (C1 – C10). It should be noted that this PID <u>does not measure methane</u> (and only weakly detects ethane).[1]

This particular PID was chosen because of the ability of the ppb-RAE to detect VOCs at concentrations as low as 1 ppb, and as high as 199 ppm. One drawback of this monitoring device is that it measures the total concentration of VOCs (excluding methane), but cannot tell the user which particular gases are present when there is a mixture of VOCs.

Measurement Dates and Locations

Measurements were taken over a five-day period of August 1-5, 2005.

Data were collected from sites in Monroe, Conecuh and Escambia counties in Alabama. Numerous sites were selected based on their possibility of being sources of H_2S and VOCs (e.g., oil and natural gas facilities; wood product facilities). Residential sites were selected based on their proximity to the various sources of air emissions.

In a few cases, measurements were taken along transects when it appeared that a particular source was emitting high concentrations of H_2S or VOCs. The purpose of the transects was to determine the potential areal extent of influence of the emissions source.

H_2S and VOC concentrations were measured at the perimeter or in the parking areas of wells sites, gas processing plants, and other industrial facilities. Consequently, the distance between the measurement location and air emission sources (e.g., spilled fluids; flares; other equipment) varied from one location to the next.

Measurement of ambient H_2S and VOC concentrations took place in residential areas, at varying distances from the potential H_2S /VOC sources. In some cases, where there was a suspected major source, measurements were taken along rough transects away from the source in the direction that the wind was blowing. Based on GPS locational data, it is possible to determine the air-distance from the source to the sampling locations.

Monitoring Conditions

The monitoring project was limited to a five-day period in August. During this time, the weather was extremely variable, and included sunny days, rain, fog, and at time, fairly strong winds.

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[1] RAE Systems. 2006. *Conversion Of PID Readings To Methane Equivalent Or Hexane Equivalent FID Response*. Technical Note TN-158. http://www.raesystems.com/~raedocs/App_Tech_Notes/Tech_Notes/TN-158_PID-FID_Conversion.pdf

3.0 LITERATURE REVIEW

3.1 Hydrogen Sulfide

Hydrogen sulfide is a gas that is produced from natural and industrial sources. It has a tell-tale "rotten egg" odor at low concentrations, and is fatal if inhaled at high concentrations. Being heavier than air, H_2S tends to sink and flow into low-lying areas where it can accumulate in concentrations that can injure or kill livestock, wildlife and human beings.

3.1.1 Sources of H_2S releases

The majority of sources of H_2S to the environment are natural.[2] Hydrogen sulfide is released into the air as a product of the decomposition of dead plant and animal material, especially when this occurs in wet conditions with limited oxygen, such as in swamps. There are also geothermal sources of H_2S, such as hot springs and volcanoes.

In addition to natural sources, human activities also result in the release of H_2S to the atmosphere. The principal source of anthropogenic H_2S is as a by-product in the purification of natural gas and refinery gases.[3] It may also be produced during the extraction oil and natural gas, and other industrial sources of H_2S include pulp and paper manufacturing,[4] sewage treatment plants, manure-handling operations, leather tanneries, rayon production,[5] and coke oven plants.[6]

There are several potential sources of H_2S in Monroe County. These include sewage treatment plants, concentrated animal feeding operations (CAFOs), lumber and wood product operations, and oil and gas facilities.

H_2S from Oil and Natural Gas

Natural gas that contains measurable concentrations of hydrogen sulfide (H_2S) is often terms "sour gas." Depending on the jurisdiction, the official definition of sour gas varies. For example, in Canada, the petroleum industry considers natural gas to be sour if it contains more than 1% H_2S. The U.S. Environmental Protection Agency considers

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[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] Chou, S. 2003. *Hydrogen Sulfide: Human Health Aspects.* Concise International Chemical Assessment Document 53. Prepared for the World Health Organization. p. 6. http://www.who.int/ipcs/publications/cicad/en/cicad53.pdf
[4] New York State Department of Health: available at http://www.health.state.ny.us/nysdoh/environ/btsa/sulfide.htm
[5] Ammann, 1986, p. 4, in Collins, James and David Lewis, Air Toxicology and Epidemiology Section, California Office of Environmental Health Hazard Assessment (OEHHA). September 1, 2000. *Hydrogen Sulfide: Evaluation of Current California Air Quality Standards with Respect to Protection of Children.* Prepared for California Air Resources Board, CA OEHHA.
[6] "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

natural gas to be “sour” if H_2S is present in amounts greater than 5.7 milligrams per normal cubic meters (mg/Nm^3), which is equivalent to 0.25 grains per 100 standard cubic feet (gr/100 scf).[7]

It has been estimated that between 15 – 25% of natural gas in the U.S. may contain hydrogen sulfide.[8] Worldwide, the percentage could be as high as 30%. It has been reported, as well, that new drilling is increasingly focused on deep gas formations that tend to be sour.[9]

Although the exact number of sour gas wells are not available, the U.S. EPA has reported that in the U.S. “the potential for routine H_2S emissions [at oil and gas wells] is significant.”[10]

Releases of H_2S from sour gas wells or facilities may occur in a number of ways. The U.S. EPA has collected documentation of sour gas well blowouts, line releases, extinguished flares, collection of sour gas in low-lying areas, and leakage from idle or abandoned wells that have impacted the public near oil and gas extraction sites.[11] In addition to releases from sour gas well sites, hydrogen sulfide also may be routinely or accidentally released into the atmosphere at oil refineries, natural gas processing facilities and desulfurization plants.

In areas with coalbed methane production, hydrogen sulfide gas has been detected in surface soils, groundwater and the atmosphere (in association with methane gas).[12]

3.1.2 Studies on H_2S from oil and natural gas production

State agencies from across the United States have received H_2S-related complaints from citizens. In 2006, Lana Skrtic, a Masters degree student at the University of California at Berkeley, collected information on studies that have been done by states in response to H_2S complaints related to oil and gas operations in Arkansas, Louisiana, New Mexico, and North Dakota. According the Skrtic, “These studies are of varying quality and scope,

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[7] U.S. Environmental Protection Agency. 1995. “Petroleum Industry,” *Compilation of Air Pollutant Emission Factors, Vol. 1, Stationary Point and Area Sources.* http://www.epa.gov/ttn/chief/ap42
[8] 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. 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.
[9] 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.
[10] U.S. 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. p.III-35.
[11] EPA, “Report to Congress on Hydrogen Sulfide Emissions,” p.III-38.
[12] La Plata County, Colorado. 2002. *La Plata County Impact Report.* p. 3-105. http://co.laplata.co.us/publications.htm

but each sheds some light on the topic of hydrogen sulfide emissions and oil and gas operations."[13]

The following paragraphs provide brief summaries of the studies conducted in the four states. For a more in-depth analysis, you can download Lana Skrtic's Masters' paper.[14]

During the 1990s, the Arkansas Department of Environmental Quality conducted hydrogen sulfide monitoring studies in response to health and welfare related complaints from residents living close to gas processing plants.[15] An initial scoping study confirmed the presence of hydrogen sulfide in ambient air, and so between March 1998 and March 1999, a more rigorous study was undertaken. At one site, the average H_2S concentration was 3.4 ppb; while the maximum H_2S level was 35 ppb. At a second site, the average H_2S S concentration was 5.5 ppb, and the maximum concentration was 127 ppb.

In Louisiana, numerous odor complaints from residents prompted the state's Department of Environmental Quality to undertake monitoring of hydrogen sulfide and sulfur dioxide concentrations downwind of the Calumet Refinery in Shreveport.[16] 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.

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, including oil and gas operations, were in compliance with the state's ambient standards.[17] The data clearly demonstrated that H_2S was present at elevated levels near oil and gas facilities in southern New Mexico. Hydrogen sulfide levels measured at flaring, tank storage, and well drilling sites, averaged from approximately 100 to 200 ppb (compared to an average of 7 ppb at two "control" sites (i.e., sites without expected sources of H_2S).

Between 1980 and 1992, the North Dakota State Department of Health and Consolidated Laboratories monitored hydrogen sulfide emissions from oil and gas wells in the state. The study found that hydrogen sulfide was routinely being emitted near oil and gas wells in that state: At one site, six miles north of the Theodore Roosevelt National Park, the one-hour average H_2S concentrations frequently exceeded 200 ppb.[18] At another site, in a

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[13] Skritic, L. May, 2006. *Hydrogen Sulfide, Oil and Gas, and People's Health.* A paper submitted for the fulfillment of a Masters Degree, Energy Resources Group, UC Berkeley. p. 35.
[14] Skritic, L. May, 2006. *Hydrogen Sulfide, Oil and Gas, and People's Health.* A paper submitted for the fulfillment of a Masters Degree, Energy Resources Group, UC Berkeley. p. 35.
http://www.earthworksaction.org/publications.cfm?pubID=168
[15] Pleasant Hills H_2S Study, obtained February 2006 by mail from Jay Justice, Senior Epidemiologist with the Arkansas DEQ.
[16] 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.)
[17] 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.
[18] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-26.

valley with several wells within one mile from the monitor, H_2S concentrations reached 250 ppb.[19]

Table 1. Summary of average and maximum H_2S concentrations (parts per billion) near oil and gas facilities in Arkansas, Louisiana, New Mexico and North Dakota.

Monitoring Location	H_2S concentration measured at monitoring site (ppb)	
	Average	Max.
Arkansas		
Rural residential 1 - near gas processing facility	2.4 – 3.4	24 - 35
Rural residential 2 - near gas processing facility	4 – 5.5	55 - 127
Louisiana		
Downwind of refinery	2.56	50.15
New Mexico		
Indian Basin Hilltop (control site)	7	8
Indian Basin Compressor Station	6	9
Indian Basin Active Well Drilling Site	114	190
Indian Basin Flaring, Production, and Tank Storage Site	203	1,200
Marathon Indian Basin Refining and Tank Storage Site	16	370
Carlsbad City Limits, near 8 to 10 wells and tank storage sites	6	7
Carlsbad City Limits (control site)	7	8
Compressor station, dehydrators – Location A	4	5
Compressor station, dehydrators – Location B	1372	15,000
Huber Flare/Dehydrating Facility	77	12
Snyder Oil Well Field	4	5
Empire Abo Gas Processing Plant	300	1,600
Navajo Oil Refinery	7 - 8	14
North Dakota		
Lostwood Wildlife Refuge	-	88
Lone Butte, 6 miles N. of Theodore Roosevelt Park	> 200	-
Unnamed valley, several wells in vicinity of monitor	-	250

These monitoring studies reveal that hydrogen sulfide is present at or near oil and gas facilities, including oil and gas wells, tank batteries, gas processing plants, flares, compressor stations and refineries. When facilities such as these are situated near residential areas, there is the possibility that residents will be routinely exposed to hydrogen sulfide.

The levels of H_2S in the four monitoring studies ranged from the relatively low concentration of 2 ppb recorded in Louisiana to concentrations in the 1000 ppb range observed in New Mexico. Even the lowest average H_2S concentration at these sites is higher than normal urban background levels, which are typically less than 1 ppb.[20].

[19] EPA, "Report to Congress on Hydrogen Sulfide Emissions," p.III-30.
[20] 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.

As reported by Skrtic, "The levels measured in this study may be expected to produce a persistent odor, which has been shown in one study to have a negative effect on the mood of nearby residents."[21] Furthermore, chronic exposure to low-level concentrations of hydrogen sulfide may result in neurological symptoms such as fatigue, loss of appetite, irritability, impaired memory, headaches, and dizziness.[22]

It is possible, too, that exposures to these levels of H_2S could cause more serious, long-term health effects. One of the studies discussed in Section 3.1.3, below, 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.[23]

3.1.3 Health Issues associated with H_2S

Exposure to H_2S is one of the leading causes of sudden death in the workplace.[24] At high concentrations (greater than 500 parts per million[25]) inhalation of H_2S can lead to immediate collapse and unconsciousness. A single breath at 1,000 ppm results in immediate loss of consciousness, cardiac arrest and death unless the unconscious victim is successfully revived.[26] Unconsciousness and death have occurred in situations of prolonged exposure to H_2S at concentrations of 50 ppm.[27]

Table 2 outlines the various types of health effects that have been associated with hydrogen sulfide in air.

Many occupational and community studies have documented the adverse health effects of exposure to relatively high levels of H2S.28 Most organ systems are affected by H2S, but the most susceptible are those with exposed mucous membranes (eyes, 29 noise and

[21] 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. Cited in: Skrtic. Skritic, L. May, 2006. *Hydrogen Sulfide, Oil and Gas, and People's Health.* A paper submitted for the fulfillment of a Masters Degree, Energy Resources Group, UC Berkeley. p. 19.
[22] 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.
[23] Legator, M., Singleton, C. ,Morris, D. and Philips, D. 2001. "Health effects from chronic low-level exposure to Hydrogen Sulfide," *Archives of Environmental Health*. 56:2:123-131.
[24] U.S. Environmental Protection Agency. 1992. *Health assessment document for hydrogen sulfide*. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment. Research Triangle Park, NC. EPA/600/8-86/026F. LEG
[25] Beauchamp, 1984. In NC Scientific Advisory Board. 2003. *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*
[26] Kilburn, Kaye. "Effects of Hydrogen Sulfide on Neurobehavioral Function." *Southern Medical Journal*. **96**: (7) 639-646. 2003.
[27] Henderson, R. 2005. "Toxic gas accidents affect far more than the workers on site," *Petromin*.
[28] Various citations in: Legator, M., Singleton, C. ,Morris, D. and Philips, D. 2001. "Health effects from chronic low-level exposure to Hydrogen Sulfide," *Archives of Environ. Health*. 56:2:123-131.
[29] Symptoms affecting the eyes are generally associated with repeated exposures to 50 ppm. H_2S NC Scientific Advisory Board. 2003. *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

throat) and those with high oxygen demands (lungs, brain). Neurotoxicity of the central nervous system (causing nausea, dizziness, confusion, headaches and sleeping problems) and pulmonary edema (build-up of fluid in the lungs) are other well-documented effects of H_2S poisoning. Cardiovascular toxicity and gastrointestinal disturbances are also associated with H_2S exposure.

