Stray Gas Migration and Applications in the use of Isotope Geochemistry

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Methane Is the Principal Hydrocarbon Detected in All of Our Stray Gas Investigations

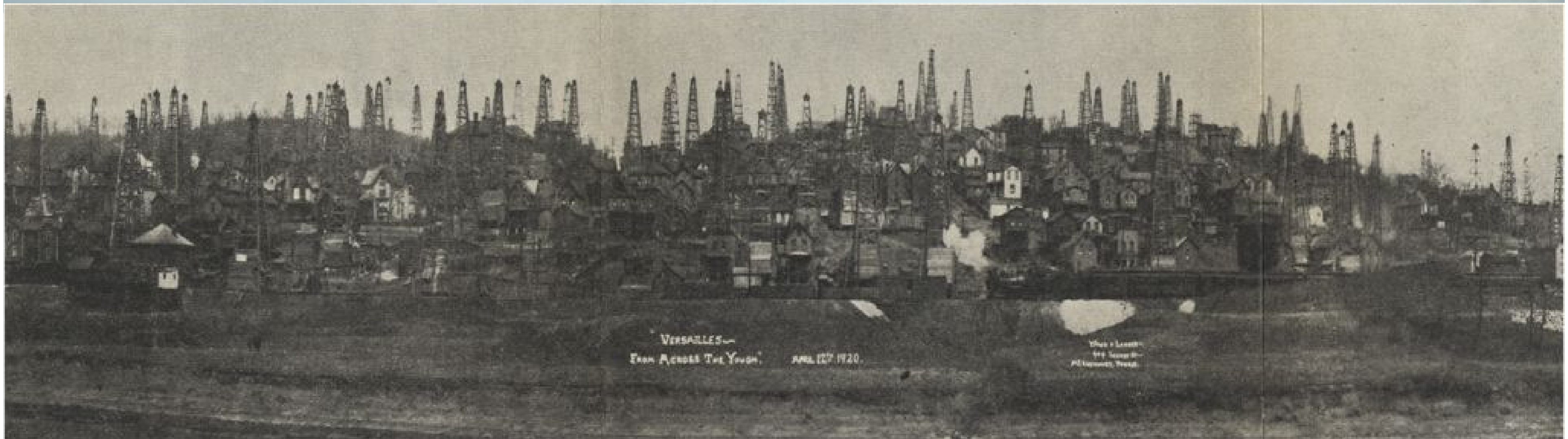
- **Methane (CH_4) is the simplest paraffin hydrocarbon gas.**
- **Flammable, colorless, odorless.**
- **Specific gravity: .555**
- **Explosive range: 5-15%**
- **Solubility in water: 26-32 mg/l**

Potential Stray Gas Sources Are Numerous in Western PA.

- **Abandoned & operating gas wells**
- **Natural gas storage fields**
- **Natural gas pipelines**
- **Abandoned & operating coal mines**

- **Abandoned & operating landfills**
- **Shallow formations – microbial/thermogenic**
- **Drift gas**

Stray Gas…Legacy



The Consequences of the Undetected Migration of Stray Gas in the Subsurface Can Be Devastating.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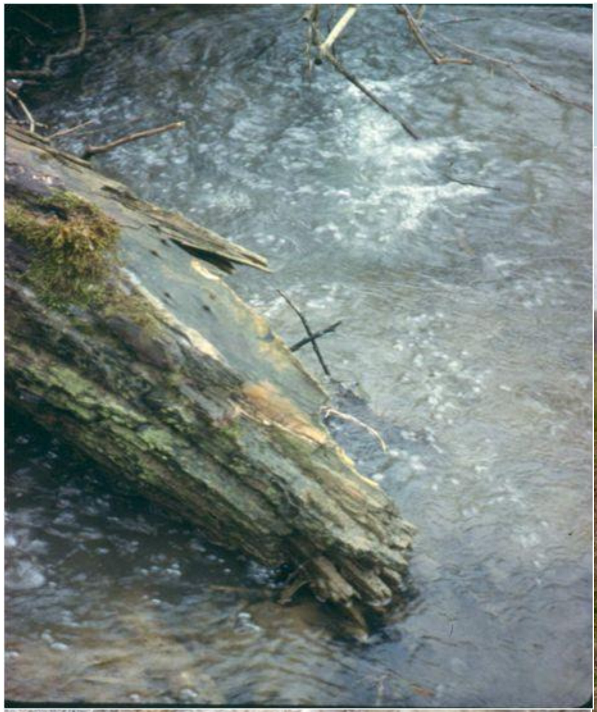
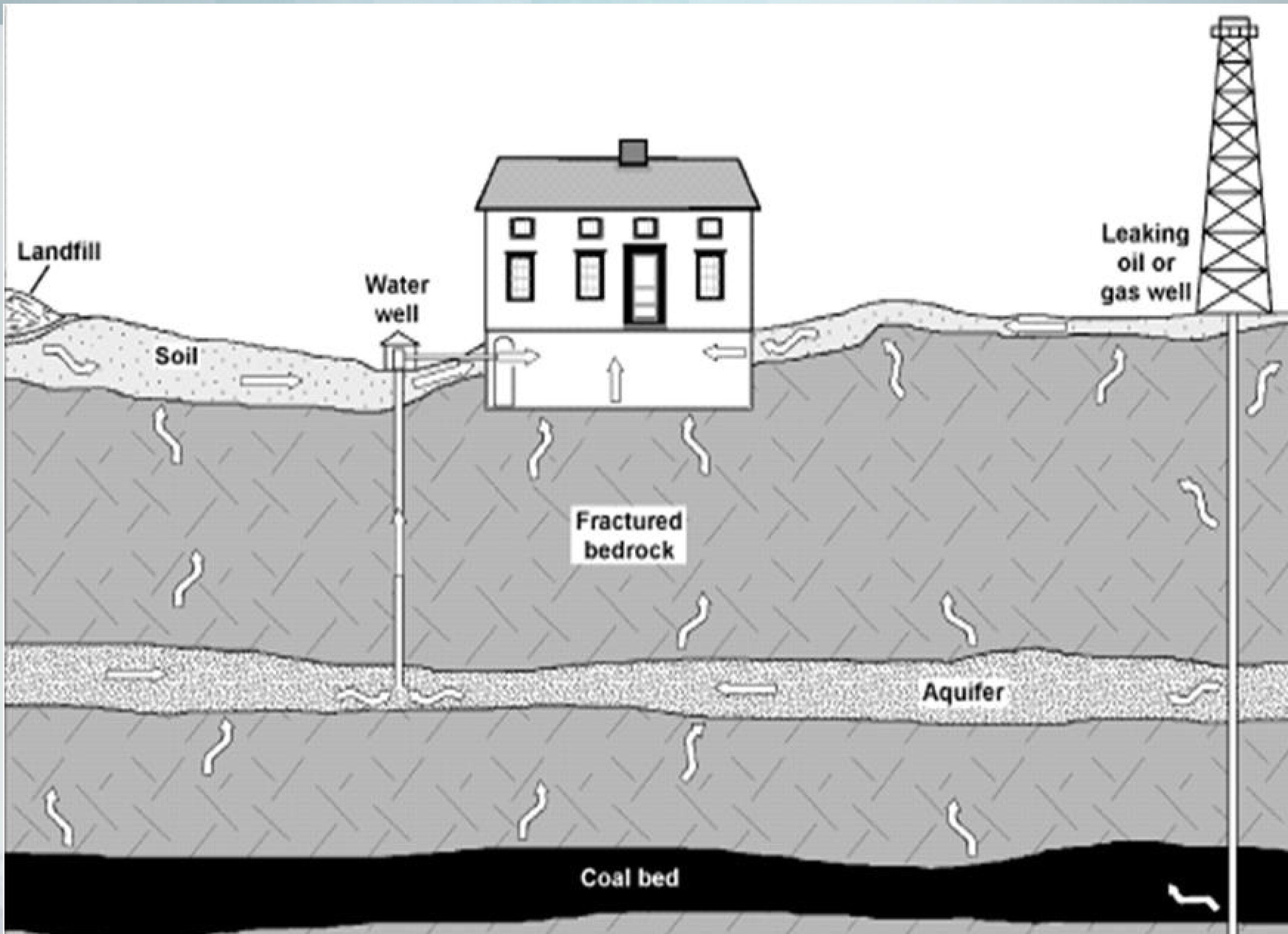
Stray Gas




