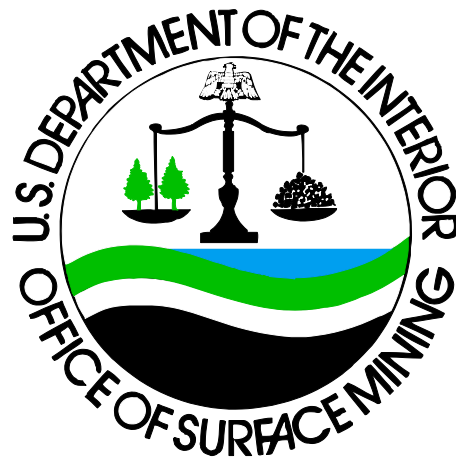




**TECHNICAL MEASURES FOR THE
INVESTIGATION AND MITIGATION
OF FUGITIVE METHANE HAZARDS
IN AREAS OF COAL MINING**

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PREFACE

Explosive levels of methane are occasionally a problem near or in homes, wells, and other structures. The methane can be generated or liberated from active or abandoned underground mining that is occurring or has occurred underneath or adjacent to these structures. The methane may also come from other sources such as oil wells, gas wells, wetlands, landfills, and septic systems.

The Office of Surface Mining Reclamation and Enforcement (OSM) recognizes that hazardous situations may occasionally be caused by current or past coal mining. Methane is not specifically regulated under the Surface Mining Control and Reclamation Act of 1977 (Act). However, the Act at Section 521(a)(2) states that “When... any condition or practices exist which condition, practice, or violation also creates an imminent danger to the health and safety of the public the secretary shall immediately order a cessation of surface coal mining and reclamation operations or the portion thereof relevant to the condition, practice, or violation.” Methane at explosive levels is an imminent danger. Thus, when methane related to active coal mining causes an imminent harm situation, OSM or the State regulatory authority has the responsibility to act.

The Act also addresses abandoned mine lands (AML) at Section 410(a): “ The Secretary is authorized to expend moneys from the fund for the emergency restoration, reclamation, abatement, control, or prevention of adverse effects of coal mining practices... if...(1) an emergency exists constituting a danger to the public health, safety, or general welfare...” Methane accumulation in or near homes from abandoned mines can pose a safety risk and therefore warrants action.

Other Federal and State agencies may have comparable responsibilities. However, little compiled literature exists on how to determine when methane levels pose an imminent harm or safety problem or on how to locate the source. This document gathers, summarizes, and references the literature to facilitate future methane evaluations.

OSM provides this manual as a public service. While the primary target guidance of this document is government scientists, geologists, and engineers, it should also be helpful to the public and industry representatives.

Glenda Owens
Acting Director

PURPOSE

Fugitive methane is the uncontrolled release of methane into the atmosphere. It may create an imminent harm to the public or private property. Ultimately, methane should not be allowed to accumulate to explosive levels in wells or structures. This document outlines testing and evaluation protocols for methane in wells, dwellings and soils near coal mines and recommends when action is prudent to prevent or mitigate methane accumulation. These technical guidelines to evaluate fugitive methane are established to:

- T evaluate the scope of the problem,
- T define investigative procedures,
- T develop sampling protocols,
- T assess hazard potential, and
- T delineate potential mitigation techniques.

Disclaimer

Nothing in this manual is a substitute for thoughtful and thorough investigative procedures in circumstances involving a potentially serious methane problem. This manual is intended to provide guidance regarding methane and is solely for the benefit of the users. No duties, rights, or benefits, substantive or procedural, are created or implied by this manual. The contents of this manual are not enforceable by any person or entity against the Office of Surface Mining Reclamation and Enforcement or the United States.

Acknowledgments

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Abbreviations

ACGIH-	American Conference of Governmental Industrial Hygienists
AQMO-	Air Quality Management District
ATM-	Atmosphere
CGI-	Combustible Gas Indicator
CM³/G-	Centimeters Per Cubic Gram
DO-	Dissolved Oxygen
GC-	Gas Chromatography
GPM-	Gallons Per Minute
GPS-	Global Positioning System
IC-	Information Circular
IR-	Infrared
LEL -	Lower Explosive Limit
MG/L-	Milligrams Per Liter
ML-	Milliliters
MPA-	Millipascals
MSHA-	Mining Safety and Health Administration
MSW-	Municipal Solid Waste
NIOSH-	National Institute for Occupational Safety and Health
OSHA-	Occupational Safety and Health Administration
OVA-	Organic Vapor Analyzer
PADEP-	Pennsylvania Department of Environmental Protection
PPM-	Parts Per Million
PSI-	Per Square Inch
STP-	Standard Temperature and Pressure
TDS-	Total Dissolved Solids
LV-	Threshold Limit Values
TLV-C-	Threshold Limit Values Ceiling
TLV- STEL-	Threshold Limit Values--Short-Term Exposure Limit
TLV- TWA-	Threshold Limit Values--Time-Weighted Average
UEL-	Upper Explosive Limit
USBM-	United States Bureau of Mines
VOC-	Volatile Organic Compound

SECTION I CHARACTERISTICS AND OCCURRENCE OF METHANE

1.0 INTRODUCTION

Methane (CH_4) is a colorless, odorless, tasteless gas and can be referred to as natural gas, light carburetted hydrocarbon, firedamp, and marsh gas. High methane concentrations can cause oxygen-deficient atmospheres, flammable situations, or explosive environments.

When methane enters the atmosphere as a point source, it can be readily ignited if the concentration exceeds 5 percent. Atmospheric methane can ignite at concentrations between 5 and 15 percent at Standard Temperature and Pressure (STP). Higher levels can quickly dilute to flammable levels. In either case, if methane is allowed to accumulate in an enclosed area, an explosive environment may develop. An explosive environment exists when a mixture of gases can self-propagate a flame throughout the mixture, independent of, and away from, the source of ignition. An ignition source can be an electrical outlet, pilot light, well pump, or match.

Occasionally, the subterranean migration of methane presents a hazard at the ground surface, primarily in structures (buildings). Potential sources include: decaying organic matter, swamps, abandoned/improperly constructed gas wells, natural seeps, leaking pipes, landfills, and abandoned or active coal mines. Entry into a structure can occur through cracks in the floor, along buried utilities, or as a dissolved component of water. When allowed to accumulate in a structure, an explosion may result as shown in Figure 1.



Figure 1. Remains of a two story residence as a result of an explosion from uncontrolled fugitive methane.

Combustion requires fuel (methane), oxygen, and a source of ignition (Figure 2). Most methane problems are usually associated with confined spaces or enclosed structures where the gas can build up to explosive levels.

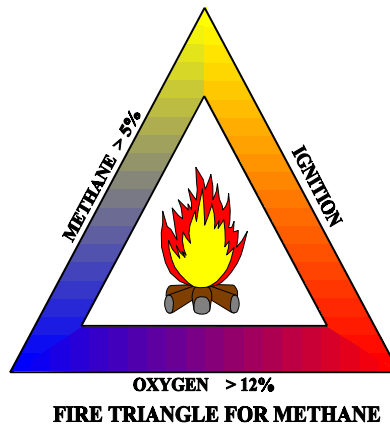


Figure 2. Fire Triangle.

In addition to the danger of homes exploding, other occurrences and/or undesirable effects of fugitive methane include:

- T Explosion of well houses
- T Igniting of spigots
- T Igniting of well heads
- T Human suffocation
- T Gas bubbles in streams
- T Fires at surface cracks
- T Dead surface vegetation
- T Cracking or blistering of pavement

Information about methane is important to public safety officials and inspectors, who should have at least a practical knowledge of how the gas might be produced, where it might be encountered, and what its effects are. Such knowledge reduces the likelihood of hazardous situations developing or at least identifies them at the earliest possible time.

Tests for methane and other dangerous gases are often made by officials and workers in response to citizen complaints. Proper use of the detecting devices requires at least a basic knowledge of these gases. The properties of normal air and other gases are important to know in the relation of the physical and chemical properties of methane. Portable gas meters are the best “on-the-spot” investigative tools allowing for dangerous concentrations to be immediately identified.

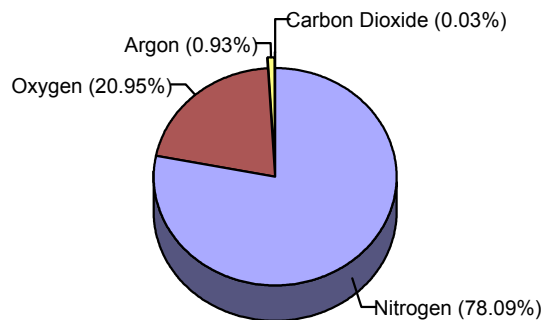
2.0 GAS CHARACTERISTICS

The physical and chemical properties of gases allow their movement to be predicted and their reactions in the atmosphere to be determined. Methane migrates from high to low pressure zones, from higher to lower levels of concentration, and by molecular diffusion. Molecular diffusion becomes a prominent factor when flow rates are extremely low to stagnant.

2.1 Normal Air: Normal or ambient air is a mixture of several gases which, though ordinarily invisible, can be weighed, compressed to a liquid, or frozen to a solid. All gases are affected by temperature, water vapor, and pressure. The global movement of air caused by these changes defines the weather patterns. These factors also affect the migration of methane. Thus, the way the atmosphere reacts with methane is important in investigating and controlling fugitive methane.

Dry air at sea level at standard temperature and pressure (STP, 20°C, 1 atmosphere) contains mostly nitrogen, oxygen, and argon with a small amount of carbon dioxide (Figure 3). Concentrations of gases are usually reported in two distinct ways:

- T Percent volume (%)
- T Parts per million (ppm)



Principal Components of Dry Air

Figure 3. Atmospheric air components.

Large components of gas such as oxygen and nitrogen in air are represented as a percentage of the total volume. Smaller constituents of the atmosphere, including toxic gases, are usually reported as parts per million (ppm) of the total volume. The relationship between ppm and

percentage is as follows:

Percentage	1.0	0.1	0.01	0.001	0.0001
PPM	10,000	1,000	100	10	1

Traces of other gases are also present in air. Table 1 shows the common components of normal air.

Table 1. Composition of Normal Dry Air

Constituent	Symbol	Percentage	PPM
Nitrogen	N ₂	78.084	
Oxygen	O ₂	20.946	
Argon	Ar	0.934	
Carbon Dioxide	CO ₂	0.033	
Neon	Ne		18.18
Helium	He		5.24
Methane	CH ₄		2.0
Krypton	Kr		1.14
Xenon	Xe		0.087
Nitrous Oxide	N ₂ O		0.5
Hydrogen	H ₂		0.5

Air may be contaminated by small concentrations of other gases such as carbon monoxide, sulfur dioxide, hydrogen sulfide, oxides of nitrogen, and excess carbon dioxide. These components change slightly depending on the effects of pollution and the associated geographic area.

2.2 Physical Properties of Gases: Gases behave according to the basic physical properties of the Ideal Gas Law (gravity, pressure, and temperature). Gases expand or contract as the temperature changes. Unlike solids and liquids, gases can be compressed. However, an analysis of normal air, regardless of where a sample may be collected, should contain the same proportions of oxygen, nitrogen, argon, and trace gases per unit volume. Changes in pressure or temperature do not affect the normal air proportions; they only change the unit volume of gases. This change in unit volume is obvious at high elevations where less oxygen is available to breathe.

2.2.1 Specific Gravity: Specific gravity is the relationship by weight of a volume of gas to a like volume of air under the same pressure and temperature conditions. The specific gravity of air is 1.000. Thus, methane at a specific gravity of 0.555 is lighter than air

and will rise in air.

A simple approximation of the specific gravity of a gas at STP is done by dividing the molecular weight of the gas by the molecular weight of air, 28.8. The molecular weight and specific gravity of common gases are listed in Table 2:

Table 2. Common naturally occurring gases.

Gas	Chemical Symbol	Molecular Weight	Specific Gravity
Air	---	---	1.000
Hydrogen	H ₂	2	0.070
Methane	CH ₄	16	0.555
Propane	C ₃ H ₈	44	1.562
Ethane	C ₂ H ₆	30	1.049
Water	H ₂ O	18	0.625
Nitrogen	N ₂	28	0.967
Carbon Monoxide	CO	28	0.967
Oxygen	O ₂	32	1.105
Hydrogen Sulfide	H ₂ S	34	1.191
Carbon Dioxide	CO ₂	44	1.529

2.2.2 Diffusion: Diffusion is the gradual mixing of two or more gases that come in contact with each other. Even without mass air movement, molecules are always moving. For example, if smoke is injected into one part of a closed room, it will eventually spread throughout the room, resulting in an even mixture.

It should be noted that diffusion speeds up as temperature increases and slows as temperature drops. Graham's Law of Diffusion states that the relative rates of diffusion of two gases are inversely proportional to the square root of their densities (molecular weight).

2.2.3 Atmospheric Pressure: The pressure of the air upon an object on the earth's surface is equal to the weight of the column of air extending from the object to the upper limits of the atmosphere, a distance estimated to be 200 miles (322 km). The pressure of the atmosphere decreases when measured at an elevation above sea level and increases below sea level. At sea level, when the temperature is 0EC (32EF) and at standard gravity, the atmosphere exerts a standard pressure of 14.7 pounds per square inch (psi) or 0.1 millipascals (MPa). This pressure is called one atmosphere. Barometric pressure is the measurement of atmospheric pressure and can be measured in any one of the equivalents

in Table 3.

Table 3. Equivalent units of atmospheric pressure.

Gravity	Mercury		Water		Pressure	
1 atm	760 mm	29.9 in	10.3 m	33.9 ft	14.7 psi	0.1013 MPa

Changes in atmospheric pressure strongly affect the migration of gases. Fluctuating barometric conditions are known to cause changes to soil-gas chemistry and ground-water levels. For example, low barometric pressure (stormy-weather indicator) produces less atmospheric pressure and results in soil outgassing or can cause a rise in ground-water levels. High barometric pressure (fair-weather indicator) produces more pressure on the atmosphere and results in infusion of ambient air into the soil/rock matrix and a possible drop in ground-water levels. In abandoned mines, gas outflow problems are often triggered or become worse during rapid reductions in barometric pressure.

In active underground mines, a fan creates a low-pressure zone that draws air through the mine to remove mine gases. Ventilation is designed to compensate for atmospheric pressure changes.

2.2.4 Boyle's Law: This physical law is important when considering atmospheric pressure changes, as measured by a barometer, on gases. At constant temperature, the volume of a given quantity of any gas varies inversely in relation to the pressure to which the gas is subjected. That is, if a gas is subjected to double its original pressure, the volume of gas is reduced to one-half of its original volume. If the pressure of gas is increased four times the volume is decreased by one-quarter its original size, etc.

Boyle's Law can be demonstrated as follows:

$$\begin{array}{ccccccc} \text{INITIAL} & : & \text{FINAL} & & \text{FINAL} & : & \text{INITIAL} \\ \text{VOLUME} & & \text{VOLUME} & = & \text{ABSOLUTE} & & \text{ABSOLUTE} \\ & & & & \text{PRESSURE} & & \text{PRESSURE} \end{array}$$

$$V_1 : V_2 = P_2 : P_1$$

$$\text{or } V_1 * P_1 = V_2 * P_2$$

These pressure changes influence gas emissions from underground coal mines and the behavior of mine air occupying abandoned mine workings.

The following mine gas problem can be solved using Boyle's Law:

In the morning, an abandoned mine contains a 1,000,000 cubic feet volume of methane- rich air at a barometric pressure of 29.8 inches of mercury. Later that day, the barometric pressure drops by 0.5 inches of mercury. How much gas

would be expected to exhaust from the mine due to expansion?

Substituting the relevant values into Boyle's Law:

$$1,000,000 : V_2 = 29.3 : 29.8$$

$$V_2 = 1,000,000 \times 29.8 / 29.3$$

$$V_2 = 1,017,065 \text{ ft}^3.$$

$$\hat{V} = 1,017,065 - 1,000,000 = 17,065 \text{ ft}^3.$$

Thus, the volume of air and methane forced out of the mine would be 17,065 cubic feet. Conversely, if the barometer rose, indicating an increase in air pressure, the air in the mine would be compressed and draw air into the abandoned mine.

As these examples demonstrate, the barometric pressure must be noted when measuring or sampling gases. Sampling of abandoned mines should be performed during periods when the barometer is falling to accurately characterize the gases exhausting from the mine.

2.2.5 Charles' Law: This law states that, at constant pressure, the volume of a given mass of gas at different temperatures is directly proportional to the corresponding absolute temperatures (within moderate temperature ranges). Absolute temperature (Kelvin) is the temperature in Fahrenheit plus 460, then divided by 1.8. Absolute temperatures are measured from absolute zero (-460E F) at which temperature a gas would show no pressure, if the general law for gases holds for all temperatures.

If V_1 is a volume of gas at absolute temperature T_1 , and V_2 is a volume of the same gas at absolute temperature T_2 , then the proportion may be written as:

$$\begin{array}{ccccccc} \text{INITIAL} & & \text{FINAL} & & \text{INITIAL} & & \text{FINAL} \\ \text{VOLUME} & : & \text{VOLUME} & = & \text{ABSOLUTE} & : & \text{ABSOLUTE} \\ & & & & \text{TEMPERATURE} & & \text{TEMPERATURE} \end{array}$$

$$V_1 : V_2 = T_1 : T_2$$

$$\text{or } V_1 / T_1 = V_2 / T_2$$

The following example shows an practical application of Charles' Law:

If 10,000 ft³. of air at 32E F is heated to 60E F by passing through a mine, what is the increased or expanded volume of air, assuming the pressure remains constant.

$$10,000 : V_2 = (460+32)/1.8 : (460+60)/1.8$$

$$10,000 : V_2 = 273.3 : 288.8$$

$$V_2 = 10,000 \times 288.8 / 273.3 = 10,567$$

Therefore, the increased air volume is 567 ft³ after the gas has passed through the mine.

2.3 Methane Gas Properties: Methane’s chemical formula is CH₄, which is one atom of carbon and four atoms of hydrogen, and its molecular weight is 16. Methane is the lightest of all hydrocarbons (sp. gr. 0.555); it diffuses very rapidly in air and is odorless. If allowed to accumulate in a stagnant atmosphere, the gas will stratify in relation to other gases according to their relative specific gravities (Figure 4).

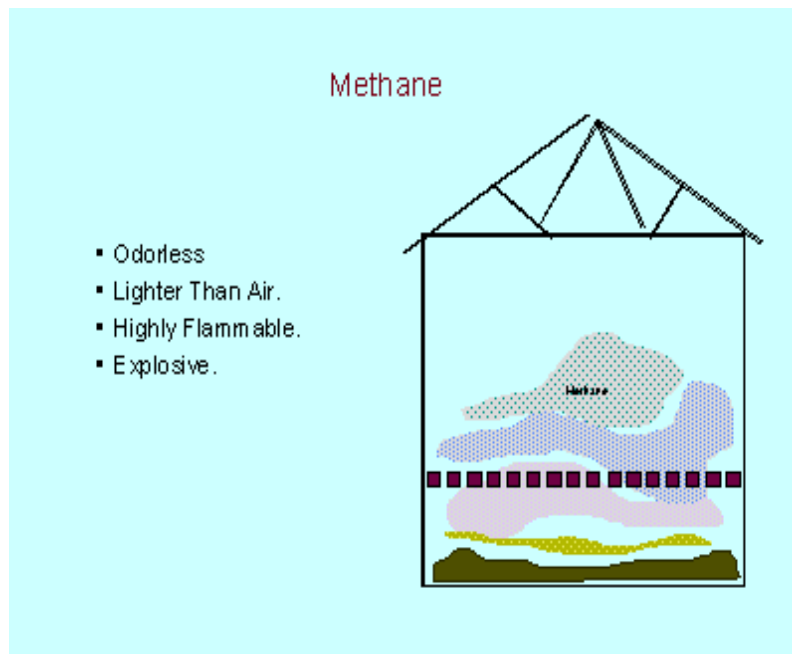


Figure 4. Conceptual model of gas stratification.(Source: ISU Extension publication #: Pm-1518k)

The inflammable and explosive range of methane is variable and “all occurrences of the gas should be considered dangerous.” With the right balance of oxygen, methane burns with a pale blue flame. Atmospheric conditions with 5 to 15 percent methane and 12 percent or more oxygen will result in an explosion. The most powerful explosive air mixture contains 9.5% methane.

Other hydrocarbon gases, including ethane and propane, can occur naturally with methane.

Ethane and propane are typically found only in small percentages or trace amounts. These compounds may come from adjacent oil and gas fields or from a coalbed.

2.3.1 Methane concentrations: Most gas concentrations are reported in percentages or parts per million. Explosive gases are frequently reported as a percentage of their explosive range.

The Lower Explosive Limit (LEL) and Upper Explosive Limits (UEL) define the range of concentrations where flammable gases or vapors are explosive when mixed with air. Methane at 5% is at the lower explosive limit, and 15% is the upper explosive limit. The concentration range is given in percentage by volume of the gas, mixed in air at standard temperature and pressure, in which ignition from an external source is possible. The values are given at 20E C and 1 atm. Other gases have different explosive limits as shown in Table 4.

Table 4. Explosive ranges of some gases.

Compound	Empirical Formula	Explosive Limits %	
		Lower	Upper
Methane	CH ₄	5.00	15.00
Ethane	C ₂ H ₆	3.00	12.50
Propane	C ₃ H ₈	2.12	9.35
Hydrogen	H ₂	4.00	74.20
Carbon Monoxide	CO	12.50	74.20

CRC Handbook of Chemistry & Physics 55TH Edition 1974

Methane is often measured in the range of 0-100 percent of the LEL. However, many methanometers (combustible-gas indicator calibrated to methane) and older gas meters measure only in the range of LEL for the particular gas for which they are calibrated. Modern equipment is usually selectable between a range of 0.0 and 5.0% methane (0-100 % LEL) or the full percentage range. Care must be observed not to misunderstand the display ranges. Simply put: %CH₄ = % LEL × 0.05 or % LEL = % CH₄ × 20. The relationship of LEL to percent methane or parts per million of methane are displayed in Table 5.

2.3.2 Methane Combustion: The ideal stoichiometric mix for methane combustion is 9.5% methane in air. At this concentration, combustion consumes all of the available methane and oxygen, resulting in the formation of only CO₂ and H₂O. This mix produces the most energetic methane combustion, reaching a flame temperature of about 1,915E C.

Table 5. Methane level equivalent units.

%-CH ₄	ppm-CH ₄	%-LEL
0.05	500	1
0.1	1,000	2
0.5	5,000	10
1.0	10,000	20
2.0	20,000	40
3.0	30,000	60
4.0	40,000	80
5.0	50,000	100

An oxygen-deficient reaction results in the formation of products other than CO₂ and H₂O. Since there is insufficient oxygen for a complete reaction, products are formed that require less oxygen. The order of these other products is CO, C (carbon, i.e. smoke) and H₂, with a possibility of a small increase of C₂ to C₅ hydrocarbons including unaturates (Kim,1978). Since not all of the methane is consumed, there is also CH₄ remaining.

Oxygen-deficient combustion is much less energetic than stoichiometric combustion. This is mainly due to the large specific heats of formation of the other products. Energy adsorption increases with methane concentration, until at greater than 15% methane in air the combustion process cannot be sustained. The flame temperature of, say, an 11% mixture in air is about 1,840°C.

An oxygen-rich reaction results in the formation of the usual CO₂ and H₂O but also oxygenates that require a lot of O₂ such as formaldehyde (CH₂O), methanol (CH₄O), and ethanediol (C₂H₆O₂). The reaction yields much less energy because the excess O₂ absorbs energy from the reaction to form the other byproducts. Combustion becomes increasingly inhibited, until at less than 5% methane the combustion process cannot be sustained. The flame temperature of an 8% mixture in air is less than 1,800°C.

In practical terms, for combustion at or below 9.5% methane in air, the products of combustion are CO₂ and H₂O. For combustion above 9.5% methane in air, the products of combustion are CO₂, H₂O, CO, C and H₂.

3.0 HAZARDOUS EFFECTS OF METHANE

Air is composed of gases balanced by the activities in nature. People require normal air to breath and to function efficiently. Although mankind has affected the atmosphere through pollution and other activities, this balance of gases has changed little. Thus, the components of air remain

relatively constant.

Many hazardous gases are deceptive and difficult to identify. Methane is difficult to identify because it is colorless, odorless, and tasteless. Hazardous gases may affect people in three adverse ways:

- T Explosion
- T Toxic reaction
- T Asphyxiation

Each of these must be discussed to understand all of the risks of working with gases. All three are potential hazards where methane exists. Burning or exploding methane can produce a toxic environment. Elevated methane levels can cause asphyxiation.

3.1 Explosive Gases: Explosive gases can be ignited by open flames, sparks from tools machinery, or electric connections. The explosive creates hazards in the following ways:

- T Percussion from the rapid expansion of gases.
- T Burning from the increase in heat.
- T Asphyxiation from the consumption of oxygen.
- T Toxic gases from the chemical reaction.

When methane is allowed to accumulate in an enclosed space, an explosion may occur, as shown in Figure 5. The experiment depicted in the figure was conducted by the BRE Fire Research Station in England. A constructed room or explosion chamber containing 10% methane gas in air was ignited using a capacitive discharge spark. The ensuing explosion began near the television and propagated outward. It resulted in the ignition of the contents of the waste paper bin in the corner of the room and some singeing of the carpet and soft furnishings. Major damage was caused by the plasterboard walls detaching from the chamber due to the explosion pressure. The remnants of a house that suffered a blast from a similar explosion mechanism are shown in Figure 1.

Methane concentrations above 15 percent are also dangerous. High concentrations quickly dilute to explosive or flammable levels near the source. Figure 6 shows a water well that vents 95% methane and has been ignited by a spark from the wiring of a submersible pump. Note the proximate location of the front entrance to the home. With care, the flame can be extinguished by capping the well (Figure 7).

In coal mines, methane was historically a common cause of death because it was allowed to accumulate to explosive levels. Methane is now controlled by dilution with fresh air (via a ventilation system) and/or degasification or drainage before mining. Modern mining techniques such as longwall mining liberate more methane than room-and-pillar mines because the method



Figure 5. A methane gas explosion propagates through a living room. Experiment conducted by BRE's Fire Research Station for Fire Investigators at the BRE Cardington Laboratory (UK).



Figure 6. Burning ground-water well venting methane.



Figure 7. Extinguishing the flame.

rapidly exposes large coal surface areas and pockets that store methane.

3.2 Toxic gases: These gases are the most difficult to detect and can be composed of a wide range of substances. Toxic gases are usually measured by volume in parts per million and their identification requires sensitive field equipment or laboratory testing. Some toxic gases are combustible and all will act as asphyxiants as they replace oxygen.

Very low concentrations of toxic gases can affect an individual immediately upon exposure. Most toxic gases have a cumulative effect on the body which may not be reversible or may take a long time to neutralize. For example, carbon monoxide (CO) takes a long time to be removed from blood. The CO bonds to the red blood cells with a higher affinity than either oxygen or carbon dioxide. Thus, it cannot easily be respired out of the body.

The presence of toxic gases in an atmosphere may be due to any of the following:

- T Blasting or other explosions.
- T Fires.
- T Liberation from ore or country rock, as with methane.
- T Decaying organic material.
- T Use of diesel and gasoline motors in enclosed areas.
- T Gas carried with geothermally derived water or carbon dioxide.
- T Gas carried chemically by various chemicals and reagents.

Methane itself is not toxic but may produce toxic gases during combustion. Depending on the source, it is sometimes associated with other toxic gases. As described above, the combustion process can yield high levels of CO. If toxic gases are suspected, the area must be ventilated before entry.

The degree of toxic effect of both gaseous and particulate contaminants depends largely upon the airborne concentration and the length of exposure. A list of threshold limit values (TLVs) is published yearly by the American Conference of Governmental Industrial Hygienists (ACGIH). Since methane is not toxic, it is not listed. However, many gases associated with methane are listed. According to the ACGIH, the TLVs refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. The three categories of TLVs are described as follows:

Threshold Limit Values - Time-Weighted Average (TLV-TWA): The time-weighted average concentration, for a normal 8-hour workday and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse health effects.

Threshold Limit Values - Short-Term Exposure Limit (TLV-STEL): 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 materially reduce work efficiency. The STEL should not exceed 15 minutes and should not occur more than four times per day, with at least 60 minutes between successive exposures.

Threshold Limit Values - Ceiling (TLV-C): The concentration that should not be exceeded during any part of the working exposure.

These TLVs serve as guides for exposure concentrations that, it is believed, a healthy individual normally can tolerate without harmful effects. An example of the TLVs of carbon monoxide are a TLV-TWA of 35 ppm and a TLV-C of 200 ppm.

Agencies such as Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) provide guidelines for toxicity levels.

3.3 Asphyxiant Gases: Asphyxia comes from the Greek word meaning the stopping of the pulse and is defined as a lack of oxygen or an excess of carbon dioxide in the body, usually caused by interruption of breathing leading to unconsciousness. Asphyxiant gases affect people by reducing the amount of oxygen available in the air.

In the atmosphere, oxygen can be consumed by chemical reactions or replaced by other gases. High concentrations of methane can displace oxygen and become an asphyxiant. When oxygen levels are reduced from their normal 20.9% to 16%, breathing becomes difficult. At 10%, unconsciousness usually occurs.

Methane when ignited consumes oxygen and produces an asphyxiant atmosphere. Even minor reductions in the level of oxygen in the air can affect an individual's breathing rate, concentration ability, and judgment. Where methane is suspected or known, adequate ventilation to dilute the gas to a harmless concentration is essential to produce a safe atmosphere.

