

Some applications of isotope geochemistry for determining sources of stray carbon dioxide gas

Christopher D. Laughrey and Fred J. Baldassare

ABSTRACT

High concentrations of stray carbon dioxide in buildings are an emerging environmental hazard in some areas of the Appalachian coalfields. In western Pennsylvania, potentially lethal concentrations of CO₂ (>25%) and low volumes of O₂ (<10%) have caused several private homes to become uninhabitable. The CO₂ is primarily anthropogenic, although the specific source is commonly uncertain. Carbon isotope geochemistry provides the most useful technique for identifying the specific gas source.

Carbon dioxide derived from organic substrates by microbial activity is enriched in ¹²C, whereas CO₂ derived from carbonate materials is enriched in ¹³C. The activity of ¹⁴C can support the identification of geologically recent microbial gas generation. Ground-water chemistry can support interpretations of an inorganic CO₂ source based on stable-isotope data. Case studies from western Pennsylvania demonstrate the utility of isotopic analyses in identifying specific sources of stray CO₂ in buildings.

INTRODUCTION

In western Pennsylvania and adjacent areas of the central Appalachian basin, carbon dioxide (CO₂) contamination of building spaces is an emerging environmental problem (Ehler, 2002; Laughrey et al., 2002; K. Hackley, 2002, personal communication). In some locations, CO₂ concentrations in excess of 25% and oxygen (O₂) levels less than 10% have driven families from their homes. Carbon dioxide concentrations as high as these are dangerous and potentially lethal (see information about CO₂ toxicity at <http://www.osha.gov/>). Humans lose consciousness in only a few minutes when exposed to air containing 10% or more CO₂, and respiratory paralysis and death may follow. Lower concentrations of CO₂ can lead to high pulse rates and hyperventilation, as well as clumsiness,

AUTHORS

CHRISTOPHER D. LAUGHREY ~ *Pennsylvania Department of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey, 500 Waterfront Drive, Pittsburgh, Pennsylvania 15222; cloughrey@state.pa.us*

Christopher D. Laughrey is a senior geologic scientist with the Pennsylvania Geological Survey, where he has worked since 1980. He worked as a geophysical analyst for the Western Geophysical [Company] in Houston, Texas, before taking his present position in Pittsburgh, Pennsylvania. He also teaches sandstone petrology at the University of Pittsburgh. Laughrey's research interests include isotope and organic geochemistry, carbonate and clastic petrology, and borehole geophysics.

FRED J. BALDASSARE ~ *Pennsylvania Department of Environmental Protection, Environmental Cleanup, 400 Waterfront Drive, Pittsburgh, Pennsylvania 15222*

Fred Baldassare is a hydrogeologist with the Pennsylvania Department of Environmental Protection. He has 15 years experience investigating incidents of subsurface stray gas migration. Fred currently serves as a project manager providing technical reviews of chemical and hydrological data generated at industrial sites with ground-water contamination. He also serves as an advisor on the regulations and technical guidance for Pennsylvania's Land Recycling Program. Fred's current research interests include natural gas isotope geochemistry and contaminant fate and transport.

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severe headaches, and dizziness. Humans suffer hypoxia at O₂ concentrations less than 16%.

Stray CO₂ can vary in origin. Potential geologic sources include volcanoes, caves, and deep natural gases (Hunt, 1996). There are no active volcanoes in the Appalachian basin, however, and there are no caves adjacent to any of the homes contaminated by CO₂ that we investigated. Deep natural gases in western Pennsylvania are unlikely founts of large-surface concentrations of CO₂; measured concentrations of CO₂ in the region's gas wells range from 0.02 to 1.9 mol% (Laughrey and Baldassare, 1998). The most likely sources are anthropogenic and include fossil-fuel combustion, lime and cement manufacture, and waste combustion. Other possible sources of CO₂ include soda ash manufacture and use, commercial beverage carbonation facilities, microbial activity in landfills, limestone and dolostone use, and coal-mining activities.

In western Pennsylvania, an additional source of stray CO₂ is so-called blackdamp from abandoned underground mines. Blackdamp is a miner's term for a nonexplosive, mine atmosphere with high CO₂ and low O₂. Shafts at abandoned mine workings provide conduits for the CO₂ to migrate to surface structures. Overburden fractures, sometimes enhanced by mine subsidence, may also provide a conduit for gas migration. Gas migration is directly linked to variations in atmospheric pressure, weather conditions, and mine ventilation. The CO₂ associated with blackdamp spreads to the surface during periods of low atmospheric pressure. The mechanisms of gas invasion and accumulation in buildings are functions of the construction materials and style and of the local geology. The U.S. Department of Interior's Office of Surface Mining (OSM) has worked to abate problems with blackdamp CO₂ in buildings in western Pennsylvania and elsewhere for several decades.

Recently, stray CO₂ has accumulated in buildings near abandoned, reclaimed, and active surface mines in western Pennsylvania and threatened the safety of the occupants. In these instances, the sources of the CO₂ were not evident. Carbon isotope analyses proved to be a very useful technique for identifying the source of gas.

In this paper, we present carbon isotope analyses of stray CO₂ sampled from private residences contaminated with the gas and from monitoring wells drilled adjacent to these homes (Figure 1). We also present gas and ground-water chemical data that, in conjunction with the isotope data, helped us to identify the sources of stray CO₂. In each case that we investigated, the CO₂ originated from ground-water reactions with carbonate minerals in surface-mine spoil. Each site, however, has several potential sources of CO₂. It was imperative to accurately identify the actual source at each site to correctly mitigate the hazard and to assign responsibility for the remediation. Our data illustrate that identifying a CO₂ source based solely on a geological site assessment and gas chemistry alone can be uncertain, and that minor sources of CO₂ (carbonate use and coal mining activity) have a significant environmental impact on individuals and communities. Our data also

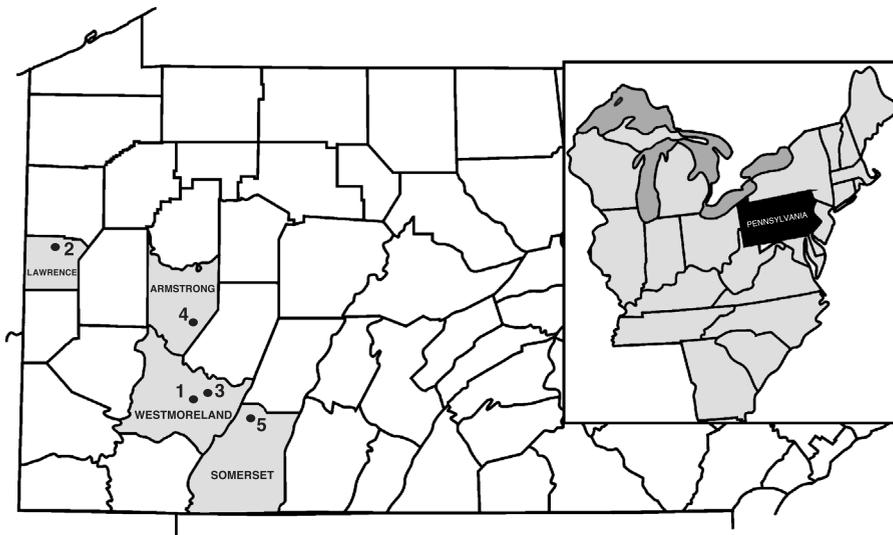


Figure 1. Locations of the five sites of CO₂ migration into private homes in western Pennsylvania discussed in this paper.

identify potential environmental problems associated with subsurface carbon sequestration.