Table 2: Health Effects Associated with Hydrogen Sulfide (adapted from Skrtic, 2006).[30]

Concentration of H_2S in air (ppm)	Length of Exposure	Effect	Source[31]
0.003 – 0.02	Immediate	Detectable odor	EPA Report 1993, p.III-5
0.2	Not reported	Detectable odor	Fuller, p.940
0.250 – 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 min.	New York State Department of Health
> 30	Prolonged	Fatigue, paralysis of olfaction from prolonged exposure	Snyder, p.200
50	Not reported	Eye and respiratory irritation	Fuller, p.940
50 – 100	Prolonged	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 1993, p.III-5
150 - 200	Not reported	Olfactory nerve paralysis	EPA Report 1993, p.III-6
200	Not reported	Respiratory and other mucous membrane irritation	Snyder, p.200
250	Not reported	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
320 – 530	Not reported	Pulmonary edema with risk of death	Kilburn (1999), p.212
500	30 minutes	Systemic symptoms after 30 minutes	Fuller, p.940
500 –1000	Immediate	Stimulation of respiratory system, leading to hyperpnoea (rapid breathing); followed by apnea (breathing stops)	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 1993 p. III-5.
750 – 1000	Immediate	Abrupt physical collapse, with possibility of recovery if exposure is terminated; if not terminated, fatal respiratory paralysis	Milby, p.192
1000 – 2000	Not reported	Immediate collapse with paralysis of respiration	Kilburn (1999), p.212
5000	Immediate	Death	Fuller, p.940

[30] Skritic, L. May, 2006. *Hydrogen Sulfide, Oil and Gas, and People's Health.* A paper submitted for the fulfillment of a Masters Degree, Energy Resources Group, UC Berkeley. p. 13.
[31] See Bibliography for complete references.

Research conducted by Kaye Kilburn, a medical doctor and professor of medicine at the University of Southern California, suggests that exposure to H_2S may cause long-term, irreversible human health effects. Kilburn performed physiologic and psychological measurements on nineteen exposed individuals, and compared results with 202 unexposed subjects.[32] Of the 19 exposed subjects, 10 were exposed at work sites, which included four oil and gas operations, and nine were exposed in their residences, which were near various sources of H_2S. The concentrations to which the subjects were exposed are not known. Kilburn found that depression, anger, fatigue, tension and confusion and respiratory ailments were all significantly higher in the exposed subjects as compared to the control group. Recently, scientific studies have provided more evidence that chronic exposure to low concentrations (in the low parts per million or even the parts per billion range) of H_2S can also affect human health. For example, a study of sewer workers, evidence indicated that low-level exposure to H_2S may be associated with reduced lung function.[33]

Increasingly, research is revealing that even low concentrations of H_2S can affect human health, especially when exposure occurs over an extended period of time. The following list of studies provides more information on the potential association between low-level exposures to H_2S and health effects.

1) One study of H_2S in the workplace found that workers complained of eye pain at a level of 6.4 ppm. (Van Hoorne, *et al.* 1991).[34]

2) Based on observations from clinical studies, short-term exposure to H_2S at concentrations of 2 ppm may induce bronchial obstruction. In a study investigating the effects of H_2S on asthmatics, two out of ten subjects exhibited a pronounced response when exposed to 2 ppm H_2S. Airway resistance and conductivity were affected by more than 30%, suggesting significant bronchial obstruction (Jappinen, P. *et al.* 1990).[35]

3) Former workers and residents living downwind of a crude oil processing plant had neurophysiological abnormalities. Residents in this study were exposed to H_2S at 10 ppb, although H_2S concentrations occasionally reached 100 ppb (Kilburn, K.H., Warsaw, R.H. 1995).[36]

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[32] Kilburn, Kaye H. "Effects of Hydrogen Sulfide on Neurobehavioral Function." *Southern Medical Journal*. **96**: (7) 639-646. 2003.

[33] Richardson, D. 1995. "Respiratory effects of chronic hydrogen sulfide exposure." Am J Ind Med. 28:99-108. LEG

[34] Van Hoorne, et al. 1991. "Survey of chemical exposures in a viscose rayon plant." *Ann Occup Hyg*. 35(6):619-631. In NC Scientific Advisory Board. 2003. *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

[35] Jappinen, P. et al. 1990. "Exposure to hydrogen sulfide and respiratory function." *British J Ind Medicine*. 47:824-828. In NC Scientific Advisory Board. 2003. *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

[36] Kilburn, K.H., Warsaw, R.H. 1995. "Hydrogen sulfide and reduced-sulfur gases adversely affect neurophysiological functions." *Toxicology and Industrial Health*. 11:185-197. LEG

4) Residents near pulp and paper mills in Finland have reported an excess of health symptoms compared to residents living in a community without any industrial H_2S sources. The annual mean concentrations of H_2S in the affected community was 8 $\mu g/m^3$ (5.7 ppb). Symptoms included respiratory, eye and nasal problems). Residents in the pulp and paper community were also exposed to other sulfur compounds, but H_2S accounted for more than two-thirds of the sulfur compounds monitored in the community (Marttila, O., Jaakkola, J.J.K., Partti-Pellinen, K. 1995).[37]

5) Symptoms of adverse health effects experienced by residents in Odessa, TX and Puna, Hawaii, two communities with industrial sources of H_2S were compared to the same symptoms in three communities without industrial sources of H_2S. The residents in Odessa were exposed to H_2S concentrations of 7-27 ppb (annual average), with maximum 8-hour measurements between 335 and 503 ppb. Exposure in Puna is less clear, but some data from the 1990s indicate hourly averages in the low-ppb range, with most below 1 ppb. Between June 1996 and 1997, peak H_2S concentrations was 301.7 ppb. In other years, releases of H_2S between 200-500 ppb were reported.

   The two H_2S-exposed communities were similar with respect to the adverse health effects (e.g., central nervous systems, ear/nose/throat, respiratory, muscle/bone, skin, immune, cardiovascular, digestive, teeth/gums, urinary, blood) reported by residents. Percentages of affected residents in the H_2S-exposed communities were statistically different (higher) than the non-exposed communities (Legator, M. *et al*. 2001).[38]

The results of other community and occupational studies indicate a considerable variety of adverse health effects from low-level, chronic H_2S exposure.[39]

3.1.4 H_2S Regulations

There are no international health-based standards for H_2S. The World Health Organization (WHO) does have an air quality guideline for H_2S of 150 $\mu g/m^3$ (10.6 ppb) averaged over a 24-hour period.[40] This guideline is based on the avoidance of eye

[37] Marttila, O., Jaakkola, J.J.K., Partti-Pellinen, K. 1995. South Karelia air pollution study: daily symptom intensity in relation to exposure of malodorous sulfur compounds from pulp mills." *Environ Res.* 71:122-27. LEG

[38] Legator, M., Singleton, C. ,Morris, D. and Philips, D. 2001. "Health effects from chronic low-level exposure to Hydrogen Sulfide," *Archives of Environmental Health*. 56:2:123-131.

[39] Mehlman, M.A. 1992. Dangerous and cancer-causing properties of product and chemicals in the oil refining and petrochemical industry. VII. Adverse health effects and toxic manifestations caused by exposure to hydrogen sulfide. *Journal of Occupational Med Toxicol.* 1:143-158. LEG

[40] World Health Organization. 2003. *Concise International Chemical Assessment Document 53, Hydrogen Sulfide: Human Health Aspects*. Geneva, Switzerland: World Health Organization. p. 21. Available from URL: http://www.who.int/entity/ipcs/publications/cicad/en/cicad53.pdf

irritation. Also, WHO recommends that H_2S concentrations not exceed 0.005 ppm (5 ppb; 7 $\mu g/m^3$), over a 30-minute period, to avoid substantial complaints about odor.[41]

Table 3. State Ambient Hydrogen Sulfide Standards[42]

State	Standard	Duration	Justification
Arizona	128 ppb	1 hr	AAAQG, health based, on OSHA guidelines
	78 ppb	24 hr	
California	8 ppb	Chronic exposure	Odor/nuisance guideline.
	30 ppb	1 hr	
Delaware	60 ppb	avg. not to be exceeded over any consecutive 3 min.	
	30 ppb	avg. not to be exceeded over any consecutive 60 min.	
Hawaii	25 ppb	1 hr	Combination of health and nuisance
Iowa	30 ppb	1 hr daily maximum	"Health effects standard"
Kentucky	10 ppb	1 hr maximum	Public health and welfare
Louisiana	330 ppb	8-hr average	1/42 of NIOSH/OSHA safety standard
Massachusetts	0.65 ppb	24-hr and annual limit	Based on EPA RfC, Threshold Effects Limit and Allowable Ambient Limit
Minnesota	50 ppb	1/2-hr avg. not to be exceeded > twice/yr	
	30 ppb	1/2-hr avg. not to be exceeded > twice in any 5 consecutive days	
Missouri	50 ppb	1/2 hr avg. not to be exceeded > twice/yr	
	30 ppb	1/2 hr avg. not to be exceeded > twice in any 5 consecutive days	
Montana	50 ppb	hourly avg. not to be exceeded > once/yr	Health based
Nevada	80 ppb	1-hr average	Health based
New Mexico	10 ppb	1-hr avg. not to be exceeded >once/year	
	100 ppb	1/2 hour average	for the Pecos-Permian Basin (PPB) Intrastate Air Quality Control Region
	30 ppb	1/2 hour average	within 5 miles of municipalities in PPB with > 20,000 people
New York	10 ppb	1-hr average	Odor and aesthetic
North Dakota	10,000 ppb	ceiling, maximum instantaneous concentration not to be exceeded	Health based
	200 ppb	1-hr avg. not to be exceeded > once/mo.	
	100 ppb	24-hr avg. not to be exceeded >once/yr	
	20 ppb	max. arithmetic mean concentration averaged over 3 consecutive months	
Oklahoma	200 ppb	24-hr average concentration	
Oregon	0.3 ppb*	annual average concentration	EPA's RfC, proposed benchmark
Pennsylvania	5 ppb	24-hr average	
	100 ppb	1-hr average	
Texas	80 ppb	30-min average	if H_2S affects a residential, business, or commercial property
	120 ppb	30-min average	if H_2S affects only property not normally occupied by people.
Vermont	24 ppb	24-hr	Health based

[41] *ibid.*
[42] See Appendix 2 for state-by-state references.

Wyoming	50 ppb	1/2-hour avg. not to be exceeded > twice/yr	
	0.03 ppm 30 ppb	1/2 hour avg. not to be exceeded > twice/5 consecutive days	

Within the United States, there is no federal ambient air quality standard for H_2S, but more than 30 states have chosen to independently regulate H_2S levels to protect the public from adverse effects related to H_2S exposure. Some states have standards based on short-term H_2S levels (average H_2S concentrations over 15 minutes), while others use an average of H_2S concentrations over much longer periods of time (extending up to one-year).[43] Table 3 includes information for states that have ambient air quality standards (or guidelines) for H_2S.

The most stringent one-hour standard – found in New Mexico, New York and Kentucky – is 10 parts per billion (ppb). In other words, those states believe there will be some effect on citizens who are exposed to H_2S at a level of 10 ppb for at least one hour. The effects may be health-related or the odors may create a nuisance for the citizens.

At least twelve states have standards for H_2S measured over a 24-hour period. These levels are lower than the 1-hour limits, and vary from concentrations of 0.65 ppb (Massachusetts) to 200 ppb (Oklahoma).

3.2 Volatile Organic Compounds (VOCs)

3.2.1 Sources of VOCs

General sources of VOCs include motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, degreasing operations, pharmaceutical manufacturing, and by-products from dry cleaning and other industrial operations.[44]

3.2.1.1. VOCs from oil and natural gas

Oil and gas extraction, processing and distribution results in the release of dozens of volatile organic compounds.

Table 4 provides a list of the VOCs that were emitted in high volumes during oil and gas extraction and distribution in the United Kingdom in 2003. More than 50 VOCs are associated with oil and gas extraction and distribution in the UK,[45] but not all of them are emitted in high volumes. Table 4 lists the 29 most significant VOCs, as identified by the UK Department for Environment, Food and Rural Affairs.

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[43] State Survey of Ambient Air Standards. http://daq.state.nc.us/toxics/studies/H2S/H2S_Survey.pdf
[44] California Air Resources Board. "Toxic Air Contaminants Monitoring" (page updated February 15, 2005) Accessed Jan. 2, 2006. http://www.arb.ca.gov/aaqm/toxics.htm
[45] DEFRA (the Department for Environment, Food and Rural Affairs. United Kingdom. "E-Digest Statistics about: Air Quality: Volatile organic compounds (VOCs)." http://www.defra.gov.uk/environment/statistics/airqual/aqvoc.htm

Table 4. The 29 most significant VOCs from UK fossil fuel extraction and distribution.

Volatile Organic Compound	Amount of VOC (metric tonnes)	Volatile Organic Compound	Amount of VOC (metric tonnes)
Butane	69,492	Toluene	232
Ethane	38,261	Formaldehyde	209
Propane	34,026	m-xylene	86
Pentane	28,640	Dichloromethane	65
Heptane	14,999	Nonane	61
Hexane	14,786	o-xylene	41
Octane	13,239	Ethylene	37
2-methylpropane	12,597	Ethylbenzene	25
2-methylbutane	10,781	Decane	23
2-methylpentane	2,078	Propylene	21
2-pentene	1,408	p-xylene	20
3-methylpentane	1,147	Acetylene	19
2-butene	804	1,3-butadiene	8
Benzene	663	1,2,4-trimethylbenzene	5
2-methylpropene	256		

During oil and gas extraction and distribution (which includes gas compression and transport via pipelines), there are numerous opportunities for VOCs to be released to the atmosphere.

Natural Gas Dehydration: Natural gas may be associated with liquid hydrocarbons; hydrogen sulfide; carbon dioxide; water; water vapor; mercaptans; nitrogen; helium; and solids (sediments). The gases from a well can be piped directly to a gas plant for processing or may need to be dehydrated at the well site before being piped to the plant. Dehydration is accomplished by several methods, of which glycol dehydration is of significance since glycol absorbs benzene and other organic compounds as well as water from the gas streams. During regeneration of the glycol, it is heated to remove the water. This process also emits volatile organic compounds.[46]

Venting: the direct emission of natural gas (which includes varying amounts of VOCs) to the atmosphere. Venting of waste gases, which contain VOCs, may occur at well sites, during the separation and dehydration of natural gas, oil and gas processing facilities, and at pipelines, e.g., during maintenance activities.

Flaring: the combustion of natural gas prior to release to the atmosphere. Combustion converts VOCs into carbon dioxide and water. Even when flaring occurs, some VOCs will be emitted to the atmosphere, because complete combustion never occurs. Complete

[46] Vermaa, Dave K., Johnson, Diane M., and McLean, James D. 2000. "Benzene and Total Hydrocarbon Exposures in the Upstream Petroleum Oil and Gas Industry," *AIHAJ* (American Industrial Hygiene Assn Journal). 61:255–263.

combustion requires sufficient combustion air and proper mixing of air and waste gas. Properly operated flares achieve at least 98 percent combustion efficiency in the flare plume, meaning that less than two percent of hydrocarbons will be emitted in the gas stream.[47]

A field study conducted in Alberta, Canada found that sweet gas flared at oilfield battery sites burned with an efficiency of only 62 – 71%. Flaring of a sour gas solution burned with 82-84% efficiency. Hydrocarbons found in the emissions above the flames included benzene, styrene, ethynyl benzene, ethnyl-methyl benzenes, toluene, xylenes, and others. Emissions from the sour gas flame also contained reduced sulfur compounds and thiophenes.[48]

Tank emissions: there are three types of emissions from hydrocarbon storage tanks: working losses (i.e., displacement of vapors as a tank is filled), breathing losses (i.e., displacement of vapors due to changes in tank temperature and pressure), and flashing losses. Flashing losses occur when a liquid with entrained gases goes from a high to a low pressure situation. As the pressure drops, some of the lighter (volatile) compounds that are dissolved in the liquids are released or flashed. These flashing losses/VOC emissions are often vented to the atmosphere through a tank's "pressure relief valve or hatch."[49]

Fugitive Emissions: The U.S. EPA reports that on average, natural gas plants release 45-128 million cubic feet of natural gas as fugitive emissions.[50] Fugitive emissions also occur from wellheads, pipelines and storage vessels.