4.0 GEOLOGIC ENVIRONMENT OF METHANE

Hydrocarbon gases, primarily methane, are generated and stored in sedimentary rocks associated with oil and gas fields or coalbeds. However, the presence of methane does not necessarily indicate that a large gas reservoir underlies an area. Methane in appreciable amounts can exist over a large area and be widely disseminated in a variety of rocks (Figure 8). Other hydrocarbon gases such as ethane and propane often occur naturally with methane

Methane is a valuable resource if it can be collected at concentrated levels. Gas that is below the explosive limit or not marketable is normally vented into the open atmosphere. Methane naturally enters the atmosphere at various concentrations through cracks, drilled holes, or water bodies

(Figure 9). Low levels may disperse naturally through the ground or atmosphere. High concentrations venting under pressure may ignite.



Figure 8. Location map of counties with total methane emission in excess of 1 Mmcf/d in 1975, from USBM Information Circular 8733 (Irani, 1977).

Methane is formed as a result of microbial or thermal alteration of organic matter. Microbial methane forms when bacteria in the environment digest organic matter and oxygen. They create carbon dioxide and low levels of methane. Methane is produced by methanogenic (methane-generating) archaeobacteria which are common in organic-rich soils. Soil biochemical reactions may also produce low-oxygen levels and occasionally methane.

Thermogenic methane forms as organic matter is buried deep under sediments. As sedimentary layers build, progressively higher temperature ($>165^{\circ}\text{C}$) and pressure regimes develop, and the thermal decomposition (cracking) of the organic matter begins (Friedman, 1978). Methane can then form through the cracking of oil in reservoir and nonreservoir rocks, or from the direct cracking of other organic matter dispersed in sedimentary rocks (Hunt, 1996).



Figure 9. Methane bubbles in a stream.

Much of the methane in consolidated strata is thermogenic in origin. The methane often originates from a carbonaceous shale or coal unit. Subsequently it migrates to other units conducive to storage, such as overlying, permeable sandstones.

Modern sediments and man-made deposits (e.g., landfills) produce new versus old methane that can be identified through the sourcing process (see Section III).

Coalbed methane is generated microbially or thermogenically during coal formation. The amount of methane commonly varies between 100 and 300 cm³/g of coal (Rice, 1993). Methane may also be stored under pressure in the rocks above a coalbed. Methane is sorbed in the coal micropores as a function of reservoir pressure. Pressure reductions will then cause these gases to be liberated. For example, mining can liberate the gas from its pressurized environment by the excavation of the coal and subsequent fracturing of the overlying strata.

Coalbeds and rocks above drainage rarely store much methane because coal exposed at an outcrop has lost the methane during the erosional process. Thus, methane is most likely to come from deeper sources.

Storage and migration of methane is affected by regional geologic structure and the permeability and porosity of the storage medium. Low permeability strata trap methane in features such as stratigraphic reservoirs, anticlines, and faults.

4.1 Methane Storage: Regional structural and stratigraphic features influence the storage of methane. Methane is often stored in these structural or stratigraphic “traps.”

Structural features include but are not limited to fractures, faults, folds, and bedding plane separations. Folding of rock units creates the most significant structural traps. Anticlines provide structural highs that trap gasses as they migrate toward the ground surface. Methane frequently tends to get trapped in porous strata in anticlines that have an overlying low-permeability unit.

Methane also commonly accumulates in stratigraphically formed traps. These traps occur where somewhat impermeable material overlies a more permeable rock unit and the rocks are such that a domal or ridge-like structure exists in the more permeable unit. These traps are created by lateral changes in the depositional environment, which deposit finer-grained material overlying and surrounding a relatively coarser-grained material. An example of this is a channel sandstone being commonly enclosed by shale. Figure 10 shows a number of structural and stratigraphic features that typically affect methane storage.

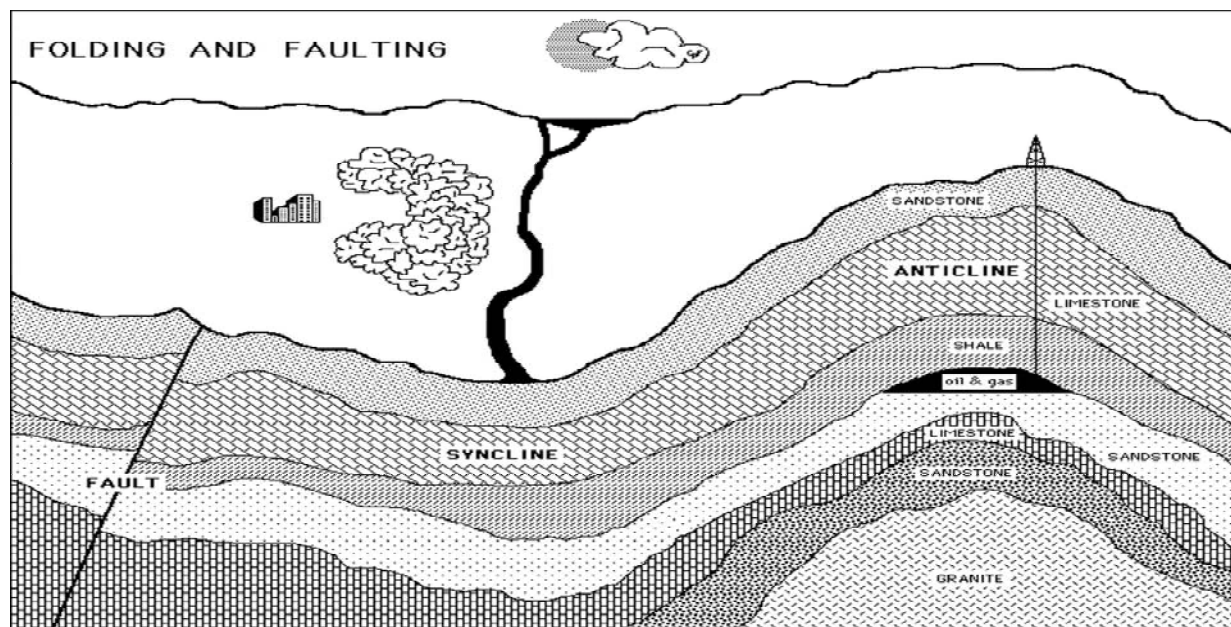


Figure 10. Examples of methane-trapping conditions.

Geologic faults exist where there has been physical displacement along a fracture in strata. However, these tend to be lesser storage mediums. Fault-line barriers, depending on the orientation of the rocks and/or of the fault, can also create a structural trap for methane.

4.2 Migration Pathways: Methane travels through the rock pores and fractures. The porosity and permeability of the transmitting medium significantly affect the migration. Methane, being lighter than air, tends to migrate vertically. However, pressure gradients cause methane to migrate to areas of lower pressure. These migrations may be in directions other than vertical.

Fractures provide a significant migration pathway. They include natural breaks produced by jointing and stress relief. For example, fractures in the Appalachian Plateau have been created through stress-relief from the removal of overlying rock mass from erosion (Wyrick and Borchers, 1981), glacial rebound, tectonic action or orogenic (mountain building) action. The fractures are avenues for methane to move from one area or level to another through differing rock units.

Faulting may also produce a conduit for gas to travel far from its source. As noted in Section 4.1

Methane Storage, ground-water and methane can easily flow along and be stored in these fault planes. Conversely, faults can form a barrier against movement when permeable units on one side of the fault are in contact with less permeable units on the other side.

Methane migration in relatively shallow rock units in the Appalachian Plateau may be related to the ground-water flow regime. Ground-water flow occurs mainly via secondary porosity and permeability (fractures in the rock units). Primary porosity and permeability (intergranular) are not important to methane transmission because they are generally very low in consolidated rocks of this region. Intergranular pore spaces are commonly filled with cementing minerals (e.g., calcite, quartz, or iron oxides). Hence, there is very little intergranular ground-water flow in this region, except in the geologically-recent unconsolidated alluvium associated with stream and river valleys or colluvium associated with the shallow weathered system. Fractures in the rocks store and transmit most of the shallow ground-water and similarly the fugitive methane in the Appalachian Plateau.

Ground-water and natural-gas flow and storage systems in the Interior and Western Regions are significantly different from those exhibited in the strata of the Appalachian Plateau. Intergranular (primary) porosity is a significant factor in the coal-bearing strata of the Interior and Western Regions. In general, the rocks of the Interior and Western Regions are less tightly consolidated, with significant primary porosity and permeability values. Williams and Driver (1987) reported median porosity values of 36.9 percent for the Denver aquifer. The Ferron Sandstone of the Emery coalfield of Utah exhibits a porosity range of 15 to 20 percent (Lines, 1987). These porosity and permeability values facilitate the transmission and storage of substantial quantities of ground-water or natural gas. The paleocene sandstones of the northern Great Plains yielded a mean hydraulic conductivity (i.e., coefficient of permeability) of 1.45×10^{-6} meters per second (Rehm and others, 1980). While some ground-water and natural gases are also stored in and flow through fractures and faults in these regions, primary porosity and permeability are the predominant factors in these ground-water and natural gas flow systems.

Generally, substantial quantities of methane do not migrate to the surface under pressure unless an event has recently changed the natural state. Methane released to the atmosphere will eventually drain the reservoir. Human activities can also cause or accelerate the release or migration of methane. Fracturing of the overlying rock strata above mines and the drilling of boreholes can alter the pressure gradients and create open pathways for the gas to migrate to the surface. Fractures occurring in shales and other more soft rock can heal over time and seal the methane into a new trap or at its original source.

Natural overburden pressure is a mechanism that force gas to the surface. High hydrostatic pressure in flooded mines can cause compression of the gas. A change in the volume of void space caused by subsidence in a mine will liberate gas. Similarly, changes in water levels in a well can cause a reduction in hydrostatic pressure, allowing methane to come out of solution and enter the well space.

4.3 Coalbed Lithology: Coal-bearing strata are mainly composed of sandstone, siltstone, shale,

and some thinly bedded limestones. Common rock sequences in coal-bearing strata for three United States regions are shown below:

<u>Appalachian Region</u>	<u>Interior Region (Illinois)</u>	<u>Western Region (NM)</u>
Siltstone and shale	Siltstone	Sandstone
Shale	Marine shale	Conglomerate
Coal	Marine limestone	Shale
Seat earth (clays/claystones or shales)	Marine black shale	Coal
Sandstone	Coal	Seat Earth
	Seat earth	Shale
	Freshwater limestone	
	Shale	
	Sandstone	

Thick sequences of predominantly shale, siltstone, or sandstone are common throughout the Appalachian coalfields. Commercial quantities of methane are generally associated with sandstone (oil and gas sands) units that are sufficiently porous and permeable. Methane commonly resides in shales, siltstones, and coals. Coals can also contain significant quantities of methane.

Wells drilled into unmined coalbeds can produce significant amounts of methane. Often this is done in advance of longwall mining in order to degas the coalbed. Degassing of coal prior to and after mining has significantly reduced the cost and hazards of methane in the gassy coal regions. In some areas, this gas is even being collected and marketed.

4.4 Methane in Coal: The most common gases found in coal are carbon dioxide and low molecular-weight hydrocarbons, predominately methane and ethane. These gases are byproducts of coalification of plant materials. Coalification is the biochemical and geochemical processes that transform organic materials into a combustible-carbonaceous solid.

Coal is a porous material with both macropores and micropores. The macropores are mainly formed by the joint systems (referred to as cleat), cracks, and fractures in the coal. The bulk of gas is adsorbed in the micropores of the coal. The micropores in coal provide a large surface area, approximately 200 to 300 square meters per gram of coal. Gas in the micropores can be liberated when environmental conditions change.

Due to the enormous surface area of the micropores, coal has the capacity to store large volumes of methane. When saturated, coal can contain greater than 21 cubic centimeters of methane per gram of coal (684 cubic feet per ton) or 28 times the volume of coal at standard conditions. An acre foot of coal has the capacity to produce more than 1.2 million standard cubic feet of methane.

As coal is mined, gas flow from the coal occurs in two steps:

- T Flow from solid coal to fractures/wells.
- T Flow through the fractures/wells to the mine.

Coals classified as "blocky" contain prominent fractures (face cleat) and secondary fractures (butt cleat). Butt cleats normally occur at right angles to the face cleats. Generally, coalbed permeability is greatest in the direction of the face cleat, and therefore the methane emission rate is higher along the face cleat. In coals classified as "friable," the fracture spacing is less than 2.5 centimeters, both sets of fractures are equally prominent, and the methane emission rate tends to be more uniform in either direction.

Deeper underground coal mines often are more gassy and produce the highest daily methane emissions during mining. The emissions are relative to the production rates, size of the mine and amount of methane in the coal. A compilation of these data is provided in US Bureau of Mines (USBM) Information Circular (IC) 8733 (Irani, 1977). The amount of gas per ton of coal produced is generally from deeper underground mines as shown in Table 6, compiled from the referenced report:

Table 6. Methane liberated from coal.

Mine Name	Coalbed	Cu. ft. gas per ton of coal mined	Age of Mine in years	Average depth of shaft or slope
Island Creek Coal Company, Buchanan Co., VA Virginia Pocahontas No. 2 Mine	Pocahontas No. 3	3,091	8	1,250
Mid Continent Coal & Coke, Pitkin Co., CO L. S. Wood Mine	Basin B	2,083	11	6,200
Consolidated Coal Company, Marion Co., WV Mountaineer Div, Consol No. 9	Pittsburgh	2,333	34	592*
Eastern Associated Coal Corp. Marion Co., WV Federal No. 2 Mine	Pittsburgh	2,025	8	830*
Bethlehem Mines Corp. Cambria Co., PA Bethlehem No. 32 Mine	Lower Kittanning	1,500	59	690 953*
Walter Resources, Inc. Jefferson Co., AL No. 3 mine	Blue Creek	1,533	2	1300

5.0 FUGITIVE METHANE SOURCES

Methane becomes a problem when it migrates from its source to the surface. If high enough concentrations of methane enter a structure, then a fire or explosion is possible. A structure could be a home, shed, well house or well bore. Potential sources include gas wells, transmission lines, landfills, wetlands, or coal mines. Each source can be specifically identified based on the site characteristics and the composition of the gas.

5.1 Gas Wells and Transmission Lines: Methane as well as natural gas in wells and transmission lines are usually thermogenic in origin. The natural gas is produced from the cracking of petroleum in deep reservoirs. The occurrence of natural gas can be far from its origin.

Gas wells are commonly associated with brines and marine-deposited connate waters. If well casings fail or are improperly abandoned, they can contaminate overlying shallow ground-water aquifers with methane. Ground-water containing concentrations of sodium and chloride can be indicative of deeper connate waters. Other indicators that the gas source is a gas well or transmission line include the presence of strontium and barium. For additional insight into using ground-water to help identify methane sources, see Hem (1989) or Stumm and Morgan (1996).

Leaky underground transmission lines can produce a shallow reservoir of gas in soil or weathered bedrock. Unlike other sources of methane, this particular problem is best identified with soil surveys. Leaky transmission and supply lines can be caused by decay of old lines, damage from construction activities such as drilling or excavation, and ground movement from earthquakes, landslides, freeze-thaw, or subsidence. The origin is usually obvious because of the mercaptain, a sulfide-based odorant, added to facilitate identification of pipeline gas.

5.2 Landfills: Present-day landfills are lined to prevent toxic and hazardous compounds, including methane, from uncontrolled migration or emission. Methane generated in landfills is microbial in origin because of the organic decay. Pre-regulation landfills pose the biggest threat as a methane source.

Most states regulate the construction, monitoring, and mitigation of methane from landfills. Monitoring systems provide an early warning for fugitive methane problems. Methane monitoring systems are typically monitored with some frequency at active landfills. Occasionally, however, methane from an active landfill may migrate undetected and outside of the landfill perimeter.

5.3 Coal Mines: Mine gases, principally methane, have been a hazard to coal miners since the beginning of underground coal mining. Years ago the miners were not educated about the different mine gases nor were they equipped to determine the actual composition of the deadly atmospheres encountered. They simply applied descriptive terms to each gas or mixture of gases depending on its effect on a person or the surrounding atmosphere. The gases or mixtures of gases were then referred to as "damps," a term probably derived from the German word "dampf", meaning vapors or gases. Firedamp is a flammable mixture of methane and air which would

either burn or explode when ignited. Firedamp, although an obsolete term, accurately defines the principal hazard of methane.

Many coal miners died from asphyxiation or explosions, in most instances the result of the migration and accumulation of methane. Today, active mines use large fans to create a low-pressure zone to move fresh air through the entries of the mine, which dilutes and removes the hazardous gases. Air in abandoned mines, where active ventilation has ceased, will stagnate and develop a “mine atmosphere” with a mixture of potentially asphyxiant, toxic, or explosive gases.

5.3.1 Mining Methodology: Coal mining is performed by either surface or underground methods depending on the depth and quality of the coal.

Types of Surface Mining include:

- T contour mining,
- T area mining,
- T mountain top removal,
- T block cut, and
- T auger and highwall mining.

Methane hazards during surface mining are rare because the gas is freely vented to the open atmosphere. Furthermore, near surface coal seams over time have lost or bled much of their methane into the atmosphere through the coal crop.

After mine reclamation, the backfill can be a source or pathway of methane. Methane can be produced from the decaying carbonaceous material left in the backfill (e.g., trees, brush or trash). This process is similar to methane being produced in landfills. If abandoned underground mine entries were encountered during surface mining, underground mine gases could also enter the backfill. Thus, the backfill can act as a conduit through which methane travels, trapped by a low-permeability cap of soil or clay materials.

Three underground mining methods are principally used to extract coal:

- T room and pillar mining,
- T room and pillar with secondary (retreat) mining, and
- T longwall mining.

Methane in underground mines is a substantial problem that must be constantly monitored and controlled. Underground mining exposes large surface areas of coal in confined spaces which can readily allow methane to concentrate to explosive levels. The principal method used to control methane in underground mines is ventilation. Powerful exhaust fans draw fresh air from main entries past the working face of the mines. Gob areas are usually ventilated with the exhaust air.

The methane level in coal mines is regulated closely by MSHA according to the standards described in Section II. Methane levels are monitored closely by personnel and equipment at all working faces and other parts of the mine. Longwall mining production is often limited below the capacity of the equipment because of the large amount of methane that is quickly released at the face. In areas of gassy coal seams, extra effort is spent to control methane ahead of mining by drilling degassification wells. In some regions, the methane is collected and marketed to the natural gas industry. Thus, coalbed methane is becoming an increasing percentage of the total natural gas production.

5.3.2 Gas Flow in Mines: Overburden thickness and rock types generally affect the amount of methane that is available in a coalbed. The deeper the coalbed and the more shale overburden, the better the chance that methane is trapped in the coalbed or adjacent permeable strata. Once the natural environment is disturbed by mining, methane is liberated.

Gas flow is different in active and abandoned mines. The differences are described below.

Active underground coal mines. In active mines the control, detection, and ventilation of methane has evolved to include sensitive detection devices and sophisticated ventilation systems. Federal and State regulations require strict methane detection and ventilation standards.

Mine workings are at atmospheric pressure. As a coalbed is mined, a pressure gradient is created. The pressure differential causes the gas to flow out of the coalbed into the mine. During the life of a large coal mine, enormous quantities of gas may be removed. However, large volumes of gas may still be retained in the remaining coal or associated strata when the mine is closed, sealed, and abandoned.

In some instances, lowering of the ground-water table or the piezometric level in confined aquifers, along with increased fracturing that accompanies mining-induced subsidence, can cause the release of diffused methane into the overlying coalbeds and rock. Mine subsidence can increase the aperture of existing fractures and open bedding planes, creating new transmissive fractures that expose methane-containing strata and allowing methane to migrate toward the ground surface.

Wells in southwestern Pennsylvania vent large quantities of methane from fractured overburden as the longwall panel passes beneath. Subsidence of 3 feet is commonplace. Methane liberated from the Pittsburgh coalbed during mining flows towards the mine mouth because of the low pressure ventilation system. The subsidence fractures extending to the surface liberate gas from the stratigraphic units above the Pittsburgh coal.

Methane will find and travel the path of least resistance, which is frequently a well. In one well, 33% methane was recorded, venting within days of the panel passage.

Abandoned underground coal mines: Abandoned mine gas is most responsive to atmospheric pressure swings. A mine will inhale and exhale as atmospheric pressures increase and decrease, respectively. If a mine entry, well bore or subsidence crack is near the foundation of a house, mine air may quickly vent into the building with rapidly dropping atmospheric pressures.

An example of mine air venting into a building is provided by a church in Eckart, Maryland, where the pilot light of a gas furnace would occasionally extinguish and people in the basement recreation hall would become dizzy. The furnace room had an entryway into the crawl space beneath the chapel. The floor of the crawl space was dirt and at the back was a 10-foot diameter subsidence hole. It was discovered that, during low pressures or rainy days, the mine vented CO₂ into the furnace room and extinguished the pilot light.

Rising water levels can also force methane upwards. This phenomenon has been observed in the Appalachian coal fields. The hydraulic pressure of flooding in abandoned underground mines has been observed to force methane upward into overlying water wells and strata. The rising water levels can force the methane upward.

Subsidence can cause cracks to migrate upwards. If mine pressures are equalized, new avenues of flow from the mine level to the surface may be created. In 1980, an abandoned mine in Graysville, Alabama, subsided causing large quantities of methane to be liberated at the surface. The mine was over 1,000 feet below the surface. It was found that subsidence had intercepted a regional fault, creating a direct pathway to the surface.

5.3.3 Active Underground Coal Mine Atmospheres: The amount and composition of gases associated with coal highly variable. The gases native to coal are mixed with normal air during mining and diluted. An abandoned mine atmosphere may also be mixed with normal air and often affected by gases from ground-water and confined spaces. It is important to consider mine gases compared to the makeup of normal clean air. Table 7 shows the average gas composition of some representative coalbeds. These samples were taken prior to mining activities.

Table 7. Average composition of gas from representative coalbeds, in percent by volume (Kim, 1973).

Coalbed	Pocahontas No. 3	Pittsburgh	Pittsburgh	Upper Kittanning	Mesa Verde	Lower Hartshorne	Mary Lee	Anthracite
State	VA	PA	WV	PA	CO	OK	AL	PA
CH ₄	94.9	91.1	95.86	97.4	87.8	99.2	96.0	98.7
C ₂ H ₆	1.3	0.3	0.01	0.01	0.05	0.01	0.01	0.1
C ₃ H ₈	0.004	ND	ND	ND	0.005	ND	ND	Trace
C ₄ H ₁₀	0.002	ND	ND	ND	0.001	ND	ND	ND
C ₅ H ₁₂	Trace	ND	ND	ND	ND	ND	ND	ND
CO ₂	0.3	8.2	2.54	0.1	0.1	0.1	0.1	0.1
O ₂	0.2	0.2	0.06	0.2	12.0	0.1	0.1	ND
N ₂	3.2	0.5	0.46	2.3	0.1	0.6	3.5	1.0
H ₂	0.02	ND	ND	ND	ND	ND	Trace	0.1
He	0.04	ND	ND	ND	ND	ND	0.3	Trace
Btu/scf	1,030	975	975	1,037	935	1,037	1,022	1,053

ND - not detected by the analytical methods used.

5.3.4 Abandoned Underground Coal Mine Atmospheres: Methane often collects in underground mines after abandonment. The gob and coal left underground degasses over time. The open mine voids, fractured overburden rock, and permeable gob act as reservoirs for these mine gases. These gases may exhaust to the surface through drifts, shafts, borings and fractures. Numerous hazards and fatal accidents have occurred from improperly sealed shafts that have exploded due to methane. Table 8 shows the composition of some representative atmospheres of abandoned mine lands.

Abandoned mine atmospheres can be diverse and are encountered in various ways. Methane is often encountered in abandoned mines while drilling for investigation or subsidence stabilization work. Usually the gas is under low pressure at various concentrations. These conditions can easily be controlled by ventilation. Occasionally, the atmosphere becomes pressurized by flooding mine conditions or other mechanisms. These conditions are difficult to control and can be very hazardous. Methane should be routinely monitored while drilling into abandoned mines.

Table 8. Composition of selected Abandoned Mine and Anomalous Atmospheres, in percentage by volume.

	Ambient Atmosphere in water well	Vertical Vent Hole	Ambient Atmosphere in Drift Mine Entry	Boring atmosphere in Strip Mine Backfill	Vent hole into flooded Mine	Ambient Atmosphere in water well
Coal Seam		Pocahontas No. 3	Upper Freeport	Upper Freeport	Pittsburgh	
Location	Buchanan Co., VA	Buchanan Co., VA	Armstrong Co., PA	Westmoreland Co., PA	Greene Co., PA	Washington Co., PA
Oxygen	13.47	4.59	16.44	10.82	0.30	16.07
Nitrogen	61.17	17.01	73.46	79.56	87.77	49.29
Carbon Dioxide	0.78	0.42	1.96	8.64	8.96	0.28
Carbon Monoxide	----	----	0.0322	0.0004	0	0.3264
Argon	0.731	0.2033	0.8779	0.9508	1.05	0.5891
Methane	23.80	77.46	7.00	0.03	1.88	33.02
Ethane	0.048	0.2681	0.181	0.0003	0.014	0.3766
Propane	0.001	0.0301	0.0335	0.0002	0	0.0426
Butane	0.0006	0.0065	0.0146	0.0003	0	0.0107
Pentane	0.0021	0.0011	0.0054	----	0	0.001

Methane under pressure, in excess of 30 psi, can be encountered in mines where methane has been trapped by flooding. The flooded mine forces methane to structural highs in the mine and compresses the gases. Drilling suddenly releases these gases, often bringing water with it to the surface and creating a potential hazard.

Methane may also occur in abandoned mines at portals and shafts. The flow and concentration of methane and other gases in these features will vary depending on barometric pressure and conditions in the mine. Dangerous levels of methane can occur at portal and shaft entrances. This was exemplified when a teenager, sitting in front of an abandoned set of mine portals, was critically burned when the portal exploded. The methane concentration was about 7.0% and was ignited when the youth celebrated the end of the school year by lighting a cigar.

6.0 HAZARD POTENTIAL

The hazard potential of fugitive methane is based on the type and size of the threatened structure, the methane level resident in either the soil, ground-water, or air, and the availability of fresh air. Other factors that may influence the hazard potential are the source of the methane (e.g., mines, landfills, etc.), the interconnectivity of pathways (natural or manmade) between the source and point of concern, and the geologic setting.

Any assessment must address the severity of the hazard as expediently as possible. Thus, the initial assessment must focus on atmospheric methane and the potential for a structure to explode. An immediate hazard always warrants a full assessment (Section III) to develop mitigation plans (Section V). When no immediate hazard exists, but methane levels are present above ambient levels, a full assessment may or may not be needed. If mitigation is recommended and implemented, a post-assessment is appropriate to gauge success.

This section provides a discussion of the assessment process. The details of how to perform an investigation and conduct sampling are addressed in Sections III and IV, respectively.

6.1 Preliminary Assessment of Potential Hazard: The preliminary assessment must focus on methane at the surface or in the atmosphere. Methane can reach the surface quickly through a high-permeability conduit, such as a fracture, or slowly through a low-permeability material, such as a fine-grained soil. In any case, methane can accumulate to a hazardous level in a confined atmosphere. Key questions to keep in mind include:

- T Is there an imminent potential for an explosion?
- T Does the situation constitute a potential future hazard?

When a landowner or tenant believes that methane exists on their property and reports the problem to the appropriate State or Federal agency, an immediate site visit and preliminary assessment are necessary.

The results of the preliminary assessment dictate the extent of any further investigation. Foremost, the first site visit must assess the immediate hazard potential. The investigator has three primary tasks at this time:

- T interview the landowner,
- T observe and record site conditions,
- T test for atmospheric methane (Section IV).

In making a preliminary assessment, the investigator should take a conservative approach. If it is believed that the condition could potentially change in the future, then periodic monitoring and further evaluation should occur.

Atmospheric methane is frequently the only parameter tested during the initial investigation.

Explosive concentrations of methane may be rapidly released from boreholes, mine shafts, drift entries, faults, or areas of subsidence. It is critical to determine, as early as possible, if an explosive environment exists. Methane measurements should focus on all areas of the property, with the testing equipment set on the most sensitive measuring level.

Any indication of methane levels above 1% by volume in an occupiable space warrants immediate evacuation of the premises and/or disconnection of electrical service. The quickest way to subsequently reduce the immediate hazard is to thoroughly ventilate the area with fresh air. Once the immediate hazard is abated, evaluate the obvious sources of high gas concentrations such as furnaces, gas grills, water heaters, clothes driers, gas lines, stoves, gas wells, etc. If such obvious sources are not the problem, then a full assessment of the potential hazard is appropriate.

6.2 Comprehensive Assessment of Potential Hazard: If actionable levels (0.25 - 1.0% for occupiable spaces and 1.0 -3.0% for unoccupiable spaces) exist, then a comprehensive assessment of the potential hazard is warranted. Often a hazardous level of methane may not exist at the time of the first site visit or preliminary assessment. The purpose of a comprehensive assessment is to gather and interpret information to determine if methane levels have been exceeded in the past or could be exceeded in the future and to determine the source. A comprehensive assessment is not necessarily complicated nor sophisticated, but must be logical and based on a good understanding of gas properties and migration principles. Proper interpretation of monitoring data requires a detailed understanding of site and geological conditions and confidence in the sampling procedures and equipment.

The investigator must maintain impartiality, objectivity, and integrity. Remember that methane from several sources may migrate through a variety of pathways. Over the course of the comprehensive investigation, the unlikely methane sources should be documented as well as the probable sources. The source(s) should be identified and ruled out through a process of elimination based on the weight of available information and data. Determination of the source(s) and migration pathway(s) of the methane should be based on the investigator's best professional judgment, based on multiple lines of supporting evidence, and be defensible with a reasonable degree of scientific certainty.