CARBON AND THE ISOTOPE GEOCHEMISTRY OF NATURAL GASES

Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. There are two fundamental kinds of isotopes, stable and unstable (radioactive) species. Stable isotopes are not subject to radioactive decay. Their abundance in nature is controlled by biological and physical processes, such as photosynthesis and equilibrium reactions in the case of the stable isotopes of carbon (¹²C and ¹³C). Differences in isotopic mass lead to subtle but significant differences in the behavior of the stable isotopes of an element during natural processes. Unstable isotopes experience radioactive decay. Each radioactive isotope has a characteristic decay time known as the half-life, and these isotopes may be used in age dating, e.g., ¹⁴C.

Carbon occurs in a wide variety of compounds, from highly oxidized inorganic materials such as CO₂ and sedimentary carbonate rocks to highly reduced organic substances in the biosphere. Sedimentary carbonates and organic matter possess distinct stable carbon isotope compositions because of the operation of two different reaction mechanisms (Hoefs, 1997):

1. Isotope equilibrium exchange reactions in the inorganic carbon system (atmospheric CO₂-dissolved bicarbonate-solid carbonate) lead to an enrichment of ¹³C in carbonate rocks.

2. Kinetic isotope effects during photosynthesis concentrate ¹²C in organic matter.

The stable isotopic composition of carbon in a sample of any material is expressed using the delta (δ) notation,

$$\delta^{13}\text{C}_{\text{sample}} = \left\{ \left[\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}} \right] \div \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{standard}} \right\} \times 1000$$

δ¹³C_{sample} is in parts per thousand or per mil (‰). The standard is the internationally recognized Peedee Belemnite (PDB) reference standard for carbon (see Hoefs, 1997). The PDB standard has been assigned a value of 0‰. Negative δ-values mean that the sample is enriched in the lighter isotope (¹²C) relative to the standard, whereas positive δ-values mean that the sample is enriched in the heavier isotope (¹³C) when compared with the standard.

Stable isotope geochemistry provides a powerful method for distinguishing natural gases from different sources (Schoell, 1983). Although methane is the primary constituent of most natural gases, other important components include higher hydrocarbons, nitrogen, hydrogen sulfide, and CO₂. The δ-values of carbon in hydrocarbon gases and CO₂ are useful for determining microbial, thermogenic, and inorganic sources of the gases (Schoell, 1983; Hoefs, 1997). Table 1 is a list of the variations in δ¹³C_{CO₂} from different sources.

The geochemistry of radioactive ¹⁴C is also useful for discerning different sources of gases. Atmospheric testing of nuclear devices in the 1950s and 1960s

Table 1. Variations in $\delta^{13}\text{C}_{\text{CO}_2}$ from Different Sources*

Atmospheric CO_2	– 8 ‰
Volcanic degassing	– 8 ‰
Thermal destruction of carbonates	+4 to – 5 ‰
Thermal degradation of organic matter	– 8 to – 12 ‰
Bacterial oxidation of methane	– 20 to – 59 ‰
CO_2 in coal bed gases	+ 18.6 to – 26.6 ‰

*Data from Rice (1993), Hunt (1996), and Hoefs (1997).

produced large amounts of ^{14}C -enriched CO_2 , and all biological material that has lived and grown since about 1960 has ^{14}C concentrations above natural, equilibrium levels. This elevated ^{14}C is a useful tracer for recently generated organic gases, such as those generated in swamps, marshes, landfill, and spoil fills. The ^{14}C activity of these materials ranges from about 30 to as much as 150% modern carbon (pMC), where 100 pMC is defined as the natural (equilibrium), prebomb ^{14}C concentration of atmospheric CO_2 (Coleman, 1994, p. 5).

STRAY CO_2 IN WESTERN PENNSYLVANIA

Between December 1996 and April 2003, we investigated five separate cases of stray CO_2 migration involving seven private residences in western Pennsylvania (Figure 1; Table 2). Our measurements of elevated carbon dioxide concentrations in the homes ranged from 2.21 to more than 25% (air contains 0.035% CO_2). Oxygen concentrations in the homes ranged from less than 10 to 20.9%. Carbon dioxide and O_2 flux varied with changes in barometric pressure, with the highest CO_2 values and lowest O_2 values occurring during the passage of low-pressure fronts.

All of the homes with elevated CO_2 were built on or adjacent to spoil in abandoned or reclaimed surface coal mines. Carbon dioxide is generated in the spoil atmosphere of reclaimed strip mines by aerobic respiration of plant roots and microorganisms and by the neutralization of acid from pyrite oxidation through reactions with carbonates (Jaynes et al., 1983; Lusardi and Erickson, 1985; Rose and Cravotta, 1998). Although elevated CO_2 in mine spoil atmospheres is well documented, it was not thought to migrate (Jaynes et al., 1983; Lusardi and Erickson, 1985; Rose and Cravotta, 1998; Ehler, 2002). In addition to the mine spoil, there were several other potential sources of CO_2 at all of these locations. These potential sources included

abandoned underground mines, oil and natural gas wells, wetlands, glacial sediments, subbase materials beneath the homes (slag and limestone), abandoned mine drainage reactions with carbonate bedrock, and active surface-mining activities.

Preliminary reconnaissance at each site involved analyzing the air chemistry inside the affected homes with Dräger MultiWarn II gas monitors equipped with infrared CO_2 , O_2 , and CO sensors and flame ionization detectors for hydrocarbon gases. Gas samples were collected from home and monitoring well atmospheres for geochemical analyses by connecting tygon tubing to the sampling point and purging the line until consistent gas concentrations were observed. We measured and recorded gas concentrations before and after sampling. The gas samples were hand pumped into Cali-5-Bond™ bags; the hand aspirator pumps had one-way valves. All samples were shipped to Isotech Laboratories in Champaign, Illinois, for molecular and isotopic analyses. Samples were prepared offline and then analyzed by dual-inlet isotope ratio mass spectrometer (IRMS).

The δ -values for all of the CO_2 samples collected in the various contaminated homes indicate that the gas was generated by ground-water reactions with carbonate minerals in the surface-mine spoil (Figure 2; Table 2). The $\delta^{13}\text{C}_{\text{CO}_2}$ of gases collected in the homes ranges from – 5.52 to – 2.96 ‰. These gases are relatively depleted in ^{12}C , i.e., isotopically heavy, and we interpret them as having an inorganic carbonate source. By comparison, CO_2 generated by biological processes in mine spoil is relatively enriched in ^{12}C , or isotopically light. Sample MB-4 from site 3 in Table 2 has a $\delta^{13}\text{C}_{\text{CO}_2}$ of – 23.14 ‰. We interpret this CO_2 as having a microbial or plant source in the spoil (discussed below in site 3).

We discovered that the CO_2 migrating into homes in western Pennsylvania can be generated both in abandoned, reclaimed surface mines and in active surface mines, where alkaline addition is practiced to maintain water quality. Two of the sites we investigated (sites 2 and 3 in Figure 1) illustrate this observation particularly well, and a detailed discussion of these sites is instructive for understanding the production and migration of high concentrations of CO_2 in the Appalachian coalfields.