3.2.1.2 Studies on VOCs from oil and natural gas production

A recent study conducted in Colorado confirms that volatile organic compounds associated with oil and natural gas production have the potential to be released at concentrations that are harmful to human health.

In 2002, concerns about air pollution from natural gas wells raised by residents in Garfield County, Colorado, prompted the county, state and the federal government to undertake a collaborative study to sample for air toxics around oil and gas sites within the county.[51] Twenty air samples were collected from seven locations, and sample sites

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[47] U.S. Environmental Protection Agency. AP-42, CH 13.5: Industrial Flares http://www.epa.gov/ttn/chief/ap42/ch13/final/c13s05.pdf

[48] Strosher, M. Alberta Research Council. 1996. *Investigations of Flare Gas Emissions in Alberta*. Report prepared for Environment Canada, the Alberta Energy and Utilities Board and the Canadian Association of Petroleum Producers. 157 pp.

[49] Oklahoma Department of Environmental Quality. 2004. *Calculation of Flashing Losses/VOC Emissions from Hydrocarbon Storage Tanks.* Fact sheet. http://www.deq.state.ok.us/factsheets/air/CalculationLosses.pdf

[50] U.S. Environmental Protection Agency. *Directed Inspection And Maintenance At Gas Processing Plants And Booster Stations.* Lessons Learned From Natural Gas STAR Partners. http://www.epa.gov/gasstar/pdf/lessons/ll_dimgasproc.pdf

[51] Colorado Department of Public Health and Environment. October, 2002. *A Community-based Short-term Ambient Air Screening Study in Garfield County for Oil and Gas Related Activities –*

included two natural gas wells (one with an air emissions control device, one without); a well with an active flare; a residence; and three other locations. The samples were analyzed for 42 VOCs. Six were present at detectable concentrations: acetone; methyl ethyl ketone; benzene; toluene; m,p-xylene and o-xylene. It was acknowledged, however, that other VOCs may have been present, but that the equipment may not have been sensitive enough to detect a number of other VOCs.[52]

In 2005, a second round of air quality monitoring was initiated in Garfield County. This time, the effort was solely funded by the County. The two-year study, expected to cost approximately $300,000, was designed to characterize county-wide ambient air quality, as well as localized odor/emission problems from oil and gas facilities. The samples are being analyzed for 43 VOC compounds. To date, 17 VOCs have been detected.

The benzene levels measured in Garfield county in 2002 ranged from 0 – 6.5 $\mu g/m^3$. [**Note:** 6.5 $\mu g/m^3$ benzene = 2.04 ppb benzene][53] As of February, 2006, 89 samples had been taken in the second air quality study. The average benzene level was 5.7 $\mu g/m^3$, and there was a maximum benzene reading of 180 $\mu g/m^3$. Benzene at these concentrations may pose health risks to residents living in the area (see Section 3.2.3 of this report).

When the concentrations of all of the measured VOCs were added together, the total VOC concentrations were in the parts per billion range.[54]

3.2.2 Health Issues associated with VOCs

VOCs are organic compounds that vaporize easily at ambient temperatures. Some VOCs are highly reactive and play a critical role in the formation of ozone. Other VOCs have adverse chronic and acute health effects. In some cases, VOCs can be both highly reactive and potentially toxic.[55]

Examples of harmful VOCs include 1-3 butadiene, benzene, ethylbenzene, toluene and xylenes.

Results and Discussion. http:// oil-gas.state.co.us/Library/ piceancebasin/GarfieldFinalReport10-31.pdf

[52] Gordon Pierce, Colorado Department of Public Health and Environment. November, 2002. *Garfield County Air Monitoring Results.* *http://oil-gas.state.co.us/Library/piceancebasin/GarfieldCountyMonitoring.pdf*

[53] Columbia Analytical Services. Q. Unit conversions – How do I convert µg/m^3 to ppbv? A. µg/ m^3 * 24.45 / molecular weight of compound = ppbv. http://www.caslab.com/FAQsv.php#q2
For benzene (molecular weight = 78), the conversion from µg/m^3 to ppb(volume) is: ppbv = x ug/m3 * 24.45 / 78.

[54] Pers. Comm. Lisa Sumi, OGAP, and Jim Rada, Garfield County Health Department. Oct. 25, 2006.

[55] California Air Resources Board. "Toxic Air Contaminants Monitoring" (page updated February 15, 2005) Accessed Jan. 2, 2006. http://www.arb.ca.gov/aaqm/toxics.htm

British researchers studying childhood cancers and atmospheric carcinogens have found that, "(1) that childhood cancers and leukaemias in Great Britain exhibit geographical clustering of birth places; (2) they occur at increased densities around industrial sites with large scale combustion processes or using volatile organic compounds (VOCs). . .".[56]

The authors conclude that, "Childhood cancers/leukaemia births are closely associated with high atmospheric emissions from combustion processes, mainly oil based, and from organic evaporation. Demonstrated associations with 1-3, butadiene, dioxins and benz(a)pyrene, but possibly others as well, are probably causal. Such toxic emissions may account for a majority of all cases."[57]

According to the Oregon Department of Human Services, human exposure to benzene, toluene, ethylbenzene and xylene (BTEX) can occur either through ingestion (drinking water from contaminated wells), or by inhalation (exposure via showering or laundering).[58] The following section summarizes health effects related to VOCs that are known to be associated with oil and gas development. Given that our study relates directly to the presence of VOCs in air, the health effects information for these selected VOCs included in this section refers to human exposure via inhalation (unless otherwise noted).

1,3-Butadiene: 1,3-butadiene is usually found in ambient air at low levels in urban and suburban areas. Studies show that short-term inhalation of elevated levels of 1,3-butadiene results in irritation of the eyes, nasal passages, throat, and lungs. Also, studies have reported a possible association between 1,3-butadiene exposure and cardiovascular diseases. EPA has classified 1,3-butadiene as a Group B2, probable human carcinogen.[59]

Benzene: Studies suggest that acute exposure to benzene (e.g., greater than 50 ppm) may depress the central nervous system. Common symptoms of acute exposure include drowsiness, fatigue, dizziness, headaches, nausea, vomiting, nose and throat irritation, slurred speech, loss of balance, and death.[60]

Prolonged exposure to benzene mainly affects the skin (e.g., redness, drying and cracking of the skin) and blood (e.g., may suppress the production of red and white blood cells, and clotting cells). Benzene may also increase the incidence of a specific type of

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[56] Knox, E.G. 2005. "Childhood cancers and atmospheric carcinogens," *Journal of Epidemio. Community Health*. 2005:59:101-105. p. 101,

[57] *ibid*. p. 104.

[58] Oregon Department of Human Services, Health Division. Feb. 1994. *Technical Bulletin – BTEX*. http://www.oregon.gov/DHS/ph/dwp/docs/fact/btex.pdf

[59] U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics Website. *1,3-Butadiene*. "Hazard Summary" (revised January, 2000). http://www.epa.gov/ttn/atw/hlthef/butadien.html

[60] Canadian Association of Petroleum Producers. 2006. *Best Management Practices - Conntrol of Benzene Emissions from Glycol Dehydrators*. p. 65 http://www.capp.ca/default.asp?V_DOC_ID=763&PubID=80610

leukemia (acute myelogenous leukemia) and other forms of leukemia and lymphomas.[61] According to the U.S. Environmental Protection Agency, there is sufficient evidence to show that benzene is a human carcinogen (cancer-causing agent).[62]

When benzene exposure occurs with exposure to other chemicals, the health effects may be enhanced. For example, exposure to benzene and ethanol can increase the effects to the blood system; and toluene decreases the ability of the body to remove benzene by competing with benzene for metabolic pathways.[63]

Ethylbenzene: Short-term, acute exposure to ethylbenzene results in respiratory effects, such as throat irritation and chest constriction, as well as irritation of the eyes and dizziness. Animal studies have shown effects on the blood, liver, and kidneys from chronic inhalation exposure to ethylbenzene. In a study by the National Toxicology Program (NTP), exposure to ethylbenzene by inhalation resulted in an increased incidence of kidney and testicular tumors in rats, and lung and liver tumors in mice.[64]

Toluene: The central nervous system (CNS) is the primary target organ for both short and long-term toluene exposures. Symptoms of CNS dysfunction resulting from short-term inhalation include fatigue, sleepiness, headaches and nausea. Chronic inhalation exposure causes irritation of the upper respiratory tract and eyes, sore throat, dizziness, and headache.

Human studies have also reported developmental effects in the children of pregnant women exposed to toluene. These effects included attention deficits, as well as craniofacial and limb anomalies. An association between exposure to toluene and an increased incidence of spontaneous abortions has also been noted. The Environmental Protection Agency notes, however, that these studies are not conclusive.[65]

Xylenes: Exposure to xylenes via short-term inhalation causes irritation of the eyes, nose, and throat, gastrointestinal effects and neurological effects. Chronic inhalation exposure results in central nervous system (CNS) effects, such as headaches, dizziness,

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61 Canadian Association of Petroleum Producers. 2006. *Best Management Practices - Conntrol of Benzene Emissions from Glycol Dehydrators.* p. 65 http://www.capp.ca/default.asp?V_DOC_ID=763&PubID=80610

62 U.S. Environmental Protection Agency. 2002. *Integrated Risk Information System (IRIS) on Benzene*. National Center for Environmental Assessment, Office of Research and Development. http://www.epa.gov/iris/subst/0276.htm

63 Canadian Association of Petroleum Producers. 2006. *Best Management Practices - Control of Benzene Emissions from Glycol Dehydrators.* p. 65 http://www.capp.ca/default.asp?V_DOC_ID=763&PubID=80610

64 U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics Website. *1,3-Ethylbenzene*. "Hazard Summary" (revised January, 2000). http://www.epa.gov/ttn/atw/hlthef/ethylben.html

65 U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics Website. *1,3-Toluene*. "Hazard Summary" (revised January, 2000). http://www.epa.gov/ttn/atw/hlthef/toluene.html

fatigue, tremors, and decrease in coordination. Respiratory, cardiovascular, and kidney effects have also been reported.[66]

3.2.3 Regulation of VOCs

There are a number of oil-and-gas-related VOCs that are regulated as air, soil and water contaminants.[67] Several of the VOCs emitted from oil and gas facilities are regulated as toxic air pollutants under the federal *Clean Air Act*. These compounds include BTEX, formaldehyde, hexane and 1,3-butadiene.[68]

The U.S. Environmental Protection Agency (EPA), Region 9, has developed risked-based exposure guidelines for a number of air contaminants at Superfund Sites. These concentrations, known as Preliminary Remediation Goals (PRG) are deemed to be protective of human health. EPA uses the PRG concentrations as a screening tool – if the concentrations of the air contaminants are below the PRG concentrations, EPA generally will not require any action to further reduce concentrations. EPA has set ambient air PRGs for a number of VOCs. The table below includes some examples of PRG concentrations. For a complete list, visit: http://www.epa.gov/region09/waste/sfund/prg

Table . Examples of Selected

Volatile Organic Compound	**EPA Region 9 Preliminary Remediation Goals for Volatile Organic Compounds in Ambient Air ($\mu g/m^3$)**
Acetone	3300
Chloroform	0.083
1,4-Dichlorobenzene	0.31
Benzene	0.25
Toluene	400
Ethylbenzene	1100
Xylenes	110

66 U.S. Environmental Protection Agency. Technology Transfer Network Air Toxics Website. *1,3-Xylenes*. "Hazard Summary" (revised January, 2000). http://www.epa.gov/ttn/atw/hlthef/xylenes.html

67 EPA has set Maximum Contaminant Levels (MCLs) for BTEX in drinking water: 0.005 ppm benzene; 1.0 ppm toluene; 0.7 ppm ethylbenzene; and 10 ppm xylenes (total). The MCL is set so that a lifetime exposure at the MCL concentration would result in no more than 1 - 100 excess cases of cancer per million people exposed. (U.S. Environmental Protection Agency. *List of Contaminants & their MCLs.* http://www.epa.gov/safewater/mcl.html)

68 U.S. Environmental Protection Agency. *Health Effects Notebook for Hazardous Air Pollutants.* http://www.epa.gov/ttn/atw/hlthef/hapindex.html

The California Environmental Protection Agency (CalEPA) has established chronic inhalation reference exposure levels for 80 air contaminants,[69] including a number of VOCs. For example, they have established an inhalation reference exposure level of 0.06 mg/m^3 (60 μg/m^3) for benzene based on hematological effects in humans.[70] The CalEPA reference exposure level is a concentration at or below which adverse health effects are not likely to occur.

EPA Rfc CHRONIC - IRIS

For some VOCs, occupational exposure limits have been set to protect human health and safety. In some cases, the limits are "advisory," e.g., those provided by the American Industrial Hygiene Association (AIHA) or the American Conference of Governmental and Industrial Hygienist (ACGIH). Other exposure limits, such as those set by the Occupational Safety and Health Administration (OSHA), have been incorporated into government regulations.

These levels are much higher than the ambient air quality guidelines above, because these represent short-term exposures to the air contaminants.

Table 5. Examples of health-and-safety-based exposure limits for various VOCs.[71]

	AIHA ERPG 2[72] (1-hour exposure – no irreversible or serious health effects)	AIHA ERPG 1[73] (1-hour exposure – only mild, transient adverse health effects)	ACGIH STEL[74] (15-minute exposure)
1,3-Butadiene	442 mg/m^3 200 ppm	22.1 mg/m^3 10 ppm	-
Benzene	489 mg/m^3 150 ppm	163 mg/m^3 50 ppm	8 mg/m^3 2.5 ppm
Ethylbenzene	-	-	545 mg/m^3 125 ppm

[69] California Office of Environmental Health Hazard Assessment. Chronic Reference Exposure Levels Adopted by OEHHA as of February 2005. http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html

[70] California Environmental Protection Agency (CalEPA). *Air Toxics Hot Spots Program Risk Assessment Guidelines: Part III. Technical Support Document for the Determination of Noncancer Chronic Reference Exposure Levels. SRP Draft.* Office of Environmental Health Hazard Assessment, Berkeley, CA. 1999. Available for download at: http://www.oehha.ca.gov/air/chronic_rels/pdf/relsP32k.pdf

[71] All data from the U.S. Environmental Protection Agency. *Health Effects Notebook for Hazardous Air Pollutants.* http://www.epa.gov/ttn/atw/hlthef/hapindex.html

[72] **AIHA ERPG 2**-- is the maximum airborne concentration below which it is believed nearly all individuals could be **exposed up to one hour without experiencing or developing irreversible or other serious health effects** that could impair their abilities to take protective action.

