IDENTIFYING SOURCES OF STRAY CARBON DIOXIDE GAS CONTAMINATION IN WESTERN PENNSYLVANIA

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CO_2 contamination of building spaces is an emerging environmental problem in western Pennsylvania.

CO2 contamination of building spaces

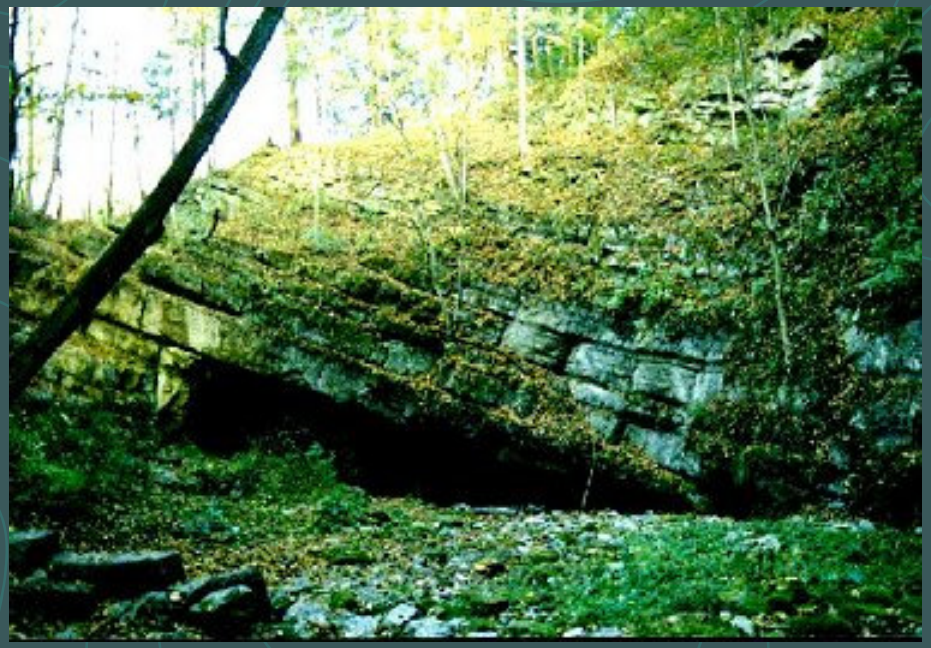
- Ambient atmosphere = 0.03%
- TLV = 0.5%
- TLV-STEL=1.5%
- Humans lose consciousness in atmosphere containing 10% or more CO_2; respiratory paralysis and death may follow
- At lower concentrations: Increased pulse and breathing rates, clumsiness, headaches, and dizziness.

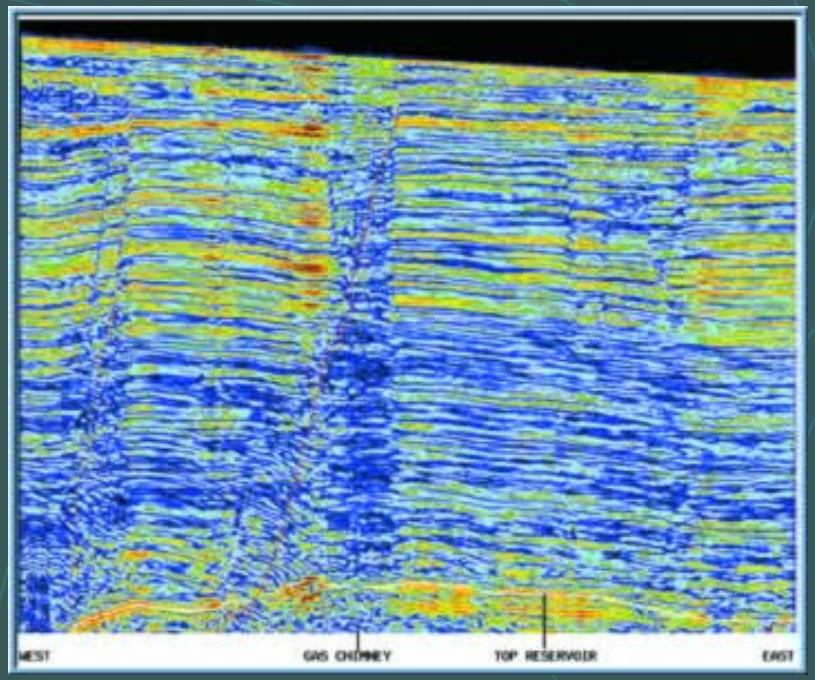
- In some instances:
  - CO_2 concentrations in excess of 25%
  - Corresponding O_2 concentrations less than 10%
  - Dangerous and potentially lethal

Potential sources of stray CO_2 in western Pennsylvania

- Geologic sources
- Anthropogenic sources

Potential geologic sources
(unlikely)





Potential anthropogenic sources

- Fossil fuel combustion
- Lime and cement manufacture
- Beverage Carbonation
- Waste combustion
- Soda ash manufacture
- CO_2 consumption and use
- Landfills
- Limestone and dolostone use
- Coal mining activities

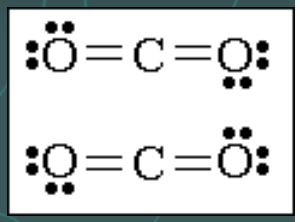
CO_2 from abandoned deep mines in western Pennsylvania

- "Blackdamp"
- Usually associated with communication of abandoned mine atmosphere with surface structures via old shafts or fractured bedrock
- 12 – 15 % CO_2 in abandoned mine atmosphere
- Driven in large part by changes in barometric pressure

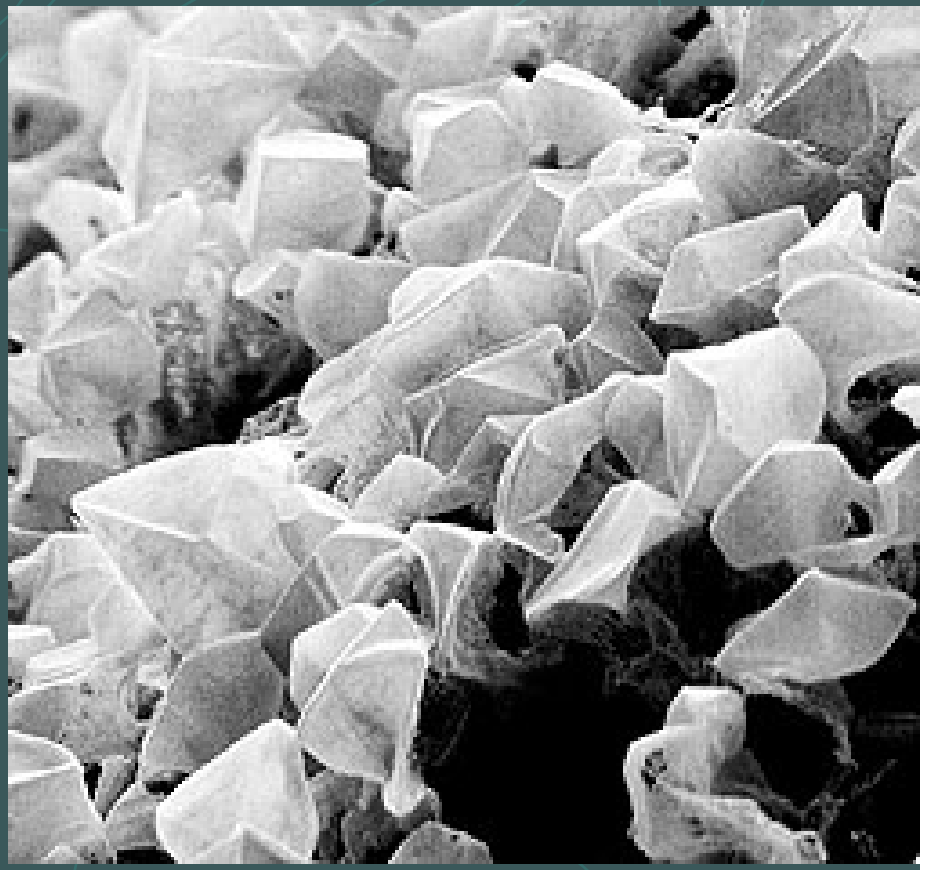
CO_2 from surface mines

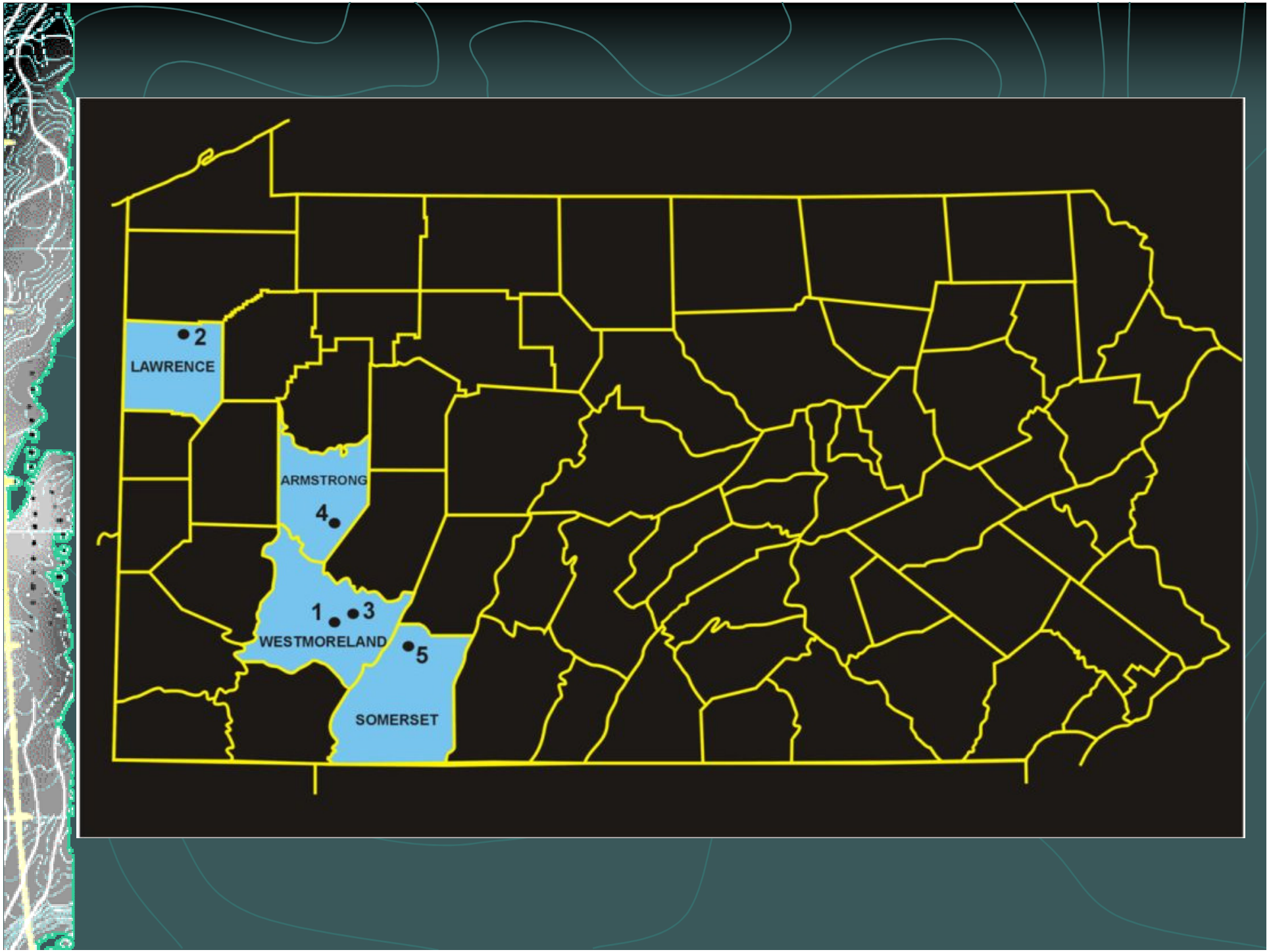
- Abandoned mines
- Reclaimed mines
- Active mines

CO2 contamination in western Pennsylvania

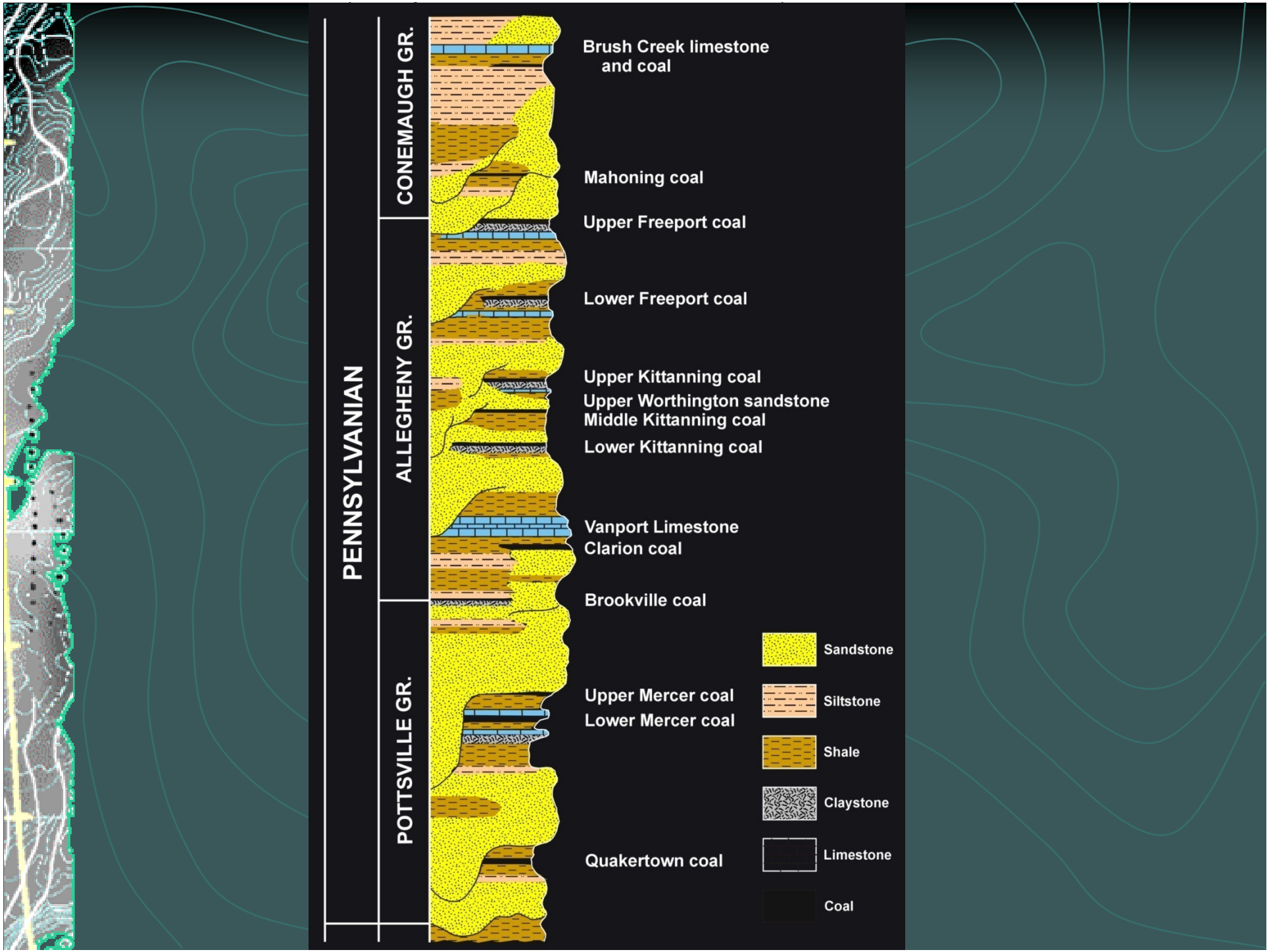


- Sources are not evident
- Utility of isotope geochemistry
- Impact on individuals and communities
- Potential problems with subsurface carbon sequestration