Landfill
Water well
Soil
Leaking oil or gas well
Fractured bedrock
Aquifer
Coal bed

Methane dissolved in water

Methane dissolved in groundwater is not uncommon in many areas of Pa. It should not be evaluated the same as methane gas in or around a building.

~ 26-32 mg/l at atmospheric pressure, however, solubility in water is proportional to pressure. Every foot of water exerts .43 psi or 2.31 feet of water is under 1 psi.

Because of the difficulty in determining the concentration of CH_4 in water at depth, it may be advisable to evaluate CH_4 dissolved in groundwater conservatively.

Estimating theoretical worse case CH_4 concentration in groundwater

$$C_W = \frac{(H_W)\ (0.43\ \text{psi/ft})(28\text{mg/l})}{14.7\ \text{psi}} + 28\text{mg/l}$$

Where:

C_W = max. theoretical concentration at bottom of water column

H_W = height of water column in feet

0.43 = hydrostatic pressure due to overlying water – weight of one square inch column of water one foot high= water pressure in psi

28 = assumed solubility of methane at atmospheric conditions

14.7 psi = one atmosphere

Ex: Consider a hydrostatic head of 200’. Groundwater at the bottom of this water column is under 5.9 atmospheres of pressure and could theoretically contain 193.3 mg/l of methane. Almost 6 times the concentration that is possible at atmospheric conditions. As the pressure is reduced, approx. 165 mg of methane could evolve for every liter of water.

Principles of gas migration in the subsurface…important variables for evaluating monitoring data

Gas migrates from areas of high pressure to areas of low pressure (advective transport)

Gas migration in the subsurface is influenced by:

- **Changes in barometric pressure**
- **Soil/bedrock porosity, permeability**
- **Precipitation - Pore water**
- **Diurnal/Temperature contrasts**

Changes in atmospheric pressure strongly influence the migration of gases in the subsurface. Fluctuating barometric conditions cause changes to soil-gas chemistry and groundwater levels.

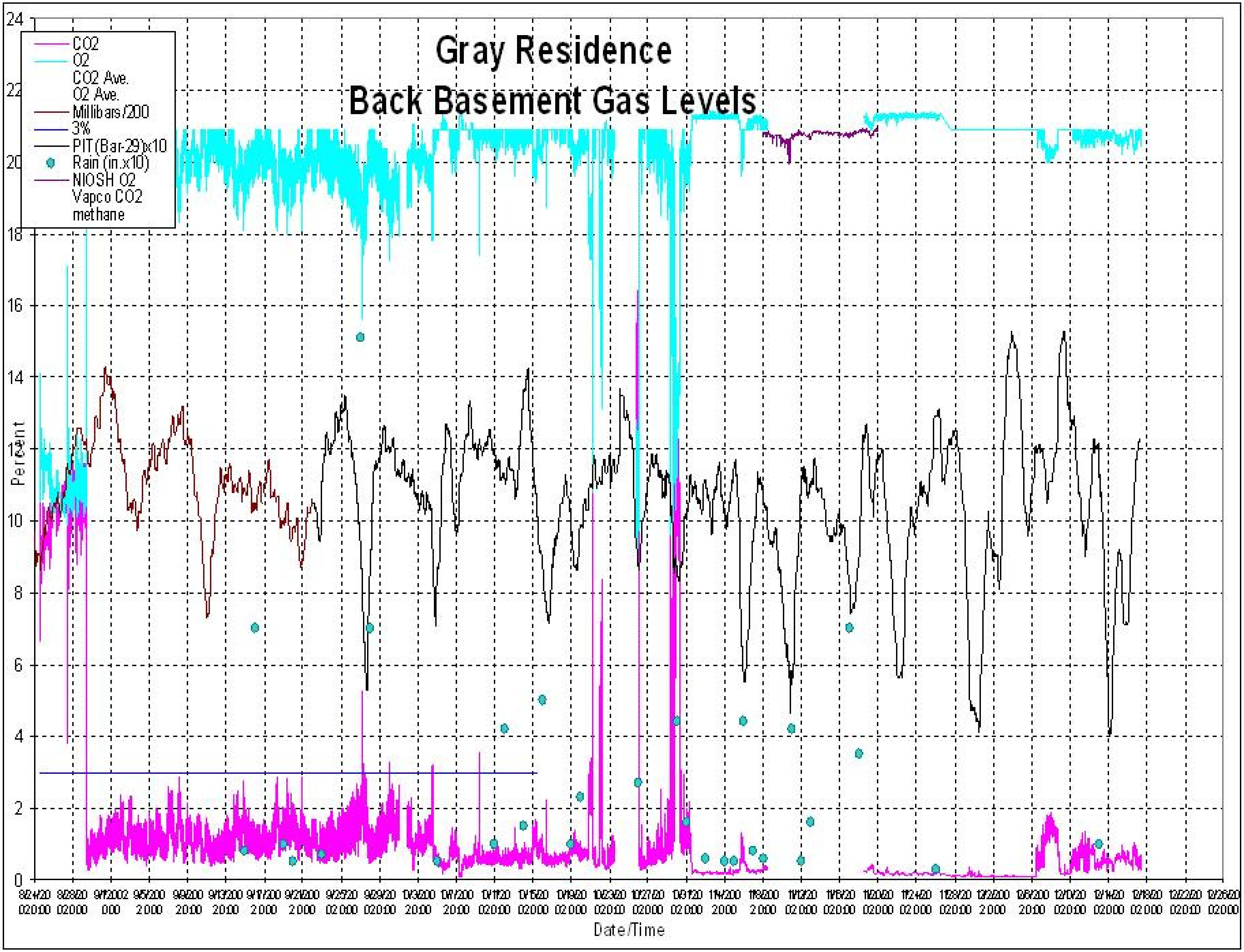
* Approaching low barometric pressure conditions results in a reduction in pressure on the soil/atmosphere boundary resulting in soil out-gassing or a rise in groundwater levels.