[73] **AIHA ERPG 1**--American Industrial Hygiene Association's emergency response planning guidelines. ERPG 1 is the maximum airborne concentration below which it is believed nearly all individuals could be **exposed up to one hour without experiencing other than mild transient adverse health effects** or perceiving a clearly defined objectionable odor.

[74] **ACGIH STEL**--American Conference of Governmental and Industrial Hygienist's threshold limit value short-term exposure limit; a **15-minute exposure, not be exceeded** at any time during a workday.

Toluene	1130 mg/m^3 300 ppm	188 mg/m^3 50 ppm	-
Xylenes	-	-	655 mg/m^3 151 ppm

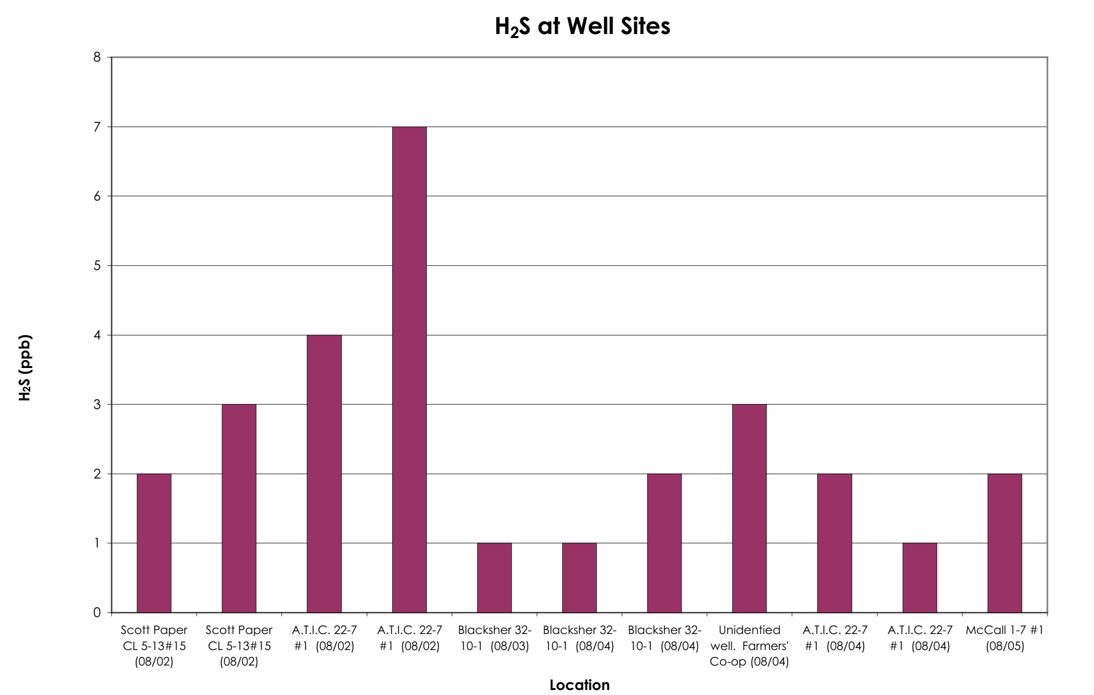
4.0 RESULTS

Appendix 2 includes information on all of the sample sites from our study where there were measurable concentrations of H_2S and/or VOCs. The following sections provide summaries and graphical representations of the sampling results.

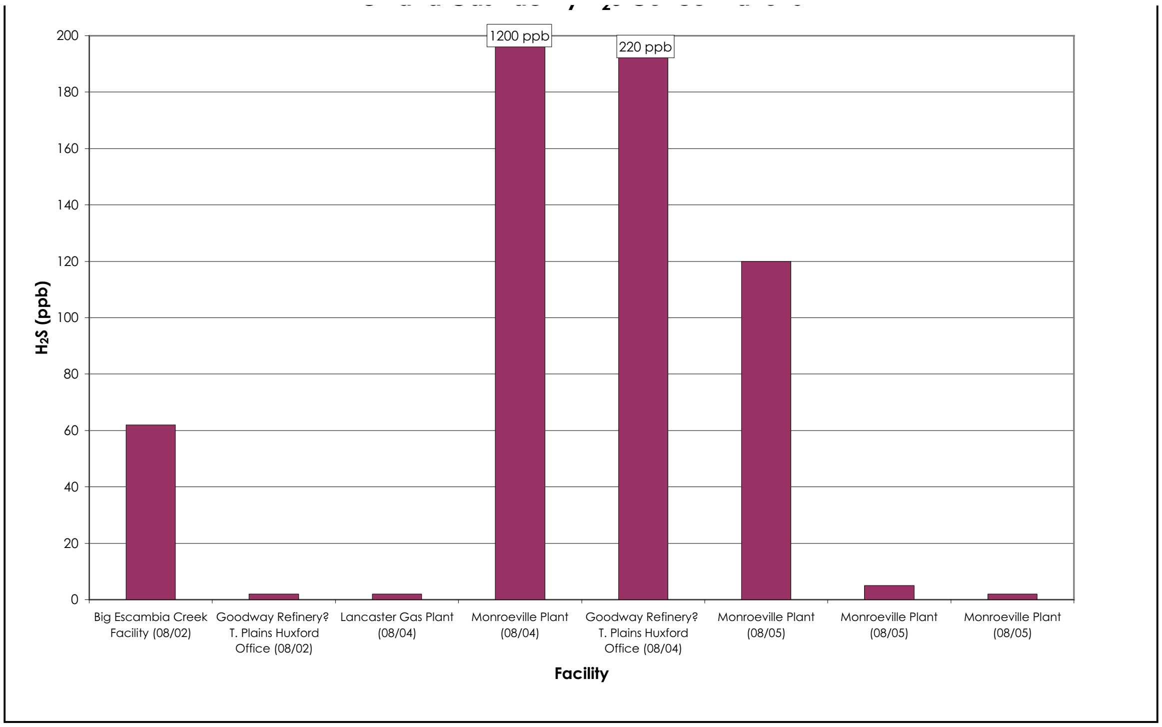
4.1 Hydrogen Sulfide

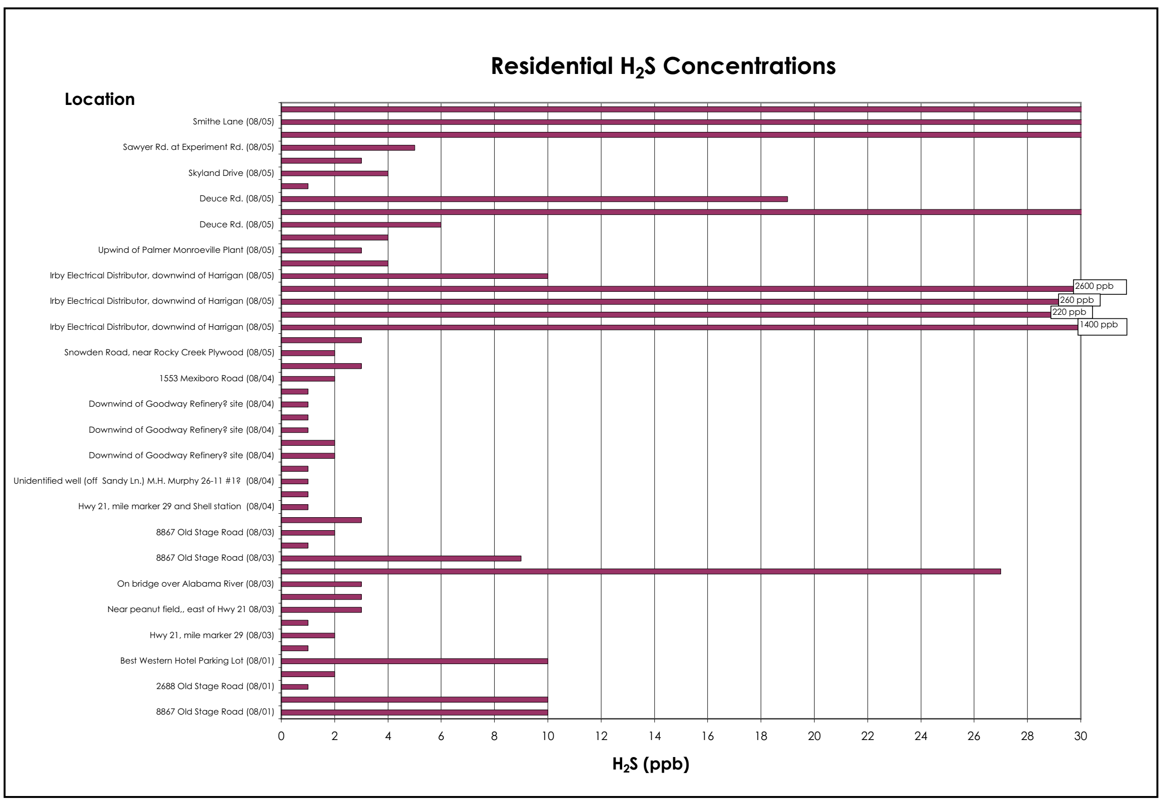
Hydrogen sulfide concentrations varied over the five-day monitoring period. The highest H_2S concentrations were experienced on August 5, and the highest reading, 2.6 ppm (2600 ppb) occurred in a residential areas (downwind from wood processing facilities).

Oil and Gas Wells – H_2S concentrations in the vicinity of well sites were below 8 ppb.



Oil and Gas Facilities (gas plants, tank batteries, metering stations, refinery) – concentrations ranged from 0 – 1,200 ppb. The known sour gas facilities (e.g., Gallagher and Escambia) did not have the highest readings. Rather, the Monroeville plant had the highest measured H_2S concentrations.


H2S (ppb)
200
180
160
140
120
100
80
60
40
20
0
1200 ppb
220 ppb
Big Escambia Creek Facility (08/02)
Goodway Refinery? T. Plains Huxford Office (08/02)
Lancaster Gas Plant (08/04)
Monroeville Plant (08/04)
Goodway Refinery? T. Plains Huxford Office (08/04)
Monroeville Plant (08/05)
Monroeville Plant (08/05)
Monroeville Plant (08/05)
Facility


Residential H2S Concentrations
Location
Smithe Lane (08/05)
Sawyer Rd. at Experiment Rd. (08/05)
Skyland Drive (08/05)
Deuce Rd. (08/05)
Deuce Rd. (08/05)
Upwind of Palmer Monroeville Plant (08/05)
Irby Electrical Distributor, downwind of Harrigan (08/05)
Irby Electrical Distributor, downwind of Harrigan (08/05)
Irby Electrical Distributor, downwind of Harrigan (08/05)
Snowden Road, near Rocky Creek Plywood (08/05)
1553 Mexiboro Road (08/04)
Downwind of Goodway Refinery? site (08/04)
Downwind of Goodway Refinery? site (08/04)
Downwind of Goodway Refinery? site (08/04)
Unidentified well (off Sandy Ln.) M.H. Murphy 26-11 #1? (08/04)
Hwy 21, mile marker 29 and Shell station (08/04)
8867 Old Stage Road (08/03)
8867 Old Stage Road (08/03)
On bridge over Alabama River (08/03)
Near peanut field,, east of Hwy 21 08/03)
Hwy 21, mile marker 29 (08/03)
Best Western Hotel Parking Lot (08/01)
2688 Old Stage Road (08/01)
8867 Old Stage Road (08/01)
2600 ppb
260 ppb
220 ppb
1400 ppb
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
H2S (ppb)

Wood Product Operations – H_2S concentrations were between 1 and 7 ppb at all facilities except Harrigan Lumber, a particle board plant on Hornady Drive in Monroeville. This location had H_2S readings as high as 1,400 ppb.

Sewage Treatment Plant – the concentrations of H_2S measured at a sewage treatment plant that serves the municipality of Monroeville, were in the 3 – 4 ppb range.

Residential areas – the majority of H_2S readings in residential areas were below 10 ppb, five readings were between 150 and 300, and three readings were between 1,400 and 2,600 ppb. There were downwind of Harrigan Lumber.

4.2 Volatile Organic Compounds

Concentrations of volatile organic compound varied over the five-day monitoring period. They ranged from non-detectable to 199 parts per million (the maximum concentration that the ppb-RAE monitor can record). Since 199 ppm is the upper limit of the VOC monitor, it is probable that when we recorded readings of 199 ppm, the actual concentrations were above 199 ppm.

The highest VOC readings (199 ppm) were experienced on August 2 and 4. These readings occurred at a well site, and in residential areas (downwind of a gas processing plant).

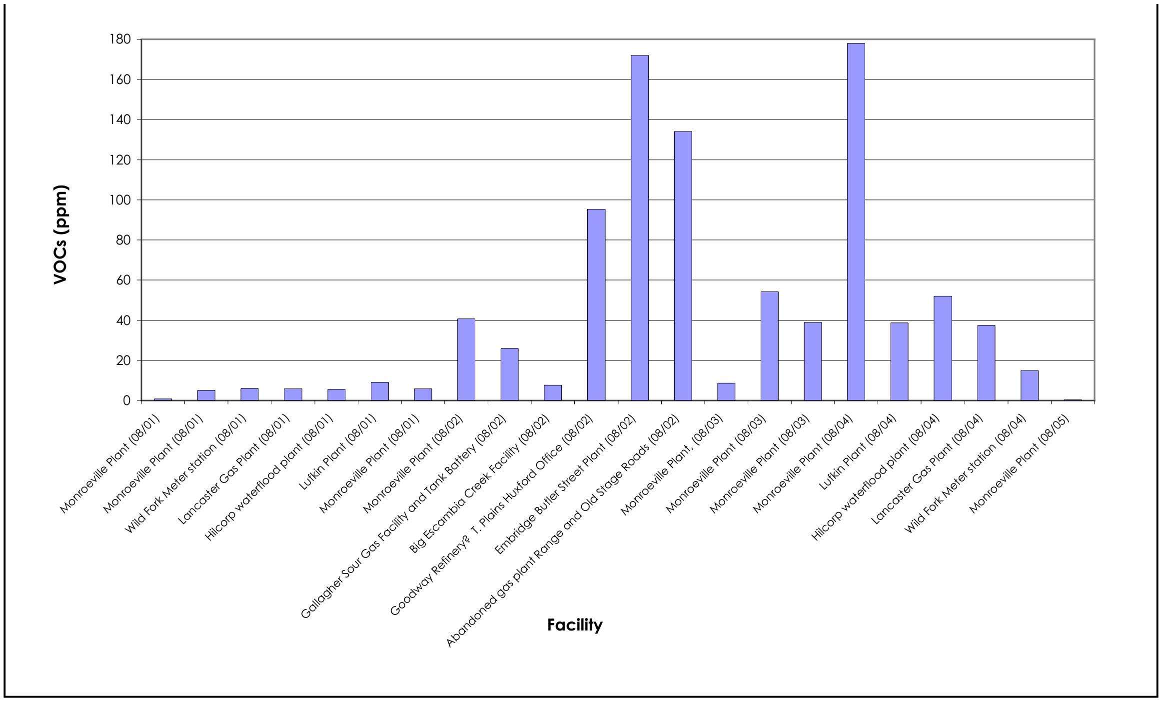
Oil and Gas Wells – concentrations ranged from 870 ppb 199 ppm. Eight wells had readings greater than 100 ppm.

