Air

Report to Congress on Hydrogen Sulfide Air Emissions Associated with the Extraction of Oil and Natural Gas

&EPA

Office of Air Quality

Clean   Air

OAQPS

Planning and Standards
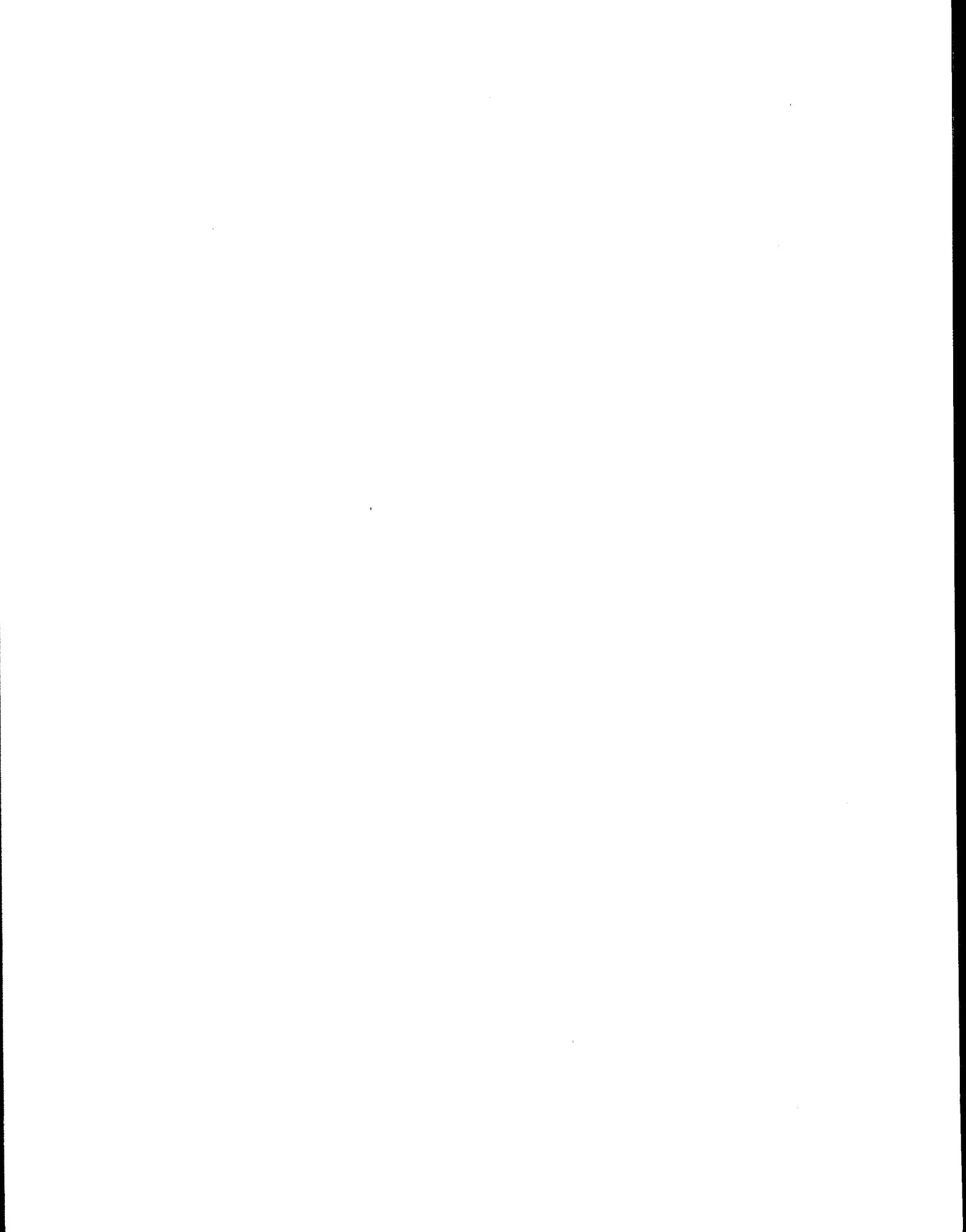
HYDROGEN SULFIDE REPORT TO CONGRESS -- EXECUTIVE SUMMARY

Under section 112(n)(5) of the Clean Air Act (CAA), as amended, Congress required the Administrator of the United States Environmental Protection Agency (EPA) to carry out a study to assess the hazards to public health and the environment resulting from the emission of hydrogen sulfide (H_2S) associated with the extraction of oil and natural gas. The assessment must include a review of existing State and industry control standards, techniques, and enforcement. This report, developed in fulfillment of section 112 (n)(5), evaluates the hazards to the public and the environment posed by these emissions.

This study was added to the CAA by the Committee on Environment and Public Works, chaired by the late Senator Quentin N. Burdick of North Dakota, because of concern about the health and environmental hazards associated with H_2S emissions from oil and gas wells. Witnesses testified before Congress that these emissions resulted in deterioration of air quality, death and injury to livestock, and evacuation and hospitalization of residents located near the release point of such emissions.

Congress considered listing H_2S as a hazardous air pollutant (HAP) under section 112(b) of the CAA, which regulates industrial sources of routine emissions of HAPs. On the basis of information contained in accident records, it was determined that H_2S is a concern from an accidental release standpoint and it would be listed under the accidental release provisions in section 112(r) of the Act, and not under section 112(b). Substances regulated under 112(r) are known or may be anticipated to cause death, injury, or serious adverse effects to human health or the environment upon accidental release.

Hydrogen sulfide is produced in nature primarily through the decomposition of organic material by bacteria. It develops in stagnant water that is low in oxygen content, such as bogs, swamps, and polluted water. The gas also occurs as a natural constituent of natural gas, petroleum, sulfur deposits, volcanic gases, and sulfur springs. Natural sources constitute approximately 90 percent of the atmospheric burden of H_2S. Ambient air concentrations of H_2S due to natural sources are estimated to be between 0.11 and 0.33 ppb (0.15 and 0.46 $\mu g/m^3$).

H_2S is a colorless gas with an offensive odor characteristic of rotten eggs. H_2S is flammable and highly corrosive to metals. It is toxic and care should be exercised in its presence. There have been several incidences in the United States of deaths of workers exposed to H_2S gases. Other symptoms of exposure include irritation, breathing disorders, nausea, vomiting, diarrhea, giddiness, headaches, dizziness, confusion, rapid heart rate, sweating, weakness, and profuse salivation. Levels above 1.5×10^5 ppb are considered life threatening. Few studies exist measuring effects of natural or accidental exposure of wildlife to H_2S; however, wildlife deaths have been reported in connection with blowouts (a sudden expulsion of gas or oil well fluids with great velocity).

Natural gas and oil formations may be composed of many gases. The largest volume and most beneficial gases in this composition are generally the light hydrocarbons (methane, ethane, propane, and butane). H_2S is the most common impurity in hydrocarbon gases. If an oil and gas formation contains H_2S, it is said to be "sour." Although a sour well's oil and gas can be sweetened by removing the H_2S after extraction, the well is always considered sour once H_2S is present.

Certain areas of the United States are especially prone to contain H_2S in oil and gas reservoirs at varying depths underground. Vulnerability zones have been characterized as 14 major H_2S prone areas found in 20 States. Texas has four discrete H_2S prone areas. Concentrations as high as 42 percent H_2S (by volume) have been found in gas from central Wyoming.

In the oil and gas industry, H_2S may be emitted or released during exploration, development, extraction, crude treatment and storage, transportation (e.g., pipeline), and refining. This report focuses on potential hazards of routine emissions and accidental releases of H_2S from the extraction and storage of crude oil and natural gas at well sites. Potential sources of emissions include flares/vapor incinerators, heater-treaters (an oil/water/gas separation device), storage tanks, equipment (valves, flanges, etc.), and both active and abandoned wells.

When H_2S is released to the air from an oil or gas well, several factors determine its possible effects on surrounding residents and the environment. Accidental releases of sour gas, such as from a well blowout or pipe rupture, are usually at high pressure and will entrain surrounding air. This causes significant, immediate dilution of the H_2S and other components of the gas, thereby reducing the potential magnitude of the consequences of the release. Factors such as chemical composition of the expelled gas, release rate, release orientation, topography and meteorological conditions also determine the effects of such a release.

Human fatalities from H_2S exposure from oil wells in the United States have virtually all been work-related. Significant public impacts are rare although evacuations have been initiated in response to accidental releases and at least one case of loss of consciousness has been reported as a result of exposure.

Eighteen states have developed ambient air quality guidelines for H_2S. Most, however, do not collect continuous data but rather only monitor for H_2S when a complaint is made. These guidelines range from 160 ppb per 24-hr averaging time to 14 ppb per 24-hr averaging time. Little data exist to determine actual levels of H_2S near oil and gas extraction sites. North Dakota was the only State found to have a continuous record of H_2S atmospheric levels at several sites. Exceedences of the North Dakota air quality standard have been minimal in recent years at these monitoring locations. No specific H_2S environmental (i.e., ecological) protection standards were found to exist. Some States require notification of the regulatory authority upon accidental release of H_2S from oil and

gas wells but few maintain an inventory of such incidences. Reporting of routine emissions (emissions of small quantities from equipment, pipelines, flares, and storage tanks) was not required by the States reviewed in this report.

H_2S is regulated under a number of United States statutes. It is listed as a hazardous substance under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). It is listed under the Emergency Planning and Community Right-to-Know Act (EPCRA) for emergency planning and preparedness, community right-to-know reporting, and toxic chemical release reporting. The Occupational Safety and Health Administration (OSHA) has established General Industry Standards that list worker exposure concentration limits, and Respirator Standards. The National Institute for Occupational Safety and Health (NIOSH) has produced a criteria document containing recommendations for safe worker exposure levels and work practices. The United States EPA has the potential for regulation of new oil and gas well sources through the Prevention of Significant Deterioration (PSD) program and, as mentioned previously, H_2S is listed under the CAA section 112(r) accidental release provisions.

Other standards for worker and public protection from H_2S emissions come from the Bureau of Land Management, Minerals Management Service, and the American Conference of Governmental Industrial Hygienists.

The oil and gas production industry has guidelines for safe practices regarding H_2S. The American Petroleum Institute, an industry-wide technical organization, has published six documents regarding H_2S in the industry. They pertain to safety practices for drilling, operation, and equipment.

Findings and Recommendations

As a result of this study, EPA finds that the potential for human and environmental exposures from routine emissions of H_2S from oil and gas wells exists, but insufficient evidence exists to suggest that these exposures present any significant threat. On the other hand, an accidental release of H_2S from an oil or gas well could have severe consequences because of its toxicity and its potential to travel significant distances downwind under certain circumstances. The likelihood (and thus the risk) of an accidental release of H_2S or any other hazardous substance, can be greatly reduced if facility owners/operators exercise the general duty and responsibility to design and operate safe facilities and if they comply with existing industry standards and practices, existing regulations, and future guidance and regulations. Such actions should result in: (1) the safe management of H_2S and other hazardous substances with an emphasis on accident prevention; (2) the preparedness to properly and quickly respond to chemical emergencies and to provide specialized medical treatment if necessary; and (3) community understanding of the risks involved. Industry should ensure that H_2S is safely handled and that accidental releases are prevented; that any releases that do occur are quickly discovered, controlled, and mitigated; and that workers and the community are informed and prepared to properly respond to a H_2S emergency.

From the limited data available, there appears to be no evidence that a significant threat to public health or the environment exists from routine emissions from sour oil and gas wells. States and industry are encouraged to evaluate existing design, construction, and operation principles within the framework of process safety management. EPA recommends no further legislation pertaining to routine H_2S emissions or accidental releases from oil and gas wells at this time. However, the Agency does recommend that the owner/operators of oil and gas extraction conduct drills and exercises with workers, the community, first responders, and others to test mitigation, response, and medical treatment for a simulated H_2S accident. Sour oil and gas extraction facilities should be able to rapidly detect, mitigate, and respond to accidental releases in order to minimize the consequences. The Agency will continue to investigate the need for additional rulemaking under the accidental release prevention provisions of the Clean Air Act.

Table of Contents

Table of Contents (continued)

Table of Contents (continued)

Table of Contents (continued)

Figures

Figures (continued)

Tables

CHAPTER I
INTRODUCTION

STATUTORY REQUIREMENTS

Section 112(n)(5) of the Clean Air Act (CAA or Act), as amended in 1990, requires the Environmental Protection Agency (EPA) "to assess the hazards to the public and the environment resulting from the emissions of hydrogen sulfide (H_2S) associated with the extraction of oil and natural gas resources." This assessment must reflect consultation with the States and shall include a review of State and industry control standards, techniques, and enforcement. To avoid duplication of work by other EPA offices, the assessment must build upon a report from the Office of Solid Waste conducted under Section 8002(m) of the Solid Waste Disposal Act. The Section 8002(m) study is a three-volume report to Congress entitled *Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy* (1987).

The EPA Administrator is required by the Act to report to Congress with the findings of the assessment along with any recommendations. Moreover, under Section 112(n)(5) (or 42 U.S.C.7412(n)5), the Administrator "shall, as appropriate, develop and implement a control strategy for emissions of hydrogen sulfide to protect human health and the environment."

This study was added to the Act by the Committee on Environment and Public Works chaired by the late Senator Quentin N. Burdick of North Dakota. The study was included in the Act because of concern about the health and environmental hazards associated with H_2S emissions from oil and gas wells. In 1987, Congress received testimony in which witnesses urged that H_2S should be listed as a hazardous air pollutant under the provisions of Section 112 of the Clean Air Act. The witnesses testified that lack of emission controls resulted in significant deterioration of air quality. There was also testimony that H_2S releases from oil and gas facilities caused death and injury to livestock and required the evacuation and hospitalization of residents from affected areas.

Congress considered listing H_2S as a hazardous air pollutant (HAP) under Section 112(b), which regulates industrial sources for routine emissions of HAPs. On the basis of information contained in accident records, it was determined that H_2S is a concern from an accidental release standpoint and should be listed under the accidental release provisions in Section 112(r) of the Act. The substances regulated under Section 112(r) are known or may be anticipated to cause death, injury, or serious adverse effects to human health or the environment from accidental releases. Under the provisions of Section 112(r) of the Act, the EPA must develop a list of at least 100 substances that pose the greatest risk from accidental releases. The Act listed 16 chemicals, including H_2S, which must be included in the Section 112(r) list.

A clerical error led to the inadvertent addition of H_2S to the Section 112(b) list of HAPs. However, a Joint Resolution to remove H_2S from the Section 112(b) list was passed by the Senate on August 1, 1991, and the House of Representatives on November 25, 1991. The Joint Resolution was approved by the President on December 4, 1991. It should be emphasized that the purpose of this report is not to examine whether or not H_2S should be included in the Section 112(b) list.

SCOPE OF REPORT

The scope of this report is determined by the Congressional directive found in Section 112(n)(5), which is quoted in its entirety in Exhibit 1. For clarity, the Agency has designed the report to respond to specific items in the directive within separate chapters or sections of chapters. It is important to note that although all issues relevant to this study have been weighed in arriving at the conclusions and recommendations of this report, no single issue has a determining influence on the conclusions and recommendations.

The directive in Section 112(n)(5) is expanded upon in the paragraphs below. Detailed methodologies used to analyze and respond to the directive can be found later in this report and in the supporting documentation and appendices. The principal components of the Congressional mandate are:

1. **Review existing State and industry control standards, techniques, and enforcement programs.**

Currently, there are no Federal ambient air quality standards for H_2S. Most oil- and gas-producing States have their own regulations and enforcement programs. Some States, such as some hosting major producers, have large H_2S programs in place. However, the risk may exist in States that do not have large programs simply because of the lack of State regulatory overview. Although Occupational Safety and Health Administration (OSHA) standards exist that are applicable to oil and gas production, there are no industry-specific standards. However, the industry has developed recommended practices and technologies to reduce the potential for H_2S emissions.

Current State regulations regarding H_2S emissions from the extraction of oil and gas are summarized in this report, with emphasis on four oil-producing States—California, Michigan, Oklahoma, and Texas. Industry safety procedures as well as regulations promulgated and proposed by OSHA and other Federal regulatory programs are reviewed.

2. **Assess the hazards to public health and the environment resulting from the emission of H_2S associated with extraction of oil and natural gas resources.**

Hydrogen sulfide is a colorless gas almost as toxic as hydrogen cyanide and 5 to 6 times more toxic than carbon monoxide. The principal threat of H_2S gas to human life is poisoning by inhalation (Dosch and Hodgson, 1986). Over the years, there have been

112(n)(5) **Hydrogen Sulfide.**– The Administrator is directed to assess the hazards to public health and the environment resulting from the emission of hydrogen sulfide associated with the extraction of oil and natural gas resources. To the extent practicable, the assessment shall build upon and not duplicate work conducted for an assessment pursuant to section 8002(m) of the Solid Waste Disposal Act and shall reflect consultation with the States. The assessment shall include a review of existing State and industry control standards, techniques, and enforcement. The Administrator shall report to the Congress within 24 months after the date of enactment of the Clean Air Act Amendments of 1990 with the findings of such assessment, together with any recommendations, and shall, as appropriate, develop and implement a control strategy for emissions of hydrogen sulfide to protect human health and the environment, based on the findings of such assessment, using authorities under this Act including sections 111 and this section.

Exhibit 1. **1990 Clean Air Act Amendments: Mandate for a Report to Congress on H_2S Emissions Associated with Oil and Gas Extraction.**

incidents involving exposure to H_2S resulting from accidental releases from oil and gas extraction facilities that have caused death or injury to humans or animals (Layton, D.W., et al; Texas Oil and Gas Pipeline Corporation).

Oil and gas extraction, as defined in this study (see Appendix A), includes only the activities involved in removing oil and/or gas from an established (developed) well. This report includes not only a review of oil and gas extraction, but also other associated components of oil and gas extraction such as piping to a separator, separation, and storage. However, in following the Congressional mandate to address extraction, this report does not cover activities primarily associated with exploration or well development, nor does it cover sources such as gas processing plants. It is noteworthy that these plants are potential sources of H_2S releases since one of their functions is to remove impurities such as produced water, H_2S and/or carbon dioxide. Personnel at these plants are trained in H_2S safety. However, this operation falls outside the definition of extraction.

In addition to assessing the sources of H_2S emissions in the extraction industry, this report discusses related control technologies as well as the health and environmental effects associated with exposure to accidental H_2S releases and routine H_2S emissions during extraction and closely associated production activities. When possible, monitored ambient air concentrations of H_2S and cases of death or injury to humans, wildlife, and/or livestock from exposure to H_2S releases and emissions are documented.

The report culminates with a hazard assessment of H_2S routine emissions and accidental releases from oil and gas extraction activities based on information obtained in the efforts described in the previous paragraphs. Past and potential hazards from both routine emissions and accidental releases are identified, the degree of hazard is assessed, and potentially exposed human and ecological populations are identified.

3.   Recommend and, as appropriate, develop and implement a control strategy for H_2S emissions to protect human health and the environment, based on the findings of such assessment, using authorities under this act including sections 111 and 112.

As stated in a 1987 Senate report on the Clean Air Act Amendments, "Although many State [H_2S regulatory] programs are implemented conscientiously, in some instances concerns have been raised that some oil- and gas-producing States may not be enforcing their regulatory programs sufficiently or may have deficient regulatory programs. The purpose of this subsection is to assess the effectiveness and the level of enforcement of various hydrogen sulfide control programs. The assessment should assure more uniform application of control technology, standards and enforcement. The Administrator should examine in particular means of preventing accidental releases of hydrogen sulfide at remote facilities" (U.S. Senate, 1987). [EPA identifies and reviews current State and Federal regulatory programs and industry-recommended procedures to reduce routine emissions and accidental releases. However, the ability to assess the effectiveness of these programs is limited by the lack of

available emissions-monitoring data and the limited information available on accidental release incidents.]

In this report, EPA makes recommendations regarding the release of H_2S from oil and gas extraction activities. The recommendations presented in this report do not constitute a regulatory determination. The Agency is, in several important areas, presenting optional approaches involving further research and consultation with the States and other affected parties.

ORGANIZATION OF REPORT

This report addresses two forms of H_2S losses to the atmosphere: routine emissions and accidental releases. (These terms are defined in the Glossary and examples are provided in Chapter II.)

Chapter II provides an overview of H_2S formation in oil and natural gas deposits and its presence in numerous industries. Potential sources of routine emissions and accidental releases from the oil and natural gas extraction industry are identified along with their causes. Chapter III is a hazard assessment of H_2S losses from oil and gas wells. It contains information on the nature of hydrogen sulfide's hazardous properties; exposure and consequence analyses for routine emissions and accidental releases; protective guidelines, prevention, mitigation, and emergency response procedures; and a characterization of land use around wells and of affected human populations and environmental settings. Chapter IV reviews and evaluates current State, Federal, and industry-recommended procedures related to H_2S in the oil and natural gas extraction industry. At the end of both Chapters III and IV are lists of findings to provide the reader with a condensed summary of key information identified during the development of this report. Chapter V completes the report with EPA recommendations regarding routine emissions and accidental releases of H_2S from oil and gas extraction operations.

This report contains a glossary of terms commonly used, and three appendices providing:

- background information on oil and gas production;
- subjects of State H_2S regulations and guidelines; and
- atmospheric dispersion calculations for accidental H_2S releases.

REFERENCES

Dosch, M.W., and Hodgson, S.F. 1986. *Drilling and Operating Oil, Gas, and Geothermal Wells in an H₂S Environment*, Publication No. M10. California Department of Conservation, Division of Oil and Gas, Sacramento, CA.

Layton, D.W., et al. 1983. *Accidental Releases of Sour Gas From Wells and Collection Pipelines in the Overthrust Belt: Calculating and Assessing Potential Health and Environmental Risks*. Lawrence Livermore National Laboratory Report UCRL-53411, Prepared for the Division of Fluid Mineral Operations, Bureau of Land Management, U.S. Department of the Interior, Washington, DC.

Texas Oil and Gas Pipeline Corporation. 1976. 6-inch Natural Gas-Gathering Pipeline Failure, Meridian, Mississippi, May 21, 1974, PB-250 935, National Transportation Safety Board, Washington D.C. February 4, 1976.

U.S. Senate. 1987. Clean Air Standards Attainment Act of 1987 Report of Committee on The Environment and Public Works. U.S. Senate to accompany S. 1894. Nov. 20, 1987, Report 100-231. U.S. Government Printing Office.

CHAPTER II
HYDROGEN SULFIDE FORMATION AND ITS ROLE IN
OIL AND GAS PRODUCTION

OVERVIEW

Petroleum oil and natural gas originate in organic-rich sedimentary source rocks composed of decayed marine algae and bacteria and terrestrial plants. In rock formations, temperature increases with depth. The organic matter (kerogen) in sedimentary rock is thermally converted to oil and gas at a specific temperature and migrates from the source rock formation into a reservoir, or trap, formed by less porous cap rock, usually shale. Once the well has been drilled into the reservoir, the oil and gas flow through the interconnected pore spaces to the well.

Natural gas may be composed of many gases. Only a few of these gases are typically found in large concentrations. The largest volume and most beneficial gases in natural gas are the light hydrocarbons (methane, ethane, propane and butane). Other gases that may occur in large concentrations are carbon dioxide, nitrogen, and hydrogen sulfide. H_2S is the most common impurity in hydrocarbon gases.

H_2S is generated under reducing conditions from high-sulfur kerogens or oils and is most commonly formed in sedimentary rock formations such as limestone (calcite or calcium carbonate). H_2S can also be generated from hydrocarbon reactions with sulfates in carbonate rock formations containing anhydrites. Oil and gas formations that do not contain H_2S are called "sweet." Oil and gas formations that contain H_2S are described as "sour." Sour gas is defined by the U.S. EPA as natural gas with an H_2S concentration greater than 0.25 grains per 100 cubic feet (GRI, 1990). Others have defined sour gas as having H_2S concentrations greater than 1.0 grain per 100 cubic feet (Amyx, Bass, and Whiting, 1960) or greater than 2 percent (Curtis and Showalter, 1989). The American Petroleum Institute recommends special practices (described in Chapter IV) for sour gas when the natural gas's total pressure is greater than or equal to 65 psia (448 kPa) and the partial pressure of H_2S in the gas is greater than 0.05 psia (0.34 kPa) (API, 1987). It is not known how many sour wells exist in the United States. Sweet oil wells can become sour due to the introduction of sulfur-reducing bacteria during enhanced oil recovery injection. Once an oil or gas field becomes sour, it cannot be made sweet again. However, after extraction from the well, the oil and gas can be sweetened by processing to remove H_2S, and this is a common procedure.

In relatively low concentrations, H_2S has a strong rotten-egg odor (Landes, 1953). However, the sense of smell rapidly becomes fatigued and cannot be relied on to warn of the continuous presence of H_2S. In fact, high concentrations of H_2S may cause a loss of smell. Concentrations of H_2S in crude oil vary greatly. In California alone, the Shiells Canyon oil field measures only 6×10^4 ppb of H_2S, while the Santa Maria Valley oil field has reported H_2S concentrations of 2.7×10^7 ppb (27 percent by weight) (Dosch and Hodgson, 1986).

Table II-1. Physical/Chemical Properties of H$_2$S

Chemical Formula: H$_2$S

Molecular Structure:

H   H
   S
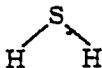
Molecular Weight: 34.08

Boiling Point: -60.33 °C (-76.59 °F)

Specific Gravity (H$_2$O=1): 0.916 at -60 °C (-76 °F) (Liquid) 1.54 g/L vapor at 0 °C (32 °F)

Vapor Pressure: 20 atmospheres at 25.5 °C (77.9 °F)

Melting Point: -85.49 °C (-121.9 °F)

Vapor Density (AIR=1): 1.19

Solubility in Water: 1 gram dissolves in 242 mL at 20 °C (68 °F)

Flammable Limits: Lower Explosive Limit – (4.3 x 10^7 ppb)
                    Upper Explosive Limit – (45.5 x 10^8 ppb)

Odor Threshold: 20 ppb[a]

Olfactory Fatigue Level: 1 x 10^5 ppb[a]

Conditions or Materials to Avoid: Avoid physical damage to containers; sources of ignition; and storage near nitric acid, strong oxidizing materials, and corrosive liquids or gases (NFPA, 1978). Hydrogen sulfide is incompatible with many materials, including strong oxidizers, metals (NIOSH/OSHA, 1978, p. 112), strong nitric acid, bromine pentafluoride, chlorine trifluoride, nitrogen triiodide, nitrogen trichloride, oxygen difluoride, and phenyl diazonium chloride (NFPA, 1978).

Hazardous Decomposition or Byproducts: When heated, it emits highly toxic fumes of oxides of sulfur (Sax, 1984, p. 1552)

Source: U.S. EPA, 1993.
[a]NIOSH, 1977.

Hydrogen sulfide is also called hydrosulfuric acid, sulfurated hydrogen, sulfur hydride, rotten-egg gas, swamp gas, and stink damp. Table II-1 lists some of the chemical and physical properties of H_2S. It is colorless, has a very low odor threshold, and being more dense than air, it tends to settle to the ground when released to the atmosphere as a pure gas (NIOSH, 1977). H_2S oxidizes to form sulfur dioxide (SO_2).

Exposure to H_2S is one potential health and environmental concern associated with extraction and related operations. H_2S is found in Paleozoic carbonates in the Rockies, Mid-Continent, Permian Basin, and Michigan and Illinois Basins (GRI, 1990). Figure II-1 shows the areas of naturally occurring H_2S. The Gas Research Institute reported in 1990 that H_2S can often occur in association with carbon dioxide (CO_2) within the deep portions of a basin and can comprise more than 30 percent of the composition.

Among the natural gas deposits in the United States, large deposits in central and north-central Wyoming, in western Texas, in southeastern New Mexico, and in Arkansas were singled out as rich in H_2S. The Health Effects Research Laboratory (HERL) also reported that H_2S concentrations as high as 42 percent may be present in gas from central Wyoming. According to the *Wyoming State Review* (1991), released by the Interstate Oil and Gas Compact Commission (IOGCC), gas reserves in Wyoming were estimated to be approximately 11 trillion cubic feet. The IOGCC also reported that the reserves of liquid hydrocarbons found in western Wyoming are approximately 5 percent H_2S. Fifty percent of the oil produced in Wyoming in 1989 was reported to be sour.

HYDROGEN SULFIDE IN INDUSTRY

Hydrogen sulfide has been cited as a potential hazard for approximately 125,000 employees in 73 industries (U.S. EPA, 1993). Industries with a potential exposure are listed in Table II-2. The health effects of H_2S were recognized in the petroleum industry more than 50 years ago with the discovery of large deposits of high-sulfur oil in the United States (Davenport, 1945). In the oil and gas industry, H_2S may be emitted or released during exploration, development, extraction, crude treatment and storage, transportation (e.g., pipeline transmission), and refining. This report focuses on potential hazards of H_2S routine emissions and accidental releases from the extraction and storage of crude oil and natural gas.

POTENTIAL H_2S EMISSION SOURCES IN THE OIL AND NATURAL GAS EXTRACTION INDUSTRY

Appendix A provides a general overview of the oil and gas extraction industry. Both the exploration/development and extraction sectors of the industry are described along with production data for recent years.

Hydrogen sulfide (H_2S) complicates oil and gas extraction operations because of its toxic effects and its corrosive properties. H_2S exists as a gas at atmospheric pressure, but it
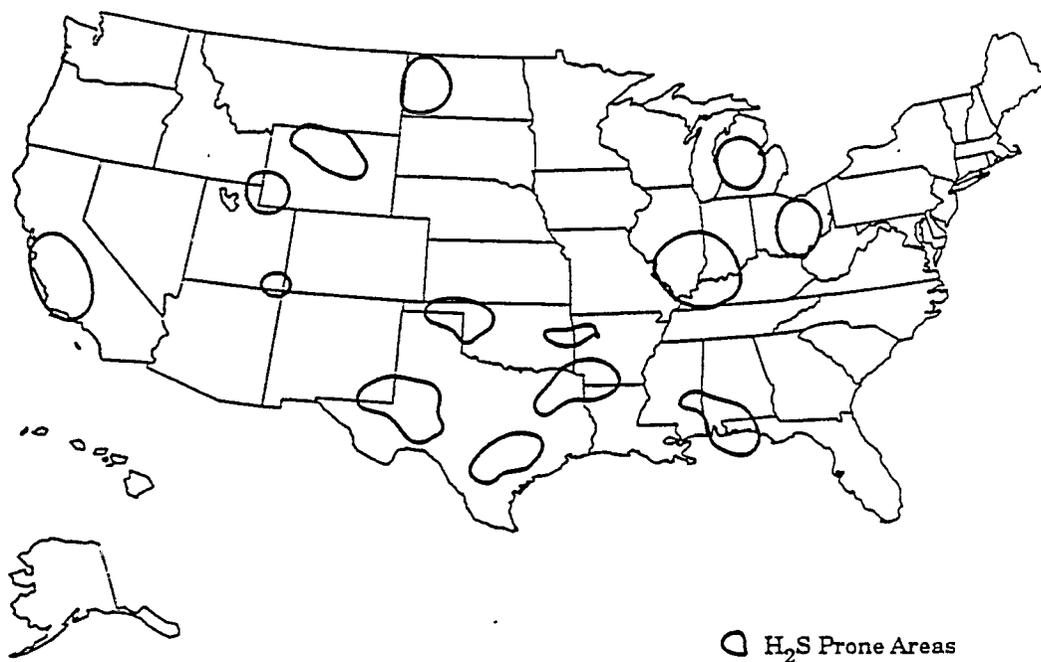
○ H$_2$S Prone Areas

Source: Gas Research Institute. 1990.