* Approaching high barometric pressure 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.

* Stray gas problems become more pronounced during rapid reductions in barometric pressure.

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


Gray Residence
Back Basement Gas Levels
CO2
O2
CO2 Ave.
O2 Ave.
Millibars/200
3%
PIT(Bar-29)x10
Rain (in.x10)
NIOSH O2
Vapco CO2
methane
Percent
Date/Time
0
2
4
6
8
10
12
14
16
18
20
22
24

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:

Initial Volume	**:**	**Final Volume**	**=**	**Final Absolute Pressure**	**:**	**Initial Absolute Pressure**
V1	**:**	**V2**		**P2**	**:**	**P1**

or V1 * P1 = V2 * P2

The following mine gas scenario 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:

$1{,}000{,}000 : V2 = 29.3 : 29.8$

$V2 = 1{,}000{,}000 \times 29.8 / 29.3$

$V2 = 1{,}017{,}065\ ft^3$.

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

hence, 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.

Genetic Characterization

Isotope Geochemistry

Thermogenic: C1 – C6 hydrocarbons generated. Formed during the thermal alteration of organic materials.

Microbial: C1 – C3 hydrocarbons generated. Formed by the bacterial decomposition of organic matter.

Molecular Analysis Not Always Conclusive & May Be Misleading

Gas composition may be affected by subsurface processes:

- **Fractionation**
- **Barometric Pressure (influences soil gas flux)**
- **Oxidizing bacteria**

Combustible gas migrating from the surface casing of an operating gas well.

The gas well is the conduit for the stray gas… not the source.

Isotope geochemistry focused the investigation… other lines of evidence confirmed the source

Stray gas detected throughout soils in a residential community…natural gas service terminated…isotope analysis reveals origin after significant resources expended…

Isotope Geochemistry

Carbon & Hydrogen Isotopes

Various researchers have determined by examination of stable hydrogen and carbon isotopes of methane that there are common hydrogen and carbon isotopic compositions for thermogenic gas associated with coal and natural gas, drift gas, and other near-surface microbial gases (Craig, 1953; Coleman and others, 1977; Deines, 1980; Schoell, 1980; Rice and Claypool, 1981; Schoell, 1983; Whiticar,1986; Wiese and Kvenvolden, 1993; Coleman, 1994; Baldassare and Laughrey, 1997; Kaplan and others, 1997; and Rowe and Muehlenbachs, 1999).

Isotopes of Carbon: C12, C13, C14

- **C12 (98.9%) & C13 (1.1%) stable**
- **C14 radioactive– decays to N14. Half life 5,570 years**
- **3 Isotopes of Hydrogen: H1, H2, H3**
- **H1, H2 stable**
- **H3 (tritium) radioactive – decays to 3He Half life: 12.6 years.**
- **C13/C12 and D/H isotope ratios**

The isotopic and compositional variations in natural gas can be described in terms of:

1) **processes during the formation of gases (bacterial fermentation, maturation of organic matter) and**
2) **processes during secondary migration (mixing of primary gases). The carbon and hydrogen isotopic compositional ranges of methanes from different sources are based on the genetic classification scheme of Schoell (1980)**

Stable carbon isotope compositions are expressed as the ratio of 12C to 13C of the sample compared with that of the international standard (produced from fossil belemnite, PeeDee formation) used by Craig (1953).

Isotopic fractionations are normally small. The C13/C12 of carbon is expressed as the per mil (parts per thousand, 0/00) and expressed as $\delta 13C$ values as follows:

$$\boldsymbol{\delta 13C\ \text{‰} = [(13C/12C_{sample} - 13C/12C_{standard}) / (13C/12C_{standard})] * 1000}$$

A C13 value of –40 0/00 indicates that the material is 40 parts per thousand. That is, the material is enriched in C12 by 40 0/00 (or 4% lighter) relative to the standard.

Isotopic signatures of methane

In general:

Microbial methane - acetate fermentation (marsh gas & landfill gas)

