

Fugitive Carbon Based Gases Blasting Related or Not

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Abstract

Surface mine blasting was recently investigated as a potential source of high concentrations of stray gases found in nearby residences of western Pennsylvania. In one incident carbon monoxide was detected in a home and in the other, high concentrations of carbon dioxide were found in a home. Both carbon monoxide and carbon dioxide are by-products of blasting. However, other potential sources of these gases may also exist in a residential setting. In each case, gas chromatography (GC) and carbon isotopic analyses were used to define atmospheric concentrations inside the homes, and to determine the source of a stray gas. Molecular and isotopic analyses provide geochemical evidence as to the origin and source of the stray gas. This paper discusses elements of a stray gas investigation and the analyses necessary to identify the source of a stray gas.

Introduction

Elevated concentrations of various gases have long been known to be dangerous to underground miners. Prior to active mine ventilation, stagnant mine atmospheres allowed gases to accumulate, sometimes to lethal levels. Common terms were associated with their detrimental effect and continue to be used today. Black damp is caused by an oxygen deficient atmosphere and is often a result of carbon dioxide (CO₂) displacing oxygen. White damp is caused by elevated levels of carbon monoxide (CO). Fire damp refers to explosive levels of methane (CH₄). As a result of research and advances in mining law, most of the gas sources are currently identified and either eliminated or diluted with active ventilation. Today all active mines are required to provide active ventilation to vent unwanted gases.

One of the identified potential sources of black damp and white damp in underground mines is blasting. To minimize the volume of adverse gases generated by blasting, permissible explosives were developed for application in underground coal mines. This was done as an effort to protect miners from overexposure to toxic gases. With the addition of active mine ventilation, most, if not all, of the black damp and white damp in the underground miner's workplace have been eliminated.

Other explosives continue to be used at surface mines and quarries. Contrary to underground mining applications, surface blasts occur in the open atmosphere and any fumes are quickly dissipated into the atmosphere. However, as blasting nears a residential area, in both construction and mining, the designs become more confined in order to prevent flyrock. As the blasts become more confined, the gases are trapped in the ground. If venting to the atmosphere is not allowed, the gases will follow the path of least resistance. Occasionally, the gases will migrate into nearby residences and cause the occupants to become ill.

Since 1988, at least eleven incidents of stray CO migration from blasting sites have been documented^{1,2,3}. In a separate instance, elevated levels of CO₂ were alleged to have been caused by blasting⁴. Although both gases are generated in the blasting process, is blasting the source of the stray gases causing a problem?

Gas Properties

The physical and chemical properties of gases allow their movement to be predicted and their reactions in the atmosphere to be determined⁵. Gases migrate from high to low pressure areas and from high to low concentrations by molecular diffusion. Molecular diffusion becomes a prominent factor when flow rates are very low or stagnant. Blasting gases when confined in the ground are under pressure and will migrate to a lower pressure area through the path of least resistance. Once the pressure has equalized, the gases in the ground will dissipate through molecular diffusion or in response to changes in barometric pressure. Residual gases in the ground could last for years. The physical properties of CO and CO₂ are a factor in how they may migrate and are important considerations in sampling.

CO is a colorless, odorless, and tasteless gas with a specific gravity of 0.97 (compared to air). Its presence is due to incomplete oxidation or combustion of carbon. Very few natural CO sources exist. The most common source is automobile exhaust. Appliances, including gas cook tops, gas heaters, furnaces, and wood stoves can also contribute CO. Inadequate maintenance, broken

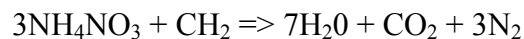
parts, or back drafting due to the design and construction of a house can make these devices dangerous. CO binds strongly with hemoglobin (carrier of oxygen from the lungs to the organs) in the blood. The CO-hemoglobin bond is 200 times stronger than O₂-hemoglobin. It is not easily respired out of the human body. Thus the blood cannot carry enough O₂ to sustain bodily functions.

Carbon dioxide is odorless, colorless, and tasteless and has a specific gravity of 1.53. It is a basic by-product of respiration and combustion. With a specific gravity heavier than air, the gas will stratify in a non-ventilated, confined area with highest concentrations at the base of a structure. CO₂ is not toxic to humans but in elevated concentrations, it can displace O₂ and result in asphyxiation (lack of oxygen).