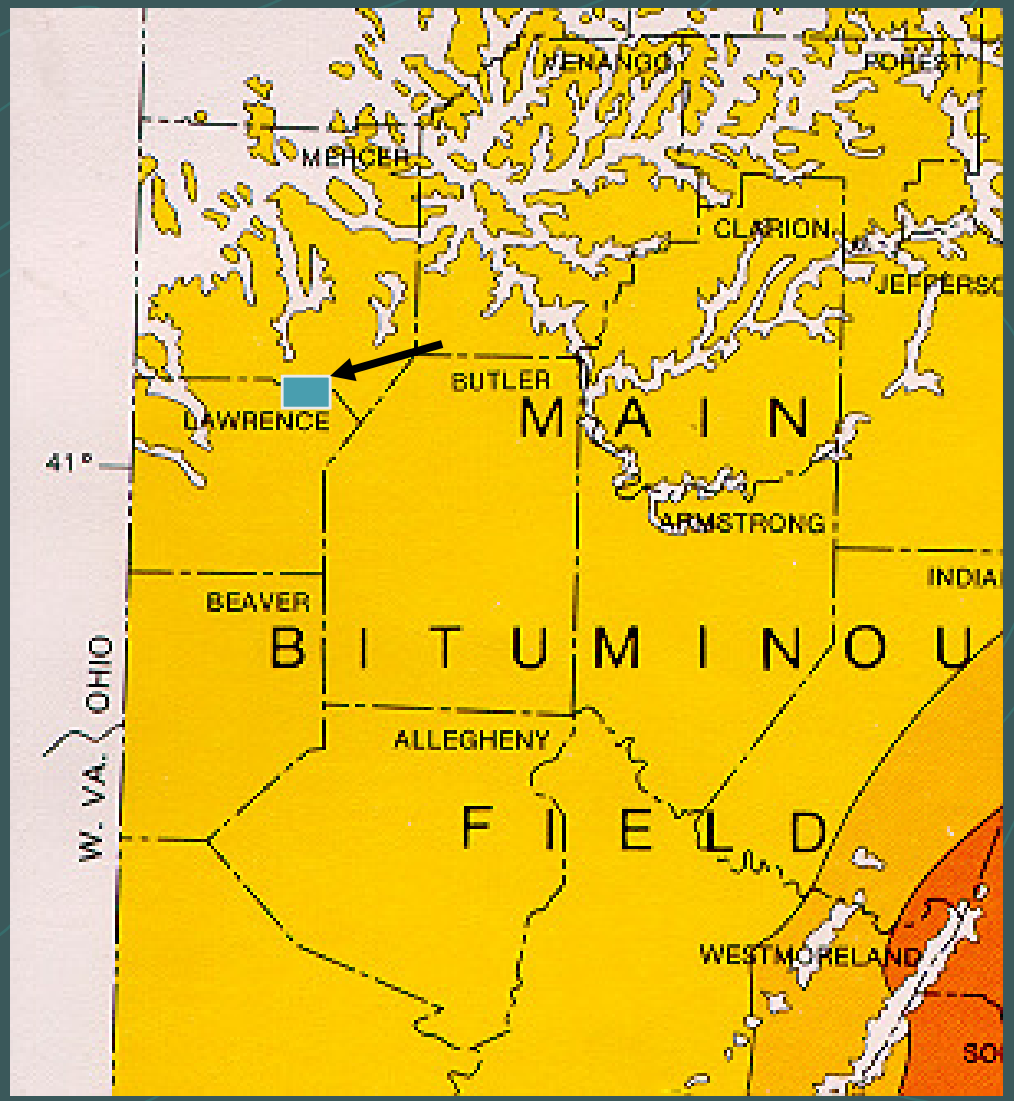

2
LAWRENCE
ARMSTRONG
4
1
3
WESTMORELAND
5
SOMERSET

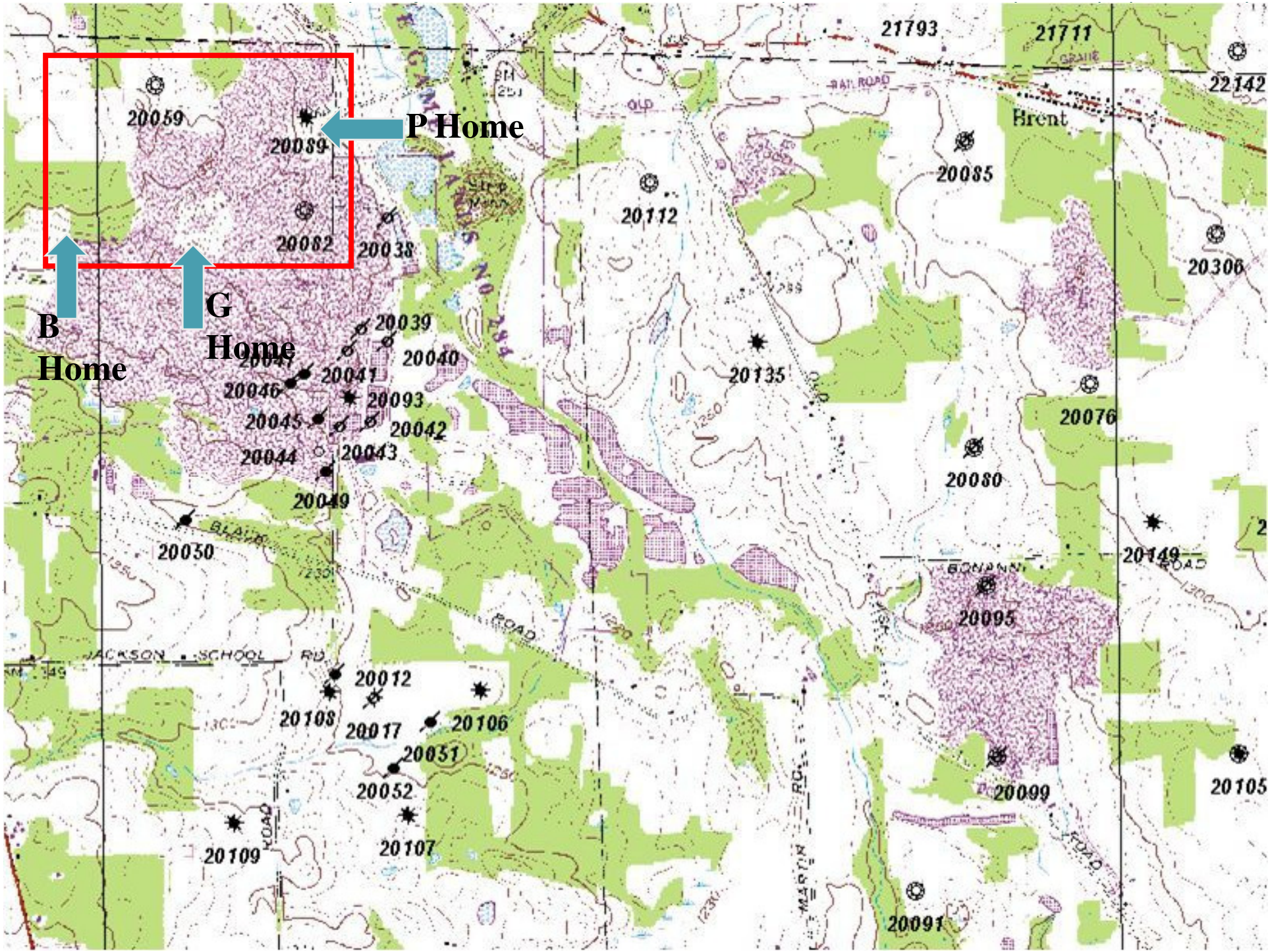
CO2 in basements, laundry rooms, game rooms


PENNSYLVANIAN
CONEMAUGH GR.
ALLEGHENY GR.
POTTSVILLE GR.
Brush Creek limestone and coal
Mahoning coal
Upper Freeport coal
Lower Freeport coal
Upper Kittanning coal
Upper Worthington sandstone
Middle Kittanning coal
Lower Kittanning coal
Vanport Limestone
Clarion coal
Brookville coal
Upper Mercer coal
Lower Mercer coal
Quakertown coal
Sandstone
Siltstone
Shale
Claystone
Limestone
Coal

Washington Township, northern Lawrence County

- Three homes
- CO_2 levels > 25% measured inside the homes
- Corresponding O_2 levels depressed as low as 10% inside the homes
- CO_2 levels >25% measured in monitoring wells around the homes
- *Low barometric pressure*
- AML funding