SITE 2: LAWRENCE COUNTY, PENNSYLVANIA

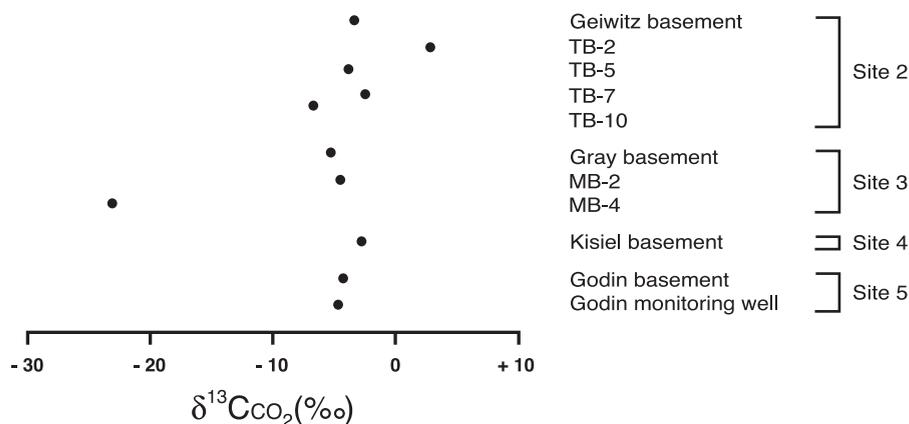
In August 2000, Pennsylvania State Representative Frank LaGrotto filed a complaint with OSM about

Table 2. Gas Geochemistry Data for Five CO₂ Contamination Sites in Western Pennsylvania

Sample	CO ₂ %	δ ¹³ CO ₂ (‰)	¹⁴ CO ₂ (pMC)	O ₂ (%)	N ₂ (%)	Ar (%)	He (%)	CO (%)	CH ₄ (%)	C ₂ +
Site 1										
Basement A	2.21	nm	nm	18.79	79.0	nm	nm	nm	nm	nm
Basement B	3.52	nm	nm	17.48	79.0	nm	nm	nm	nm	nm
Monitoring well 1	1	nm	nm	20.2	77.8	0.93	nm	0.0011	0.0018	nd
Monitoring well 2	12.4	nm	nm	10.02	76.6	0.91	nm	0.0004	0.0004	nd
Monitoring well 3	11.5	nm	nm	19.75	67.82	0.93	nm	0.0004	0.0004	nd
Monitoring well 4	15.7	nm	nm	16.95	66.38	0.97	nm	0.0003	0.0033	0.0001
Monitoring well 5	16	nm	nm	14.89	68.18	0.93	nm	0.0001	0.0003	nd
Monitoring well 6	7.5	nm	nm	17.72	73.86	0.92	nm	0.0001	0.0008	nd
Monitoring well 7	13	nm	nm	nm	nm	nm	nm	nm	nm	nm
Monitoring well 8	14	nm	nm	16.62	68.42	0.96	nm	0.0001	0.0012	0.0001
Monitoring well 9	16	nm	nm	10.91	72.08	1.01	nm	0.0005	0.0044	0.0001
Monitoring well 10	16	nm	nm	16.38	66.65	0.97	nm	0.0004	0.0017	nd
Monitoring well 11	14	nm	nm	10.82	74.21	0.95	nm	0.0004	0.0253	0.0005
Site 2										
Geiwitz basement	8.96	-3.99	15	13.05	77.08	0.91	0.004	nm	nd	nd
TB-2	2.19	+2.86	21.2	18.73	78.15	0.92	0.0052	nm	nd	nd
TB-5	15.58	-4.02	13.2	9.08	74.45	0.88	0.0047	nm	0.0097	nd
TB-7	17.46	-2.64	7.8	7.83	73.82	0.88	0.0062	nm	0.0015	nd
TB-10	10.86	-7.01	24.5	7.87	80.31	0.96	0.0028	nm	nd	nd
Site 3										
Gray basement	8.86	-5.52	nm	9.82	80.35	0.96	nm	nm	0.015	nd
MB-2	10.65	-4.76	nm	7.20	81.09	0.96	nm	nm	0.013	nd
MB-4	1.43	-23.14	nm	19.3	78.0	0.93	nm	nm	0.0087	nd
Site 4										
Kiesel basement	10.7	-2.96	nm	10.94	77.43	0.93	nd	nd	nd	nd
Site 5										
Godin basement	9.51	-4.07	nm	13.43	76.13	0.93	nd	nd	nd	nd
Monitoring well	8.92	-4.18	nm	12.66	77.47	0.95	nd	nd	nd	nd

nm: not measured.
nd: not detected.

Figure 2. Graphical presentation of the stable carbon isotope data discussed in this paper and summarized in Table 2. All but one of the $\delta^{13}\text{C}_{\text{CO}_2}$ values are relatively enriched in ^{13}C , indicating an inorganic carbonate source for the gas. Sample MB-4 (from the Darmac mine, site 3) is isotopically light, indicating an organic carbon source for the CO_2 collected in that monitoring well.



CO_2 accumulations in the homes of two of his constituents in Washington Township, Lawrence County, Pennsylvania (Figure 1). A third home was discovered to also have high concentrations of CO_2 . The Office of Surface Mining personnel installed gas meters in the homes and drilled a total of 10 groundwater-monitoring wells around the buildings (Figure 3). The gas meters installed in the three homes (Dräger MultiWarn II monitors) measured O_2 , CO_2 , carbon monoxide (CO), and methane (CH_4). These instruments continuously recorded the levels of the gases at 10-min intervals for 28 days at a time. The Office of Surface Mining routinely downloaded the data from the meters and continued monitoring at the homes for more than 1 yr while investigating the source of the CO_2 . Carbon dioxide concentrations as high as 25% and corresponding O_2 levels as low as 10% occurred in the homes during periods of low barometric pressure. Carbon dioxide levels in the atmosphere directly above the water table in some of the monitoring wells exceeded 25% at these times, and corresponding O_2 levels dropped to 3%. Trace amounts of CO and CH_4 were noted occasionally during the monitoring period. The Office of Surface Mining assisted the families in constructing temporary remediation systems so that they could safely occupy their homes during the site investigation. If the CO_2 problem was related to an abandoned mine, then federal funding from OSM would be available to construct a permanent abatement system.

Potential Gas Sources

There are many possible sources of CO_2 at the Lawrence County site. Entries to an abandoned deep mine in the lower Pennsylvanian Brookville Coal (Figure 4) were encountered during surface-mining activities in

the late 1980s, but we quickly eliminated blackdamp from this mine as a possibility. The mine, located updip of the contaminated homes, is completely flooded and discharges abandoned mine drainage (AMD) at volumes as much as $2.83 \text{ m}^3/\text{s}$ ($100 \text{ ft}^3/\text{s}$) into a large mine pool. This water drains south into a wetland updip of both spoil from a large reclaimed surface-mine and glacial-till deposits (Figure 3).

Other potential sources of CO_2 included the spoil in the reclaimed surface mine, subsurface AMD reactions with the lower Pennsylvanian Vanport Limestone (Figure 4), gas migration from caves in the Vanport Limestone, glacial drift gas, swamp gas from wetlands adjacent to the site, active deep gas wells in the area, and an abandoned oil field (Figure 3). We suspected organic matter buried in spoil at a reclaimed strip mine, or AMD reactions with carbonate in the spoil or the Vanport Limestone beneath and adjacent to the homes. Calcium carbonate was added to the spoil to help increase the alkalinity (i.e., HCO_3^- concentration) of acidic ground water in the material (Smith and Brady, 1998). Abandoned mine drainage discharging from the abandoned deep mine entry could react with the carbonate material in the spoil and produce CO_2 through a series of chemical reactions involving several carbonate species, including CO_3^{2-} , HCO_3^- , H_2CO_3 , and CO_2 . In addition, organic matter in the spoil could produce CO_2 through microbial processes. We used isotope geochemistry to determine if the CO_2 had an organic or inorganic source. This information would clarify the process responsible for generating CO_2 on site.