The purpose of a comprehensive assessment is to field verify the historical information and to obtain the data required to assess the extent and source of the fugitive methane. The first step is to collect any available historical information. The information includes, but is not limited to: topographic maps, geologic maps, mine maps, hydrologic studies, historical reports on methane emissions, and methane mitigation controls. Any nearby methane sources, underground transmission pathways, and existing control facilities must be identified. Map information is best verified by walking the site. Personal interviews or phone interviews may also be needed to verify information. On-site interviews are helpful in obtaining a historical perspective of the site conditions. The investigator must consider the area well beyond the immediate site of concern since methane can migrate laterally considerable distances. For example, a landfill may generate methane that leaks into glacial drift and propagates thousands of feet away in a residential structure. Finally, atmospheric, ground-water, and soil methane levels need be evaluated.

6.3 Post-Mitigation Assessment: After mitigation has been started and the methane hazard has been reduced or abated, follow-up testing is appropriate to gauge the success. A post-mitigation assessment should include an evaluation of the sources, potential for continued release of methane, the success in eliminating methane pathways from the source to the problem area, the success of eliminating atmospheric methane from the problem area, and a determination of the length of time required for the post-mitigation assessment.

Post-mitigation assessment should always include atmospheric methane testing and/or testing of dissolved or soil methane based on the source and mitigative technique. If methane remains above actionable levels, further assessment is necessary to identify pathways not identified earlier.

SECTION II

ACTION LEVELS FOR METHANE CONCENTRATIONS

1.0 INTRODUCTION

As discussed in the previous section, methane may reside in different lithologic units and can be transmitted to the atmosphere in numerous ways. Occasionally, methane accumulates near or in manmade structures. When the concentration exceeds approximately 5 percent, the methane may explode. An explosive environment exists when a mixture of gases can self-propagate a flame throughout the mixture, independent of, and away from, the source of ignition. An ignition source can be an electrical outlet, pilot light, well pump, or match. This chapter will focus on methane levels in structures, soil, and ground-water that may necessitate remedial actions due to potential accumulation of explosive levels of methane.

The recommended action levels in Table 9 are guidelines when mitigative actions may be prudent to ensure the safety of structures and the public. The recommended action levels are based on the existing scientific literature and are dependent on the amount of methane present in the air, soil, or water, and the confined space within the structure of concern. Examples of a confined structure could be a well bore, a well house, or the basement of a building. By establishing action levels, investigators are better prepared to identify imminent harm situations. The means to measure methane levels will be discussed in Section IV.

Table 9. Recommended Action Levels for Methane

Action Level	Atmospheric (Percent Volume)		Dissolved in Water (mg/liter)	Soil Gas (Percent Volume)
	Occupiable Spaces (homes)	Un-Occupiable Spaces		
Immediate Action	>1.0%	>3.0%	>28 mg/L	>5.0%
Warning, Investigate	>0.5% but <1.0%	>1.0% but <3.0%	>10 mg/L but <28 mg/L	>3.0% but <5.0%
Monitor to Determine Concentration Trends	>0.25% but <0.5%			<3.0% but >1.0%
No Immediate Action	<0.25%	<1.0%	<10 mg/L	

The recommended action levels are based on site-specific information, application of scientifically valid methodology, and the exercise of common sense. Accuracy and consistency of the field investigation is the basis for application of the recommended action levels. There may be occasions when the investigator will determine that a potentially harmful situation may later develop and immediate action is required even though recorded methane concentrations are

below the recommended action levels. One example is where the investigator believes that methane is accumulating at a rate that would produce explosive levels in a relatively short time period.

The action levels should be considered guidelines. All investigations should be evaluated based on their site-specific circumstances with the ultimate goal of 0% methane. Thorough evaluation of potential sources and trend analysis of the data are key to making decisions regarding future monitoring and mitigation.

2.0 ATMOSPHERIC METHANE

2.1 Explosibility of Methane Mixtures: Methane may originate from many sources as discussed in Section I. If methane is liberated into the atmosphere as a point source, it can be readily ignited if the concentration exceeds 5 percent. Atmospheric methane will ignite at concentrations between 5 and 15 percent at Standard Temperature and Pressure (STP). Higher levels can quickly dilute to flammable levels. In either case, if methane is allowed to vent into an enclosed area, an explosive environment may develop.

2.2 Regulatory Standards for Methane in Atmospheres: As a reference for recommending action levels, the following governmental agencies have established guidelines for methane in the atmosphere. See Appendix A to Section II for the full citations.

2.2.1 Occupational Safety and Health Administration (OSHA) - in underground construction regulations (29 CFR 1926.800), standards are set at levels of 0.25, 0.50 and 1 percent with specific actions recommended for each level. The three-tiered action levels are based on corrective actions which provide an increased margin of safety to protect workers. At 0.25%, they require steps to be taken to increase ventilation or lower gas concentrations to below 0.25%. At 0.50%, work activities involving welding, cutting, or other hot work are prohibited. At 1%, all employees must be withdrawn and all electrical power must be shut off, except that necessary to ventilate the area. The types of construction activities covered in this section include underground tunnels, shafts, chambers, and passageways. OSHA's philosophy centers around ventilation coupled with effective air monitoring. Ventilation is presented as the key to risk control.

2.2.2 Mine Safety and Health Administration (MSHA) - at 30 CFR 75.323, Actions for Excessive Methane, the rules require adjustments to the ventilation of an underground coal mine when methane reaches 1.0% and closure of the mine section when 1.5% is reached. At 30 CFR 75.342, Methane Monitors, the monitors on mining equipment must automatically de-energize the equipment when methane reaches 2.0%. These action levels anticipate the existence of other potentially explosive materials (e.g., coal dust) which in combination could cause an explosion.

2.2.3 California Code of Regulations - at Section 8424, Airborne Contaminants, (c) specifies

that all underground work shall cease, employees shall be removed, and re-entry, except for rescue purposes, shall be prohibited when the methane exceeds 1.0%.

2.2.4 The South Coast Air Quality Management District (AQMD), by law, is required to achieve and maintain healthful air quality for its residents. At municipal landfills, mitigation measures such as compaction, additional cover, and/or watering are required when methane is above 0.5% at any place on the final grade surface.

2.2.5 Pennsylvania Department of Environmental Protection (PADEP) - is proposing a plan for municipal solid waste (msw) landfills. This includes reporting methane levels within a well when concentrations are in excess of 0.05% (500 ppm) above background levels.

2.3 Literature on Methane Levels in the Atmosphere: The following research documents recommend levels for methane in the atmosphere.

2.3.1 Iowa State University Extension Publication #: Pm-1518k, Jeff Lorimor, Extension Engineer; Charles V. Schwab, Extension Safety Specialist, Agricultural and Biosystems Engineering, and Laura Miller, Extension Communications, Iowa State University, February 1994.

Methane is dangerous because it is highly combustible. At concentrations of 50,000 ppm or more (a level of 5 percent), methane can explode. Methane gas is produced as animal wastes decompose, and high temperatures accelerate this process. Another problem is that this colorless, odorless, tasteless gas is difficult to detect. Methane is lighter than air and will accumulate in the top of unvented areas, such as closed pits. The maximum allowable concentration is 1,000 ppm, or 0.1 percent.

2.4 Recommended Action Levels - Atmospheric: Based on the current literature and regulatory limits, the following action levels are recommended for occupiable and unoccupiable spaces. An occupiable space is an area large enough that a person can enter. An unoccupiable space is any area that is smaller than an occupiable space.

2.4.1 Action Levels in Confined, Occupiable Spaces

a. **>1.0% methane:** One percent methane indicates that potentially explosive or flammable quantities of the gas or vapor are being liberated in the immediate environment. This concentration of methane should result in immediate evacuation of the premises and priority remediation. A sign should be posted on the premises at a location easily observable. This warning should include information that the concentration of methane is above 1.0 %, that smoking is prohibited, and that remediation is needed to reduce the methane concentration. Active ventilation would be considered the best option for immediate risk control.

b. **>0.5% but < 1.0% methane:** Methane levels at 0.5% should be viewed as a warning

that gas is not only present but that the concentration may be increasing. Appropriate actions would be to warn the occupants and/or place a sign on the premises at a location easily observable. This warning should include information that the concentration of methane is above 0.5 %, that smoking is prohibited, and that remediation is needed to reduce the methane concentration. Also, any work to be conducted should proceed with extreme care.

c. **> 0.25% but <0.5% methane:** Methane concentrations between 0.25% and 0.50% pose no immediate threat to the inhabitants but warrant periodic monitoring. Investigators must use caution since the source of methane may be higher in concentration than observed. The monitoring data must be evaluated for trends and sampling protocol must be followed as described in Section IV, Protocol for Methane Sampling and Gas Analysis Techniques.

d. **< 0.25% methane:** Methane levels at concentrations below 0.25% warrant no immediate action. Periodic monitoring should be performed to verify that the gas concentration has not changed.

2.4.2 Actions Levels in Confined, Unoccupiable Spaces

a. **>3.0% methane:** When the methane concentration in an unoccupiable space is greater than 3%, immediate action is necessary. This action would include notifying the property owners of a potential buildup of methane to an explosive level, posting a sign in the vicinity of the unoccupiable space, and immediate venting of the space. The notification and sign should include information that, in the vicinity of unoccupiable space, the concentration of methane is above 3%, that smoking is prohibited, and that mitigation is needed to reduce the methane concentration to less than 1.0%. Also work conducted in the vicinity should not be allowed except those actions necessary to reduce the methane levels.

b. **>1.0% but < 3.0% methane:** Methane concentrations between 1% and 3% warrant monitoring at sufficient time intervals to determine a trend in methane concentration. The trend would show whether methane is accumulating, dissipating, or is unchanged. Care should be taken to remove any ignition source near the unoccupiable space.

c. **< 1.0% methane:** Levels of methane less than 1% warrant no immediate action. Periodic monitoring should be performed to verify that the gas concentration has not changed.

3.0 METHANE IN WATER

3.1 Explosibility of Methane in Water. Dissolved methane and pure gaseous methane in water are not explosive. The solubility of methane in water is between 28 and 30 mg/L at STP (Harder, 1963). Methane does not react with silica, carbonates, iron, or any other substances commonly found in ground-water. It does not impair the odor, taste or color of the water, nor does it in any

way affect the potability of the water. As water is agitated or reduced in pressure, small bubbles may form and appear to make the water milky or translucent. The water will quickly clear as the gas escapes into the atmosphere. However, when water containing dissolved methane comes in contact with the atmosphere, some of the methane exsolves from the water and mixes intimately with the air. This gas mixture, if liberated in a confined space, could possibly ignite or, if allowed to accumulate, explode. The question is “What level of methane in water can exsolve into an explosive atmosphere in a confined space?” In a house, the most common place water would be exposed or aerated in large volumes, typically via a shower or clothes washing machine.

3.2 Literature on Methane in Water: The following information is pertinent to establishing action levels on dissolved methane in ground-water.

3.2.1. “Methane in the Fresh-Water Aquifers of Southwestern Louisiana and Theoretical Explosion Hazards” by A. H. Harder *et al.* (1963) The report discusses methane sources and minimum methane concentrations in water that can produce explosive atmospheres. Methane has been known to occur naturally in significant concentrations in aquifers. The methane in water will exsolve into the surrounding atmosphere. Harder et al reported, in oil and gas producing fields, methane concentrations as great as 127 ppm (mg/L) in aquifers as deep as 700 feet. The paper reports that the volume of methane that exsolves from ground-water is dependent on four variables:

- T temperature
- T pressure
- T quantity of water pumped
- T volume of air which the gas exsolves

The authors presented an equation that may be used to calculate the theoretical minimum volume of methane-bearing water required to produce an explosive hazard under specific conditions. The equation is used in this report as the basis for recommended action levels for methane-laden water.

Harder *et al.* charted explosive levels in confined spaces using dissolved methane concentrations. Explosive levels of atmospheric methane resulting from dissolved methane are influenced by the size of the confined area exposed to the water and the volume of water available. For example, a small shower stall is 3' X 3' x 8' for a total volume of 72 cubic feet. Assuming no air exchange in the stall, an explosive atmosphere would be obtained at 28 mg/L with 779 gallons of water. While this is an excessive volume of water for a typical shower, it is based on 5% methane in the atmosphere. (See Figure 11).

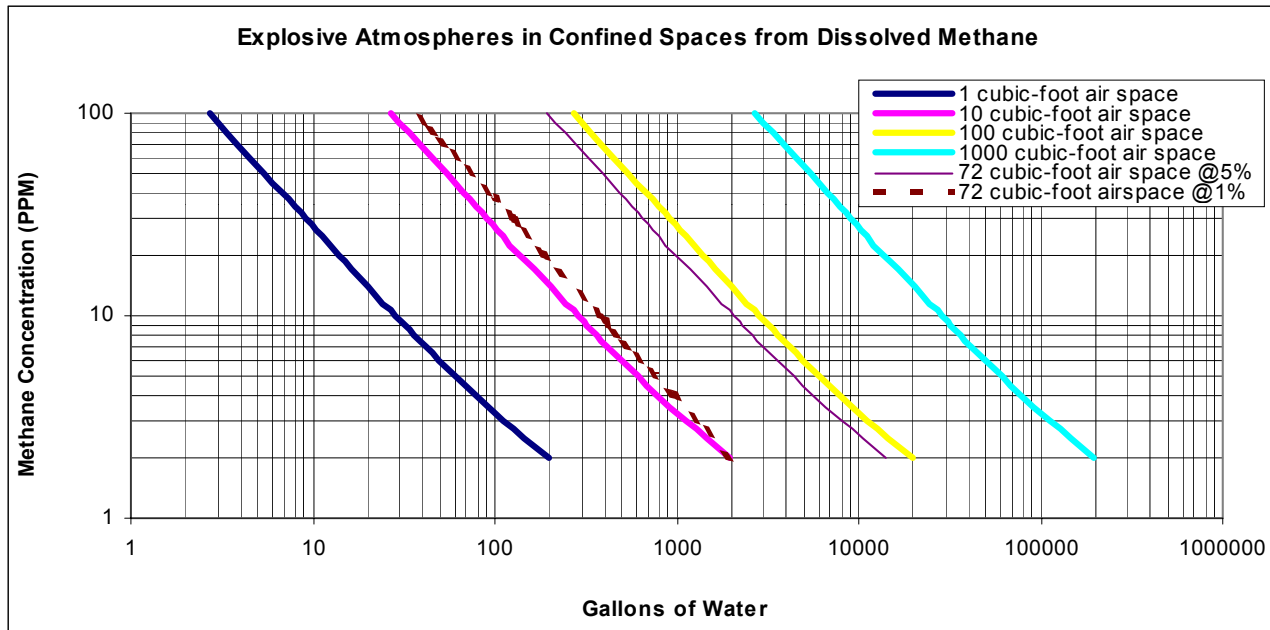


Figure 11. Explosive Atmospheres in Confined Spaces from Dissolved Methane.

Restructuring of the equation recommended by Harder et al. yields:

$$\frac{g}{V} = 5.09 \left[\frac{22259}{(22.3 - Q)^2} * \ln \frac{.99Q}{(Q - .223)} - \frac{10.10}{(22.3 - Q)} \right]$$

where g is gallons, V is volume of air space, and Q is the concentration of methane.

As specified above, action is recommended at 1% methane in the atmosphere. In a shower stall with a volume of 72 ft³, this action level is attained at about 130 gallons of water. The 1% action level line is dashed in Figure 11.

3.2.2 “Composition of Natural Gas from Water Wells, Gas Wells, and Seeps, Northern San Juan Basin, Colorado”. Augusta Warden *et al.* 1995, Department of the Interior, US Geological Survey, Administrative Report for the Bureau of Land Management. The solubility of methane in water at STP (standard atmospheric pressure of 1 atm and temperature of 15°C (59° F)) is 28mg/L. However, the concentration of methane found in a sample can be greater than this depending on pressure (depth) and temperature. For example, a sample taken from a well with a pump intake about 200 feet below the surface and with a sustained water level 100 feet below surface can theoretically have a methane concentration of about 110 mg/L at the pump intake.

3.2.3 “Standard Methods for the Examination of Water and Wastewater”. Method 6211,

(Franson,ed.,1992). The method states that water with a methane concentration of 0.7 mg/L and temperature of 68°C (154°F) at atmospheric pressure in a confined poorly ventilated space can produce an explosive atmosphere. No size of the confined space is mentioned. Note, however, that the specific conditions of temperature, confined space, and pressure all play an integral part in the formation of methane atmosphere in air.

3.3 Regulatory Standards for Dissolved Methane in Water - Review of available information found no recommended action levels or established guidelines for methane in water.

3.4 Recommended Action Levels - Methane in water: Based on the literature cited above, the following action levels are recommended for dissolved methane in well water. In-line samples represent the water conditions at the point of production or use. It is assumed that the water delivery system is a closed system. In the event that a point of accumulation exists within the system (such as a cistern), investigation should proceed as if the methane is atmospheric. Changes in pressure and temperature will affect the methane concentration. See Sections III and IV for specific criteria on collecting in-line samples.

3.4.1 In-Line samples

a. **>28 mg/L.** A dissolved methane concentration greater than 28 mg/L indicates that potentially explosive or flammable quantities of the gas are being liberated in the well and/or may be liberated in confined areas of the home. This concentration of methane should result in immediate ventilation of the well head to the atmosphere. Additionally, methane concentration in excess of 28 mg/L may require further mitigation and modifications to the water supply system.

b. **> 10 mg/L but < 28 mg/L.** When a dissolved methane concentration exceeds 10 mg/L, it should be viewed as a warning that gas is not only present but that the concentration may be increasing. Appropriate actions would be to warn the occupants. This warning should include information that the concentration of methane is above 10 mg/L, and that remediation may be prudent to reduce the methane concentration to less than 10 mg/L. Additionally, the warning should include a recommendation that ignition sources be removed from the immediate area.

c. **< 10 mg/L.** Levels of methane less than 10 mg/L require no immediate action. Periodic monitoring should be performed to verify that the gas concentration has not changed.

4.0 METHANE IN SOILS

4.1 Explosibility of Methane in the Vadose Zone: The vadose zone is defined as the unsaturated zone above the ground-water table. In this zone, void spaces between soil particles are filled with water and gases, including oxygen and, in some cases, methane. Methane in soil is not explosive unless it accumulates in a confined space or void. The methane usually does not have an available

source of ignition in the soils. It generally does not partition to soil particles and will vent easily into the atmosphere. However, fractures and permeable layers overlain by impermeable layers may trap the gas. This situation can produce a point source where the trapped gas layer is intersected by a foundation, hole, or anything protruding through the soil, and methane may vent to the surface. In structures, the large surface area of the foundations in contact with methane-laden soils may foster an influx of methane similar to the way radon enters buildings. Then, as the liberated gas mixes with air, it may ignite or explode if the concentration meets or exceeds 5%.

4.2 Literature Search - No documents were found that discussed action levels for methane in soils.

4.3 Reference regulatory standards for methane in vadose zone - Review of available information found no recommended or established guidelines for methane in soil.

4.4 Recommend action levels - Soils: Recommended action levels for methane in the vadose zone are based upon a sampling program that shows a *sustained* methane concentration in soils. While no documented action levels are available, the need exists for an evaluation criteria that is useful in determining the existence of a hazardous situation. The following recommendations are based on the explosive levels of gas found in the soil.

a. **>5% methane:** When a sustained methane concentration of > 5% (explosive range) is recorded in the vadose zone of soils, immediate action is recommended. This action would include notifying the property owners of a potential buildup of methane to an explosive level, posting a sign in the vicinity of the problem area, and immediate venting of the space. The notification and sign should include information that, in the vicinity of the problem area, the concentration of methane is above 5% (the explosive level), that smoking is prohibited, and that remediation is needed to reduce the methane concentration to less than 3%. Also work conducted in the vicinity would not be allowed except those actions necessary to reduce the methane levels. Work should proceed with extreme care.

b. **>3.0% but < 5.0% methane:** Sustained methane concentrations of less than 5% but greater than 3% warrant monitoring at sufficient time intervals to determine the trend in methane concentration. The trend would show whether methane is accumulating, dissipating, or unchanged. Property owners should be notified of the potential for methane accumulation and that potential ignition sources should be removed from the immediate area.

c. **< 3.0% methane:** Sustained levels of methane less than 3% not affecting a structure warrant no immediate action. The source and extent of the methane in the ground should be determined and the potential of affecting any structures should be evaluated.

The potential for soils themselves to create an explosive hazard is remote but the soils are conduits for methane. The first indicator of a hazard in any investigation is the atmospheric methane concentration. Most investigations will identify either atmospheric

methane or dissolved methane in water as the problem. When all other sources have been eliminated and problematic atmospheric methane levels persist, the soils need be evaluated. It is necessary to determine if the source is deep (methane from mining activity or gas or oil wells) or from shallow sources (methane produced from degradation of organic material such as in a sanitary landfill). Methane in soil should be evaluated as a possible conduit much like methane dissolved in water. Soil surveys may quickly help determine if the source is shallow, such as from a gas line or buried organic matter. This methodology is often used to search for leaky gas lines and volatile organics from underground storage tanks.

Section II Appendix A REGULATIONS

Occupational Safety and Health Administration at 29 CFR 1926.800

(h) Hazardous classifications.

(h)(1) Potentially gassy operations. Underground construction operations shall be classified as potentially gassy if either:

(h)(1)(i) Air monitoring discloses 10 percent or more of the lower explosive limit for methane or other flammable gases measured at 12 inches (304.8 mm) to + or - 0.25 inch (6.35 mm) from the roof, face, floor or walls in any underground work area for more than a 24-hour period: or

(h)(1)(ii) The history of the geographical area or geological formation indicates that 10 percent or more of the lower explosive limit for methane or other flammable gases is likely to be encountered in such underground operations.

(h)(2) Gassy operations. Underground construction operations shall be classified as gassy if:

(h)(2)(i) Air monitoring discloses 10 percent or more of the lower explosive limit for methane or other flammable gases measured at 12 inches (304.8 mm) + or - inch (6.35 mm) from the roof, face, floor or walls in any underground work area for three consecutive days: or

(h)(2)(ii) There has been an ignition of methane or of other flammable gases emanating from the strata that indicates the presence of such gases: or

(h)(2)(iii) The underground construction operation is both connected to an underground work area which is currently classified as gassy and is also subject to a continuous course of air containing the flammable gas concentration.

(h)(3) Declassification to potentially gassy operations. Underground construction gassy operations may be declassified to Potentially Gassy when air monitoring results remain under 10 percent of the lower explosive limit for methane or other flammable gases for three consecutive days.

(j) Air quality and monitoring.

(j)(1)(vii) Whenever five percent or more of the lower explosive limit for methane or other flammable gases is detected in any underground work area(s) or in the air return, steps shall be taken to increase ventilation air volume or otherwise control the gas concentration, unless the employer is operating in accordance with the potentially gassy or gassy operation requirements. Such additional ventilation controls may be discontinued when gas

concentrations are reduced below five percent of the lower explosive limit, but shall be reinstated whenever the five percent level is exceeded.

(j)(1)(viii) Whenever 10 percent or more of the lower explosive limit for methane or other flammable gases is detected in the vicinity of welding, cutting, or other hot work, such work shall be suspended until the concentration of such flammable gas is reduced to less than 10 percent of the lower explosive limit.

(j)(1)(ix) Whenever 20 percent or more of the lower explosive limit for methane or other flammable gases is detected in any underground work area(s) or in the air return:

(j)(1)(ix)(A) All employees, except those necessary to eliminate the hazard, shall be immediately withdrawn to a safe location above ground; and

(j)(1)(ix)(B) Electrical power, except for acceptable pumping and ventilation equipment, shall be cut off to the area endangered by the flammable gas until the concentration of such gas is reduced to less than 20 percent of the lower explosive limit.

(j)(2) Additional monitoring for potentially gassy and gassy operation. Operations which meet the criteria for potentially gassy and gassy operations set forth in paragraph (h) of this section shall be subject to the additional monitoring requirements of this paragraph.

(j)(2)(i) A test for oxygen content shall be conducted in the affected underground work areas and work areas immediately adjacent to such areas at least at the beginning and midpoint of each shift.

(j)(2)(ii) When using rapid excavation machines, continuous automatic flammable gas monitoring equipment shall be used to monitor the air at the heading, on the rib, and in the return air duct. The continuous monitor shall signal the heading, and shut down electric power in the affected underground work area, except for acceptable pumping and ventilation equipment, when 20 percent or more of the lower explosive limit for methane or other flammable gases is encountered.

Mine Safety and Health Administration (MSHA) at 30 CFR 75.323

75.323 Actions for excessive methane.

(a) Location of tests. Tests for methane concentrations under this section shall be made at least 12 inches from the roof, face, ribs, and floor.

(b) Working places and intake air courses.

(1) When 1.0 percent or more methane is present in a working place or an intake air course, including an air course in which a belt conveyor is located, or in an area where mechanized

mining equipment is being installed or removed:

- (i) Except intrinsically safe atmospheric monitoring systems (AMS), electrically powered equipment in the affected area shall be de-energized, and other mechanized equipment shall be shut off;
 - (ii) Changes or adjustments shall be made at once to the ventilation system to reduce the concentration of methane to less than 1.0 percent; and
 - (iii) No other work shall be permitted in the affected area until the methane concentration is less than 1.0 percent.
- (2) When 1.5 percent or more methane is present in a working place or an intake air course, including an air course in which a belt conveyor is located, or in an area where mechanized mining equipment is being installed or removed:
- (i) Everyone except those persons referred to in §§104(c) of the Act shall be withdrawn from the affected area; and
 - (ii) Except for intrinsically safe AMS, electrically powered equipment in the affected area shall be disconnected at the power source.

(c)Return air split. (1) When 1.0 percent or more methane is present in a return air split between the last working place on a working section and where that split of air meets another split of air, or the location at which the split is used to ventilate seals or worked-out areas changes or adjustments shall be made at once to the ventilation system to reduce the concentration of methane in the return air to less than 1.0 percent.

- (2) When 1.5 percent or more methane is present in a return air split between the last working place on a working section and where that split of air meets another split of air, or the location where the split is used to ventilate seals or worked-out areas:
- (i) Everyone except those persons referred to in §§104(c) of the Act shall be withdrawn from the affected area;
 - (ii) Other than intrinsically safe AMS, equipment in the affected area shall be de-energized, electric power shall be disconnected at the power source, and other mechanized equipment shall be shut off; and
 - (iii) No other work shall be permitted in the affected area until the methane concentration in the return air is less than 1.0 percent.

(d)Return air split alternative. (1) The provisions of this paragraph apply if--

- (i) The quantity of air in the split ventilating the active workings is at least 27,000 cubic feet per minute in the last open crosscut or the quantity specified in the approved ventilation plan, whichever is greater;
 - (ii) The methane content of the air in the split is continuously monitored during mining operations by an AMS that gives a visual and audible signal on the working section when the methane in the return air reaches 1.5 percent, and the methane content is monitored as specified in §§75.351; and
 - (iii) Rock dust is continuously applied with a mechanical duster to the return air course during coal production at a location in the air course immediately outby the most inby monitoring point.
- (2) When 1.5 percent or more methane is present in a return air split between a point in the

return opposite the section loading point and where that split of air meets another split of air or where the split of air is used to ventilate seals or worked-out areas--

- (i) Changes or adjustments shall be made at once to the ventilation system to reduce the concentration of methane in the return air below 1.5 percent;
- (ii) Everyone except those persons referred to in §§104(c) of the Act shall be withdrawn from the affected area;
- (iii) Except for intrinsically safe AMS, equipment in the affected area shall be de-energized, electric power shall be disconnected at the power source, and other mechanized equipment shall be shut off; and
- (iv) No other work shall be permitted in the affected area until the methane concentration in the return air is less than 1.5 percent.

(e) Bleeders and other return air courses. The concentration of methane in a bleeder split of air immediately before the air in the split joins another split of air, or in a return air course other than as described in paragraphs (c) and (d) of this section, shall not exceed 2.0 percent.

75.342 - Methane monitors.

(a)(1) MSHA approved methane monitors shall be installed on all face cutting machines, continuous miners, longwall face equipment, loading machines, and other mechanized equipment used to extract or load coal within the working place.

(2) The sensing device for methane monitors on longwall shearing machines shall be installed at the return air end of the longwall face. An additional sensing device also shall be installed on the longwall shearing machine, downwind and as close to the cutting head as practicable. An alternative location or locations for the sensing device required on the longwall shearing machine may be approved in the ventilation plan.

(3) The sensing devices of methane monitors shall be installed as close to the working face as practicable.

(4) Methane monitors shall be maintained in permissible and proper operating condition and shall be calibrated with a known air-methane mixture at least once every 31 days. To assure that methane monitors are properly maintained and calibrated, the operator shall:

- (i) Use persons properly trained in the maintenance, calibration, and permissibility of methane monitors to calibrate and maintain the devices.
- (ii) Maintain a record of all calibration tests of methane monitors. Records shall be maintained in a secure book that is not susceptible to alteration or electronically in a computer system so as to be secure and not susceptible to alteration.
- (iii) Retain the record of calibration tests for 1 year from the date of the test. Records shall be retained at a surface location at the mine and made available for inspection by authorized representatives of the Secretary and the representative of miners.

(b)(1) When the methane concentration at any methane monitor reaches 1.0 percent the monitor shall give a warning signal.

(2) The warning signal device of the methane monitor shall be visible to a person who can

de-energize electric equipment or shut down diesel-powered equipment on which the monitor is mounted.

(c) The methane monitor shall automatically de-energize electric equipment or shut down diesel-powered equipment on which it is mounted when--

- (1) The methane concentration at any methane monitor reaches 2.0 percent; or
- (2) The monitor is not operating properly.

[61 FR 9829, Mar.11, 1996, as amended at 61 FR 55527, Oct. 25, 1996]

California Code of Regulations

8424. Airborne Contaminants.

(a) When the air in any part of a tunnel and/or shaft is known to contain or is suspected of containing dangerous airborne contaminants, it shall be tested by means acceptable to the Division before employees are allowed to work therein, in accordance with Section 5155 (Airborne Contaminant) of the General Industry Safety Orders. These tests shall be made by a person who has been certified by the Division.