Figure II-1. Major H$_2$S prone areas.

Table II-2. Occupations with Potential H₂S Exposure

Animal fat and oil processors
Animal manure removers
Artificial-flavor makers
Asphalt storage workers
Barium carbonate makers
Barium salt makers
Blast furnace workers
Brewery workers
Bromide-brine workers
Cable splicers
Caisson workers
Carbon disulfide makers
Cellophane makers
Chemical laboratory workers, teachers, students
Cistern cleaners
Citrus root fumigators
Coal gasification workers
Coke oven workers
Copper-ore sulfidizers
Depilatory makers
Dyemakers
Excavators
Felt makers
Fermentation process workers
Fertilizer makers
Fishing and fish-processing workers
Fur dressers
Geothermal-power drilling and production workers
Gluemakers
Gold-ore workers
Heavy-metal precipitators
Heavy-water manufacturers
Hydrochloric acid purifiers
Hydrogen sulfide production and sales workers
Landfill workers
Lead ore sulfidizers
Lead removers
Lithographers

Lithopone makers
Livestock farmers
Manhole and trench workers
Metallurgists
Miners
Natural gas production and processing workers
Painters using polysulfide caulking compounds
Papermakers
Petroleum production and refinery workers
Phosphate purifiers
Photoengravers
Pipeline maintenance workers
Pyrite burners
Rayon makers
Refrigerant makers
Rubber and plastics processors
Septic tank cleaners
Sewage treatment plant workers
Sewer workers
Sheepdippers
Silk makers
Slaughterhouse workers
Smelting workers
Soapmakers
Sugar beet and cane processors
Sulfur spa workers
Sulfur products processors
Synthetic-fiber makers
Tank gagers
Tannery workers
Textiles printers
Thiophene makers
Tunnel workers
Well diggers and cleaners
Wool pullers

Source: NIOSH, 1977.

is soluble in oil and water. As a result of this solubility, H_2S can enter the environment by a variety of pathways. It can enter the atmosphere as a result of releases of gas containing H_2S or as a result of venting tanks or vessels which contain or have contained oil or water with significant concentrations of H_2S. Waters in the general environment can become contaminated with H_2S by contact with either gaseous plumes or waters that contain H_2S.

The potential sources of H_2S emissions associated with oil and gas extraction are summarized in Table II-3.

Routine emission sources may include—

- inefficient air emission control devices
- tank venting due to diurnal temperature changes;
- volatilization;
- generation by sulfur-reducing bacteria in oil deposits; and
- migration through poorly plugged wells.

Potential accidental release sources include —

- equipment failures, e.g., valves, flanges;
- piping ruptures due to corrosion, embrittlement, or stress; and
- venting due to unanticipated pressure changes.

Background information on these potential sources is provided in Appendix A.

The crude oil and natural gas industries use a large number of similar yet distinct industrial processes that together serve a common purpose: to remove hydrocarbons from subterranean deposits of oil and gas and to produce marketable products for industrial, commercial, and residential use. Figure II-2 shows the basic components of a typical oil and gas production operation. From the wellhead, the oil/gas mixture is piped to an oil/gas separator. Oil/water emulsions and mixtures are then transferred to a heater-treater, which separates the oil from the water. The treated crude oil is next piped to storage tanks, and the produced water is piped to a holding tank prior to further treatment and/or disposal. An emergency pit (a wastewater basin) is also provided. Each of these operations, as well as other equipment found at a well site, may be a source of H_2S in sour oil and gas operations.

Oil and Gas Production Operations

Crude Oil

In the crude oil production process, releases or emissions of H_2S to the environment may occur from a variety of sources, including wellheads, piping, flares, separation devices, storage vessels, and pumps.

Table II-3. Examples of Potential Routine H_2S Emission Sources and
Accidental H_2S Release Sources from Sour Oil and Gas Extraction

Source	Mechanism	Cause
Flares/vapor incinerators	Incomplete combustion	Design; lack of maintenance
Heater-treaters	Pressure change, high pressure	Pressure above design specifications
Crude oil storage tanks	Diurnal temperature change; filling operations; volatilization	Lack of controls; design
Water storage vessels	Volatilization; sulfur-reducing bacteria	Lack of controls; design
Equipment (valves, flanges, etc.) Oil/gas separator	Corrosion and embrittlement	Reaction of water with metal and H_2S; lack of maintenance; poor materials
Well plugging	Migration from well bore to atmosphere	Improper plugging
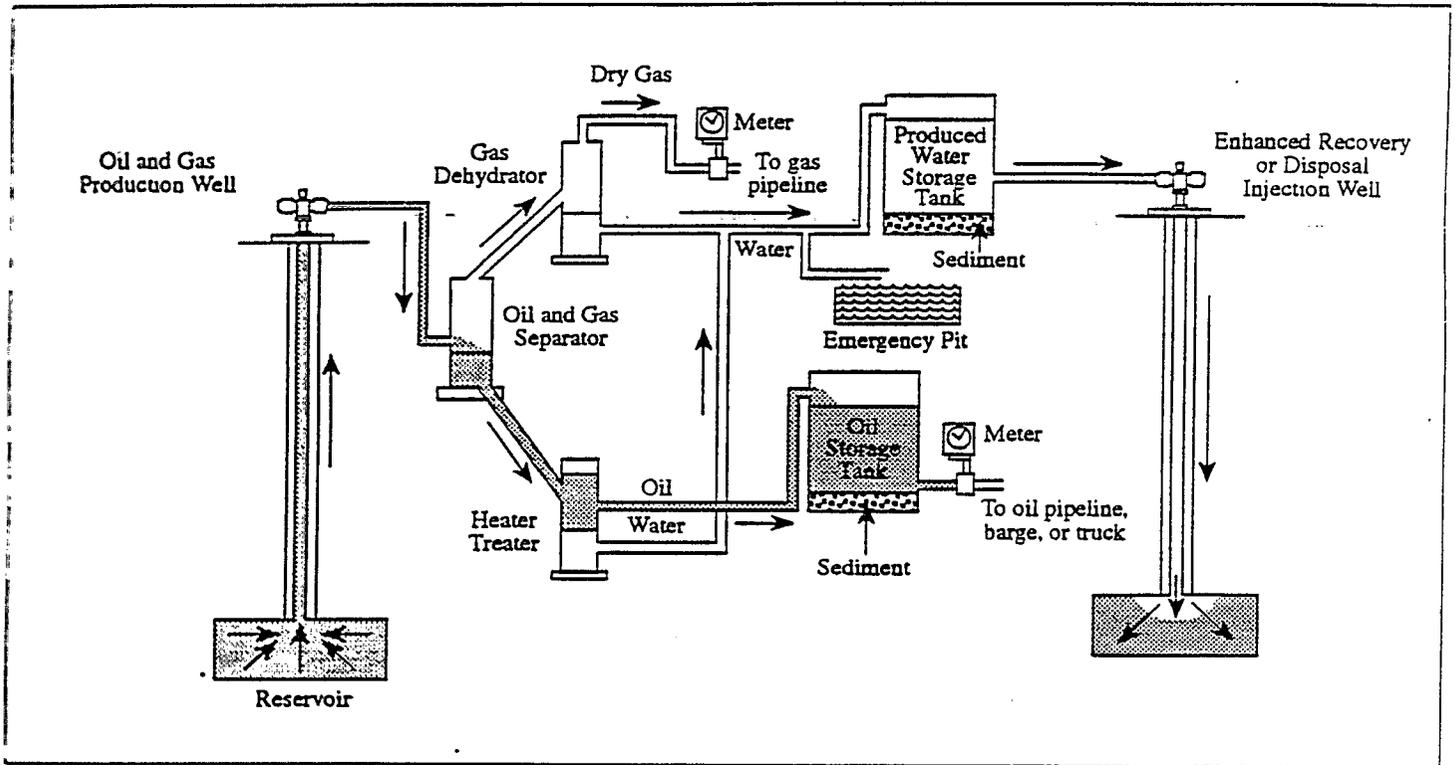
Figure II-2. Typical extraction operation showing separation of oil, gas, and water.

Flares are connected to points in the system where gas might be directed in case of an operating problem. Subject to regulatory approval, flares may also burn gases that cannot be sold. The gases are vented up a tall vertical pipe and then ignited at the top of the pipe, releasing heat and combustion products. Flares are connected to production vessel pressure-relief valves, rupture disks, and tank vents, among other places. Few data are available on the efficiency of flares used in a crude oil production setting; however, the operating efficiency of a common flare, regardless of industry application, is about 95 to 99 percent (personal communication, Donelson, Texaco, 12/9/92). The combustion product of H_2S is sulfur dioxide (SO_2). Incomplete combustion from flares is one possible source of H_2S emissions, and actual pollutant emissions vary depending on the combustion efficiency of the flare.

Devices, such as heater-treaters, break down water/oil emulsions or mixtures. These devices operate under pressure and do not normally emit H_2S. However, H_2S may be released in accidental situations when the vessel becomes subjected to pressures above design specifications. The pressure relief valve or a rupture disk will open in a high-pressure situation, and the gas will be sent through these openings via pipeline to a flare (personal communication, Donelson, Texaco, 12/9/92).

H_2S can potentially be emitted by two processes from vessels used to store water produced during extraction:

- Dissolved H_2S may be contained in the produced water and brought up from the reservoir. Pressure reductions from subsurface to surface change the solubility of H_2S in water and can release some H_2S from solution.
- H_2S may be produced by the action of sulfate-reducing bacteria in some aqueous and oil media. Biocides are used to kill these bacteria and eliminate H_2S formation.

Tanks storing crude oil are another potential source of H_2S emissions. H_2S can be discharged to the atmosphere from a storage tank as a result of diurnal temperature change, filling operations, and volatilization. The process of filling oil-transport vessels is another potential source of H_2S emissions. As the crude oil is loaded, gases containing the pollutant are displaced to the atmosphere. If the gas amounts do not warrant repressuring into the gas sales line, a flare may operate to burn the gas given off (personal communication, Donelson, Texaco, 12/9/92). There have been several accidents involving tanks that have H_2S in them. This is typically a worker safety issue.

Pumps that move the oil during the extraction process can leak oil at the seals between the moving shaft and the stationary casing, causing a possible release of H_2S.

Natural Gas

Two additional items in natural gas extraction can contribute emissions and releases of sulfur compounds into the atmosphere: (1) equipment failure (e.g., leaks and ruptured pipes) due to corrosion or embrittlement, and (2) improperly plugged wells.

Equipment Failure. H_2S can attack the crystalline matrix of the steel, leading to embrittlement and cracking of the steel, which could, in turn, lead to possible leakage of H_2S. This embrittlement is invisible and can occur in a short period of time. Corrosion, which is caused by chemical reactions of metal with water and H_2S, can also cause H_2S leakage. Because of the corrosive nature of H_2S in the presence of water, oil and gas operations take precautions to remove water from gas streams containing H_2S. The National Association of Corrosion Engineers has a "Standard Material Requirement" entitled "MR-0175-92, Sulfide Stress Cracking Resistant Metallic Materials for Oil Field Equipment" which describes corrosion prevention measures. Corrosion resistant materials, coatings, and chemical corrosion inhibitors may be used to prevent equipment failure and gas releases where H_2S and other corrosives are known to be present (personal communication, Donelson, Texaco, 12/9/92). This type of accidental release is discussed in greater detail in Chapter III.

Well Plugging. Improper well plugging may also be a potential source of H_2S emissions. After all of the recoverable natural resources have been removed from a well, it must be properly plugged to avoid degradation of groundwater and surface water. Plugging involves placing cement within a wellbore at specific intervals to permanently block the possible migration of formation fluids containing H_2S. Improper plugging may allow H_2S (if present) to migrate out of the wellbore and into the atmosphere. Well plugging is regulated by the individual states. Plugging bonds are posted and procedures are subject to the regulatory agency's approval and on-site witness (personal communication, Donelson, Texaco, 12/9/92). This type of accidental release is also discussed in Chapter III.

Stripper Wells

Stripper wells are defined in Appendix A as producing at most 10 barrels of oil per day or 100 thousand cubic feet of gas per day. The owners or operators of these wells are typically smaller producing companies. Although stripper wells are often in remote areas, many are not completely isolated from the public. The potential exists for livestock, wildlife, or humans to come into contact with high levels of H_2S from stripper wells due to routine emissions and accidental releases. Although these wells are a potential hazard, no data were available on the number of sour stripper wells in the United States.

REFERENCES

Amyx, Bass, and Whiting. 1960. *Petroleum Reservoir Engineering.*

API. 1987. *API Recommended Practice 49 (RP 49), Recommended Practices for Safe Drilling of Wells Containing Hydrogen Sulfide,* 2nd ed., Publication No. RP49. American Petroleum Institute.

Curtis, S., and Showalter, E. 1989. Pumping Units and Prime Movers, *SPE Petroleum Engineers Handbook.*

Davenport, S.J. 1945. Hydrogen Sulfide Poisoning as a Hazard in the Production of Oil, Information Circular 7329. U.S. Department of the Interior, Bureau of Mines.

Donelson, Texaco, Personal communication, 12/9/92.

Dosch, M.W., and Hodgson, S.F. 1986. *Drilling and Operating Oil, Gas, and Geothermal Wells in an H_2S Environment,* Publication No. M10. California Department of Conservation, Division of Oil and Gas, Sacramento, CA, 39.

GRI. 1990. *Chemical Composition of Discovered and Undiscovered Natural Gas in the Continental United States. Volume I.* Prepared by Energy and Environmental Analysis, Inc., Arlington, VA, for Gas Research Institute, Chicago, IL.

Landes, K.K. 1953. *Petroleum Geology.* J. Wiley and Sons, Inc., New York, NY, 106 & 167.

NIOSH. 1977. *NIOSH Criteria for a Recommended Standard.... Occupational Exposure to Hydrogen Sulfide,* Publication No. 77-158. U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, Cincinnati, OH, 2, 147.

U.S. EPA. 1987. *Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy, Volume I,* EPA/530-SW-88 003. U.S. Environmental Protection Agency, Washington, DC.

U.S. EPA. 1993. *Health Assessment Document for Hydrogen Sulfide (HAD).* EPA/600/8-86/026F. U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, DC. January 1993.

Wyoming State Review, Interstate Oil and Gas Compact Commission/EPA State Review of Oil and Gas Exploration and Production Waste Management Regulatory Programs, October 1991.

CHAPTER III
HAZARD ASSESSMENT OF OIL AND GAS WELLS

INTRODUCTION

Objective

The objective of this chapter is to evaluate the potential hazards to public health and the environment resulting from routine emissions and accidental releases of hydrogen sulfide (H_2S) from oil and gas production, i.e., extraction; piping to a separator; oil, gas, and water separation; and associated storage.

Focus of Assessment

This hazard assessment was performed in two parts. First, existing H_2S ambient air monitoring data were compared to studies of human health and environmental effects to determine whether the H_2S concentrations measured from routine emissions have potentially harmful effects. Second, the threat of accidental releases was assessed by identifying past accidents and their impacts, reviewing atmospheric dispersion analyses (i.e., modeling) of accidental release scenarios in the literature, and conducting additional analyses. The result is an assessment of whether routine emissions and accidental releases are at levels that would require a national control strategy. In addition, this assessment identifies the hazards of H_2S, recommended protective levels, and the areas of the United States potentially vulnerable to routine emissions and accidental releases of H_2S.

Scope and Limitations

This hazard assessment addresses hydrogen sulfide emissions and releases that may potentially originate from a range of sources beginning with oil and gas wells (after well development) up through their associated treatment processes, storage units, and piping. However, it does not include gas processing or oil refining plants. For the potential H_2S emission sources described in Chapter II, non-occupational health impacts are considered along with environmental impacts (i.e., wildlife, livestock, and vegetation). For wildlife and livestock, the assessment includes animals that may be exposed to H_2S when they wander onto the well site.

For routine H_2S emissions, this hazard assessment is limited by the lack of data available on ambient air quality around well sites. Only a small amount of ambient monitoring data collected by States was identified. In addition, no national statistics on the health and environmental effects of chronic H_2S exposure exist. Nor are national statistics on the frequency and severity of accidental H_2S emissions or releases available. Only case records were located for the assessment of accidental releases. Therefore, the conclusions drawn from this assessment are based primarily on predictive modeling of accidental releases

and on a semi-quantitative comparison of ambient monitoring data and non-specific health effects data.

Hazard Assessment Steps

This hazard assessment was divided into three major parts:

- Hazard Identification
- Exposure Analysis
- Consequence Analysis

Figure III-1 displays the various components of this assessment.

The first step in this assessment was hazard identification. It entailed collecting information on the physical and chemical properties of H_2S and its location in the United States as it occurs (1) naturally in petroleum deposits, and (2) where it has been generated by sulfur-reducing bacteria that are introduced by enhanced oil recovery processes. The primary component of hazard identification is determining hydrogen sulfide's hazardous properties: ignitability, corrosivity, explosivity, and toxicity to human health and the environment.

The second step, exposure analysis, included identification of the H_2S prone areas for H_2S exposure in the United States and the human and ecological populations expected to be in these zones. The final part of the assessment, consequence analysis, was an examination of H_2S routine emissions and accidental releases occurring at oil and gas wells and the severity of the consequences.

Since this report examines routine emissions and accidental releases separately, this chapter first presents hazard identification, which is the same for both routine and accidental releases. Next, routine exposure and its consequences are discussed. Finally, exposure to accidental releases and its consequences are presented.

HAZARD IDENTIFICATION

Chemical Identity

Hydrogen sulfide is a colorless, flammable gas which, in low concentrations, has a characteristic odor of rotten eggs. It is a frequent component of crude oil and natural gas. Hydrogen sulfide gas has the Chemical Abstracts Services (CAS) registry number 7783-06-4; its physical and chemical properties are summarized in Table II-1.

Hazard Identification	Exposure Analysis	Consequence Analysis
Chemical Identity Location Nature of Hazard	Vulnerable Zones Land Use in Zones Human Populations Environment	Severity of Consequences
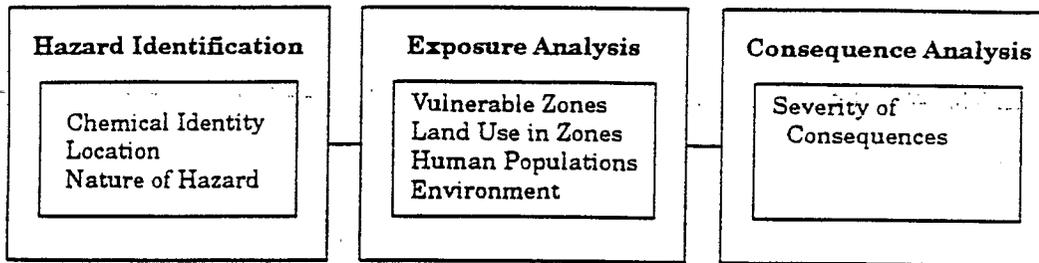
Adapted from: U.S. EPA, 1987.

Figure III-1. Components of the hazard assessment exercise.

Location

H$_2$S is found at varying depths in the earth's geological formations. Underground sources of the gas are often referred to as pockets of H$_2$S. Other natural sources of H$_2$S include volcanic gases, sulfur deposits, sulfur springs, and swamp gas from anaerobic decay. Approximately 90 percent of the air emissions of H$_2$S are produced by natural sources (U.S. EPA, 1993). A portion of this 90 percent results from the routine emissions and accidental releases resulting from the extraction of oil and gas containing H$_2$S. Figure II-1 shows major H$_2$S-prone areas of the United States.

Nature of Hazard

Exposure Routes, Absorption, Metabolism, and Elimination

As described in previous chapters, the most rapid route of exposure to H$_2$S is through the air. Although eye irritation is the basis for the OSHA Permissible Exposure Limit (PEL), inhalation is the quickest lethal exposure to humans and wildlife. The solubility of H$_2$S in water decreases as temperature increases; however, drinking groundwater has been found with noticeable H$_2$S concentrations.

Sullivan and Krieger's *Hazardous Materials Toxicology* (1992) summarizes the effects of H$_2$S exposure as follows:

> In environmental and occupational exposures, the lung rather than the skin is the primary route of absorption (Burgess, 1979; Yant, 1930). The dermal absorption of H$_2$S is minimal (Laug and Draize, 1942). Results from animal inhalation studies indicate that H$_2$S is distributed in the body to the brain, liver, kidneys, pancreas, and small intestine (Voigt and Muller, 1955). Within the body, H$_2$S is metabolized by oxidation, methylation, and reaction with metallo-or disulfide-containing proteins. Orally, intraperitoneally, and intravenously administered H$_2$S is primarily oxidized and directly excreted as either free sulfate or conjugated sulfate in the urine (Curtis et al., 1972). The importance of methylation in the detoxification processes of H$_2$S, however, is unknown (Weisiger and Jakoby, 1980). The reaction of H$_2$S with vital metalloenzymes such as cytochrome oxidase is the likely toxic mechanism of H$_2$S (NRC, 1979; Smith and Gosselin, 1979). Reaction with nonessential proteins may also serve as a detoxification pathway (Smith, Kroszyna, and Kruszyna, 1976; Smith and Gosselin, 1964). Systemic poisoning occurs when the amount of H$_2$S absorbed exceeds that which can be detoxified and eliminated (Yant, 1930; Milby, 1962). Because of its rapid oxidation in the blood, H$_2$S is not considered a cumulative poison (Yant, 1930; Ahlborg, 1951; Haggard, 1925)....

There are no animal data available regarding the exhalation of H_2S after inhalation exposure. In animals, the excretion of H_2S by the lungs is minimal after peritoneal administration of H_2S (Evans, 1967; Gunina, 1957; Susman et al., 1978). However, because rescue personnel have developed H_2S poisoning shortly after starting mouth-to-mouth resuscitation on victims who had been poisoned, it is likely that significant H_2S is excreted from the lungs (Kleinfeld, Giel, and Rosso, 1964).

Acute Human Toxicity

The odor perception threshold for H_2S is very low. At concentrations between 3 and 20 ppb, the characteristic rotten egg odor is detectable. However, higher concentrations of H_2S in the 1.5×10^5 to 2.5×10^5 ppb range can cause olfactory paralysis. At these concentrations, the olfactory sense may be lost and exposed persons may be unaware of the presence of the toxic gas. Thus, odor cannot be relied upon as a warning sign of possible exposure to H_2S. Pulmonary edema, resulting from inhalation of levels between 3×10^5 and 5×10^5 ppb, can be fatal. (See Table III-1.) Inhaling levels between 5×10^5 and 1×10^6 ppb can cause a stimulation of the respiratory system, and rapid breathing (hyperpnea) will occur followed by cessation of breathing (apnea). The effect of inhaling levels above 1×10^6 ppb is immediate respiratory paralysis followed by death.

Inhalation of levels above 2.5×10^5 ppb can damage organs and the nervous system. Much of this damage is a result of a lack of oxygen (anoxia) caused by the depression of cellular metabolism which can occur at 2.5×10^5 ppb. Instances of permanent neurological damage in humans resulting from acute exposure have been described. Furthermore, animal data have revealed that changes in the tissues of the brain, lungs and heart can occur from exposure to the gas.

Irritation of the respiratory tract and eyes is another major effect of H_2S exposure. The gas is readily absorbed through the nasal and lung mucosa. It is very irritating to the respiratory tract and eyes and can cause serious eye injury above 5×10^4 ppb. The gas can affect the epithelium of the eye causing inflammation and lacrimation. The Integrated Risk Information System (IRIS) (U.S. EPA, 1992) lists several signs and symptoms of H_2S exposure including painful conjunctivitis, sensitivity to light, tearing, and clouding of vision. In addition, permanent scarring of the cornea can occur. At high, and potentially lethal concentrations, the mucous membranes can be anesthetized so that irritation effects cannot be relied upon to warn individuals of H_2S exposure.

In addition to irritation, IRIS lists other signs and symptoms of H_2S exposure including labored breathing and shortness of breath, profuse salivation, nausea, vomiting, diarrhea, giddiness, headache, dizziness, confusion, rapid breathing, rapid heart rate, sweating, and weakness.

Table III-1. Effects of Exposure in Humans at Various Concentrations in Air

| Clinical Effect | Level of Hydrogen Sulfide | | Reference |
	ppb	mg/m^3	
Odor perception threshold	3-20	0.004 - 0.028	Indiana Air Pollution Control Board (1964)
Offensive odor (rotten eggs)	<3x10^4	<42	Ahlborg (1951)
Offensive odor (sickening sweet)	>3x10^4	>42	National Research Council (1977)
Occupational Exposure Limit (OEL)	1x10^4	14	National Research Council (1977)
Serious eye injury	5x10^4 - 1x10^5	70 - 140	National Research Council (1977)
Olfactory paralysis	1.5x10^5 - 2x10^5	210 - 350	National Research Council (1977)
Pulmonary edema, threat to life	3x10^5 - 5x10^5	420 - 700	National Research Council (1977)
Strong stimulation of respiration	5x10^5 - 1x10^6	700 - 1400	National Research Council (1977)
Respiratory paralysis, collapse and death	1x10^6 - 2x10^6	1400 - 2800	National Research Council (1977)

Source: U.S. EPA, 1993.

Hydrogen sulfide may also decrease the body's ability to withstand infection. A toxicological study exposed rats to 4.5×10^4 ppb of hydrogen sulfide for 2, 4, or 6 hours, followed by a challenge with an aerosol of *staphylococcus epidermis* (Rogers and Ferin, 1981). A significant dose-response effect was seen in the number of colonies formed, when the exsanguinated lungs were harvested from the rats at 30 minutes, 3 hours and 6 hours post-challenge, and homogenized and grown in a selective growth medium for staphylococci. Rats exposed to hydrogen sulfide for 4 hours had a 6.5-fold greater percent of colony-forming units than controls, while those exposed to hydrogen sulfide for 6 hours had a 52-fold greater percent of colony-forming units. The conclusion reached was that hydrogen sulfide significantly affected the antibacterial system of the rats by impairing alveolar macrophages.

However, Higashi et al. (1983), in a cross-sectional study of viscose rayon textile workers exposed to hydrogen sulfide (average concentration, 3×10^3 ppb) and carbon disulfide, found no difference between exposed employees and controls in respiratory and spirometric variables. Similarly, Kangas et al. (1984) found no increased prevalence of subjective symptoms among cellulose mill workers exposed to hydrogen sulfide concentrations of up to 2×10^4 ppb and methyl mercaptan levels as high as 1.5×10^4 ppb, and much smaller amounts of dimethyl disulfide.

Chronic Human Toxicity

The toxicological data based was reviewed and an inhalation reference concentration (RfC) was verified by the U.S. EPA Reference Dose (RfD)/RfC Work Group on June 21, 1990. The documentation is available via the Integrated Risk Information System (IRIS) (U.S. EPA, 1991). The Integrated Risk Information System is an on-line data base containing EPA risk assessment results and regulatory information. An RfC is defined as an estimate, with uncertainty spanning perhaps an order of magnitude, of a daily exposure to the human population (including sensitive subgroups) which is likely to be without adverse effects during a lifetime (U.S. EPA, 1990). The derivation of the RfC is based on a complete review of the toxicological literature and encompasses adjustments for exposure duration and dosimetry. It utilizes uncertainty factors to account for specific extrapolations between the population in which the effect was observed and the human population. The critical, usually the most sensitive, effect is the focus of the RfC derivation; for this effect the no-observed-adverse-effect level (NOAEL), or lowest-observed-adverse-effect level (LOAEL) if a NAOEL is not available, is identified. Detailed discussion concerning these issues can be found in U.S. Environmental Protection Agency, 1990.

The RfC for H_2S is 9×10^{-4} mg/m^3 (6.7×10^{-1} ppb) and was derived from the NOAEL for inflammation of the nasal mucosa in mice (Toxigenics, 1983). The subchronic study revealed a lowest-observed-adverse-effect level (LOAEL) of 110 mg/m^3 (8×10^4 ppb) and a no-observed-adverse-effect level (NOAEL) of 42.5 mg/m^3 (3.05×10^4 ppb). Since the RfC may change due to evaluation of additional data, the reader is referred to IRIS for the most current information regarding the RfC for H_2S.

The extrapolation of the NOAEL to the RfC follows several steps. First, the NOAEL is adjusted to account for the daily length of exposure in the study; and second, it is extrapolated to humans, and a human equivalent concentration (HEC) is calculated. Finally an uncertainty factor is applied. The RfC for hydrogen sulfide is derived using an uncertainty factor of 1000. The 1000 reflects a factor of 10 to protect sensitive individuals, 10 to adjust from subchronic studies to a chronic study (a subchronic study is carried out over a shorter period of time and may not accurately reflect cumulative effects), and 10 to adjust for interspecies conversions and database deficiencies.

Very little data exist on whether H_2S can cause carcinogenic, mutagenic, reproductive or developmental effects in humans or animals. Because of a lack of adequate test data, H_2S is currently placed in Group D, based on the weight-of-evidence criteria in the EPA's Carcinogen Risk Assessment Guidelines issued in August 1986. A Group D ranking means that the available data are inadequate to assess a chemical's human carcinogenic potential. Furthermore, data are inadequate to state that H_2S is mutagenic or that it causes reproductive effects. Limited animal data do suggest that H_2S appears to have potential to alter normal developmental processes. No data on human developmental effects of inhaled H_2S have been located (U.S. EPA, 1993).

Ecological Effects

Data on the ecological effects of H_2S are limited (Table III-2). McCallan, Hartzell, and Wilcoxon (1936) and Benedict and Breem (1955) conducted high-exposure fumigation studies, which noted that young, growing plants were the most susceptible to injury from exposure to H_2S. However, they noted that temperature, soil moisture, and species differences were important factors affecting the results. Heck, Daines, and Hindawi (1970) noted that mature leaves were unaffected while damage to the young shoots and leaves consisted of scorching. Among the plants determined to be sensitive to H_2S are clover, soybean, tomatoes, tobacco, and buckwheat.

According to the EPA *Health Assessment Document for H_2S* (U.S. EPA, 1993), few studies exist that evaluate natural or accidental exposure of wildlife and/or domestic animals to H_2S. However, H_2S has been determined to be highly toxic to some fish species. Animal surveys conducted after a gas well blowout in Lodgepole, Alberta, Canada (Lodgepole Blowout Inquiry Panel, 1984; Harris, 1986) revealed that large animals were exhibiting signs of mucous membrane irritation and were avoiding the geographic area. Most cattle in the exposed area were unaffected. Concentrations of H_2S as high as 1.5×10^4 ppb (sampling time unknown) were measured in the blowout area.

Flammability, Explosivity, and Corrosivity

"Hydrogen sulfide is generally stable when properly stored in cylinders at room temperature. However, in the air, it is flammable and explosive and may be ignited by static discharge. It may react with metals, oxidizing agents, and acids such as nitric acid, bromine

Table III-2. Effects of Ecological Exposure to H₂S

Studies	Species		Level	Source
Aquatic	Bluegill	LC_{50}	0.009 - 0.0478 mg/L	AQUIRE
	Rainbow Trout	LC_{50}	0.013 - 0.047 mg/L	AQUIRE
	Fathead Minnow	LC_{50}	0.007 - 0.776 mg/L	AQUIRE
Mammalian	Mouse	NOAEL	42.5 mg/m³ (3.05×10^4 ppb)	IRIS
		LOAEL	100 mg/m³ (8×10^4 ppb)	IRIS
	Rat	NOAEL	42.5 mg/m³ (3.05×10^4 ppb)	IRIS
		LOAEL	100 mg/m³ (8×10^4 ppb)	IRIS

AQUIRE   Aquatic Toxicity Information Retrieval
IRIS   Integrated Risk Information Service

LC_{50} Lethal Concentration 50
NOAEL   No-observed-adverse-effect-level
LOAEL   Lowest-observed-adverse-effect-level

pentafluoride, chlorine trifluoride, nitrogen triiodide, nitrogen trichloride, oxygen difluoride, and phenyldiazonium chloride. When heated to decomposition, it emits highly toxic sulfur oxide fumes" (Sullivan and Krieger, 1992). In pure form, its lower and upper explosive limits are 4.3 percent (4.3×10^7 ppb) and 45.5 percent (45.5×10^7 ppb), and its auto-ignition temperature is 260 °C (500 °F) (NIOSH, 1977). The National Fire Protection Association (NFPA) has classified hydrogen sulfide in the highest flammability class (NFPA, 1974).