Gas Isotope Analyses

The $\delta^{13}\text{C}_{\text{CO}_2}$ of samples at the Lawrence County site range from +2.86 to -7.01 ‰ (Figure 2; Table 2).

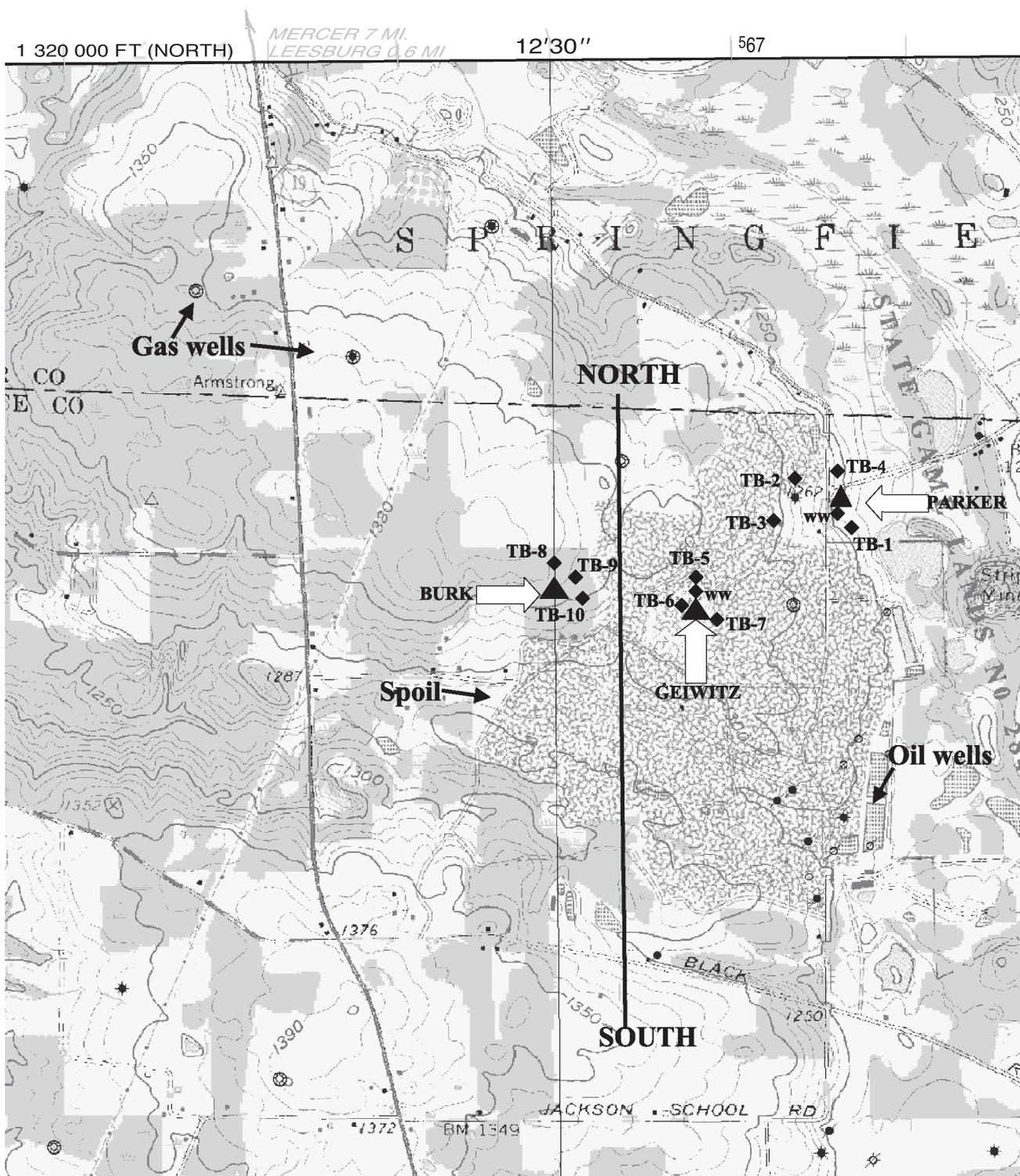
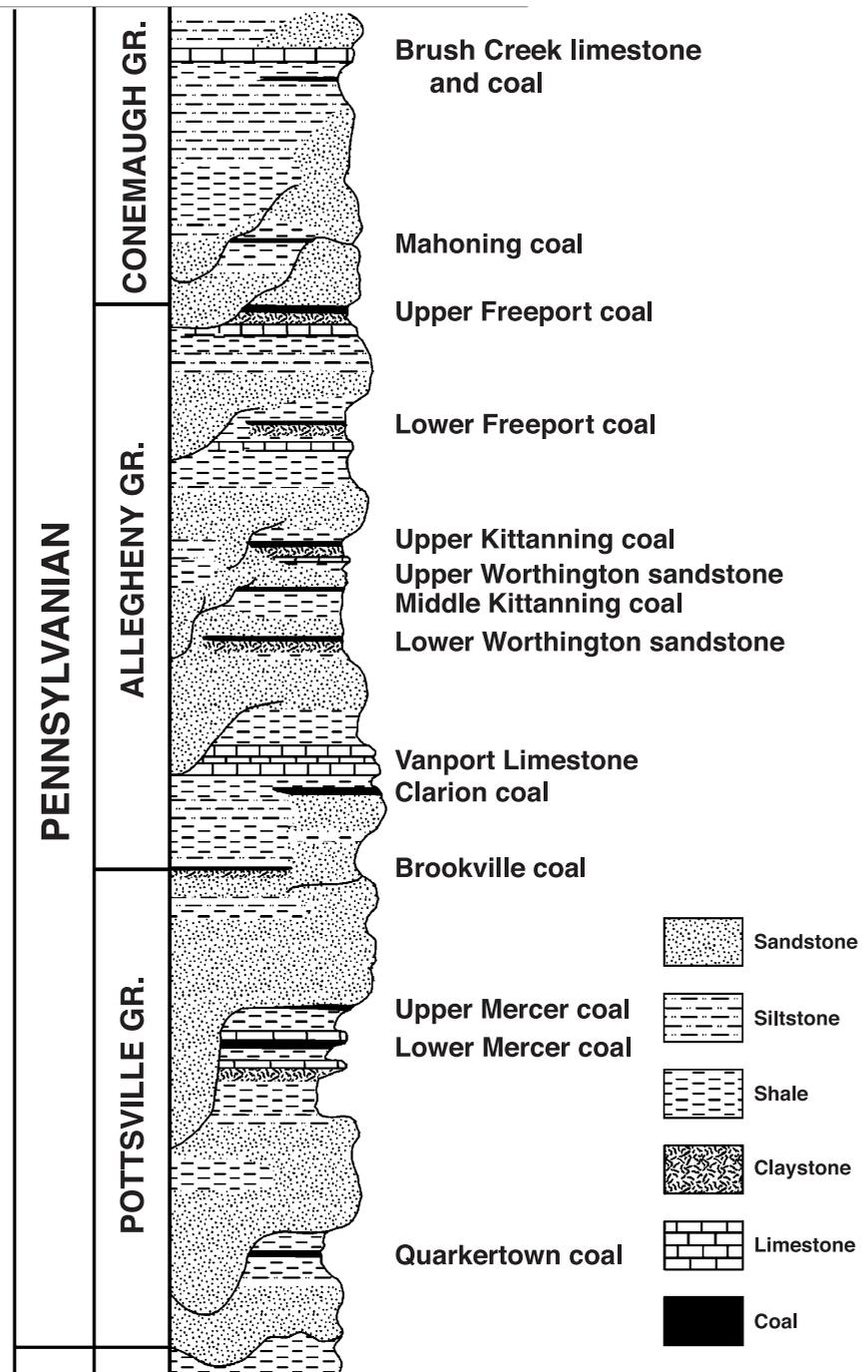


Figure 3. Portion of the U.S. Geological Survey Harlansburg 7.5-min quadrangle showing the northern Lawrence County, Pennsylvania location of the site 2 study area. Large black triangles labeled Parker, Geiwitz, and Burk are the CO₂-contaminated homes. Black diamonds are monitoring wells labeled TB-1 through TB-10; ww indicates private water wells. The deep mine drain and pool discussed in the text are just north of the letter N in Springfield. The north-south line of cross section shown here is illustrated in Figure 5. The original topography reflects the morphology of the Wisconsin Kent end moraine and glaciofluvial deposits.