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B Home
G Home
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22142
Brent
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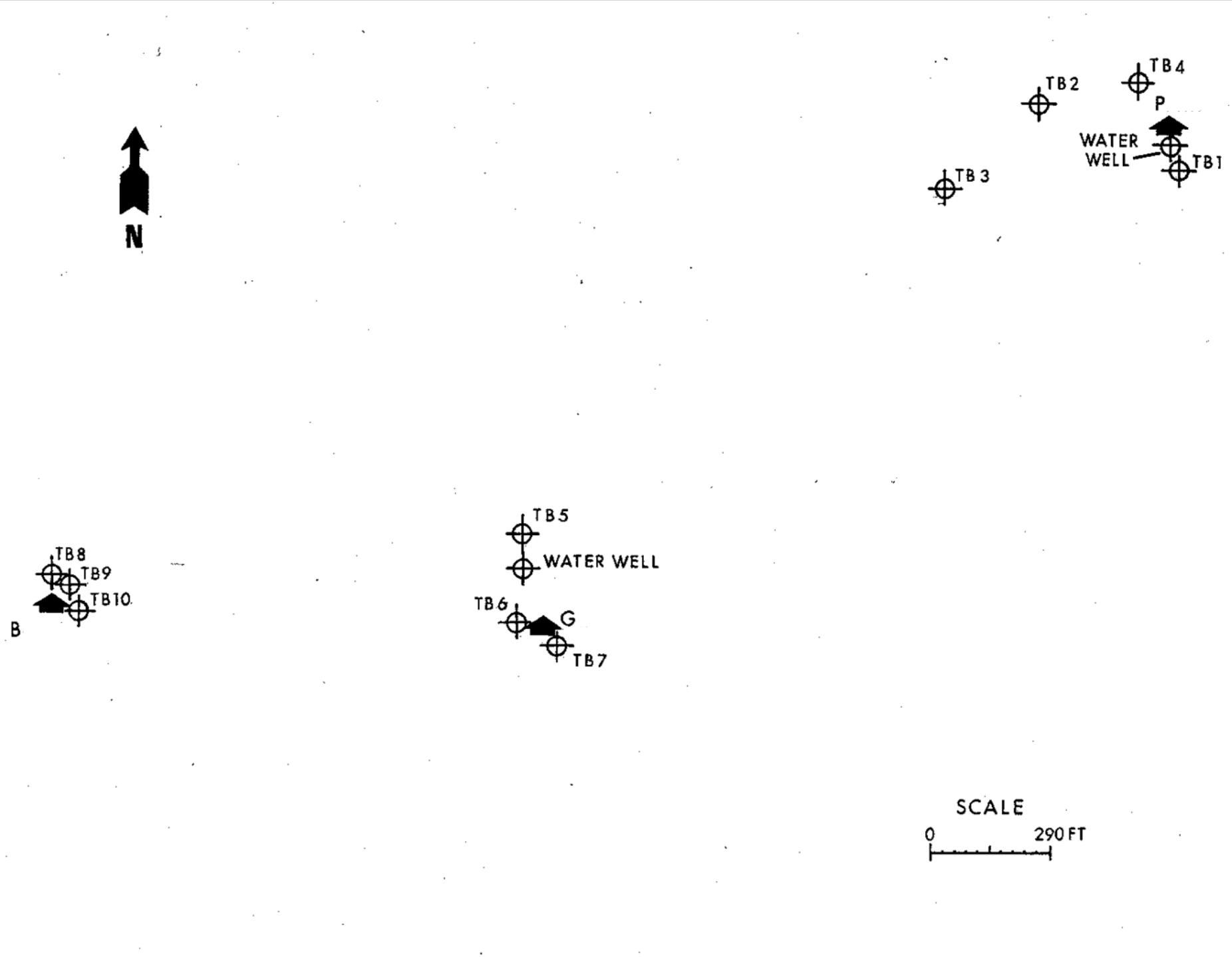
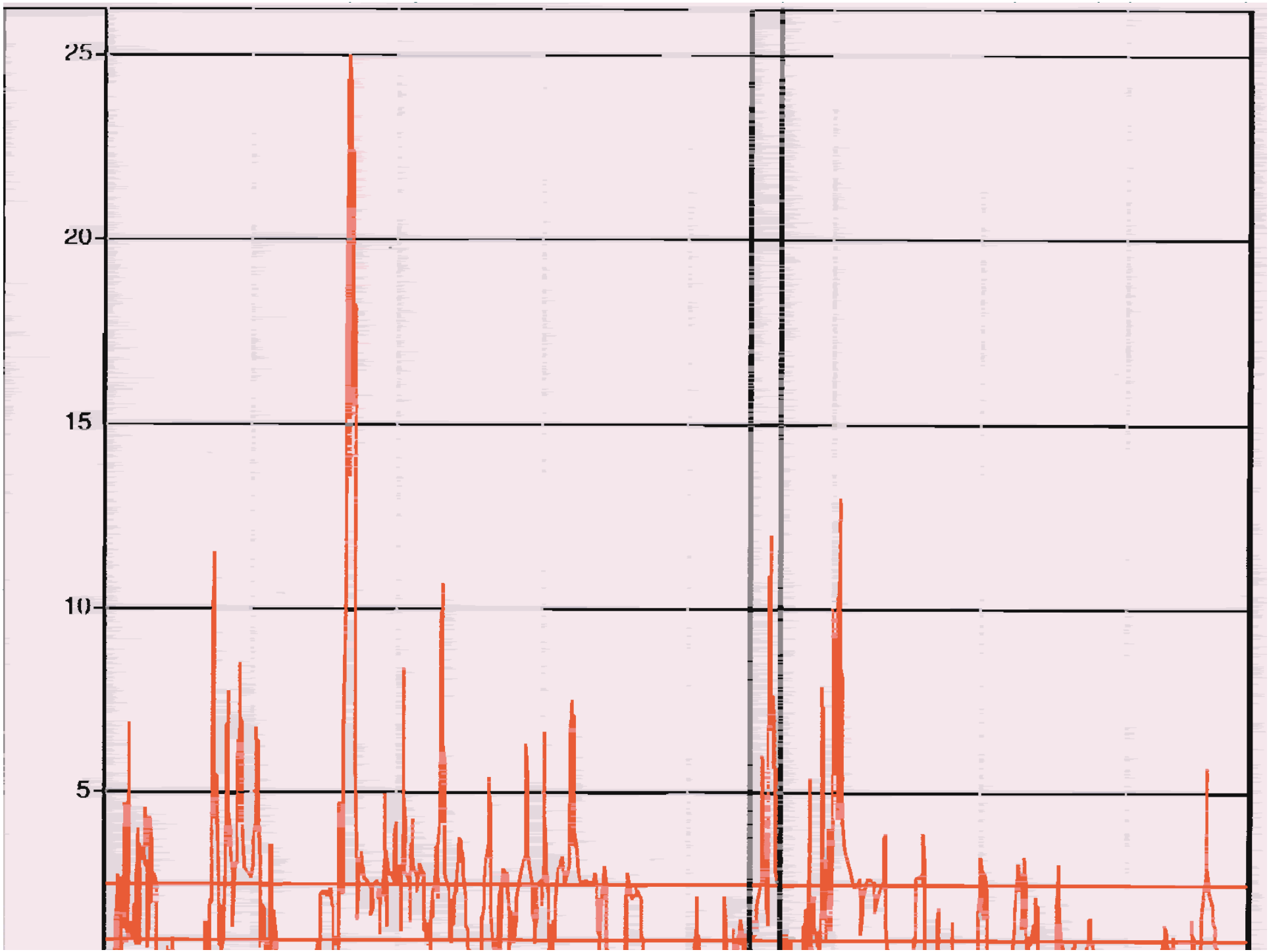
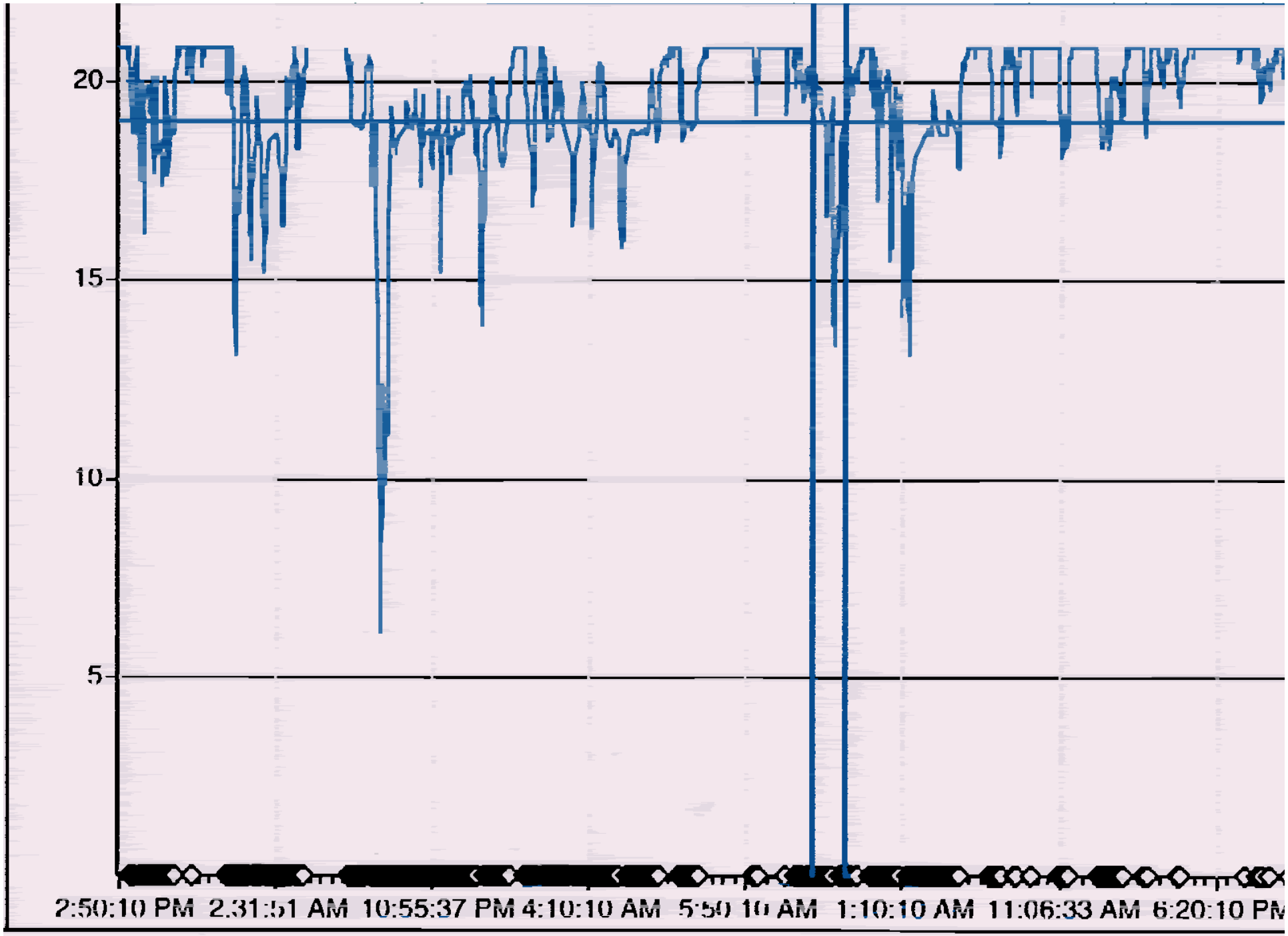
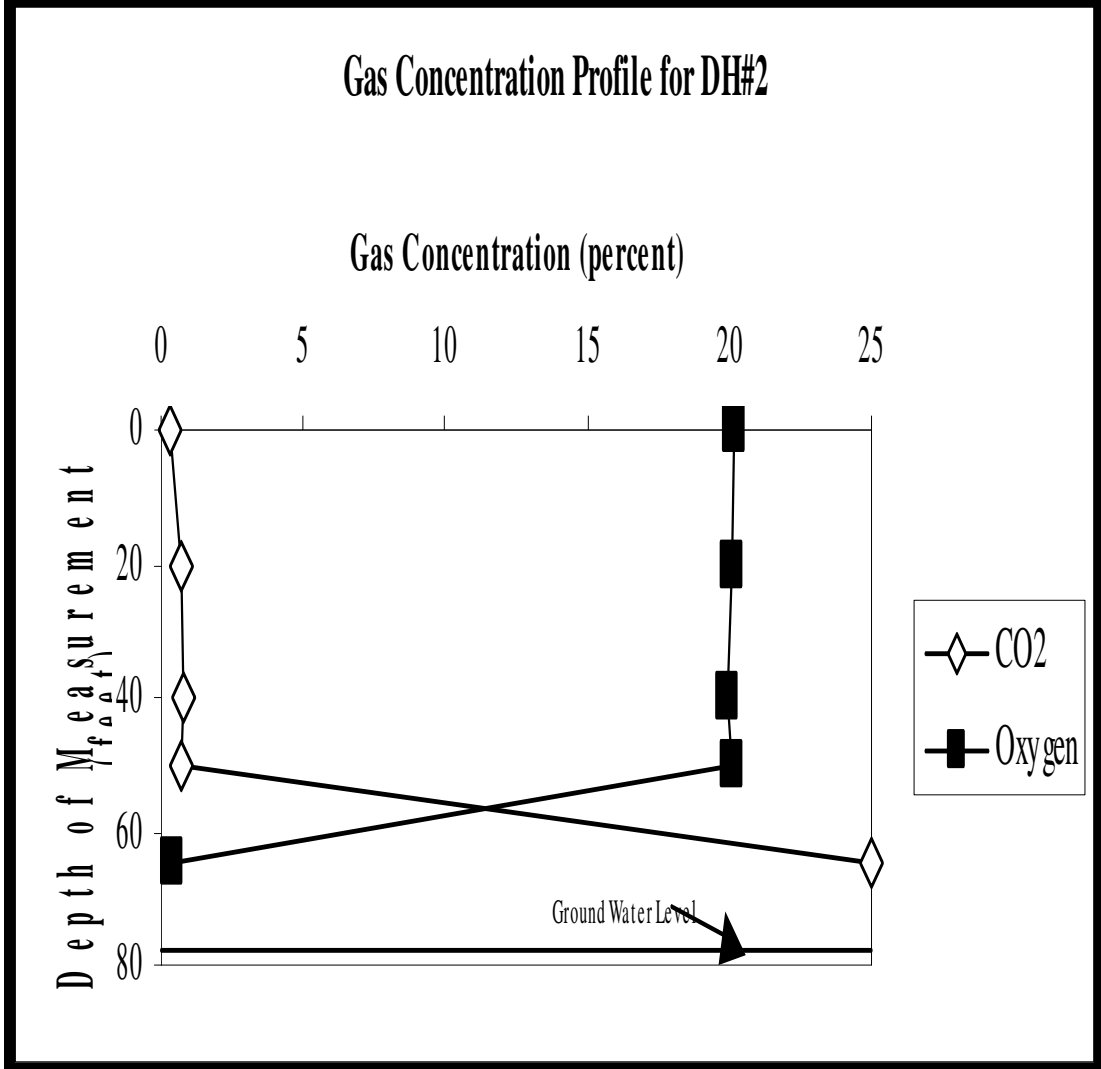
20105
20091
ROAD
JACKSON SCHOOL RD.
MARTIN RD.


N
TB2
TB4
P
WATER
WELL
TB1
TB3
TB5
WATER WELL
TB8
TB9
TB10
B
TB6
G
TB7
SCALE
0
290 FT


25
20
15
10
5


20
15
10
5
2:50:10 PM
2:31:51 AM
10:55:37 PM
4:10:10 AM
5:50:10 AM
1:10:10 AM
11:06:33 AM
6:20:10 PM

Monitoring Wells

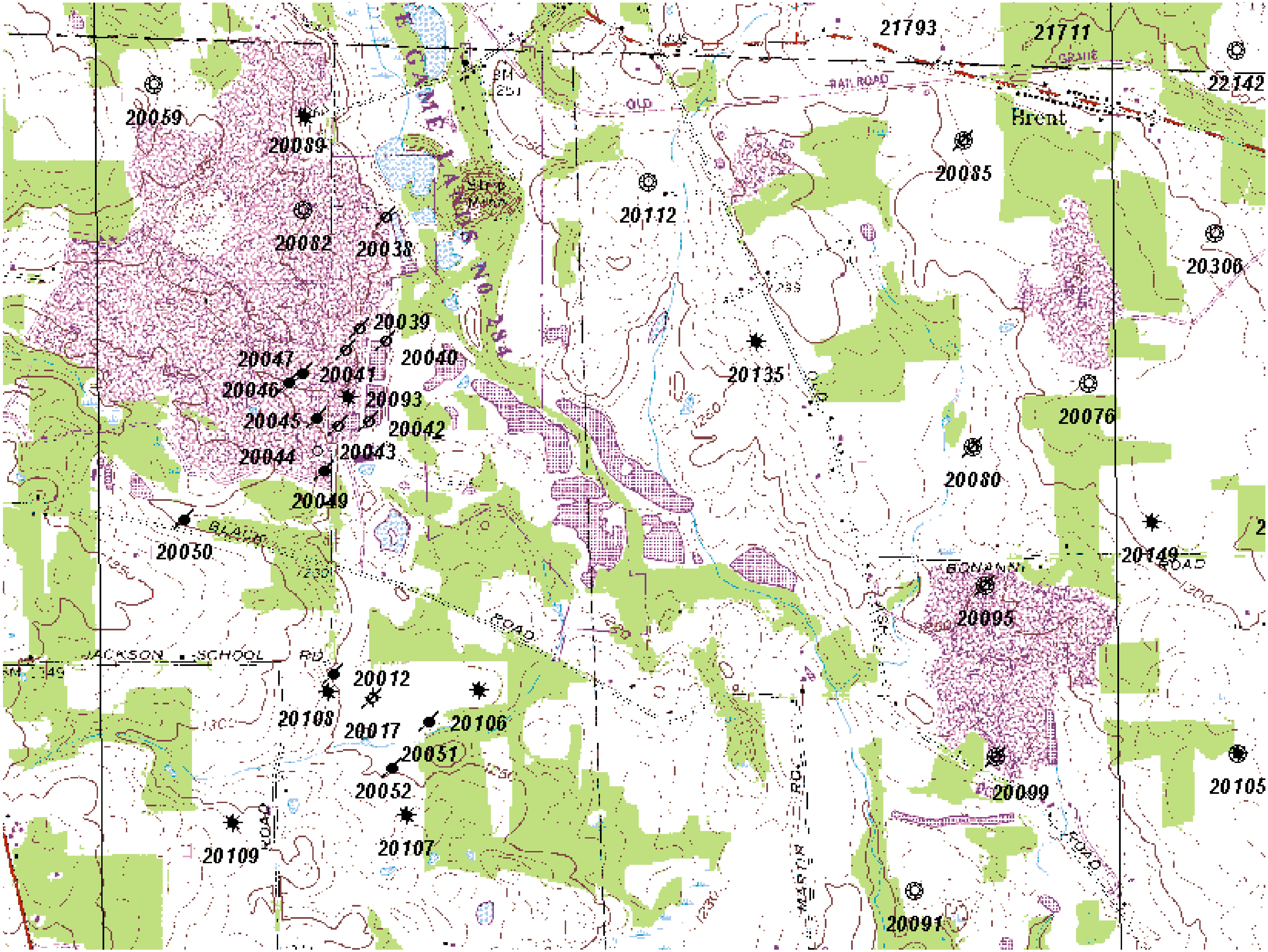


Lawrence County Potential CO_2 Contamination Sources

- Deep Mine
- Strip Mines
  - Spoil gas
- Oil and Gas Fields
- Marsh Gas
- Drift Gas
- Subsurface Geology
  - Carbonate rocks?
  - Caves?