In the presence of water, hydrogen sulfide gas is highly corrosive to metals, including high-tensile steel, which hydrogen sulfide can embrittle. These properties can lead to loss of containment and accidental releases from ruptures if not controlled. Special precautions must be taken to prevent spontaneous ignition fires when vessels that previously contained concentrated hydrogen sulfide are opened. Ignition is caused by reaction of iron sulfide with air to form iron oxide. The conversion of sulfide to oxide produces enough heat to ignite flammable vapors (Dosch and Hodgson, 1986).

ACGIH Threshold Limits

The American Conference of Governmental Industrial Hygienists (ACGIH) publishes a book of threshold limit values for chemical substances in the work environment (ACGIH, 1992). The limits are intended for use in the practice of industrial hygiene as guidelines or recommendations in the control of potential health hazards. When OSHA began setting standards for employee exposure in the 1970s, they adopted the ACGIH threshold limit values (TLV's) as their permissible exposure limits. The ACGIH standards are recommendations rather than regulations; they are updated annually and respond to current research more quickly than OSHA's regulations.

The current limits for H_2S were adopted by ACGIH in 1976. The Threshold Limit Value-Time Weighted Average (TLV-TWA) is 1×10^4 ppb or 14 mg/m^3, and the TLV short-term exposure limit (TLV-STEL) is 1.5×10^4 ppb or 21 mg/m^3. The TLV-TWA is defined as the time-weighted average concentration for a normal 8-hour workday and 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect. The TLV-STEL is defined as the concentration to which workers can be exposed continuously for a short period of time without suffering from 1) irritation, 2) chronic or irreversible tissue damage, or 3) narcosis of sufficient degree to increase the likelihood of accidental injury, impair self-rescue or reduce work efficiency, also provided that the daily TLV-TWA is not exceeded. A STEL is further defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the TLV-STEL should not be longer than 15-minutes and should not occur more than 4 times a day, and should be separated by 60 minutes each.

LC_{01}

One measure of the airborne concentrations of toxic materials that might cause fatality is the LC_{01}, which is the concentration that could prove fatal to one percent of those exposed to it. The LC_{01} is related to the exposure time, t, by a relationship of the form $LC_{01} = (k/t)^{1/n}$, where k and n are constants that depend on the material in question. This relationship is a manifestation of the probit equation, which is a well-established way of presenting the relationship between concentration, exposure time, and probability of fatality.

For H_2S, the Center for Chemical Process Safety of the American Institute of Chemical Engineers (AIChE) has a probit equation which gives $k = 83,500$ and $n = 1.43$, with C in ppb and t in minutes (AIChE, 1989). Thus, for a five minute exposure, $LC_{01} = 8.95 \times 10^5$ ppb and, for a one hour exposure, $LC_{01} = 1.6 \times 10^5$ ppb.

The Energy Resources Conservation Board (ERCB) of Alberta, Canada (Alp et al., 1990) has developed an alternative probit equation (shown in Figure III-2) which, for the LC_{01}, gives $k = 1.364 \times 10^8$ and $n = 2.5$. For a five minute exposure, this gives $LC_{01} = 3.75 \times 10^5$ ppb and for a one hour exposure gives $LC_{01} = 1.4 \times 10^5$ ppb. The ERCB values are thus more conservative.

AIHA Guidelines

The American Industrial Hygiene Association (AIHA) sets Emergency Response Planning Guidelines (ERPGs) to protect the general public in the event of an emergency release. The three ERPGs for H_2S, which are time-dependent levels for varying degrees of potential harm, are defined as follows:

ERPG-3 1×10^5 ppb, the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects;

ERPG-2 3×10^4 ppb, the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

ERPG-1   100 ppb, the maximum airborne concentrations below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.
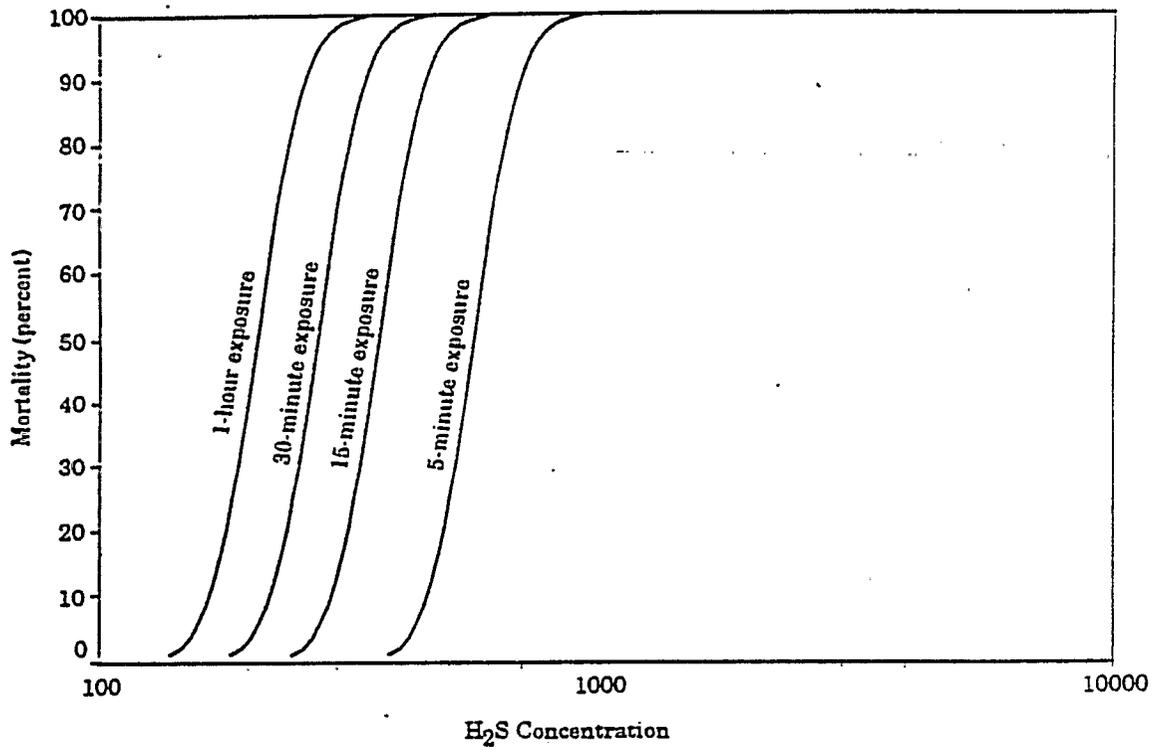
Note: Concentrations intentionally left in ppm.
Source: Alp et al., 1990.

Figure III-2. ERCB H$_2$S probit relations.

For hydrogen sulfide, the ERPG-3 is based on human experience, while the ERPG-2 is based on animal studies and the ERPG-1 is based on the fact that the objectionable odor of hydrogen sulfide is distinct at 300 ppb (AIHA, 1991). For the purposes of accidental release dispersion analysis, the ERPG-2 was considered conservative and used as a threshold for emergency countermeasures.

As stated above, these ERPG values are for an exposure time of one hour. At the time of writing, there is no definitive guidance on how to extrapolate to shorter durations of exposure. However, Gephart and Moses (1989) suggest that a constant dosage extrapolation might be reasonable; that is, (ERPG in ppb)x(exposure time, t, in minutes). = constant, k. Discussions with one of the AIHA authors have suggested that, for t < 15 min, k should be divided by two. Thus, for H_2S, the ERPG-2 is as follows:

- 3×10^4 ppb for an exposure time of one hour
- 1.8×10^5 ppb for an exposure time of five minutes.

The reader should recognize that these extrapolations are tentative and included for purposes of illustration. They represent one of the greater sources of uncertainty in the calculations.

NAS/NRC Guidelines

For the last forty years, the NRC's Committee on Toxicology has submitted emergency exposure guidelines for chemicals of concern to the Department of Defense (DOD) (NRC, 1986). These guidelines are used in planning for sudden contamination of air during military and space operations; specifically, they are used to choose protective equipment and reponse plans after non-routine but predictable occurrences such as line breaks, spills, and fires. These guidelines are for peak levels of exposure considered acceptable for rare situations, but are not to be applied in instances of repeated exposure.

An Emergency Exposure Guidance Level (EEGL) is defined as a concentration of a substance in air (gas, vapor, or aerosol) judged by DOD to be acceptable for the performance of specific tasks by military personnel during emergency conditions lasting 1 to 24 hours. Exposure to an EEGL is not considered safe, but acceptable during tasks which are necessary to prevent greater risks, such as fire or explosion. Exposures at the EEGLs may produce transient central nervous system effects and eye or respiratory irritation, but nothing serious enough to prevent proper responses to emergency conditions.

Since the 1940's, the NRC has developed EEGLs for 41 chemicals, 15 of which are listed in Section 302 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) as extremely hazardous substances (EHSs). Although acute toxicity is the primary basis for selecting EEGLs, long-term effects from a single acute exposure are also evaluated for developmental, reproductive (in both sexes), carcinogenic, neurotoxic, respiratory and other organ-related effects. The effect determined to be the most seriously debilitating,

work-limiting, or sensitive is selected as the basis for deriving the EEGL. This concentration is intended to be sufficiently low to protect against other toxic effects that may occur at higher concentrations. Factors such as age of the exposed population, length of exposure, and susceptibility or sensitivity of the exposed population are also considered in determining EEGLs.

Safety factors are used in developing EEGLs to reflect the nature and quality of the data. Safety factors for single exposures may differ from those used in chronic studies. In the absence of better information, a safety factor of 10 is suggested for EEGLs (i.e., the reported toxicity value should be divided by 10) if only animal data are available and extrapolation from animals to humans is necessary for acute, short-term effects (NRC, 1986). The safety factor of 10 takes into account the possibility that some individuals might be more sensitive than the animal species tested. A factor of 10 is also suggested if the likely route of human exposure differs from the route reported experimentally (NRC, 1986), for example, if oral data are reported and inhalation is the most likely exposure route for humans.

As noted by NRC (1986, p. 7), development of an EEGL for different durations of exposure usually begins with the shortest exposure anticipated (i.e., 10-15 minutes) and works up to the longest, such as 24 hours. For H_2S, 10-minute emergency exposure guideline level (EEGL) is 5×10^4 ppb; 1×10^4 ppb is the 24-hour EEGL. The 24-hour/day, 90-day continuous exposure guide level (CEGL) for H_2S has been recommended at 1×10^3 ppb (NCCT, 1985). Under the simplest framework, Haber's law is assumed to operate, with the product of concentration (C) and time (t) as a constant (k) for all the short periods used (Ct=k) (Casarett and Doull, 1986). If Ct is 30 and t is 10, then C is 3; if Ct is 30 and t is 30, then C is 1. If detoxification or recovery occurs and data are available on 24-hour exposures, this is taken into account in modifying Ct. In some instances, the Ct concept will be inappropriate, as for materials such as ammonia that can be more toxic with high concentrations over short periods. Each material is considered in relation to the applicability of Haber's law.

Generally, EEGLs have been developed for exposure to single substances, although emergency exposures often involve complex mixtures of substances and, thus, present the possibility of toxic effects resulting from several substances. In the absence of other information, guidance levels for complex mixtures can be developed from EEGLs by assuming as a first approximation that the toxic effects are additive. When the chemical under evaluation for development of an EEGL is an animal or human carcinogen, a separate qualitative risk assessment is undertaken in recognition of the fact that even limited exposure to such an agent can theoretically increase the risk of cancer. The risk assessment is performed with the aim of providing an estimate of the acute exposure that would not lead to an excess risk of cancer greater than 1 in 10,000 exposed persons. The following mathematical approach, taken directly from NRC (1986, pp. 26-27), is applicable for EEGL computations for carcinogens:

1. If there has been computed an exposure level d (usually in ppm in air), which after a lifetime of exposure is estimated to produce some "acceptable" level of excess risk of cancer — say, 1×10^{-6} — this has been called a "virtually safe dose" (VSD). Computation of the dose d, if not already done by a regulatory agency, will be computed by the Committee on Toxicology in accordance with generally accepted procedures used by the major regulatory agencies, i.e., using the multistage no-threshold model for carcinogenesis and the appropriate body weight/surface area adjustments when extrapolating from an animal species to humans.

2. If carcinogenic effect is assumed to be a linear function of the total (cumulative) dose, then for a single 1-day human exposure an acceptable dose (to yield the same total lifetime exposure) would be d times 25,600 (there being approximately 25,600 days in an average lifetime); the allowable 1-day (24-h) dose rate would be

$$d \times 25,600$$

3. Because of uncertainties about which of several stages in the carcinogenic process a material may operate in, and because of the likely low age of military persons, it can be shown from data of Crump and Howe (1984) that the maximal additional risk that these considerations contribute is a factor of 2.8. As a conservative approach, the acceptable dose is divided by 2.8, i.e.,

$$\frac{d \times 25,600}{2.8}$$

If a lifetime excess risk, R, is established by DOD (for example, at 1×10^{-4}, as has been suggested by the International Council on Radiation Protection for nuclear power plant workers), then the appropriate extent of risk at the EEGL would be

$$\frac{d \times 25,600}{2.8} \times \frac{R}{\text{level of risk at d}}$$

(In the example given here, the level of risk at d was no more than 1×10^{-6}.) If R is 1×10^{-4}, then R/risk at d $= 10^{-4}/10^{-6} = 100$ (NRC, 1986).

4. If a further element of conservatism is required (for example, where animal data need to be extrapolated to estimate human risk), an additional safety factor can be used as divisor.

The NRC's Committee on Toxicology has also developed special public exposure guidelines upon request from Department of Defense. The Short-term Public Exposure Guidance Level (SPEGL) is defined as an acceptable ceiling concentration for a single,

unpredicted short-term exposure to the public. The exposure period is usually calculated to be one hour or less and never more than 24 hours. SPEGLs are generally set at 0.1 to 0.5 times the EEGL. A safety factor of 2 is often used to take into account effects on sensitive subpopulations, such as children, the aged, and people with debilitating diseases. A safety factor of 10 may be used to take into account the effects of an exposure on fetuses and newborns. Effects on the reproductive capacity of both men and women are also considered. Five SPEGLs (for hydrazine, dimethylhydrazine, monomethyl hydrazine, nitrogen dioxide, and hydrogen chloride) have been developed by the NRC; all five chemicals are on the list of EHSs. (U.S. EPA, 1987).

EXPOSURE AND CONSEQUENCE ANALYSES

In this section, potential exposures to and consequences of exposure to H_2S from oil and gas wells are analyzed. The zones of the United States most likely to contain H_2S are identified and the potentially exposed human and ecological populations are discussed. Routine emissions and accidental releases of H_2S are characterized using monitoring records and dispersion modeling and the consequences are discussed. For accidental releases, prevention, mitigation and emergency response policies and procedures are also identified.

Vulnerability Zones

Vulnerability zones are estimated geographical areas that may be subject to concentrations of H_2S at levels that could cause irreversible acute health effects or death to human populations within the area following an accidental release. For detailed hazard analyses recommended under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA), see Chapter IV; vulnerability zones are based on estimates of the quantity of hazardous substances released to air, the rate of release to air, airborne dispersion, and the airborne concentration that could cause irreversible health effects or death. This concept of vulnerability is used to assess regions most likely to encounter routine emissions or accidental H_2S releases from oil and gas production. This report does not use the EPCRA methodology. Rather, the basic tools of a hazard analysis are used to alert the reader to areas with potential H_2S hazards.

Estimated vulnerability zones are shown in Figure III-3 as circles with different radii to illustrate how changing conditions or assumptions can influence the vulnerablity zone estimate. With most atmospheric releases, the actual concentration of the airborne chemical tends to decrease as it moves further downwind from the release site because of continual mixing and dilution (i.e., dispersion).

The American Petroleum Institute (API), an industry-wide technical organization, has published several recommended practices (RP) pertaining to hydrogen sulfide in the oil and gas production industry. Figure III-4 shows API's RP 49 recommended equipment layout to minimize vulnerability zones for an unconfined area, taking the potential for H_2S releases into consideration. Confinement refers to offshore sites and some land locations confined by
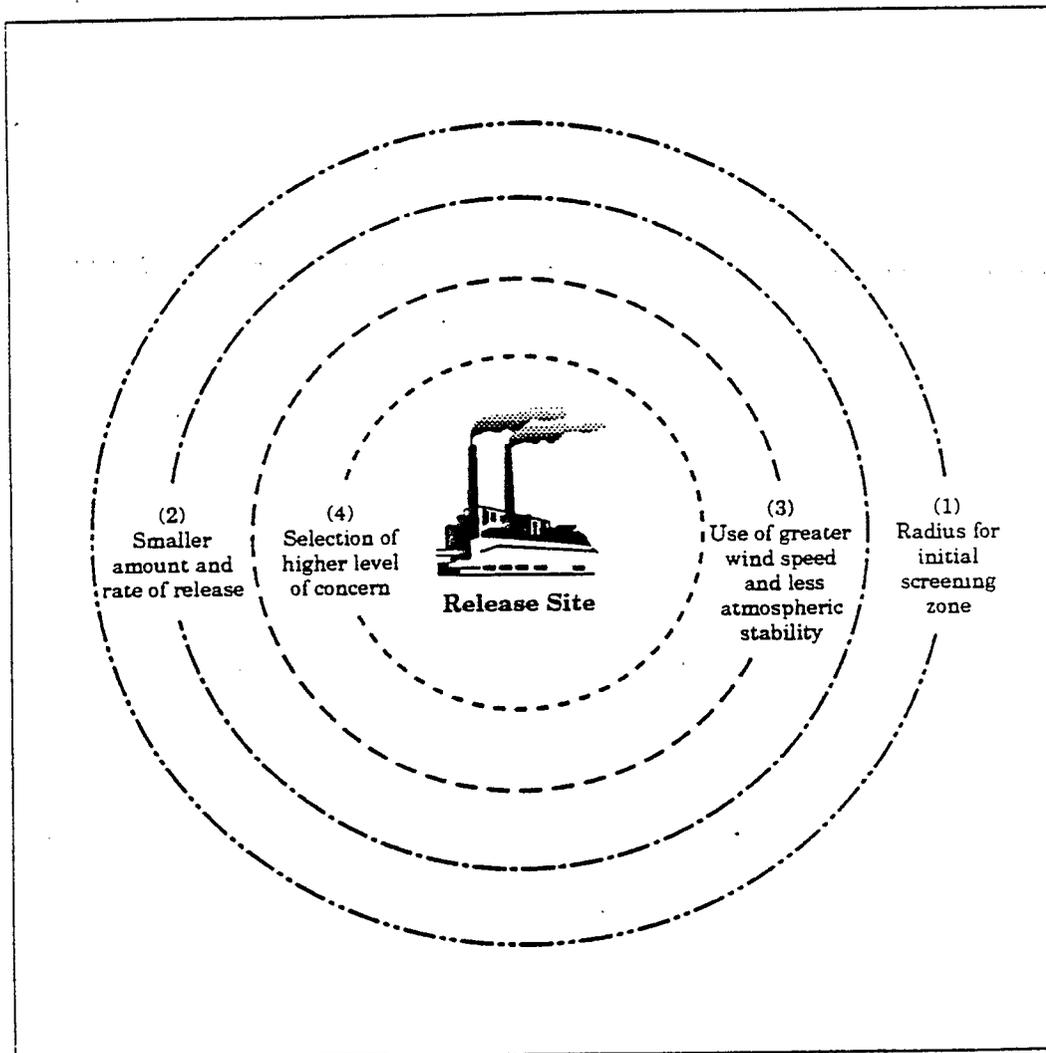
Source: U.S. EPA. 1987.

Figure III-3. The effect of different assumptions on the calculation of the radius of estimated vulnerable zones.
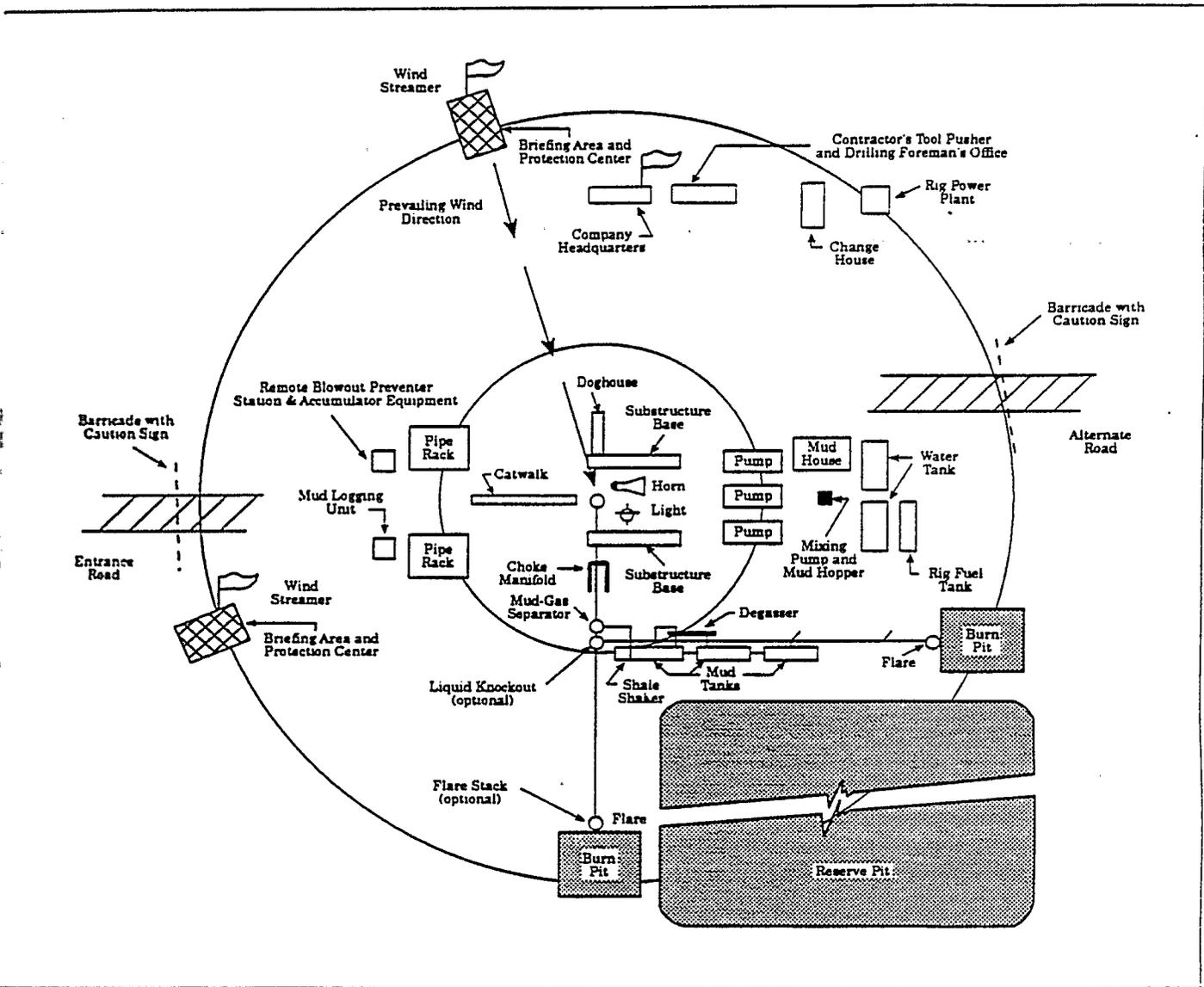
Figure III-4. Example of drilling equipment layout – unconfined location.

the restriction of area, method of access, terrain, surrounding population distribution, etc. In an H_2S environment, well plot areas should be larger than usual, (i.e.. larger reserve pits, turnaround room. etc.). The extra space allows for a greater margin of safety in well site activities and, in turn, a smaller vulnerability zone.

The California Division of Oil and Gas provides guidance on H_2S exposure prevention. In their report, *Drilling and Operating Oil, Gas, and Geothermal Wells in an H_2S Environment*, the State recommends calculating the well area's potential toxicity from H_2S emissions, if the volume of oil or gas produced and the concentration of the H_2S in the oil or gas are known (Dosch and Hodgson, 1986). From these data, the radius from the source to the 3×10^5 ppb and 1×10^5 ppb H_2S concentration area can be determined on dispersion-based scales. Potential sources of toxic gas emissions considered in calculating the toxicity of the well area include wells and associated production, treatment, processing, and storage facilities.

Calculating vulnerability zones for H_2S on a nationwide basis, as in EPCRA hazard analyses, is difficult because vulnerability zones are designed for site-specific studies. Therefore, this assessment will take a broader approach to identifying vulnerability zones, which will be referred to as H_2S prone areas. These areas are considered the major areas of the United States prone to natural occurrences of hydrogen sulfide. Figure II-1 identified 14 major H_2S prone areas in the United States. The 20 states having H_2S prone areas are Alabama, Arizona, Arkansas, California, Colorado, Florida, Idaho, Indiana, Illinois, Kentucky, Louisiana, Michigan, Mississippi, Missouri, Nebraska, North Dakota, Oklahoma, Texas, Utah, and Wyoming. Texas has four discrete areas prone to H_2S. However, some States, such as Louisiana, do not drill to depths of known H_2S deposits; in Louisiana, oil and gas wells appear to be located in more shallow depths.

Exposure Analysis — Routine Emissions

Monitoring Records

Ambient air monitoring programs measure the concentration of pollutants after they have dispersed from one or more sources. These levels are recorded and tracked continuously so that the level of exposure and air quality can be assessed over the long term and under varying meteorological and emission scenarios. Ambient air monitoring is also used to determine compliance with air quality standards by measuring pollutant concentrations. With a dispersed, relatively unreactive primary pollutant such as hydrogen sulfide, often the emissions can be traced back to the specific source.

Many States require ambient air monitoring for hydrogen sulfide at gas plants and refineries; however, monitoring is not frequently required at oil and gas extraction facilities. In the preparation of this report, six States (California, Michigan, North Dakota, Oklahoma, Texas, and Wyoming) were contacted and questioned about the availability of monitoring

data. California, Michigan, Oklahoma, Texas and Wyoming had not conducted pertinent ambient air monitoring.

The North Dakota State Department of Health and Consolidated Laboratories (NDSDH&CL) performs ambient monitoring for routine emissions of H_2S and has collected the data since 1980. The following discussion summarizes North Dakota's program to provide an indication of historical, routine emissions of H_2S from wells. Since no other States have such monitoring data available, this report relies on North Dakota's data to assess hazards and draw conclusions.

The North Dakota database contains site name, year/month/day monitored, and H_2S value measured. The database reflects three background and six special purpose monitors (i.e., monitors set up as a result of a complaint). Monitoring periods vary in length from months to over a decade for a total of 393 months (32.75 years) of data (personal communication, D. Harman, NDSDH&CL, 8/11/92). Table III-3 shows the North Dakota data. The data were in half-hour average concentrations up to January 1, 1988, when the averages recorded were changed to hourly, to correspond with the change in the North Dakota Ambient Air Quality Standards (NDAAQS). Some monitoring lasted less than a year; however, monitoring in the Theodore Roosevelt National Park-north unit was begun in 1980 and continues today.

North Dakota's Hydrogen Sulfide Standards - An Historical Review. At the time of the early monitoring activities, there were two NDAAQS for hydrogen sulfide, both based on half-hour averages and on odor thresholds but over different time spans. Adopted in 1970, they were based upon guidelines established in the Interstate Air Pollution Study conducted in St. Louis in the late 1960s. Those standards were 54 ppb (75 $\mu g/m^3$), 1/2-hour maximum concentration not to be exceeded more than twice per year; and 32 ppb (45 $\mu g/m^3$), 1/2-hour maximum concentration not to be exceeded more than twice in any five consecutive days. The 1/2-hour hydrogen sulfide standards were inconvenient because all of the other pollutants were being tracked on an hourly basis. To correct the situation, North Dakota developed a 1-hour standard that would afford the same degree of protection as the old 1/2-hour standards did, while still based on an odor threshold value. Statistically, they narrowed the proposed standard down to a range of concentrations between 48 ppb and 52 ppb. Montana had an existing hydrogen sulfide standard of 50 ppb for a 1-hour period, not to be exceeded more than once per year, and North Dakota decided to adopt the same standard to provide consistency on both sides of the North Dakota-Montana State border. The 50 ppb (70 $\mu g/m^3$) 1-hour hydrogen sulfide standard became effective October 1, 1987.

At the same time that the new standard became effective, a new chapter (Chapter 20) was added to North Dakota's Air Pollution Control Rules entitled "Control of Emissions from Oil and Gas Well Production Facilities." The oil companies expressed concern that the hydrogen sulfide standard was included in North Dakota's table of ambient air quality standards (NDAAQS) and, by law, exceptions could not be granted. Their position was that they could not guarantee compliance with the standard at all times, and that the standard was

Table III-3. North Dakota H₂S Monitoring Studies

Study	Location	Dates	Year	Ambient Std. (ppb)	Violation* (hours)	Maximum (ppb)
Roffler	Farmyard within 1/2 mile of well and tank battery	5/11/80 - 9/29/80	1980	32	0	13
Theodore Roosevelt National Memorial Park – North Unit	Little Missouri River Valley, near the north unit park headquarters	4/24/80 - 8/2/92 (1990 missing)	1980	32	0	4
			1981	32	1	220
			1982	32	34	500
			1983	32	31	158
			1984	32	27	415
			1985	32	35	·137
			1986	32	12	87
			1987	32/50	0	73**
			1988	50	0	39
			1989	50	0	10
			1990	50/200	0	10
			1991	200	0	32
			1992	200	0	6
Jorgenson	Valley with several oil wells within 1 mile	10/2/80 - 5/13/82	1980	32	8	160
			1981	32	19	230
			1982	32	13	250
Tadrmas	Farmyard within 1 mile of several wells	6/30/82 - 10/31/83	1982	32	9	541
			1983	32	7	353
Theodore Roosevelt National Memorial Park – South Unit	Painted Canyon Rest Area	10/17/85 - 6/30/90	1985	32	0	12
			1986	32	0	16
			1987	32/50	0	18.
			1988	50	0	9
			1989	50	0	10
			1990	50/200	0	0*
Lone Butte	Little Missouri River Valley near an oil tank battery in Little Knife Oil Field	1/17/84 - 7/11/89	1984	32	1808	1630
			1985	32	1859	2734
			1986	32	1653	2182
			1987	32/50	1130	2420
			1988	50	320	1515
			1989	50	25	122
Lostwood	Lostwood National Wildlife Refuge Headquarters	12/26/85 - 1/14/91	1985	32	0	0
			1986	32	0	18
			1987	32/50	0.	45
			1988	50	0	46
			1989	50	0	47
			1990	50/200	0	88
			1991	200	0	0
Olson	Farmyard within 1.5 miles of several wells	7/20/89 - 9/18/90	1989	50	2	88
			1990	50/200	0	73
Plaza	Town of Plaza, within 2 miles of several wells and tank batteries	9/4/90 - 8/3/92	1990	50/200	0	152
			1991	200	0	358
			1992	200	1	269

Source: Personal correspondence, D. Harman, NDSDH & CL, 8/11/92.