- (1) Records shall be kept of these tests.
- (2) Records of gas tests and air flow measurements shall be maintained on the surface by the employer and available to the Division upon request.

(b) Tests for dangerous or explosive gas(es) shall be taken at such times and locations to accurately represent the conditions existing in all areas where employees may be exposed to the danger(s) of these gases and specifically:

(1) In tunnels classified as Potentially Gassy a manual flammable gas monitor shall be used as needed, but at least at the beginning of each shift and at least every four hours to ensure that the conditions prescribed in Section 8422(b)(2) are unchanged.

(2) In any tunnel classified as gassy, there shall be tests for gas or vapors continually during actual operations to ensure that the conditions prescribed in Section 8422(b)(3) are not exceeded. In addition, a manual electrical shut down control shall be provided near the heading. (See Section 8425 for additional requirements for the operation of Gassy and Extra Hazardous Tunnels).

(c) Whenever any of the following conditions have been encountered, all underground work shall cease, employees shall be removed, and re-entry except for rescue purposes shall be prohibited until the Division has been notified and has authorized re-entry in writing.

- (1) An underground ignition of gas or vapor occurs.
- (2) 20 percent of LEL of flammable gas or vapor is exceeded.
- (3) A toxic or suffocating gas in concentrations dangerous to health or life is encountered.

(d) Whenever the presence of hydrogen sulfide is suspected or detected in an underground

work area, a test shall be conducted in the affected area at least at the beginning and midpoint of each shift.

(e) Whenever hydrogen sulfide is detected in an amount exceeding 5 ppm, a continuous sampling and indicating hydrogen sulfide monitor shall be used. The monitor shall be designed, installed and maintained to provide a visual and audible alarm when the hydrogen sulfide concentration reaches 10 ppm to signal that additional measures, such as respirator use, increased ventilation, or evacuation might be necessary to maintain hydrogen sulfide exposures below the permissible exposure limit.

South Coast Air Quality Management District (AQMD), by law, is required to achieve and maintain healthful air quality for its residents. This is accomplished through a comprehensive program of planning, regulation, compliance assistance, enforcement, monitoring, technology advancement, and public education. The AQMD is the air pollution control agency for the four-county region including Los Angeles and Orange counties and parts of Riverside and San Bernardino counties.

Rule 1150.1. Control of Gaseous Emissions from Municipal Solid Waste Landfills

(d) (6) Operate the collection system to prevent the concentration of TOC measured as methane from exceeding 500 ppmv above background as determined by instantaneous monitoring at any location on the landfill, except at the outlet of any control device.

(h) (2) Inactive landfills without a gas collection system:

(A) Upon discovery of TOC measured as methane exceeding 500 ppmv at any location on the landfill surface, apply mitigation measures such as compaction, additional cover, and/or watering to reduce the emissions to less than 500 ppmv. The procedure used for measurement of TOC shall meet the requirements of Section 3.0, Attachment A.

**Pennsylvania Department of Environmental Protection
Proposed State Plan for Municipal Solid Waste (MSW) Landfills
(http://www.dep.state.pa.us/dep/subject/draft_policies/emis_lan.htm)**

The initial Annual Report for a gas collection and control system must be submitted to the Department within 180 days after installation and start-up of the system as specified in 60.757(f) and (g). The initial report is required to include the Initial Performance Test Report for the gas control system and the following information:

(a) Value and length of time for exceedances of monitored parameters under 60.756. This would include reporting of monthly measurements of nitrogen or oxygen concentration and temperature within a well that exceed 20 percent or 55 °C (131 °F), and methane concentrations in excess of 500 ppm above background. Reportable exceedances for control device operating parameters include 3-hour periods when combustion temperatures are outside the ranges established in the most recent performance tests, and periods when

the pilot flame to a flare or flare flame is absent.

SECTION III INVESTIGATIVE PROCEDURES

1.0 INTRODUCTION

This section identifies techniques that can be employed during the course of a fugitive methane investigation. Two phases of investigation are recommended and together comprise the site characterization:

- 1) the *Preliminary Investigation* is an initial determination of site conditions and actions to identify immediate health hazards.
- 2) the *Comprehensive Investigation* builds on the Preliminary Investigation and may include several on-site visits to characterize the site conditions and the source of the methane.

A mitigation plan, if necessary, should be developed from data derived during the comprehensive investigation. The appropriate techniques for each investigation are largely dependent on the site-specific conditions. This section also identifies outside resources, sources of background information, and standard investigative methods.

The timing of sampling with respect to natural forces and man-induced impacts is critical to site characterization and to identifying the methane source. Background sampling is recommended prior to mining, construction, or other activities to establish a baseline by which any possible change can be measured.

2.0 PRELIMINARY INVESTIGATION

As discussed in Section I, the investigator has three primary tasks at this time: interview the landowner or occupant, observe and record site conditions, and test for possible atmospheric methane concentrations. The foremost concern is safety to the public and property. Thus, testing of atmospheric methane levels must always be conducted first and concurrently with the recording of site conditions. This will identify hazardous levels of methane at the earliest stage of the investigation.

The investigator should observe all personal safety rules and procedures at all times during the preliminary investigation. It is recommended that the investigator attend the 40-hour OSHA course or a comparable course for dealing with hazardous materials. Some safety suggestions include:

- T Always test for methane before and during entrance to a structure or other enclosure where

the problem has been reported. Your first breath of methane (low oxygen) could be your last! (Check the calibration of a hand-held electronic methane detector in fresh air just prior to use.)

- T If methane is known or suspected to be emanating at the surface, use caution while working in that area. Park your motor vehicle at a safe distance, and do not drive across the area.
- T Do not investigate a problem without a partner or other individual. These individuals may be able to help or call for assistance in case you are injured.
- T Do not turn on or use electrical devices, and preclude the use of other potential ignition sources until you have tested the atmosphere and determined that it is safe.
- T Prior to use, be sure testing equipment is explosion-and flame-safe.

2.1 Test for Atmospheric Methane: ALWAYS TEST FOR METHANE FIRST! The landowner must immediately show the investigator the problem area for evaluation and testing. If methane levels exceed 1% by volume (10,000 ppm) in the atmosphere being tested, evacuate the area immediately and ventilate with fresh air. Portable Combustible Gas Indicators (CGI) calibrated for methane detection should have a minimum sensitivity of 0.1% by volume (1,000 ppm), or a sensitivity of 5% LEL. Note that most equipment that measures methane also measures other combustible gases. Equipment and its usage are detailed in Section IV.

REMEMBER, methane gas is colorless, tasteless, odorless, and lighter than air. Testing for methane in structures, such as homes and businesses, is performed to determine the emergency nature and impact of the problem. Sampling of the ambient air in and around structures should be the first activity performed at the site. Since the problem involves hazardous gases, the atmosphere in a structure or a confined space should be considered hazardous until testing determines otherwise. The problem may be compounded with toxic, combustible, or asphyxiant gases (e.g., carbon monoxide, hydrogen sulfide, etc.) in addition to methane. The atmosphere should be tested before any possible ignition source is encountered, such as turning on a light switch.

2.1.1 Commercial Gas: If natural gas is used in the home or is available in the area, the gas company is usually the first on site to evaluate the problem. The company's findings are necessary to dismiss natural gas leaks from appliances or distribution lines. Regardless, first check all apparent places that may be a point source of methane such as gas appliances, supply lines, and volatile liquids. Many methane problems are simply a leaky supply line or a poorly operating gas appliance. Elevated methane levels on the upper floors of residential structures are almost always due to appliances.

2.1.2 Methane Sampling: Low levels of methane in a structure are usually a sign of a concentrated point source entering the building. Confined spaces must be carefully sampled to prevent normal air from diluting the atmosphere of a concentrated area. Opening a manhole cover or door will allow the confined atmosphere to disperse. Sampling should be performed through an existing opening, hole, or slightly opened door.

Beyond the obvious sources, all potential methane migration paths, traps, and potential sources of ignition in structures must be tested. Fugitive methane most often enters

structures from the basement. Since methane is lighter than air, it will collect along the ceiling of the basement and/or enclosed areas.

The investigator should start in the middle of the room to establish ambient levels of methane and then expand to other areas. Sample gas concentrations at the top of openings, between floor joists, and along ceilings within the structure. Methane will collect under slabs or pavement, especially if a gravel bedding provides a permeable reservoir. The uphill edges of slabs or paved areas should be evaluated to determine if gas is exiting to the atmosphere. Test all cracks, joints, floor drains, pipe entrances or other openings in the ground or in the basement of the structure.

Test all water faucets for methane by spraying the water into an inverted container for a few minutes to trap any released methane.

Abandoned subterranean structures, such as tanks, vaults, and drain fields may be sources or conduits of methane. These features must be checked for the presence of gas and evaluated as potential sources. Care must be taken to preserve the atmosphere of these confined spaces. For example, the gas concentration may be lost if a manhole cover is opened to test for gas. Preferably gas can be sampled through a hole in the cover.

2.1.3 Records: Sampling points should be briefly described. The best method for documenting measurements is to draw a sketch map and depict all testing locations. The sketch map should include enough detail to describe the site conditions and all anomalies. Record the initial and highest readings observed at each location or a range of readings if the measurements are highly variable.

It is important to distinguish methane readings as initial or sustained. There may be sample points where methane concentrations are not sustainable. When reviewed collectively, these readings may provide clues as to the source. Sustained readings may indicate an inflow from a concentrated source. In contrast, intermittent readings usually indicate a concentration of gas from a disperse source. All readings should be checked to determine if the measurements are repeatable.

Record atmospheric conditions during sampling. Weather conditions to be noted throughout the investigation include: barometric pressure, temperature, precipitation, and wind. Ideally, these data should be recorded at or very near the problem site, but this is not always possible. Recorded methane concentrations should be evaluated with barometric pressure readings taken at the time of sampling.

Diffusion is an important property of all gases and must be taken into account. Gas measurements in an open hole or well must extend below the surface away from the diffusive effects of wind. Gas sampling outdoors on windy days should be avoided.

2.2 Interview the Land Owner/Tenant: A significant amount of background information can be

obtained from the owner. This information will help develop a plan to characterize the extent and source of the methane.

Questions should be scripted prior to interviewing property owners and other individuals. Owner responses will likely prompt additional questions during the interview. Avoid asking leading questions and allow the owner to elaborate. Some typical questions include:

- T How long have you lived in the home?
- T When and how did you first become aware of this problem?
- T Are you aware of any methane problems with this structure/well prior to this one?
- T What was the nature of any previous problems?
- T Can you tell me any characteristics of the present problem?
- T Who drilled your well? When was it drilled? How deep is it? How was it constructed (e.g., casing, well screen, grouting, yield development, etc.)? Have yield test(s) been performed, when, and by whom? Request all available documentation.
- T How old is the dwelling?
- T Has remodeling or other nearby construction occurred recently?
- T What, if any, data do you have on methane concentrations or water quality?
- T Are you aware of any other methane problems in the area?
- T Is there any other information related to this problem that you want to discuss?
- T Have any occupants of the structure experienced health problems?
- T Are there any known underground structures in or near the dwelling such as basements, sewers, cisterns, etc.

Information obtained during an interview is important and together with a limited amount of quantitative data may be all you have to work with at this stage. Most property owners are non-technical people; therefore, the information given will tend to be qualitative rather than quantitative. The quality of the information is directly related to the strength of the individual's knowledge, memory, and objectivity. These limitations must be considered when assessing the information.

2.3 Observe Site Conditions: Take topographic and/or mine maps to the site. Note surface features that may be important to the migration of methane. Look for obvious sources of methane, including water wells, abandoned and active oil or gas wells, gas transmission lines, wetlands, landfills, and evidence of mining. All features should be identified on a map and tested for methane. Also note items that may seem to be unrelated to the methane problem such as local construction activities and history of the area.

Note or incorporate relevant features observed in the field on the base map. In the absence of a map, GPS data are useful so that the site can be plotted accurately onto a base map. With GPS data, the locations of sample points can be revisited and distances between points can easily be determined.

Occasionally, methane can be observed diffracting light when it vents. Odors may also be apparent

and may be associated with related hydrocarbons or other compounds. These observations may be relevant to the source identification and should be noted.

To the extent possible, structure and/or water well construction details should be determined or evaluated. The location, condition, and source of natural gas lines, propane lines or other potential conduit(s) of combustible gas must be identified. Solicit the help of local gas and other utilities, if available. Pertinent background information contained in any permits or other official records should be field verified for accuracy.

2.4 Action: Multiple site visits may be required. If any of the actionable levels as outlined in Section II are observed, then a comprehensive investigation is warranted. If after additional visits methane is not observed, a summary report is necessary to document the findings of the preliminary investigation. The report may dismiss the complaint or recommend a comprehensive evaluation. A comprehensive investigation is warranted if any evidence suggests that methane may achieve actionable levels.

3.0 COMPREHENSIVE INVESTIGATION

A comprehensive investigation warrants review of all historical information and extensive methane testing. The purpose is to delineate the extent of the problem, identify the magnitude of the hazard, identify the source, and recommend a mitigation plan, if necessary.

3.1 Historical Information/Data: The investigator should obtain reports for previous methane investigations in the area and review all information/data obtained during the Preliminary Investigation. Also review published research and reports specific to the area.

Historical data used in the investigation may include:

- T aerial photos
- T topographic and underground mine maps
- T county maps
- T geologic structure and geology maps
- T stratigraphic logs and cross-sections
- T isopach (lines of equal rock thickness) maps
- T isopleth (lines of equal concentration) maps
- T lineament maps
- T mine permit files
- T drillers' records and aquifer test results
- T historical methane yields of specific coals and other rocks
- T gas well records
- T well yield
- T daily water usage
- T other existing analytical data

Maps should be compiled to aid in the detailed site reconnaissance. Often, the maps will yield a good focal point from which to start. For example, the location of gas wells are shown on topographic maps. Older topographic maps will often exhibit gas wells that are no longer visible at the present time or that would require considerable searching with some idea to identify their location. The location of these wells with regard to the problem and their present condition may prove to be important in the investigation.

Historical gas line problems in the area may actually indicate the source of the gas. For example, leaky gas lines may store natural gas (predominantly methane) in the soil and shallow bedrock that can take a long time to disperse.

Weather conditions strongly affect methane migration. The Internet is a valuable resource to gather time-sensitive weather information on a local and regional scale and a historical basis. Most airports also compile this weather information. These data are also available from the National Oceanographic and Atmospheric Administration. However, the investigator must realize that differences can exist between the location at which the data was collected and the site being investigated.

3.2 Detailed Site Reconnaissance: In the Preliminary Investigation, the immediate area was assessed for any obvious methane hazards and sources. The detailed site reconnaissance expands to include all adjacent areas, take a closer look at the site conditions, and confirm the location of structures, water and gas wells, utility lines, and other surface features. Examine anything that may have an impact on the problem and record observations. Frequently, nothing is found that is previously unknown to the investigation. However, the absence of certain features will help eliminate potential sources.

3.2.1 Detailed Notes: Document all information that is personally checked or observed. If the source is in question or uncertain, the case may be litigated and contemporary notes will be valuable. Note how the information is obtained. Were they personal observations of the well condition or was the information given by the owner? If field measurements are taken, note where, when, how, and under what conditions.

3.2.2 Interviews: Interviews with other people not contacted during the Preliminary Investigation will be needed. These people include:

- T nearby property owners
- T previous landowners (both for the problem site and adjacent areas)
- T local well drillers
- T the home builder
- T officials and professionals from coal and gas companies
- T landfill personnel (if relevant)
- T geological consultants who commonly conduct work in the area
- T county or local municipal officials.

Not all of these people will be accessible or have information to add to the investigation, but it is a good practice to talk with as many as possible to determine what they do know about methane in the area.

The following officials can provide important information and may be able to provide valuable technical support:

- T Public safety officials provide critical help, in particular if the investigation uncovers an emergency condition.
- T Gas companies provide excellent technical resources and are often involved in the investigation because the problem was discovered on a routine pipeline inspection.
- T Local government officials can provide the location of methane collection systems and oil wells.

3.2.3 Structure Characteristics: Potential methane paths, traps, and sources of ignition in structures must be determined. The details of the structure construction and present integrity should be determined. Pertinent information concerning the structure includes but is not limited to:

- T age of the building
- T type, thickness, and integrity of the foundation substrate (e.g., fill, gravel, or bedrock)
- T condition of basement walls and floor
- T associated French and field drains
- T entry points of utilities (water, gas, electric, and septic lines)
- T location and construction of floor drains
- T remodeling changes
- T tanks, vaults, and other features that may impact sources and/or points of methane entry
- T crawlspace locations

Particular note should be made of foundation cracks and the location and conditions of vents to the exterior. Abandoned subterranean structures such as tanks, vaults, and drain fields may be sources or conduits of methane.

3.2.4 Water Well Characteristics: When a well is a suspected source of methane, record the details that are available or measurable. Pertinent water well data include:

- T total depth
- T depth to water
- T rock units intersected
- T extent of casing(s) and/or screen
- T surficial and annular grouting

- T age of well
- T water-bearing units
- T lithologic units
- T pump intake location
- T venting and/or cap type

Location of the well (vertically and horizontally) with respect to a mine or other potential sources is equally important. Whether or not methane is confined to the well is important, because the open bore can become a conduit for methane at depth to easily migrate to the surface. At minimum, record total depth and depth to water when investigating water wells, if the well is accessible.

Much of the well information can be obtained from the original driller's records, if available. Field check the driller's log if possible. The amount of casing, total depth, and pump setting are generally reliable. The depths when water was encountered and unusual problems will sometimes be noted in the logs.

A borehole camera can be used to determine the casing depth, depth to water, rock types, fracture orientation, level of water-bearing zones, gas entry points below water level, casing, plumbing integrity, the nature of obstructions, and the extent of biofilms on the interior walls of the well. Be certain that the camera is safe for explosive environments.

3.2.5 Water Well Quality: In areas where methane is occasionally problematic, background methane data may exist. Background data are helpful to determine if construction or mining adjacent to or beneath wells has impacted the hydrologic and/or geologic conditions and caused a change in methane levels.

Wells should be sampled at least three times. Particular attention should be paid to the relative barometric pressure and the direction of pressure change at the time of sampling. Low-pressure systems are known to cause increased atmospheric methane readings under certain circumstances.

3.3 Field Measurements and Sampling: Field measurements and methane samples are always necessary during a comprehensive investigation. If methane is present, the data will be used to determine the hazard potential. Field instrumentation and sampling can be segregated into three categories:

- T methane in the atmosphere,
- T methane in the water, and
- T methane in the soils.

Depending on the problem type, any or all of these media may need to be tested during the investigation. Regardless of the media being sampled, atmospheric methane is a hazard and should be monitored during all phases of the investigation.

3.3.1 Methane in the Atmosphere: Field measurements, sample collection, and laboratory analyses should be conducted to augment the testing performed during the preliminary investigation. If at any time methane exceeds 1% in an occupiable area, evacuate the area and ventilate. Atmospheric grab samples are essential during the comprehensive investigation.

a. Field Meters. The most common field measurements of methane are obtained from portable meters generally referred to as methanometers or combustible gas indicators. Most incorporate catalytic diffusion or non-dispersive infrared absorption as the sensors for methane.

Field measurements of atmospheric methane can be obtained using various equipment including the above referenced meters, or methane-specific detector tubes (Section IV). Generally, the gas measurement equipment used depends on the accuracy required and resources available to the field personnel.

An investigation that requires mitigation should not rely exclusively on field measurements for methane. Field measurements are not as accurate as laboratory analyses. It is very important to note that field equipment usually measures combustibility of the atmosphere and will therefore be affected by the presence of any other combustible gases.

Depending on site conditions, it may be prudent to test for other gases for safety reasons. These gases include:

- T hydrogen sulfide (H₂S)
- T carbon monoxide (CO)
- T carbon dioxide (CO₂), and
- T oxygen (O₂).

These gases can be dangerous based on their levels. Some of these gases can displace oxygen and cause asphyxiation (O₂ < 16%) , others can be toxic or explosive. For example, H₂S is toxic, corrosive, and can also be explosive.

b. Grab Samples. At some point during the comprehensive investigation, samples should be obtained for molecular analyses in the laboratory. Sample wands with an aspirator or pump are necessary to take point source samples. Small hand pumps can be used to collect a sample. Gas samples should be collected in Tedlar[®] bags, vacuum tubes, or other impermeable environmental sample bags. Most meters can be configured to obtain diffusion or point measurements. Gas analyses in the laboratory are generally conducted by gas chromatography.

Detector tubes will provide only grab sample results and are not recommended for detailed field investigations. Tubes must be selected for the particular gas to be tested, often

requiring trial and error sampling. Only qualitative methane data can be obtained from detector tubes.

c. Continuous Monitoring: The methane concentrations recorded at various points may change over time. This may be due to the effects of weather, changes to the source, and other influences. Numerous visits may be necessary before the full extent of the problem is determined because of these varying readings.

Continuous methane monitors and multi gas monitors are available for long-term deployment in the field. This equipment can be equipped with alarms and data loggers to warn of dangerous methane levels and to record changes in methane levels over time. We highly recommend the use of data logging and continuous monitors to help investigate and mitigate a methane problem.

Continuous monitors should be set with alarms at levels that can warn when conditions for imminent danger exist. These conditions should follow the action levels defined in Section II of this manual. A data logger on a continuous monitor is an important investigative tool. The data logger can improve the quality of the field data and reduce the amount of time required to obtain samples. Data recorded over a known period can be correlated with other conditions that may change at the test site. Methane levels may vary with changes in temperature, barometric pressure, or even the time of day.

As an example of the need for continuous monitoring, an anomalous short-term combustible gas level was found to occur every morning as a resident left home. The monitor was placed in the ground floor of the home near an integral garage. The timing on the gas meter showed that the anomalies occurred when the resident started the vehicle and the rich exhaust fumes were identified as a combustible gas on the monitor. Accounting for the car fumes and changing the location of the gas monitor addressed the anomaly.

The continuous monitors with data loggers have historically been available only as complicated fixed or dedicated systems usually designed for industrial use. These systems can be simply modified for residential use and incorporated with data loggers for monitoring a project site. These types of systems are recommended for long-term monitoring or incorporation into a mitigation plan. More recently, portable methane and multi-gas monitors used for confined space work have been outfitted with data loggers. These units can be left on for extended times, powered by household current, to monitor a project site. Data loggers in these portable units are usually less robust than fixed systems and have short duration logging periods of one month or less. The portability and ease of use of these systems make them ideal for field work.

Continuous monitoring with data loggers must account for all activities that may affect the readings over short time periods. For example, a unit placed next to an exterior door will be impacted by fresh, outdoor air anytime the door is opened. Monitors should be placed near the suspected gas entry point (e.g., a crack) but away from doors, windows, vents or

human activities. The data logger should be set to monitor peak readings (the highest readings during a recording period) at intervals that provide good resolution of the recorded period. Logging intervals ranging from 10 to 30 minutes provide adequate resolution to monitor peak readings for logging periods of 5 to 30 days. Longer intervals may be required for long-term monitoring. Monitoring should continue through a change in weather or a change in season unless the source of gas can be identified or abated. The data should be graphed and analyzed for trends, anomalies, and compared to any variables that may influence the gas levels over time.

Continuous monitors are often used to monitor the effectiveness of mitigation and identify system failures at the earliest possible time. Methods similar to those described above are used in mitigation work. These are discussed in greater detail in Section V.

d. Outdoor Testing: Methane is lighter than air. It will dissipate rapidly in an open air environment but can sometimes be observed as it exits a vent or well because of light diffraction. Methane will rarely be measured outdoors unless concentrations are significant (>5%) from a point source. To be effective, gas measurements taken outdoors, in an open hole or a well, must be below the surface away from the effects of wind. Also, opening a confined place outdoors can result in a representative sample being lost. For example, a measurement is inaccurate when a manhole cover is opened to test for gas. A preferred method is to sample the gases through a hole in the cover or when the lid is ajar.

e. Indoor Testing: To begin indoor testing, first recheck methane levels and review the details on the history of any construction, appliance repair or replacement, condition of the gas appliances and distribution system for changed conditions since the preliminary investigation. After the obvious sources have been rechecked and eliminated, then more indirect sources must be considered.

Methane can travel from the source through the soil, rock, or subsurface utilities to areas immediately outside the foundation. Thus, the primary point of methane entry into a structure is through openings in the basement. When sampling with a combustible gas indicator (CGI), start in the middle of the room to establish ambient levels of methane and then expand to other areas. A small amount of methane in a structure is usually a sign of a concentrated point source. Inevitably, the gas is leaking from one or more points into the structure.

Always work from an area of least concentration to the highest. Search for gas at the top of openings, between floor joists, and along ceilings of basements or crawl spaces, from all cracks, joints, or other openings in the ground or basement walls, and under slabs or pavement. The sample points that produced methane readings during the preliminary investigation must be revisited and measured. Associated areas not previously sampled such as neighboring properties should be investigated. During this phase of the investigation samples should be taken to verify measurements and to determine the molecular composition (Section III, 4.0 Sourcing of Methane).

Measure gas around construction joints, most notably the contact of foundation with the ground and floor slab. Note all openings, such as floor drains, pipe entrances and any cracks for the presence of gas. All readings should be double checked to determine if the measurements are repeatable. Gas anomalies should be recorded and the sample point briefly described. The anomalies must be compared with all data collected earlier. If the measurements are highly variable, record the initial and highest readings observed at each location or a range of readings.

3.3.2 Methane in Water Wells: Methane, along with other gases and chemical constituents, can be dissolved in water. The solubility of methane in water is directly proportional to pressure. The solubility of methane at atmospheric pressures is about 28 mg/L. Ground-water at depth can contain higher concentrations depending on the hydrostatic pressure.

Methane can be present in surface or ground-water. Since surface water can freely yield gas to the atmosphere in open spaces, testing is usually not necessary. On the other hand, ground-water pumped into a house can liberate methane inside and create a hazard. Occasionally, the levels are high enough that a kitchen faucet can be ignited with a match.

In a well, methane can exist in either a dissolved or gaseous phase. Dissolved methane in the water is kept in solution by atmospheric or hydrostatic pressure. The higher the water column, the more methane that can be held in solution. Gaseous methane enters the well bore as either bubbles in the water or as free methane from fractures above the water table. In both phases, the gas will be affected by temperature and barometric pressure.

Microbial activity can also impact dissolved-methane concentrations. Methane can be created by certain methanogenic (methane-generating) archaeobacteria from CO₂, H₂, and other constituents. Alternately, methane can be broken down or degraded by other types of methanotrophic (methane-utilizing) archaeobacteria. Methane-utilizing bacteria are particularly active in aerobic environments, such as water wells. Periodic sanitation of the well can minimize or eliminate a bacterial problem.

a. *Well Bore Gas:* Gas samples taken from the well bore atmosphere are affected by the use of the well, changes in water level, temperature, and barometric pressure. Atmospheric samples should be taken as close to natural conditions as possible. For example, when taking a gas sample in a well that is normally capped, the sample should be collected within a foot or two below the top of the casing with a clipboard or towel covering the top of the well to simulate normal operating conditions of the well. If the well has a vent, then the sample should be taken from within the vent pipe. For details on the sampling protocol, see Section IV.

The highest level of methane (as a gas or dissolved) in a well may be encountered shortly after extensive pumping (i.e., during well recovery). An example would be when a fracture system filled with methane is exposed by the falling water table and allowed to directly and

freely vent into the well bore. Conditions like this may show a high content of methane in the casing, but low dissolved methane. Recharging of the well with dissolved methane-laden waters will also subsequently yield significant amounts of gaseous methane to the well bore. It is not recommended to sample during pumping, because the lowering water table will draw air into the well bore.

b. Estimating the Dissolved Methane Level: The worse-case scenario (maximum concentration) for dissolved methane in the well is based on the water column height. This information will yield insight as to the potential hazard and gives a starting point for later reference. The calculation is relatively simple. First, determine how much standing water is in the well. Based on this information, the maximum possible dissolved methane at the bottom of the well can be estimated by:

$$C_{well} = \left[\frac{(0.43)H_w}{14.7} \times 28 \right] + 28$$

- T C_{well} is the maximum concentration of dissolved methane at the bottom of the well (mg/L).
- T multiply the height of the well water column (H_w) in feet by 0.43 lb/in²-ft (the weight of an one inch square column of water one foot high), the result is water pressure in pounds per square inch (psi).
- T given that one atmosphere (atm) is equal to 14.7 psi, divide the weight of the water by 14.7, giving the weight of the water in atmospheres.
- T finally, multiply the number of atmospheres by 28 mg/L (the average solubility of methane in water) and add 28 mg/L, for the initial ground level atmosphere, to yield the worst-case scenario for dissolved methane (mg/L).

As an example: Water is 100 feet down a well 200 feet deep, which could theoretically contain a maximum of 110 mg/L methane.

$H_w = 200'$ total depth - $100'$ depth to water = $100'$
 Water column pressure is $100' \times 0.43$ psi/ft = 43 psi
 Pressure in atmospheres (atms) is 43 psi / 14.7 psi/atm = 2.93 atms
 Maximum dissolved methane at $100'$ is 28 mg/L + $(28$ mg/L/atm \times 2.93 atms) = 110 mg/L

c. Well Purging: Water standing in a well bore for a protracted period of time undergoes physical, chemical, and biological changes that directly impact the water quality. Included in these changes is possible degassing of dissolved methane. It is imperative that the ground-water sampled has been recently derived from the aquifer. For example, when a domestic well is not being pumped for normal daily use, methane levels will not accurately represent the true site and/or ground-water quality conditions.