Abandoned deep mine

- Brookville coal
- Completely flooded
- Abandoned mine drainage (AMD)
- Discharges up to 2.83 m^3/s (100 ft^3/s)
- Not a source of black damp



21793
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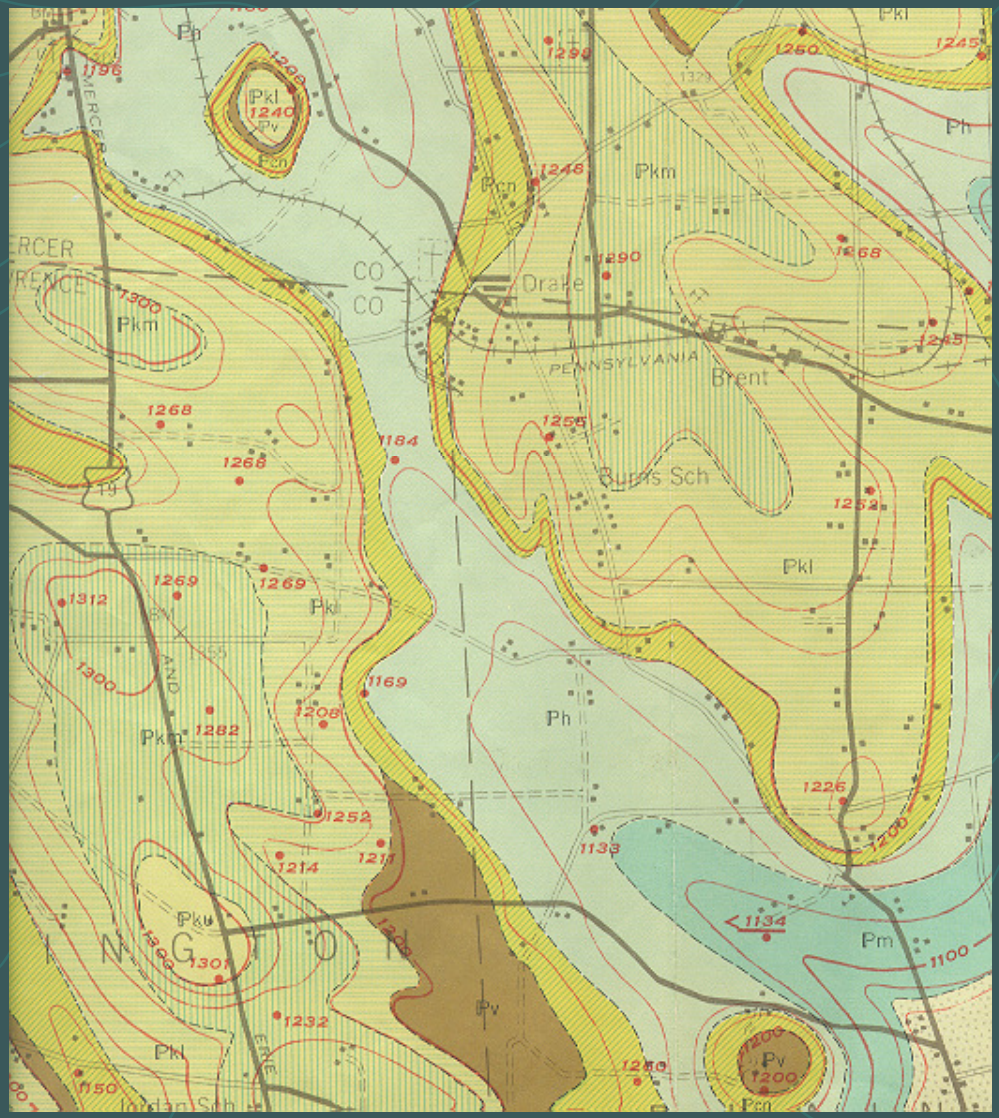
20099
20105
20109
20107
20091
Brent
GAME LANDS NO 284
RAILROAD
BLAINE
ROAD
JACKSON SCHOOL RD
BONANNI ROAD
MARTIN RD

Bedrock Geology

- Allegheny Group
  - Vanport Limestone
    - Cut out by channel ss of the Kittanning Fm in the study location
- Highly fractured bedrock (affects groundwater levels and gas migration)

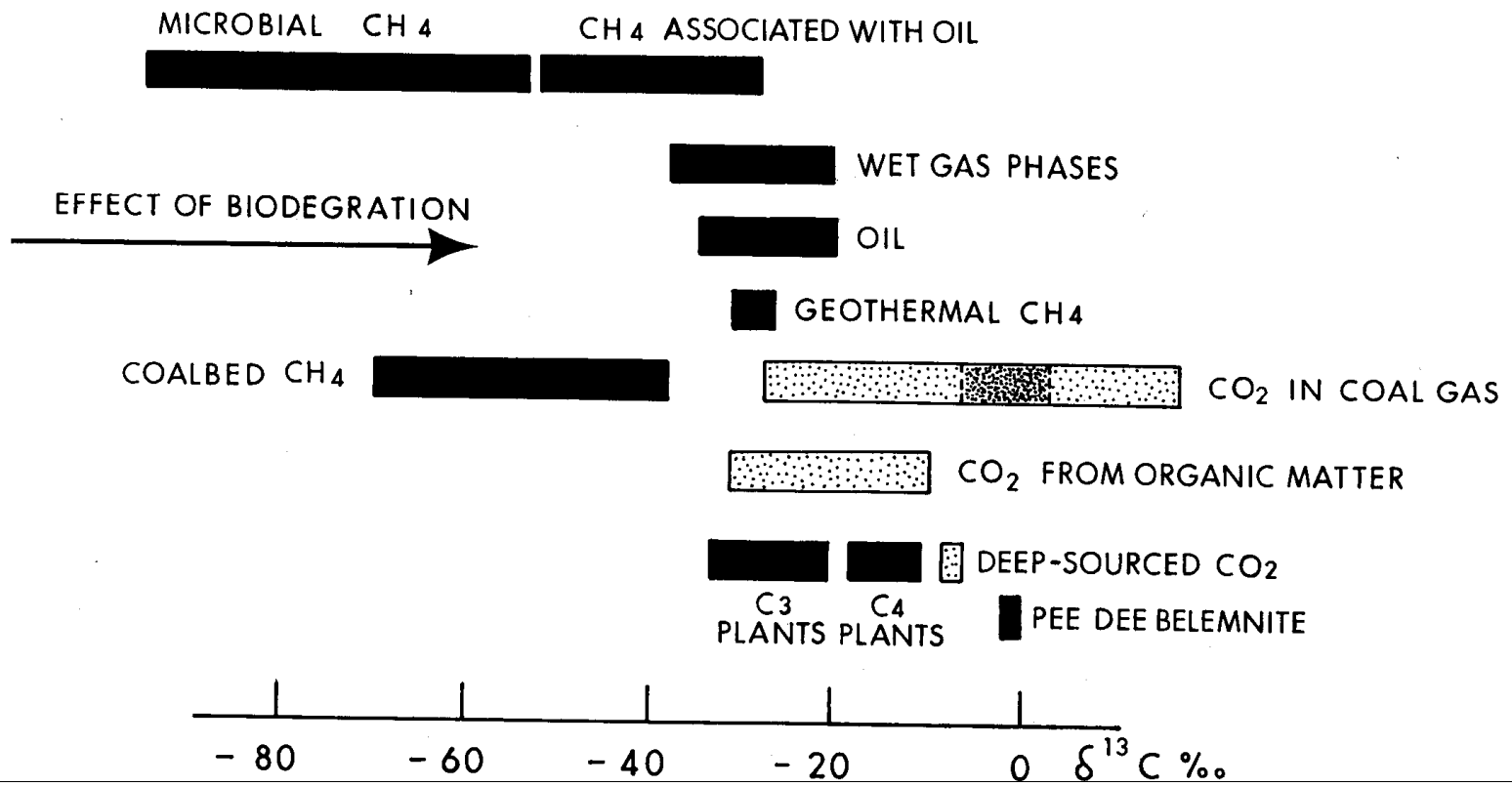


Stable Isotope Geochemistry

$$\partial\ ^{13}CO_2 = R_{sample} - R_{standard} / R_{standard} * 1000$$

- Isotopic ranges of natural gases are large in range, specific, predictable, and capable of providing diagnostic information on their source.
- Differences in isotopic mass lead to subtle but significant differences in the behavior of an element during natural processes (*fractionation*)

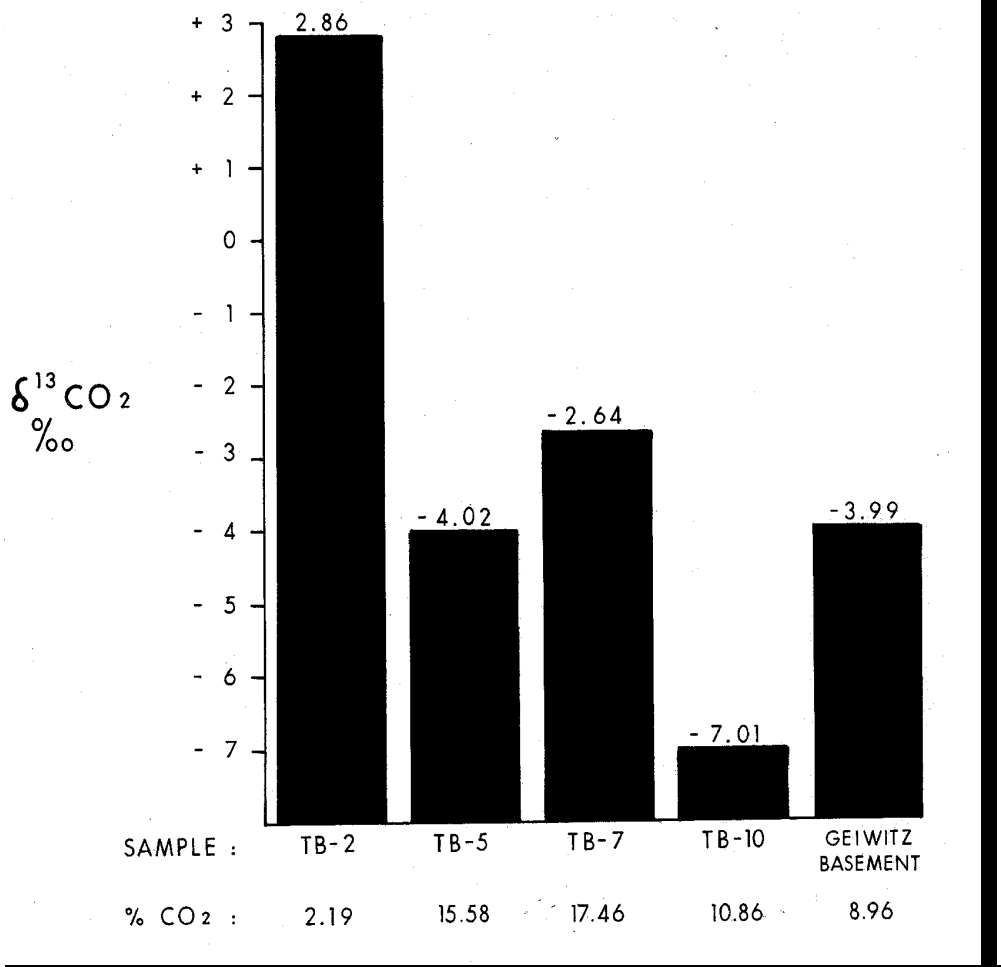
- Carbon
  - Highly oxidized compounds (CO_2)
  - Highly reduced organic compounds
  - Isotope equilibrium exchange reactions – enrichment of ^{13}C in carbonate rocks
  - Kinetic isotope effects during photosynthesis – concentrate ^{12}C in organic matter