Analysis of data prior to 10/1/87 based upon 32 ppb, 1/2-hour average standard, not to be exceeded more than twice in any consecutive days.

Analysis of data between 10/1/87 and 6/1/90 based upon 50 ppb 1-hour average standard, not to be exceeded more than once r year.

Analysis of data after 6/1/90 based upon 200 ppb 1-hour average standard, not to be exceeded more than 1 time per month.

* violation occurs the second time the standard is exceeded.

Monitor out of service much of the time period.

Exceedance defined as 2 times the standard.

not based on health-related concerns but on odor recognition levels. As a result, a joint Health Department/Industry task force was established and four new health-based standards were developed (effective June 1, 1990). These included raising the 50 ppb, 1-hr standard to a 200 ppb, 1-hr standard - a decrease in H_2S protection by a factor of four. These standards, which remain in effect today, are as follows:

- 1 x 10^4 ppb or 14 mg/m³) maximum instantaneous concentration not to be exceeded;
- 200 ppb or 280 μg/m³) maximum 1-hour average concentration not to be exceeded more than once per month;
- 100 ppb or 140 μg/m³) maximum 24-hour average concentration not to be exceeded more than once per year;
- 20 ppb or 28 μg/m³) maximum arithmetic mean concentration averaged over three consecutive months (personal communication, D. Harman, NDSDH&CL, 8/11/92).

Methodology for Analysis of Monitoring Data. For the analysis of the monitoring data, only one of the standards was evaluated for each time period. Prior to October 1, 1987, the data were compared to the 32 ppb 1/2-hour average standard, not to be exceeded more than twice in any five consecutive days. After October 1, 1987, and prior to June 1, 1990, 50 ppb was the only standard in effect, not to be exceeded more than once per year. The data collected after June 1, 1990, were compared to the 200 ppb standard which was not to be exceeded more than once per month. The results of the analysis are tabulated in Table III-3.

PSD Class I Areas. Several of the North Dakota monitoring programs were conducted to monitor air quality changes resulting from the oil and gas production industry at national parks and wildlife refuges. The Federal government established the Prevention of Significant Deterioration permit program (PSD) to protect areas with good air quality. In North Dakota, the most important, or Class I, areas include the Lostwood National Wildlife Refuge and the northern, southern and Elkhorn Ranch portions of the Theodore Roosevelt National Park (see Figure III-5). Monitoring sites for hydrogen sulfide were set up at all of these locations except the Elkhorn Ranch locations.

At the Lostwood Wildlife Refuge, data were obtained for the period from December 26, 1985, until January 14, 1991. Throughout the time period the maximum average concentration was 88 ppb, recorded as a 1-hour average in 1990. Overall, this was a site with acceptable air quality with respect to hydrogen sulfide because there were no NDAAQS violations.

In the Theodore Roosevelt National Park system (see Figures III-6 and III-7 for well distribution around the park), data were received by NDSDH&CL for the south unit (obtained at the Painted Canyon Rest Area) from October 17, 1985, to June 30, 1990. The air quality was very good, with no NDAAQS violations. and a maximum half-hour average
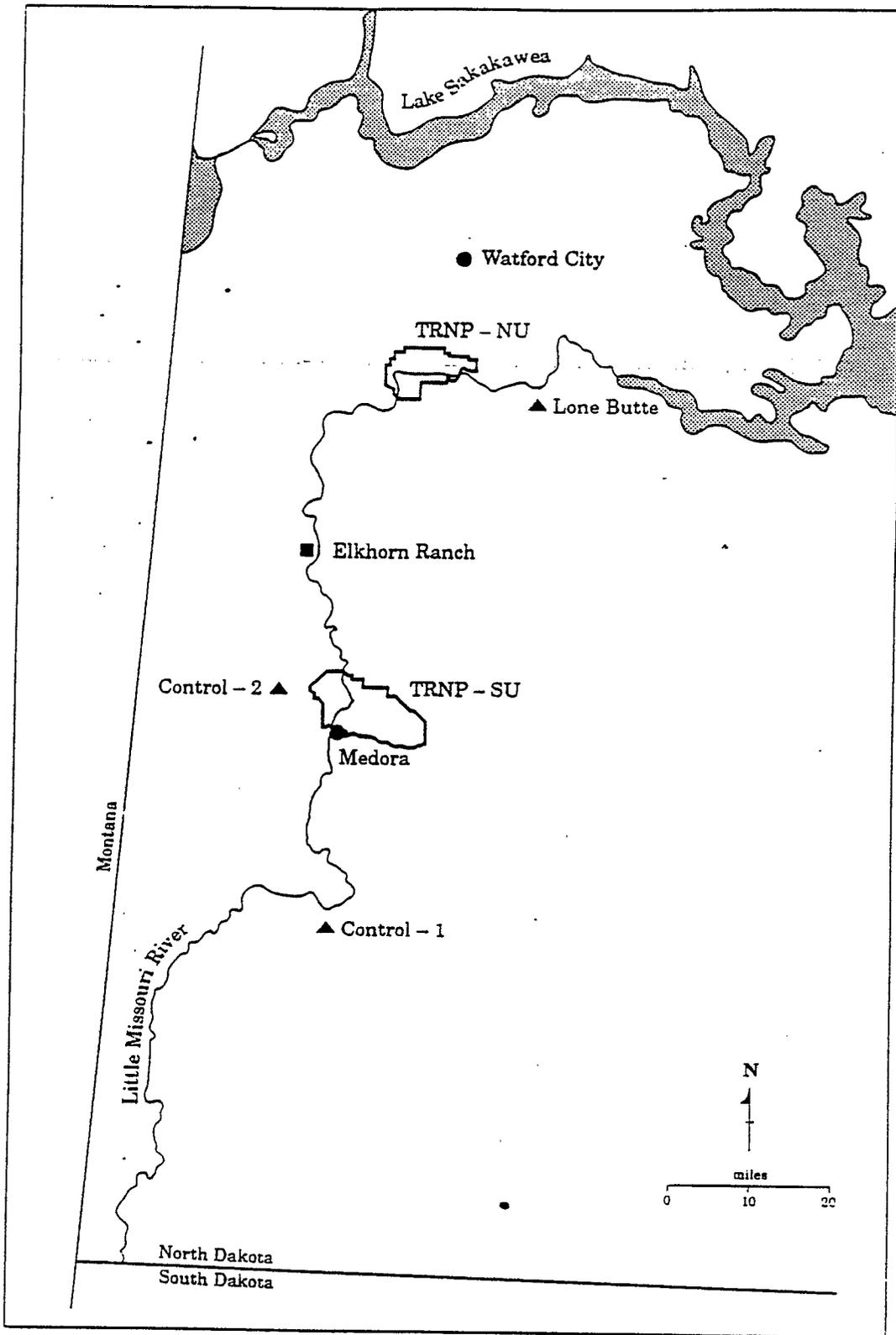
Source: Bilderbeck, 1988.

Figure III-5. Class I and II areas of North Dakota including Lone Butte and
Theodore Roosevelt National Park (TRNP). Bold outlined areas
are Class I; remaining area is Class II.
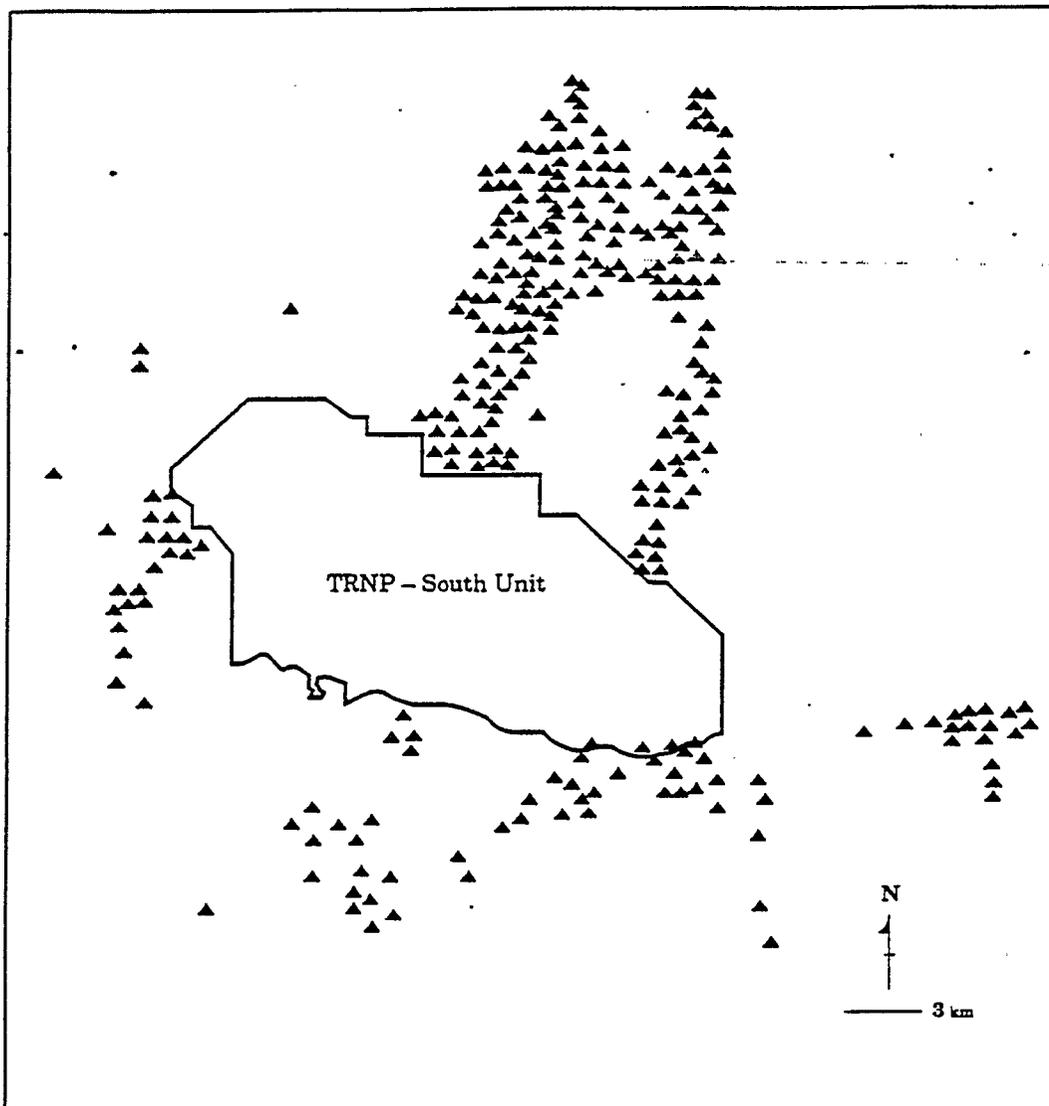
Source: Bilderbeck, 1988.

Figure III-6. Well distribution around Theodore Roosevelt National Park,
South Unit.

TRNP – North Unit

Lone Butte

N

3 km
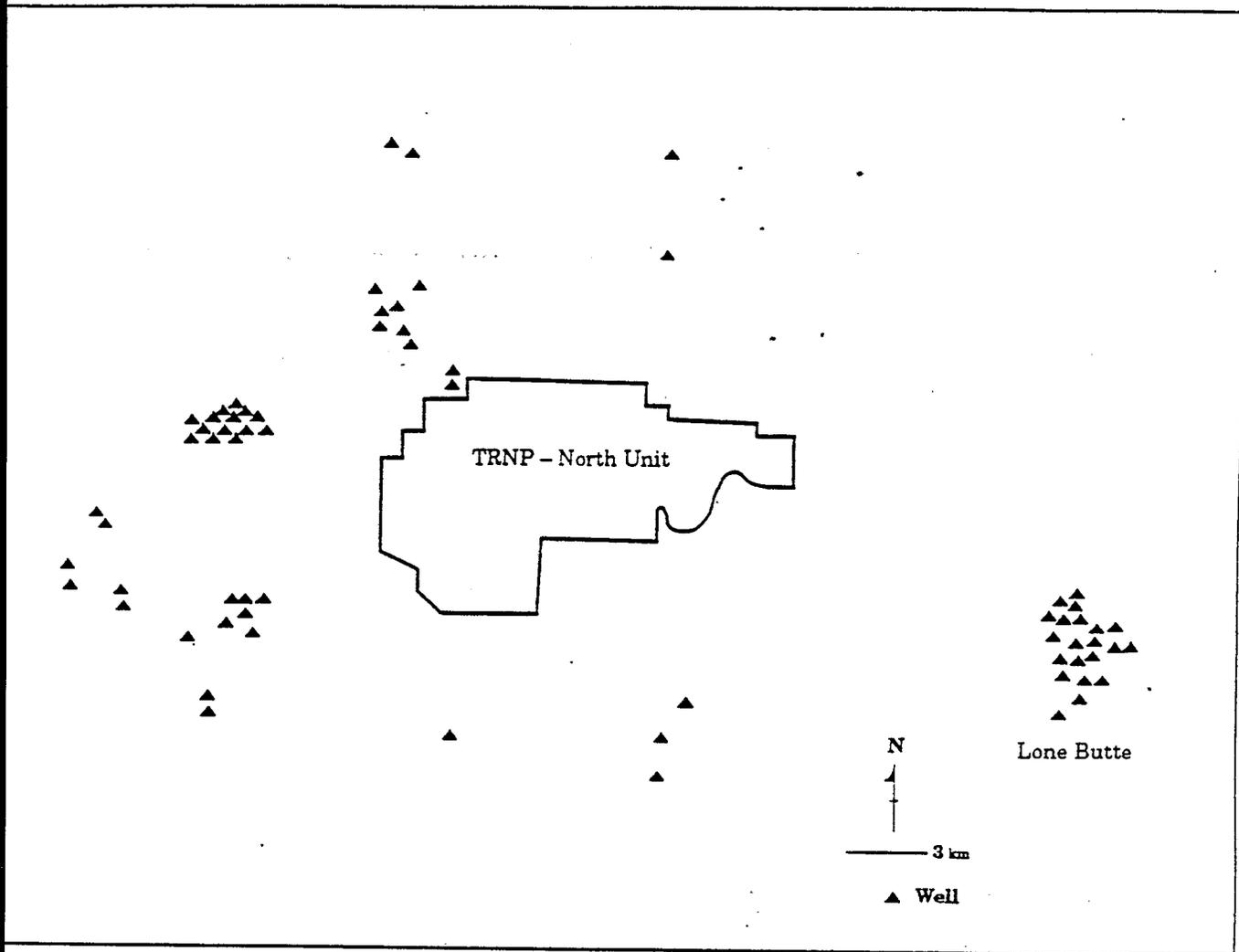
▲ Well

Figure III-7. Well distribution around Theodore Roosevelt National Park, North Unit.

concentration of 18 ppb. The longest period of monitoring data received was from the north unit (recorded in the Little Missouri River Valley), covering the period from April 24, 1980, to August 2, 1992 (1990 data were not received by NDSDH&CL). In the early years, numerous violations of the 1/2-hour, 32 ppb NDAAQS occurred (e.g., 68 in 1982, 62 in 1983, and 70 in 1985). The maximum 1/2 hr time-weighted average concentration recorded during this period was 500 ppb in 1982. Air quality did improve during the second half of the study period, with several years of no NDAAQS violations. This was a result of NDSDH&CL mandated implementation of rigorous operations and maintenance programs by well operators involved in the field and tank vapor collection. Also, expansion of a gas-gathering pipeline network contributed to the decrease in H_2S concentrations because gases were previously released to the atmosphere.

From 1988 to 1990, the Williston Basin Regional Air Quality Study (BLM, 1990) was undertaken as a joint project between North Dakota and the Bureau of Land Management (BLM) to forecast compliance with Federal standards for sulfur dioxide, the resulting product of hydrogen sulfide combustion. Figure III-8 shows the range of concentrations measured at the site. Although over the entire period, 0 ppb was the concentration most frequently recorded, a decrease in air quality is charted, from 1982 through 1987.

Lone Butte. Lone Butte, is located approximately 11 km from the north unit of Theodore Roosevelt National Memorial Park (see Figure III-5). Lone Butte had concentrations of hydrogen sulfide an order of magnitude higher than the other sites. The monitor at Lone Butte (see Figure III-9), in the Little Missouri River Valley near an oil tank battery in the Lone Butte Oil Field, recorded more than 3000 violations of the 1/2-hour average 32 ppb NDAAQS per year from 1984 to 1986. Air quality did improve at the end of the monitoring period, although not to levels continuously below the NDAAQS of 50 ppb which was the standard at that time.

Figures III-10 depicts the range of concentrations measured at the Lone Butte site. Zero ppb is recorded more than 50 percent of the time through the early years, with an improvement towards 80 percent of the time by 1989. (The detection limit of the monitoring equipment was 1 ppb.) The improving trend toward the hydrogen sulfide standard occurred when the NDSDH&CL correlated the sources of the hydrogen sulfide with the ambient monitor levels through the use of the prevailing wind direction. The possibility of NDSDH&CL requiring individual monitoring at each well site convinced the producers to reduce their emissions (personal communication, D. Harman, NDSDH&CL, 8/11/92).

Other Monitoring Sites. Data from thirteen months of monitoring during 1989-1990 were recorded at the Olson farmyard, 1.5 miles from several wells in North Dakota. A maximum 1-hour average concentration of 88 ppb was recorded. Data were also obtained from September 4, 1990, to August 3, 1992, from a monitor in the town of Plaza, North Dakota, within 2 miles of several wells and tank batteries. The maximum concentration recorded on this monitor was 358 ppb, in 1991, with one violation of the NDAAQS recorded.
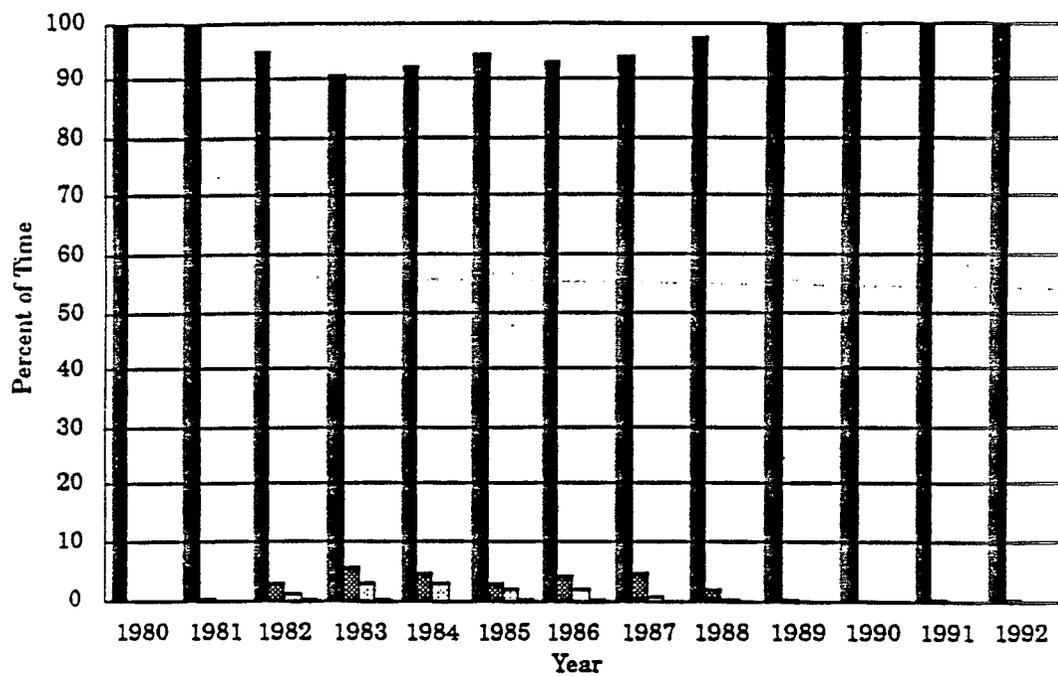
Legend:
- ■ 0 ppb
- ▨ 1-10 ppb
- ▦ 11-50 ppb
- □ >50 ppb

H$_2$S monitor detection limit = 1ppb

Source: Personal correspondence, D. Harman, NDSDH & CL, 8/11/92.

Figure III-8. Percentage of times designated H$_2$S concentrations were measured at the Theodore Roosevelt National Park – North Unit monitoring site.
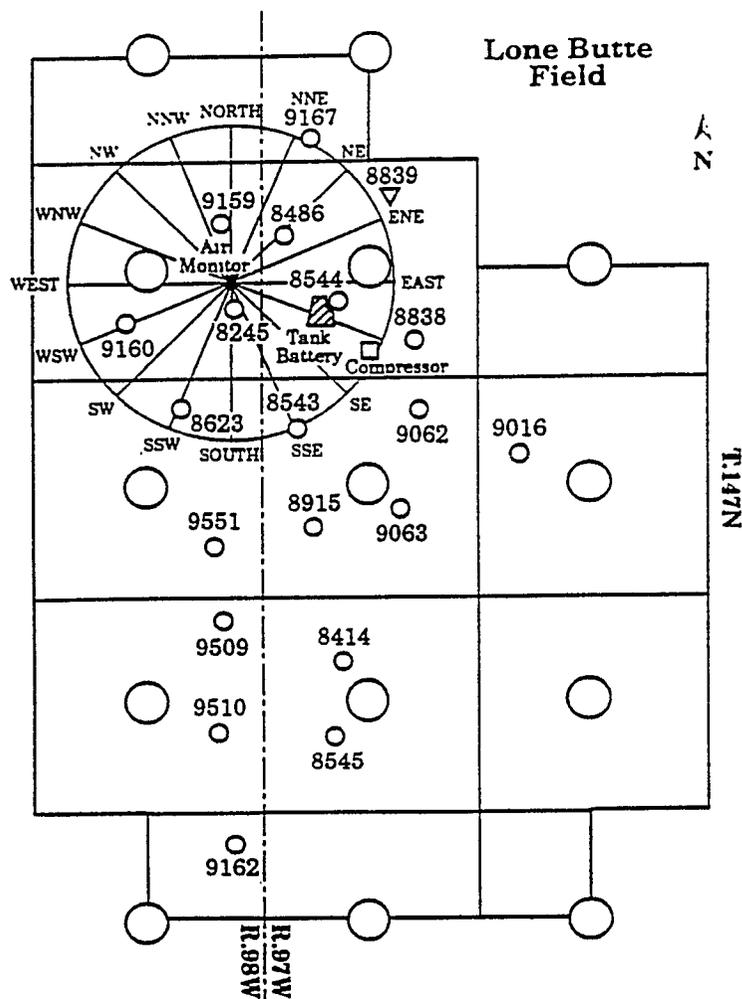
File No.	Operator	Well Name	Well No.
8245	Chevron USA, Inc.	Bob Creek Federal Unit	1-13-3B
8414	Chevron USA, Inc.	Carus Federal	1-30-1C
8486	Apache Corp.	Federal 18	1
8543	Chevron USA, Inc.	Bob Creek Federal Unit	4-19-1D
8544	Chevron USA, Inc.	Bob Creek Federal (Comm)	2-18-48
8545	Chevron USA, Inc.	Carus Federal	2-30-4B
8623	Chevron USA, Inc.	Bob Creek Federal	3-24-2A
8838	Apache Corp.	Carus Amoco Unit "A"	1
8839	Apache Corp.	Carus Amoco Unit "C" (SWD)	1
8915	Apache Corp.	Lone Butte Federal Amoco "A"	1
9016	Apache Corp.	Carus Amoco "B"	1
9062	Apache Corp.	Lone Butte Federal Amoco "B"	1
9063	Apache Corp.	Federal	19-1-
9159	Texaco, Inc.	Bob Creek	13-8
9160	Texaco, Inc.	Bob Creek	13-11
9162	Texaco, Inc.	Bob Creek	36-1
9167	Texaco, Inc.	Bob Creek	7-13
9509	Chevron USA, Inc.	Mormon Butte	5-25-2B
9510	Chevron USA, Inc.	Mormon Butte Federal	3-25-3B
9551	Chevron USA, Inc.	Foley-Stewart Federal	4-25-3C
N/A	North Dakota State Dept. of Health	Air Monitor	
N/A	Koch Hydrocarbon	Compressor Station	
N/A	Chevron USA, Inc.	Tank Battery	

Source: Personal correspondence, D. Harman. NDSDH & CL, 8/11/92.

Figure III-9. Wells producing between July 1986 and December 1987 surrounding Lone Butte H_2S ambient air monitoring site.
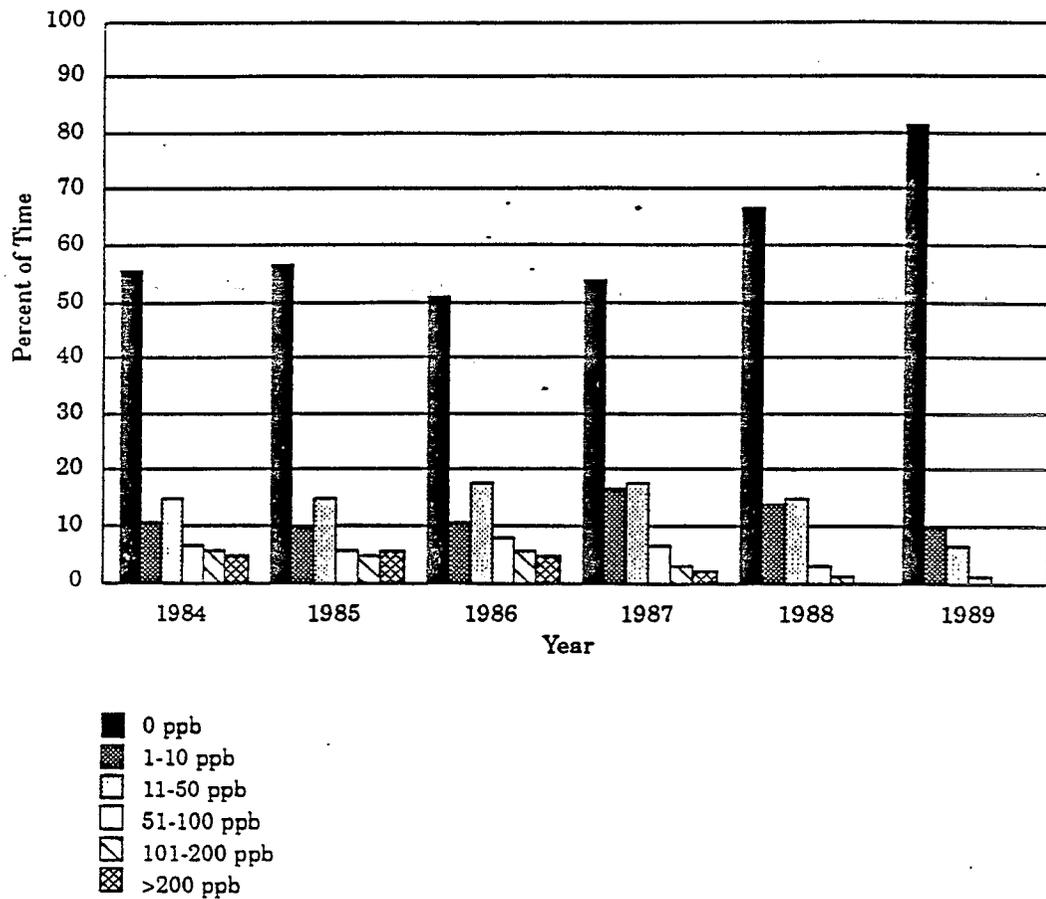
Figure III-10. Percentage of times designated H$_2$S concentrations were measured at the Lone Butte monitoring site.

H$_2$S monitor detection limit = 1ppb

Source: Personal correspondence, D. Harman, NDSDH & CL, 8/11/92.

Only four months of monitoring data from the Roffler site were received by NDSDH&CL. dating from April 11, 1980, to September 29, 1980. Located in a farmyard within 1/2 mile of a well and tank battery, the monitor measured very low concentrations (usually 0 ppb) with a maximum, time-weighted average of 13 ppb recorded. In contrast, at the Jorgenson monitor, the recorded concentration was as high as 250 ppb. The Jorgenson monitor was located in a valley within one mile of several wells, and the data received dated from October 2, 1980, to May 13, 1982. Data from sixteen months of monitoring, from June 30, 1982, to October 31, 1983, were received for the Kadrmas site. Located in a farmyard within a mile of several wells, the maximum half-hour averages recorded were 541 ppb, in 1982, and 353 ppb, in 1983. · From these three studies, an analysis was performed on the monitoring data in comparison to the 32 ppb half-hour standard. The results showed that the concentration of hydrogen sulfide never exceeded the NDAAQS during the four months of the Roffler study. Conversely, at the Jorgenson site, the 32 ppb standard was violated 16 times in 1980, 38 times in 1981, and 26 times in 1982. At the Kadrmas site, the violation count was 18 times in 1982 and 14 times in 1983.

<u>Williston Basin Study</u>. The Williston Basin Regional Air Quality Study was undertaken in the late 1980s to assess the air quality impact of oil and gas production in western North Dakota (BLM, 1990). Emissions inventories were prepared and air quality models were applied to project the impact of sulfur dioxide and hydrogen sulfide emissions in these 12 selected oil fields with respect to applicable ambient air quality standards and PSD increments. Study results suggested that exceedances of both sulfur dioxide and hydrogen sulfide ambient air quality standards could be expected for some fields. Exceedances of Class I PSD increments for sulfur dioxide were expected for three of the four Class I areas studied. Further development of the oil and gas fields, where the emissions of sulfur dioxide and hydrogen sulfide would be possible, would not be permitted unless these exceedances were addressed.

To arrive at estimated hydrogen sulfide concentrations for the study, two types of hydrogen sulfide emissions were considered. First a hydrogen sulfide concentration was obtained through back calculation of the output sulfur dioxide concentrations from the Industrial Source Complex Model. The predicted sulfur dioxide concentrations were the result of modeled dispersion of the point source emissions from heater-treaters firing on H_2S contaminated wellhead gas and from flares which burn H_2S contaminated wellhead gas when a gas gathering pipeline is not available. To provide conservative results, combustion efficiency of 75 percent was used in these calculations, meaning that 25 percent of the hydrogen sulfide remained unchanged. [Note: As stated in Chapter II, flares, in most applications, operate at 95 to 99 percent efficiency.] The second emission source used represented fugitive emissions from leaky valves, tank hatches or pipe connections. These fugitive sources were estimated as contributing a background concentration of 7 $\mu g/m^3$ (50 ppb), derived from the 99th percentile of the 1-hr average monitored ambient air concentrations at three remote monitor locations (the Theodore Roosevelt National Park's two sites and the Lostwood site) during portions of 1987 and 1988.

At the time of the study, the NDAAQS for H_2S was 50 ppb 1-hour average concentration not to be exceeded more than once a year. NDAAQS exceedances were predicted for 6 of the 12 fields studied using current emissions estimates, with exceedances predicted for 7 of the 12 fields using future emissions estimates. Of the sites where modeling suggested NDAAQS exceedances, the yearly second highest (the first occurrence of ambient hydrogen sulfide concentrations above 50 ppb would be allowed by the law) expected concentrations exceeded 700 ppb for the Lost Bridge Field and 900 ppb for the Rough Rider Field.

Modeling results are only an estimate and are often considered accurate when they are within a factor of two of the actual ambient concentrations. Except for the Lone Butte Field, ambient monitoring data were not available for the other fields to verify or contradict the modeled estimates.