- **Del 13C: -40 to -62 0/00**
- **Del D: -270 to -350 0/00**

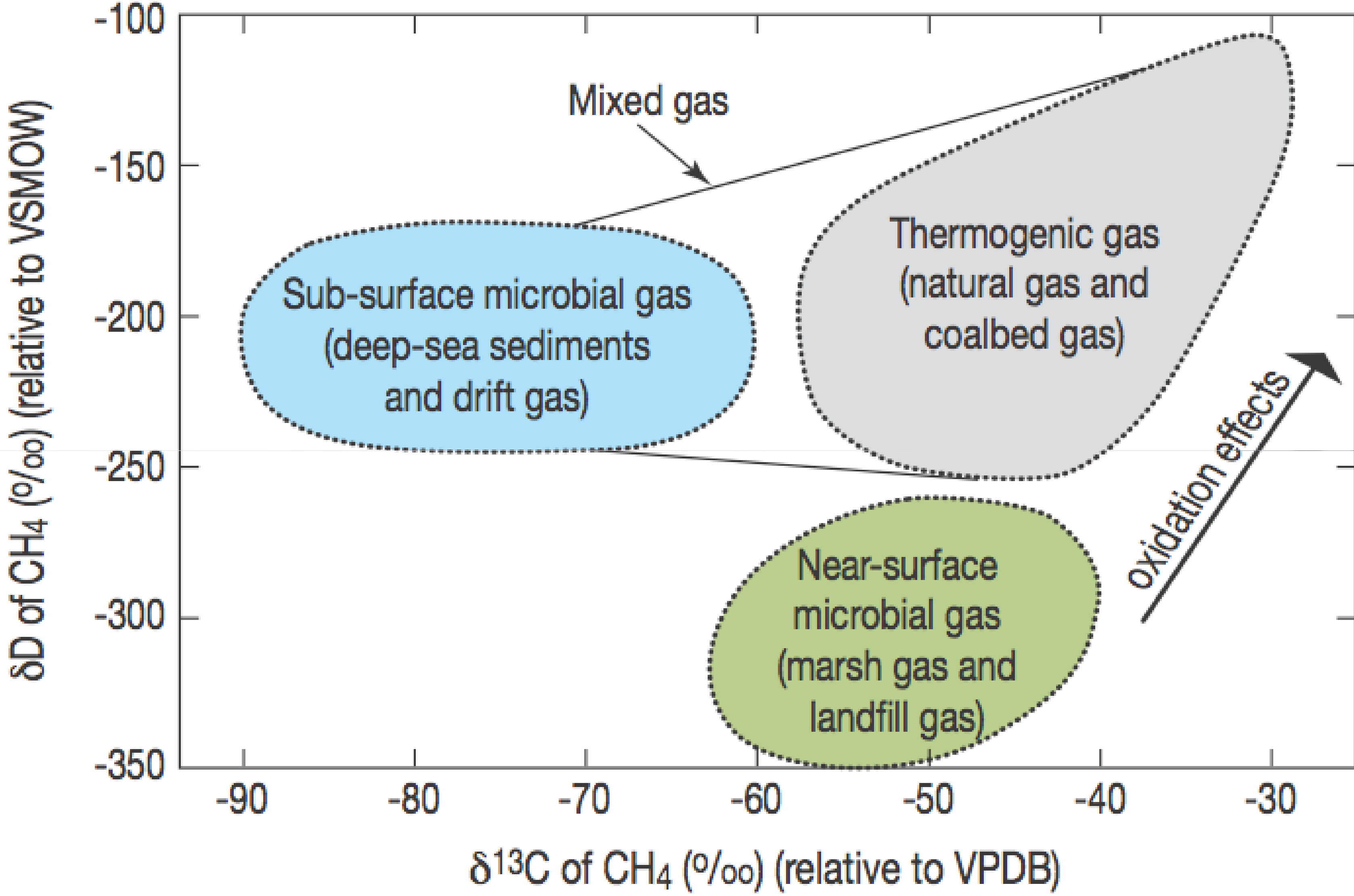
Microbial methane - CO_2 reduction (drift gas)

- **Del 13C: -62 to -90 0/00**
- **Del D: -180 to -240 0/00**

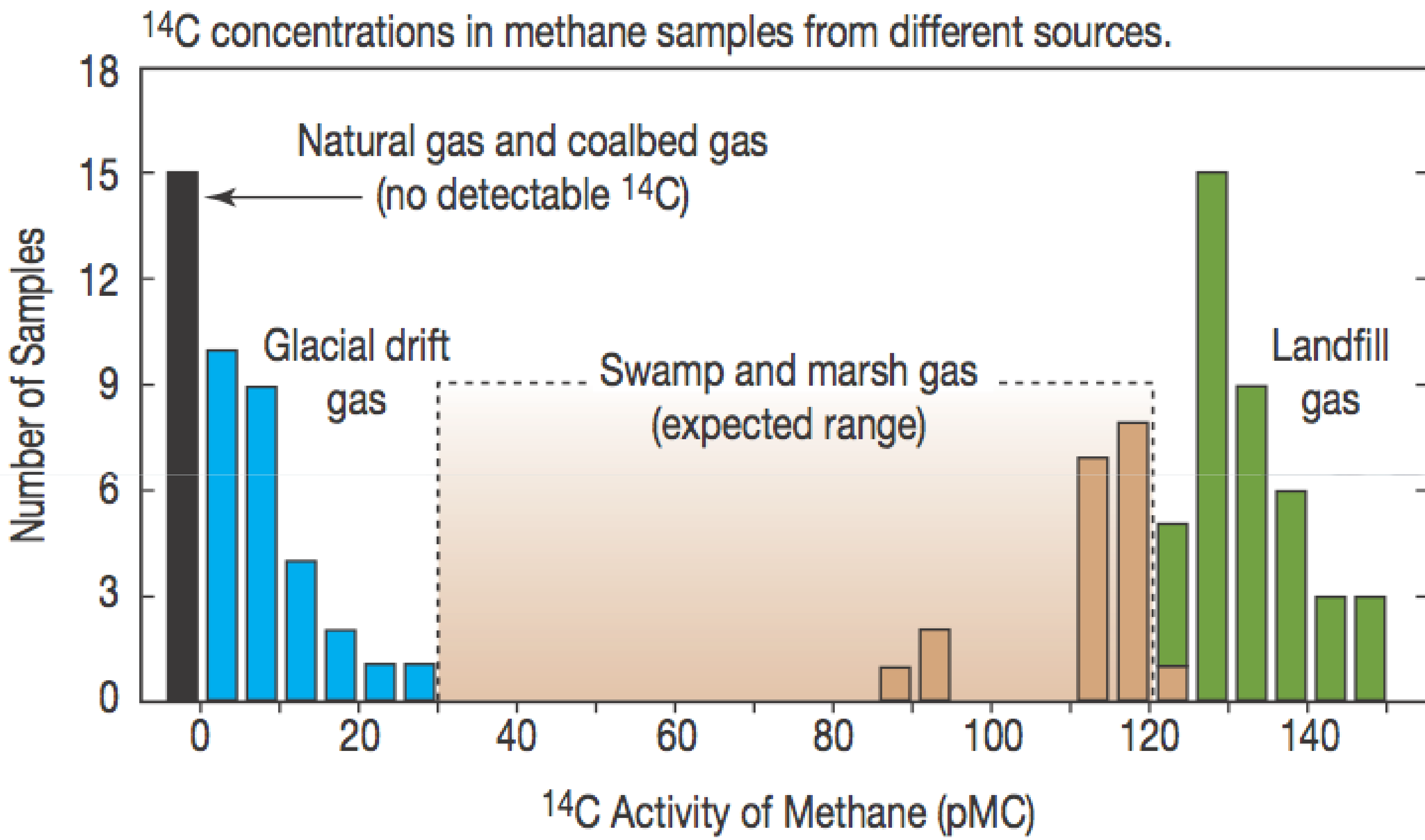
Thermogenic methane

- **Del 13C: -26 to -50 0/00**
- **Del D: -110 to -250 0/00**

Stable carbon and hydrogen isotopic compositional ranges of methanes from different sources.