Figure 4. Stratigraphic column for the Pottsville, Allegheny, and a portion of the Conemaugh Groups in western Pennsylvania.



Carbon dioxide sampled in the basement of the Geiwitz home (Figure 3) has a $\delta^{13}\text{C}$ of -3.99‰ . All other CO_2 samples are from the atmosphere directly above the water table in the monitoring wells (Figure 3). All samples are relatively depleted in ^{12}C . We interpret the CO_2 as having an inorganic, carbonate source. Variations in $\delta^{13}\text{C}_{\text{CO}_2}$ in our sample set (differences of as much as 9.87‰) are most likely caused by heterogeneity in the source carbonate material,

mixing of the CO_2 generated from carbonate in the subsurface at the site and atmospheric CO_2 , and/or mixing of the CO_2 with bacterially mediated gas in the local aquifer (Chapelle and Knobel, 1985).

We also measured the ^{14}C activity of the same five CO_2 samples. If the gases at the Lawrence County site were generated from organic matter by microbial activity in the surface-mine spoil, the CO_2 should have ^{14}C activities in excess of 100 pMC. The ^{14}C

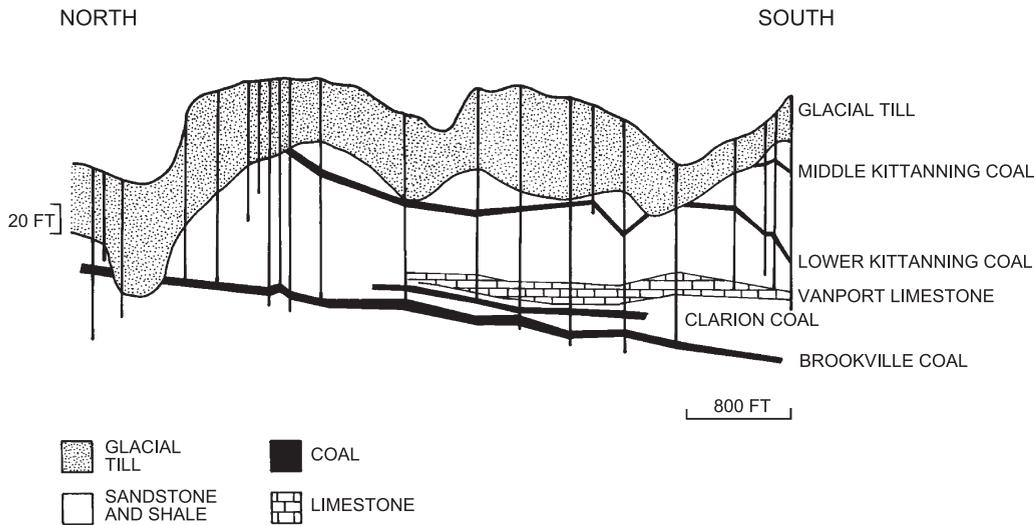


Figure 5. North-south geologic cross section for site 2. See Figure 3 for line of section. Note the Vanport Limestone pinches out south of the study area.

activity of our samples, however, ranged from 7.8 to 24.5 pMC (Table 2).

These values reflect minor mixing of the CO₂ generated from subsurface carbonates with atmospheric CO₂ and/or glacial drift gas (Coleman, 1994).

Geologic and Ground-Water Data

The isotopic data suggested that carbonate was the source of the CO₂ contamination in the homes and above the water table. We suspected that AMD discharging from the abandoned deep mine was reacting with the carbonate to produce the CO₂. Possible carbonate sources included carbonate in the glacial till used for spoil and the Vanport Limestone in the bedrock. Although the literature indicated that the Vanport Limestone occurred in the subsurface at the site (Poeth, 1963), monitoring wells drilled by OSM and exploratory wells drilled by the surface-mine operator revealed that the Vanport is absent at the site (Figure

5). Analyses of the glacial till revealed that it contained as much as 8% calcium carbonate and possessed excellent potential for increasing alkalinity in the ground water at the site if used as spoil fill after mining (Ehler, 2002). This was done, and we therefore suspected that AMD reactions with carbonate in the spoil were the source of the CO₂.

The geochemistry of ground water collected from the deep mine drain and from the various monitoring wells at the site support this interpretation. The partial pressure of CO₂ in collected ground-water samples is 0.01–0.2 atm (Table 3) (Ehler, 2002). Although moderately high in alkalinity (31.36–136.84 mg/L), and only slightly low in pH (5.82–6.55), the water is undersaturated with respect to calcite, dolomite, and siderite (Table 3; Figure 6). During reclamation, no one anticipated the high ground-water recharge from the abandoned deep mine, nor the fact that such high volumes of CO₂ could form and exsolve in the spoil and move so efficiently as a free phase through permeable

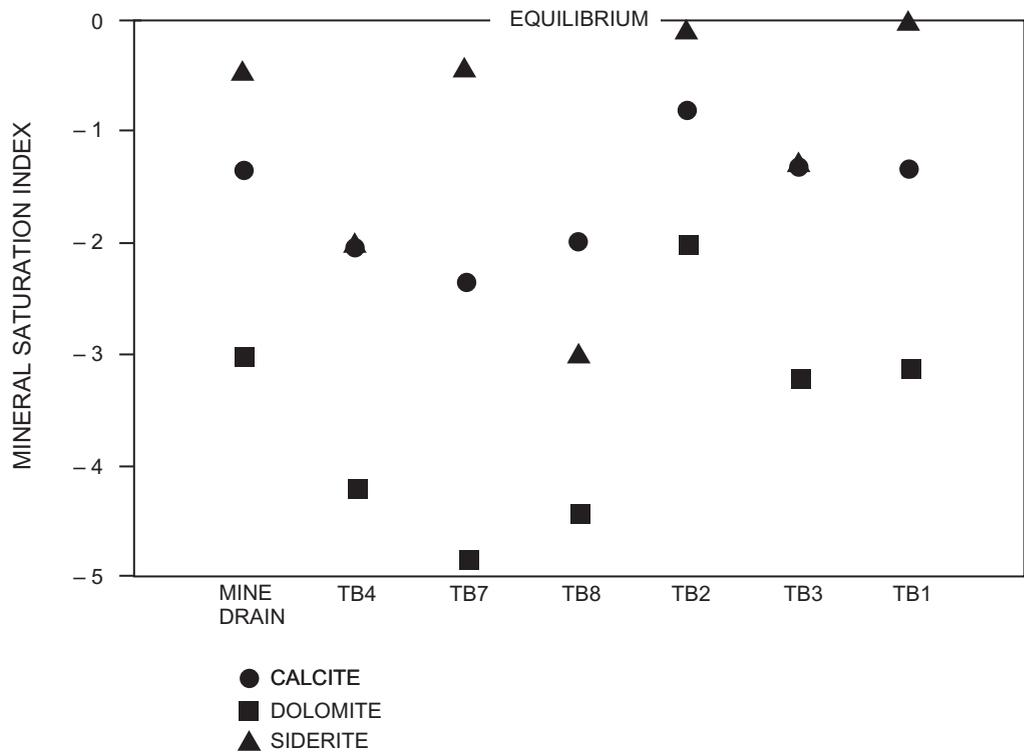
Table 3. Ground-Water Chemistry for Site 2, Lawrence County, PA