Oil and Gas Facilities (gas plants, tank batteries, metering stations, "refinery") – VOC concentrations ranged from 400 ppb to 178 ppm. Three sites had VOC readings above 100 ppm.

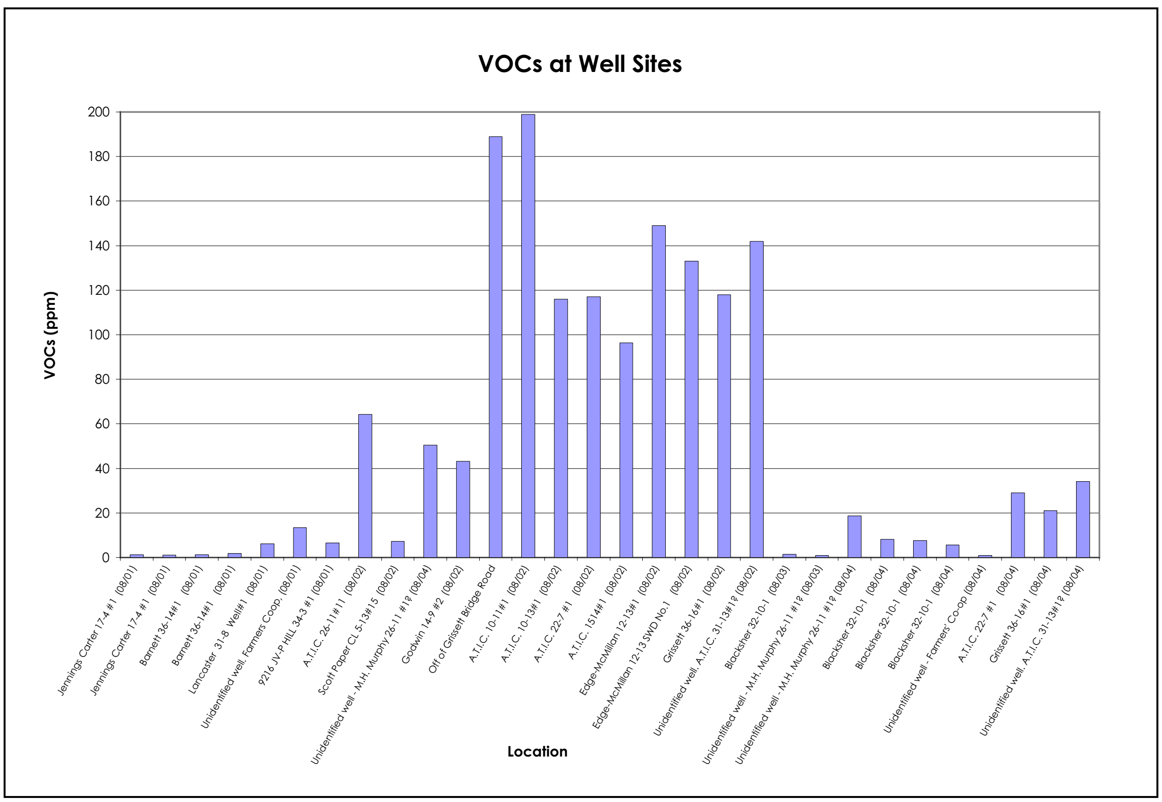
Wood Product Operations – the lowest VOC readings, which were less than 400 ppb, were at or near the Harrigan Lumber facility (but it was fairly windy when the measurements were taken, so the VOCs may have been dispersed). The Georgia Pacific operation had VOC levels of approximately 5 ppm. The Rocky Creek Plywood facility, and nearby neighborhoods, had much higher VOC concentrations, up to 60 ppm at the facility and 98 ppm in the neighborhood.

Sewage Treatment Plant – VOCs were not measured.

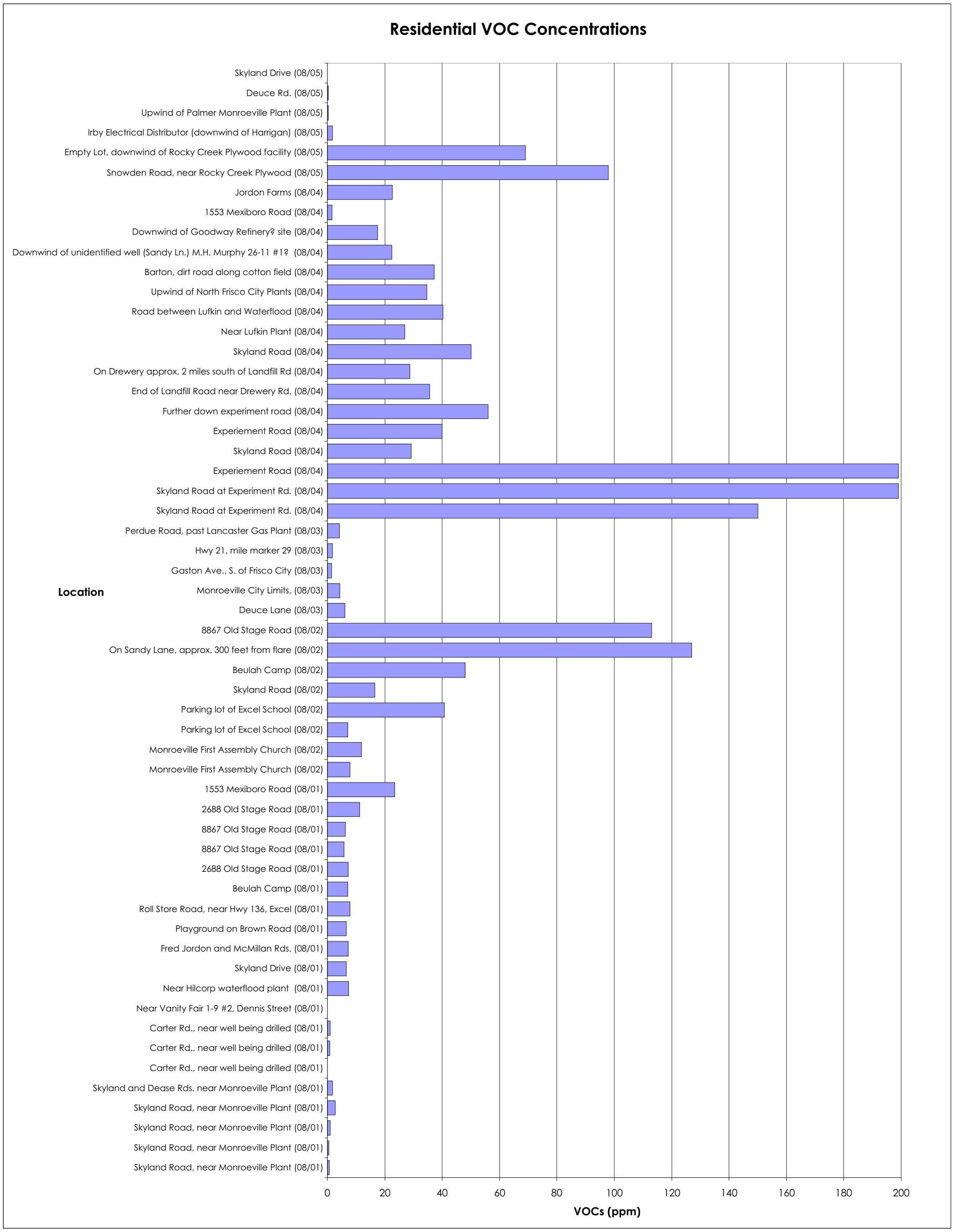
Residential areas – the concentrations varied from no detectable VOCs to 199 ppm. Four locations had concentrations greater than 100 ppm.



VOCs (ppm)
180
160
140
120
100
80
60
40
20
0
Monroeville Plant (08/01)
Monroeville Plant (08/01)
Wild Fork Meter station (08/01)
Lancaster Gas Plant (08/01)
Hilcorp waterflood plant (08/01)
Lufkin Plant (08/01)
Monroeville Plant (08/01)
Monroeville Plant (08/02)
Gallagher Sour Gas Facility and Tank Battery (08/02)
Big Escambia Creek Facility (08/02)
Goodway Refinery¿ T. Plains Huxford Office (08/02)
Embridge Butler Street Plant (08/02)
Abandoned gas plant Range and Old Stage Roads (08/02)
Monroeville Plant. (08/03)
Monroeville Plant (08/03)
Monroeville Plant (08/03)
Monroeville Plant (08/04)
Lufkin Plant (08/04)
Hilcorp waterflood plant (08/04)
Lancaster Gas Plant (08/04)
Wild Fork Meter station (08/04)
Monroeville Plant (08/05)
Facility



VOCs at Well Sites
VOCs (ppm)
200
180
160
140
120
100
80
60
40
20
0
Jennings Carter 17-4 #1 (08/01)
Jennings Carter 17-4 #1 (08/01)
Barnett 36-14#1 (08/01)
Barnett 36-14#1 (08/01)
Lancaster 31-8 Well#1 (08/01)
Unidentified well. Farmers Coop, (08/01)
9216 JV-P HILL 34-3 #1 (08/01)
A.T.I.C. 26-11#11 (08/02)
Scott Paper CL 5-13#15 (08/02)
Unidentified well - M.H. Murphy 26-11 #1¿ (08/04)
Godwin 14-9 #2 (08/02)
Off of Grissett Bridge Road
A.T.I.C. 10-11#1 (08/02)
A.T.I.C. 10-13#1 (08/02)
A.T.I.C. 22-7 #1 (08/02)
A.T.I.C. 1514#1 (08/02)
Edge-McMillan 12-13#1 (08/02)
Edge-McMillan 12-13 SWD No.1 (08/02)
Grissett 36-16#1 (08/02)
Unidentified well. A.T.I.C. 31-13#1¿ (08/02)
Blacksher 32-10-1 (08/03)
Unidentified well - M.H. Murphy 26-11 #1¿ (08/03)
Unidentified well - M.H. Murphy 26-11 #1¿ (08/04)
Blacksher 32-10-1 (08/04)
Blacksher 32-10-1 (08/04)
Blacksher 32-10-1 (08/04)
Unidentified well - Farmers' Co-op (08/04)
A.T.I.C. 22-7 #1 (08/04)
Grissett 36-16#1 (08/04)
Unidentified well. A.T.I.C. 31-13#1¿ (08/04)
Location



Residential VOC Concentrations
Skyland Drive (08/05)
Deuce Rd. (08/05)
Upwind of Palmer Monroeville Plant (08/05)
Irby Electrical Distributor (downwind of Harrigan) (08/05)
Empty Lot, downwind of Rocky Creek Plywood facility (08/05)
Snowden Road, near Rocky Creek Plywood (08/05)
Jordon Farms (08/04)
1553 Mexiboro Road (08/04)
Downwind of Goodway Refinery? site (08/04)
Downwind of unidentified well (Sandy Ln.) M.H. Murphy 26-11 #1? (08/04)
Barton, dirt road along cotton field (08/04)
Upwind of North Frisco City Plants (08/04)
Road between Lufkin and Waterflood (08/04)
Near Lufkin Plant (08/04)
Skyland Road (08/04)
On Drewery approx. 2 miles south of Landfill Rd (08/04)
End of Landfill Road near Drewery Rd. (08/04)
Further down experiment road (08/04)
Experiement Road (08/04)
Skyland Road (08/04)
Experiement Road (08/04)
Skyland Road at Experiment Rd. (08/04)
Skyland Road at Experiment Rd. (08/04)
Perdue Road, past Lancaster Gas Plant (08/03)
Hwy 21, mile marker 29 (08/03)
Gaston Ave., S. of Frisco City (08/03)
Location
Monroeville City Limits, (08/03)
Deuce Lane (08/03)
8867 Old Stage Road (08/02)
On Sandy Lane, approx. 300 feet from flare (08/02)
Beulah Camp (08/02)
Skyland Road (08/02)
Parking lot of Excel School (08/02)
Parking lot of Excel School (08/02)
Monroeville First Assembly Church (08/02)
Monroeville First Assembly Church (08/02)
1553 Mexiboro Road (08/01)
2688 Old Stage Road (08/01)
8867 Old Stage Road (08/01)
8867 Old Stage Road (08/01)
2688 Old Stage Road (08/01)
Beulah Camp (08/01)
Roll Store Road, near Hwy 136, Excel (08/01)
Playground on Brown Road (08/01)
Fred Jordon and McMillan Rds. (08/01)
Skyland Drive (08/01)
Near Hilcorp waterflood plant (08/01)
Near Vanity Fair 1-9 #2, Dennis Street (08/01)
Carter Rd., near well being drilled (08/01)
Carter Rd., near well being drilled (08/01)
Carter Rd., near well being drilled (08/01)
Skyland and Dease Rds. near Monroeville Plant (08/01)
Skyland Road, near Monroeville Plant (08/01)
Skyland Road, near Monroeville Plant (08/01)
Skyland Road, near Monroeville Plant (08/01)
Skyland Road, near Monroeville Plant (08/01)
0
20
40
60
80
100
120
140
160
180
200
VOCs (ppm)

5.0 DISCUSSION

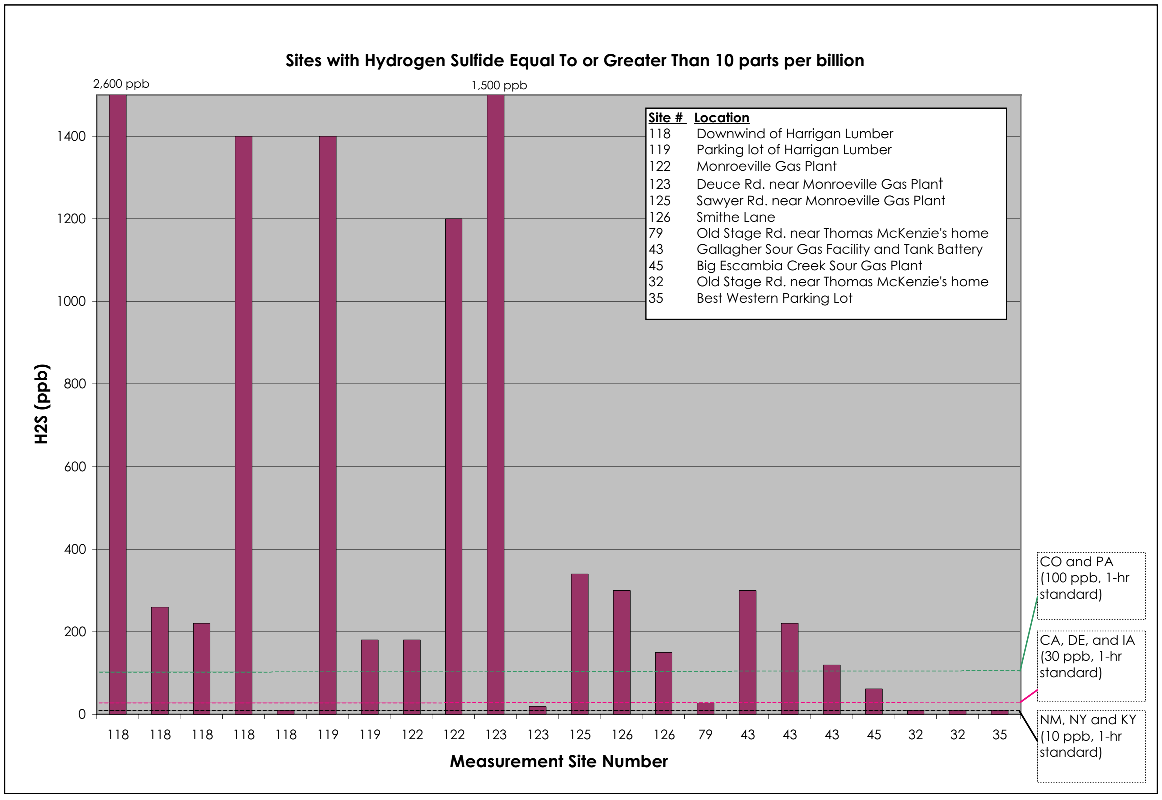
Table 6. Summary table for ranges in H_2S and VOC concentrations.