In most cases, the daily use of the well by the homeowner will sufficiently perform the purging process. However, there will be situations when the investigator will need conduct the purging. The protocols of the purging process and potential problems are described in detail in Section IV.

d. Water Samples: Water samples should be obtained whenever methane is perceived and/or the atmospheric testing near or in the well shows measurable concentrations of methane. When taking a dissolved methane sample from the well, the well should be purged and the protocols outlined in Section IV should be followed. Samples may be obtained from various kinds of pumps and bailers.

The ground-water should also be sampled for major inorganic constituents. It is recommended that the ground-water samples be analyzed at a minimum for pH, total hot acidity, total alkalinity, total iron, total manganese, total aluminum, sulfate, chloride, sodium, total dissolved solids (TDS), specific conductance, and dissolved oxygen. These parameters yield a variety of information on the aquifer geochemistry, biological activity, and relative age of the ground-water recharge. These constituents may also yield insight into the history and/or the source of the water produced by the well. Creating a specific conductance and temperature profile of the standing water in the well bore can also indicate the location and relative contribution of water-bearing fractures in rocks of the Appalachian Plateau (Hawkins et al., 1996). The location of the water-bearing zones may be indicative of the source(s) of the dissolved methane.

In the Appalachian Plateau, low TDS (<200 mg/L) is generally indicative of relatively young ground-water. Recently infiltrated water has had only a very short time to dissolve and assimilate minerals from the aquifer or water table. Higher concentrations of TDS indicate that the ground-water has been moving through soluble units for a long time. For example, high concentrations of calcium (>100 mg/L) indicate that the ground-water has been in contact with alkaline rock (e.g., limestone) long enough to become saturated or nearly so.

Elevated sulfate concentrations (>50-100 mg/L) are indicative of ground-water contaminated with mine drainage. Mine drainage will commonly have sulfate levels ranging from a few hundred to over several thousand milligrams per liter. Ground water, naturally, will seldom have sulfate concentrations exceeding 50 mg/L in the shallow sedimentary rocks of the Appalachian Plateau. If the water quality is indicative of mine drainage, the dissolved methane may have a similar origin.

Gas wells are commonly associated with brines and marine-deposited connate waters because of their depth. If the well casings fail or are improperly abandoned (i.e., without being plugged) and are under sufficient pressure, they can contaminate overlying shallow ground-water aquifers with methane and ground-water containing sodium, bromide, barium, strontium, and chloride well above background levels for the area. For example, background concentrations for sodium and chloride in shallow ground waters of western

Pennsylvania are generally below 100 mg/L and seldom naturally exceed 300 mg/L, except when brine contamination is suspected (McElroy, 1988).

In general, the older and more deeply buried the rock units, the higher the sodium and chloride concentrations (Poth, 1962). Deep brines in Pennsylvania exhibit chloride concentrations ranging from 13,800 to 207,000 mg/L and sodium concentrations ranging from 6,760 to 83,300 mg/L (Rose and Dresel, 1990). A shallow ground-water system contaminated with these brines is anticipated to have sodium and chloride concentrations falling between background and the extreme values exhibited by the brines. Certain gas and oil field brines that are high in barium have low sulfate concentrations (Hem 1989). For additional insight into using ground water to help understand where the methane is originating from, the reader is directed to Hem (1989) and Stumm and Morgan (1996).

3.3.3 Methane in Soils: Methane migrating to the surface through soils is not an uncommon occurrence in gas-producing regions. In all likelihood, it frequently goes unnoticed unless bubbling is noticed in pooled surface water, the concentration is high enough to kill some of the surface vegetation, or methane found elsewhere focuses an investigation on the soil.

A hazard can develop while excavating in methane-rich soils. Methane can be encountered in pits or trenches and go unnoticed by equipment operators. In areas of possible methane sources, confined excavations should be tested for methane. If a diesel or gas engine races for no particular reason, methane exhausting from a broken line or the soil may be the likely cause. This situation requires further investigation before any source of ignition is introduced to the area.

The same mechanisms that permit methane to enter shallow ground-water wells permit it to be released at the surface. Diffusion will force gas to migrate from areas of high concentration to areas of low concentration, even through low permeability materials. Methane flows from high-pressure toward low-pressure areas. If the pore pressure for methane in the ground exceeds atmospheric pressure, it will flow to the surface. Soil texture, compaction, and geomorphology are factors that affect permeability and allow methane to migrate through or be stored in soil.

Stress-release fractures and geologic faults may act as conduits to allow methane migration. Shallow coalbeds and gas-bearing strata can supply low-pressure gas to the surface over a very long time period.

Man-made sources of gas, including pipelines and landfills, can fill the soil and shallow bedrock with methane quickly. Mining-induced fracture accentuation or fracture creation will permit the release of additional methane above natural conditions and provide more efficient avenues toward the surface.

Methane in soil is not usually hazardous, since it is not available to normal combustion and naturally dissipates into the atmosphere. However, the gas can become hazardous where it

becomes trapped in a crawl space or shed built over methane-laden soils.

a. Methane migration: Methane is lighter than air and it migrates up-gradient or more accurately to areas of decreasing pressure. Permeability and porosity are important considerations for methane migration in soils. The presence of methane in soil is in part a function of the different textures of soils. Testing the texture, permeability, and porosity of soil may provide useful information on the storage capacity of methane. Depth and geomorphology of the soil are also helpful. Some glacial and especially peat-type soils can be a source of methane.

Methane migration in soil is similar to methane migration in bedrock. For example, a non-cohesive sandy soil is highly permeable and can allow gases to migrate. In contrast, tight clay soils will impede migration of gas but may trap methane in the underlying weathered bedrock.

The scenario described above occurred at a structure built on a monolithic slab. Methane was recorded at cracks in the slab and around electric outlets in the wall. Soil probe holes around one side of the foundation indicated high levels of methane but no methane was observed at the surface. Further investigation found that the weathered bedrock above a low-pressure pipeline contained the methane. The pipeline was being used to collect methane from an underground coal mine in the area for commercial distribution and was determined to be broken. Methane was being trapped under a clay soil layer in the fractures of the shallow weathered bedrock and migrating about 100 feet horizontally into the structure. The pipeline was subsequently repaired and the methane was purged from the rock.

b. Soil gas monitoring: Soil samples readily lose gases when disturbed and samples are rarely collected. Methane in the soil is measured by the amount of atmospheric methane that accumulates in a long narrow hole. The holes are made with tile probes, steel rods, or sophisticated probes with sample ports or retractable tips designed specifically for gas sampling. Depths of the holes are usually 2-5 feet depending on soil type and length of probe. If soils are cohesive and a slide or power hammer is used, holes can be advanced 10 feet or more, depending on the depth and hardness of bedrock.

Many holes can be driven in a short time in a predetermined grid, to define the areal extent of the problem and pinpoint the source (soil gas survey). Soil gas surveys should be conducted in accordance with ASTM D 5314 (Standard Guide for Soil Gas Monitoring in the Vadose Zone).

A sketch map is necessary to compile the information from soil probing. Methane levels are typically highest in the holes closest to the source. For example, soil probing and sampling along a pipe or drain alignment can identify the point of a leak. Similarly, the perimeter of a building can be checked to identify the direction from which the gas is migrating. Soil probing may extend radially from an anomaly to determine the direction of

a more concentrated source.

Gas companies frequently use soil probing to determine the areal extent of the problem from a leaky gas line. By contour mapping equal concentrations (isopleths), the methane can be traced toward the highest concentrations, hence the probable source area. As with any subsurface exploration, care must be taken to not damage buried utilities and other structures that may be hidden underground.

The different atmospheres in soil must be considered in the evaluation of soil probe holes. Testing for organic material in soils may prove helpful in determining the source of methane. Methane from human development including leaky gas lines, septic systems, or landfills can travel through backfill and soils. Deeper methane sources from mining or drilling may be redirected or trapped in the soil horizon. Methane in the soils may migrate and collect in a location substantially removed from the source.

c. Soil testing equipment: The atmosphere in a small hole is representative of the soil gases because dispersion and diffusion draw the surrounding gases into the hole. Testing the hole for methane uses equipment similar to testing for atmospheric methane. A Combustible Gas Indicator calibrated to detect methane with an extension wand and a pump are required. The procedure for using a CGI is as follows:

- T Gas is drawn through the hollow rods of a gas probe by an aspirator or small hand pump and measured by a gas meter.
- T Solid rods are retracted and a tube or wand is placed into the hole at a depth away from the influence of the ambient air to measure gas.
- T Enough gas is drawn to purge the sample lines, but not at a rate to evacuate the hole and draw in air from the surface.
- T Samples are drawn from as close as possible to the bottom of the hole, with the surface opening blocked.

4.0 SOURCING OF METHANE

The source of methane and the migration pathway should be identified in order to develop an effective mitigation plan. It is important to consider all information/data when attempting to identify the source. Eventually, data/information obtained during the Preliminary and Comprehensive Investigations can be synthesized and interpreted to identify the source of the methane, with recommendations for mitigation. There are several geochemical and statistical techniques that can be employed to determine the source of fugitive methane.

Molecular analyses of gas samples are fundamental to attempt to identify the source of gases during investigations of fugitive methane. Results for molecular analyses combined with other aspects of a site specific investigation may be sufficient to interpret the source of the gas. However, due to other environmental processes in the subsurface, molecular analyses may not

always be reliable to interpret the source of gas. Fluctuating barometric conditions, chemical fractionation, and bacterial oxidation may alter the composition of a gas as it migrates from the source area. Additionally, in areas where several potential methane sources occur, it is often advisable to sample gas for carbon and hydrogen isotopic analyses. Carbon and hydrogen isotopic analyses together with results of a site specific investigation generally provides a definitive answer regarding the source of methane. Interpretation of isotopic analyses for gas samples should be conducted by professionals experienced in this field of geochemistry.

Different gas sources generally exhibit significantly different ratios of combustible gases and isotopic signatures. Specifically, the ratio of hydrocarbon components is often useful in determining the source of gas. Thermogenic and microbial methane sources can often be distinguished by their stable carbon and hydrogen isotopic concentrations as well as their chemical composition (Coleman, 1994; Baldassare and Laughrey, 1997).

Isotopes are different forms of the same element. Methane can occur in three different isotopes of carbon (^{12}C , ^{13}C , and ^{14}C), and hydrogen also has three different isotopes (1H, protium, 2H, deuterium, and 3H, tritium). Carbon-14 and hydrogen-3 are radioactive. They are formed by cosmic rays in the upper atmosphere. The other isotopes of carbon and hydrogen are stable. Measuring the relative concentrations of the isotopes of carbon and hydrogen generally allows us to distinguish methane from different sources. (Coleman et al. 1977; Fuex, 1977; Stahl, 1977; Schoell, 1980; Coleman, Benson, Hutchinson, 1990; and Baldassare, 1997).

Hydrocarbon gases are generally categorized as microbial or thermogenic in origin. Microbial methane form via one of two predominant metabolic processes active in methanogenic bacteria - the reduction of CO_2 in marine environments and fermentation of acetate in freshwater settings (Wiese and Kvenvolden, 1994). Landfill and marsh gases are gases of microbial origin. Thermogenic methane forms as organic matter is buried in sediments and subjected to progressively higher temperature regimes, which facilitates the decomposition of the organic matter and the generation of hydrocarbons. Thermogenic methane forms through the thermal decomposition of oil in reservoir and nonreservoir rocks and in coal, and from the direct thermal decomposition of organic matter dispersed in sedimentary rocks. (Hunt, 1996) Natural gas from producing formations, pipeline gas, and coalbed gas are, generally, examples of thermogenic gas. However, increasingly pipelines convey microbial and mixed microbial thermogenic gases and coal can contain methane of microbial origin.

Isotopic analyses allow differentiation between microbial and thermogenic methane, however, they may not provide results that can be interpreted to distinguish different thermogenic sources. For example, methane from a coalbed may have a similar stable carbon and hydrogen isotopic composition when compared to methane from an active or abandoned gas well. In problematic areas, a regional isotopic database can help overcome these ambiguities. It is also important to consider other elements of an investigation when attempting to identify the source of methane.

Different gas sources generally exhibit different ratios of methane, C_2+ hydrocarbons and isotopic signatures. The ratio of C_2+ hydrocarbons is often useful to determine if the gas is microbial or

thermogenic in origin. Chapter 5 provides an example of calculating hydrocarbon ratios. High concentrations of C₂+ hydrocarbons are an indication that the gas is thermogenic in origin, however, the absence or low concentrations of C₂+ hydrocarbons does not indicate the gas is microbial in origin. (Coleman, 1994). Stable carbon and hydrogen isotopic analyses are powerful tools to distinguish microbial and thermogenic gas sources. (Baldassare, 1997).

During investigations where microbial gas is suspected as the potential source, ¹⁴C (carbon 14) analyses provides definitive results. Thermogenic methane was formed from organic materials that are millions or hundreds of millions of years old and does not contain any detectable ¹⁴C. Landfill gases are enriched in ¹⁴C, and are, therefore, readily distinguished from thermogenic sources by ¹⁴C analyses. (Coleman, 1994)

Age dating of ground-water is also useful in determining the source of the methane. Extremely old connate water is expected to be associated with deeper-sourced thermogenic-derived methane. On the other hand, for relatively young and recently recharged ground-water, age dating of the ground water can be performed using tritium or chlorofluorocarbons, whereas methane can be dated using carbon-14 (¹⁴C) (Wassenarr et al., 1992; Avarena et al., 1995). Younger ground-water is generally expected to be associated with shallow microbially formed methane.

4.1 Gas Wells: Methane produced from gas wells drilled into producing geologic formations is generally thermogenic in origin. Because thermogenic gases may have similar stable carbon and hydrogen isotopic concentrations, identifying methane from thermogenic sources represents a challenge in areas where several potential thermogenic sources exist. Figure 12 illustrates this point where results for delta ¹³C and delta D are plotted for gas samples collected from various sources

A comprehensive investigation including samples for molecular and stable carbon and hydrogen analysis from all potential sources is recommended during investigations where 2 or more thermogenic sources are suspected. These data combined with a thorough physical investigation should provide sufficient information to interpret the source.

4.2 Collection, Transmission, and Distribution Lines: The vast majority of gas transported through gas lines is of thermogenic origin. In some areas of the country however, gas of microbial origin or a mixture of the two types is transported. The composition of the transmitted gases may

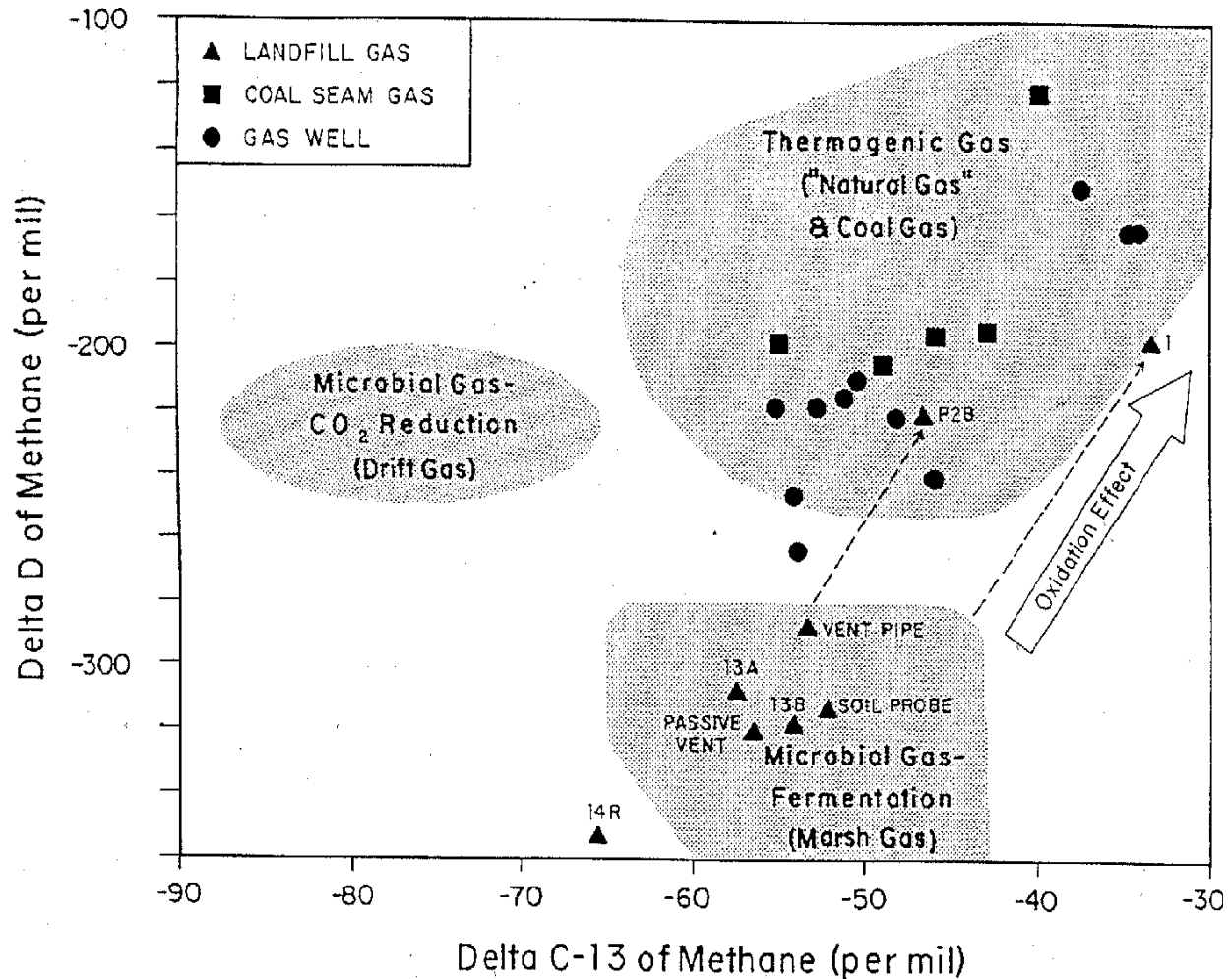


Figure 12. Identifying the sources of Stray Methane by using Geochemical and Isotopic Fingerprinting (Baldassare, 1997).

vary greatly over time. Collection pipelines carry gas from a point source to a storage facility. Transmission lines are high pressure, high volume pipelines used to convey gas to the distribution points from storage. Distribution pipelines carry gas along the streets and into people's homes. Gas from transmission and distribution lines almost always contains mercaptain as an odorizer and is thus easily identified. Occasionally a small or local gas company will not add mercaptain.

4.3 Landfills: Methane generated in landfills is microbial in origin. Most states regulate the control, monitoring, and mitigation of methane from landfills. Methane monitoring systems are common at active landfills. The monitoring systems provide an early warning for fugitive methane. Occasionally, however, methane from an active landfill will migrate undetected and outside of the landfill perimeter. Unpermitted, pre-regulation landfills may also represent methane sources with the potential for migration to other areas, thus creating a hazard.

Coleman (1993) documented that low concentrations (up to 100 ppm) of ethane, propane, and butane are not uncommon in landfill gas. Further, the composition of gas in an aerobic environment such as the shallow-soil zone or near-surface waters can be altered by oxidizing bacteria (Coleman, 1994). These bacteria preferentially deplete the ^{12}C components (James, 1984). It is apparent, then, that these factors may alter the composition of a gas making molecular analyses alone potentially unreliable as a means to identify the source. If molecular analysis cannot be interpreted with confidence for source identification, isotopic analyses of the carbon and hydrogen isotopes generally can (Coleman, 1994).

The radioactive isotopes of carbon and hydrogen are particularly useful to identify the source of fugitive methane from landfills. Methane generated at landfills is from the decomposition of waste including paper, wood, and food materials that were grown in the previous 40-50 years (Coleman, 1994). Carbon 14 (^{14}C) is the radioactive isotope of carbon. The half-life of ^{14}C is 5,730 years. Because most landfill gas is generated from materials grown within the last 40-50 years and since natural gas and coalbed gas were produced from materials millions of years old, they contain no ^{14}C .

During the 1950s and 1960s, above-ground testing of nuclear devices produced substantial amounts of ^{14}C -enriched CO_2 . Materials grown since 1960 have ^{14}C above normal levels. Similarly, the radioactive isotope of hydrogen (tritium) was also enhanced during nuclear testing. The half-life of tritium is 12.4 years. Tritium is also found at elevated concentrations in landfills because of materials such as luminous paints and other luminous items that apparently exist in landfills. Tritium analysis of methane can identify landfill methane and provide a technique to distinguish landfill gas from other microbial methane such as sewer gas, marsh gas, and swamp gas (Liu, 1996).

Figure 13 provides a graphical representation of the ^{14}C concentrations from various sources. As illustrated, if landfill gas is suspected as the source of gas in a fugitive methane migration incident, the radioactive isotopes of carbon and hydrogen provide definitive results to distinguish microbial methane from thermogenic methane and landfill gas from other microbial gases.

4.4 Abandoned Mines: Many mine shafts and portals were abandoned before regulations on their closure were in effect. Therefore, these shafts and portals may be open, capped, or improperly sealed. They often exist in old mining communities. Occasionally, old mining structures and new structures are adjacent to or over old shafts. Open mine portals are an attractive danger, especially to inquisitive children. Explosive levels of methane from the mine may be venting through the shafts and portals to the surface where there is oxygen and sources of ignition.

Gas produced from abandoned mines is microbial and thermogenic in origin. Abandoned underground coal mines are methane sources with the potential for migration to areas of decreasing pressure. These mines are generally below drainage, hold methane in reserve, and

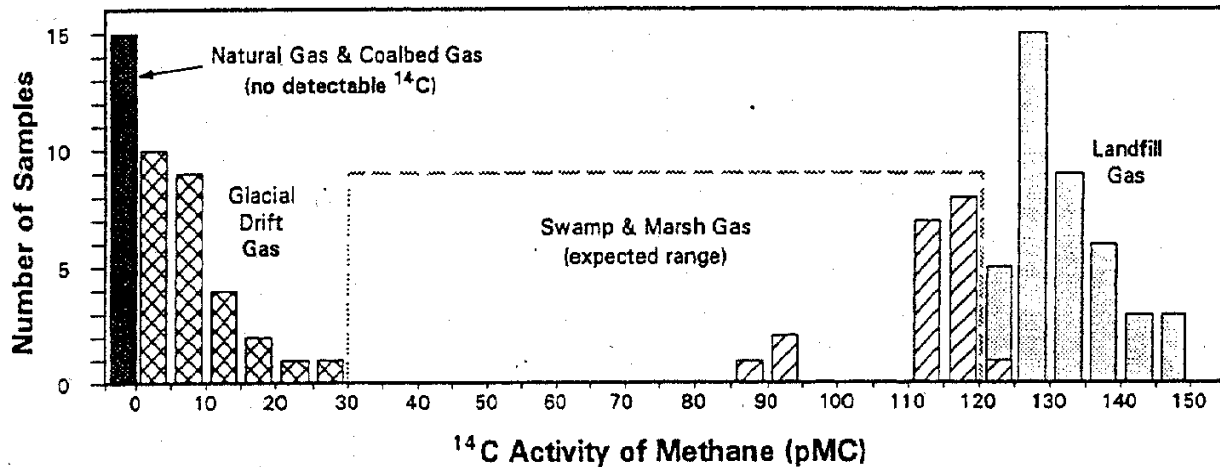


Figure 13. Use of Geochemical Fingerprinting for Gas Identification (Coleman, 1994).

create a pressure differential to release gas through fractures or wells. The extent, proximity, and conditions of an abandoned coal mine are important to evaluate as are overburden conditions. The overburden and abandoned mine can be assessed by the installation and monitoring of properly sited soil gas surveys, unsaturated zone monitoring points, and ground-water monitoring wells. The number of monitoring points and type of monitoring are dependent on site-specific conditions. At a minimum, gas samples should be collected from all monitoring points for molecular analyses at similar intervals and under the same barometric conditions.

Fluctuating barometric conditions often drive the migration of methane from shallow abandoned coal mines. Pressure is reduced at the soil/atmosphere interface under falling barometric conditions, resulting in soil outgassing. The depth to which barometric conditions affect the soil gas chemistry varies widely, but has been reported to exceed tens of meters.

Barometric pressure, air temperature, and weather conditions should be recorded during sampling. Several sampling episodes under various barometric conditions are recommended to interpret the results.

4.5 Active Mines: When high-extraction mining is conducted, such as longwall or room-and-pillar with retreat mining, most of the ground subsidence occurs shortly thereafter. Coe and Stowe (1984) stated that 90 percent of the subsidence occurs within a few days of longwall mining. Subsidence creates new or accentuates existing fractures in the overlying strata. The fractures in the overburden can serve as avenues of methane flow to the surface. Occasionally, subsidence cracks are observed at the surface, indicating that a transmissive conduit may exist from depth to the surface. If building foundations are cracked from the subsidence, methane can more easily infiltrate the building from fractures in the underlying subsoil and strata.

Furthermore, subsidence can cause dramatic changes in the hydrologic regime as the ground-water percolates downward. Subsidence can cause the release of methane and increase the transmissivity of the rock. Previously impermeable lithologic units may be fractured and become

semi-permeable to permeable. Where subsidence causes a lowering of the ground-water levels, the reduced hydrostatic pressures facilitate the flow of methane from the rock units into well bores and to the surface (Naftz et al., 1998). The timing of methane arrival in a well is the most useful tool to establish active mining as the source. It is highly recommended that the well bore atmosphere and the groundwater in a water well in the area of longwall or other high-extraction mining be sampled prior to mining

In the Appalachian Region, methane is commonly produced by or stored in coals, sandstones, and carbonaceous shales. Subsidence from high-extraction mining can greatly impact the overlying ground-water system and in turn directly or indirectly cause the liberation of methane.

Ultimately, methane enters wells as either a gas through unsaturated rock units or as a dissolved component in ground-water. Water wells open to the atmosphere generally represent low-pressure zones compared to the high pressures exerted by strata and ground-water. Gas migrates from areas of high pressure to low pressure areas and therefore, water wells especially those where the water level has been lowered as a result of mining, become natural avenues for methane migration. After subsidence is complete, the low-permeability units may partially heal, the water levels are partially to completely re-established, and the methane concentrations may restabilize at or near background levels.

Methane sampling to gauge the effects of mining-induced subsidence should be conducted prior to mining and through the period of expected subsidence. As soon as the physical changes related to mine subsidence are noted, shortly after the passage of the high-extraction mining equipment (longwall), the initial post-mining sampling should be collected. These physical changes include but are not limited to: dwelling structural damage, surface cracking, general lowering of the ground surface, complete loss or substantial lowering of well water levels, visual changes to the water (e.g., dissociating gases, discoloration), and/or audible gas entering the well. Overlying wells have been observed to vent over 30% methane within a few days of mining. Periodic sampling may be appropriate for up to one year.

Regardless of whether or not subsidence-induced changes are observed, the well should be sampled at least three times after the mining passes or until methane returns to ambient levels. A suggested sampling program, including water levels and ground-water methane concentrations, is as follows:

- T Initially sample at least one week after passage of mining.
- T The second sample should be collected six months after mining occurs.
- T The tertiary sample should be collected at the one-year mark after mining.
- T Sampling may extend beyond one year after mining.

The frequency of this sampling is based on known geologic and hydrologic responses to longwall mining-induced subsidence, as discussed above. However, it is anticipated that additional research into the nature of methane released by mining subsidence may result in changes to the sampling protocol. Depending on the methane concentration recorded, additional and more frequent

sampling may be required after the mining has passed.

SECTION IV PROTOCOL FOR METHANE SAMPLING AND GAS ANALYSIS TECHNIQUES

1.0 INTRODUCTION

Accurate and reproducible sampling is fundamental to proper assessment of the hazard potential of fugitive methane. This chapter recommends procedures and protocols for methane sampling in the field and analysis in the laboratory. Sampling procedures for methane in the atmosphere, wells, and soils will be discussed. Additionally, procedures are recommended for collecting water samples to evaluate methane dissolved in water. Details of sampling include sample collection techniques, use of field instruments, sample handling and preservation, and procedure/chain-of-custody documentation. Potential problems are also discussed in this chapter.

2.0 TESTING FOR ATMOSPHERIC METHANE

Atmospheric methane is measured as a normal component of air. Field testing for methane with portable meters provides instantaneous readings necessary to identify hazardous areas and to potentially locate sources. Samples for molecular analysis in the laboratory via gas chromatography (GC) are usually essential at some point during the investigation. Laboratory analyses are necessary to verify field measurements, identify and quantify other components in the sample, and to attempt to identify the source.

2.1 Portable Equipment: Most commonly, field measurements of methane are obtained with portable meters capable of detecting trace levels of gas. The meter sensitivity for testing atmospheric methane is typically in the range of 0.005% (50 ppm or 0.1% LEL) to 0.1% (1000 ppm or 2% LEL).

Portable meters use one or more indirect methods to calculate the concentration of combustible gases to a standard gas, usually methane. With microprocessors, the equipment has become more accurate and easier to use over the past 10 years. Some meters have dual sensor capability to measure low concentrations of gas with the catalytic bead sensor and the full range of gas above the LEL with the infrared (IR) sensor. Table 10 lists some of the meters available.

Portable meters fall into three basic categories:

2.1.1 Catalytic Bead System: The most common meters use a catalytic bead system. Catalytic bead detector operation is based on a simple principle. When hydrocarbon comes in contact with a catalytic bead filament, heat is generated, which changes the resistance across one side of a circuit. The reference side remains unchanged. The concentration of gas is proportional to the difference in the resistance across the two circuits. This system can be calibrated to detect low concentrations on the order of 10 parts per million or the more normal range of the lower explosive limit of gas. Limitations associated with these

types of meters include:

- T The meter will not measure methane in a diluted oxygen atmosphere, or where the methane concentration is above 12%.
- T The catalytic bead sensor will measure, but cannot distinguish between the types of combustible gases, including methane, hydrogen, carbon monoxide, hydrogen sulfide, ethane, propane, and other hydrocarbons.
- T The meters become poisoned with repeated exposure to silicon and lead compounds or may destruct from high concentrations of combustible gases.