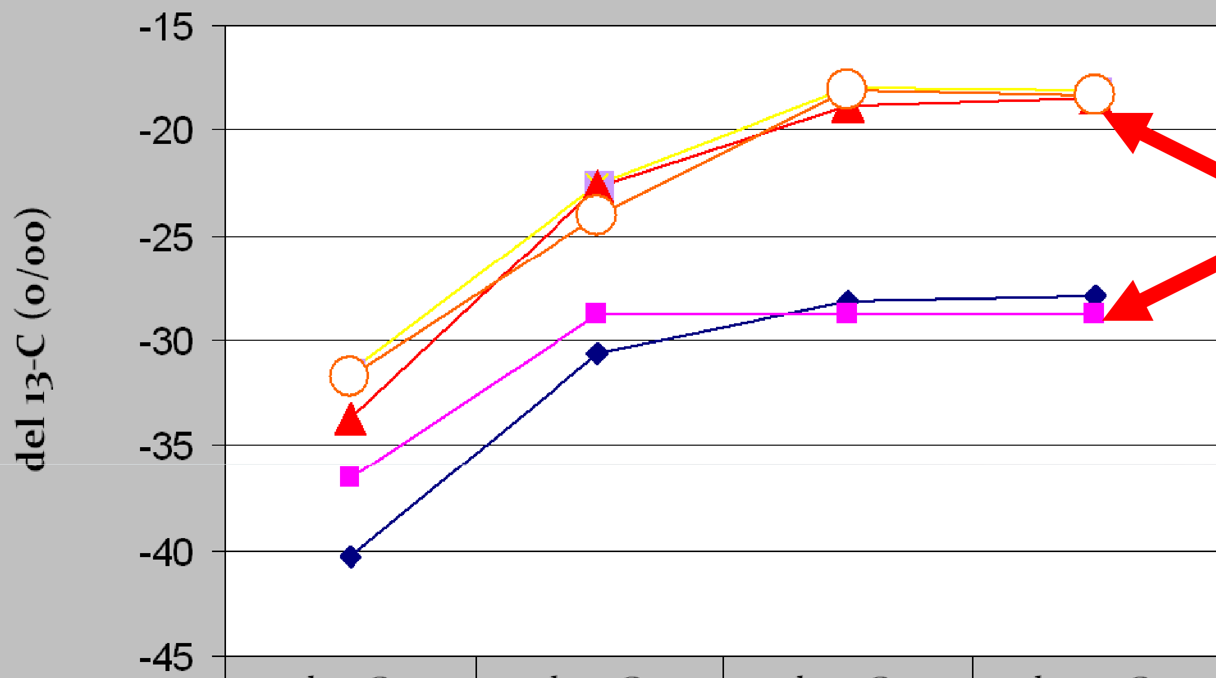


After Coleman and others (1993) based on the data set of Schoell (1980)



Coleman and others (1993)

Compartmentilization
Gas Isotope signatures



	d13-C1	d 13-C2	d 13-C3	d 13-nC4
A	-40.26	-30.63	-28.09	-27.86
B	-36.51	-28.73	-28.76	-28.82
C	-31.48	-22.56	-17.99	-18.08
D	-33.76	-22.71	-18.85	-18.48
E	-31.71	-24.01	-18.04	-18.4

A B C D E

Del 13-C for C2, C3, C4 can allow discrimination of thermogenic gases from different sources

2 Source Rocks

B1
B2
A1
A2
A2

4 Flow Units
(modeled after Schoell,et al., 2003)

Isotope geochemistry
Interpretations, Considerations, Challenges

Dosing – isotope geochemistry can provide additional line of evidence as to source strength

Oxidation – under certain conditions the isotope signature can be altered due to bacterial oxidation in the subsurface

Mixing – stray gases of different origins can mix in the subsurface creating a composite signature of the gas **–** In some areas, gas from abandoned gas wells has migrated to more shallow formations mixing with microbial gas or thermogenic gas of a different origin

Variability – the stable carbon and hydrogen isotope signature from a source can change over time due to production variability

Thermal maturity (diagenesis, catagenesis, metagenesis)

- Natural gas sources can vary regionally
- Formations can serve as a source or reservoir
- Isotope reversals (C_2, C_3)

Elements of the Investigation
Rapid Assessment Protocol

- **Interviews…**
- **Establish a timeline**
    - **When and how did you become first aware of the problem?**
    - **Can you relate the occurrence with any recent activity in the area?**
    - **How long have you lived at this residence?**
    - **Are you aware of any methane problems with this structure/well prior to this one?**
- **Identify all potential sources in the immediate area of investigation**
    - **Gas wells:**
    - **Record pressure for each casing interval**
    - **Sample/characterize gas for each casing interval**
    - **Review well records & completion reports, drillers log, cementing tickets, frac records, maintenance & repair records, electronic logs**

    - **Coal mining:**
    - **Overburden type & thickness**
    - **Mining method: Longwall/room & pillar**
    - **Review/Record head levels for aquifer(s) and/or mine pool from area mine degas boreholes, and piezometers.**