	Oil and Gas Wells	Gas Plants	Wood Products	Sewage	Residential
H_2S (ppb)	< 8	0 – 1,200	1 - 1,400	3 - 4	10 – 2,600
VOCs (ppb)	870 – 199,000	400 – 178,000	<400 – 60,000	-	0 – 199,000

5.1 Hydrogen Sulfide

Alabama does not have an ambient air quality standard for H_2S. Thus, we have taken the liberty of comparing H_2S concentrations measured in these three Alabama counties to standards that have been set by other states.

The chart below depicts our sampling sites that had measured H_2S concentrations equal to or greater than 10 parts per billion (ppb). Ten parts per billion is the value that some states (NM, NY, KY) have set as the average value not to be exceeded when H_2S is monitored over a one-hour period. Twenty-two measurements at ten separate sites exceeded the 10 ppb value.

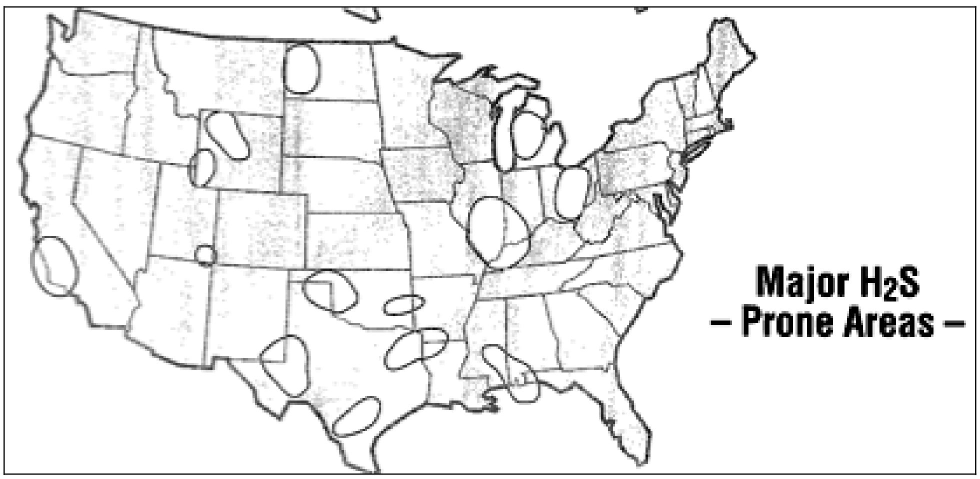


We did not take an average measurement over a 1-hour period; rather, our readings reflect the average taken over less than a minute. Regardless of our measurement technique, however, these results still serves as an indication that ambient concentrations at some of the sites far exceeded many state regulatory standards that have been set to protect human health, welfare and quality of life.

These levels of hydrogen sulfide are between 10 and 2600 times greater than normal urban background levels, which are typically less than 1 ppb.[75] In unpolluted areas, concentrations of H_2S may be as low as 0.03 – 0.1 μg/m3 (0.02 – 0.07 ppb).[76]

5.1.1 Gas wells and processing plants

As seen in the map below, the southwest region of Alabama contains some oil and gas reservoirs that have a high content of hydrogen sulfide.



Source: Gas Research Institute, 1990.[77]

In Alabama, the Oil and Gas Board (OGB) defines a sour gas operation as a facility that handles hydrogen sulfide concentrations equal to one hundred (100) parts per million (ppm) or more.[78]

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[75] 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.

[76] Chou, S. 2003. *Hydrogen Sulfide: Human Health Aspects.* Concise International Chemical Assessment Document 53. Prepared for the World Health Organization. p. 7. http://www.who.int/ipcs/publications/cicad/en/cicad53.pdf

[77] Energy and Environmental Analysis. Nov. 1990. *Chemical Composition of Discovered and Undiscovered Natural Gas in the Lower-48 United States.* Prepared for the Gas Research Institute. 90/0248. p. 1-13.

[78] Alabama Oil and Gas Board. *Rules and Regulations of the State Oil and Gas Board of Alabama Governing Onshore Lands Operations*. 400-1-1-.05. Definitions. (69) "Sour gas operations." http://www.ogb.state.al.us/HTMLS/OGBRULES/4001.htm#400-1-1-.05

Within Alabama, there are numerous oil and gas fields that contain sour gas, and several facilities that process sour gas. The Alabama Oil and Gas Board has identified fifteen fields in Escambia and Conecuh counties in southwest Alabama that produce natural gas containing hydrogen sulfide at 100 parts per million or greater; and three gas processing plants that process the hydrogen-sulfide-laden gas (Table 7).[79]

Table 7. Producing Fields and Plants in Conecuh, Escambia, and Monroe Counties with 100 parts per million (ppm) or greater of Hydrogen Sulfide.[80]

FIELDS	COUNTY
Appleton	Escambia
Big Escambia Creek	Escambia
Big Spring	Escambia
Fanny Church	Escambia
Flomaton	Escambia
Huxford	Escambia
Little Cedar Creek	Conecuh
Little Escambia Creek	Escambia
Little Rock	Escambia
Northwest Appleton	Escambia
Northwest Hall Creek	Escambia
Northwest Smiths Church	Escambia
South Burnt Corn Creek	Escambia
West Appleton	Escambia
Wild Fork Creek	Escambia
PLANTS	**COUNTY**
Castleberry Plant	Conecuh
Big Escambia Creek Plant	Escambia
Flomaton Plant	Escambia

The oil and gas wells located in these fields, as well as the plants themselves (due to fugitive or intentional releases of gas) are likely to be sources of H_2S. Table 8 contains a list of some of the sour gas wells in Escambia and Conecuh counties. The table includes the H_2S content of the gas extracted from these wells.[81]

We did not have the opportunity to sample around most of these well sites to determine H_2S emissions coming off of the equipment (e.g., through leaky values and connections or on-site venting). We did sample near one sour well (A.T.I.C. 22-7 #1), and measured H_2S concentrations between 1 and 7 ppb.

[79] Alabama Oil and Gas Board gas plant data. Letter from Berry H. Tew, Jr., Oil and gas supervisor, to Thomas McKenzie and Audrey Silcox. June 20, 2005. The letter included a chart entitled "Producing fields and plants in Conecuh, Escambia and Monroe Coutnies with 100 parts per million (ppm) or greater of Hydrogen Sulfide."
[80] Information included in a letter from Alabama Oil and Gas Board to Audrey Silcox and Thomas McKenzie. June 20, 2005.
[81] Data from the Alabama State Oil and Gas Board "PVT database", which includes reservoir engineering parameters such as formation volume factor, solution gas/oil ratio, full well stream hydrocarbon analyses, and API gravity. Database can be accessed at: http://www.ogb.state.al.us/HTMLS/dbpvt.htm

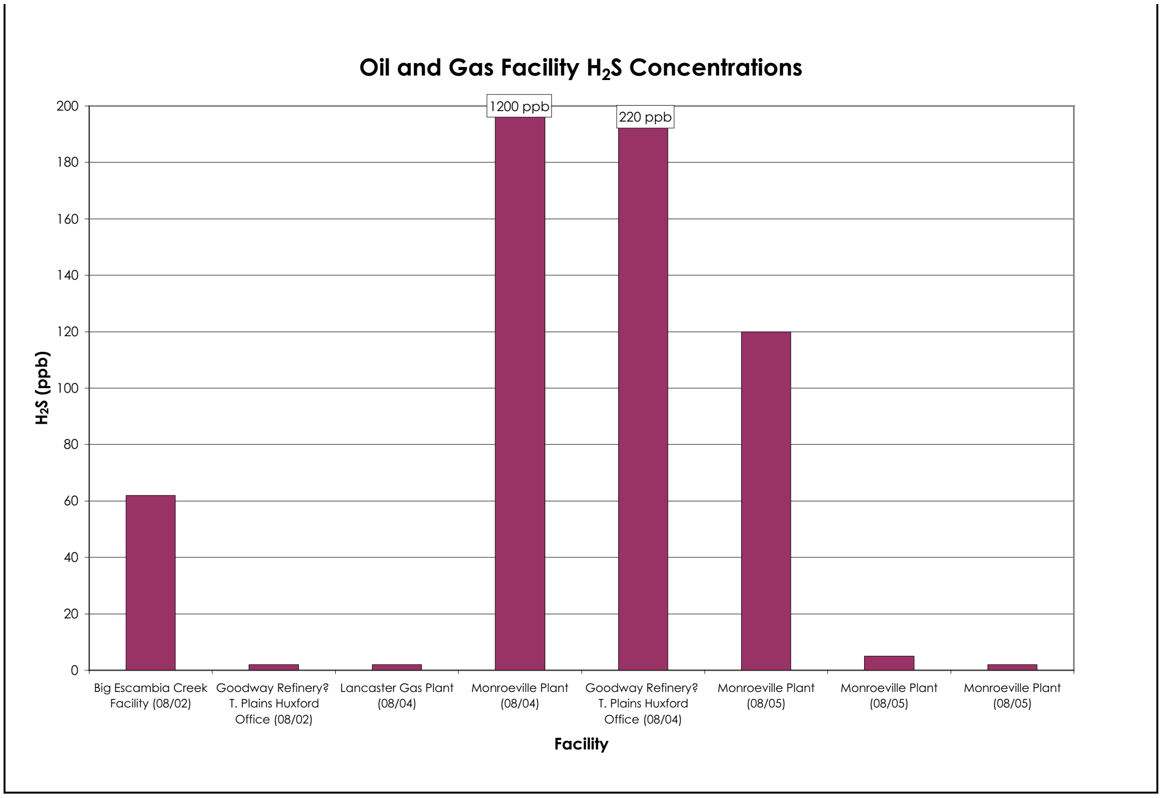
Table 8. Wells in Escambia and Conecuh Counties with greater than 100 ppm H_2S in the gas stream.

County	Permit #	Well name	H_2S Mol %	H_2S ppm[82]	Field
Escambia	1869	DORA J. STEELY #36-2	2.2	22000	Fanny Church-Oil
Escambia	3581	ATIC 35-6 #2	0.03	300	Huxford-Oil
Escambia	3584	APPLETON UNIT 2-14 #1	1.75	17500	Appleton-Oil
Escambia	3986	APL UNIT TR 5: MCMILLAN TRUST 11-1 #2	1.6	16000	Appleton-Oil
Escambia	4693-B	PARSONS 4-16 #2	3.45	34500	Catawba Springs-Oil
Escambia	5178	HUXFORD 34-2 #1	0.67	6700	Hanberry Church-Oil
Escambia	5272	EARL H. WEAVER 22-15 #1	0.68	6800	South Burnt Corn Creek-Oil
Escambia	5411	IPC 5-10 #1	4.2	42000	Wild Fork Creek-Oil
Escambia	5757	P.H. GALLAGHER 16-3 #1	0.69	6900	West Appleton-Oil
Escambia	6943	EDGE-WEFEL TRUST 24-5 #1	3.64	36400	North Smiths Church-Oil
Escambia	10166	A.T.I.C. 34-4 #1	3.42	34200	Northwest Smiths Church-Oil
Escambia	10217	A.T.I.C. 10-10 #1	0.1	1000	Chitterling Creek-Oil
Escambia	10572	A.T.I.C. 21-5 #1	0.7	7000	East Robinson Creek-Oil
Escambia	11030-B	MCMILLAN 3-9 #1	2.54	25400	Northwest Appleton-Oil
Escambia	11116-B	A.T.I.C. 22-7 #1	2.27	22700	Southwest Canaan Church-Oil
Escambia	13756	ATIC 27-8 #1	1.52	15200	Wildcat
Conecuh	10560	CEDAR CREEK LAND & TIMBER CO. 30-1 #1	0.29	2900	Little Cedar Creek-Oil
Conecuh	13472	PUGH 22-2	0.07	700	Little Cedar Creek-Oil

As seen in the graph on the next page, the concentrations measured at the perimeter of some the gas processing plants were in the range of 2 to 1200 ppb. Interestingly, the concentration near Big Escambia, the one "sour" gas plant in our study, did not register the highest H_2S concentration.

There are a couple of possible reasons for this: (1) we were not directly downwind of any H_2S emissions from the plant; (2) the plant was not venting at the time; (3) the plant is well maintained (e.g., leaky fixtures and valves are immediately addressed) because it is not safe to allow H_2S into the working environment of the plant.

[82] If H_2S contents are reported in ppm or grains (gr) per 100 scf, use the following factors to convert to mole %: 10,000 ppm H_2S = 1 mole % H_2S; 627 gr H_2S/100 scf = 1 mole % H_2S.
Source: U. S. Environmental Protection Agency. *AP-42 Emissions Factors, Ch. 5, Petroleum Industry, S. 5.3, Natural Gas Processing.* http://www.epa.gov/ttn/chief/ap42/ch05/final/c05s03.pdf p.5.3-1.



In Alabama, there are regulations that pertain to acceptable H_2S concentrations near refineries and gas plants. Section 335-3-5-.03 of the Alabama Administrative Code applies to facilities that handle natural gas or refinery gas that contains more than 0.10 grain of hydrogen sulfide per standard cubic foot (SCF). The regulation states:

> *No person shall cause or permit the emission of a process gas stream containing more than 0.10 grain of hydrogen sulfide per SCF into the atmosphere unless it is properly burned to maintain the ground level concentrations of hydrogen sulfide to less than twenty (20) parts per billion beyond plant property limits, averaged over a thirty (30) minute period.*[83]

While we do not have the capability of proving that H_2S measured near the gas processing plants originated from the plants, the above graph shows that four measurements taken at the fence-line of gas plants/refineries exceeded the 20 ppb standard. On August 4 and 5, the Monroeville plant had readings of 120 and 1,200 ppb, respectively. The Big Escambia Plant had a reading of 62 ppb on August 2, and the "Goodway Refinery"[84] had a reading of 220 ppb on August 4.