Table 10. Portable Gas Meters (Compiled From: Buyer's Guide to Portable Gas Monitors, Tara Nemer, Environmental Technology, November/December 1997, pgs. 44-49)

Company	Phone	Gas types	Sensor Types	Data Loggers & Pumps	Notes
AIM Safety USA Inc. Austin, TX	(512) 832- 5665	Combustible, multi-gas	IR, Cat Bead, Semiconductor, Electrochemical	Exposure Logger, Integral Pump	Hazmat uses.
Bacharach Inc. Pittsburgh, PA	(412) 963- 2625	Combustible, multi-gas, toxic, CO ₂	Cat Bead, Semiconductor, Optical Electrochemical	Logger, Attached Pump	Fixed Systems
Biosystems Inc., Middletown, CT	(800) 711- 6776	Combustible, multi-gas, toxic	Cat Bead, Electrochemical	Logger	
CEA Instruments, Emerson, NJ	(201) 967- 5660	Combustible, toxic, Volatile Organics, CO ₂	IR, Cat Bead, Electrochemical	Logger, Integral Pump	Land fill monitor
Draeger Safety Inc., Pittsburgh, PA	(800) 615- 5503	Combustible, toxic, CO ₂ , multi- gas	IR, Cat Bead, Electrochemical	Long term logger, Integral Pump	Long life Sensors
Gas Tech Inc., Newark, CA	(510) 745- 8700	Combustible, multi-gas, toxic	Cat Bead, Electrochemical		Remote sensor
Industrial Scientific Corp., Oakdale, PA	(412) 788- 4353	Combustible, multi-gas, toxic	Cat Bead, Electrochemical	Optional logger, Integral pump	
MSA Instrument Division, Pittsburgh, PA	(800) 672- 2222	Combustible, multi-gas, toxic	Cat Bead, Electrochemical		

2.1.2 Flame Ionization System: This type of meter operates on flame ionization, a sensor similar to a catalytic bead. These are also known as “sniffers” or “spotters” that detect the lowest trace levels of methane.

- T The meter relies on a separate fuel, usually hydrogen, to burn across two electrodes. Hydrocarbons entering this sampling system and passing through the flame will increase the current in the electrodes.
- T Typically, the meter has two ranges: the search scale, which measures from 0 to 100% of 50 parts per million of combustible gas and the high scale, which measures from 0 to 100% of 5,000 parts per million (< 10% LEL).

2.1.3 Infrared (IR) System: The IR system includes a combustible gas meter which operates on more recent technology based on point infrared sensors. The infrared detectors use the diffraction of light in the presence of methane to measure methane concentration. IR equipment is more expensive than catalytic beads. Other features of an IR system include:

- T Less sensitive to very low concentrations of gas.
- T Sensors have a long operation life.
- T Is not susceptible to the sensors being polluted by contaminants.
- T Is able to measure to 100% gas without the presence of oxygen.

One limitation of the IR sensor is that it will not measure the full combustibility of a gassy atmosphere that may have other non-hydrocarbon combustible gases, including hydrogen or carbon monoxide.

2.1.4 Calibration: Instrument calibration is necessary to ensure accurate methane measurements. Meters should be routinely calibrated, at least monthly. Sensors that do not hold calibration should be replaced. Prior to usage at each site, the gas meter must be zero calibrated in a fresh clean atmosphere at temperatures and air pressures similar to those at the investigation site.

2.2 Sample Containers: Gas samples for laboratory analysis can be collected in a variety of containers available commercially, including glass sampling bulbs, sampling bags, vacutainers, and various glass bottles. Sampling bulbs or sampling bags may require purging to remove any atmosphere in the vessel.

Evacuated bottles and vacutainers under a vacuum have a shelf life of approximately 3 months. Samples should be analyzed within a few days of sample collection. Some gases may react with the rubber stopper or septum. Over extended periods of time, bacteria, even in evacuated samplers, can produce trace levels of methane and oxygen.

Tedlar™ bags are often used to collect gas samples from sources under low pressure for laboratory analysis. Samples in Tedlar bags may be subject to the effects of adsorption and condensation, resulting in loss of sample over a period of several days. However, Tedlar bags have been found superior to polyethylene, saran, and Mylar (Schuetzle, 1975). The authors also found that the polar gases (most odorous), such as H₂S, were highly susceptible to adsorptive effects.

Overall, the characteristics of methane and other hydrocarbon gases associated with most fugitive methane migration problems are not greatly affected by adsorption and condensation. Any potential effects of condensation and adsorption can be greatly reduced if samples are immediately transported and analyzed in the laboratory.

Non-reactive stainless-steel gas cylinders are recommended for samples from sources under pressure.

2.3 Laboratory Equipment: Samples collected for laboratory analysis should be submitted to the laboratory shortly after collection for optimum accuracy. Methane concentrations can be determined using an organic vapor analyzer (OVA) coupled with a gas chromatograph (GC) column. An OVA with GC is capable of separating methane, ethane, and other heavy hydrocarbon gases. The integral detector is a flame-ionization type. The fuel and carrier gas is usually hydrogen (Chafin et al., 1996).

2.4 Sampling Methodology - Atmospheric Methane: Methane in the ambient atmosphere must be tested first (normal atmosphere in the center of the room). Initial testing for ambient methane levels will determine if immediate action, such as ventilation or site evacuation, must take place. If a safe environment exists but detectable methane remains in the area, then the entry points and/or source area(s) should be determined.

2.4.1 Indoor Sampling: Methane discovered in a residence should be sampled with doors and windows closed to avoid dilution with the outside atmosphere. All fans, including HVAC units, ceiling fans, and exhaust fans, must be turned off to obtain a good sample. Any prior attempt to ventilate the structure should be noted and sufficient time allowed for the atmosphere to stabilize prior to any sampling.

Ambient methane concentration in a residence is usually low, even if the source of the methane is emerging directly into a room. Dilution greatly affects most natural methane sources in ambient atmospheres unless the source is concentrated and under pressure. A quick reconnaissance of the structure with a sensitive methane detector is recommended. Sample locations include:

- T the ceiling
- T any visible cracks in the basement.
- T the atmosphere in the center of any suspect room near the ceiling, because methane is lighter than air and may collect at higher levels.
- T in each corner of the room, especially any corner away from doorways or windows that may ventilate the area.
- T the top of stairways and above the headers of internal doorways, including the top of a basement stairway.
- T possible methane entry points in each room, such as floor drains, open sewer lines or utility entrances, and
- T gas appliances and lines.

The investigator must search for detectable levels of methane from room to room and note any areas with detectable concentrations of methane. Rooms with little or no methane relative to the problem area must be eliminated and the search refined to those areas with detectable measurements. Any potential sources of volatile organic compounds in the area(s) of investigation must be identified. Sources such as gas cans, lawnmowers, or paint cans may interfere with some types of instrumentation and cause false readings.

In general, field instruments are incapable of detecting extremely low concentrations of methane. An ambient atmosphere with only 1-2 ppm is at the detection limits of most GC setups and may be the normal background level in some atmospheres. Trace methane levels may also represent a diluted point source and may warrant additional work. Ambient methane levels of 10-100 ppm indicate that a source of methane may exist. Low levels of methane are not hazardous since they are not explosive, but require additional investigation to identify the source and migration paths. A thorough testing of the atmosphere will usually help define the extent of the problem. The open areas that have anomalously higher gas concentrations are likely to be closer to the source of the gas.

The investigator must first determine if any gas appliances or gas lines are in or adjacent to the suspect area, then eliminate the possibility of methane coming from these sources. If methane is coming from an unknown source outside the structure, then the path is most likely subterranean. In such cases, the investigator must change search patterns to review the areas outdoors.

2.4.2 Outdoors Sampling: A search similar to that described above should be performed outdoors along the edge of the foundation. Detectable gas readings observed indoors should correlate with the location of the exterior search. Extra effort to search the gas line and meter or any other utility alignment should be done. All cracks and holes adjacent to the foundation should be checked for gas.

Repeatable results in outdoor ambient atmospheres are difficult to obtain because the gas is usually low in concentration and easily disturbed by ventilation or even the process of sampling itself. Revisiting a site for additional testing may be necessary to determine trends and obtain additional information to identify the source of gas. Sampling should be completed at locations where methane was previously detected, with samples collected for laboratory analysis at locations with the highest recorded readings.

3.0 TESTING FOR METHANE IN WELLS

Methane enters water wells as a free gas or as a dissolved component of ground water.

Frequent occurrences of methane in domestic water wells of the Appalachian Plateau illustrate the need for a standard method or protocol for sampling the dissolved methane in ground-water and the gaseous methane in the well bore.

The methods for sampling methane that are discussed below are aimed at achieving accurate measurements. This sampling methodology is meant to be simplistic and performed with the use of inexpensive, commonly available equipment. If this protocol is followed, consistent, reproducible, and accurate measurements will be obtained.

3.1 Portable Equipment: The portable meters for evaluating atmospheric methane around wells in this section are the same as outlined in Section IV, 2.0. However, well sampling requires some additional equipment to obtain water samples and pump the well. Portable sampling equipment includes, but is not limited to:

- T Portable submersible pump (e.g., the GRUNDFOS Redi-Flo 2)
- T Kemmerer-type sampler

The investigator must maintain a record of the purging procedure and flow characteristics of the well. Because of the potential for degassing, it is strongly recommended to not use a bailer for purging or sampling when methane or other gases are the targeted constituents. Use of a jet pump is likewise not recommended, because it can entrain air into the water.

3.2 Preliminary Test: A simple qualitative field check for dissolved methane can be performed by aerating water into an enclosed container such as a wide-mouth jar. Water is simply sprayed into the overturned jar, allowing the water to drain away and the methane to become trapped in upper portion of the container. Aeration into the container should proceed for at least one minute. A gas meter with a sampling wand is then quickly inserted into the overturned container to measure the gas level in the trapped atmosphere. A sample can also be obtained for additional analytical testing. This should not be used for quantitative analysis because the longer the water is aerated the more gas is produced. Also, the high humidity may affect readings.

3.3 Sampling Methodology - Well Preparation: Wells must be purged (pumped) prior to sampling because a "fresh" water sample is needed to assess ground-water quality. When sampling for water quality, a well should be purged to ensure that a fresh and representative sample is collected (Koterba et al., 1995).

Water standing in a well for a period of time undergoes changes that can affect and alter the water quality. Examples of these changes include:

- T Temperature changes
- T Gases (e.g., oxygen, carbon dioxide, methane, or hydrogen sulfide) entering or escaping from solution
- T Oxidation/reduction reactions
- T Biological activity

- T Precipitation of metals
- T Reactions with the well casing or exposed rocks

3.3.1 Pumping: Typically, purging a monitoring well of 3 well volumes is considered sufficient to obtain a valid water sample. The well volume is the amount of water contained inside the well initially, based on the height of the water column and the well diameter. Occasionally, 3 well volumes are inadequate, if so, the investigator must continue to purge the well. The following are indications that the well has not been adequately purged:

- T the water becomes cloudy or discolored during purging,
- T the field parameters (discussed below) do not become stabilized, or
- T foreign material falling from the sides or surface of the borehole into the water can be heard.

Water samples taken from the bottom of the water column can hold the highest concentrations of dissolved methane in solution (worst-case scenario). However, the best place to sample from a well is at the water-bearing zones. In the Appalachian Region, the water-bearing zones are usually high in the well in the upper reaches of the water column, where the fractures are more numerous and fracture apertures are wider (Stoner, 1983; Hawkins et al., 1996).

Sampling at the level of the water-bearing strata will yield the truest representation of the ground-water quality in the aquifer. Sampling at lower levels in the well may not truly represent the dissolved methane concentrations in the water. As the water column is drawn down, the water-bearing fractures are exposed and the ground-water is susceptible to degassing.

There are times when a low-yielding well will be completely dewatered during purging. The investigator should try to avoid dewatering the well. However, if this happens, the investigator should allow the well to partially recover and then sample. Significant water quality changes for many parameters, as discussed above, may occur if the water is allowed to sit for several days. However, because of the rapid nature in which methane degasses from water, the well should not be permitted to sit idle for more than a half hour to an hour after dewatering.

Determination that a well has been adequately purged can also be achieved by monitoring one or more field parameters (pH, temperature, specific conductance, and/or turbidity). Dissolved oxygen (DO) can be used as a field parameter at wells with a submersible pump. However, DO, or dissolved methane sampling, is not recommended to be performed at a well with a jet pump and cannot be used when the well is purged with a bailer. For dissolved methane samples, it is recommended that DO be one of the field parameters used. *ALL* field parameters need not be monitored. However, it is recommended that at least two of them are monitored; however, one may be acceptable. These parameters will help standardize the data collected from the well and will be especially useful when future

samples are collected.

Readings should be taken every 3 to 5 minutes. Once field parameters have stabilized for at least 15 minutes, a water sample can be taken. Stabilization is reached when:

- T pH is within ± 0.1 of a standard unit,
- T temperature is within ± 0.2 CE,
- T specific conductance is within 5% for values equal to or less than 100 microsiemens and 3% for values >100 microsiemens, or
- T turbidity is within 10% for values <100 NTU.

(After Koterba et al., 1995).

With this purging method, the investigator is not limited by the amount of water purged. However, if purging continues until 5 well volumes or more are removed, sampling can proceed, even if the field parameters have not stabilized. However, the investigator must be sure to record any problems that occurred during the purging and sampling process.

Artesian wells do not need to be purged. They can be sampled them from the plumbing system, as discussed below, at the overflow point, or as close as possible to the well head.

3.3.2 Inaccessible Well Heads: In the Appalachian Region, domestic wells are frequently inaccessible because they have been buried, the well cap cannot be removed, or centralizers impede complete access. In these cases, it is recommended that the field-parameter method be used to determine when to sample. If the field parameter method cannot be used, estimate the well dimensions, water level and the purge volumes at the time of sampling. This method should be used only when the other methods cannot be performed. As stated before, the investigator must be sure to record how the purging amounts were determined and how the method was performed.

For domestic wells that are used daily, extensive purging prior to sampling may not be needed. If the well has been used for normal domestic purposes within the previous 24 hours, this process will perform most of the required purging. However, the investigator will need to run water at 1-2 gpm for approximately 10-30 minutes prior to taking a sample. This will completely clear the plumbing system and allow for a "fresh" water sample to be taken unless a large storage system such as a cistern is used in the system. In most cases, the homeowner's delivery system will be used, so this method of well purging and sampling should be adequate.

3.3.3 Degassing: There are some potential problems with the purging of low-yielding wells in the Appalachian Plateau. Domestic wells in this region tend to receive most of recharge from relatively shallow ($<100'$ from the surface) fractures created by stress-relief forces (Ferguson, 1967). Domestic wells are generally drilled much deeper to create a reservoir. When pumped down, water emanating from the shallow fractures cascades down the inside of the well bore and/or casing and drips from offsets in the well bore, ultimately

physically impacting the standing water in the well. These actions permit ample time, a large surface area, and a mechanism for dissolved methane to degas. This condition will dramatically lower the dissolved methane concentration levels in the water. Great care must be taken to minimize this interference. It is recommended to pump low-yielding wells at a relatively low rate for an extended period of time to prevent substantial dewatering below the water-bearing zones. A pumping rate of 0.1-1.0 gallons per minute is likely to minimize the cascading problem for the average well of the Appalachian Plateau. However, it is recommended to have prior knowledge of the well's yield potential and to adjust the purge rate accordingly. The well should be pumped at a rate nearly equal to the known recharge rate.

If the water-bearing zones are well-documented, a single packer or a straddle pack could be used to simplify the purging and sampling as well as improve the accuracy. When conducting this type of low-flow purging, the field parameter stabilization method should be used to determine when to initiate sampling. Puls and Paul (1995) observed stabilization of water quality parameters with as little as 7.5 liters purged in two-inch monitoring wells. All wells stabilized after purging less than 10 liters.

3.4 Sampling Methodology - Well Head Sampling. For well head sampling, ground-water samples are collected in 40-50 ml glass vials with Teflon[®] septa closures. Once purging is completed, the discharge rate should be reduced to a low rate to the point of achieving laminar flow for sampling. Too high of a flow rate will create turbulent flow, which facilitates degassing of methane. Laminar flow can also be accomplished by tapping a portion of the total flow with a Y-splitter and small diameter tubing, using a valve, or having a variable speed pump. The vial should be completely filled directly from the tubing or a hose inserted into the bottle. Caution should be taken to minimize splashing and aeration in the vial. The vial should be filled to overflow and allowed to continue overflowing for about 1 minute. A replicate sample is recommended to be taken each time a sample is taken to determine sampling consistency and potential variability of the dissolved methane.

Once filled, approximately one-third to one-half of the sample is rapidly decanted and the sample quickly sealed. Removal of part of the sample creates a head space for the methane to exsolve from the water. The investigator must make sure the septum is seated properly and that the cap is on tight, then the sample is shaken vigorously for a few seconds. Based on work conducted by the Colorado Oil and Gas Conservation Commission and Bureau of Land Management (1995), the sample should not be analyzed for at least 45 minutes after sampling. This permits ample time for the dissolved methane to exsolve.

Ground-water samples collected for GC analysis should be collected in 40 ml glass vials with Teflon[®] septa. The sample bottles must be filled to the top with a meniscus and contain no air bubbles. Samples should be refrigerated to 4EC for transport to the laboratory.

If microbial degradation is a concern and analysis will not be conducted within 24 hours, then the sample will need to be fixed with a microbicide or germicide to inhibit methane-utilizing bacteria.

If isotope analyses are planned, a germicide that will not interfere with the analyses, such as benzalkonium chloride, should be used. A portable gas chromatograph can be taken into the field if results are needed immediately or if there is a concern the sample will degrade rapidly.

Regardless of the type of equipment used, its use should be continued throughout the length of a project for consistency of sample comparison. Time of sampling, water temperature, and barometric pressure should be recorded for each sample. If possible, the ambient air temperature and the methane level in the surrounding atmosphere should be measured and recorded. These conditions can influence the methane concentration that is ultimately recorded.

Water samples for dissolved methane received at the laboratory are in air-tight containers with air space to allow methane to degas. A gas-tight syringe is inserted through the Teflon[®] septa of the vial to extract a sample of the gas from the head space. This sample is then injected into the OVA for analysis. The extracted air sample is then subjected to the same test as outlined in Section IV, 2.0 Laboratory Equipment. Determination of the dissolved methane content of the water sample is detailed in Standard Methods for the Examination of Water and Wastewater (Franson, ed., 1992). The method defined is entitled the Combustible-Gas Indicator Method and utilizes Henry's Law. Concentration of methane dissolved in water can be calculated from a bottle sample with adequate head space using the method described in Appendix A.

3.5 Sampling Methodology - Gaseous Methane in the Well Bore: Methane in the well bore may come from methane dissolved in the water and exsolving into the well head space or from free methane flowing through fractures above or below the water table. Methane flowing through the water column will generate bubbles that can usually be heard in the well or even observed in shallow wells where the water table is visible. Sampling of the well head atmosphere can help evaluate the hazard potential of the well and estimate dissolved methane concentrations.

To sample the well bore atmosphere, first purge the well, as discussed above. Once the purging is completed, the well should be permitted to sit idle for two hours or longer, simulating periods of non-water use of a domestic well. This idle time will allow, if present, dissolved methane to degas and gaseous methane to flow into the well unrestrained. During this period, the well casing should be capped or covered with a low-permeability material (e.g., sheet plastic, a thick towel, or something similar) to impede venting.

The investigators should allow the water level in the well to stabilize or allow sufficient time for dissolved methane to exsolve into the well head space. The speed at which an equilibrium is reached is a function of contact surface to volume of liquid and solubility. The greater the proportion of surface area the sooner equilibrium is reached.

Weather conditions can affect the sampling of wells for atmospheric methane. Special attention should be paid to barometric pressure changes before and during sampling. If a low-pressure front is moving through the area, this can draw higher amounts of gas from the strata intersected by the well, whereas a high-pressure area can cause the infusion of ambient air into the ground. Precipitation preceding gas sampling can create a wetting front moving downward through the soil

and shallow strata pushing gases ahead of it thus influencing the pore gas quality. Windy conditions are usually associated with changes in barometric pressure and can make sampling difficult by displacing the well atmosphere.

Collecting a gas sample can also be difficult. The very act of uncovering the well casing and inserting the sample vial or sensor has the potential to disturb the in-well atmosphere. The methane at the top of the well bore can be vented freely, or atmospheric gases can enter the casing to displace and/or dilute the methane concentration. Ideally, place a tube with a pump or aspirator bulb attached through the well cover to obtain a sample from the well bore.

3.5.1 Grab Samples: Gas grab samples are collected in a vacuum vial that is opened and then resealed while inside of the well casing or through a septum cap of a vacutainer. As the well cover is removed, obtain the sample as quickly as possible to avoid dilution. The gas analysis can be achieved with a gas chromatograph or an organic vapor analyzer. Regardless of which type of equipment is used, it must be used throughout the length of a project for consistency of comparison.

3.5.2 Meter Testing: The easiest method to determine the methane concentration in the well bore is to take field measurements. The investigator inserts the wand of a gas meter into the casing, or through a small hole in the cover, and covers the remainder of the casing or hole with the sheet plastic or towel. The setup should be allowed to stabilize for at least 2 minutes prior to testing the atmosphere of the well bore.

3.5.3 Field Estimating Dissolved Methane Concentration: From the methane concentration in the well atmosphere, assuming no venting, the dissolved methane concentration can be estimated. The same formulae used to determine dissolved methane of water samples in the laboratory can be slightly modified and used to estimate the dissolved methane of the standing water column in the field. These formulae are described in Standard Methods for the Examination of Water and Wastewater (Franson, ed., 1992). Using the known volume of the standing water column, the volume of the head space over top of the water to the top of the casing, and using field or laboratory determinations of atmospheric methane concentration from the head space, an estimate of the dissolved methane is possible.

This method works with a reasonable degree of certainty. As shown in Table 11, field estimates compared well to laboratory samples at a site in Washington County, Pennsylvania. These results are not admissible in court in the event of litigation, but they can be used as a first cut to determine the potential hazard from dissolved methane in the ground water. An example of how this estimate is made is given in Appendix B.

Table 11. Laboratory analysis versus field estimate methane concentrations.

Sample	Laboratory Concentration (mg/L)	Field Estimate (mg/L)	Difference (mg/L)
1	0.0071	0.0042	(0.0029)
2	0.0048	0.0066	0.0018
3	2.7 and 1.23	0.68	(2.02) and (0.55)
4	0.016	0.0156	(0.0004)
5	0.071	0.045	(0.026)

It should be noted that this estimate is not valid under fracture flow conditions. For example, in one instance 33% methane was recorded in a well bore. This sample was back- calculated to 185 mg/L of dissolved methane in the water, which, given the water level in the well, was not physically possible. Therefore, gaseous methane had to be entering the well, thus interfering with the results. The landowner stated that substantial "boiling" or bubbling was audible at the time the gas sample was taken.

Additional work is required to refine and make this method of estimation a more viable tool. However, this method can be employed when other data are not available.

The relationship between the methane dissolved in the well water and methane in the well head space will hold as long as the well is reasonably well-sealed and sufficient time is allowed for the establishment of an equilibrium between the gaseous and liquid phases. This estimate does not consider gaseous methane produced as a result of fracture flow.

3.5.4 Fracture Flow Methane: Methane above the water table is most likely flowing through fractures and bedding plane separations into the well bore below the casing. The location, concentration, and pressure of methane entering the well can be determined with the use of an inflatable packer, sample tube, sensitive pressure gauge, vacuum pump, and methanometer.

The testing process involves lowering the packer down the well at appropriate intervals, inflating the packer, closing the sample line, and testing the pressure with an appropriate range gauge (head pressures are commonly in the range of 1-10 inches of water), then purging the line with the vacuum pump for the time required to clear the line finally and measuring the level of methane. The methanometer and pressure gauge should be observed for 1-2 minutes or until conditions stabilize. Testing should proceed from the bottom of casing to the top of the water column. At least one test should be taken in the casing to determine the quality of the casing seal.

Occasionally, testing should extend into the water column. This will identify methane bubbling through the water column. No significant gas pressure should be measured in the

water column unless fracture flow is encountered. Care should be observed not to pump water into the methanometer when below the water table.

If available, borehole camera work should be used to augment this test to accurately locate the depth and condition of casing, fractures, and the water level.

3.6 Sampling Methodology - In-House Sampling: When sampling from a faucet, the water should be sampled as close to the well as possible. Ideally, samples should be taken from a faucet prior to the holding (pressure) tank, in-line filter or treatment system. Always sample a cold water line. If the holding tank is an older type with an air-water interface, this can also cause an interference with the sampling. The newer bladder type holding tanks are less problematic. If taken from a sink spigot, the aerator should be removed before attaching any tubing or taking the sample.

The sample is obtained in glass vials as described in the previous section. A method for calculating the concentration of dissolved methane in the well water, is performed using equation (1). The background methodology for deriving this equation and an example of it's use are illustrated in Appendix A of this section.

$$C_{well} = P_{barom} \%CH_4 \left[\frac{160V_s}{RT_s} \% \frac{8.9 \times 10^3}{K_{CH_4}} \right] \quad (1)$$

Where:

- C_{well} = Concentration of methane dissolved in the well water (mg/liter)
- $\%CH_4$ = Measured concentration of methane in the head space of the sample (percent)
- V_s = Measured volume of the head space of the sample (liters)
- P_{barom} = Measured barometric pressure (atmospheres)
- T_s = Measured temperature of the sample. (degrees Kelvin)
- R = Gas constant (0.0821)
- K_{CH_4} = Equilibrium constant for methane at temperature at the well site (Table 12).

Table 12. Derived from solubility data given in
 “Handbook of Chemistry and Physics 72nd Edition” page 6-5

T(°C)	K_{CH_4}
15	3.203×10^4
20	3.564×10^4
25	3.918×10^4
30	4.263×10^4

4.0 TESTING FOR METHANE IN SOILS

Shallow probing and soil gas sampling are useful to identify and delineate the areal extent of methane in soils. Soil gas surveys can also be valuable in helping to locate sources. The environmental remediation industry has developed various techniques for investigating non-methane-VOC pollutants in the soil. In general, soil gas surveys to determine the extent of methane in the shallow overburden and to locate the source area should be conducted in accordance with ASTM 5314 (Standard Guide for Soil Gas Monitoring in the Vadose Zone).

As with water and atmospheric testing, it is important to consider the impact of barometric pressure changes before and during soil gas sampling. If a low-pressure front is moving through the area, this can draw higher amounts of gas from the soil and underlying strata, whereas a high-pressure area can cause the infusion of ambient air into the subsurface. Precipitation preceding soil gas sampling can create a wetting front moving downward through the soil, pushing soil gases ahead of it and thus influencing the pore gas volume.

4.1 Portable Equipment: The portable meters for evaluating atmospheric methane in this section are the same as outlined in Testing for Atmospheric Methane, Section IV, 2.0. However, soil sampling requires some additional equipment to create a void in the soil. This equipment is available as gas/vapor probes. Tile, rebar, or steel probes can also be used to open small holes in the ground. Probes are usually $\frac{3}{8}$ to 1 inch in diameter. Hammer drivers and power hammer drills can extend the depth to the weathered bedrock. Specialty soil gas probes with hollow stems, sample ports, and valves are available for specific depths and can be sampled through the hollow stems with pumps.

4.2 Laboratory Equipment: Testing equipment for methane in soils involves the same laboratory equipment as that described in Section IV, 2.3.

4.3 Sampling in Soils: To begin soil sampling, a solid or hollow perforated steel tube is driven into the ground. The depth of insertion generally ranges from 2 to 5 feet. The resistance of the

ground to driving the probe is important to help determine when bedrock is encountered. Methane will pool and migrate in the horizontal fractures and permeable bedding of soils that often occur at the weathered rock and soil interface. Special probes with extensions can be used to extend to depths of 10 feet or more depending on soil conditions. Most probing is designed to extend to the depth of buried pipelines.

4.3.1 Meter Testing: Once the hole is driven, gases are then withdrawn from the hole or a hollow probe with a vacuum pump or aspirator into a portable gas meter. The length of the sample lines will determine how much gas needs to be aspirated or how long the lines must be pumped in order to obtain a representative sample. Gas should be drawn from the hole until all of the sample line is purged and a peak reading on a gas meter is observed. Time of evacuation can take up to 2 minutes in porous soils with long sample tubes. Sustained and peak reading should be recorded. Care must be taken not to draw normal atmosphere from the surface down into the hole. Blocking the top of the hole with dirt or other inert material will minimize the potential for sample dilution. The investigator should not evacuate for such a protracted period that the natural flow system of the gas is disturbed. Over-evacuation may draw atmospheric gases into the soil.

4.3.2 Grab Samples: Once the evacuation is complete, a gas sample is extracted from the steel tube using a gas-tight syringe, vacutainer, or pump and sample bag. The samples can be analyzed in the field with gas chromatography (Chafin et al., 1996) or sent to the laboratory. If a sample is taken, care should be taken to secure the syringes from being compromised prior to laboratory analysis.

4.3.3 Sample Location: Deciding when and where to probe soils for methane is at the discretion of the investigator. Probing along linear features, such as buried pipelines, cracks, and adjacent to pavement is a good starting point. Features that divert or cause alternative pathways for the lateral flow of gas, such as a foundation footer or backfill material for a utility line, are possible locations with elevated methane concentrations. Distressed or lack of vegetation may also be evidence at the surface of an area of methane migration. Methane displaces oxygen in the root zone which can kill plants.