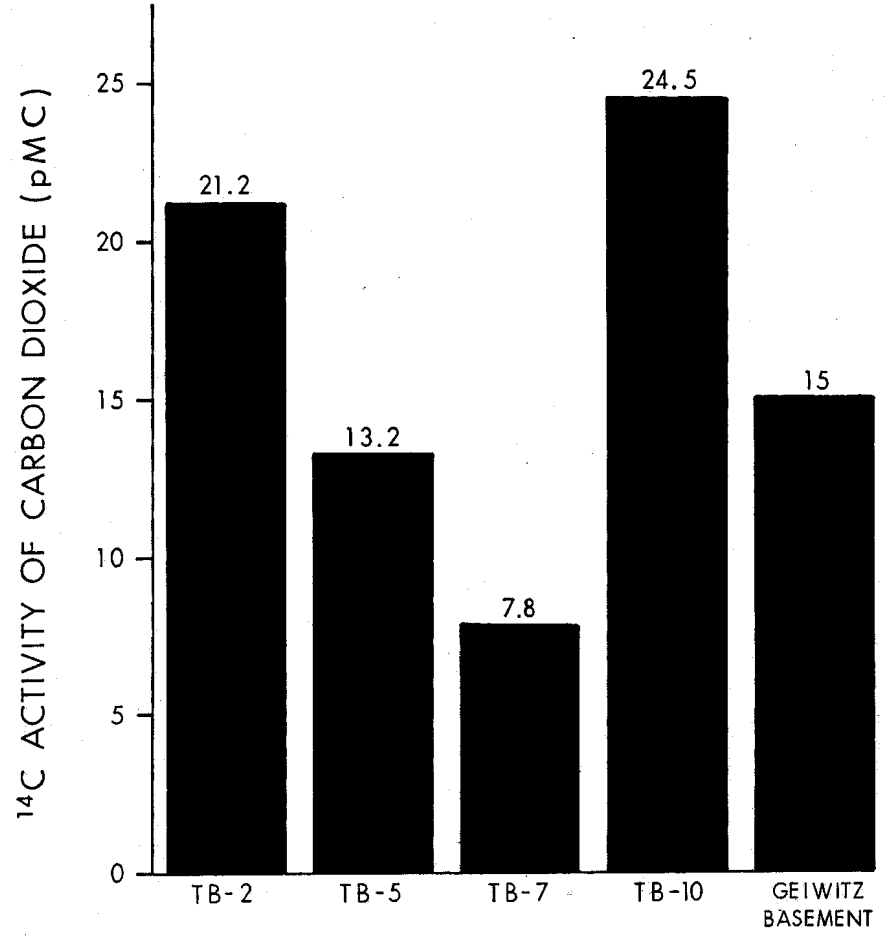

MICROBIAL CH4
CH4 ASSOCIATED WITH OIL
WET GAS PHASES
EFFECT OF BIODEGRATION
OIL
GEOTHERMAL CH4
COALBED CH4
CO2 IN COAL GAS
CO2 FROM ORGANIC MATTER
DEEP-SOURCED CO2
C3 PLANTS
C4 PLANTS
PEE DEE BELEMNITE
- 80
- 60
- 40
- 20
0
δ13C ‰

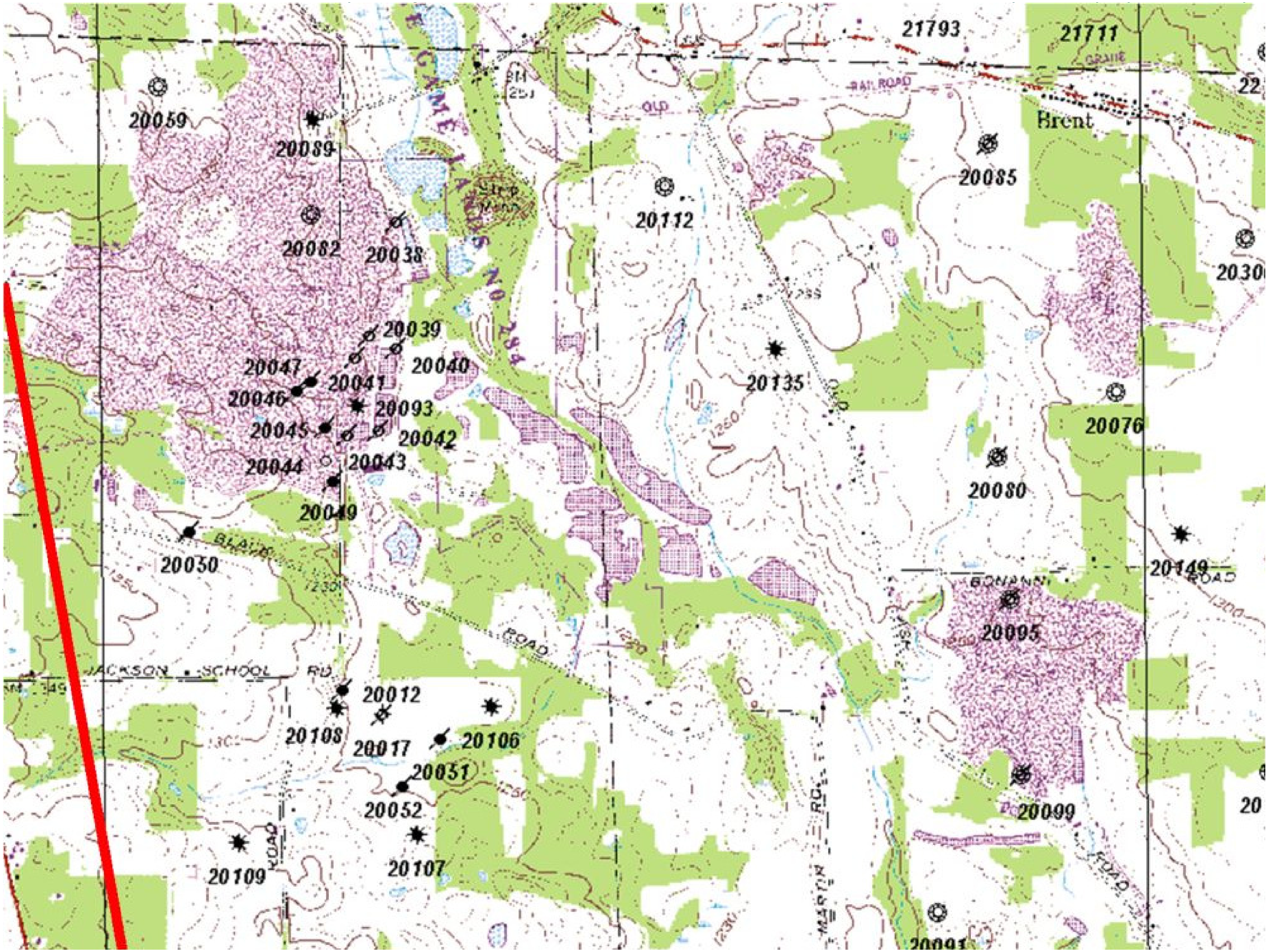
^{14}C Activity of CO_2

- Atmospheric testing of nuclear devices in the 1950's and 1960's produced substantial amounts of ^{14}C-enriched CO_2.
- All plant or animal material that has grown since approximately 1960 has ^{14}C concentrations above natural levels.
- This ^{14}C concentration can be used as a tracer for microbial gas.
  - ^{14}C activity 30 – 150 percent modern carbon (pMC)
  - 100 pMC defined as natural (equilibrium) pre-bomb ^{14}C concentration of atmospheric CO_2

Isotope Geochemistry Data






21793
21711
Brent
RAILROAD
OLD
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20046
20093
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BLAIR
20149
ROAD
BONANNI
20095
JACKSON SCHOOL RD.
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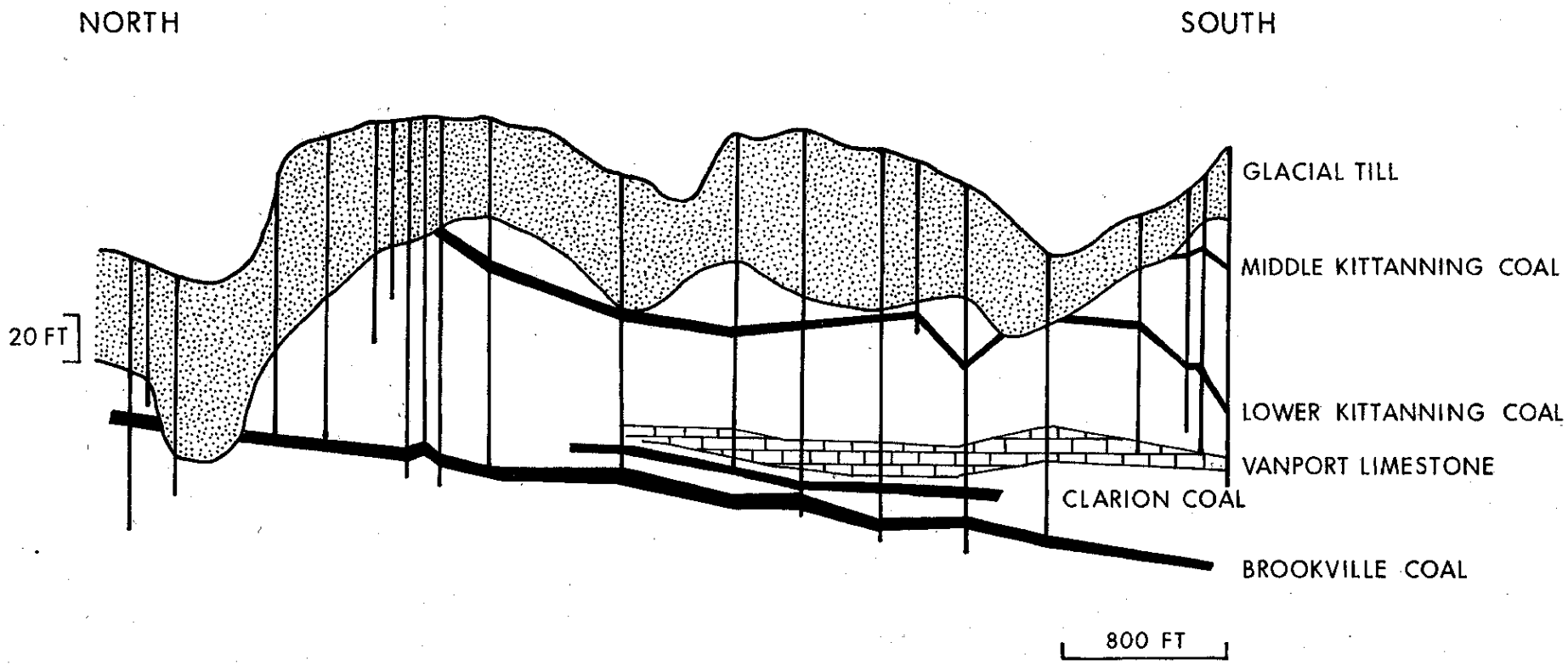
ROAD
MARTIN RD.
ROAD
20091


NORTH
SOUTH
20 FT
GLACIAL TILL
MIDDLE KITTANNING COAL
LOWER KITTANNING COAL
VANPORT LIMESTONE
CLARION COAL
BROOKVILLE COAL
800 FT
GLACIAL TILL
COAL
SANDSTONE AND SHALE
LIMESTONE

Carbonate Source?

- No Vanport Limestone beneath the study area
- Other bedrock units lack carbonate minerals
- Glacial till contains 4 – 8% $CaCO_3$
- Glacial till was used as fill (high neutralization potential)

Groundwater Chemistry

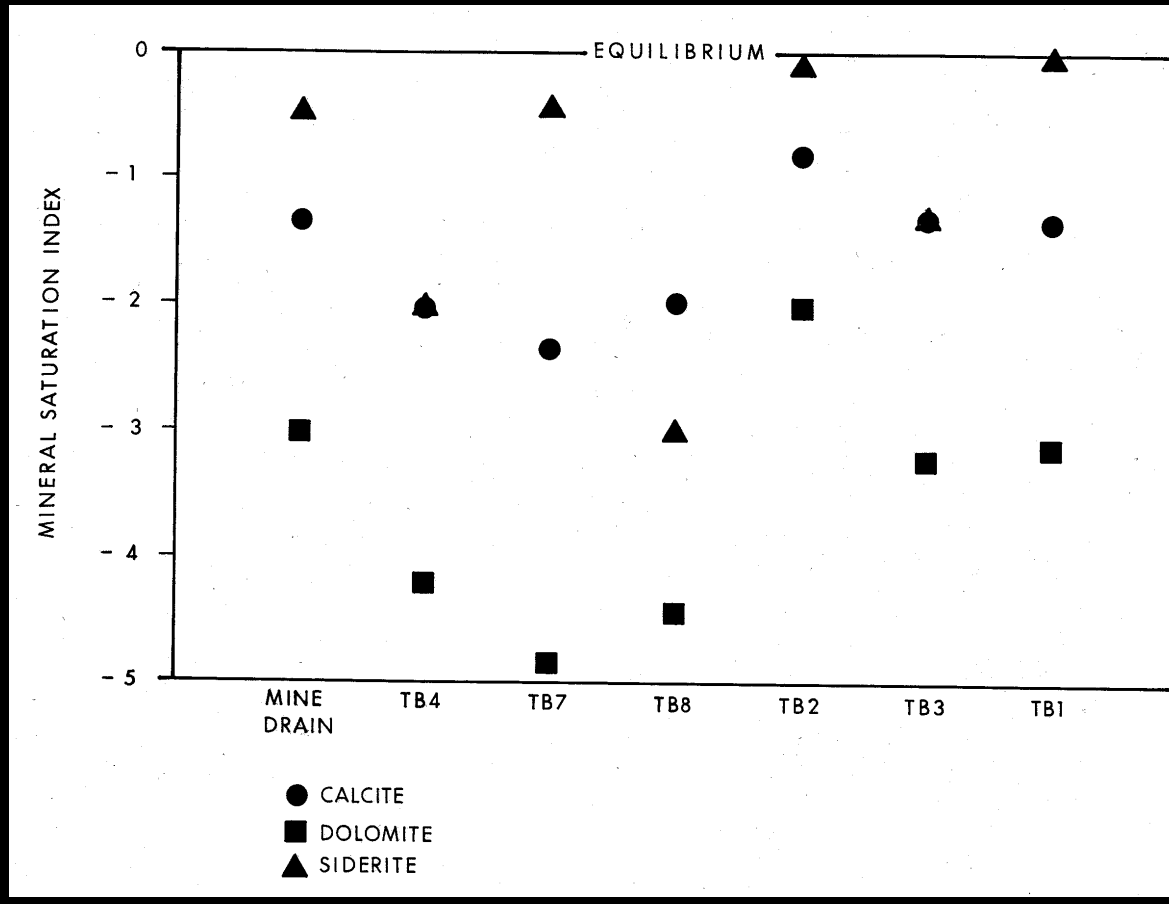
The groundwater onsite is under saturated with respect to calcite and dolomite. Groundwater can react with reported carbonate in the fill to produce the observed volumes of CO_2.