Conclusions. At several locations, for example, Lostwood and the Theodore Roosevelt-south unit, the monitoring program served as a verification that the air quality was within the levels allowed by the law. In two cases, the monitoring programs were of too short of a duration to support any conclusions. When an area is monitored for a short period of time, as at the Roffler and Olson sites, the full range of meteorological conditions and emissions scenarios are not represented in the ambient air measurements. Monitoring was discontinued at Jorgenson and Kadrmas (both monitored in the early 1980s) and at Lone Butte (the site with the worst air quality) even though numerous NDAAQS violations were experienced during their last monitored year. This occurred because rigorous inspection and maintenance scheduling was established and/or the data indicated no air quality problems existed (personal communication, D. Harman, NDSDH&CL, 11/9/92).

Ambient concentrations of hydrogen sulfide varied for the sites, with maximum yearly concentrations ranging from half-hour averages, below the 1 ppb detection limit, to 2734 ppb (2.734×10^3 ppb). Two common factors were the median and mode values. For all of the monitoring data received from North Dakota, the median and mode values were 0 ppb. In other words, for each site more than half of all observations recorded below the 1 ppb monitor detection limit.

Severity of Consequences. No epidemiological studies have been carried out to assess the effects of hydrogen sulfide exposure resulting from the production of oil and gas. Many States have enacted ambient air quality standards based upon odor for hydrogen sulfide, since its odor recognition threshold is so low (i.e., 3 to 20 ppb).

Annual average H_2S concentrations, which can more appropriately be compared to a long-term concentration benchmark such as the RfC, were also calculated from the Lone Butte site. These values exceeded the RfC by about an order of magnitude from 1984-1987, dropping to about the RfC level in 1988 and 1989. Since these values indicate the combined impacts of 9 separate wells, it is reasonable to conclude that: 1) the long-term impact of routine releases from any individual well is probably not significantly greater than the RfC;

and 2) the use of a gas-collection system with manifolded flares and rigorous operation and maintenance programs can significantly reduce long-term H_2S impacts.

At low concentrations, odor nuisance and eye and respiratory tract irritation are the consequences of exposure rather than the toxic properties of the gas. An explanation for an increased perception of ill health could be related to low level exposure to hydrogen sulfide and pulmonary infections. A study by Rogers and Ferin (1981) concluded that hydrogen sulfide significantly affected the antibacterial system of rats by impairing pulmonary macrophage. However, additional research would be required before any definitive judgements could be made in human exposure scenarios.

Elevated ambient concentrations in two episodes (one in the Great Kanawha River Valley, WV, in 1950, and one in Terre Haute, IN, in 1964) were reported as 0.41 mg/m³ (293 ppb) and 0.46 mg/m³ (329 ppb), respectively (West Virginia Department of Health, 1952; U.S. Public Health Service, 1964). These incidents did not result from oil and gas production; however, the ambient concentrations recorded were comparable to some measurements in North Dakota. General symptoms of malaise, irritability, headache, insomnia, and nausea were reported by exposed populations. In the Terre Haute incident, levels measured at a nearby lagoon ranged from 2×10^3 to 8×10^3 ppb). The most common symptoms reported were offensive odor, foul-tasting water, nausea, vomiting, diarrhea, throat irritation, shortness of breath, burning eyes and asthma. Milder symptoms included cough, headache, anorexia, acute asthma attacks, nervousness, weight loss, fever, gagging and heaviness of chest. The symptoms ceased when the odor disappeared. In an episode in Alton, IL in 1973 similar symptoms were reported (Illinois Institute for Environmental Quality, 1974; NRC, 1979). Ambient hydrogen sulfide levels ranged from 25 ppb to higher than 1×10^3 ppb. Other contaminants, such as ozone and nitrogen oxides were also detected during this episode (Hoyle, 1973).

A study of the levels of sulfur compounds in vegetation near the Lone Butte oilfield and Theodore Roosevelt National Park, was conducted during the summer of 1987 (Bilderback, 1988). The study's conclusions confirmed what ambient monitoring had suggested: the South Unit of the national park may have been impacted by moderately high levels of atmospheric sulfur pollution, and the Lone Butte oil field was impacted by high levels of reactive atmospheric sulfur. Visible signs of vegetation damage were also detected at the Lone Butte oilfield. Furthermore, Bilderback attributes the elevated levels of hydrogen sulfide at the North Unit of the Park to the Lone Butte oilfield.

Consequence Analysis — Routine Emissions

As described in Chapter II, several potential sources of routine H_2S emissions can be found at oil and gas production facilities. Figures III-11 and III-12 indicate that 8 States have a significant overlaps of well fields and H_2S prone areas. Using the estimated number of producing wells in these States (Figure III-12) as a conservative measure, it appears that as many as 280.000 oil wells and 54,000 gas wells have the potential for location in an H_2S
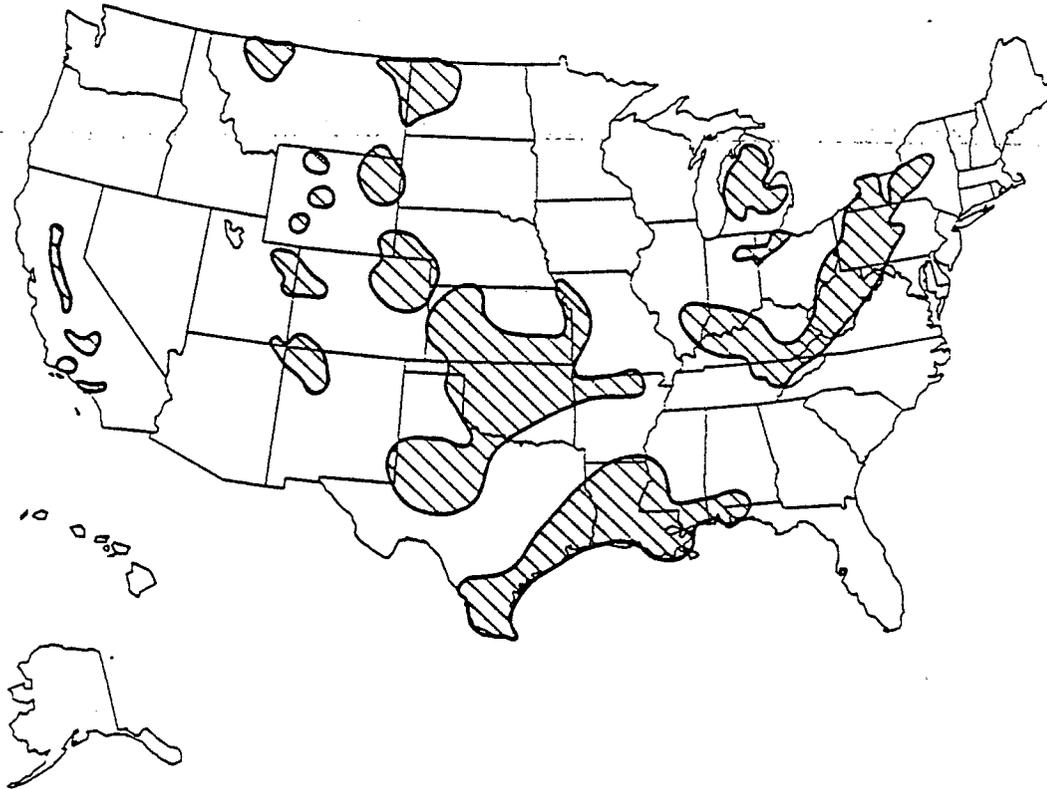
Figure III-11. Oil and gas fields.

Legend: # Oil wells / # Gas wells

Federal Waters $\frac{4868}{3591}$

Other $\frac{25}{147}$

US Total $\frac{601,520}{268,367}$

N/A = Data not available
0 = No wells registered in State
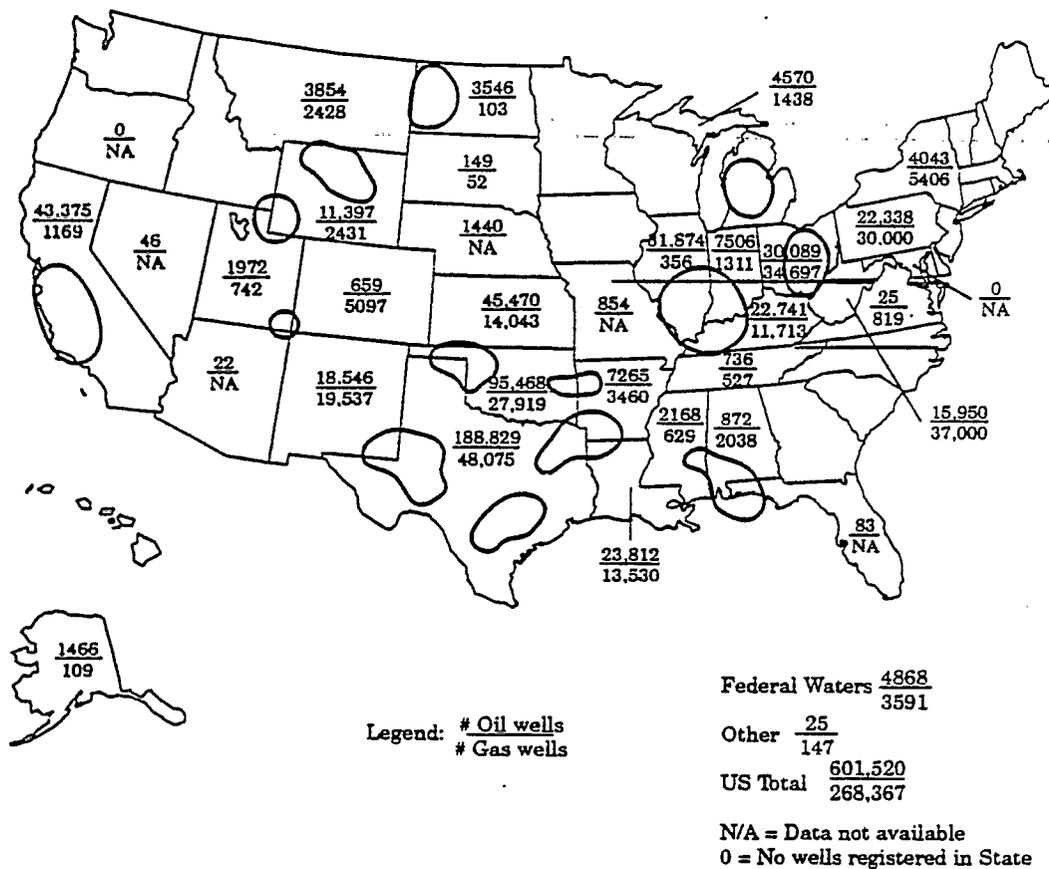
Source: Gas Research Institute, 1990.

Figure III-12. Major H$_2$S prone areas shown in relation to number of producing oil and gas wells in 1990.

prone area. Although only a fraction of these wells would actually be sour, these figures imply that the potential for routine H_2S emissions is significant. However, no national statistics are available to predict the probability of such emissions. The only record of routine emissions identified is ambient air quality monitoring data from the State of North Dakota. Nine monitoring studies in 12 years resulted in more than 3,300 violations of the NDAAQS. The majority of these violations occurred when the standard was developed based on the more conservative odor threshold rather than on health considerations. Only one violation was recorded after the health-based (higher concentration limits) standards were implemented.

A routine emission scenario would be the incomplete combustion of the wellhead gases, allowing some percentage of the hydrogen sulfide to be emitted. In the oilfields of North Dakota, the concentration of hydrogen sulfide in waste gas stream to flares can reach 30 percent, with the conversion efficiencies of the flaring operations varying from 30 to 100 percent (NDSDH&CL, 1983). (Note, however, that in Chapter II, the common efficiency of a flare, regardless of industrial application is 95-99 percent.) This scenerio would result in releases of 0 to 70 percent of the hydrogen sulfide contained in the wellhead gas. In western North Dakota, the amount of natural gas flared exceeded 1 million cubic feet per month in mid-1982, dropping to less than half of that amount by mid-1985, as more wells were tied into a central gas collection system (Liebsch, 1985). As a worst case scenario, if the gas content were 30 percent hydrogen sulfide, and the combustion efficiency were 30 percent (70 percent of the hydrogen sulfide was emitted unconverted), 210,000 cubic feet of hydrogen sulfide per month could have been routinely emitted in the mid-1982 time period.

No H_2S health or ecological effects studies have been conducted which specifically target oil and gas production. The most common consequences of exposure to routine emissions of H_2S are the odor nuisance and eye and respiratory tract irritation.

Exposure Analysis—Accidental Releases

The discussion of accidental releases begins with a description of examples of accidental releases of sour oil and gas in the United States that have impacted the public and wildlife. These examples are then supplemented by calculations of the consequences of a series of hypothetical accident scenarios using atmospheric dispersion models. The risk to the public from an accidental release of H_2S is a function of both the potential consequences and the likelihood of occurrence of an accidental release. Risks from a major accidental H_2S release will vary from facility to facility depending on site-specific factors such as the population density and distribution of nearby populations and the quality of process safety management and risk management practiced at the facility. Since risk is a product of both consequences and likelihood, risk reduction must take both into account. The accidental release discussion concludes with an assessment of accident prevention, mitigation, and emergency procedure measures that, if systematically implemented, could help to prevent or reduce the likelihood of accidental releases of H_2S from sour oil and gas, and mitigate the

consequences in the event that a release occurs. Supporting details for the atmospheric dispersion calculations may be found in Appendix C.

Accidental Release Records

A variety of sources were investigated to locate documentation of accidental sour gas releases. These sources include: Congressional testimony; literature searches; database searches; state regulatory authorities; emergency response organizations; and industry officials. No national statistics regarding sour oil or gas releases were identified. Data base sources were the Accidental Release Information Program (ARIP) database which is maintained by the EPA, the Acute Hazardous Events (AHE) database which was developed by EPA, and the Emergency Response Notification System (ERNS) database. ARIP has records of chemical accidental releases that have occurred since October 1986 with some detailed information on accident cause. AHE has incident records covering the time period 1982 to 1986 and was developed from various sources including press reports, spill reports to the National Response Center, and some state and EPA regional office records. ERNS contains records of releases reported to the National Response Center.

A review of available sources revealed several documented examples of incidents in oil and gas extraction operations in the United States where accidental releases of H_2S have impacted the public and/or the environment since 1974. There was also a very large sour gas release that caused some environmental damage in Alberta, Canada during this time period. Examples of some of these accidents are summarized in Table III-4. It should be noted that these incidents include two accidents related to carbon dioxide injection to improve recovery rather than from the accidental releases of sour natural gas. One of these accidents resulted in eight fatalities, and another accident resulted in two injuries. The other incident resulting in fatalities was the result of fire associated with a natural gas release. However, effects on the public that are directly related to oil and gas extraction activities have most often been limited to evacuation. Isolated incidents resulting in hospital treatment have also occurred. Evacuation may occur as a conservative measure whether or not a life-threatening situation exists. There have been several documented incidents involving livestock and wildlife fatalities. In addition to toxicity, the flammability of accidental releases of sour oil and gas may also present a significant hazard.

Information from the State of Texas shows that there were 145 incidents of sour oil and gas release during the years 1985 through 1992 (Hall, 1992). These accidents were generally related to sour oil and gas rather than specifically from extraction activities. In these incidents, there were 10 deaths (all occupational), and 109 injuries (100 occupational and 9 public). The Texas incidents may be illustrative of the relative hazard to operating personnel, the general public, and the environment. These statistics indicate that the major hazard from oil and gas operations involving H_2S would be to workers rather than the public or wildlife. Workers are more often in close proximity to the wells and associated equipment.

Table III-4. Examples of Accidental Releases of H_2S from Oil and Gas Extraction Operations with Impact on the Public or Environment

Date and Location	Effects on Public	Effects on Environment	Comments	Source
5/21/74 Meridian, MS	5 deaths due to associated fire	40 acres burned	Sour gas gathering pipeline rupture and subsequent fire	Texas Oil and Gas Pipeline Corporation, 1976
2/2/75 Denver City, TX	8 occupants of house 200 ft from well were overcome by the gas and died.	None identified	Gas escaped from gas injection well. Gas was 93 v/o CO_2 and 5 v/o H_2S.	Layton et al., 1983
5/21/81 Big Piney, WY	No impact on public	Deaths of some jackrabbits and blackbirds	Well blowout lasting 8 days. Nearest residence was 2 miles away	Layton et al., 1983
10/7/82 Calgary, Canada	No impact on public	A number of moose and other large animals died	Release of 10 million ft³ H_2S per day of accident	Oil Daily, 1982
/88 Lea County, NM	1 person physically incapacitated	1 horse died	An individual changing a tire was overcome with H_2S	Correspondence NM Oil Conservation Division, 1992
/20/89 Scurry County, TX	Evacuation of nearby residents, 2 treated at hospital	None identified	CO_2 injection line rupture	Texas Railroad Commision Hall, 93
/20/90 Laplata County, CO	2 mile radius evacuated	None identified	Well leak	ERNS, National Response Center Report #01425
/29/90 Heidelberg, MS	No deaths but 2,000 local residents were evacuated	None identified	Well blowout and consequent fire	Platt's Oilgram News, 1990
16/91 Lambert, MT	12 people were evacuated	None identified	Incident was caused by corrosion of gathering line. Evacuation due to smell.	National Response Center
19/91 Yoakum County, TX	None identified	7 cows, 1 coyote, and rabbits died	Sour gas gathering line rupture, 1.2% H_2S	Texas Railroad Commision Hall, 93
2/17/91 Gaines County, TX	None identified	Unspecified number of wildlife died	Sour gas gathering line rupture, approximately 6% H_2S	Texas Railroad Commision Hall, 93

Atmospheric Dispersion Analysis

Atmospheric dispersion analyses of sour oil and gas releases by computer model were both reviewed in the literature and conducted. The following issues are discussed prior to analyses of the consequences of sour gas release scenarios:

- Choice of scenarios;
- Sour gas composition and density;
- Behavior of sour gas upon release; and
- Choice of atmospheric dispersion models.

Choice of Scenarios. The objective in choosing scenarios was to investigate a representative range of potential accidental release situations including hypothetical worst case scenarios. Scenarios for atmospheric dispersion analysis were chosen from documented accidental releases, expressions of public concern, and literature analyses in which dispersion models were applied to sour gas release scenarios.

The accidental sour gas releases documented in the previous section show some common causes. Well blowouts and line releases are examples of accidents that have occurred and resulted in offsite impact. Therefore, these accident scenarios were included in the atmospheric dispersion analyses. Investigation of some public complaints resulted in concerns regarding sour gas releases from extinguished flares, collection of sour gas in low-lying areas, leakage from temporarily abandoned or idle wells, and line leakage (NDSDH&CL, 1989; U.S. EPA, 1992). These concerns were also investigated as accidental release scenarios.

Several literature sources provided descriptions of hazards associated with the operation of sour oil and gas wells in addition to sour gas dispersion analysis to support scenario development. Hazard/risk analyses and data on the composition of sour gas of wells in Alberta, Canada (Alp et al., 1990), southwest Wyoming and northern Utah (Quest, 1992), and western Wyoming and adjoining areas of Utah and Idaho (Layton et al., 1983) were considered in the choice of scenarios. Assessments of levels of concern (LOC), concentrations at which H_2S is of concern, for acute exposure to H_2S were also provided in these sources. Although H_2S alone is more dense than air, in general, the literature pertains to sour gas mixtures that are typically less dense than air and concludes that sour gas releases from well blowouts and line ruptures are of most concern as potential causes for levels of concern to extend significant distances from the point of release.

Sour Gas Composition and Density. The density of sour gas mixtures is of importance because it is one determinant of whether an accidental release will result in a plume that travels downwind at ground level or will result in a buoyant plume that rises and disperses. A dense plume may have a greater impact on humans and wildlife because it remains at ground level for a period of time. The density of sour gas mixtures at atmospheric pressure (to which accidental releases of sour gas are discharged) is dependent

on the temperature and composition of the mixture. The density of a given gas mixture increases as temperature decreases. Expansion of natural gas released from a pressurized system results in cooling of the gas. The colder a gas, the higher its density.

There is a wide variety of potential compositions of sour gas mixtures, depending on the reservoir. The density of these mixtures depends on their composition. In addition to hydrogen sulfide, natural gas can also contain some or all of the following: hydrogen, helium, carbon dioxide, nitrogen, methane, ethane, propane, isobutane, n-butane, isopentane, n-pentane, hexanes, heptanes, and higher molecular weight hydrocarbons. The largest component is typically methane, with hydrogen sulfide, ethane and possibly carbon dioxide (CO_2) likely to be present in significant proportions. Natural gas must contain some proportion of hydrogen sulfide in order to be considered sour.

Figure III-13 illustrates the variability of sour gas composition by showing the distribution of H_2S composition by number of sour gas wells in Alberta, Canada (Alp et al., 1990). Figure III-14 presents the same information as a function of the total number of tons of sulfur from natural gas produced each year. The H_2S composition can range from a small fraction of a percent to over 40 percent. A statistical analysis was performed of the sulfur composition of wells in the Overthrust Belt in western Wyoming and adjoining areas of Idaho and Utah (Layton et al., 1983). Volume percentages of sulfur were found similar to those in the Alberta wells. The sulfur composition ranged from less than 1 percent through 35 percent, with a mean of about 10 percent. Data on H_2S in California oil and gas fields shows fields with H_2S concentrations varying from less than 1×10^5 ppb (0.01 percent) to 20 - 30 percent (Dosch and Hodgson, 1986).

In addition to increasing the density of a sour gas mixture, carbon dioxide in sufficiently large concentrations can extinguish sour gas flares, resulting in uncombusted H_2S being released. CO_2 concentrations in various parts of the Overthrust Belt were found to vary from less than 5 percent by volume to more than 50 percent (Layton et al., 1983).

Some example sour gas compositions are presented in Table III-5. Composition D is the single composition considered representative of all the data on producing gas wells in Alberta, Canada. Composition C is a representative gas composition produced by wells in a southwestern Wyoming sour gas field (Quest, 1992). Data were collected for a producing well in western North Dakota (U.S. EPA correspondence, 26 October 1992), and the compositions of streams after processing to recover hydrocarbon condensate at that well are given by compositions A and B of Table III-5. Composition A shows the gas composition after high pressure separation, and Composition B shows the composition after low pressure separation. The low pressure stream has a significantly higher H_2S concentration than the high pressure stream although its flowrate is lower.

H_2S alone is more dense than air, while methane alone is less dense than air. Natural gas mixtures of H_2S and light hydrocarbons are typically less dense than air to the extent that methane predominates in the mixture. The approximate molecular weight of air is 29. The

Legend:
- 0% to 5%
- 5% to 20%
- 20% to 40%
- > 40%

Y-axis: Volume ($10^6 \, m^3$)
X-axis: Year
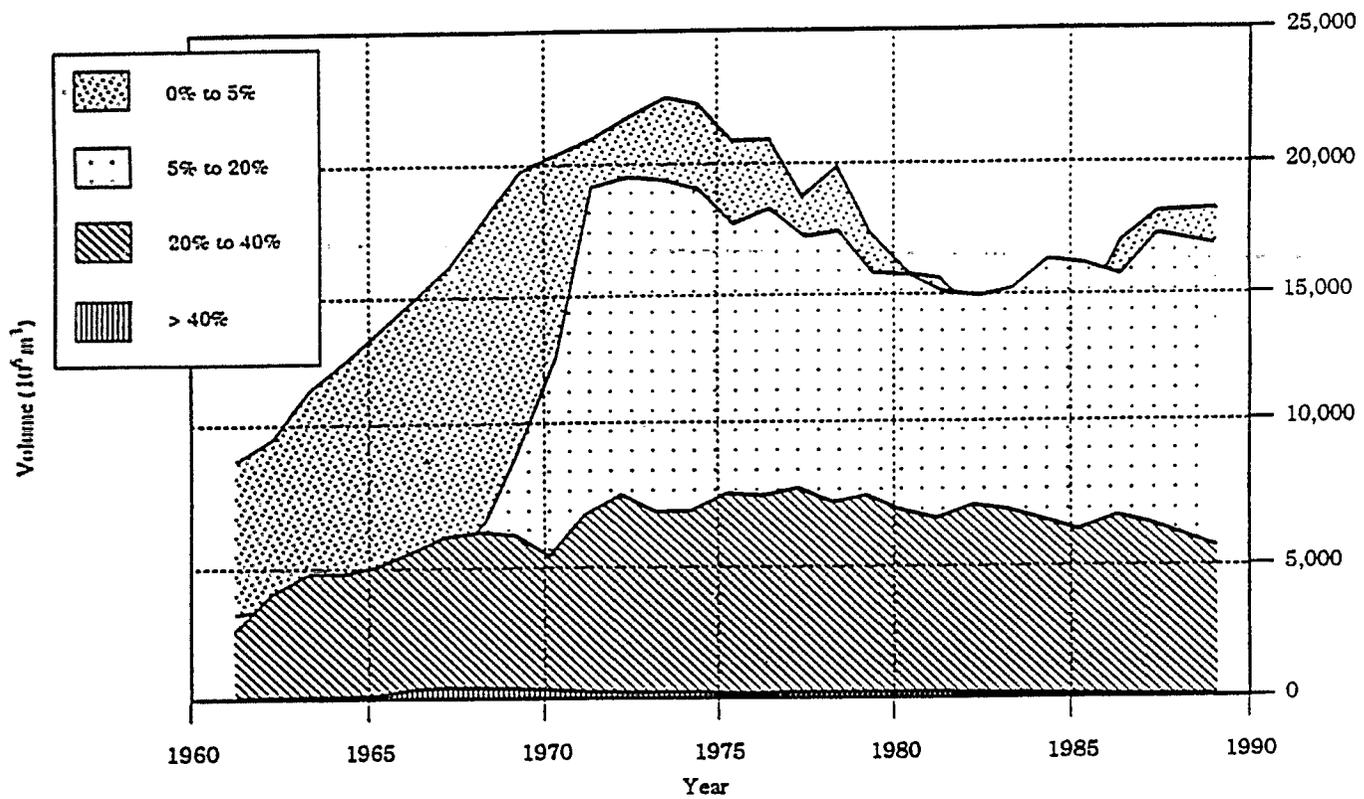
Source: Alp et al., 1990.

Figure III-13. Distribution of producing sour gas wells in Alberta by H_2S content.
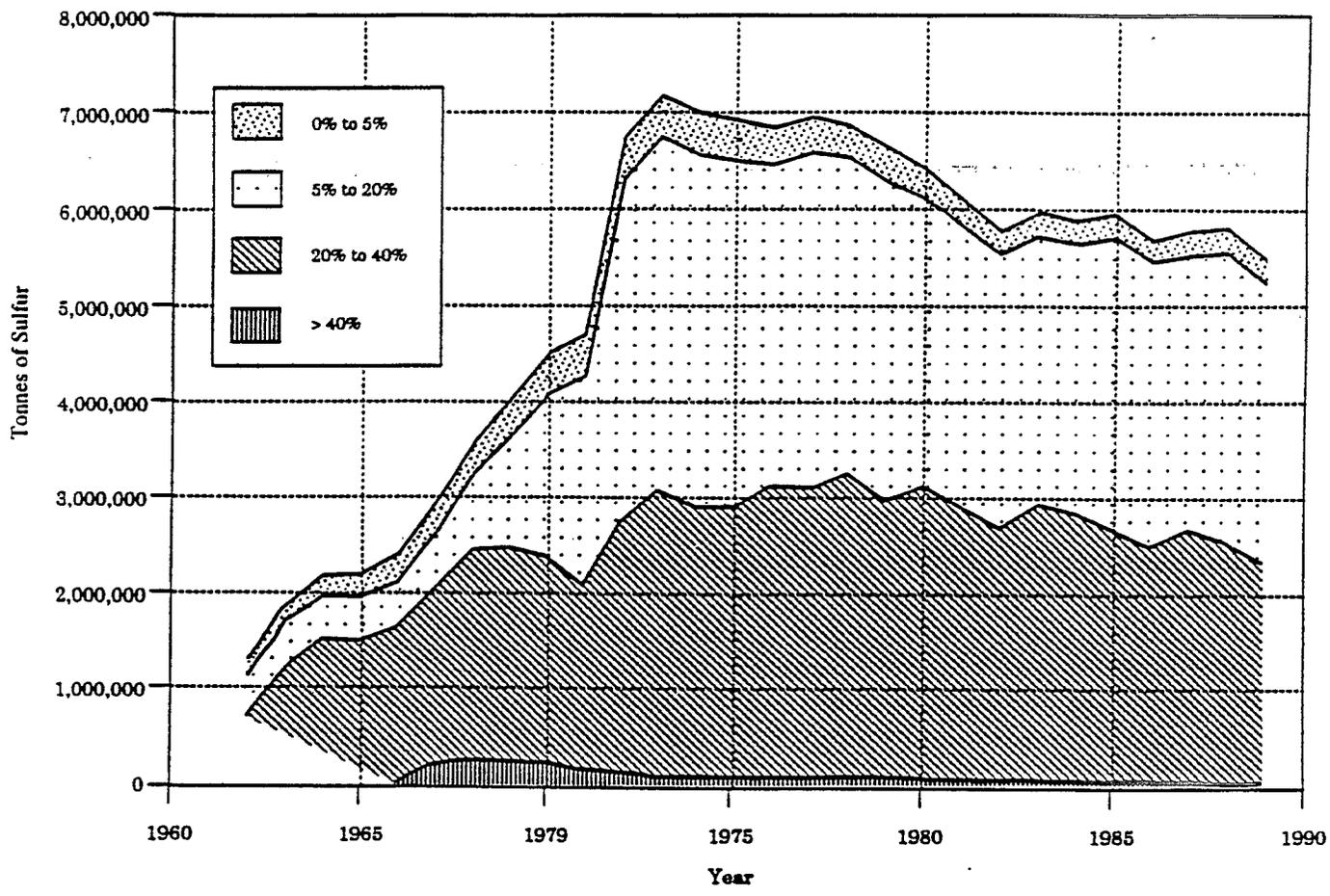
Source: Alp et al., 1990.

Figure III-14. Total sulfur generated from producing gas wells
in Alberta by H$_2$S composition of well.

Table III-5. Example Gas Stream Compositions

		Mole Fraction			
		Sample Well		Composition Used in Cave Creek Risk Assessment (C)	Composition Used by ECRB (D)
Component	Molecular Weight	High Pressure (A) (well flow)	Low Pressure (B) (vapor recovery systems)		
drogen Sulfide (H_2S)	34	0.075	0.277	0.146	0.30
rbon Dioxide (CO_2)	44	0.01	0.013	0.027	0.123
trogen (N_2)	28	0.003	-	0.017	0.02
thane (CH_4)	16	0.83	0.45	0.699	0.55
hane (C_2H_6)	30	0.047	0.10	0.058	0.005
opane (C_3H_8)	44	0.012	0.064	0.018	0.001
utane (C_4H_{10})	58	0.0032	0.024	0.0042	0.001
Butane (C_4H_{10})	58	0.0038	0.026	0.0050	—
entane (C_5H_{12})	72	0.0016	0.011	0.0022	—
Pentane (C_5H_{12})	72	0.0020	0.0086	0.0018	—
xanes (C_6H_{14})	86 }	0.0034	0.019	0.0031	
ptanes+ (C_7H_{16})	100+ }			0.0176	
erage Molecular Weight		19.25	28.9	23.2	25.2

two composite compositions and the high pressure stream shown in Table III-5 have molecular weights less than 29. Thus, these streams are less dense than air at the same temperature and pressure. CO_2 is also more dense than air at similar conditions and may cause the density of a gas mixture to be higher than that of air if present in large concentrations. The low pressure stream has a molecular weight very close to that of air and with some modification in composition, such as more H_2S or CO_2 and less methane, could be more dense than air.