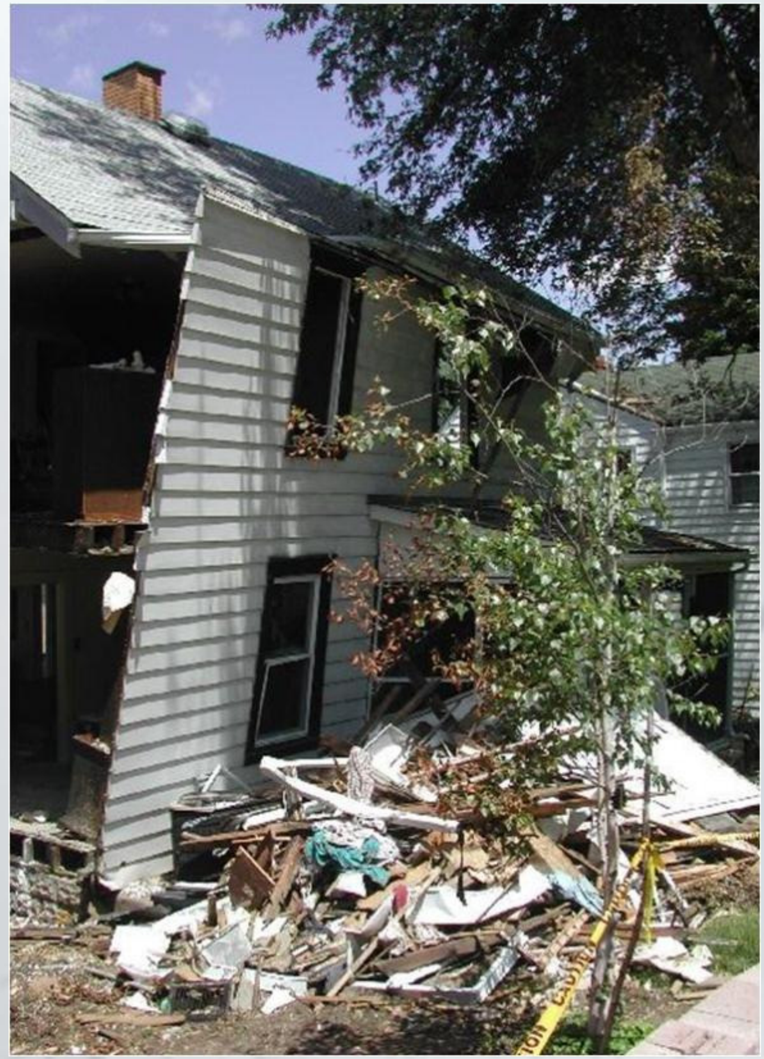
- Collect samples of the stray gas, and potential sources for molecular and isotopic analyses
- Identify and evaluate each potential source for potential mechanisms of migration
- Soil Gas Survey - Establish monitoring points & conduct combustible gas monitoring on specified frequency. Monitor soil gas (~2'-4' below grade) for combustible gas
  - Expand out from areas of high concentration
  - Establish sampling grid: delineate the boundaries of stray gases in the soils, identify tested locations
  - Select locations at boundaries, and in areas of high concentrations for follow-up monitoring
  - Construct soil gas monitoring points for long-term monitoring
- Focus investigation on the basis of molecular and isotopic analyses
- Support your thesis and conclusions with multiple lines of evidence

Sampling


PA DEPARTMENT OF ENVIRONMENTAL PROTECTION


100
200
300
400
psi
ISOTECH

Case History – Bridgeville Explosion



Bridgeville Explosion

In May 2003 the Bridgeville VFD answered a fire call at 673 Chestnut Street in Bridgeville, Pennsylvania.

Shortly after the fire was extinguished an explosion occurred at 667 Chestnut Street resulting in the destruction of the home and injuring three occupants.

Several potential sources of the explosion were identified in the immediate area

Chestnut St. - Bridgeville

Potential Sources

- **Active Natural Gas Service Lines**
- **Operating Natural Gas well**
- **Abandoned Natural Gas well**
- **Abandoned Coal Mine**

Natural Gas Service Line

The PUC required pressure testing of main gas line and service lines. This work revealed several leaks along the main service line.