Alkalinity: 31.36 – 136.84 mg/l

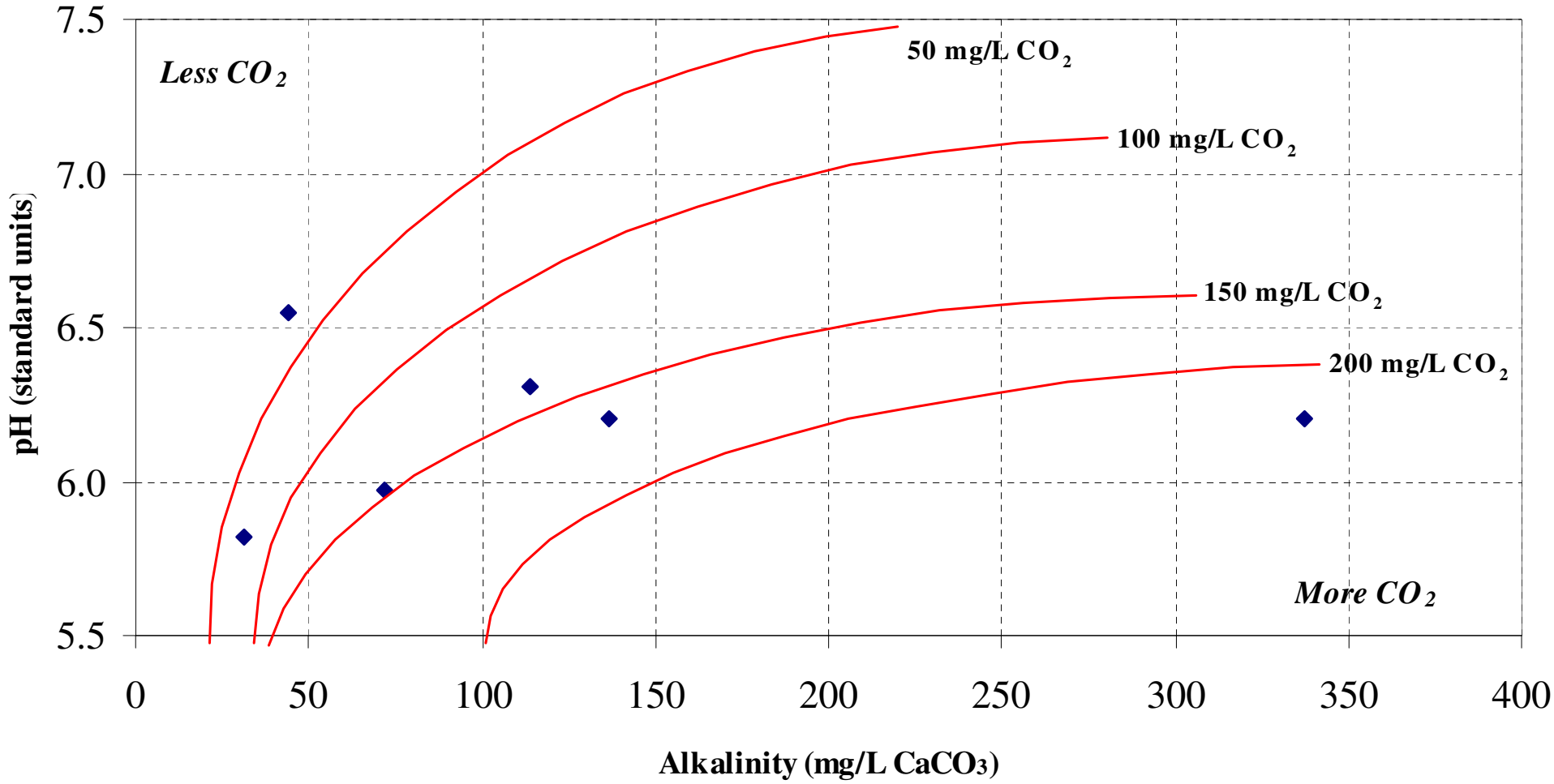
pH: 5.82 – 6.55

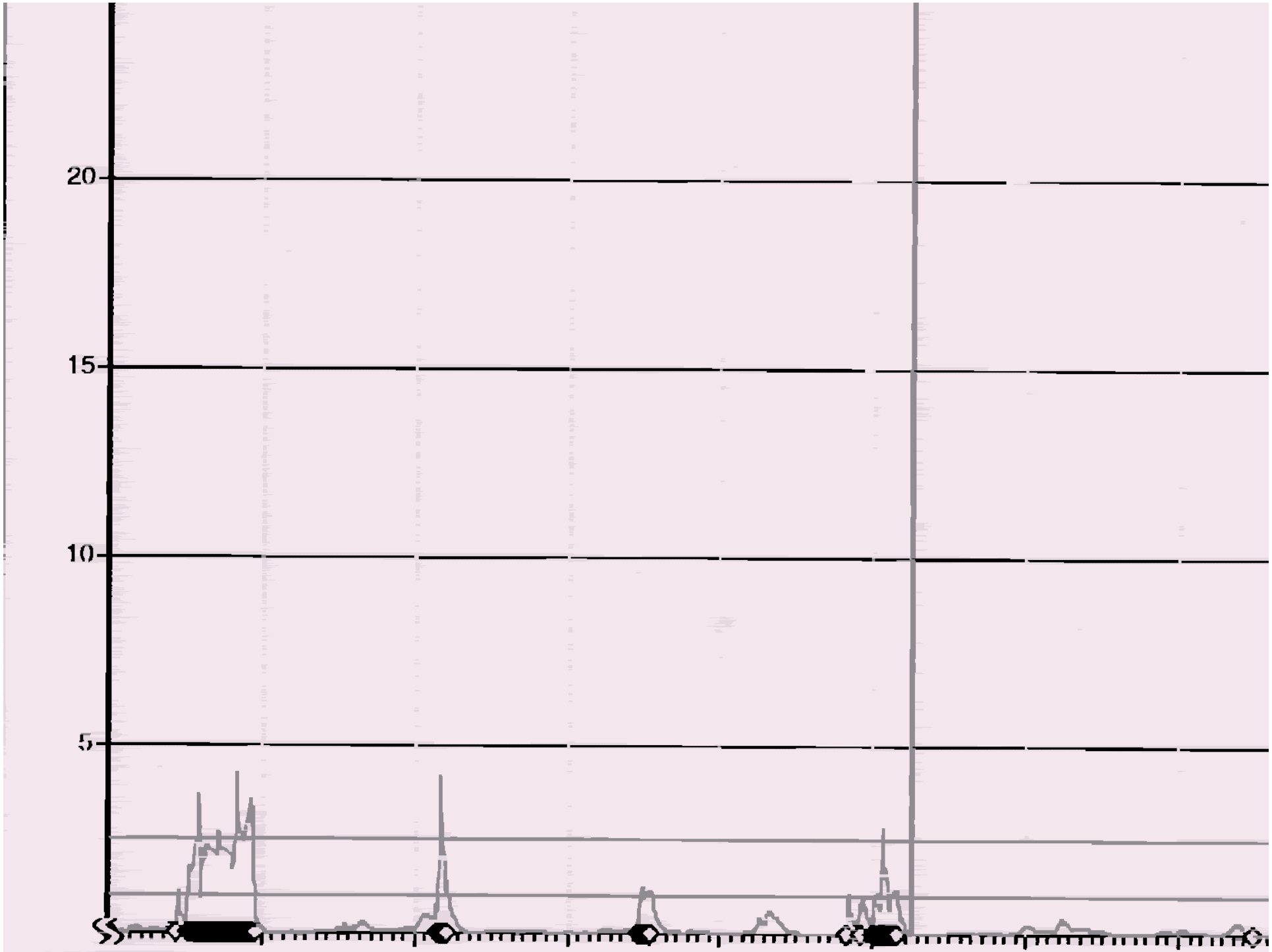
PCO_2: 0.01 – 0.2 atm; groundwater PCO_2 ranged from 0.5 - 0.2 atm during low barometric pressure events.

Local pockets of tipple refuse in fill allow areas of more acidic water and enhance carbonate dissolution.