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[83] *ADEM Admin. Code R. Chapter 335-3-5 Control of Sulfur Compound Emissions* Section. 03 Petroleum Production. http://www.adem.state.al.us/Regulations/Div3/Div3%207-06.pdf

[84] There was no identifying sign on this facility. The only sign in front of the facility read: "Thomas Plains Huxford Office. We referred to it as "Goodway Refinery." It is referenced as Site 49 in Appendix 2 of this report. It appeared to be a gas plant/fueling station.

Interestingly, one of the plants that processes sweet gas (i.e., Monroeville) appeared to be one of the larger H_2S emissions sources in the sampling area.

It is possible that this is because the gas at Monroeville does contain some H_2S (but not enough to have it considered "sour"), and that the facility's flare does not efficiently burn the H_2S. Or perhaps, assuming that the gas contains some H_2S, the fugitive emissions from the site are large enough to allow these high readings. Alternatively, the H_2S measured at the Monroeville facility had a source other than the Monroeville plant.

5.1.2 H_2S Near wood product facilities

In Alabama, there are H_2S-related regulations for pulp mills.[85] Our highest readings were near a particle board plant (Harrigan Lumber). There may be cause for health concerns for residents living near this plant. Concentrations measured at and downwind from the facility were as high as 1400 ppb.

5.2 Volatile Organic Compounds

As mentioned in the methods section of this report, the equipment used to measure VOC concentrations did not provide information on concentrations of individual VOCs. Rather, the reading reflected the sum of all volatile carbon compounds in the C1 to C10 range (excluding methane). The intention of our study was simply to identify whether emissions from the various industries in the counties may be creating an unhealthy level of VOCs.

We measured VOC concentrations as high as 199 ppm, which was the upper limit of the PID monitor (indicating that in all likelihood, concentrations exceeded 199 ppm in some locations). These levels may be a cause for concern. As mentioned in the Literature Review section of this report, other oil and gas producing regions have measured elevated levels of VOCs. In Garfield County, Colorado, benzene was found to be present in some air samples at levels that could pose a threat to human health (i.e., the average and max concentrations. . . greater than EPA PRGs and Cal … 50 ppb).[86]

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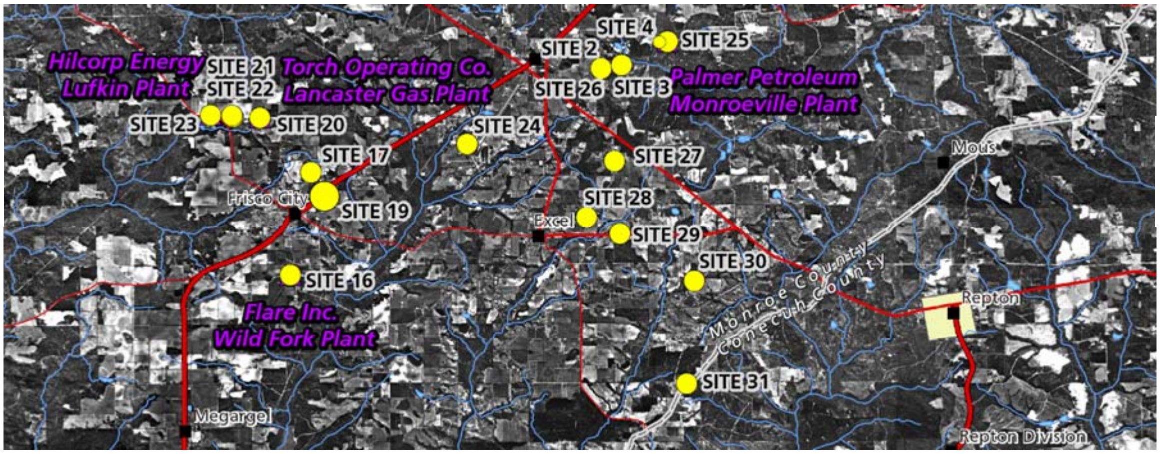
[85] *ADEM Admin. Code R. Chapter 335-3-5 Control of Sulfur Compound Emissions*. Section 04 Kraft Pulp Mills. "(a) No person shall cause or permit the emissions of total reduced sulfur (TRS) from recovery furnaces, lime kilns, digesters, and multiple effect evaporators to exceed 1.2 pounds (expressed as hydrogen sulfide on a dry gas basis) per ton of air-dried pulp from kraft pulp mills. (b) The pulp production rates for kraft pulp mills referred to in this Rule shall be calculated as provided in Rule 335-3-4-.07(3). (c) Notwithstanding the specific limits set forth in this Rule, in order to maintain the lowest possible emission of air contaminants, the highest and best practicable treatment and control for TRS currently available shall be provided for new kraft pulp mills."

[86] Columbia Analytical Services. Q. Unit conversions – How do I convert $\mu g/m^3$ to ppbv?
A. $\mu g/m^3 * 24.45$ / molecular weight of compound = ppbv.
http://www.caslab.com/FAQsv.php#q2
For benzene (molecular weight = 78), the conversion from $\mu g/m^3$ to ppb(volume) is: ppbv = x ug/m3 * 24.45 / 78.



In addition to venting of natural gas, and losses from equipment due to fugitive emissions, a likely source of VOCs and other potentially hazardous air emissions related to oil and gas operations are flares.

Recently, Midroc Operating Company was fined by the Alabama Department of Environmental Management (ADEM) for violating provisions of its air quality permits. Between September 28 and October 6, 2005, an ADEM staff member conducted visible emissions observations on twelve flares located at oil and gas production and separation sites in Conecuh County. The visible emissions observations resulted in nine flares having periods in which visible emissions exceeded allowable levels outlined in the company's air permits.[87]

A report by the Environmental Integrity Project, "Smoking Guns," contends that large volumes of air pollution are released because flares are poorly operated and do not burn cleanly.[88] The U.S. Environmental Protection Agency (EPA), as well, has identified visibly smoking flares as being, "far less efficient than properly maintained flares." [89]

During the week of August 1-5, 2005, when we conducted our sampling operations, we found a number of sites that had smoking flares (see photographs on the following pages). While ADEM appears to have taken a good first step in penalizing operations with inefficient flares, the problem may be more widespread than the department realizes.

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87 Alabama Department of Environmental Management. Consent Order No. 06-___-Cap. In The Matter Of: Midroc Operating Company, Castleberry, Conecuh County, Alabama, Air Facility ID No. 103-0011, Air Facility ID No. 103-0017, and Air Facility ID No. 103-0018. http://www.adem.state.al.us/PublicNotice/Mar/AO/Midrock.pdf

88 USEPA Office of Air Quality Planning and Standards, Regulatory Impact Analysis for the Petroleum Refinery NESHAP, Revised Draft (1994). Cited in: Environmental Integrity Project. 2002. *Smoking Guns*. http://www.environmentalintegrity.org/pub75.cfm

89 *ibid.*

Gallagher Sour Gas Facility and Tank Battery (Conecuh County, Aug. 2, 2005)

This facility is owned by Vintage Petroleum.

There were visible emissions from the flare stack, and H_2S odors. The maximum H_2S reading immediately downwind of this site was 300 parts per billion (ppb).

The maximum VOC reading at the site was 26 parts per million (ppm).

Unidentified well off of Sandy Lane (Escambia County, Aug. 2, 2005)

There was no identification sign at this site. Based on the GIS data, it was most likely Stetson Petroleum Corporation's M.H. Murphy 26-11 #1 well, permit #4577. (Latitude 31.19187; Longitude 87.43942)

Clearly, there were visible emissions from the flare stack. No H_2S was detected on August 2, but a VOC reading of 50 ppm was recorded. There are homes located as close as approximately 300 feet from the well site.

Lancaster Gas Plant (Monroe County, Aug. 4, 2005)

Torch Operating Company operates this gas plant, which is located next to two other gas facilities in Monroe County.

There were visible emissions from the flare at this facility.

VOCs ranged from 27 to 52 ppm over a 25-minute period.

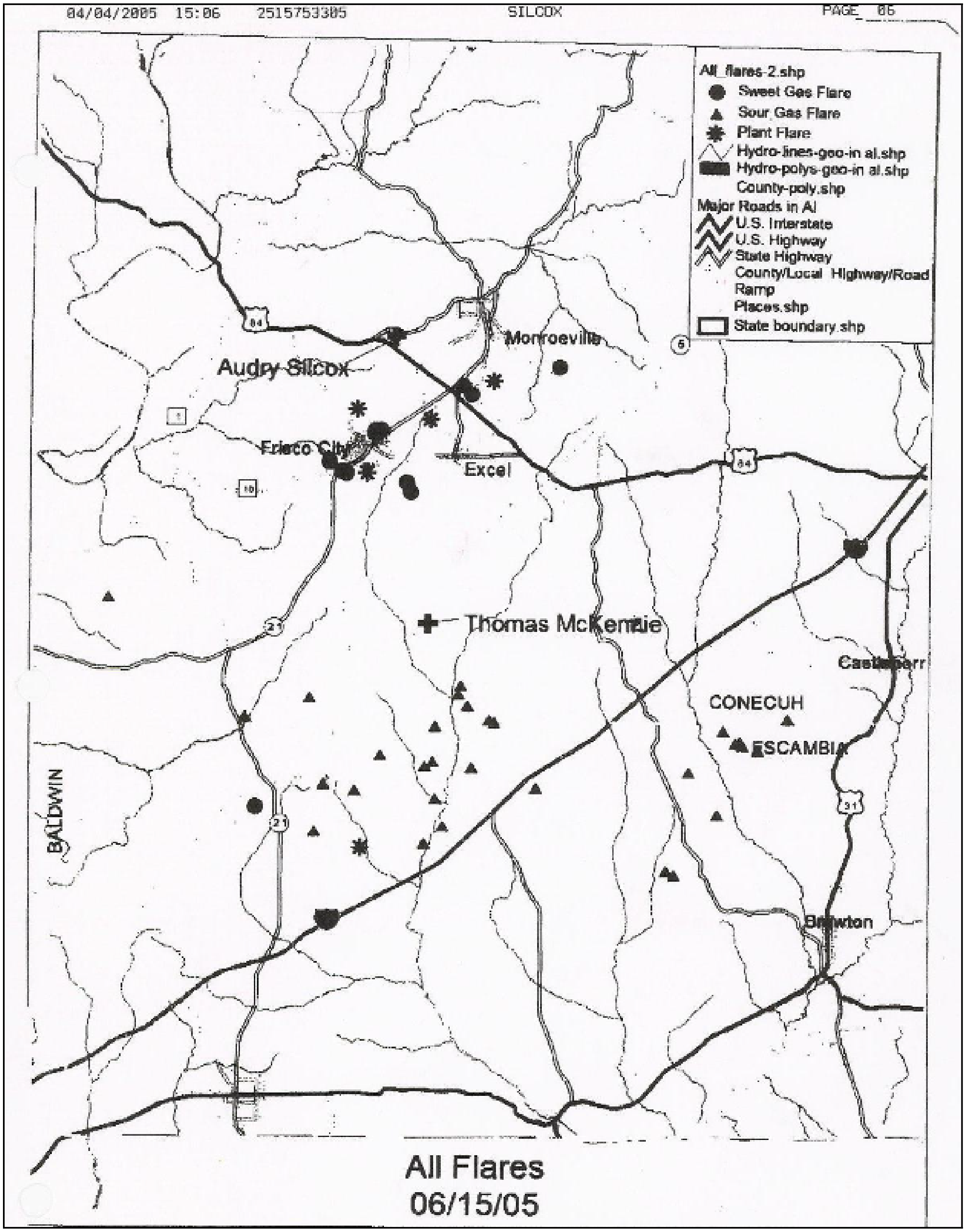

Figure 1. Sweet and sour gas flares from oil and gas wells and gas plants in Escambia, Conecuh and Monroe Counties in Alabama.

Figure 1 shows there are many flares that are operating in the region (Conecuh, Escambia, Monroe counties).

In addition to VOC emissions, these flares may be emitting other hazardous air pollutants such as polycyclic aromatic hydrocarbons (e.g., Chrysene and Benz(a)Anthracene, which are recognized carcinogens),[90] as well as others such as Acenaphthene, Acenaphthylene, Anthracene, Pyrene, which have known health effects).[91] If the gas being flared is "sour," incomplete combustion can lead to the emission of hydrogen sulfide, as well sulfur dioxide, water and other sulfur compounds.

It is possible that collectively, the routine emissions from these flares may be emitting high enough levels of air pollutants to be contributing or causing health problems in the region.

It is also possible, however, that these flares undergo "upset" situations, where large amounts of gas are vented without being burned. Upset emissions are non-routine events, such as equipment breakdowns, startup, shutdown and maintenance, at industrial facilities. As the result of upsets, pollution is often routed to a flare or vented directly to the air and normal pollution controls are bypassed.[92]

According to the Environmental Integrity Project (EIP), "Upsets are a significant source of air pollution. In some cases, releases from upsets actually dwarf a facility's routine emissions."[93]

EIP obtained upset reports for 57 facilities (18 refineries, 6 natural gas plants, 32 chemical plants, and a carbon black plant) in five states (Alabama was not included). Four of the six natural gas plants' 2003 upset emissions of VOCs were greater than the total VOC emissions that each plant reported to the state in 2002.

The EIP report found that even though it is illegal under the *Clean Air Act* to emit more pollution than is allowable under a permit or rule, "approximately half of the states have created loopholes that allow pollution resulting from upsets to exceed those limits."[94]

Alabama has created such a loophole. An Alabama rule expressly exempts companies from complying with pollution permit limits during upsets. It states: "The Director may, in the Air Permit, exempt on a case by case basis any exceedances [sic] of emission limits

[90] State of California. Environmental Protection Agency. *Proposition 65. Chemical Listed Effective August 11, 2006 as Known to the State of California to Cause Cancer or Reproductive Toxicity.* http://www.oehha.ca.gov/prop65/prop65_list/files/P65single081106.pdf
[91] Strosher, M. Alberta Research Council. 1996. *Investigations of Flare Gas Emissions in Alberta*. Report prepared for Environment Canada, the Alberta Energy and Utilities Board and the Canadian Association of Petroleum Producers. 157 pp.
[92] Environmental Integrity Project. 2004. *Gaming the system: How off-the-books, industrial emissions cheat the public out of clean air*. p. 1 http://www.environmentalintegrity.org/pub240.cfm
[93] Environmental Integrity Project. 2004. *Gaming the system: How off-the-books, industrial emissions cheat the public out of clean air*. p. 1
[94] Environmental Integrity Project. 2004. *Gaming the system: How off-the-books, industrial emissions cheat the public out of clean air*. p. 1

which cannot reasonably be avoided, such as during periods of start-up, shut-down or load change."[95]

5.3 Are the data representative?

There were several constraints on the ability to obtain representative samples of the H_2S and VOC concentrations in air. First, the monitoring occurred during one five-day period in August. This period is but a snapshot in time. There were no other data with which to compare our readings, so it is not possible to know for sure if the concentrations were "average," worse or better than the typical air quality in the three counties. The measured values were simply the concentration of H_2S and VOC in the air at the exact time and location measurements were taken.