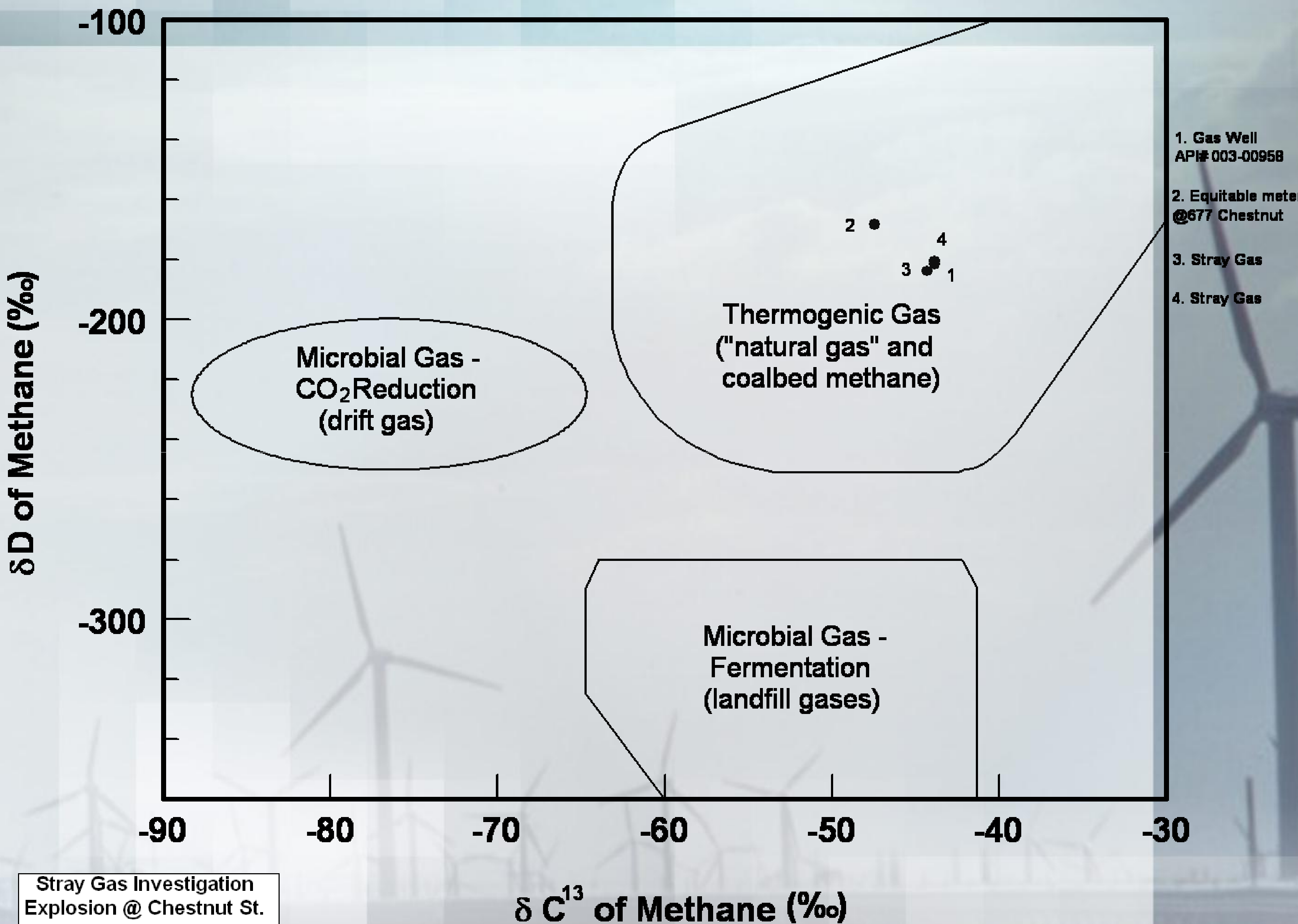
Deep mining of the Pittsburgh Coalbed

Mine Maps reveal deep mining of the Pittsburgh coalbed in the area at a depth of 60-80’ below the surface by room and pillar methods beginning in 1901.

A mine entry was driven below some of the homes on Chestnut St.

An operating and abandoned gas well were identified in the area of investigation

ISOTOPE CROSSPLOT



Stray Gas Investigation
Explosion @ Chestnut St.
Bridgeville, PA

Potential Mechanism of Migration

- **Isotopic analysis revealed that the gas produced by the active well was similar in origin to the gas from the monitoring point at the explosion site.**

- **Well was shut in at time of explosion. Operator was required to evaluate casing integrity and cement bond of the suspect gas well.**

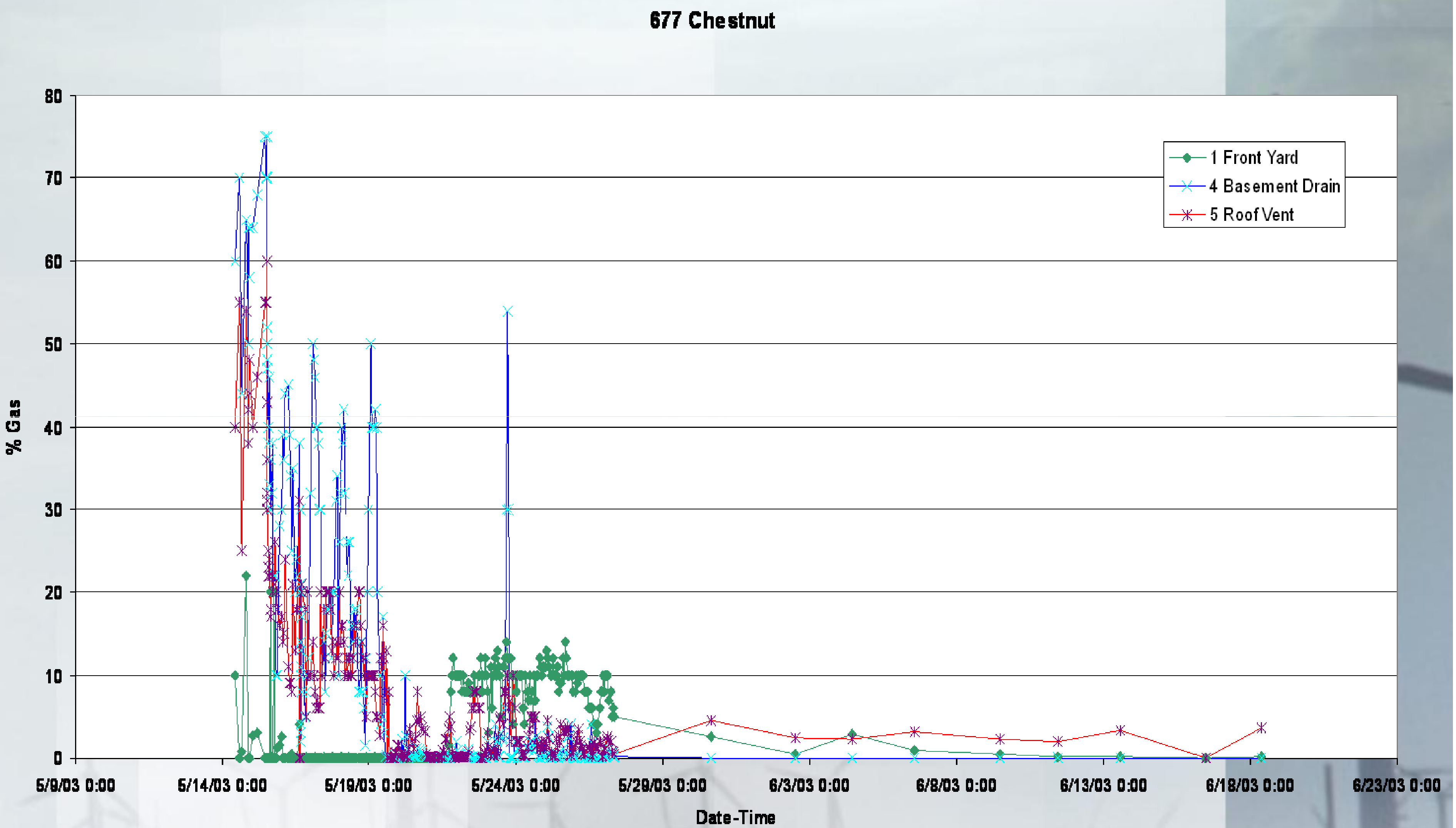
- **Results revealed a hole in the well casing at approximately 130' below grade.**

- **DEP personnel theorized that gas from the active well was leaking into shallow abandoned deep mine workings and migrating to the area on Chestnut Street.**

- **The operating gas well was subsequently shut in and DEP personnel stationed at the monitoring points to try to determine if a change occurred as a result of that shut in. Within minutes of shutting in the well a dramatic increase in gas was seen at the monitoring point of the explosion site verifying the migration pathway.**

- **The active well was repaired by using a single set production-injection packer.**