Sample	pH	Alkalinity	pCO ₂	SI (CO ₂)	SI (Calcite)	SI (Dolomite)	SI (Siderite)
Mine Drain	6.31	113.64	0.0544503	–1.264	–1.3352	–3.0419	–0.4581
TB-1	6.36	110.7	0.0489779	–1.31	–1.37	–3.17	0/06
TB-2	6.2	337.1	0.2009555	–0.6969	–0.838	–2.0382	–0.1099
TB-3	6.2	136.84	0.0888383	–1.0514	–1.4216	–3.2502	–1.4181
TB-4	5.97	71.6	0.0786502	–1.1043	–2.0199	–4.2497	–2.0108
TB-7	5.82	31.36	0.0284315	–1.5462	–2.3601	–4.8631	–0.4786
TB-8	6.55	43.98	0.0125516	–1.9013	–2.0002	–4.4499	–3.0787

pCO₂ = partial pressure of carbon dioxide.

SI = saturation index.

Figure 6. Mineral saturation indices for the water samples from site 2, Lawrence County, Pennsylvania. See Table 3 for the ground-water chemistry data used to construct this graph.



earth materials to nearby structures. A crossplot of the pH and alkalinity of the water samples (Figure 7) reveals that the theoretical dissolved CO₂ concentrations at the site are high enough to produce the observed gas volumes in the homes and wells. See Ehler (2002) for a discussion of the CO₂ migration on the site.

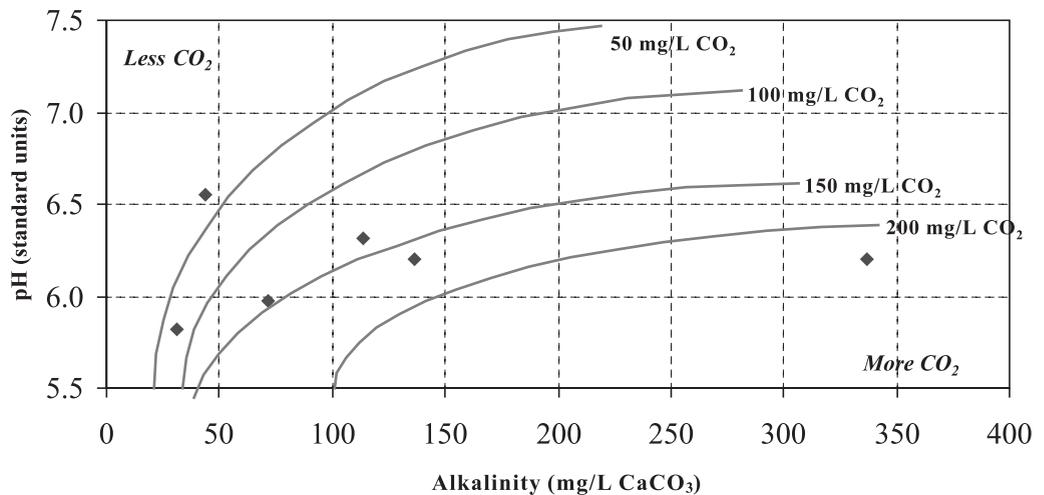
Remediation

Geochemical data and interpretations indicated that the CO₂ contamination of the homes and ground wa-

ter at the Lawrence County site was related to past surface mining activity. This conclusion allowed OSM to provide funds for remediation. The remediation process consisted of several steps:

- filling concrete foundation blocks with a special grout mix to decrease the permeability of the basements to gas;
- installation of vapor barriers and constructing basement subfloors impermeable to gas;
- installation of vents; and

Figure 7. Plot of pH vs. alkalinity for the case 2 water samples.



- installation of fan systems to create positive pressure beneath the homes that maintains a meter-scale buffer zone between migrating CO₂ and the basements.

The remediation effort succeeded in reducing CO₂ levels in all of the homes to normal atmospheric levels (0.03%), including during periods of low atmospheric pressure.

SITE 3: DERRY, PENNSYLVANIA

In August 2002, family members in a home near the community of Derry (Figures 1, 8) experienced relatively serious symptoms of CO₂ toxicity and hypoxia. Two daughters, whose bedrooms were in the basement, awoke on several nights with accelerated heart rates, difficulty breathing, and tightness in the chest. Their father experienced similar symptoms upon entering the basement. The Department of Environmental Protection's (DEP) Emergency Response Team evacuated the family and examined the home. They recorded CO₂ concentrations of 2% and O₂ levels of 15% in the basement. We documented CO₂ levels in excess of 10% and O₂ levels below 10% in the home during our investigation in August–December 2002. The CO₂ was detected entering the home at numerous locations in the basement.

DEP personnel assisted the homeowner with installation of an interim gas recovery system in the basement. This measure temporarily reduced CO₂ concentrations in the basement. The OSM and National Institute of Occupational Safety and Health (NIOSH) set up uninterrupted monitoring of the gas flux in the home. They also pursued periodic monitoring of gas flux at several points outside of the home. Carbon dioxide levels sometimes exceeded 20% at two monitoring locations during the investigation.

Potential Gas Sources

This residence is on the northwest flank of the Chestnut Ridge anticline about 0.5 km (0.3 mi) southeast of the community of West Derry. The home sits on steeply dipping bedrock of the Allegheny Group; numerous coals crop out in the area (Figure 9). These coals have been both deep mined and surface mined (Skema, 1988). The upper Worthington Sandstone (Figure 4) crops out in a large crawl space behind the basement and beneath the kitchen and back patio floors. The sandstone is intensely fractured. A bedding plane in this exposed sandstone yields the highest detected concentrations of CO₂ in the house. Upper Kittanning coal is actively surface mined 152.4 m (500 ft) up the hill from the house.