Carbon Dioxide Concentrations at Varying pH and Alkalinity Values

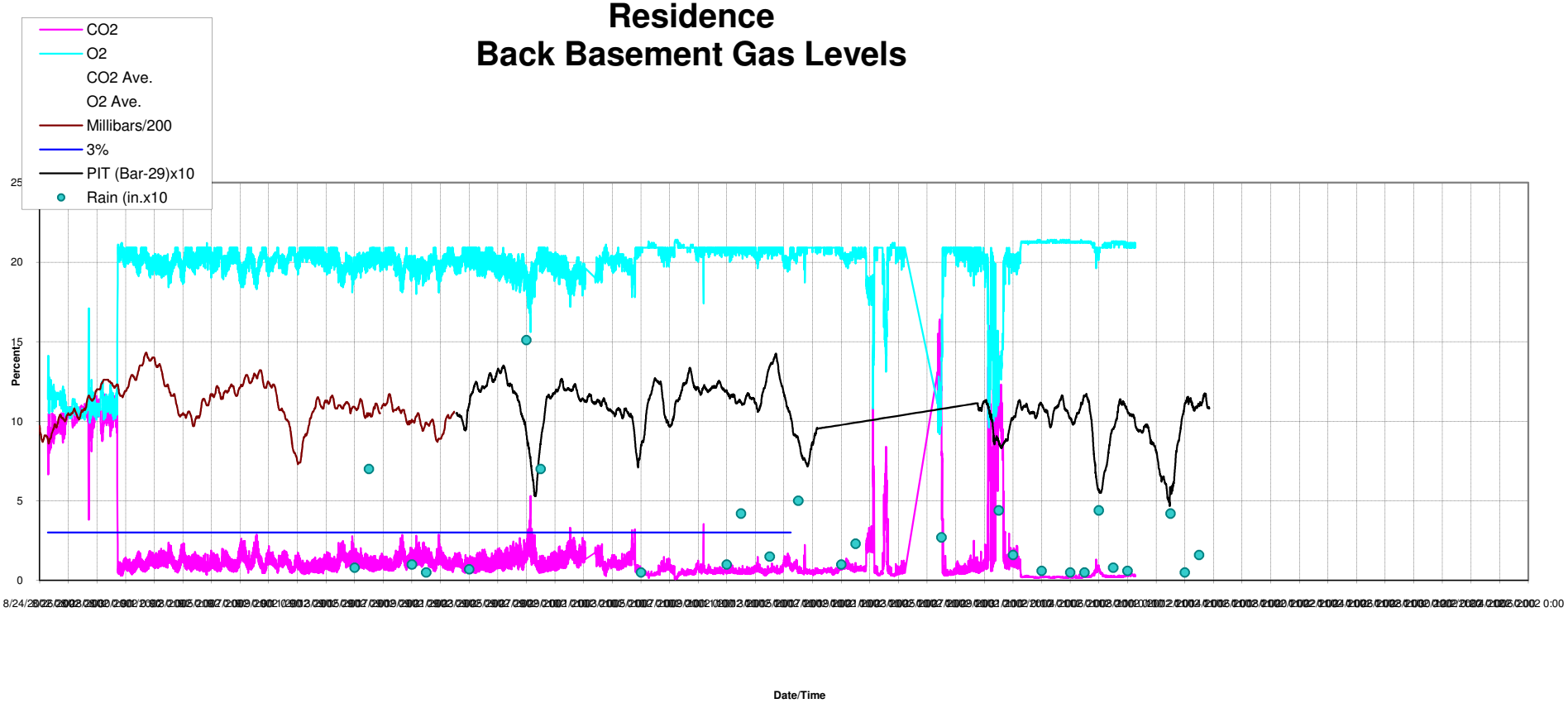


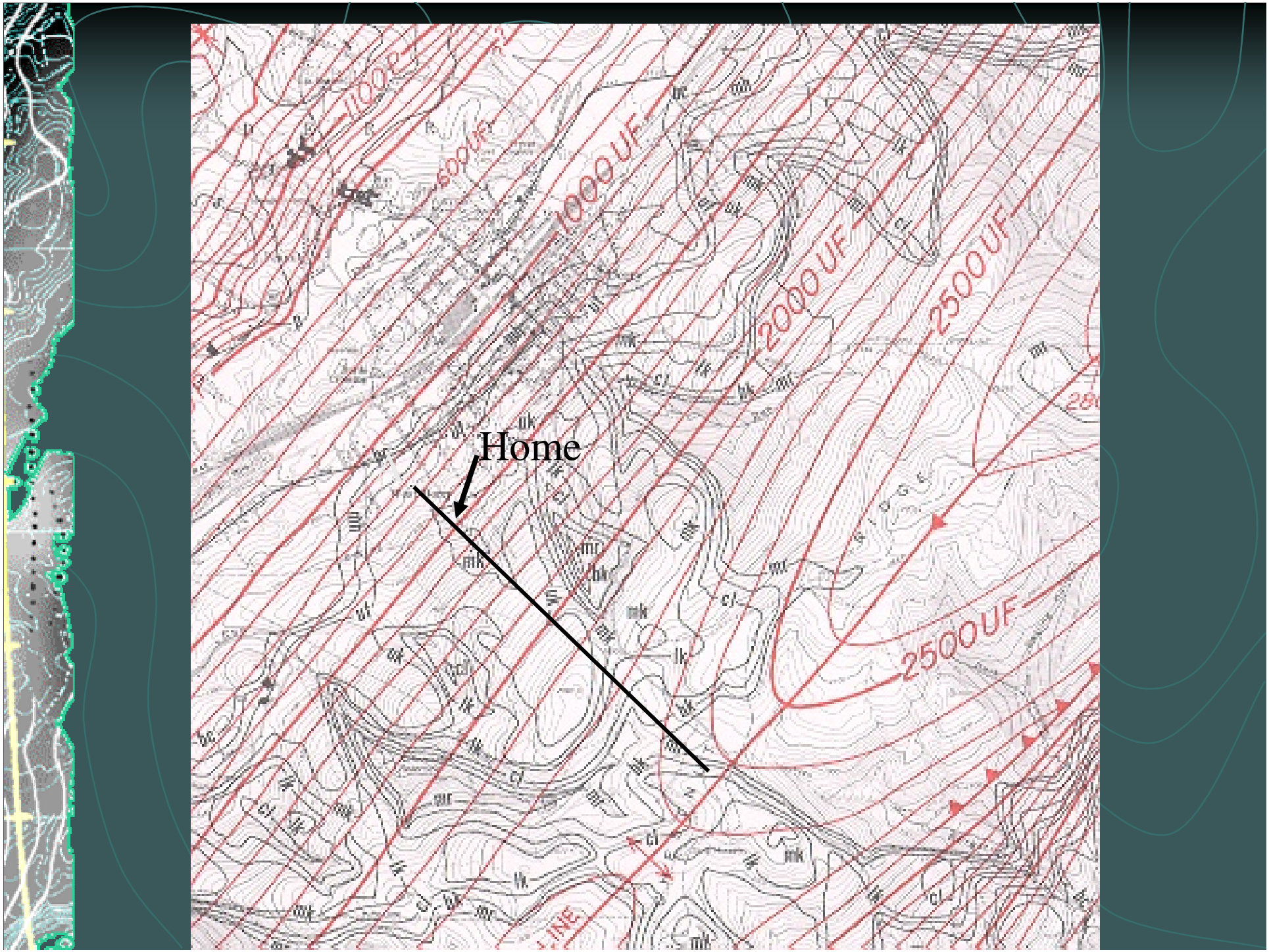

20
15
10
5

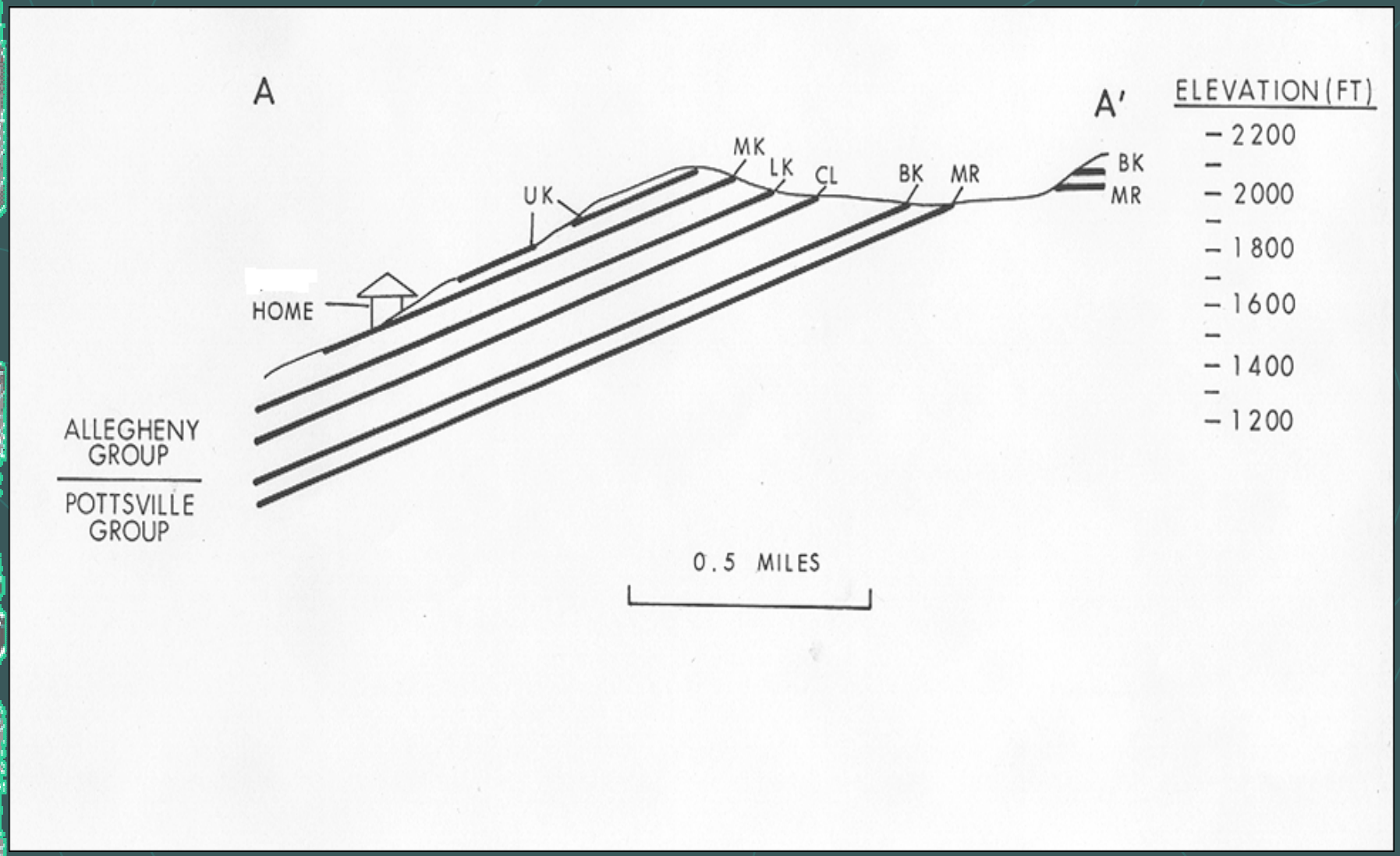
Westmoreland County, Pennsylvania

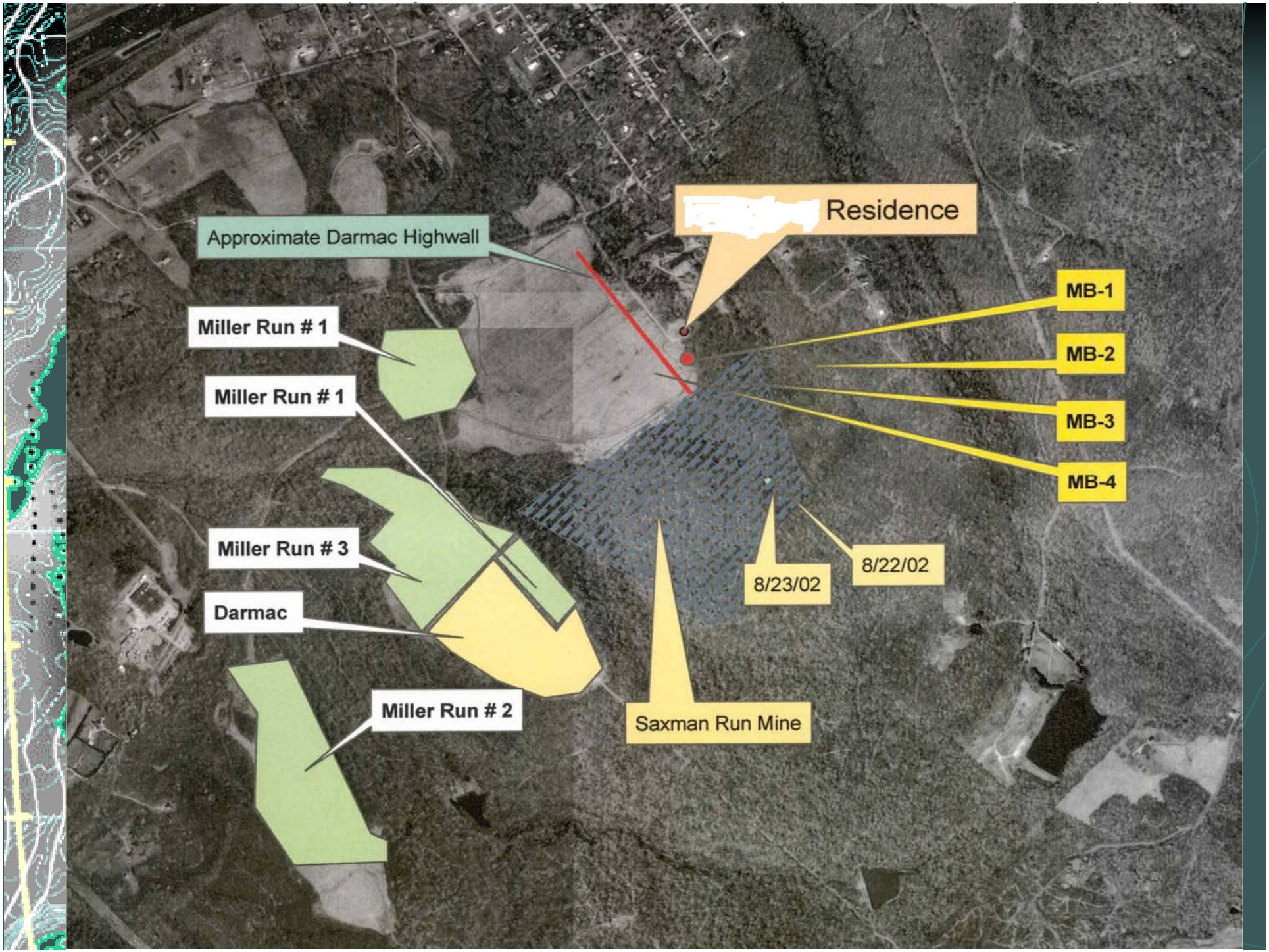
- August 2002: Family members experienced serious symptoms of CO_2 toxicity.
- CO_2 levels as high as 10%
- O_2 levels as low as 15%