If during the course of the investigation a possible methane source is discovered, soil gas sampling should focus on the source. However, attention to a possible source should not preclude sampling elsewhere. Sampling in other areas performs several functions:

- T may indicate multiple sources.
- T provides background data about the ambient methane content in the soil.
- T indicates the source(s) and the direction of migration.

Sample spacing and configuration are important. Initial sampling should extend radially away from an identified point source. Linear features such as a utility or foundation should have samples spaced parallel to that feature. Probing should be performed to extend underground features such as cracks in pavement or the ground. A minimum of three

nonaligned samples should be taken to develop a three-dimensional view of the gas concentration of the area. An isopleth map can be developed if enough readings are obtained.

The sampling points should be separated by enough distance that they are not influencing each other. The spacing will depend to some extent on the soil types and length of time required for tube evacuation.

5.0 SAMPLE HANDLING, PRESERVATION, AND CHAIN-OF-CUSTODY

Proper handling, preservation, and documentation of samples are as important as proper sampling technique. These protocols are important to produce valid and consistent results and for investigations that may culminate in litigation. Data can be excluded from testimony if the documentation is lacking or incorrect.

The people responsible for taking, handling, and delivering the sample to the laboratory, as well as the identity of the chemist or technician who analyze the sample should be recorded. The specific details on how, under what conditions, the date, the time, and where the sample was taken also need to be recorded. The general location (e.g., John Doe's residence) and the exact location (e.g., 6 inches above the floor of the basement along the northwest wall) need to be specified. Weather conditions (e.g., temperature, recent precipitation, barometric pressure, rising or falling barometric trends, wind speed) should be observed and recorded. If the sample was fixed or required special handling, this information should be documented. If anything occurred prior to sampling that could impact the results (e.g., the well was dewatered or the windows and doors of the structure were left open shortly prior to sampling), this should be detailed. In short, everything that may have an impact on the sample should be noted.

Section IV - Appendix A
Determining the Concentration of Methane in Well Water
When There Is No Direct Access to the Well

To determine the concentration of methane dissolved in well water when there is no direct access to the well, a water sample must be collected at a water tap, such as a faucet. Consider that the water sample is collected in an empty bottle. The bottle is immediately sealed. In the bottle, let the volume of the headspace be V_s . Shortly, the methane will begin to degas from the water into the headspace. This process will continue until the partial pressure of the gaseous methane in the headspace is in equilibrium with the remaining concentration of methane dissolved in the water. The methane that was in the water at the time the sample was collected is now distributed between the water and the headspace. Thus, the concentration of methane in the well water is the sum of the methane contained in the sample headspace and the remaining methane dissolved in the water of the sample.

To determine the concentration of methane, C_b (mg/L), dissolved in the well water the following measurements are required:

1. concentration, i.e., mole fraction of methane, in the sample headspace, $X_{CH_4(g)}$
2. volume of the sample headspace, V_s (liters)
3. temperature of the sample, T (can be assumed to be room temperature, K).
4. atmospheric pressure, P_{atmos} (atmospheres)

Then from the conservation of mass:

$$\Delta C = C_b - C_a \quad (1a)$$

Where:

- C_b = Concentration of methane dissolved in the water sample before any degassing (mg CH_4 /liter H_2O)
- C_a = Concentration of methane dissolved in the water of the sample after equilibrium is reached (mg CH_4 /liter H_2O)
- Delta C = Change in concentration of the methane dissolved in the water sample (mg).

Re-writing Equation (1a):

$$C_b = \Delta C + C_a \quad (1b)$$

From the ideal gas law:

$$P_{CH_4} = \frac{n_{CH_4} RT}{V_s} \quad (2)$$

Where : P_{CH_4} = Partial pressure of methane gas in the sample headspace (atmospheres)
 V_s = Volume of sample headspace (liter)
 T = Temperature of gas in sample headspace (°K)
 R = Gas constant = .0821 (atmospheres liters/mole °K)
 n_{CH_4} = Moles of methane degassed from the water of the sample into the headspace of the sample

Since the molecular weight of methane is 16,000 milligrams, the moles of methane, n_{CH_4} , can be expressed as:

$$n_{CH_4} = \frac{\Delta C}{16000} \quad (3)$$

Using equation(3) in (2):

$$P_{CH_4} = \frac{\Delta C RT}{16000 V_s} \quad (4)$$

or solving equation(4) for *Delta C*

$$\Delta C = 16000 \frac{V_s P_{CH_4}}{RT} \quad (5)$$

Since in the sample bottle the partial pressure of methane in the vapor phase is in equilibrium with the methane dissolved in the water, Henry's Law can be used. From Henry's Law:

$$K_{CH_4} = \frac{P_{CH_4}}{X_{CH_4}(w)} \quad (6)$$

Where:

$X_{CH_4}(w)$ = Mole fraction of methane remaining in the water of the sample at equilibrium

K_{CH_4} = Equilibrium constant for methane (atmospheres/mole fraction). Note that K_{CH_4} is a function of temperature (Table 12)

Solving (6) for $X_{CH_4}(w)$, we get:

$$X_{CH_4}(w) = \frac{P_{CH_4}}{K_{CH_4}} \quad (7)$$

But from the definition of mole fraction, $X_{CH_4}(w)$ can be written as:

$$X_{CH_4}(w) = \frac{n_{CH_4}(w)}{n_{H_2O}} \quad (8)$$

Where:

$n_{CH_4}(w)$ = Moles of methane dissolved in the water of the sample at equilibrium
 $n_{H_2O}(w)$ = Moles of water in the sample

Now the molecular weight of water is 18g, while the molecular weight of methane is 16g, so that:

$$n_{H_2O} = \frac{m_{H_2O}}{18} = \frac{\rho_{H_2O} V_{H_2O}}{18} = \frac{1000 V_{H_2O}}{18} \quad (9)$$

and:

$$n_{CH_4}(w) = \frac{m_{CH_4}(w)}{16000} \quad (10)$$

Where:

ρ_{H_2O} = Density of water ~1000 (gm/liter)
 V_{H_2O} = Volume of water in the sample (liters)
 m_{H_2O} = Mass of water in the sample (gm)
 $m_{CH_4}(w)$ = Mass of methane dissolved in the water of the sample at equilibrium (mg)

Using equations (9) and (10) in (8), we get:

$$X_{CH_4}(w) = \frac{m_{CH_4}(w)}{16000} \cdot \frac{18}{1000V_{H_2O}} \quad (11)$$

Using equations (7) and (11) and solving for $m_{CH_4}(w)$:

$$m_{CH_4}(w) = \frac{16000 \times 1000 V_{H_2O} P_{CH_4}}{18 K_{CH_4}} = 8.9 \times 10^5 \frac{V_{H_2O} P_{CH_4}}{K_{CH_4}} \quad (12)$$

The quantity $m_{CH_4}(w)$ is the mass of methane dissolved in the sample water after equilibrium has been established. In terms of concentration, we may write:

$$C_a = \frac{m_{CH_4}(w)}{V_{H_2O}} = 8.9 \times 10^5 \frac{P_{CH_4}}{K_{CH_4}} \quad (13)$$

Using Equations (5) and (13) in Equation (1b), we get:

$$C_b(mg/L) = P_{CH_4} \left[\frac{16000 V_s}{RT} \% \frac{8.9 \times 10^5}{K_{CH_4}} \right] \quad (14)$$

The partial pressure of methane in the sample headspace, p_{CH_4} , is directly related to the mole fraction of methane in the headspace, $X_{CH_4}(g)$

or:

$$p_{CH_4} = P_{atmos} X_{CH_4}(g) \quad (15)$$

Where:

P_{atmos} = Atmospheric pressure (atmospheres)

$X_{CH_4}(g)$ = Mole fraction of gaseous methane in the sample headspace

Using equation (15) in equation(14), we get the concentration of methane in the well water:

$$C_b(mg/L) = P_{atmos} X_{CH_4}(g) \left[\frac{16000 V_s}{RT} \% \frac{8.9 \times 10^5}{K_{CH_4}} \right] \quad (16)$$

Example:

A water sample is collected from a faucet into a 50cc bottle and immediately sealed. At the time the sample was taken, the atmospheric pressure was 29.80 inches of Hg. The headspace volume is

20cc. A gas sample is taken from the headspace of the water sample; at that time the sample is at room temp (20°C). The subsequent analysis shows 36% CH₄.

Thus:

$$\begin{aligned}V_s &= 20 \text{ cc} = 0.02 \text{ liters} \\X_{\text{CH}_4}(\text{g}) &= 36\%/100 = 0.36 \\P_{\text{atmos}} &= 29.80 \text{ inches of Hg} = 0.996 \text{ atmospheres} \\T &= 20^\circ\text{C} = 293^\circ\text{K} \\R &= 0.0821\end{aligned}$$

From the Table:

$$K_{\text{CH}_4} = 3.546 \times 10^4 \text{ (atmospheres/mole fraction)}$$

Using equation (18):

$$C_b(\text{mg/L}) = (0.996)(0.36) \cdot \left[\frac{(16000)(0.04)}{(0.0821)(293)} \% \frac{8.9 \times 10^5}{3.456 \times 10^4} \right] = 18.7 \text{ (mg/L)}$$

Section IV - Appendix B
Field Estimating Dissolved Methane Concentrations in Well Water

The dissolved methane in the well water can be estimated from the methane concentration in the well bore atmosphere. This assumes that no fracture flow methane is entering the well.

Required Information:

- T Total well depth.
- T Depth to water.
- T Well diameter (d) or radius (r).
- T Methane concentration in the well headspace above the water level. This is measured with field instruments or from laboratory analysis.

The investigator needs to determine the volume of water in the well and the volume of the overlying headspace, each of which is the volume of a cylinder. The volume of a cylinder is equal to: $\pi r^2 h$, where h is equal to the height of water column for the volume of water calculation and equal to the distance from the water surface to the ground surface for the headspace calculation. The value of π is given as 3.1416.

Given: The well is 220 feet deep and the water level is 100 feet below the surface, the well is 6 inches in diameter (3 inch radius), and the methane concentration field measured in the headspace is 2 percent.

Determination of the volume of water:

Height of the water column is $220' - 100' = 120'$

Well radius is $3''/12 \text{ in/ft} = 0.25'$

Water volume is $3.1416 \times 0.25^2 \times 120' = 23.56 \text{ ft}^3$

Determination of the headspace volume:

Height of the headspace is $100'$

Well radius is $3''/12 \text{ in/ft} = 0.25'$

Water volume is $3.1416 \times 0.25^2 \times 100' = 19.63 \text{ ft}^3$

Field estimation of the dissolved methane in the well water:

g = volume of water (ft^3)

Q = methane concentration in the water (mg/L)

V = head space volume (ft^3)

Rf = atmospheric methane reading (%)

Simplified equation from Standard Methods for the Examination of Water and Wastewater:

$$Q = Rf \left(6.7 \left(\frac{V}{g} \right) + 0.24 \right)$$

Plug in the values for the example:

$$Q = 2 \left(6.7 \left(\frac{19.63}{23.56} \right) + 0.24 \right)$$

$$Q = 11.6 \text{ mg/L}$$

SECTION V METHANE MITIGATION

1.0 INTRODUCTION

When fugitive methane is identified in or near structures at unsafe levels, prompt action is required to reduce or eliminate the hazard. This section provides procedures and recommendations to reduce and mitigate fugitive methane in areas of concern. Depending on the source of gas, or suspected source of gas, interaction with State or Federal regulatory agencies may be required for concurrence or approval of the mitigation procedure.

This section does not address mitigation of gas leaks from a pipeline or other commercial sources. Gas companies are governed by the Interstate Commerce and Transportation Agency and must fix leaks associated with their lines. Of course, they also have a strong financial incentive to fix leaks in terms of lost revenues because of lost gas or for fear of litigation in the event of an accident.

Methane is often difficult to eliminate at the source, so most remediation efforts focus on hazard mitigation at the point of concern. Usually methane is redirected away from the problem area and vented into the atmosphere. Other alternatives are to seal the migration pathways or retain the gas close to its source. Normally, mitigation is conducted at or near the ground surface. However, high volume or high-pressure leaks, may require elimination at the source (e.g. improperly abandoned gas well).

A methane mitigation plan is based on the source strength, surface and subsurface features, and structure characteristics. Frequently, methane emissions are associated with water wells, oil or gas wells, high permeability soils, mine portals, and shafts. Full mitigation may involve more than one of these features.

Remember that an important part of abatement is monitoring and frequent or continuous assessment. Monitoring of the project for at least four months after abatement is required to ensure success. Continuous monitoring with data logging is the best post-abatement assessment method because methane gas will vary in concentration depending on atmospheric conditions and as the source is depleted or recharged.

Caution: One should not directly apply the mitigation techniques discussed herein to other mine gas problems because of different characteristics of those gases in relation to their toxicity, density, origin, etc.

2.0 SAFETY CONCERNS

Once a hazard is identified, qualified professionals are needed to design a plan, implement the

plan, operate the equipment, and monitor the success. Continuous monitoring is prudent through these stages to ensure safety and observe changes that may warrant modifications to the mitigation technique. Always be mindful of the action levels specified in Section II. Safety of the public and workers must always be the main concern.

2.1 Design: As a mitigation plan is being designed, continuous monitoring at the site may be necessary to identify changing conditions. The plan must state the hazard, outline a clear plan to mitigate the hazard, and require construction by professionals with qualifying experience. A conservative design must be provided at public facilities such as a school.

2.2 Construction: Workers must be knowledgeable about explosive hazards and the site must be routinely checked for methane. In severe cases or in a confined environment, permissible tools and machinery, and ventilation equipment may be required. Guidelines for safely working around methane as they apply to the appropriate work setting are published both by OSHA and MSHA.

2.3 Operation: Operation of methane-mitigation systems must be performed by knowledgeable individuals who understand the hazards and principles of gas migration. Equipment must be maintained to detect the limits designed within a factor of safety. All equipment exposed to the LEL of methane should be permissible and sealed from general access. Any and all facilities venting gas that approach the LEL of methane should be posted as to their flammable condition.

2.4 Monitoring: An organized program is recommended during all phases of construction and after completion of the project. Monitoring points, to assess system performance, should be installed in active and passive vents and in areas where fugitive methane was previously detected. These points should be monitored and readings recorded on a specified frequency. In public buildings, automatic alarm systems should be used to warn the occupants of elevated methane levels.

The post assessment monitoring is essential to the safe and long-term operation of the mitigation system. Additionally, depending on the complexity of the site and mitigation system, post mitigation monitoring may also be necessary to adjust and optimize system performance.

3.0 METHANE AT THE SOURCE

Eliminating or sealing methane at the source of the problem is often difficult, impossible, or impractical to do, even when the specific source and path of migration can be identified. For example, when methane is dissolved in water, sealing the source or migration route would likely prevent water from flowing into the well. In many cases, the source of methane is diffuse and may require large areas to be grouted or sealed to contain it. The occasional source of methane that is concentrated in a small area is most likely to be successfully abated by treatment of the source. These conditions could be a leaky gas well, vertical vent holes from mining, or isolated gas pockets.

3.1 Gas and Oil Wells: Gas and oil wells are the most likely methane sources to be successfully sealed or plugged. However, due to the uncertainty of well construction/integrity some older leaking or improperly abandoned gas and oil wells, proper abandonment can be costly, time consuming and present a challenge. Most often, methane from gas or oil wells is from a deep source and comes to the surface through a breach in the casing or well seals. This may be caused from over pressurized production strings or cracked grout in the annulus. The annulus is the space between the casing and the boring, or casing and the production string that is normally grouted closed.

Proper well plugging and abandonment will prevent gas migration to the surface or to groundwater. Plugging requires special equipment readily available in the petroleum industry. Equipment may be required to perforate casings and inject cement grout under very high pressures. Often the work must be performed when the well is pressured with gas through special surface provisions like blow-out preventers or stuffing boxes. In worse-case scenarios, the casing may need to be removed or drilled out and the hole plugged. The oil and gas drilling industry has the knowledge and resources to mitigate problems with leaking wells. Most states with commercial natural gas production have regulations that specify gas well plugging criteria.

3.2 Landfills: Methane from municipal waste landfills is produced as the result of the decomposition of waste materials. Methane and carbon dioxide are the principal gases produced at near equal ratios. Methane monitoring at the landfill perimeter is typically required by State regulation. This monitoring usually identifies fugitive methane before a hazardous situation develops at or near a building, however, in some instances gas generated from the landfill migrates beyond the landfill footprint. The mechanics of methane migration patterns are complicated because of the variability in the permeability of soils and refuse. Methane migration distances greater than 1,500 feet have been observed (O’Leary, Walsh, 1991). Methane mitigation techniques include passive venting to the surface or active venting that entails drawing the methane away from the landfill through a series of lateral tubes with a fan.

Passive vent systems rely on natural barometric pressure and convection mechanisms to vent landfill gas. Passive vents are often installed and monitored in an iterative method to gauge their success in controlling gas migration. Often, passive systems are sufficient to control gas migration. Shallow gas venting trenches within the landfill may also be effective to vent the gas. These systems are typically constructed with flares to burn off the gas in order to prevent odors.

Passive vent systems are not always adequate to mitigate offsite migration. This may be due to insufficient pressure on the gas within the landfill to move it to the passive system (O’Leary and Walsh, 1991). The effects of fluctuating barometric conditions can also impact the effectiveness of passive systems. Active gas recovery systems remove gas under a vacuum from a landfill or landfill perimeter. Active systems require gas recovery wells and vacuum pumps. Recovery wells should be installed in areas of high permeability since gas will more readily migrate to these areas and recovery is more efficient. Recovery wells are typically two to three feet in diameter. Larger diameter wells provide more surface area and therefore, require less vacuum. Wells should be individually valved so that the vacuum to each well can be regulated. This provides flexibility for

changing conditions. If gas migration continues after a well is in operation, additional vacuum can be applied. In areas where wells produce low concentrations of methane, the vacuum can be reduced.

3.3 Mine Shafts and Portals: Mine shafts and portals provide a migration path for coal bed methane to reach the surface. Shafts and portals provide access and fresh air ventilation for underground coal mines during operation. These surface facilities are regulated by MSHA during mining and when a mine is shut down. During active mining, methane from the coal is vented to the atmosphere through the mine ventilation network.

In an inactive mine, the methane migration may be prevented by backfilling the mine openings and grouting of the fractures that may act as conduits for the methane. However, it is difficult and extremely expensive to effectively seal all fractures. Ventilating the mine and keeping the source under negative pressure will better mitigate the problem; however, this requires long-term and high-energy maintenance costs.

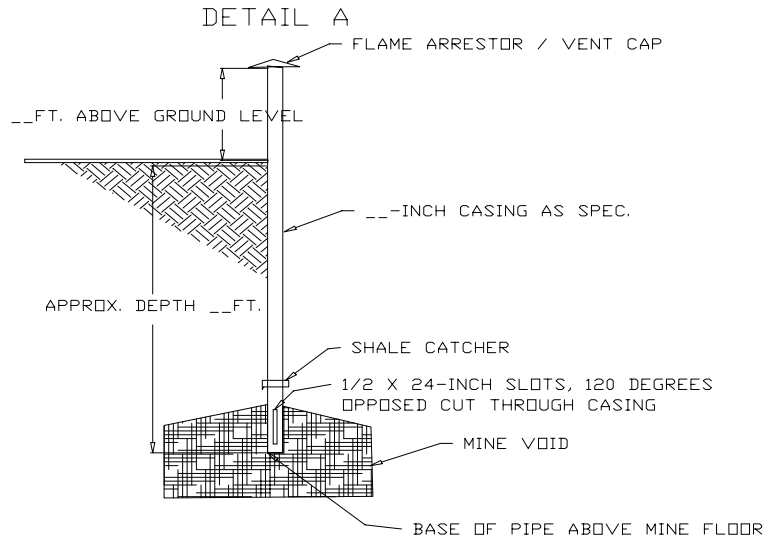
Mitigation of methane from abandoned portals and shafts depends on the concentration of gas, overburden characteristics, and surrounding land use. Similar to other mitigation techniques, the control of hazardous levels of methane from shafts and portals involves ventilation, sealing, or a combination of both.

The following sections provide general guidelines for mitigating methane from coal mines.

3.3.1 Vents: Vents for portals and shafts are designed to safely conduct methane away from the source to the atmosphere, where it is less likely to impact normal human activity. In general, the mitigation of a shaft is similar to a portal or drift entry. The horizontal axis of portals and drifts must account for the upward flow of methane gas.

The vent should be constructed of durable materials such as schedule-40 steel pipe. The diameter and routing of the pipe must minimize any restrictions to the flow of gas. Ideally, the pipe should extend straight up for a minimum of 10 feet above the ground. If structures or other features are nearby that may hamper the dispersion of gas, the vent should be extended higher. Rain caps or an inverted J-bend are useful to keep the weather, animals and debris from interfering with the top of the vent. Figure 14 shows a specification drawing of a typical vent.

Vent designs differ for a portal or shaft depending on the condition of the entry and mine level. In general, four possible conditions exist: a) open shaft, b) improperly backfilled shaft, c) collapsed shaft or d) abandoned portal.



TYPICAL VENT INSTALLATION
 Figure 14 Sketch design of basic vent (OSM-FRPD)

a) Open Shaft: The intent of a shaft vent is to collect the methane gas trapped below the seal and conduct it safely to the surface before it permeates into the shallow bedrock or permeable soils. An open shaft that is venting methane should be sealed at the surface and a vent stack should be lowered into the shaft with openings in the pipe below the seal. The openings in the subsurface vent pipe should be above the mine level and directly below the area of the seal. Ideally, this zone is backfilled with permeable stone to allow the gas to migrate through the fill and into the vent pipe.

The vent stack above and through the impermeable seal should not be perforated. The perforations in the subsurface vent stack should begin directly at the base of the cap seal to prevent gas from being trapped under the cap. The cap must be designed air-tight to prevent gas from migrating around the cap and short-circuiting the vent. The cap must be structurally sound and extend into competent rock to form a stable seal.

b) Improperly Backfilled Shaft: A shaft that has been improperly abandoned and filled with debris, construction materials, or unknown materials should be explored to determine if an adequate seal can be constructed. Often the materials placed in an abandoned shaft include large fragments of the shaft support and related structures such as timbers and steel beams and concrete. Also, shafts create disposal sites for discarded appliances and automobiles. These materials create voids in the backfill that may trap gas and are difficult to remove from the shaft.

The problem with unclassified material backfilling of a shaft is that dangerous pockets of gas can exist within the fill. Excavation of some if not all of the debris from the shaft will

provide long-term abatement. Removal is usually performed by a clamshell. Sometimes other equipment is needed to breakup the material prior to removal, like an iron ball.

If the objectionable material cannot be removed then drilling vent holes into the mine from an adjacent area often is the most practical mitigation plan. This requires a good mine map. The vent holes are drilled to the mine level to relieve any positive gas pressure. Casing is extended to the mine level and to 10 feet above the ground.

If the surface is stable, drilling vent holes that intersect the shaft is also an alternative mitigation plan. These holes can be angled into the shaft and debris to vent pockets of methane to the surface. Often times, it takes numerous holes to explore, vent, and seal sections of the shaft. Usually, an impermeable cap is required to reduce the impact of gases not intercepted. Any holes that do not encounter methane can be used for sealing with grout.

c) Collapsed Shaft: Collapsed shafts are similar to improperly backfilled shafts but have the added hazard of unstable ground conditions. Depending on the degree of collapse, most of the work to vent and seal the shaft must be performed by angle drilling adjacent to the shaft.

If the shaft is partially collapsed and methane is being produced in the shaft, permeable backfill should be placed into the open interval up to the level of competent bed rock. The remainder of the hole should be backfilled with impermeable material such as clay or concrete to the surface. A vent stack open and perforated in the permeable zone and non-perforated in the seal zone can be placed consecutively with the fill or drilled into the stabilized backfilled shaft.

Innovative construction techniques are required to work safely around unstable shafts venting methane. Often times, the abatement is best implemented in a phased approach to stabilize, seal, and vent the collapsed shaft.

d) Abandoned Portal: The same basic procedures for mitigation of methane venting from shafts are required for portals (either slope or drift entries). Most often the vent for a portal will be drilled from the surface directly above an open, stable entry that is directly inside the portal seal (Figure 15). The vent is open and perforated in the mine interval and nonperforated and sealed through the overburden. The portal is then backfilled or sealed to redirect



Figure 15 Installation of vent at gassy abandoned portal, entry backfilled with concrete.

the gas through the vent. The design of the backfill must prevent the vent from being blocked by the fill.

If the area over the portal is inaccessible and the entry is mostly open, a vent can be installed along the roof of the entry and directed out the opening and up into the atmosphere (Figure 16). The vent then forms an 'L' shape with the apex of the legs supported by a foundation. The external part of the vent extends vertically as in a typical vent surface facility and the subsurface part of the vent extends horizontally or slightly down-grade into a stable section of the entry. The surface is then sealed with impermeable material such as clay or concrete. If the mine is wet then a wet seal, as described below, must also be installed.

Flame arresters are used extensively in the gas and petroleum industry but are also useful in controlling ignition of methane mitigated by venting. Flame arresters are relatively simple devices that prevent the migration of flame into a vent. Methane within the explosive range can propagate quickly and explode even with low oxygen levels. A flame arrester will allow the gas to burn, but will prevent the flame from propagating below a set of screens or holes set at specific dimensions. This device quickly reduces the burning temperature and stops the migration of flames.

The use of flame arresters on vents is necessary where the vent may be exposed to combustion. In residential areas, children playing with fireworks have ignited methane vents, but the most common source of ignition are lightning strikes. Flame arresters are not recommended on plastic vent pipe since the operating temperature of the arrester may melt

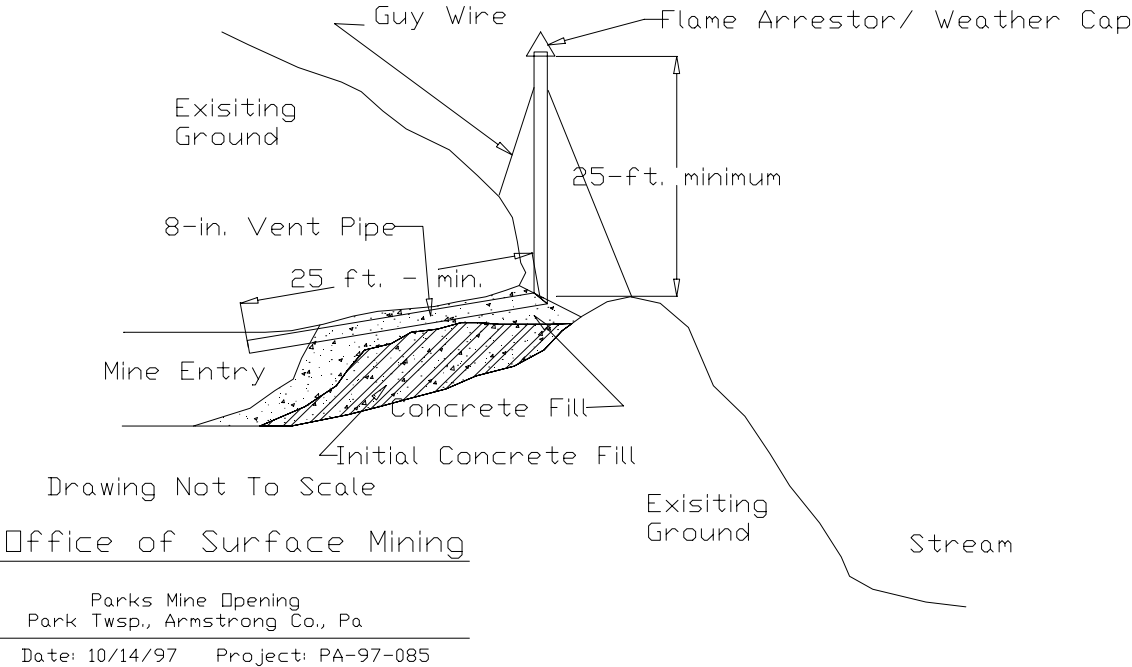


Figure 16 Sketch of vent and seal in abandoned drift entry.

the pipe.

Vents should be as maintenance-free as possible. The life-expectancy of a vent should be at least 25 years. A sample port installed in the vent pipe at waist level is useful for collecting samples during the post mitigation assessment. Valves or tap holes for sampling must be routinely lubricated to prevent them from rusting shut. The vent stack should be painted or made of materials that will not corrode.

The cap and flame arrester should be inspected annually to ensure they are not blocked by corrosion, bird nests, or other debris. If sampling shows a significant reduction in gas levels the subsurface part of the vent should be inspected to ensure that the hole has not collapsed or otherwise been blocked. If the vent is working well and the problem with methane is mitigated, the purpose of the vent may soon be forgotten. Maintenance of the vent must be described to the property owner. The vent should not be used for other purposes such as a yard light or sign and other sources of combustion must be kept away from it.

3.3.2 Seals: Mine seals are a necessary part of a mitigation plan for methane exhausting from shafts and portals. Mine seals are usually used in combination with vents or in cases where the methane is low in concentration and can be adequately trapped near its source. Seals for mine closure have been perfected over the years by various agencies, including many state mine reclamation agencies, MSHA, and USBM. In general, these techniques incorporate methods to provide a stable surface but do not always provide techniques to seal gases.

Seals must be founded into stable rock and be durable enough to prevent vandalism or reopening of the mine. At abandoned mines, the degree of collapse of a mine opening often dictates the type of seal used to close the mine. The availability of local materials and access to the opening control the type of materials to be used.

a) Dry Seals: A dry seal is used where no water drainage is anticipated from the entry (Figure 17). Construction material must be appropriate for the intended purpose, collecting or sealing for gas or water. In general, permeable backfill is inserted into the mine first and then finished with impermeable backfill. Permeable backfill is composed of coarse stone or riprap. Large pore spaces are



Figure 17. A concrete block dry seal placed at an abandoned mine land reclamation project in West Virginia. (West Virginia Division of Environmental Protection).

required to provide high permeability for gases. If possible, open voids for collecting methane should be incorporated in the design.