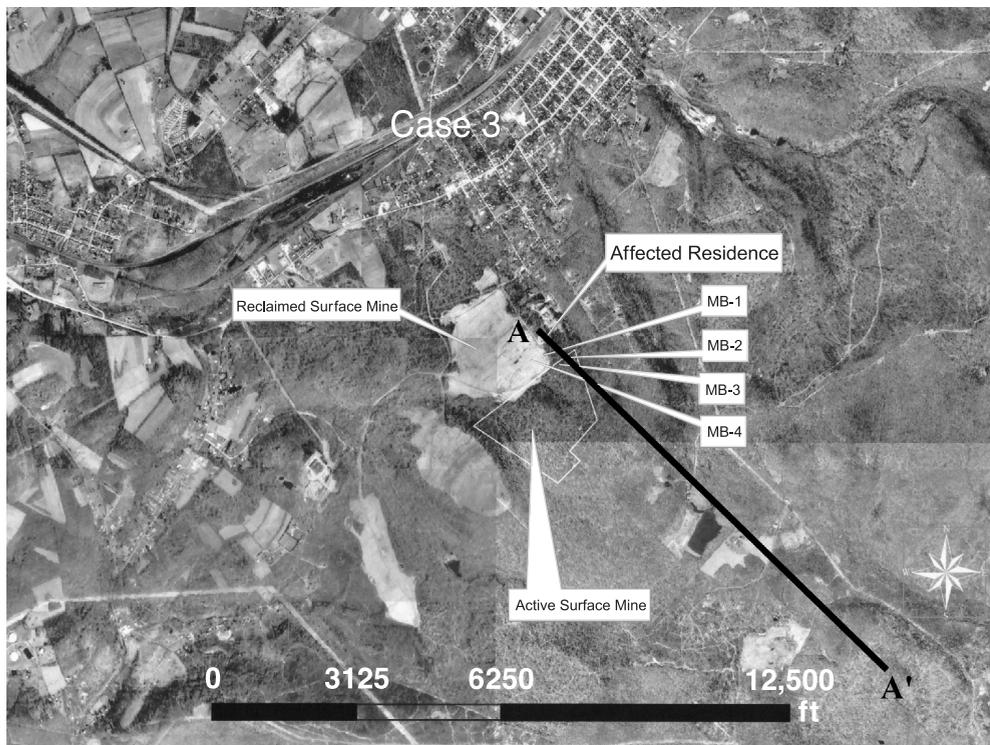
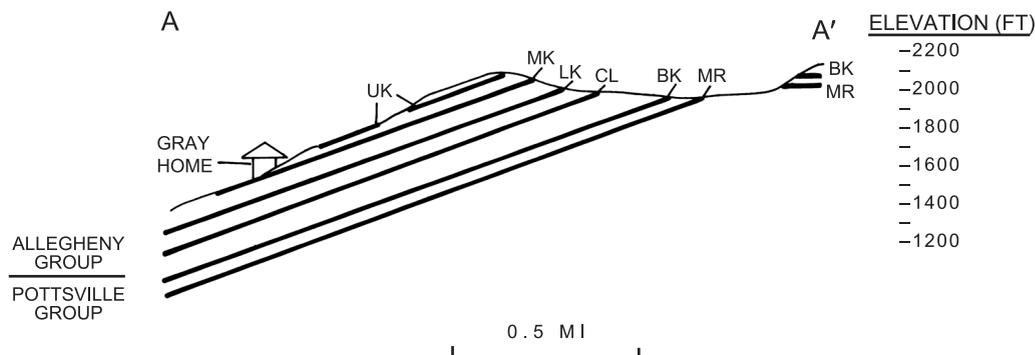


Figure 8. Aerial photo showing site 3 with CO₂-contaminated home, monitoring wells (MB-1 – MB-4), surface mine locations, and the line of cross section presented in Figure 9.

Figure 9. Structural and geologic cross section for site 3. See Figure 8 for line of section. UK, MK, and LK denote upper, middle, and lower Kittanning coals, respectively. CL = Clarion coal. BK = Brookville coal. MR = Mercer coal.



There are several potential sources of the CO₂:

- the middle Kittanning coal beneath the home;
- the spoil in a reclaimed surface mine (Darmac mine) adjacent to the home;
- a reported abandoned deep mine downdip of the home;
- the active surface mine (Saxman Run mine) updip and above the home;
- blasting at the active surface mine; and
- deep natural gas wells updip of the home.

The deep gas wells were eliminated as a source because all are properly maintained, and compositional analyses of the produced gases show that CO₂ is only a trace constituent.

DEP, OSM, and NIOSH conducted a detailed investigation to determine if blasting at a nearby active surface mine was the source of CO₂. Their investigation did not reveal any direct relationship between blasting and CO₂ in the private residence.

The coal beneath the home is an unlikely source. The CO₂ content of coal-bed gases in Pennsylvania is highly variable, but the median value is only 4.1% (Markowski, 2001). Natural gases in undisturbed, subsurface coals tend to be strongly adsorbed on the coal surfaces and in micropores (Hunt, 1996). The middle Kittanning coal exposed at the surface is aurally limited and would have reached outgassing equilibrium in the geologic past.

The atmosphere and mine pool elevation in the abandoned deep mine approximately 274.3 m (900 ft) downdip of the home was unknown; therefore, the deep mine was considered as a potential, but unlikely, source.

Spoil in the reclaimed Darmac surface mine or in the active surface mine updip of the residence were the most likely sources of the CO₂. Alkaline addition

was not employed in the reclamation of the Darmac mine, and the spoil is low in carbonate minerals. We suspected that CO₂ generated in this spoil is caused by plant and microbial respiration. At the active mine, AMD reactions with crushed limestone used to neutralize ground water in backfilled sections was a potential source of CO₂. The crushed rock is used in the reclaimed areas of the active mine site at an application rate of approximately 205 t/ac.

Gas Isotope Analyses

We used stable isotope geochemistry to determine the genetic origins of the CO₂ in the residence and correlate it to one of the three remaining possible sources: the active or abandoned surface mines, or the deep mine. We collected three gas samples for molecular and stable carbon isotopic analyses and one sample of the crushed rock used in the reclaimed areas of the surface mine for isotopic analyses (Table 2). The gas sample from the residence was collected from the bedding plane in the rock face exposed in the unfinished area of the basement where the highest CO₂ concentrations were observed. Sample MB-2 was collected from a monitoring point installed to the pit floor in a reclaimed section of the active surface mine, updip of the residence. The pit floor is at approximately 12 m (39.4 ft) below grade in MB-2. The third sample was collected from monitoring point MB-4 installed in the spoil of the reclaimed Darmac surface mine adjacent to, and just downdip of, the residence. The pit floor is at approximately 10.2 m (33.5 ft) below grade. Total depth for MB-4 is 10.7 m (35 ft) below grade.

Table 2 and Figure 2 show the geochemical data for the three gas samples. The δ¹³C_{CO₂} of the gas collected in the home is -5.52‰. This gas is depleted in ¹²C (isotopically heavy) and is derived from an

inorganic, carbonate source. The $\delta^{13}\text{C}_{\text{CO}_2}$ of the gas collected from the reclaimed section of the active mine pit floor (MB-2) is -4.76% . This gas also is derived from carbonate. The CO_2 from the residence is slightly more depleted in ^{13}C when compared to the CO_2 from MB-2 (a difference of 0.76%). This difference may be caused by mixing with atmospheric CO_2 and/or variation in the carbonate source material. There is excellent correlation of the $\delta^{13}\text{C}_{\text{CO}_2}$ of the gases from the home and MB-2. Furthermore, the concentration of CO_2 and other gases are similar and in the same relative proportions for the residence and MB-2, an indication that the gases may be from the same source.

The $\delta^{13}\text{C}_{\text{CO}_2}$ of the crushed limestone used at the surface mine is -2.20% . The CO_2 samples from the residence and the mine are slightly more enriched in ^{12}C than their interpreted source because of mixing with atmospheric CO_2 .

The CO_2 from the reclaimed Darmac mine (sample MB-4) is organic in origin. It has a $\delta^{13}\text{C}_{\text{CO}_2}$ of -23.14% . This gas formed through plant and/or microbial respiration. The isotopic results for MB-4 clearly indicate this CO_2 is not from the same source as the CO_2 found in the residence, MB-4, or the crushed rock used at the active mine site.