Gas mixtures which are denser than air due to high concentrations of CO_2 have caused fatalities as described in the discussion of release histories. A well blowout near Big Piney, Wyoming, on June 21, 1981, killed small animals up to about 0.8 km from the well (Alp et al., 1990) The gaseous emissions from the well were composed of 70 percent CO_2, 20 percent methane and 3 to 4 percent H_2S. It is not clear that H_2S caused the animal fatalities in this case. However, these emissions were clearly denser than air. The literature generally describes mixtures that are less dense than air; the studies of hazards/risks associated with sour gas (Alp et al., 1990; Quest, 1992) referred to in this report used gas compositions that are buoyant.

In conclusion, sour gas as produced is typically buoyant. There can be atypical cases where natural gas contains high concentrations of H_2S and/or CO_2 which results in a denser-than-air mixture. Also, gas processing such as separation for condensate (liquid hydrocarbon) recovery at the well site may affect the density of a gas stream.

Behavior of Sour Gas Upon Release. High pressure sour gas releases from well blowouts and line ruptures are initially high momentum jets which can vary directionally between the extremes of vertical and horizontal. The jet (high velocity) nature of such releases is caused by the differential pressure between the contained gas and the atmosphere and results in entrainment of the surrounding air into the released gas. Entrainment of air results in dilution of the released gas and causes its density to approach that of air. Thus, as air is entrained, both positively and negatively buoyant gas mixtures with air will tend to have densities approaching that of air. A high velocity jet (such as from a high pressure source) will entrain air more rapidly and to a greater extent than a low velocity jet from a low pressure source. Depending on the release conditions, it is possible for a gas mixture to retain its initial positive or negative buoyancy. Negative buoyancy releases are of greatest concern because of dense gas behavior and their tendency to travel to ground level where exposure is likely to occur.

As previously discussed, the effective molecular weight (and thus, the density) of sour gas mixtures as produced is generally less than that of air with isolated exceptions. Therefore, models for these cases should consider the various mechanisms that describe the near-field (near the point of release) and far-field (downwind) behavior of the plume of released gas and its interaction with the surrounding air. In particular, the models should contain mechanisms for simulation of the following sequence of effects occurring along a plume of released gas from the point of release: a) near-field momentum jet modeling; b)

subsequent positively-buoyant rise or negatively-buoyant sinking; c) potential for a nominally buoyant plume that is initially on the ground to rise or, if negatively-buoyant, to stay at ground level; and d) far-field transition to a subsequent Gaussian (passive modeling) phase. The Gaussian or passive phase assumes random mixing in the far-field due to the action of atmospheric turbulence; whereas, close to the source, entrainment of air is affected or sometimes dominated by the released material itself.

Choice of Atmospheric Dispersion Models. The models reviewed in the literature for analysis of the dispersion characteristics of sour gas were GASCON2, FOCUS, and a Gaussian dispersion model. Confirmatory, independent atmospheric dispersion analyses were conducted for most of the scenarios with the SAPLUME, SLAB, and DEGADIS models.

The computer model GASCON2 was specifically developed in Canada to model sour gas releases from well blowouts and line ruptures (Alp et al., 1990). The model incorporates high pressure gas jet releases, plume rise or sinking (depending on density) and subsequent passive atmospheric dispersion. GASCON2 was validated by comparison with experiment. The associated literature also contains extensive discussions on uncertainties and the work was reviewed by a science advisory board.

The proprietary model, FOCUS, contains a treatment of momentum and buoyancy effects and transition to subsequent passive atmospheric dispersion (Quest, 1992). The model has been available for several years and has been used in a number of risk assessments of toxic and flammable vapors.

The Gaussian dispersion model is suitable for passive releases (Layton et al., 1983). Therefore, jet momentum effects are neglected and the results are not expected to be reliable close to the emission source. However, at large distances where low concentrations of H_2S would result (e.g., in the low part per million range), all three of the above models should converge to similar results.

A well-established model developed by Ooms (1974, 1983) for jet releases of vapors can model the dispersion of both buoyant and heavier-than-air momentum jets. The EPA has sponsored the incorporation of the Ooms model into the well-known DEGADIS model (Spicer, 1988), which can only simulate vertical, but not horizontal releases. Another proprietary model, SAPLUME, is also based on the Ooms model and can simulate jets at any orientation (SAIC, 1990).

SLAB was developed by Lawrence Livermore National Laboratory (Ermak, 1989). This computer model also accepts jets of vertical or horizontal orientation. However, it was specifically developed for heavy vapors and has not been carefully validated for use with buoyant plumes, so results must be interpreted with care.

Consequence Analysis — Accidental Releases

In the following sections, the consequences of accidental releases for a variety of scenarios are presented.
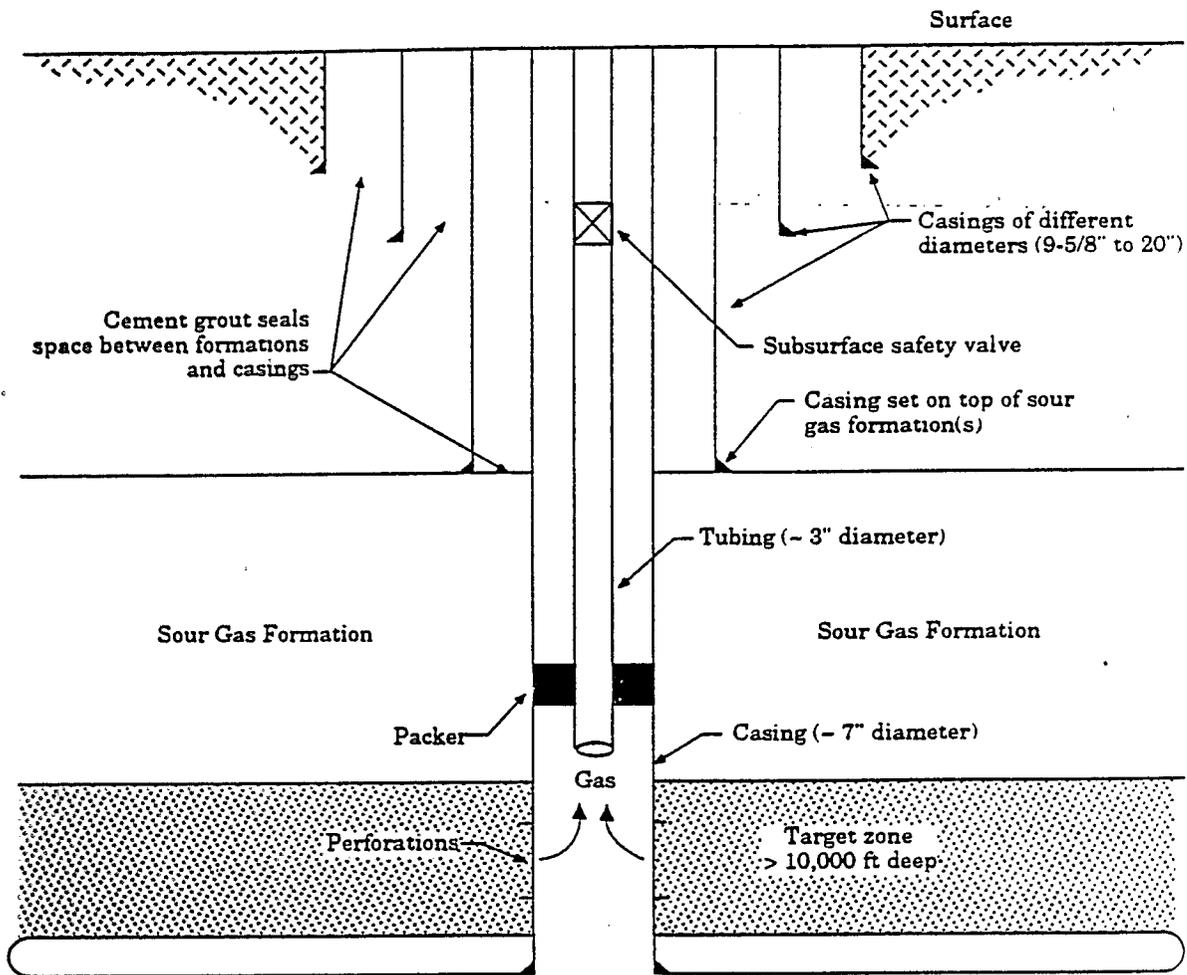
It should be noted that the calculated consequences of some of the modeled scenarios are based on very conservative assumptions in order to examine the worst case. The worst-case scenario is designed to generate the maximum impact off-site. It is considered to be extremely unlikely and does not take into account a variety of factors that can significantly reduce downwind impacts. However, the worst-case scenario is useful to facilities and communities surrounding facilities in gaining an understanding of the potential magnitude of severe situations. The potential for severe consequences should be taken into account along with more probable scenarios when setting priorities for community emergency planning.

Consequence Analysis of Jets from Well Blowouts

Figure III-15 shows the layout of a typical completed sour gas well. A well blowout is an uncontrolled release from a well during drilling, servicing, or production operations. Such an accident could occur if a blowout preventer failed during drilling or a subsurface safety valve fails to operate during production. The possible types of flow from a ruptured well are shown in Figure III-16. A useful simplification is that an accidental release into the casing is possible during drilling or servicing, while flow would likely be restricted to the production tube if there were a blowout during normal production operations. Potential flow orientations are shown on Figure III-17. Examples evaluated for the purposes of this study included the extremes of a vertical jet and a horizontal downwind jet.

Flow rates for the scenarios identified in Figure III-16 are functions of such items as rock permeabilities, gas properties, depth, and tubing and casing diameters. Overall, there are large variabilities in these parameters. One measure of the potential rate of flow from a well is the Calculated Absolute Open Flow Rate (CAOF), which is the rate of flow of gas into the well bore when the pressure is atmospheric. This measure represents a maximum possible flow rate. The actual flow rates out of a ruptured well will be less than the CAOF because of frictional effects in the pipework. Thus, the use of CAOF for a release rate is conservative. Table III-6 gives some representative examples of how the CAOF is reduced for a specific set of well parameters. A flow rate of 2×10^7 standard cubic feet per day (scf/d) was chosen for representative calculations, with a flow rate of 10^8 scf/d being taken as an example of a very high flow rate. The bases for these assumptions are presented in Appendix C.

For the scenarios analyzed for this report, it was assumed that the gas emerges as a vapor. Since typical pressures are very high (e.g., in excess of 1,000 pounds per square inch gauge (psig)), the flow is choked (limited) at sonic velocity.

Surface

Casings of different
diameters (9-5/8" to 20")

Cement grout seals
space between formations
and casings

Subsurface safety valve

Casing set on top of sour
gas formation(s)

Tubing (~ 3" diameter)

Sour Gas Formation

Sour Gas Formation

Packer

Casing (~ 7" diameter)

Gas

Perforations

Target zone
> 10,000 ft deep

Source: Layton et al., 1983.

Figure III-15. Simplified representation of a completed sour-gas well.
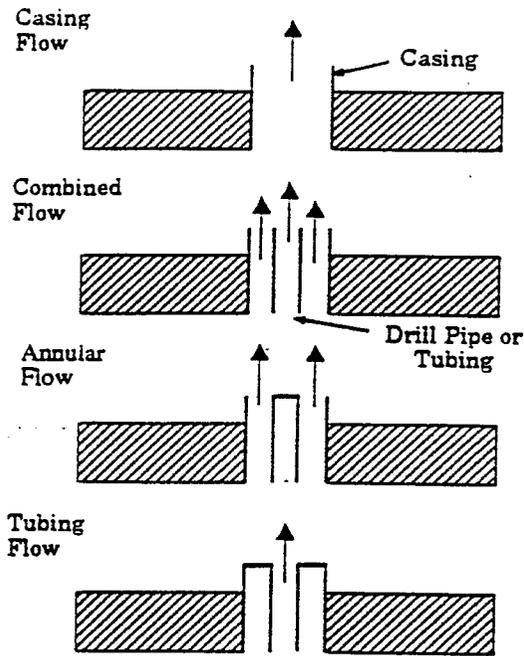
Source: Alp et al., 1990.

Figure III-16. Possible well flow scenarios.
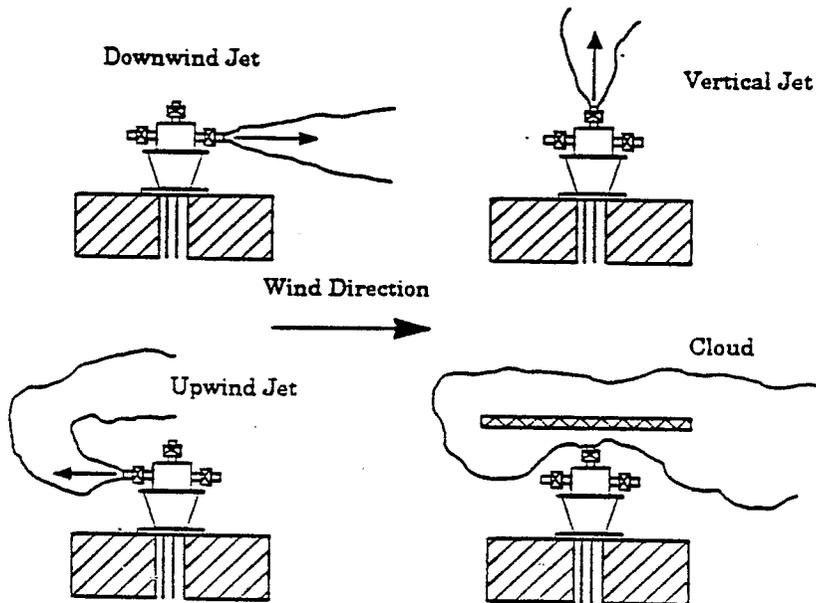
Source: Alp et al., 1990.

Figure III-17. Possible well accidental release geometries.

Table III-6. Surface Deliverability as a Function of Well CAOF

CAOF $(10^3 m^3/d)$*	Casing Flow	Annulus and Tubing Flow	Annulus Flow	Tubing Flow
5000	57.4 %	52.2%	39.3%	8.5%
1000	95.0	82.5	76.0	26.0
500	98.0	96.0	92.0	46.0
100	99.0	98.0	97.0	90.0
50	99.2	99.2	99.2	98.6

Source: Alp et al., 1990.
* At 15°C and 101.3kPa.

The values in Table III-7 were based on the following well conditions:

- Well depth (m)   2660
- Casing inside diameter (mm)   156.3
- Tubing outside diameter (mm)   73.0
- Tubing inside diameter (mm)   62.0
- Reservoir pressure (kPa)   15,900
- Reservoir temperature (°C)   75

The temperature of the gas in the well prior to expansion to atmospheric pressure through the rupture depends on the depth of the gas reservoir. The amount of cooling depends on the initial pressure and the composition. For the purposes of this analysis, an expanded gas temperature of 0°C (32°F) was assumed. This assumption is further discussed in Appendix C.

For a well blowout, the release could continue indefinitely. For illustrative purposes, it was assumed that any nearby individuals could be evacuated within one hour. The calculations of distances of concern discussed below assume that the duration of release and possible duration of exposure is one hour.

For vertical releases of sour gas from well blowouts, the independent dispersion modeling (SLAB, DEGADIS, SAPLUME, and the Gaussian model) and results reported in the literature (Alp et al., 1990; Quest, 1992) indicate that there will be no concentrations above levels of concern at ground level, either at the emergency countermeasure (ERPG-2) or potential fatality (LC_{01}) level. The jet is oriented upwards and, for either buoyant or negatively buoyant sour gas, dilutes rapidly due to its high momentum.

For horizontal releases from well blowouts, results calculated using the SLAB and SAPLUME models are given in Table III-7 for low wind speed and stable conditions. Releases in the direction of the wind were assumed. Depending on composition, release rate, and the model used, distances to the LC_{01} range from 700 meters (approximately 0.4 miles) to greater than 10 kilometers (approximately 6 miles). Distances to the ERPG-2 range from 2.8 kilometers (approximately 1.7 miles) to greater than 10 kilometers (approximately 6 miles). The atmospheric conditions input into the models represent conditions of high stability and little atmospheric mixing. Thus, these conditions represent the "worst-case" because levels of concern will be exceeded for predicted distances from the point of release that will exceed those for other weather conditions. The results were calculated neglecting the possibility of slight buoyancy of the plume even after dilution. DEGADIS results are not quoted because the jet module of that computer model can only handle vertical releases. For all the models, results in the range greater than 10 km (6 miles) should be regarded as beyond the limit of validity and probably conservative (see below).

For comparison, the GASCON2 model calculates an estimated distance of 1.6 km (1 mile) to the LC_{01} for a composition D flow rate of 2.4×10^5 m³/d (cubic meters per day), or 8.5×10^6 scf/d, and an estimated distance of approximately 5 km (3 miles) for a composition D flow rate of 9.5×10^5 m³/d (3.4×10^7 scf/d)(Alp et al., 1990). From Table III-7, for composition D with a flowrate of 6×10^5 m³/d (2.1×10^7 scf/d), SLAB and SAPLUME predict a distance of 2.9 km and 3 km (both approximately 1.8 miles) to the LC_{01}, respectively. These distances and release rates are intermediate to those values in the GASCON2 model. Therefore, the results calculated with GASCON2 are consistent with the results generated by SLAB and SAPLUME (to within the uncertainties expected in such models).

Table III-7. SLAB and SAPLUME Results – Horizontal Releases from a Well Blowout

Composition (from Table III-6) and Flow Rates (m^3/d)	Predicted Distance 1 h Exposure (SLAB)		Predicted Distance 1 h Exposure (SAPLUME)	
	LC_{01}	ERPG-2	LC_{01}	ERPG-2
A, 6×10^5 m^3/d (7.5% H_2S)	700 m	2.8 km	1 km	3.1 km
B, 6×10^5 m^3/d (27% H_2S)	2.8 km	7 km	2.7 km	10 km
C, 6×10^5 m^3/d (15% H_2S)	1.5 km	4.7 km	1.5 km	5.7 km
D, 6×10^5 m^3/d (30% H_2S)	2.9 km	7 km	3 km	10 km
D, 3×10^6 m^3/d (30% H_2S) (extreme case)	7 km	>10 km	>10 km	>10 km

By contrast, the FOCUS model calculates an estimated distance of 0.7 km to the LC_{01} for composition C with a flow rate of 6×10^5 m^3/d (2.1×10^7 scf/d)(Quest, 1992). This prediction is about half that given by the SLAB and SAPLUME calculations, which predict a distance of 1.5 km (0.9 miles) to the LC_{01} for composition C with a flowrate of 6×10^5 m^3/d (by implication, GASCON2 would predict similar distances). This difference in predictions may lie within the range of uncertainty of vapor dispersion models; the precise reason for the difference cannot be determined from the information available about the proprietary model FOCUS.

Figure III-18 shows the results of the comparison of observations from actual well blowouts in Alberta, Canada, with GASCON2 predictions. The actual blowouts were at Lodgepole (October 17 through December 23, 1982), Clovesholm (September 24-28, 1984) and Rainbow Lake (December 9-14, 1985). The air quality data associated with each blowout were collected with public safety interests in mind and not model verification or validation. As a consequence, most of the observations were poorly documented with respect to magnitude, location, averaging time and meteorological conditions. Screening of the data to select only measurements in which there could be reasonable confidence produced a data set of 50 (45 of which were from the Lodgepole blowout). For the Lodgepole case, seven stationary and five mobile units collected data within 50 km of the site.

As can be seen, GASCON2 significantly overpredicts, especially when its predicted concentrations are in the greater than 3×10^4 ppb range, where overpredictions are by as much as a factor of 10. This concentration is the range of interest for ERPG-2 and LC_{01}. These overpredictions tentatively (because of the poor quality of the data) suggest that the GASCON2 results are conservative and, by implication, that the results from the SLAB and SAPLUME calculations are also conservative.

Possible reasons for conservatism include underestimating the effect of the plume lifting off the ground. For distances in the several km to the greater than 10 km (6 mile) range, neglect of dry deposition (fallout, transfer from the air to other surfaces) of the highly reactive H_2S may also lead to overestimation of airborne concentrations. However, it is more likely that the poor quality of the observations is reponsible for the apparent disagreements.

Standard text-book calculations indicate that flammable mixtures will not propagate more than 100 m from the point of release (Quest, 1992). If ignition occurs, potentially fatal thermal radiation loads could be received up to approximately 100 meters from the source. Although not pertinent to a discussion of hazards from H_2S releases, it should be noted that SO_2 will be emitted as a result of igniting a sour gas stream and may present a toxicity hazard.
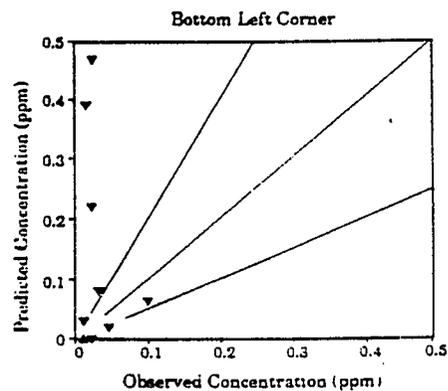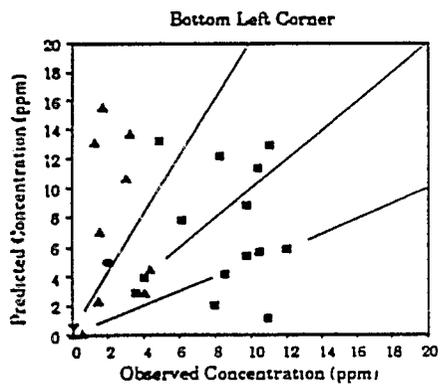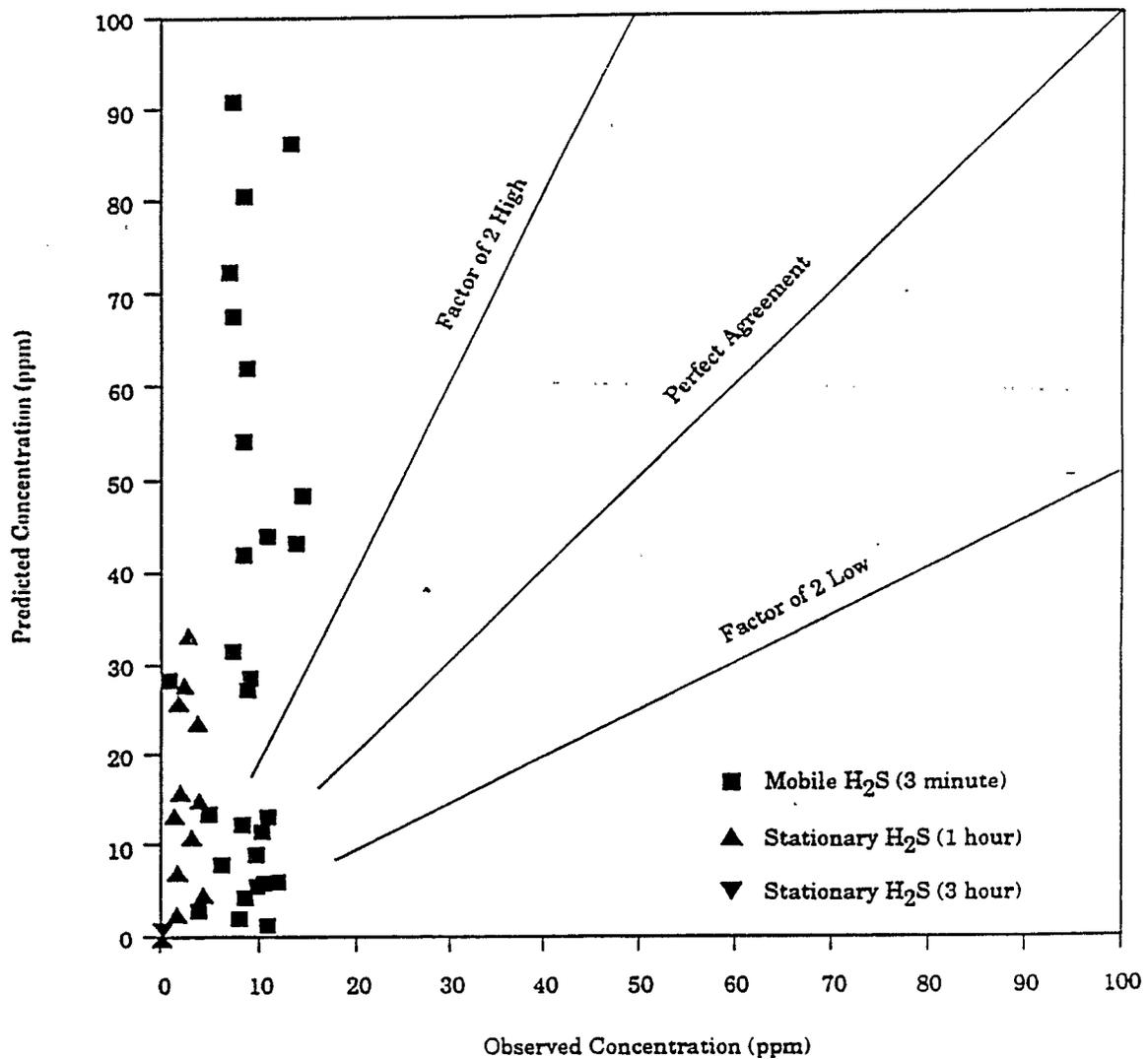
Figure III-18. Predicted H_2S and SO_2 concentrations for selected well blowout observations.

Consequence Analysis of Line Ruptures

Releases from line ruptures will behave much like well blowouts unless there is a means to isolate the rupture. Most gathering systems are not equipped with isolation systems, and aging pipework presents integrity concerns (particularly when not properly maintained). Advanced gathering line systems may have emergency shutdown valves (ESDs) that are remotely or locally operated. ESDs may be manually or automatically operated (e.g., by a signal from an H_2S detector). Figures III-19 and III-20 show some typical configurations for ruptures of lines that are equipped with ESDs. For such releases, the total mass released is limited by the quantity of gas between ESDs. The valves may be 1 km to 3 km apart (0.6 mile to 1.8 mile) (Alp et al., 1990).

Figure III-21 shows typical mass release rates for the rupture cases identified in Figure III-20, assuming a 6" diameter pipe at a pressure of approximately 5,000 kPa (725 psi). Rupture Scenario 4 (no ESD) follows Scenario 1 until a steady state of 2.4×10^5 m^3/d (8.5×10^6 scf/d) is reached after about a minute.

Figure III-22 shows mass release rates as a function of time for various pipe diameters and various ESD separations with an assumed line pressure of approximately 50 atmospheres (735 psi). The variable, t_d, listed on Figure III-22 is the time in seconds taken for 99 percent of the line contents to be depleted after closure of the ESD valves. M_d is the total mass released in kg. As can be seen, for many of the cases, a puff release (rather than a continuous release) is a reasonable approximation because of the short duration.

The predicted distances of concern for lines with ESD valves that close promptly are smaller than those for wellhead blowouts because the duration of release is shorter, the total mass released is smaller, and because shorter exposure times allow higher tolerable levels of concern.

Calculations from SADENZ, a companion model to SAPLUME for puff releases, predict that distances to the LC_{01} for compositions A-D in Table III-5 and released masses specified in Figure III-22 range from 600 m (0.4 miles) to 4.3 km (2.6 miles). Predicted distances to the ERPG-2 adjusted for shorter exposure time (method described by Gephart and Moses, 1989) range from 750 m (0.45 miles) to approximately 5.6 km (3.4 miles). This is consistent with the calculated results from the GASCON2 model (Alp et al., 1990) and, as before, somewhat higher than those calculated from the FOCUS model (Quest, 1992).

Consequence Analysis of Line Release Seepage

A survey of several gas pipeline incidents that were investigated by the National Transportation Safety Board (NTSB) indicated that, for buried gas pipelines operating above 600 psig, a 1" diameter hole will blow away the soil above the line (Quest, 1992). This will result in the formation of a crater from which the gas will escape as an unobstructed jet. For smaller holes (e.g., a 1/4" diameter hole caused by corrosion), the soil remains in place

End Pipe Rupture

ESO Value Operates ESO Value Operates ESO Value Operates

Centre Pipe Rupture

ESO Value Operates ESO Value Operates ESO Value Operates

ESD Valve Failure

ESO Value Operates ESO Value Operates ESO Value Operates

Decay to Steady State

ESO Value Operates ESO Value Operates ESO Value Operates
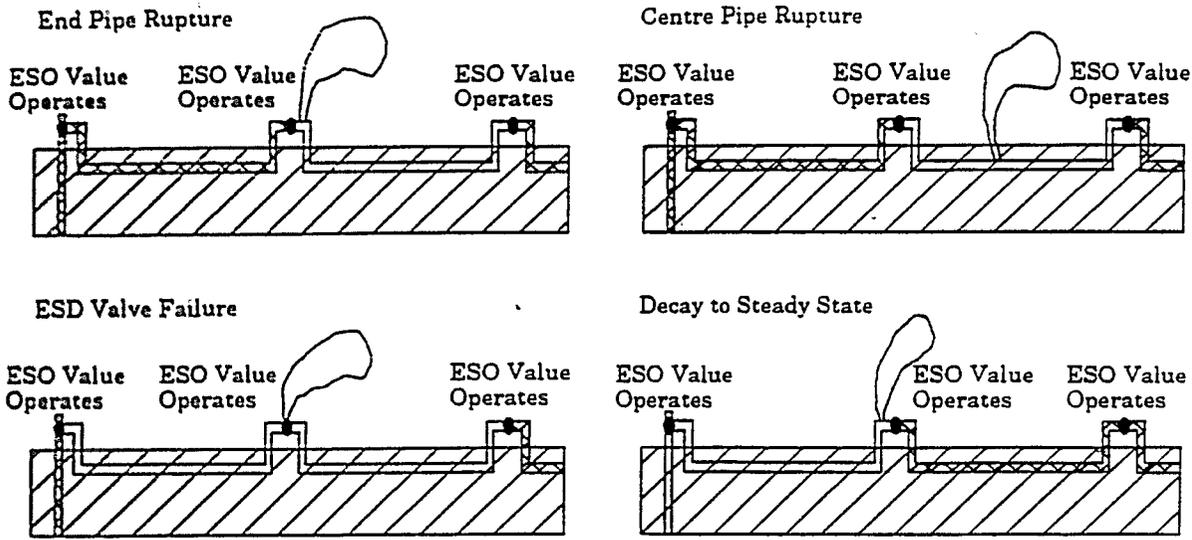
Source: Alp et al., 1990.

Figure III-19. Possible pipeline rupture scenarios.

Long Rupture

Short Rupture

Leak
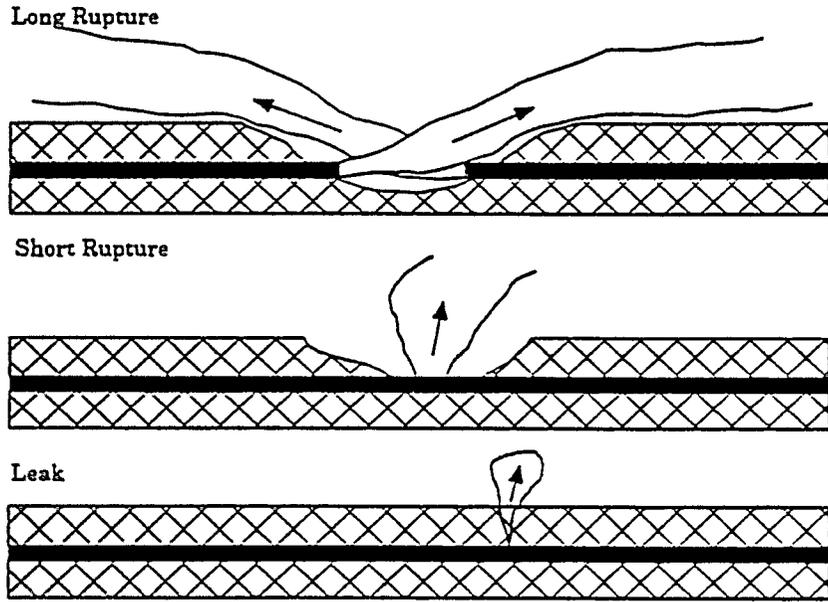
Source: Alp et al., 1990.