Impermeable backfill is clay, bentonite, coal ash, cinder block, cement, or concrete. Materials with low permeability to water generally provide good barriers to methane. The permeability of “soft” backfill can be decreased by compaction in layers. Clay soil backfill must be enveloped in less cohesive materials to provide drainage and stability. Clay materials must be protected from erosion and slip failure. In areas where clay is not available, bentonite can be mixed with local soils, cement, or other materials to create a low permeability barrier. Concrete and other cement materials such as shotcrete provide a durable impermeable material. These type of materials are often emplaced by pumping if access is limited.

b) Wet Seals: Wet seals are required in portals and drifts that are draining water (Figure 18). Wet seals are designed to safely conduct the water through the seal but still restrict access into the mine opening. The design problem is compounded by methane, which needs to be safely vented out of the mine or sealed into the mine. If vented, the methane should exit separate from the water, where it cannot be ignited by human activity.



Wet seals should have pipes with traps installed to prevent gas from migrating through the system. Traps can be designed similarly to systems used in plumbing like P- traps or in catch basins. Vents can be incorporated with the drains or as isolated systems. Routine maintenance and inspection are required to ensure the traps are functioning or that the system is still draining water.

Figure 18. A hydraulic wet seal was constructed with a gravel bulkhead for water and subsidence control (Douglas Abandoned Mine Land Reclamation Project).

Systems must be designed recognizing the potential of iron and other sediment to routinely block these systems. The pipes should be constructed of non-corrosive materials such as plastic and must be of diameter to provide protection from growth of scale or precipitate.

Monitoring of seals should be performed routinely to determine if the material is stable, not saturated, and not vandalized. Occasionally, redressing the surface of earthen seals is required. The contacts of the seal with the surrounding rock or earth should be inspected with a methanometer to ensure that they are not leaking. Cracks and ground failures around the seal should be inspected routinely and during various climatic conditions. Water levels associated with wet seals must be routinely monitored to determine whether

seals are functioning or the water has dried up.

4.0 METHANE IN WATER WELLS

Mitigating methane in water wells depends on the location of the well, the volume and pressure of the emanating gas, the depth that gas enters the well, and resources available to fix the problem. For example, a low concentration of gas in an abandoned well will require minimal mitigation, such as venting to the surface or grouting. In contrast, a high concentration of methane venting under pressure from a well next to an occupied residence may require active venting or abandonment and abatement similar to plugging (sealing) a commercial gas well. The time period required for mitigation may be short-term, if the source of gas is limited and recently discharged, or may continue for an unlimited time until conditions change or the source is exhausted.

Knowledge of the construction and use of the well is required and must be investigated as described earlier in Section III. The general strategy is to remove the gas from any ignition source such as sparks or open flames. Mitigation of methane found in water wells is commonly performed by either venting, water aeration systems and in some cases, plugging of the well. Plugging of a well requires abandoning that source of water, unless a specific horizon of methane can be identified and isolated by grouting. Venting of a well or well enclosure is the preferred mitigation, unless another source of water is economically feasible.

4.1 Venting Water Wells: Venting of a water well is a simple technique to allow methane and other gases, such as carbon dioxide, to freely and safely exhaust into the atmosphere. The technique requires that the well bore have an open avenue to the surface, away from any potential source of ignition. Methane is lighter than air, so it will flow upward and out of a vented well.

4.1.1 Well location: The location of the well, gas pressure, and the volume and concentration of methane yielded are important to consider when designing a vent. A well with methane concentrations below the lower explosive level, located away from any structures, such as a residence or out-building, may require only a nominal opening in the well cap and a short vent. Methane gas exhausting from a well with concentrations near or above the lower explosive limit must be vented into the atmosphere away from easy access by the public or source of ignition. This is performed by extending the pipe vent vertically a minimum of 10 feet above the surface. Greater pressure or increase in volume of gas requires a larger diameter vent to minimize back-pressure on the well system. This removes the combustible gas from potential ignition sources and away from obstacles that may affect efficient release into the atmosphere. Methane in a well next to or within 10 feet of a structure requires venting the gas away from the structure at least 10 feet above the top of the nearest structure. The potential for downdrafts and the trapping of gas under eaves of a structure must be considered in the design of vertical vents.

If the well is in a well house, pump house, vault, or a structure, such as a business or residence, additional precautions must be taken during venting. If possible, the area of the

structure with the well should be isolated and sealed from areas normally occupied. Elsewhere, areas must be adequately vented to minimize methane collection or pooling of methane. Well houses are a particular hazard and should be treated as a confined space according to OSHA standards. Explosions have occurred in well houses without adequate venting.

4.1.2 Vent Type: Vent pipes can be constructed of durable materials depending on the designed life of the mitigation (Figure 19). Pipe should be smooth-walled on the inside to minimize restriction of flow. Wall diameter or schedule thickness should be such that the pipe is rigid. Plastic pipe may melt if the vented methane burns. Steel pipe may require painting or other weather proofing, but is generally durable, if appropriate gage is used.

At a minimum, venting is performed by connecting a small diameter pipe (~1") to a hole in the well cap or near the top of the casing. The pipe extends above the ground surface and usually ends in an inverted "J." This prevents the accidental introduction of foreign materials. If the methane problem is significant, it is recommended to run the pipe away from structures and away from normal public access. A larger diameter pipe with fewer bends is less restrictive and provides a more efficient vent. Ideally, for wells yielding large amounts of methane, the vent should be the same diameter as the well casing and extend up vertically, safely away from the surface. Pipe vents less than 1" diameter should only be used in short vent heights with low gas flow rates. All connections to the well and well casing, including the well caps, pitless adapter, and other access points should be sealed to ensure methane exhausts as planned from the vent. A screen material is usually placed in the opening to prevent insects and other small animals from entering.



Figure 19. Water well vent.

4.1.3 Vent Seating: The integrity of the casing's seal with the surrounding ground is important to the efficiency of the vent. The casing must not be breached and should be tightly sealed into bedrock to prevent gas from leaking into the annular space around the casing and flowing uncontrolled to the surface. Methane may also leak into fractured bedrock or permeable soil materials, if any significant pressure is not controlled by the casing. Vents

installed in poorly grouted or dilapidated casing or in open boreholes may require the installation of new casing and may need to be re-grouted prior to installing the vent. Soil gas surveys will help identify if gas is permeating through the soil. A vent pipe installed inside or outside of the original well casing may be required to seal gases leaking into the soil or fractured bedrock. Any caps, unions or other connections must be vapor-tight to prevent gas from leaking from any place except from the vent exhaust.

4.1.4 Disadvantages of Venting: Vents in water wells do not remove methane dissolved in water or eliminate the source of methane. Well water may still require treatment to remove high concentrations of methane in water that may exsolve in an enclosed atmosphere. Methane-stripping systems can be expensive and require considerable space. Another disadvantage is that vents are aesthetically unsightly and do require periodic maintenance.

4.2 Sealing Water Wells: In some cases where the methane inflow into a domestic well or other boring is severe, the optimum abatement is to abandon and plug it. It is necessary to determine the source and flow path to abate methane in a well so as not to simply redirect the gas to the surface. The grout should be tremmied into the well bore to minimize the separation and to prevent bridging. A grout of neat cement or mixture of cement and bentonite is recommended. The grout should be emplaced under pressure to ensure the sealing of all avenues of methane migration. In some cases, it may be possible to use a single or straddle packer to effectively seal a specifically determined zone or rock unit, rather than grouting the entire well shut.

In cases where the methane is leaking out of the annular space between the well bore and the casing, the casing will need to be removed or it will need to be perforated to allow for complete grouting of the well. Casing removal is preferable, but may not always be achievable, especially in older wells and wells where the casing was originally grouted in place. If the casing is to be perforated, the investigator must be sure the entire annular space can be accessed and sealed by grout.

After the well is abandoned and plugged, the piping, wiring and any permeable backfill around them to the home should be removed. Once these lines are removed, the ditch should be filled with a low-permeability material, like a packed clay. This procedure removes any avenue by which methane could potentially enter the dwelling or other structure.

If the well requires grouting and abandonment, some analysis regarding a new well location, construction, and depth must be evaluated prior to abandoning the old well. Drilling a new well may not be an option because of location restrictions, potability or the possibility of drilling into the same methane producing horizons. Drilling a new water well or provisions for an alternative water source is advisable prior to abandoning the old well.

4.3 Water Treatment or Aeration Systems: Where high concentrations of dissolved methane are encountered and the well is the most viable or only economical source of water, treatment of the water is an option. Methane is easily removed from water by aeration, which can also improve other water quality parameters.

Commercial aeration units are readily available; however, site-specific systems can also be inexpensively made from off-the-shelf components. The aeration system should be designed for the specific well and its use. The worst-case scenario in terms of the amount of water use and methane concentration should be considered during the design phase.

To lower dissolved methane concentrations by aeration, the water needs exposure to the atmosphere and time. In an aeration system, the water is usually sprayed into a large holding tank. Spraying exposes the water to the atmosphere and facilitates degassing. The configuration of the spray heads will to a large extent be determined by the dissolved methane concentrations (Figure 20).



Figure 20. Aeration system and holding tank.

The size of the tank is determined by the minimum length of time the water will need to sufficiently degas. The bigger the tank, the longer the detention time for the methane to exsolve. The tank must be vented similarly to a well to reduce methane concentrations. In most cases, a positive ventilation system (i.e., fan may be required) to remove the exsolved methane.

Large sand filtering systems or conventional cisterns can also be used for stripping methane from the water. However, depending on the amount of water in need of treatment, significant space may also be needed for the facility. Water should also be treated to prevent contamination from bacteria and other micro- and macro-organisms.

4.3.1 Disadvantages of Aeration: Disadvantages of aeration systems include:

- T Electrical power is needed to augment the spraying system and run the positive ventilation system.
- T An additional pump is required to provide water pressure to the home.
- T More maintenance is required than for a system that simply pumps the water from the well into the home.
- T Systems are bulky and heavy.
- T Systems must be protected from freezing.

5.0 METHANE IN SOIL

Methane migrating through the soil and into the atmosphere is not uncommon and occurs naturally when a source of methane is near the surface. In rural areas, away from residences the risk is

small. In general, the gas quickly dissipates at the surface. Gas companies must routinely check gasline corridors for methane and monitor any natural occurrences of gas. The U.S. Department of Transportation and Commerce requires that gas lines must be checked at least every three years.

Mitigation is most often required when methane in soils affects a structure or occurs in a densely populated area. Anyone abating methane in soils should first evaluate if the source can be controlled. This may involve repair of a gaslines, plugging a gas wells, or venting or sealing underground mines as described in the sections above. After the source is controlled, purging the remnant methane in the soil will quickly eliminate this hazard. Occasionally, a large volume of gas can be stored in the soil and may require extensive purging and trenching to exhaust the supply of stored methane.

If the source of the methane cannot be controlled and long-term mitigation of the soil is required, various techniques can be employed to reduce the hazard. As with other mitigation techniques, methane in soils can be vented or sealed.

5.1 Venting: Venting is the preferred option in populated areas, since sealing may force the gas to other properties and expand the hazard. Sealing should be used in unpopulated areas to contain a concentrated source. As with other mitigation problems, abatement is often best achieved by a combination of sealing and venting (Figure 21).

Venting large areas of methane in soils is often not practical. Smaller areas can be controlled by installing collection fields above the vadose zone to direct the gas through surface vents into the atmosphere. The collection fields can be as simple as a gravel subbase under pavement or an extensive drain field with gravel envelopes and perforated pipe. The drain field system is tied to a manifold and vented to the surface.



Figure 21 Red gas vent along gas pipeline right of way is used to safely conduct gas from a shallow mine subsidence. (OSM-FRPD)

5.2 Sealing: Methods to seal point sources of gas involve crack sealing or grouting, clay, and earth seals over outcrops or fracture areas. Lateral migration of methane can be intersected from the soil by the use of cutoff walls. For example, this technique may be used to isolate a gassy coal outcrop from adjacent properties. However, this method would not be practical in sealing an entire outcrop. Leaks from the ground are often sealed by pavement and the gas comes to the surface along the pavement edges. Techniques of sealing the surface combined with venting can control and redirect methane safely into the atmosphere. The landfill industry often uses synthetic liners to seal the migration of gases and polluted water into the disposal area.

5.3 Monitoring: Monitoring the mitigation of soil methane is similar to monitoring vents and seals for shafts and portals. Monitoring must be conducted routinely to determine if the vents are functioning and correctly sized. Seals must be checked to determine if they have been breached or broken. The perimeters must be observed to determine if the problem has enlarged or if the system is functioning as designed.

Monitoring of areas where the soil has been purged or treated to remove remnant methane must be preformed routinely after the problem has been solved to evaluate the success of the repair. Gas utilities will monitor an area more frequently after a gas line is repaired for an extended time. If no problems are observed over a year, then gas utilities return to a normal long-term monitoring schedule, typically every 3 to 5 years.

6.0 METHANE IN STRUCTURES

When methane is identified in a structure at dangerous levels the area must be ventilated and/or evacuated immediately. The source or pathway into the structure must be identified to develop a mitigation plan (Section III). Within or immediately outside a structure, the following mitigation techniques are available to effectively lower the methane levels.

6.1 Long-term or short-term remedies: Long-term and short-term remedies depend on the source and pathway of the methane migration. Problems associated with longwall mining stop as the ground heals and establishes a new equilibrium. This may take anywhere from months to a few years.

Short-term remedies are often associated with the need to control the immediate hazard. These include temporary vent stacks, trenching, or ventilation with fans. One often sees temporary vents provided by gas utilities to ventilate an area affected by a leaky gas line (Figure 19). The intent is to remove the immediate hazard and provide a safe atmosphere to continue the investigation. If the source is limited or can be isolated, short-term treatment is all that is required.

Long-term remedies should only follow detailed investigations that identify the source and migration path. Long-term remedies usually involve both venting and sealing. Active systems in structures should always provide positive pressure ventilation to dilute gases. Negative pressure systems (vacuum) create new migration paths for methane, since gases seek negative pressure. However, negative pressure systems do not provide a fail-safe and can create a greater hazard when disabled by power failures. In contrast, positive pressure systems provide a better fail-safe condition by diluting the hazardous atmosphere. Mitigation is often constructed in phases to provide the most economical solution to the problem. In general, methane should be vented at high-pressure sources and sealed at low-pressure sources.

6.2 Venting: The first and most effective mitigation procedure for methane in an enclosed area, like a building, is venting. Ventilation is directly applicable to control methane in structures by

reducing the explosive level of gas. Venting of methane from a structure must take into account the construction of the building or residence and the principal migration path. Ideally, the migration path should be intercepted as close to the source as possible. When the migration of gas cannot be pinpointed or is diffuse, the structure itself must be remediated. The radon mitigation industry provides useful methods and technology that can also be used to abate methane hazards.

Methane with its low density and rapid diffusion can be easily vented. The gas easily rises into the open atmosphere and is quickly dispersed with fresh air. Ventilation systems can directly vent concentrated sources of methane or dilute the hazardous atmosphere to safe levels by introducing fresh air. The investigator should always provide fresh air with positive pressure towards the source of the problem.

As with surface vents (Figure 22), the materials used for ventilation are varied. Common supply sources are companies that mitigate radon, HVAC, and water seepage. Vents and drains for methane must be installed with minimum restrictions of flow. Smooth-walled pipe, 45-degree bends, and gradual transitions provide the most efficient air flow. Particularly important in passive systems, the diameter of the pipe or duct must be designed to not restrict the natural flow of air.



Figure 22. Vent stacks outside of residential structures.

Ventilation systems can be made passive by capitalizing on the natural properties of methane or be made active with blowers to force the movement of air.

6.2.1 Passive Systems: Passive systems require no power and can provide mitigation if the source of methane is low in concentration and will not change over time. Passive systems are often used in combination with tile drains or drain fields located above the vadose zone to collect gas in the subsurface and vent to the atmosphere. A passive vent can be incorporated with a tile drain around the perimeter of a house to intercept lateral movement of methane in permeable substrata of soil or rock.



Figure 23. Active vent on a landfill near an elementary school.

6.2.2 Active Systems: Active systems that draw

vacuum on the soil or a point source are not recommended except in special conditions to isolate a point source or remove a limited source of methane. A zone of negative pressure invites more gas to the area and can therefore expand the methane hazard. Active vent systems are often used in mitigation of gas line leaks when the soil is purged. This method rapidly drains the gases in the soil and shallow fractured bedrock. Fresh air is then drawn into the soil and fractures to replace the methane. If the source is not eliminated, soil purging will not be successful.

Similarly, active vents drawing gases from the soil or fill materials are often used to remove VOCs such as leaking underground storage tanks (Figure 23). Active systems such as sub-slab suction may be required in some mitigation plans. Fresh air intakes must be provided to reduce back-pressure in the slab that would draw gases from the soil. Active vents should be designed to take advantage of dilution with fresh air.

6.3 Dilution: Dilution is the most effective method to reduce the hazards of methane if the source of the methane cannot be intercepted and vented away. Dilution can be considered a subgroup of ventilation but is important enough for specific discussion. Dilution is simply providing fresh air to reduce the concentration and therefore the explosiveness of methane. This can be done simply by opening doors and windows to allow fresh air in a structure. A more active system may involve fans or blowers to temporarily reduce the level of methane. Dilution is the theory behind ventilation in underground coal mines, by facilitating rapid exchange of air across the working face. Dilution can be provided by either passive or active systems.

6.3.1 Passive Dilution: Passive dilution can be relatively easy to design into a mitigation plan. It is often as simple as maintaining ventilation in a crawl space or confined space with strategically placed openings. Often this technique is combined with sealing of the ground and/or the floor of the structure. Other passive dilution plans can incorporate the natural convection of air and the low density of methane to direct gas through a subsurface drain system. Many passive systems can be readily converted to active systems and provide a good approach for phased projects. Passive systems are applied best to smaller areas such as residential and small structures.

6.3.2 Active Dilution: An active dilution system requires power, maintenance, and constant monitoring. An active system is used if the hazard exposure and risk are high. An active system requires fans or blowers to draw fresh air into the problem area and dilute the concentration of gas. This system is effective on large structures such as schools or apartment buildings. The dilution of gas is most effective if isolated in its own environment such as a crawl space or sub-drains beneath the structure. Diluting the ambient atmosphere in the occupied areas is not usually practical as in coal mine ventilation. The amount of air to exchange is usually too large and must be maintained at comfortable temperatures for occupancy. Both require significant amounts of energy. There are efficient air exchangers that can be used to provide fresh air, but the exchange air volume rate is low.

6.4 Sealing: Sealing buildings from fugitive methane should be considered as secondary mitigation or in combination with venting. Gases are very difficult to seal completely, but seals can be effective at redirecting gas to a vent. Sealing of structures or the ground is always open to failure from holes, cracks, or tears in the barriers. Seals are effective when incorporated with ventilation, especially in new construction. In the Los Angeles area, subdivisions have been constructed where methane in the soil exists from a shallow oil field. The methane is controlled by ventilating and sealing the crawl spaces of the new homes as claimed by the sealant manufacturer. Sealing is best performed on the exterior of the foundation. The most difficult part of an effective seal is to achieve a competent air-tight seal at transitions of materials and the entrances of utilities, drains, and other conduits through the floors or walls. The radon mitigation industry provides useful strategies to seal and vent low concentrations of methane.

6.4.1 Foundations: Foundations often provide the migration pathways for methane to enter a structure. It must be determined if the migration is taking place laterally through the foundation walls, such as in a basement, or up through the floor. Deep footers, pilings or caissons can provide an avenue for gas from the subsurface into the structure. This can occur if deep foundation members are extended through coal beds, peat, or landfills. Disturbed rock materials, soil, or fill adjacent to foundation members is often permeable and provides avenues for gas to migrate.

Sealing of the foundation should be performed on the external surfaces. For example, a vapor barrier should be placed along the building walls adjacent to a tile drain. Concrete floors should be underlain with a flexible vapor barrier that would bridge any natural cracking in the concrete. Materials such as concrete block or frame construction can be coated with flexible impermeable sealants. Spaces between seals like a crawl space should be ventilated. For example, an earthen floor would be sealed with a quality vapor seal protected by a layer of well-graded gravel, the overlying floor would be sealed with another vapor barrier between the floor coverings or the underfloor coated with an asphaltic sealant. The space between the gravel protection and the underfloor should be vented.

Similarly, in the case of a concrete floor on grade, the gravel backfill should be vented and ideally installed with a drain system. As in the example above, a vapor barrier is installed to seal the exposed earth, a well-graded gravel bed is laid on top and then another vapor barrier is laid before the concrete is poured. The vapor seal should be bonded to all walls. The concrete floor is then finished with wire mesh to minimize any cracking. All joints and protrusions such as a drain or utility are sealed with a quality caulk that will remain flexible after curing. Venting of the gravel sub-base can be performed in a manner that is common in the radon mitigation field by placing a blower in the inlet to force air across the gravel and drain out the opposite side.

6.4.2 External Seals: External seals to the property can be placed on foundation walls where it is practical to expose them. Materials including synthetic liners, coatings, and sealants can be used with various foundation materials including concrete, cinder block, and stone. If gas

is migrating upward through the overburden from a deeper source, an external seal must be constructed to envelop the structure.

External seals below a structure are difficult to construct. Common technology to seal under and around a structure include pressure grouting and in- place mixing of soils. Indirect sealing through grouting and other techniques rarely produces a complete barrier to methane, but may reduce the flow and effective concentration of gas on the structure to reduce the hazard.

Lateral seals external to the structure most commonly are constructed by using a cutoff trench. These trenches are usually backfilled with combinations of clay, bentonite or cement to form an impermeable barrier. These barriers are very effective and can eliminate the hazard of methane migrating laterally from a coal crop or landfill (Figure 24).



Figure 24 Soil-Bentonite cut-off trench excavated into collapsed mine voids. (OSM-FRPD)

6.5 Monitoring of Structures: Monitoring the mitigation work on structures is important to ensure the success of the project. The property owner must assume some responsibility to maintain and monitor the condition of all equipment, seals, and barriers. Routine checks with a methanometer should be incorporated in all monitoring plans. All vents, air inlets, and sealed construction joints should be checked. Observations must be made during various climatic conditions to determine the effects of barometric pressure and temperature on the mitigation. Monitoring of the mitigation work should also be performed if any modifications or remodeling is performed on the structure. This will ascertain if the system is damaged.

Electronic monitoring systems that detect methane are readily available. These detectors vary from small self-contained units similar in appearance and cost to a common household Carbon Monoxide Detector to sophisticated monitors with relay circuits and data recorders. The degree of risk and long-term mitigation plan dictate which monitoring equipment is best. If a problem is well-mitigated with durable passive equipment, then monitoring may be quite simple but should be continued until the source of the gas is controlled or depleted. The small homeowner units provide cost-effective monitoring to warn the occupants of immediate danger.

Larger, high-risk locations such as a school, office, or apartment building should be monitored with multi-channel monitors with sensors placed at various strategic locations in the building. Alarms and warning circuits can be activated at central locations and the problem evaluated before an evacuation alarm is triggered. Monitoring systems may provide additional protection from the hazard by energizing backup equipment such as fans or blowers.

Monitoring by electronic equipment and sensors provides an added level of protection to the occupants or residents of a structure. However, the systems are expensive and require routine maintenance and calibration. A schedule and budget to calibrate equipment and replace sensors must be developed and adhered to. A monitoring system should not be taken out of service without careful consideration and evaluation of the project.

7.0 POST-MITIGATION ASSESSMENT

Monitoring the success of the mitigation efforts is essential. Mitigation that involves sealing or redirecting of methane gases away from the site should be diligently monitored directly after construction is complete and for an extended time to ensure that the abatement is successful. Adjacent properties must be investigated to check that the methane has not been redirected to create another hazard. It is important to monitor the effects that drive the fluctuating gas levels such as changes in temperature and barometric pressure. Climatic factors often require at least a season and often more time to monitor the complete effects.

Temporary methane problems that could be associated with subsidence or leaky pipe lines should be monitored frequently. The mitigation system should be constructed so that it can be easily removed and modified as the problem is repaired and gas concentrations return to safe levels. The change in conditions must be investigated with enough detail to ensure that the problem has ended. Long-term abatement devices such as vents should be designed with sample ports and other access so that routine samples can be easily collected.

Post-mitigation monitoring can be as simple as taking routine samples after mitigation or may involve more constant monitoring on sensitive projects that can only be achieved by data recording at regular intervals. Active systems usually require more detailed monitoring to ensure that the equipment is functioning properly and is durable. Fixed methane monitoring and alarm systems are available from commercial vendors. Passive systems should be monitored to ascertain if the abatement is properly sized for the worse-case scenario.

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Glossary

- Abate-** To stop or eliminate.
- Action Level-** Exposure level at which action must be taken to protect employees or residents. Exposure at or above the action level is termed occupational exposure. Exposure below this level can also be harmful.
- Aerobic-** Oxygen-dependent or requiring oxygen.
- Alluvium-** Clay, silt, sand, gravel, or other rock materials transported by flowing water and deposited recently in terms of geologic time.
- Ambient-** The environment surrounding a body but undisturbed or unaffected by it or encompassing on all sides.
- Anticline-** When beds are arched upward so as to incline away from each other, they form an anticline.
- Asphyxiation-** Local or systemic deficiency in oxygen and excess carbon dioxide in living tissues, usually a result of interruption of respiration.
- Aquifers-** A stratum of permeable rock, sand, or gravel that yields sufficient water for the required use.
- Bedding Plane-** In sedimentary or stratified rocks, the division surfaces that separate the individual layers.
- Bentonite-** Absorptive and colloidal swelling clay used as a sealing agent, as in lining ponds.
- Biofilm-** A thin layer culture of microbes.
- Blocky-** Strata that break into thick blocks.
- ¹⁴C-** Carbon 14. A heavy radioactive isotope of carbon of mass number 14, used especially in tracer studies and in dating archaeological and relatively recent geological materials.
- Carbonaceous-** Rich in carbon.
- Coal Ash-** Noncombustible matter remaining after burning coal.
- Coal bed-** A bed or layer of coal. Coal seam is more commonly used in the U.S. and Canada.
- Colluvium-** Applied to loose and unconsolidated weathered deposits, usually at the foot of a slope or a cliff and brought there chiefly by gravity.
- Connate-** Applied to waters buried with sedimentary and volcanic rocks. These waters are essentially stagnant, except as they are incorporated in new minerals found in the rock.
- Damps-** Any mine gas, or a mixture of gases, particularly those deficient in oxygen.
- Detector Tubes-** A way of collecting a grab sample of air to be tested. They obtain only qualitative data.
- Diffusion-** A random process in which something spreads out or scatters.
- Disseminate-** To spread; to diffuse.
- Explosive Limit (Upper and Lower)-** Range of concentration where flammable gases and vapors are explosive when mixed with air.
- Friable-** Easy to break or crumble naturally.
- Fracture-** Breaks in a rock due to stress.
- Fugitive Methane-** Methane gas that is migrating to unwanted areas in an uncontrolled way.
- Geomorphology-** A science that deals with the land forms of the earth.

Grout- A pumpable slurry of cement or a mixture of cement and fine sand, commonly forced into a borehole to seal crevices in a rock to prevent ground-water or gases from seeping or flowing into an excavation.

Hydrostatic Pressure- The pressure developed by a water.

In-situ- In place.

Joint- A fracture in the rock where there has been no measurable movement.

Lithology- The character of a rock described in terms of structure, color, mineral composition, grain-size, and arrangement of its component parts.

Macroporosity- Porosity visible without the use of a microscope.

Mercaptan- A class of compounds analogous to alcohols and phenols but containing sulfur instead of oxygen. Some have very disagreeable odors and are used to scent natural gas in pipelines.

Microbial (methane)- methane formed when bacteria in the environment digest organic material and oxygen. These bacteria create carbon dioxide and low levels of methane.

Microporosity- Porosity visible only with the aid of a microscope.

Orogenic- Of or relating to the processes by which mountains are formed.

Outgassing- The release of gases into the earth's atmosphere from the ground.

Permeability - For rock or earth material, the ability to transmit fluids.

Plugging- The filling of an abandoned borehole with inert impermeable material in order to stop flow.

Porosity - Percentage of void space or interstices in rock or other earth material.

PPM- Parts Per Million.

Purging- Sufficiently pumping a well to obtain a fresh unbiased water sample.

Safety Factor- A limit above or below the critical value that provides an extra level of assurance that a disastrous event will not occur.

Sniffer- A device that monitors gases in the atmosphere.

Specific Conductance- A measure of the ability of water to conduct an electrical current, related to the type and concentration of ions in solution.

Stratigraphic- Pertaining to the sequence of stratified rocks.

Stoichiometric- Describing the quantitative relationship between chemical substances, in which proportions of reactants and products are characteristic for each reaction.

STP- Standard Temperature and Pressure (20 degrees Celsius and 1 atmosphere).

Syncline- A concave fold in which the rocks on each side slope toward the middle.

Tedlar® Bags- A vacuum bag or impermeable environmental sample bag.

Thermogenic (methane) - As buried sediment layers build up pressure and temperature, thermal decomposition takes place, producing methane.

TLV- Threshold Limit Values. The concentration and condition of a substance a person can be exposed to daily without adverse health effects.

TLV-TWA- Time Weighted Average concentration for a normal work day and work week to which all workers can be exposed without adverse health effects.

TLV-STEL- Short-Term Exposure Limit. The concentration to which workers can be continuously exposed for a short period of time without irritation, chronic tissue damage, or narcosis.

TLV-C- Ceiling. The concentration that should never be exceeded.

Trenching- The digging of shallow trenches to expose a coal seam or vein.
Vadose Zone- The unsaturated zone in soil.