One way to estimate the amount of pollutants in air is to look at air emission data from various emission sources. The Alabama Oil and Gas Board requires companies to report the amount of gas vented to the atmosphere from its gas processing plants. Figure 2 shows that emissions of raw gas vented to the atmosphere (which would be a source of VOCs and possibly H_2S) were lower in August, 2005 than most other months of the year. In other words, it is quite possible that the concentrations of VOCs and H_2S that we were measuring near the gas processing plants were actually lower than average.

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[95] Alabama Department of Environmental Management. *ADEM Admin. Code R. 335-.3.14-.03(1)(h).* **Cited in**: Environmental Integrity Project. 2004. *Gaming the system: How off-the-books, industrial emissions cheat the public out of clean air.* p. 14.

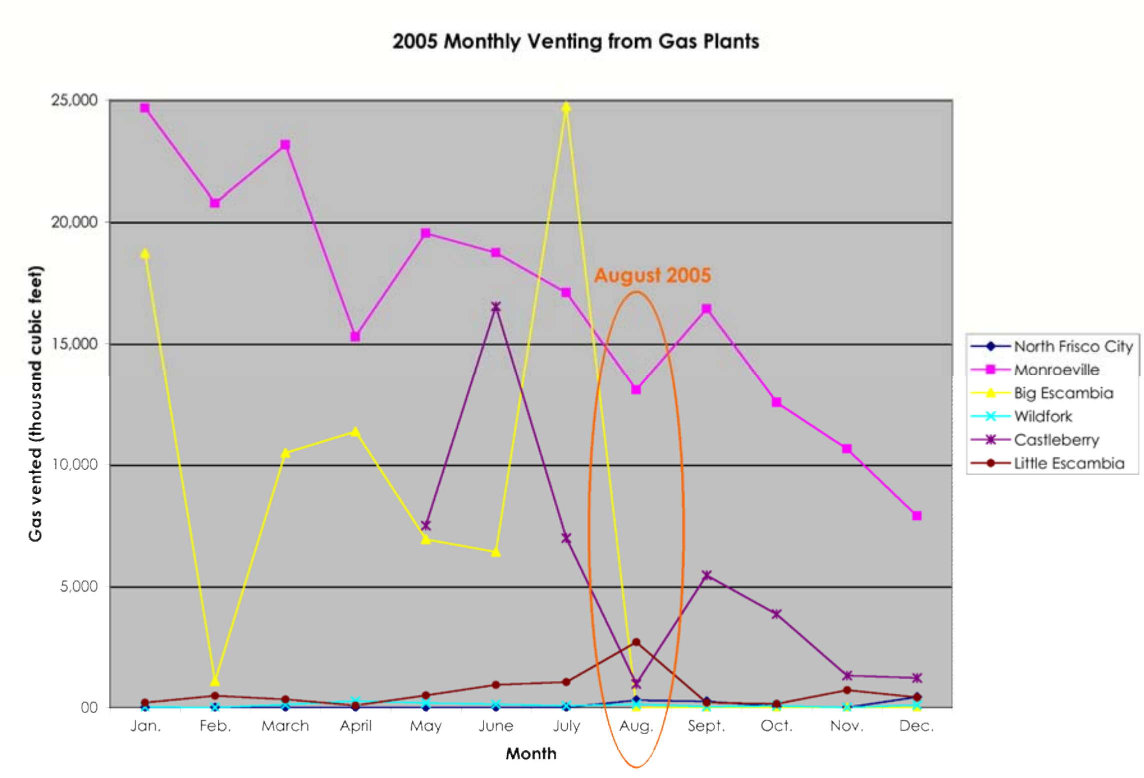

Figure 2. Monthly emissions from natural gas plants in Monroe, Conecuh and Escambia Counties.[96]

6.0 Conclusions and Recommendations

Hydrogen Sulfide

Hydrogen sulfide levels sampled in residential areas of Monroe County, averaging from approximately 100 ppb to 2000 ppb (i.e., 2 ppm), are significantly elevated compared to normal urban background levels, which are typically less than 1 ppb. Studies conducted in other oil and gas producing regions in the U.S. have found comparable levels of H_2S (100 – 15,000 ppb range) in the vicinity of wells and facilities.

It is not known whether or not concentrations in the 100 – 2000 ppb range are experienced for extended periods of time in Conecuh, Monroe or Escambia counties, since our study was conducted over only a few days.

According to health literature, concentrations in the parts-per-billion range produce a nuisance due to odors. These odors, in turn, may lead to headaches, nausea and sleep disturbances if exposure is constant. One study discussed in the Literature Review Section, above (i.e., Legator *et al*., 2001) found central nervous system, respiratory

[96] Data from Alabama Oil and Gas Board on-line database http://www.ogb.state.al.us/ogb/plant_production.aspx

system, and ear, nose and throat symptoms associated with annual average hydrogen sulfide levels ranging from 7 to 27 ppb.

Considering that there is the potential for long-term health effects from exposure to H_2S, (e.g., see references to Kilburn's and Legator's research in the Literature Review section) a better characterization of H_2S exposure levels in this region of Alabama is imperative.

Long-term monitoring sites should be set up in both residential areas, as well as near oil and gas facilities in the region.

Strosher et al. (1996) measured concentrations of hydrocarbon compounds emitted from sweet and sour gas flares in Alberta. They were then able to predict ground-level concentrations of HAPs at various locations around the well location. Predicted values of some polycyclic aromatic hydrocarbons in the vicinity of sweet and sour gas flares were comparable to concentrations found in large industrial cities, while predicted values of hazardous VOCs released during flaring were below ambient air quality standards.[i]

Volatile Organic Compounds

Based on our findings of VOC levels in the parts per million range, it is strongly advised that attempts be made by the agencies to identify and monitor the concentrations of VOCs present in the air in Monroe, Escambia and Conecuh counties. Not only may individual VOCs, such as benzene, be contributing to health problems in the area, the total emission of VOCs may also be contributing to the formation of low-level ozone (smog), which is itself is a health hazard.

It is recommended, as well, that VOC identification and monitoring occur not only in residential areas, but also in the vicinity of oil and gas operations. This will help to hone in on operations that may be emitting large quantities of VOCs due to fugitive emissions; venting from dehydration units; or VOC emissions due to inefficient burning of waste gas during flaring operations.

APPENDIX 1

Letter from Alabama Department of Environmental Management to Audrey Silcox. June 20, 2005.

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ADEM

ALABAMA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

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Laboratory: 277-6718
Mining: 394-4326

June 20, 2005

Mrs. Audrey Silcox
P. O. Box 1360
Monroeville, Al 36461

Dear Mrs. Silcox:

At your recent meeting with Mr. Trey Glenn, ADEM agreed to consider installing a hydrogen sulfide (H_2S) monitor near you. ADEM's Air Division has investigated the feasibility of establishing a continuous H_2S monitoring site in your area. At the present, the Department does not have the equipment needed for this task. The price for a continuous H_2S monitor ranges from $15,000 to $40,000. With the addition of operational and related equipment (data logger, computer, meteorological equipment, utility building, chain link fence, electrical power) expenses, the cost for initial startup for a project of this type could exceed $70,000. The facility would require additional personnel resources to establish and maintain the site. Weekly visits to the site by personnel from the Montgomery office would be required to download data (H_2S, meteorological) and to maintain the site.

Given the above, ADEM does not have the resources to purchase and operate an H_2S monitor in your area.

Please find enclosed three maps showing locations of natural gas facilities in your area.

Sincerely,

Timothy S. Owen, Chief
Energy Branch
Air Division

TSO/jpk

Birmingham Branch
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Birmingham, Alabama 35209-4702
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(251) 432-6598 [Fax]

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APPENDIX 2

State Ambient Hydrogen Sulfide Standards

State	Standard	Duration	Justification	Source
Arizona	0.128 ppm 128 ppb	1 hr	AAAQG, health based, on OSHA guidelines	Arizona Ambient Air Quality Guidelines. http://www.azdeq.gov/environ/air/permits/download/ambient.pdf
	0.078ppm 78 ppb	24 hr		
California	8 ppb	Chronic Exposure	Odor/nuisance	California Office of Environmental Health Hazard Assessment http://www.oehha.ca.gov/air/chronic_rels/pdf/7783064.pdf
	0.03 ppm 30 ppb	1 hr		California Air Resources Board, Nov 2005: http://www.arb.ca.gov/aqs/aaqs2.pdf
Delaware	0.06 ppm 60 ppb	avg. concentration not to be exceeded taken over any consecutive 3 min.		Delaware Ambient Air Quality Standards, http://www.dnrec.state.de.us/air/aqm_page/docs/pdf/reg_3.pdf
	0.03 ppm 30 ppb	avg. concentration not to be exceeded taken over any consecutive 60 min.		
Hawaii	25 ppb	1 hr	Combination of health and nuisance	Hawaii State Ambient Air Quality Standards, http://www.hawaii.gov/health/environmental/air/chart.pdf
Iowa	30 ppb	1-hr daily maximum	"health effects standard"	Iowa Administrative Bulletin. Aug. 18, 2004. http://www.legis.state.ia.us/Rules/2004/Bulletin/IAB040818.pdf
Kentucky	10 ppb	1 hour	Public health and welfare	401 KAR 53:010. Ambient air quality standards http://www.lrc.state.ky.us/kar/401/053/010.htm
Louisiana	330 ppb	8-hr average	NIOSH/OSHA safety standard, took 1/42 of their level	Personal Communication, Lana Skrtic, OGAP, and Jim Hazlett, Air Quality Assessment, Louisiana Department of Environmental Quality
Massachusetts	0.65 ppb	24-hr and annual limit	Based on EPA RfC, Threshold Effects Limit and Allowable Ambient Limit	Massachusetts Rule 310: Ambient Air Exposure Limits for Chemicals http://www.mass.gov/dep/air/aallist.pdf
Minnesota	0.05 ppm 50 ppb	1/2 hr avg. not to be exceeded over 2 times/yr		Minnesota Pollution Control Agency, State Ambient Air Quality Standards, Chapter 7009.0080 http://www.revisor.leg.state.mn.us/arule/7009/0080.html
	0.03 ppm 30 ppb	1/2 hr avg. not to be exceeded over 2 times in any 5 consecutive days		
Missouri	0.05 ppm 50 ppb	1/2 hr avg. not to be exceeded over 2 times/yr		Missouri Ambient Air Quality Standards CSR 10-6.010, http://www.sos.mo.gov/adrules/csr/current/10csr/10c10-6a.pdf
	0.03 ppm 30 ppb	1/2 hr avg. not to be exceeded over 2 times in any 5 consecutive days		
Montana	0.05 ppm 50 ppb	hourly avg. not to be exceeded more than once/yr	health based	Montana Rule 17-8-214 deq.mt.gov/dir/legal/Chapters/CH08-02.pdf
Nevada	0.08 ppm 80 ppb	1-hr average	health based	Nevada Chapter 445B – Air Controls, section 22097, http://www.leg.state.nv.us/NAC/NAC-445B.html#NAC445BSec22097
New Mexico	0.010 ppm 10 ppb	1-hr avg. not to be exceeded more than once/year		New Mexico Ambient Air Quality Standards, Title 20, Chapter 2, Part 3 http://www.nmenv.state.nm.us/aqb/regs/20_2_03nmac_103102.pdf
	0.100 ppm 100 ppb	1/2 hour average	for the Pecos-Permian Basin Intrastate Air Quality Control Region	
	0.030 ppm 30 ppb	1/2 hour average	within five miles of municipalities in Pecos-Permian Basin with > 20,000 people	

State	Standard	Duration	Justification	Source
New York	0.01 ppm 10 ppb	1-hr average	odor and aesthetic	New York Rules and Regulations, Chapter III, Subpart 257-10; http://www.dec.state.ny.us/website/regs/subpart257_10.html
State	**Standard**	**Duration**	**Justification**	**Source**
North Dakota	10 ppm 10,000 ppb	ceiling, maximum instantaneous concentration not to be exceeded	health based	North Dakota Ambient Air Quality Standards, Chapter 33-15-2 http://www.legis.nd.gov/information/acdata/html/..%5Cpdf%5C33-15-02.pdf
	0.20 ppm 200 ppb	maximum 1-hr average concentration not to be exceeded more than once per month		
	0.10 ppm 100 ppb	maximum 24-hr average concentration not to be exceeded more than once per year		
	0.02 ppm 20 ppb	maximum arithmetic mean concentration averaged over three consecutive months		
Oklahoma	200 ppb	24-hr average concentration		Oklahoma Air Pollution Control Rules, Title 252, Chapter 100-31-7 http://www.deq.state.ok.us/rules/100.pdf
Oregon	0.3 ppb*	annual average concentration	based on EPA's RfC, proposed benchmark	Personal Communication, Bruce Hope, Senior Environmental Toxicologist, Oregon Department of Environmental Quality, Air Quality Division. Feb. 10, 2006.
Pennsylvania	0.005 ppm 5 ppb	24-hr average		Pennsylvania Article III, Chapter 131, http://www.pacode.com/secure/data/025/chapter131/025_0131.pdf
	0.1 ppm 100 ppb	1-hr average		
Texas	0.08 ppm 80 ppb	30-min average	if the downwind concentration of hydrogen sulfide affects a property used for residential, business, or commercial purposes	Texas Administrative Code, Title 30 Part 1, Chapter 112, subchapter B; info.sos.state.tx.us/pls/pub/readtac$ext.ViewTAC?tac_view=5&ti=30&pt=1&ch=112&sch=B&rl=Y
	0.12 ppm 120 ppb	30-min average	if the downwind concentration of hydrogen sulfide affects only property used for other than residential, recreational, business, or commercial purposes, such as industrial property and vacant tracts and range lands not normally occupied by people.	
Vermont	0.024 ppm 24 ppb	24-hr	health based	Current standard is equivalent to 33.3 μg/m³. Proposing 1 μg /m³ annual average, to be determined in April; current standard available at http://www.anr.state.vt.us/air/docs/apcregs.pdf
Wyoming	0.05 ppm 50 ppb	1/2 hour average not to be exceeded more than 2 times per year		Wyoming Department of Environmental Quality, Air Quality Division, Ambient Air Quality Standards, Chapter 2: deq.state.wy.us/aqd/stnd/Chapter2_2-3-05FINAL_CLEAN.pdf
	0.03 ppm 30 ppb	1/2 hour average not to be exceeded more than 2 times in any 5 consecutive days		

* Proposed, to be reviewed April 2, 2006