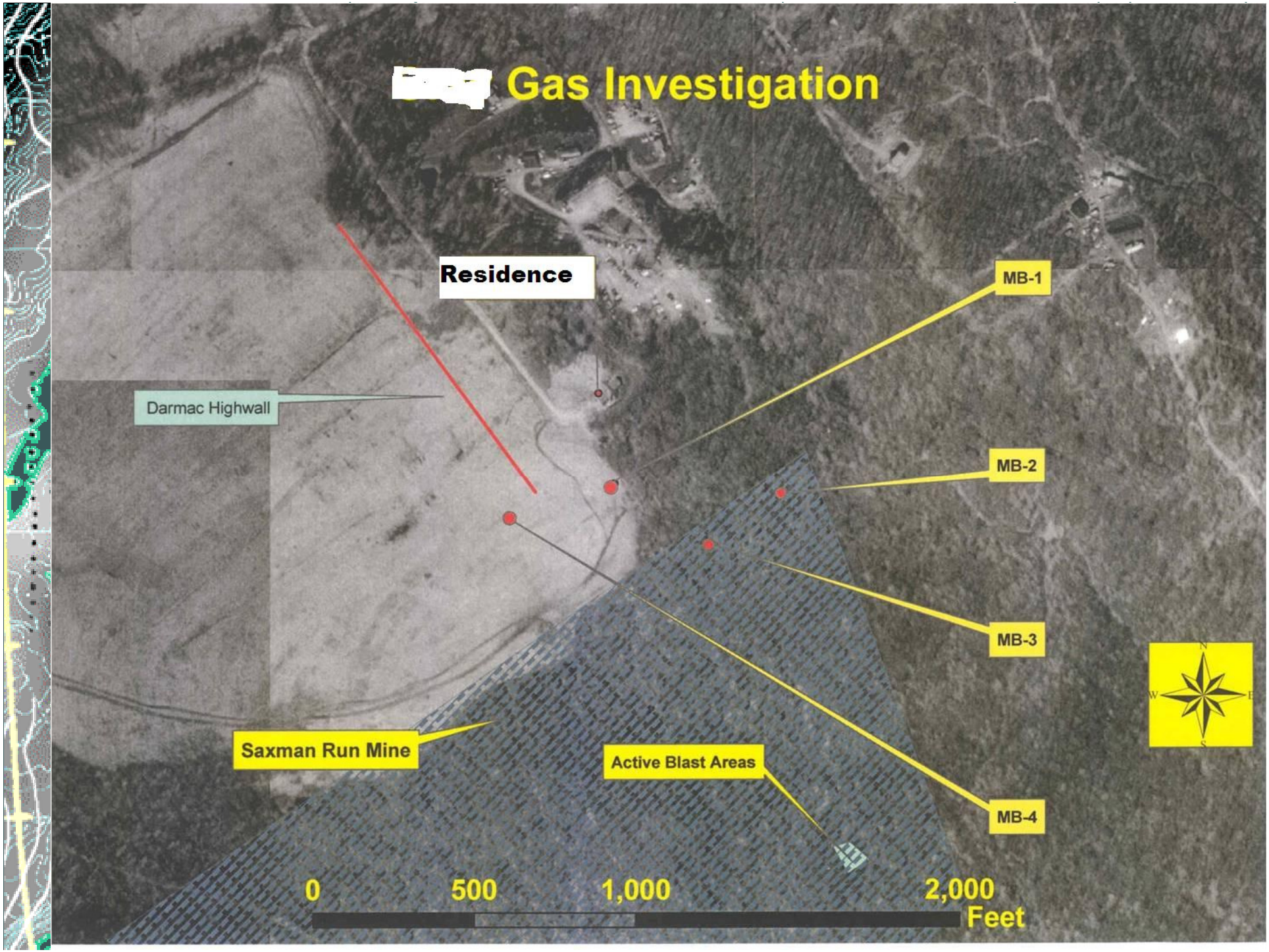
Residence
Back Basement Gas Levels

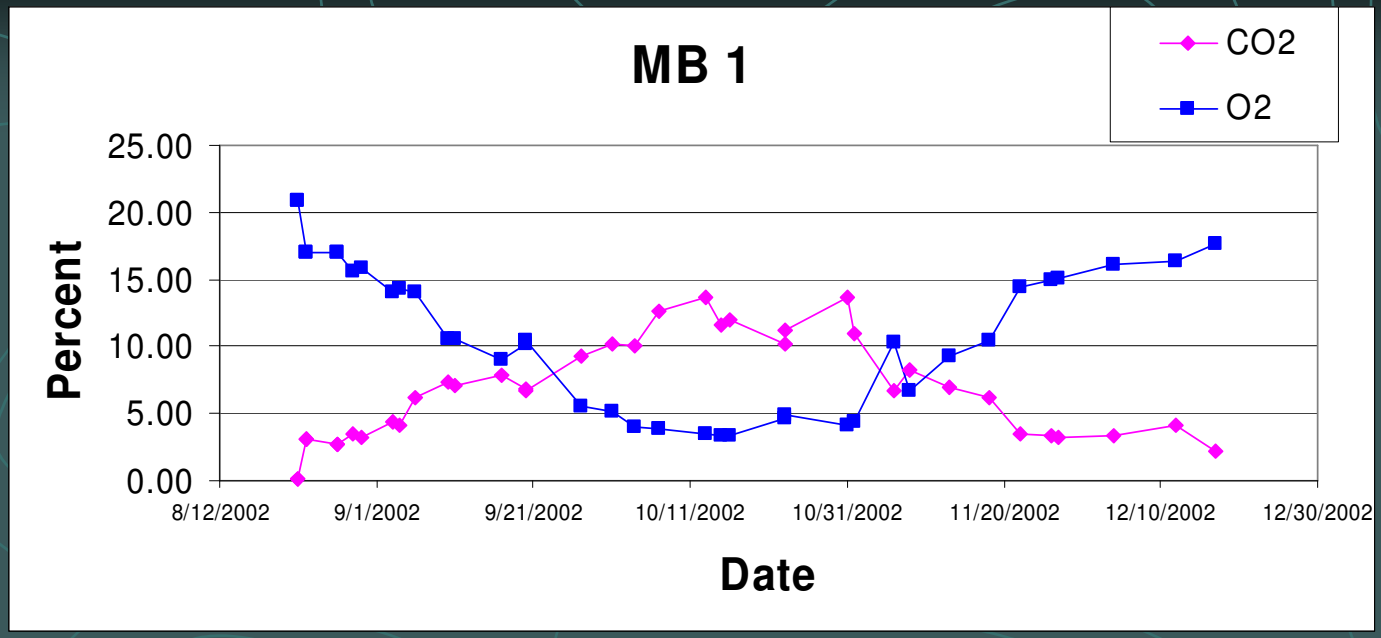


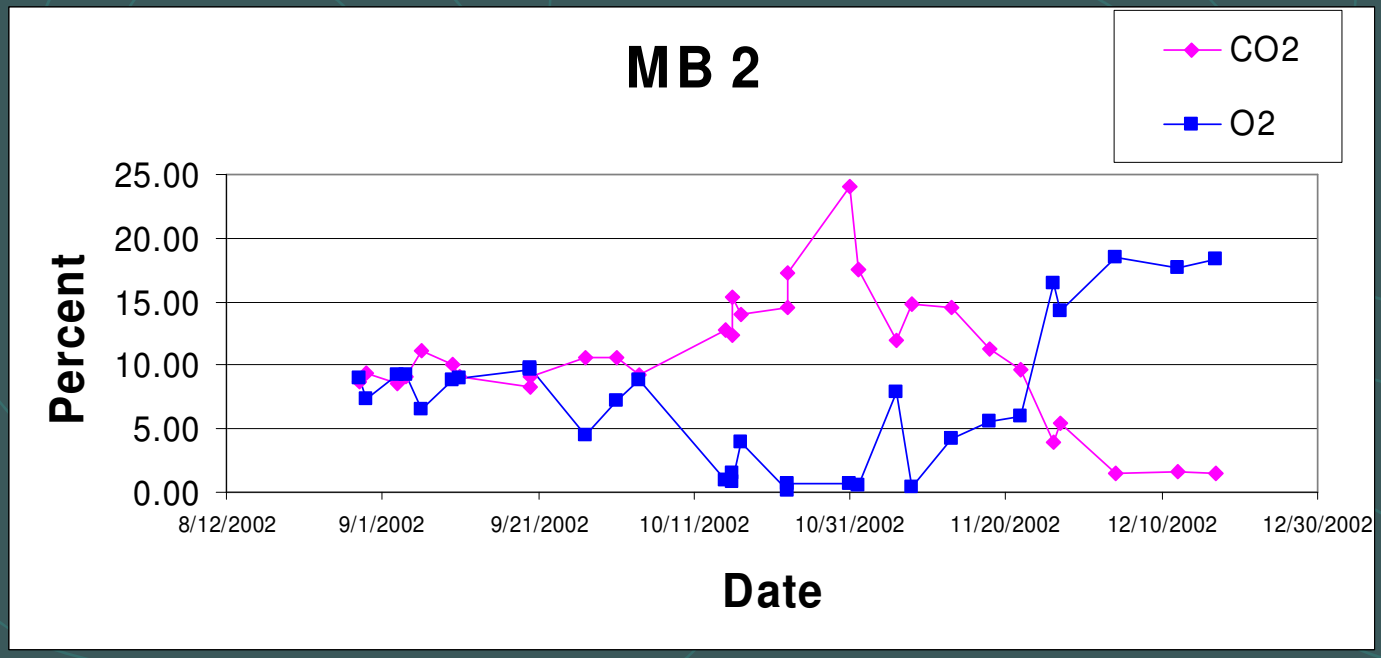

Home
1000 UF
2000 UF
2500 UF
2500UF

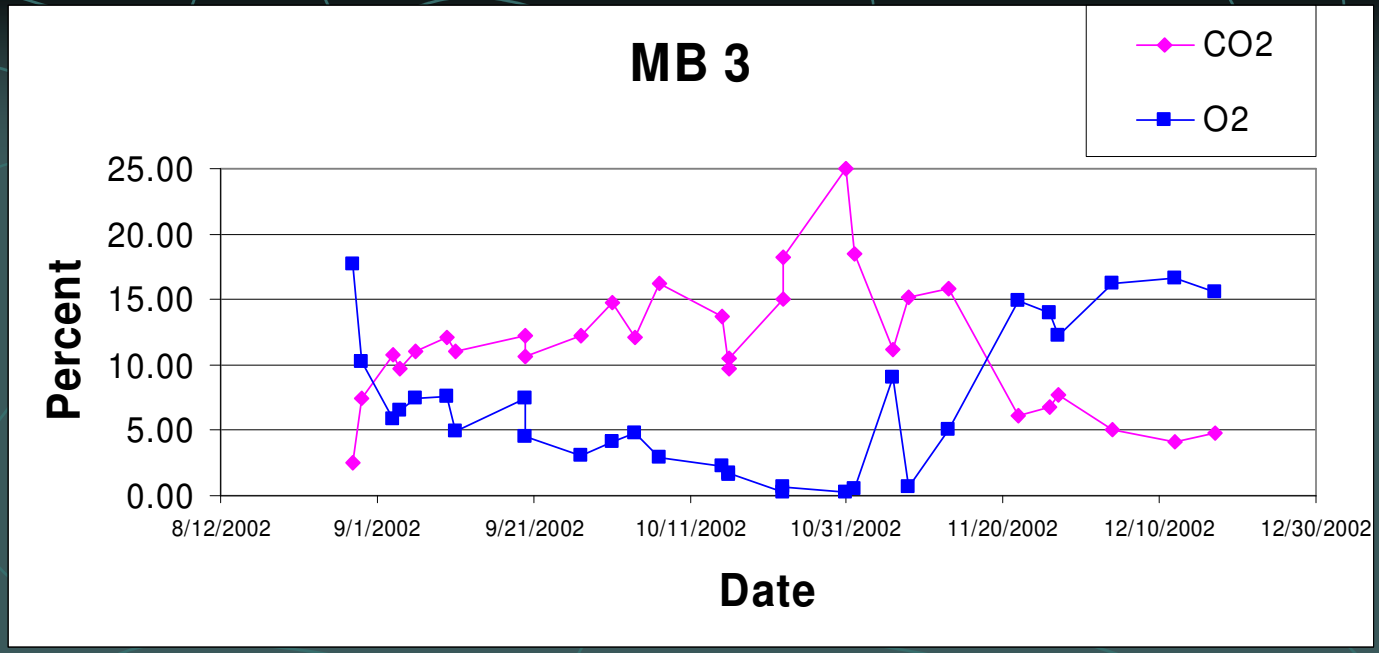

A
A'
ELEVATION (FT)
2200
2000
1800
1600
1400
1200
MK
LK
CL
BK
MR
UK
BK
MR
HOME
ALLEGHENY GROUP
POTTSVILLE GROUP
0.5 MILES


Approximate Darmac Highwall
Residence
MB-1
MB-2
MB-3
MB-4
Miller Run # 1
Miller Run # 1
Miller Run # 3
Darmac
Miller Run # 2
8/23/02
8/22/02
Saxman Run Mine


[redacted] Gas Investigation
Residence
MB-1
Darmac Highwall
MB-2
MB-3
Saxman Run Mine
Active Blast Areas
MB-4
0
500
1,000
2,000
Feet


MB 1
CO2
O2
25.00
20.00
15.00
10.00
5.00
0.00
Percent
8/12/2002
9/1/2002
9/21/2002
10/11/2002
10/31/2002
11/20/2002
12/10/2002
12/30/2002
Date


MB 2
CO2
O2
25.00
20.00
15.00
10.00
5.00
0.00
Percent
8/12/2002
9/1/2002
9/21/2002
10/11/2002
10/31/2002
11/20/2002
12/10/2002
12/30/2002
Date


MB 3
CO2
O2
25.00
20.00
15.00
10.00
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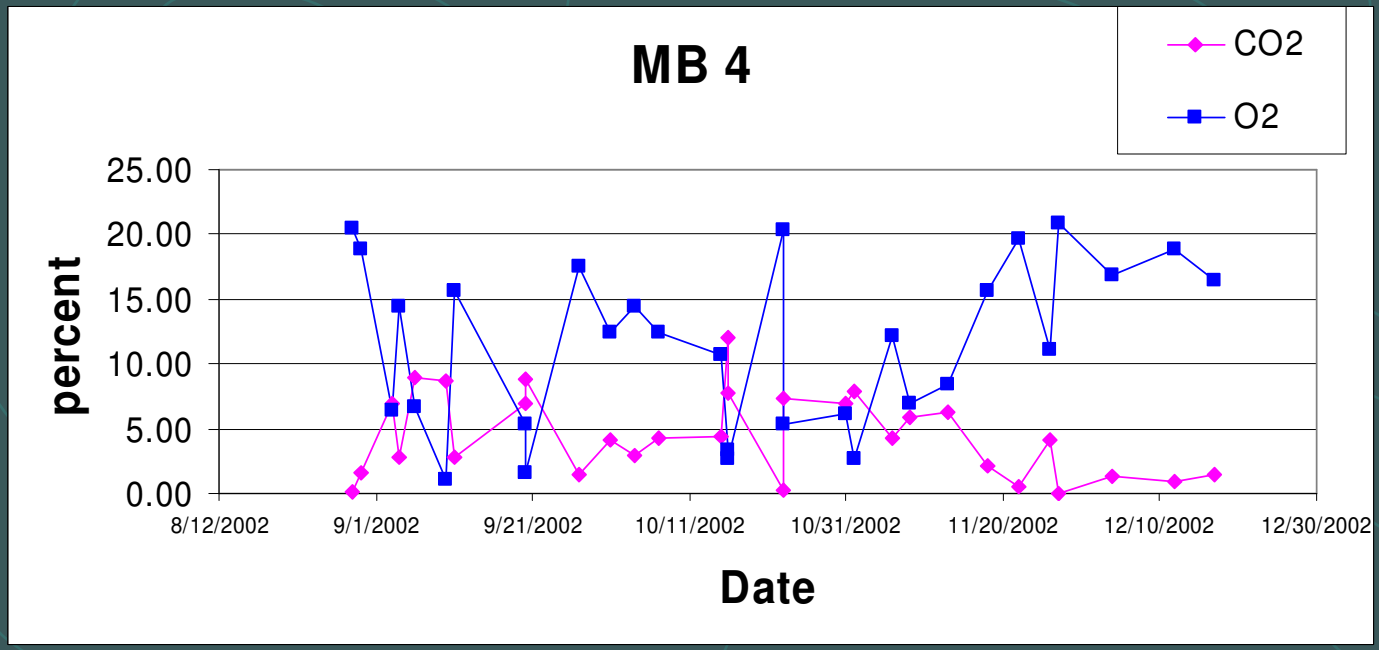
Percent
8/12/2002
9/1/2002
9/21/2002
10/11/2002
10/31/2002
11/20/2002
12/10/2002
12/30/2002
Date


MB 4
CO2
O2
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20.00
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percent
8/12/2002
9/1/2002
9/21/2002
10/11/2002
10/31/2002
11/20/2002
12/10/2002
12/30/2002
Date

Molecular & Isotopic Results

	Residence	MB-2 (Saxman Run Mine - active)	MB-4 (Darmac Mine - reclaimed)	Crushed Limestone (Used as reclamation at active Saxman Run Mine)
CO_2	8.86%	10.65%	1.43%	
CH_4	0.015%	0.013%	0.0087%	
N_2	80.35%	81.09%	78.00%	
O_2	9.82%	7.29%	19.30%	
Ar	0.96%	0.96%	0.93%	
N_2O	est. at <100 ppm			
C_3H_8			0.17%	
i-C_4H_{10}			0.013%	
n-C_4H_{10}			0.074%	
C_6+			0.071%	
$\delta^{13}CO_2$	-5.52	-4.76	-23.14	-2.20

Interim Remedial Action

Current stray CO2 cases

Potential for future problems…

CO_2 Migration From Subsurface Sources In Western Pennsylvania

- Relevant to CO_2 sequestration research
- Indicates possible problems related to CO_2 migration
- Exemplifies the myriad sources of CO_2 ("*noise*") in potential sequestration sites