Figure III-20. Possible pipeline release geometries.
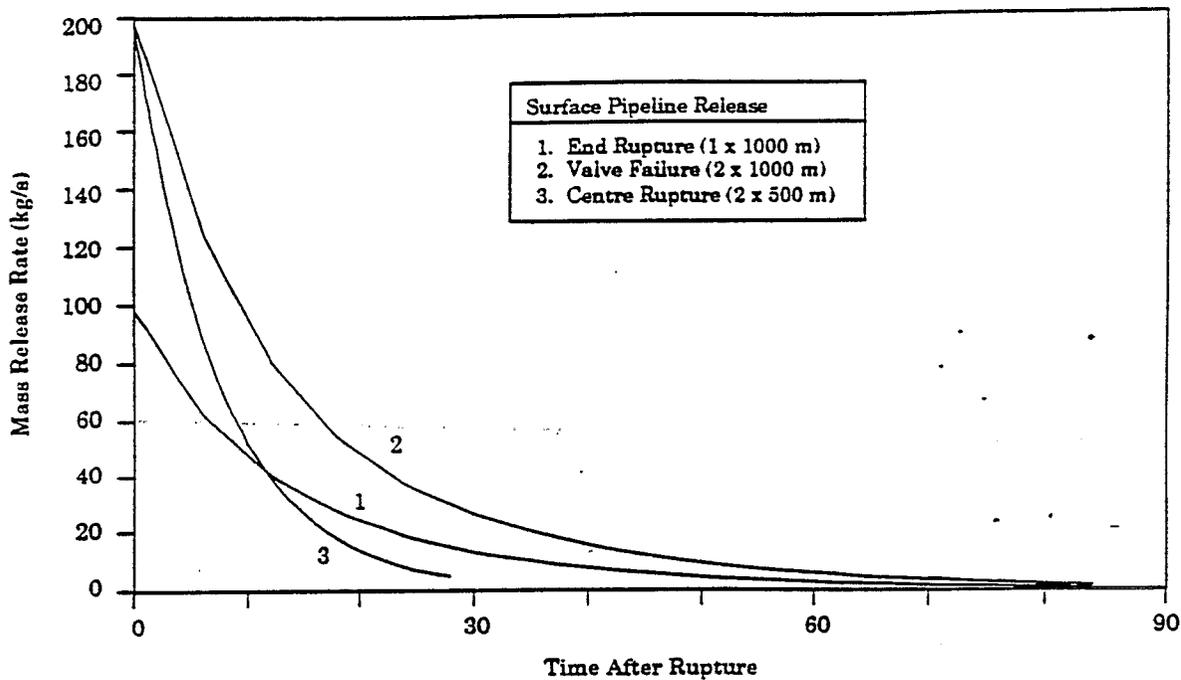
Source: Alp et al., 1990.

Figure III-21. Predicted mass release rates - rupture of 6" pipe.
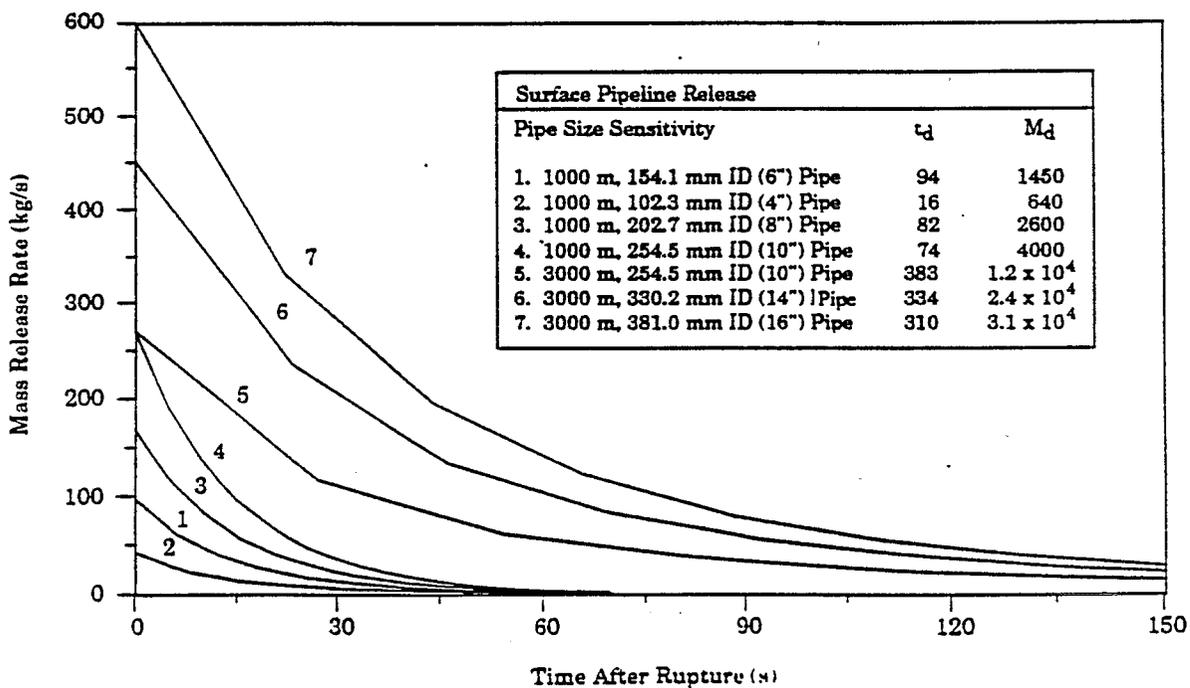
Source: Alp et al., 1990.

Figure III-22. Predicted mass release rates - rupture of pipes of differing diameters.

and the vapors migrate to the surface where they are released without any momentum (although the resulting vapor cloud may still be buoyant enough to lift off).

For a 1/4" diameter hole in a line containing gas at a pressure of 1,000 psig, the calculated release rate (using standard text book formulae for choked flow) is about 1 lb/sec, assuming that the surrounding soil does not reduce the emission rate by physically impeding the flow. If this gas seeps to the surface, the predicted distance to which the ERPG-2 would be exceeded for a person who inadvertently enters the plume for five minutes is about 400 m (0.2 miles) and the predicted distance to the LC_{01} is about 250 m (0.15 miles) when the atmospheric stability category is F and the windspeed is 1.5 m/sec (4.9 feet per second), utilizing composition C from Table III-5. These results neglect the possibility that the plume might lift off the ground or exhibit dense gas behavior.

Consequence Analysis of Flare Stack Releases

Results calculated using the GASCON2 (Alp et al., 1990) and FOCUS (Quest, 1992) models and those carried out independently with the SAPLUME model show that, with or without sour gas ignition, the plume emitted from a flare stack is a momentum jet with dilution of the discharge and will rise sufficiently high to avoid concentrations above the ERPG-2 at ground level.

It is possible that a release of very dense gas from an unignited flare could exhibit dense gas behavior. For example, in 1950 in the town of Poza Rica, Mexico, 22 people died from exposure to hydrogen sulfide emitted from a malfunctioning flare at a gas purification plant (McCabe and Clayton, 1952). However, in this case, the gas from the well contained 3 percent by volume of H_2S and 15 percent by volume of CO_2. During the startup period for the desulfurization units to which the gas was sent, partially processed gas containing 81 percent CO_2 and 16 percent H_2S was sent to a flare. It was this processed, heavy vapor and not the produced gas that, upon failure of the flare, descended to ground level. However, despite the limitations in applicability and the unlikelihood of occurrence, this incident is illustrative of the potential for severe consequences when managing a dense gas stream.

Consequence Analysis of Releases Collecting at Ground Level

The specific cases listed in Table III-5 are all less dense than air. This has been the case for all the gas streams investigated for this report for which detailed compositions were documented. Also, note that the most dense composition on Table III-5, stream B which has a density close to that of air, was obtained after some separation and processing for vapor recovery. It appears that the concern about heavy vapors containing H_2S settling or collecting in low-lying areas may be justified for only a fraction of wells such as the previously described Big Piney, Wyoming well blowout and Poza Rica, Mexico flare incident. It is pertinent to address other situations where this concern is justified.

Nine people were killed in an incident in Denver City, Texas, when they were exposed to gas escaping from a well injecting gas into an oil reservoir as part of an enhanced oil recovery project (Layton et al., 1983). The injected gas was composed of 93 percent by volume CO_2 and 5 percent by volume H_2S - clearly denser than air, but as before, gas that was previously processed and not of as-produced composition.

In general, it is possible that releases directly from wells with unusually dense sour gas compositions or associated lines could settle in low-lying areas at ground level. These releases would not be of typical composition. It is also possible that people entering areas of seepage such as those previously described for line releases could confuse these with settling on the ground. It is therefore reasonable to speculate that, in some cases, such concerns could possibly have arisen from seepage events.

The modeling described in the foregoing applies to plumes over flat terrain. In complex terrain, it is unlikely that released gas of typical composition will flow into lower elevations such as valleys because, as previously noted, it is generally not denser-than-air. However, it is very likely that a small or chronic release will follow the flow of the wind. Thus, for example, on cold, still nights there could be flows of air with relatively little turbulence from higher elevations into valleys (katabatic flows). This could carry slowly diluting H_2S with it and potentially cause odors within houses in valleys some distance from the well. This situation would likely not occur during the day when such air flows are uncommon. However, as previously discussed, it is possible for sour gas of unusually dense composition to remain at ground level. Therefore, for such releases, it is conceivable that flow could "channel" through terrain of low elevations such as valleys. This possibility is highly uncertain. The study of the behavior of dense gas flow around obstacles and through rough terrain is controversial and is an area where further research is needed.

Accidental Releases—Prevention, Mitigation, and Emergency Response

The design and operation of sour gas systems require special consideration as a result of the potential hazards presented by a release of H_2S. The hazards of exposure to H_2S can be significantly reduced by the implementation of process safety management principles. A primary emphasis on containment together with design features for the detection and mitigation of losses in containment are necessary for safe operations. The degree of sophistication of individual sour gas system designs will vary depending on site-specific circumstances and age. Older systems may incorporate relatively simple safety designs when compared with current state of the art. The presence of sour oil and gas operations in remote locations or near populated areas may both be justification for the use of advanced designs. Remote areas may be subject to extended releases if accessibility is limited. Process safety management and major safety considerations are discussed below.

Process Safety Management

Facilities that handle hazardous materials have a responsibility to understand the hazards present at their sites and to take steps to ensure that chemical accidents due to these hazards are prevented. Many organizations, including the American Institute of Chemical Engineers - Center for Chemical Process Safety (AIChE-CCPS) and the EPA, have found that major chemical accidents cannot be prevented by hardware or by technology alone. Prevention requires comprehensive management systems designed to identify and control hazards (AIChE, 1989; U.S. EPA, 1988). These management systems are known as Process Safety Management (PSM) and consist of "comprehensive sets of policies, procedures, and practices designed to ensure that barriers to major incidents are in place, in use, and effective. The management systems serve to integrate process safety concepts into the ongoing activities of everyone involved in the process - from the chemical process operator to the chief executive officer" (AIChE, 1989). The Occupational Safety and Health Administration (OSHA) has set standards for process safety management, which are discussed in Chapter IV.

PSM consists of several essential elements that work together to allow safe operation of a facility;

- Management Commitment: Management must adopt a philosophy that makes safety an integral part of operation from the top down; an attitude that all accidents can be prevented and that business must always be conducted safely.

- Process Hazards Analysis or Hazard Evaluation: The purpose of the process hazards analysis is to systematically examine the equipment, systems, and procedures for handling a hazardous substance; to identify the mishaps that could occur, analyze the likelihood that mishaps will occur, and evaluate the consequences of these mishaps; and to analyze the likelihood that safety systems, mitigation systems, and emergency alarms will function properly to eliminate or reduce the consequences of the incident. Thorough process hazards analysis is the foundation for the remaining elements of the PSM system.

- Process Knowledge and Documentation: Facilities document the details of the technology and design of the process, its standard conditions and consequences of deviation from these standards, the known hazards of the chemicals and processes involved and protective systems for protection of workers, the public, and the environment. ·

- Standard Operating Procedures (SOPs): These are procedures that describe the tasks to be performed by the operator or maintenance worker to ensure safety during operation and maintenance.

- Training: A program to teach those responsible for designing, operating, and maintaining the unit or plant. Elements in a management training system include development of training programs, training of instructors, measuring performance and determining the effectiveness of training. Training is typically carried out by facility managers and training staff.

- Maintenance (Process and Equipment Integrity): A formal program to ensure that equipment is constructed according to design, installed properly, and adequately maintained.

- Prestartup Review: The purpose of this review is to ensure that all elements of process safety, including hardware, procedures, and control software, are in place prior to startup, and that all prior issues of concern have been resolved.

- Management of Change: Management must instruct personnel to recognize change and to evaluate change with regard to process safety.

- Safety Audits: The purpose of safety audits is to measure facility performance, to verify compliance with a sound process safety program, and to determine that risks are being appropriately managed.

- Accident Investigation: Accident investigation is a management process by which the underlying causes of an incident are identified and steps are taken to prevent similar incidents.

- Emergency Planning and Response: Emergencies involving highly hazardous substances can have catastrophic results if not handled properly. Employees need to know and be trained in proper emergency procedures, evacuation requirements, and notification steps.

Major Safety Considerations

Siting. The magnitude of the potential consequences from human exposure to an H_2S release decreases with distance from the sour oil or gas source. Therefore, operations involving H_2S should be situated as far as possible from residential and commercial structures to minimize potential hazards to the public. Prevailing weather patterns (e.g., wind direction), terrain features, transportation routes, population centers, the potential for evacuation, and the potential for access control are some additional factors to be considered in siting decisions. These are site-specific factors that must be determined for each location.

At a minimum, well sites should be fenced to maintain some obstacle to approaching the wellhead.

Materials Selection and Corrosion Prevention. Materials must be chosen that are suitable for the service into which they are placed. Sour oil and gas operations are often conducted under high pressure and corrosive conditions. Therefore, in addition to temperature and pressure considerations, system designs for the wellhead, downhole equipment, and pipelines must incorporate features to minimize the effects of corrosion in order to prevent a breach of containment and accidental release of H_2S. Several national engineering standards governing the choice of materials are applicable. Standards include those by the American Petroleum Institute (API), American Society of Mechanical Engineers (ASME), and the National Association of Corrosion Engineers (NACE). One such standard is NACE Standard MR0175, "Material Requirements for Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment." Also applicable are the API 6A specifications for equipment in high H_2S concentrations in close proximity to occupied structures.

In addition to proper selection of materials, corrosion inhibiting fluids can be used to prevent internal corrosion and cathodic protection can be used to prevent external corrosion. Inhibitor applications include the filling of wells with inhibitor during extended periods of shut-in and injection into pipelines.

Corrosion monitoring programs should be a normal part of the operations and maintenance for sour oil and gas systems so that corrosion problems can be anticipated and repairs made before an accidental release occurs. The need for a corrosion control program and program monitoring was discussed in the first edition of API RP 55, "API Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide" (API, 1983). This document has been withdrawn pending publication of an updated, second edition. Additional discussion of RP 55 can be found in Chapter IV. Corrosion monitoring systems can take a variety of forms including external monitoring (ultrasonic or X-ray inspection), corrosion coupons and spool pieces (test pieces), instrumented "pigs", or in-place instrumentation. Pigs are instruments that can be transmitted through lengths of larger diameter piping to take measurements of internal surfaces.

Leak Detection and Mitigation. While systems should be designed to meet the appropriate standards, there is still the potential for releases to occur as a result of human error or equipment failure (e.g., corrosion, impact, etc.). A possible design feature for oil and gas operations is the use of detection systems which monitor for evidence of system leaks and then isolation systems that can be used to shut off leaks. For H_2S-containing systems, detection systems can focus directly on measurement of H_2S, on measurement of pressure changes which could be indicative of a leak, or temperature indicators that can be indicative of a loss of containment and subsequent fire. Signals from such detection systems can be used in modern, sophisticated systems to automatically initiate additional containment measures such as well shut-in or isolation of sections of pipeline. There are national

standards for performance and use of H_2S monitoring equipment such as these set by the Instrument Society of America, ISA-S12.15 "Part I: Performance Requirements of Hydrogen Sulfide Detection Instrumentation" and "Part II: Installation, Operation, Maintenance of Hydrogen Sulfide Detection Instruments." Not all systems have leak detection or signalling devices associated with them. Such systems may present a greater hazard potential than those that have devices because detection would have to be by visual means or by smell. Any release would continue until detected.

Flares may malfunction resulting in extinguishment of the flame. This may occur due to several causes including flow of noncombustible compounds (e.g., nitrogen or carbon dioxide) and high winds. Flares can be equipped with automatic ignition devices to reignite extinguished flames and supplemental fuel systems to maintain ignition of the flare gas in the presence of inert gas. Flares should also be constructed at a height that provides for sufficient dispersion of the discharge.

The equipment used to mitigate releases depends on the operations. For well drilling and workover operations, a blowout preventer is used. This piece of equipment consists of high-pressure valves that allow the operator to shut in the well. For operating wells, there can be subsurface shutoff valves which are located in the well as well as above grade valves located at the wellhead and in the lines around surface equipment such as separators. Shut-in may be accomplished automatically via a signal (H_2S concentration, pressure change, temperature) that is received indicating a potential leak. For pipelines, there may also be isolation or shutdown valves located along the pipeline and these may be automatically activated if there is an indication of a leak in the pipeline or at the well. Not all systems will have automatic mitigation capability and isolation would have to be manual in these cases.

Inspection and Monitoring Practices. API RP 55 made recommendations for actions that were intended to monitor performance of the containment system for the sour oil and gas. API RP 55 specifically called for inspection of equipment and system performance to look for indications of corrosion that are indicators of degradation of the sour oil and gas containment equipment. Inspections were specifically recommended for changes in lift performance; changes in pressures associated with packed off annuli; and for the condition of valves, flanges, and connections. The document also recommended that any equipment failures be evaluated to determine the cause of the failure. Particular attention should be paid to the effectiveness of the corrosion control program at a site and corrective action should be considered if there is any indication that the program is inadequate.

API RP 55 also called for the monitoring, maintenance and recalibration of monitoring equipment (temperature, pressure, composition, etc) to make sure it is functioning as intended.

Emergency Procedures. In the event of loss of containment of the sour oil and gas, emergency procedures must be implemented to both restore containment and to protect the public. API RP 55 called for the preparation of a contingency plan for operations involving

sour oil and gas. The plans are to contain information that would be needed by personnel responding to the accident at the site. Among the information that should be in the plan according to the API recommended practices are:

1. Location of wells and details on the equipment including flow lines, isolation valves, processing facilities, and tank batteries;
2. Location of safety and life support equipment;
3. Location of telephones and other communication equipment;
4. Potential location of roadblocks for excluding unauthorized personnel for the areas associated with the accidental release;
5. Location of residences, businesses, parks, schools, roads, medical facilities;
6. Areas that could experience elevated H_2S concentrations (e.g. levels greater than 1×10^5 ppb);
7. Potential evacuation routes; and
8. Designated safe areas for operations personnel.

In addition to this information, the plan should have a list of emergency telephone numbers including company supervisors; residences, schools and businesses; nearby operators and service companies; local law enforcement agencies; officials responsible for public facilities that could be impacted; medical assistance personnel, facilities and equipment; and concerned local, state, and Federal agencies.

Beyond the information listed above, the contingency plan should have an immediate plan of action. Among the elements in an immediate action plan are the determination of the potential hazard to the public from the discharge and then an identification of actions to respond to the hazard (e.g. immediate measures to eliminate the discharge, notification of responsible supervisors, establishment of a restricted access zone, evacuation of personnel). API RP 55 also recommended consideration of advanced briefing of public and public officials so they understand the nature of the hazard, the necessity for emergency response plans, and the general steps that would be taken in the event of an emergency. Finally, API RP 55 called for the updating of the plan as necessary to keep the information in the plan current and conducting periodic drills so that personnel are familiar with the type of situations to which they may have to respond.

The Department of the Interior has promulgated regulations that are applicable to sour oil and gas operations on Bureau of Land Management (BLM) property (BLM, 43 CFR 3160). These regulations call for the preparation of public protection plans for drilling and production operations where (1) the 1×10^5 ppb H_2S radius is greater than 50 feet and the area includes locations where the public could reasonably be expected to be (e.g. occupied residences, schools, churches, parks); (2) the 5×10^5 ppb H_2S radius is greater than 50 feet and includes any part of Federal, State, or county or municipal road or highway; or (3) the 1×10^5 ppb H_2S radius is greater than 3,000 ft. where facilities and roads are principally maintained for public use. The requirements for the content of these public protection plans are very similar to those called for in API RP 55.

Abandonment Practices

The termination of sour oil and gas production operations normally results in the plugging of the well with cement prior to abandonment by the operator. As a result, a potential exists for H_2S to be released from sour oil and gas from the well and associated equipment if proper precautions are not taken. API RP 55 identified actions that should be taken at the end of operations. The document specifically called for precautions to ensure that H_2S does not present a hazard to the public and the environment. The document called for either air purging or water flushing of equipment followed by opening to the atmosphere. Pipelines then were to be purged and capped. API RP 55 also called for the setting of cement across formations that could produce H_2S.

In some cases, wells may be temporarily abandoned. These wells may also be called "idle" or "inactive." In temporary abandonments, the well will not be plugged with cement but perforations may require isolation. Typically, application must be made and approval given by a state authority to temporarily abandon a well. Conditions justifying temporary abandonment to a State most often include economic conditions and future utility (IOGCC, 1992). Approval is temporary and of limited duration although extensions may be granted at the discretion of the state authority. Depending on the state, initial approval periods range from 6 months up to 10 years. Extensions may be granted for up to an unlimited number of time periods. In many states, but not all, periodic testing is required on idle wells. For example, mechanical integrity and pressure tests may be required. These practices are intended to prevent releases of oil and gas.

Of 215,000 oil and gas wells estimated to have been idle in 1992, approximately 68,000 were thought to have been idled without State approval (IOGCC, 1992). 50,000 of these wells, known as orphan wells, were believed to have been idled by operators who were unknown or insolvent. Although the fact that a temporarily abandoned well has not been reported to the State does not mean the well will be the source of an accidental release, the lack of control and supervision does represent an unsafe situation and may present a greater risk to the public and the environment. The majority of States have developed some funding mechanism and implemented programs to plug and abandon orphan and preregulatory wells although these activities vary widely from state to state (IOGCC, 1992).

Land Use Around Well Sites

Land use can vary enormously around oil and gas wells. The wells may be found in urban areas or open rangelands. Figure III-23 shows current land-use patterns by EPA region (Southerland, 1992). In Regions 6, 8, and 9, which contain the majority of wells in naturally occurring H_2S areas, between 50 and 60 percent of the land is used as range. The three regions represent about 60 percent of the oil and gas producing wells. In the Midwest's Region 5, which contains 12 percent of the nation's producing oil and gas wells, over 50 percent of the land is farmed (U.S. EIA, 1990; U.S. EIA, 1991).
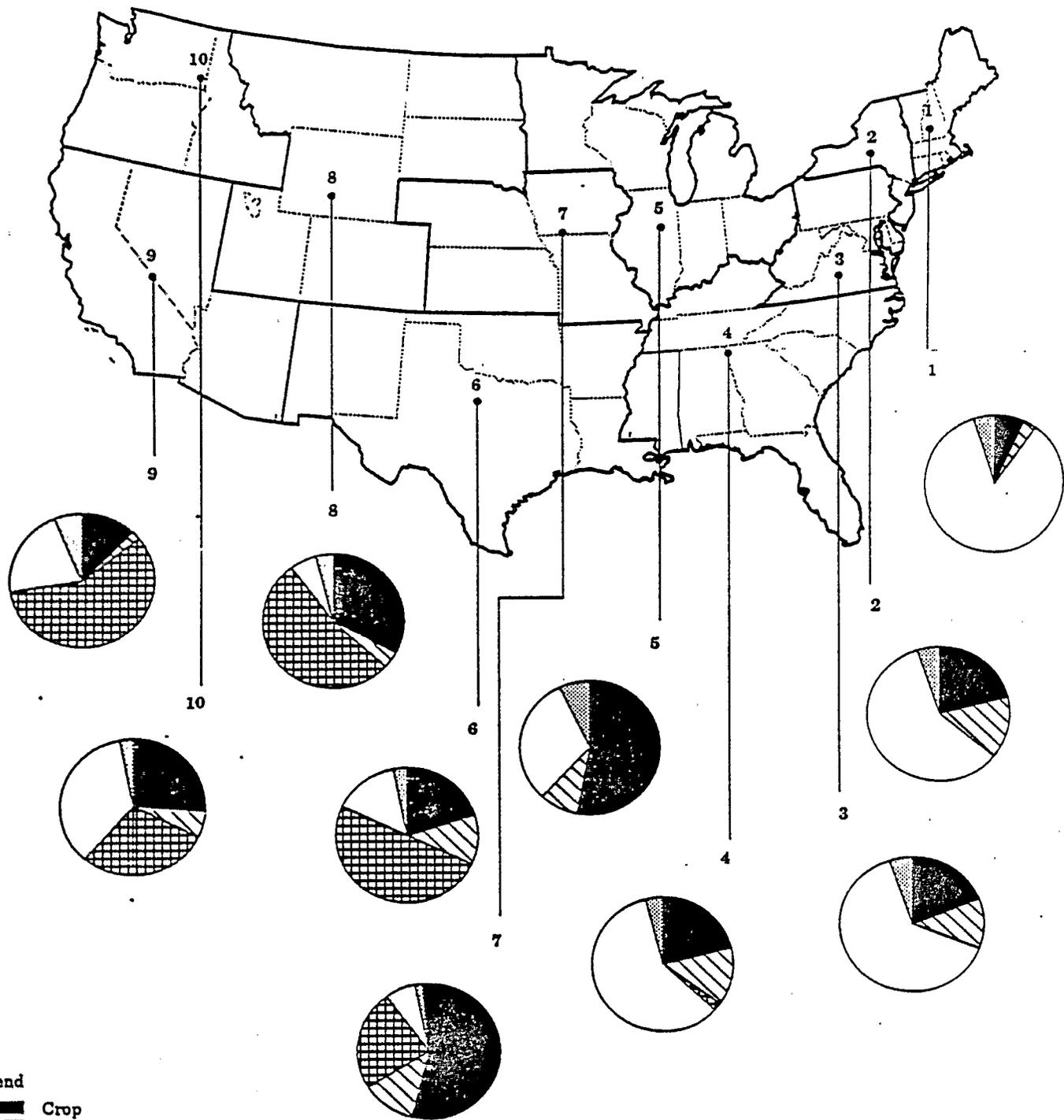
Legend
▮ Crop
▧ Pasture
▤ Range
▭ Forest
▯ Minor

Figure III-23. Current land-use pattern by EPA region

Regarding urban areas, in California, for example, the Division of Oil and Gas reports that "one-third of California's 1.7 billion barrels of oil reserves are in urban areas or in areas where residential development is increasing. (The H_2S content of these reserves was not available.) The Los Angeles Basin both typifies the situation and is the most complex example. Here, a large metropolitan area lies over one of California's major petroleum-producing provinces. Because oil and gas are so fundamental to the U.S. economy, any recoverable amounts cannot be ignored. Ways have been developed to produce oil and gas safely in urban areas, with minimum negative effects. Urban planners, administrators, and California Division of Oil and Gas engineers work together to ensure a safe partnership between urban life and oil and gas development" (CDC, 1988).

Affected Human Populations

Figure III-24 overlays 1980 census data on the H_2S prone areas to show the proximity of major populations to H_2S deposits. The figure shows that a wide range in population density can be found in H_2S deposit areas. However, a look at the locations of well fields in the United States (Figure III-11) and the number of wells per State (Figure III-12) clarifies the potential exposure of large human populations to H_2S from oil and gas wells.

Data were not available to arrive at statistics on individuals exposed to H_2S emissions. Because the number of wells in the U.S. is so great and the diversity of population density around wells so large, it was not possible to arrive at an estimated affected population. The photographs in this report show that wells may be found in urban, suburban, and rural areas. Populations that could be exposed include adults in work settings (e.g., fire stations), children in schools, shoppers in downtown areas, and people in residential areas.

Affected Environmental Settings

A 1991 study in Wyoming found that, in two years, 237 animals had been killed by H_2S gas. In many oil fields this gas was vented through flare stacks. The researcher stated that when flare stacks are used, it is possible to install devices which would prevent raptors and other birds from using flares as perch sites. Also, wildlife mortality caused by H_2S would be reduced by ensuring that igniters were operating efficiently so that the gas would be properly flared and not accidentally vented directly into the environment (Esmoil, 1991). Based on other accident history, one impact on environmental settings has been the loss of livestock attributed to exposure to H_2S. Sixty percent of the U.S. wells are located in EPA Regions that contain more than 50 percent rangeland. However, many other species of animals and plants are potentially exposed to H_2S concentrations that could cause adverse effects. Testimony for the Clean Air Act Amendments included statements about episodes in the Great Plains that resulted in livestock dying and humans being hospitalized (Audubon Society, 1987).

Twelve percent of all wells are located in EPA Region 5, which is more than 50 percent cropland. As noted in a previous section of this report, soybeans have been

Urbanized Population
⬤ 250,000 or more
▲ 100,000-249,999
• 50,000-99,999
◊ H₂S Prone Areas
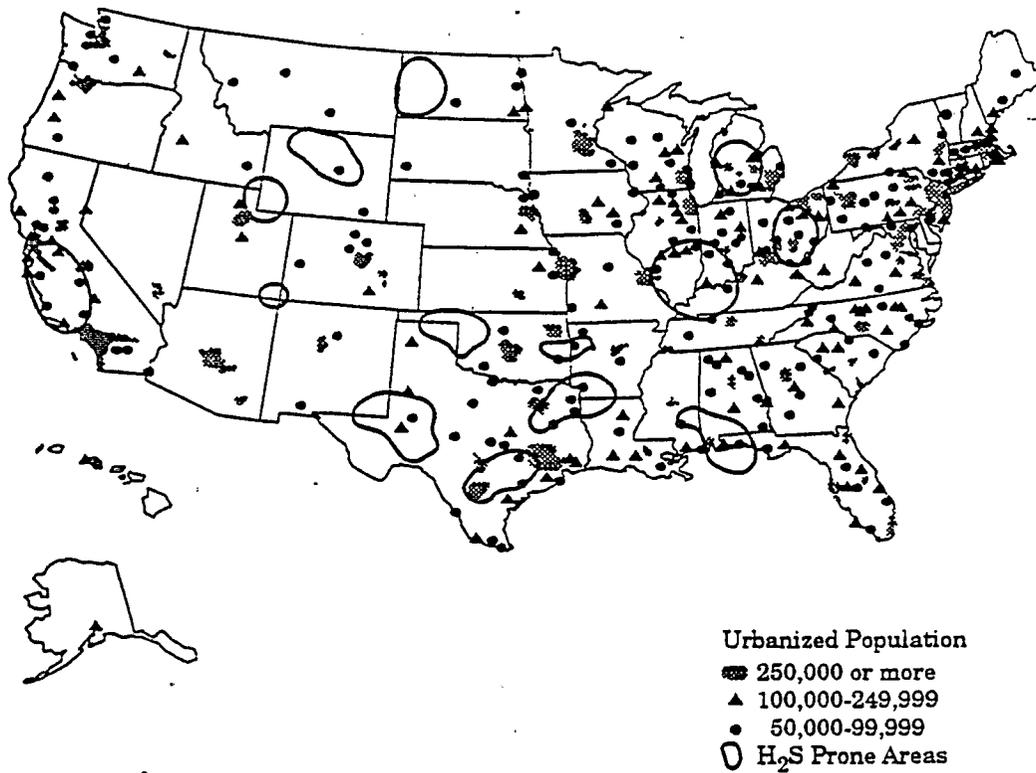
Figure III-24. Major H₂S prone areas shown in relation to 1980 census data.

determined to be sensitive to H_2S along with other crops. There has been evidence of scorching to young leaves and shoots but no effect on mature leaves (Heck et al., 1970).