We did not sample any gases from the abandoned deep mine down-dip of the home. The exact location of this mine is uncertain, and we are not aware of any monitoring wells drilled into the mine void. The steep dip makes migration of large concentrations of CO_2 up to the residence unlikely. Stray gases from abandoned mines typically include percentage range concentrations of CH_4 ; we did not detect any CH_4 in the gas samples collected during this investigation. Furthermore, we expect any CO_2 from this mine to be organic in origin (Kim and Kissell, 1988) and isotopically light, similar to the gas from sample MB-4 (Rice, 1993). The strong stable isotopic correlation between the CO_2 in the house and the active mine pit floor indicate the latter is the source of the problem. Additionally, the extensive monitoring conducted by OSM and NIOSH exhibits a revealing profile. For a period of several days following a rain event, the concentrations of CO_2 in onsite/offsite monitoring wells and inside the impacted residence increased substantially. This phenomenon was observed on several occasions and was determined to be the most significant factor in the migration of CO_2 from the source. We attribute the CO_2 increase to the reaction of acidic surface/ground water with the limestone amended to

the active surface mine site. For a brief period, the rain also served as a wetting front, resulting in less diffusion with ambient air, allowing the gas to migrate at higher concentrations.

Remediation

After isotopic results and other data collected during this investigation were presented to the mine operator, officials with DEP requested an onsite mitigation plan to eliminate the migration of CO_2 from the active surface mine. The company responded by proposing an interceptor trench at the downgradient edge of their site, 396.7 m (1140 ft) in length through backfill spoil that is 10.7–12.2 m (35–40 ft) thick (Figure 10). After excavation, the trench was left open to the atmosphere. Monitoring data from all stations show the trench to be highly effective in eliminating the migration of CO_2 from the active mine site to the impacted residence.

ADDITIONAL DATA

In addition to the two sites discussed above, the data listed in Table 2 include gas analyses from three other sites in western Pennsylvania where CO_2 migrated into and accumulated in private homes. At Site 1 in Westmoreland County (Figure 1), we measured CO_2 levels as high as 3.52% and O_2 levels as low as 16% in the basement of the Sweezy residence (see Table 2). The Office of Surface Mining and Pennsylvania's DEP installed monitoring wells around the home. Carbon dioxide concentrations as high as 16% occurred in these wells during periods of low barometric pressure. At first, investigators suspected blackdamp, but there was no apparent deep mine source for the CO_2 . The home rests along the crop line of the middle Pennsylvanian upper Freeport coal, and the upper Freeport and Mahoning coals were strip mined at the site (Figure 4). Possible sources of CO_2 included spoil in the former strip mine and natural gas wells adjacent to the property. Chemical analyses of the deep-well gases revealed only traces of CO_2 . By default, OSM determined that the CO_2 in the Sweezy residence originated in the strip-mine spoil and initiated remediation. The exact mechanism of this CO_2 occurrence remains undefined, and the source of the gas remains obscure.

In January 2003, we responded to a complaint at the Kisiel residence in Armstrong County, Pennsylvania

Figure 10. Photograph of the trench excavated at the low wall to intercept CO₂ from the active surface mine at site 3. The affected home is visible through the woods in the upper right portion of the photo (arrow).



(site 4 in Figure 1). We measured CO₂ and O₂ concentrations of 14.7% and 6.8%, respectively, in the basement. On different days, CO₂ levels at the top of the basement stairs ranged from 0.13 to 3.48%, and O₂ levels there ranged from 17.5 to 20.5%. Isotopic analyses yielded a $\delta^{13}\text{C}_{\text{CO}_2}$ of -2.96‰ for the gas accumulating in the basement. The Kiesel home is built on spoil from a reclaimed surface mine. The isotopic results indicate a carbonate source for the CO₂. The likely source is AMD reactions with carbonate material in the mine spoil.

In March 2003, we responded to yet another emergency case of CO₂ accumulation in a private residence. Carbon dioxide levels in the basement of the Godin residence (site 5 in Figure 1; Table 2) exceeded 11%, and O₂ dropped to 13% during our first visit to the home. Carbon dioxide concentrations exceeded 25% during continuous gas monitoring over several weeks. The home is newly constructed (the residents had lived there 2 weeks when we first visited the site). It is on spoil at a reclaimed surface mine; the spoil is 21.3 m thick (70 ft) beneath the home. Alkaline addition was used in the spoil at the site. There is also a deep mine 122 m (400 ft) west of the home. There are natural gas wells adjacent to the site. Isotopic analyses yielded a $\delta^{13}\text{C}_{\text{CO}_2}$ of -4.07‰ for the gas accumulating in the basement (Table 2). Gas that we collected from a monitoring well drilled through the spoil to the pit floor directly adjacent to

the house has a $\delta^{13}\text{C}_{\text{CO}_2}$ of -4.18‰ . These results again indicate that AMD reactions with carbonate minerals in the spoil are the source of the CO₂ gas.

Remediation at sites 1, 4, and 5 was similar to that described above for site 2 in Lawrence County. Remedial efforts were successful in reducing the levels of CO₂ to safe levels at all locations.

CONCLUSIONS

Elevated concentrations of CO₂ and depressed concentrations of O₂ in building spaces is an arising environmental hazard in western Pennsylvania and other areas of the Appalachian coalfields. This problem was restricted to blackdamp from abandoned deep mines in the past, but serious CO₂ hazards related to surface mining activity have emerged in the past few years. Carbon dioxide in the spoil of reclaimed surface mines may be organic or inorganic in origin. Organic CO₂ in spoil forms through aerobic respiration of plant roots and organisms. Inorganic CO₂ forms in spoil treated with alkaline addition by neutralization of acid from pyrite oxidation through reactions with carbonate minerals. Even near-neutral AMD waters can be undersaturated with respect to carbonate and react with calcite and dolomite in reclaimed mine spoil to produce CO₂ under certain geochemical conditions. Active

and reclaimed surface mines historically were located in rural regions isolated from homes and commercial real estate. Contemporary urban expansion, suburban sprawl, and Brownfield development, however, now juxtapose surface mining and building spaces in many parts of the Appalachian basin. More problems like those discussed in this paper are likely to appear. Although not widespread, this problem is dramatic and potentially lethal when it does occur.

Correct identification of the source of stray CO₂ is the most important step in the mitigation process. Gas composition and ground-water chemistry data by themselves are ambiguous in defining a mechanism for CO₂ generation and a specific source. Isotope geochemistry, particularly stable isotope work, is the most powerful tool available for discriminating CO₂ from different sources. Accurate recognition of a CO₂ source facilitates the assignment of liability, the procurement of appropriate remediation funds, and the design of adequate abatement protocols in stray gas migration cases.

The practice of alkaline addition to surface mines has saved hundreds of kilometers of streams in western Pennsylvania from degradation caused by AMD. The unintended consequence of CO₂ offgassing caused by this practice can be mitigated by using recommended building construction techniques. Abatement of stray CO₂ and other gases in new building construction is accomplished by using existing building code requirements for radon-resistant construction with the recommendation that the ventilation system is reversed to create a positive pressure system. These techniques are identified in Appendix F, Radon Control Methods, of the 2000 International Code for Building Construction. Proper application of these techniques will eliminate subsurface gas entry into structures.

Subsurface sequestration of anthropogenic CO₂ is a popular technology currently advocated by many researchers for curtailing the accumulation of greenhouse gases in the Earth's atmosphere and controlling global warming (see Drahovzal and Wickstrom, 2002 and web site discussions at <http://www.netl.doe.gov/coalpower/sequestration/index.html> and http://www.fossil.energy.gov/coal_power/sequestration/index.shtml). Subsurface CO₂ sequestration involves three potential carbon storage reservoirs: (1) petroleum reservoirs; (2) coal seams; and (3) deep brine aquifers. Assuring the environmental safety of subsurface CO₂ storage is critical. Sequestered CO₂ may migrate and contaminate potable ground water or accumulate as free gas in building spaces with conse-

quences similar to those described in the paper. It is also important to recognize that there are several possible sources of CO₂ in the petroleum and coalfields of the Appalachian basin before storing CO₂ underground there.

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