Combustible Gas Monitoring Data

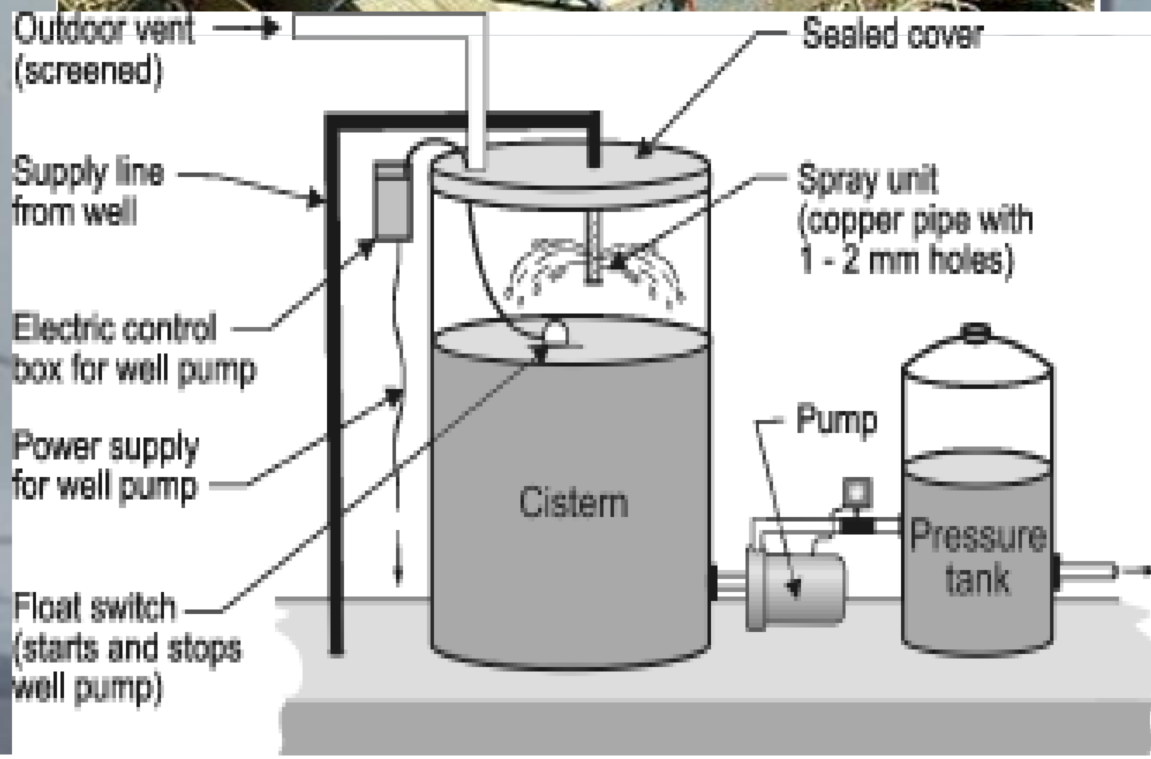


Mitigation Techniques

- **Interceptor Ventilation Trenches**
- **Passive water well vents**
- **Water aeration systems**
- **Positive pressure ventilation systems**

Ventilation Trenches

pro-active/mitigation measure designed to intercept, control, and vent stray gas before migration to structures and other areas of concern.



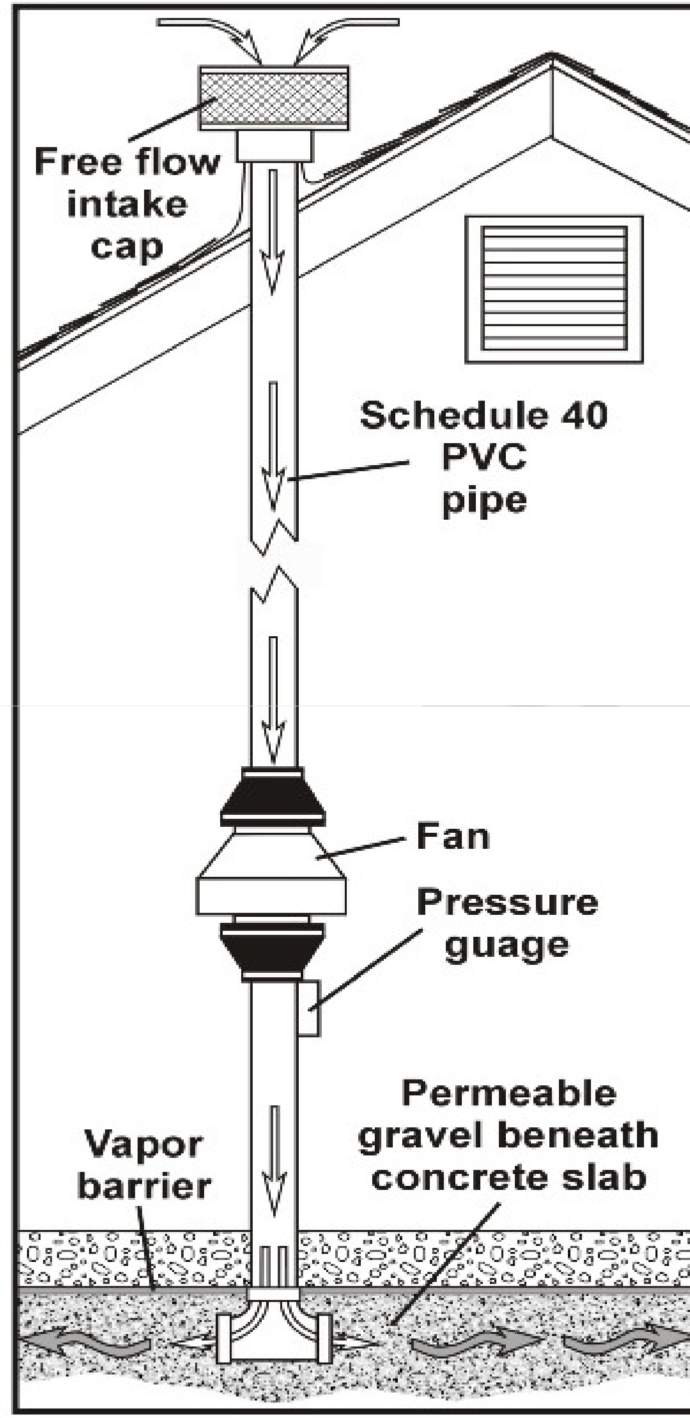
Water well vents
Aeration systems

Sub-slab Positive Pressure Mitigation Systems

* Existing technology

* Immediately effective to protect occupants

* Superior to conventional systems because the low pressure effect of the building shell is reversed, and the stray gas remains subsurface. The vent system manages clean air only.



Positive Pressure Mitigation Systems

Alarm Systems