Waterfowl habitats of major concern are located in some areas of oil deposits with H_2S, as shown in Figure III-25. Concern has also been expressed about the deterioration of air quality in Theodore Roosevelt National Park (Sierra Club, 1987). Figure III-26 shows the location of national parks and national forests in relation to H_2S deposits.

FINDINGS

1. Human exposure to H_2S may cause death, as well as symptoms including irritation, breathing disorders, nausea, vomiting, diarrhea, giddiness, headaches, dizziness, confusion, rapid heart rate, sweating, weakness, and profuse salivation. Levels greater than 1.5×10^5 ppb are life threatening.

2. No epidemiological studies were found on the effects of H_2S emissions from oil and gas extraction/production.

3. Human acute and chronic health effects data and ecological effects data are limited.

4. H_2S is classified as a Group D carcinogen, meaning not classifiable as a human carcinogen. The inhalation RfC is 9×10^{-4} mg/m³ (0.67 ppb) in chronic exposures scenarios. This RfC is not appropriate, however, for assessing concentration-response relationships in short-term or accidental exposure scenarios.

5. Few studies exist measuring natural or accidental exposure of wildlife to H_2S; however, wildlife deaths have been reported with blowouts.

6. High exposure studies have shown young, growing plants to be the most susceptible to H_2S injury (clover, soybean, tomatoes, tobacco, buckwheat).

7. Aquatic LC_{50}s show bluegill = 0.009-0.0478 mg/l.
   NAOEL for mice = 42.5 mg/m³ (3.05×10^4 ppb).
   LAOEL for mice = 100 mg/m³ (8×10^4 ppb).

8. Nationwide, vulnerability zones have been characterized as 14 major H_2S prone areas found in 20 states. Texas has 4 discrete H_2S prone areas.

9. North Dakota is the only State known to have routinely monitored ambient H_2S at well sites and surrounding areas.

10. Many oil-and gas producing States require ambient air monitoring for H_2S at gas plants and refineries, but monitoring is not frequently required at oil and gas

Legend:
⊙ Waterfowl Habitats
◊ H₂S Prone Areas
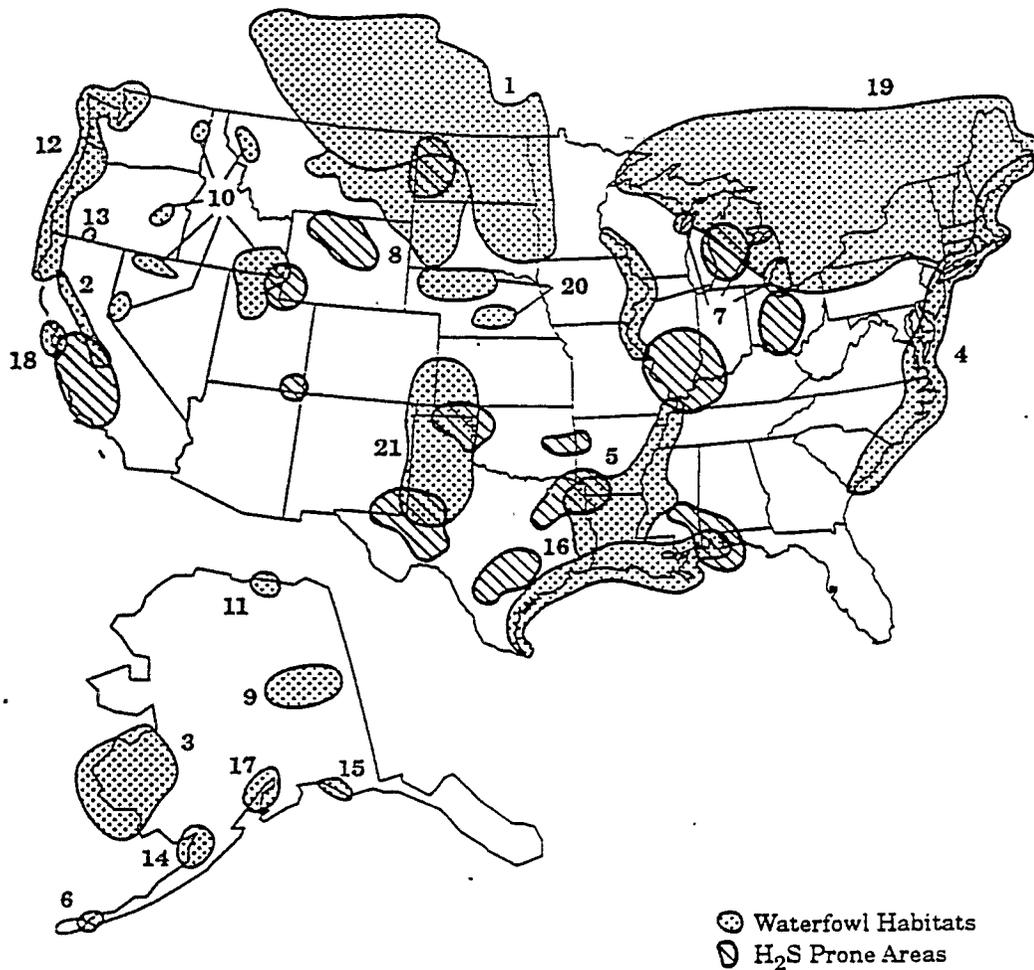
Source: Gas Research Institute, 1990.
        Coperrider, Boyd, and Stuart, 1986.

Figure III-25. Major H₂S prone areas in relation to waterfowl habitats of major concern (numbers indicate relative priority of concern).

Legend:
- ● National Forest
- ▲ National Parks
- ⬯ H₂S Prone Areas
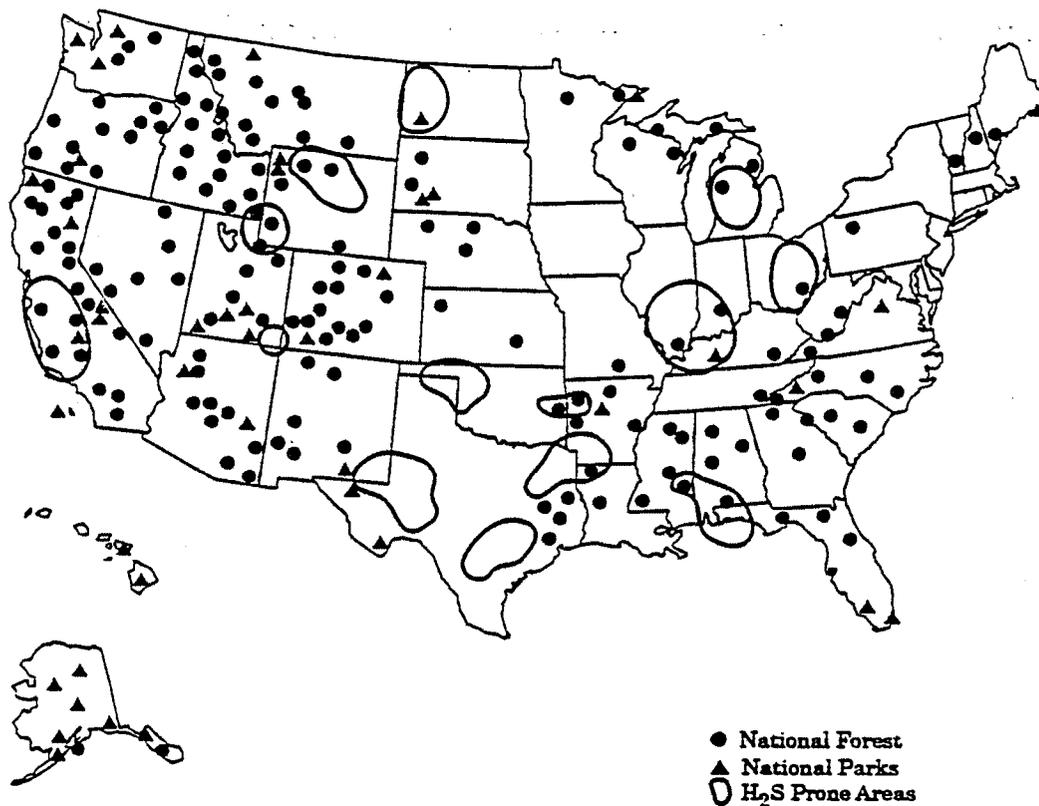
Figure III-26. Major H_2S prone areas shown in relation to National Forests and Parks.

extraction facilities, unless H_2S emission violations are suspected or complaints are filed.

11. North Dakota has three background and six special-purpose H_2S monitors. Monitoring periods vary in length from months to over a decade (32.75 years total).

12. At several locations, North Dakota monitoring data verified compliance with State H_2S standards. In two cases, data were from monitoring periods too short to support any conclusions; these were discontinued even though numerous NDAAQS violations were experienced their last year monitored.

13. North Dakota's database showed short-term H_2S concentrations ranging from 0 to 2734 ppb. The median value of all monitoring data was 0 ppb.

14. One North Dakota site had maximum short-term H_2S concentrations an order of magnitude higher than the other eight sites. At this site, more than 3,000 violations were recorded from 1984 to 1986. Concentrations improved greatly from 1986 to 1989, and only one violation occurred after the health-based standards went into effect.

15. Annual average H_2S concentrations at two sites in North Dakota approximated the RfC after introduction of a gas collection system with manifolded flares.

16. North Dakota flare operating efficiencies have been reported to range from 30 to 100 percent. (At 30 percent efficiency, H_2S can be routinely released in significant concentrations.)

17. The risk to the public of an accidental release of H_2S from the extraction of oil and gas is a function of both potential consequences and likelihood of occurrence. Judgements of risk should not be made solely on the basis of consequence analysis alone.
    a. Risks may vary from facility to facility depending on site-specific factors such as the density and distribution of nearby populations and the quality of process safety management and risk management practiced at the facility.
    b. Some facilities present greater risk than others.
    c. Risk reduction must take both consequence and likelihood of occurrence into account.

18. In addition to being toxic, H_2S is corrosive to metals in the presence of moisture and is flammable.
    a. Sour gas is flammable due to its composition of light hydrocarbons and H_2S. However, ignition of sour gas does not generally represent a thermal radiation hazard to the offsite public beyond a distance of about 100 meters.

b. The corrosivity of H₂S in the presence of moisture can cause equipment leakage and other losses in containment.

19. If accidentally released to the air under certain circumstances, H_2S can present a threat to public health and the environment.
   a. Well blowouts, line ruptures, and equipment leakage have caused accidental releases of sour gas with documented impacts on public health and the environment.
   b. The impacts on the public in the United States from sour natural gas releases from extraction activities documented in this study were limited to examples of hospital treatment and evacuation. A number of fatalities have occurred in the workplace. A single incident of the release of carbon dioxide containing H_2S from injection activities to enhance recovery resulted in the 1975 fatalities of eight members of the public.
   c. In this study, several incidents were documented as examples of both livestock and wildlife fatalities resulting from exposure to H_2S from accidental releases of sour gas.
   d. The concentration of H_2S in sour gas may vary from non-lethal levels to lethal levels above 30 percent. Unless there are high concentrations of carbon dioxide and/or hydrogen sulfide, an unprocessed sour gas mixture will usually be less dense than air and will not usually collect at ground level or in low-lying areas if accidentally released.
   e. Releases of sour gas such as from an extinguished flare or from high-pressure equipment failures (e.g., well blowouts and line ruptures) will entrain surrounding air which can cause significant dilution of the hydrogen sulfide and other components in the gas, thereby reducing the potential magnitude of the consequences of its release.
   f. A release of a sour gas mixture that is denser than air and is not significantly diluted through release phenomena (such as a jet from a high pressure source) could, under conservative atmospheric conditions, settle in low-lying areas and present a toxicity hazard. No documented incidents associated directly with oil and gas extraction were identified to support this scenario. Thus, this finding is based on theoretical premises.

20. Atmospheric dispersion modeling of worst-case scenarios shows that accidental releases of sour gas can have a range of impacts from no public impact to doses equivalent to the LC_{01} and AIHA ERPG-3 beyond 10 kilometers from the point of release.
   a. Modeling results indicate that, within a broad range of typical conditions for a vertical well blowout and emission from an extinguished flare, sour gas releases will not cause fatalities to the offsite public. This result would also apply to any similar vertical jet release at wellhead conditions resulting from equipment or line leakage.

b. Modeling results estimate that, in the worst-case, a <u>horizontal</u> release of sour gas from a well blowout (or similar high release rate jet in a horizontal orientation from equipment or piping) could produce fatalities in one percent of the human population exposed at distances up to approximately 10 kilometers.

21. Results from modeling exercises are only gross approximations of what might occur during an actual accidental release. These results are extremely sensitive to factors such as the assumed release rates and assumed meteorological conditions. Precise prediction of downwind effects from an actual release is unlikely for reasons such as:
   a. An actual release may have a different release rate than that assumed for a hypothetical scenario.
   b. The composition of an actual sour gas release may differ from that assumed in a modeling scenario.
   c. The meteorological conditions existing during an actual release may differ from those assumed in a modeling scenario.
   d. The effects of surface roughness (e.g., terrain and obstacles) are not fully understood. It is assumed in the models used that complex terrain and obstacles increase dispersion.
   e. The levels used to predict the onset of toxic effects (i.e., LC_{01} and ERPG-3) are highly uncertain.

22. While analysis of the worst-case scenario can be useful to help facilities and the community surrounding facilities to gain an understanding of the potential magnitude of severe situations, such an analysis does have its limitations. A worst-case scenario should be taken into account along with more probable scenarios when setting priorities for community emergency planning. Note, however, that the worst-case is designed to generate the maximum impact off-site and is considered to be extremely unlikely. The worst-case does not take into account a variety of factors that can significantly reduce downwind impacts.
   a. The worst-case scenario does not take into account the role of process safety management in reducing the probability of loss of containment.
   b. The worst-case scenario does not take into account mitigation actions that can reduce the amount released into the air.
   c. The worst-case scenario assumes terrain and topographical conditions that minimize dispersion of the plume. Actual conditions may result in greater dispersion.
   d. Worst-case meteorological conditions may not exist during an actual release.
   e. The dose that is actually received is uncertain and may be reduced or avoided by sheltering-in-place or evacuation.

23. Technologies have been developed to detect and reduce the amount of sour gas released as a result of breaches in containment. These technologies would serve to protect the public in inhabited areas and to protect wildlife in remote areas with

limited access by facilitating quicker mitigation. These technologies include:

   a. Subsurface safety valves;
   b. Remotely operated isolation valves;
   c. Automatically operated shutoff and isolation valves;
   e. Remotely monitored pressure and flow meters;
   f. Local and remote audible and visual warning signals; and
   g. Automatic flare ignitors and supplemental fuel sources.

In spite of the availability of detection and mitigation measures, all facilities have not uniformly adopted such measures. In addition, the reliability of such equipment and site-specific conditions must be considered before particular technologies are adopted or implemented.

24. Wells drilled in H_2S prone areas may or may not contact H_2S sources.

25. Eight States have a significant overlap of well fields and H_2S prone areas. Therefore, it is roughly estimated that as many as 280,000 oil wells and 54,000 gas wells have the potential to be located in an H_2S prone area. The actual number of sour wells in each State was not available.

26. Population densities in urban areas within ranges of 100,000-249,999 and 50,000-99,999 can be found in H_2S prone areas in California, Texas, Missouri, Florida, Illinois, Kentucky, Oklahoma, Arkansas, Ohio, Michigan, and Wyoming.

27. There have been several documented incidents of wildlife fatalities due to sour oil and gas releases. No incidents have been documented where large-scale wildlife fatalities have been caused by H_2S, and no national statistics on wildlife incidents were found. However, a Wyoming study found 237 animals killed by H_2S in two years.

28. H_2S-prone areas overlap 10 waterfowl habitats of major concern, 18 national forests and 3 national parks.

29. Land use and, therefore, potential human and ecological exposure scenarios can vary enormously around oil and gas wells:
   a. In EPA Regions 6, 8, and 9 which contain the majority of wells in H_2S prone areas (which represent 60 percent of all wells nationwide), 50 to 60 percent of the land is used as range.
   b. In Region 5 (12 percent of U.S. wells), 50 percent of land is farmed.
   c. In California, 1.7 billion bbls of oil reserves are in urban or increasingly developed residential areas.

30. ACGIH's recommended TLV-TWA for H_2S is 1×10^4 ppb (14 mg/m^3) and TLV-STEL is 1.5×10^4 ppb (21 mg/m^3).

31. AIHA ERPGs for the general public for H_2S are --
ERPG 3 - 1×10^5 ppb (1-hr exposure, not life threatening)
ERPG 2 - 3×10^4 ppb (1-hr exposure, no irreversible or serious health effects)
ERPG 1 - 100 ppb (1-hr exposure, no mild, transient adverse effects or clearly defined odor).

32. NAS/NRC H_2S guidelines for protecting the general public from the effects of accidental releases are -
90-day continuous exposure guide level - 1×10^3 ppb
24-hr emergency exposure guideline level - 1×10^4 ppb
10-min emergency exposure guideline level - 5×10^4 ppb.

REFERENCES

ACGIH. 1992. *1991-1992 Threshold Limit Values for Chemical Substances in the Work Environment*. American Conference of Governmental Industrial Hygienists.

Ahlborg, G. 1951. Hydrogen sulfide poisoning in shale oil industry. *Arch Ind Hyg Occu Med* 3:247-266.

AIChE, 1989. American Institute of Chemical Engineers, *Technical Management of Chemical Process Safety*, Center for Chemical Process Safety, New York, 1989.

AIHA. 1991. *Emergency Response Planning Guidelines: Hydrogen Sulfide*. American Industrial Hygiene Association. Akron, OH.

Alp, E. et al. 1990. *An Approach for Estimating Risk to Public Safety from Uncontrolled Sour Gas Releases*. ERCB Report 90-B (10 Volumes), Prepared by Concord Environmental Corporation for Energy Resources Conservation Board, Calgary, Alberta.

API, 1983. *API Recommended Practice 55 (RP 55), Recommended Practices for Conducting Oil and Gas Production Operations Involving Hydrogen Sulfide*, October 1981, Reissued March 1983, 1st ed., Publication No. RP55. American Petroleum Institute.

Audubon Society. 1987. Testimony of John Brophy, Co-chairman of Conservation, Fargo-Moorhead Audubon Society, North Dakota. Presented to the U.S. Senate Subcommittee on Environmental Protection, June 19, 1987, Honorable George Mitchell Chairman, in Hearings before the Subcommittee on Environmental Protection of the Committee on Environment and Public Works, U.S. Senate, 100th Congress,

First Session on S.300, S.321, S.1351, and S.1384 bills to amend the Clean Air Act-Part 2. U.S. Government Printing Office, Washington, 1987.

Bell, R.P. 1978. Isopleth Calculations for Ruptures in Sour Gas Pipelines. Energy Processing/Canada (July-August 1978).

Benedict H.M., and Breem, W.H. 1955. The Use of Weeds as a Means of Evaluating Vegetation Damage Caused by Air Pollution. *Proceedings of the Third National Air Symposium.* Pasadena, CA. Los Angles, CA National Air Pollution Symposium, 177-190.

Bilderback, D.E. 1988. The Effects of Air Contaminants on the Vegetation of Theodore Roosevelt National Park and Adjoining Areas. Final Report.

BLM. 1990. *Williston Basin Regional Air Quality Study.* U.S. Department of the Interior, Bureau of Land Management, Cooperative Effort with the North Dakota State Department of Health and Consolidated Labs; Montana State Department of Health and Environmental Sciences, and the U.S. Department of Agriculture, Forest Service.

BLM, 43CFR3160. Title 43 *Code of Federal Regulations*, Part 3160 Onshore Oil and Gas Operations; Federal and Indian Oil and Gas Leases; Onshore Oil and Gas Order No. 6, Hydrogen Sulfide Operations, Bureau of Land Management. *55 Federal Register 48958*, November 23, 1990.

Bureau of the Census. 1983. *Characteristics of the Population: General Social and Economic Characteristics.* United States Summary, Part 1, PC80-1-C1, issued December 1983, 1980 Census of Population. U.S. Department of Commerce, Washington, D.C.

Burgess, W.A. 1979. Potential Exposures in Industry: Their Recognition and Control. In: *Patty's Industrial Hygiene and Toxicology*, G.D. Clayton, ed., John Wiley and Sons, New York, NY, 1:1149-1222.

Casarett and Doull. 1986. *Toxicology.* C.D. Klassen, M.O. Amdur, and J. Doull, ed., Macmillan Publishing, New York.

CDC. 1988. *California Oil, Gas, and Geothermal Resources: An Introduction*, 4th ed. Based on the 2nd edition by D.E. Ritzius. California Department of Conservation, Division of Oil and Gas, Sacramento, CA.

Cloe, W.W. 1985. Selected Occupational Fatalities Related to Toxic and Asphxiating Atmospheres in Confined Work Spaces As Found in Reports of OHSA Fatality/Catastrophe Investigations, U.S. Department of Labor.

Cooperider, A.Y., Boyd, R.J., and Stuart, H.R., eds. 1986. *Inventory and Monitoring of Wildlife Habitat*. U.S. Department of the Interior, Land Management Service Center, Denver, CO.

Curtis, C.G., Barholomew, T.C., Rose, F.A., and Dodgson, K.S. 1972. Detoxication of sodium 35 S-sulfide in the rat. *Biochem Pharmacol* 21:2313-2321.

Crump, K.S. and Howe, R.S. 1984. The multistage model with a time-dependent dose pattern: applications to carcinogenic risk assessment. *Risk Analysis* 4:163-176.

Dielwart, J., Knox, H., and Angle, R. 1979. *A Report by the Alberta Petroleum Industry, Government Environmental Committee on Hydrogen Sulfide Isopleth Prediction: Phase II Pipe Burst Study*. APIGEC.

Dosch, M.W., and Hodgson, S.F. 1986. *Drilling and Operating Oil, Gas, and Geothermal Wells in an H$_2$S Environment*, Publication No. M10. California Department of Conservation, Division of Oil and Gas, Sacramento, CA, 39.

Ermak, D.L. 1989. *User's Manual for the SLAB Model, An Atmospheric Dispersion Model for Denser-than-Air Releases*. Lawrence Livermore National Laboratory.

Esmoil, B.J. 1991. *Wildlife Mortality Associated with Oil Pits in Wyoming*. Master's Thesis, University of Wyoming, Laramie, Wyoming. Also published as a Final Report by the Wyoming Cooperative Fish and Wildlife Research Unit, February 1991.

Evans, C.K. 1967. The toxicity of hydrogen sulfide and other sulfides. *J Exp Physiol* 52:231-248.

Gas Research Institute, Chicago, IL. 1990. *Chemical Composition of Discovered and Undiscovered Natural Gas in the Continental United States*. Volume 2: Statistics by Basin and Formation-Non-Associated Gas. Prepared by Energy and Environmental Analysis, Inc.

Gephart, L., and Moses, S. 1989. An Approach to Evaluate the Acute Impacts from Simulated Accidental Releases of Chlorine and Ammonia. *Plant/Operations Progress* 8 8-11.

Guidelines for Chemical Process Quantitative Risk Analysis. 1989. Center for Chemical Process Safety of the American Institute of Chemical Engineers, New York.

Gunina, A.I. 1957. Transformation of sulfur-35-labeled hydrogen sulfide introduced into blood. *Dokl Akad Nauk SSSR* 112:902-904.

Haggard, H.W. 1925. The toxicology of hydrogen sulfide. *J Ind Hyg* 7:113-121.

Harris, B. 1986. Study into long-term effects on livestock following the Lodgepole blowout. Alberta Agriculture, Edmonton, Alberta, Canada.

Heck, W.W., Daines, R.H., Hindawi, I.J. 1970. Other Phytotoxic Pollutants. In: *Recognition of Air Pollution Injury to Vegetation: a Pictorial Atlas*, J.S. Jacobson and A.C. Ill, eds.

Higashi, T., Toyama, T., Sakurai, H., Nakaza, M., Omae, K., Nakadate, T., Yamaguchi, N. 1983. Cross sectional study of respiratory symptoms and pulmonary functions in rayon textile workers with special reference to H2S exposure. *Ind. Health* 21:281-292.

Hoyle, W. 1973. Summary of Alton Special Project (Inter-office correspondence), Illinois Environmental Protection Agency, Springfield, IL.

Illinois Institute for Environmental Quality. 1974. Hydrogen Sulfide Health Effects and Recommended Air Quality Standard. Document No. 74-24. Chicago: State of Illinois, Institute for Environmental Quality, p27.

IOGCC. 1992. *A Study of Idle Oil and Gas Wells in the United States*. Interstate Oil and Gas Compact Commission (IOGCC) and United States Department of Energy.

Johnson, D.W. 1991. Prediction of Aerosol Formation from the Release of Pressurized, Superheated Liquids to the Atmosphere. In *International Conference and Workshop on Modeling and Mitigating the Consequences of Accidental Releases of Hazardous Vapors*. American Institute of Chemical Engineers, NY.

Kangas, J., Jappinen, P., Savalainen, H. 1984. Exposure to Hydrogen Sulfide, Mercaptans, and Sulfur Dioxide in Pulp Industry. *American Industrial Hygiene Association Journal* 45: 787-90.

Kleinfeld, M., Giel, C., Rosso, A. 1964. Acute hydrogen sulfide intoxication: an unusual source of exposure. *Ind Med Surg* 33:656-660.

Laug, E.P., and Draize, J.H. 1942. The percutaneous absorption of ammonium hydrogen sulfide and hydrogen sulfide. *J Pharmacol Exp Ther* 76:179-188.

Layton, D.W., et al. 1983. *Accidental Releases of Sour Gas From Wells and Collection Pipelines in the Overthrust Belt: Calculating and Assessing Potential Health and Environmental Risks*. Lawrence Livermore National Laboratory Report UCRL-53411, Prepared for the Division of Fluid Mineral Operations, Bureau of Land Management, U.S. Department of the Interior, Washington, DC.

Liebsch, E. 1985. State Trends in Well Flaring. North Dakota State Department of Health, Intradepartmental Memorandum.

Lodgepole Blowout Inquiry Panel. 1984. Lodgepole blowout inquiry phase I report to the lieutenant governor in council with respect to an inquiry held into the blowout of the well, Arusco Dome Brazean River 13-12-48-12. Calgary, Alberta, Canada: Energy Resource Conservation Board; report no. D84-9.

McCabe, L.C., and Clayton, G.D. 1952. Air pollution by hydrogen sulfide in Poza Rica, Mexico: An evaluation of the incident of Nov. 24, 1950. *Arch. Ind. Hyg. Occup. Med.* 6 199-213.

McCallen, S.E.A., Hartzell, A., Wilcoxon, F. 1936. *Hydrogen Sulphide Injury to Plants.* Contrib. Boyce Tompson Inst. 8: 189-197.

National Response Center, Washington, DC, Incident Report 72218

National Response Center, Washington, DC, Incident Report 76451

NCCT. 1985. Hydrogen Sulfide. National Council Committee on Toxicology, National Research Council. In: *Emergency and Continuous Exposure Guidance Levels for Selected Airborne Contaminants. Vol. 4*, Washington, DC, National Academy Press, pp. 55-68.

NFPA. 1974. *National Fire Codes--A Compilation of NFPA Codes, Standards, Recommended Practices, and Manuals: Combustible Solids, Dusts and Explosives. Volume III*, National Fire Protection Association, Boston, MA, 49-160 - 49-161.

NIOSH. 1977. *NIOSH Criteria for a Recommended Standard.... Occupational Exposure to Hydrogen Sulfide*, Publication No. 77-158. U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, Cincinnati, OH, 79.

North Dakota State Department of Health and Consolidated Laboratories. 1983. *Sulfur Dioxide Emissions Inventory for Sources near the Theodore Roosevelt National Park.* Final Report.

North Dakota State Department of Health, Oil Field Complaint File, 5 April 1989.

NRC. 1979. *Hydrogen Sulfide.* National Research Council. USA Subcommittee on hydrogen sulfide. University Park Press, Baltimore, MD.

NRC. 1986. National Research Council, Committee on Toxicology. *Criteria and Methods for Preparing Emergency Exposure Guidance Level (EEGL), Short-Term Public*

Emergency Guidance Level (SPEGL), and Continuous Exposure Guidance Level (CEGL) Documents. National Academy Press, Washington, D.C.

Oil Daily; No. 7773, November 18, 1982.

Ooms, G. 1974. A New Method for the Calculation of the Plume Path of Gases Emitted by a Stack, *Atmospheric Environment* 6 899 - 909: See also: Ooms, G., A.P. Mahieu and F. Zelis, "The Plume Path of Vent Gases Heavier than Air," First International Symposium on Loss Prevention and Safety Promotion and Safety Promotion in the Process Industries, The Hague (1974): Ooms, G. and N.H. Duijm, "Dispersion of a Stack Plume Heavier than Air," IUTAM Symposium on the Atmospheric Dispersion of Heavy Gases and Small Particles, Delft (1983) - Springer - Verlag, Berlin/Heidelberg.

Platt's Oilgram News, Vol. 68, May 31, 1990.

Quest Consultants, Inc. 1992. *Hazards Analysis/Risk Analysis Study of Union Pacific Resources Company's Wahsatch Gas Gathering Pipeline System.* Prepared for Union Pacific Resources Company, Fort Worth, TX.

Rand, McNally. 1992. *Road Atlas.* Rand McNally, Chicago, IL.

Rogers, R.E., and Ferin, J. 1981. Effect of hydrogen sulfide on bacterial inactivation in the rat lung. *Archive of Environmental Health* 36:261-264.

SAIC. 1990. *SAIC's Computer Programs for Modeling the Atmospheric Dispersion of Hazardous Vapors - Model Description and User's Guide.* Science Applications International Corporation, Reston, VA.

Sierra Club. 1987. Testimony of J.L. Lamb, Executive Committee Member, Chairman of Conservation in North Dakota, Dacotah Chapter, Sierra Club. Presented to the U.S. Senate Subcommittee on Environmental Protection, June 19, 1987, Honorable George Mitchell Chairman, in Hearings before the Subcommittee on Environmental Protection of the Committee on Environment and Public Works, U.S. Senate, 100th Congress, First Session on S.300, S.321, S.1351, and S.1384 bills to amend the Clean Air Act- Part 2. U.S. Government Printing Office, Washington, 1987.

Smith, R.P., and Gosselin, R.E. 1964. The influence of methemoglobinemia on the lethality of some toxic anions. *Toxicol Appl Pharmacol* 6:584-592.

Smith, R.P., and Gosselin, R.E. 1979. Hydrogen sulfide poisoning. *J Occup Med* 21:93-97.