Source of Carbon Based Gases from Blasting

All explosives create an amount of CO and CO₂. Depending on the oxygen balance of the formulation, some explosives produce more CO than others. The commonly used explosives contain an organic carbon. For simplicity, ammonium nitrate and fuel oil (ANFO) will be given as an example.

The byproducts of the detonation of ANFO are primarily water (H₂O), nitrogen (N₂) and carbon dioxide (CO₂), all nontoxic to people. In an ideal reaction¹:



Noxious fumes are generated when the fuel oil portion is incorrect, water is introduced into the ANFO, or optimum detonation velocities are not attained due to inadequate priming. Generally, whenever the reaction becomes less efficient, toxic gases (fumes or “smoke”) are produced. These secondary byproducts are CO and nitrogen oxides (NO_x).

The source of carbon in both CO and CO₂ is the fuel oil (CH₂). It is thermogenic in origin, derived from an organic source that was formed millions of years ago. This will play an important role when trying to determine the source as discussed later in this paper.

Migration Pathways

The migration pathways may be in multiple directions from a blast. Gases can travel through rock pores and fractures⁵. The porosity and permeability of the transmitting medium affect the travel rates. Generally, pressure gradients cause gases to migrate to areas of lower pressure. Sometimes, gases will follow man made features such as buried pipelines and other utilities.

Fractures provide a significant migration pathway. They include natural breaks produced by jointing and stress relief. The fractures are avenues for gases to move from one area or level to another through differing rock units. Faulting may also produce a conduit for gases to travel from its source. 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.

Gas Sampling and Thresholds

Gases can become dangerous in confined areas where ventilation is minimal. As the gases move through the ground and enter a residence, they will generally accumulate in the lower or below ground portions of a building. **ALWAYS TEST THE ATMOSPHERE FOR GASES BEFORE ENTERING A CONFINED AREA!** A confined area may be a basement, crawl space, closet, well house, manhole, trench, etc. Remember, CO₂ can stratify because it is more dense than air. Entry testing should include oxygen, CO₂, CO, and CH₄ (explosive at 5 %). If there are dangerously elevated levels of CO₂, the oxygen reading will be low and alarm.

NIOSH^{6,7} recommends that work areas not exceed a time weighted average of more than 35 ppm CO and 0.5 % (5000 ppm) CO₂ over an 8-hour period. For residential structures, EPA recommends no more than 9 ppm over an 8-hour period for CO. NIOSH also recommends a short term exposure limit (< 15 minutes) of 3 % CO₂ and a maximum limit of 200 ppm for CO.

Testing with Field Meters

Portable multi-gas monitors used for confined space work can be outfitted with data loggers. These units can be left on for extended periods of time, powered by household current, to monitor a project site. Their portability and ease of use make them ideal for field work. A multi-gas monitor for blasting investigations should include CO₂, CO, O₂, and CH₄.

The monitors should alarm when conditions for imminent danger exist. Because of constant changes in atmospheric conditions, 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. Gas concentrations may vary with changes in temperature and/or barometric pressure.

Generally, the gas measurement equipment used depends on the accuracy required and resources available to the field personnel. The most common field measurements of carbon gases are obtained from portable meters equipped with sampling wands and pumps. Figure 1 displays a portable meter used to sample gases. In addition to spot checking gas levels, many of the meters on the market today are capable of continuously recording gas measurements.

In homes, a low level of any gas in a confined area is usually a sign of a concentrated point source of entry or generation in a building⁵. Confined spaces must be carefully sampled to prevent normal air from diluting gases in the area to be sampled. Sampling should be performed through an existing opening or slightly opened door. Remember CO will evenly diffuse throughout the room and CO₂ will settle to the floor. Once safely inside, 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. Beyond the obvious sources, all potential entry points, traps, and potential sources of combustion in structures must be tested. Gases most often enter structures through a basement.

Construction trenches and subterranean structures such as tanks, vaults, and drain fields may be sources or conduits. These features should be checked for the presence of gas and evaluated as

potential sources. Care should be taken to preserve the atmosphere of these confined spaces. For example, the gas concentration may be greatly diluted or lost if a manhole cover is opened to test for gas. In this case, it is preferable to sample through a hole in the manhole cover.

Boreholes between the blast and problem areas should also be installed and tested to attempt to identify pathways (Figure 2). Portable meters with pumps and sampling wands can reach a depth of approximately 6 feet in the hole. If sampling is required at the bottom of a hole, tubing can be lowered to the bottom. Boreholes are best sampled on days when barometric pressures are dropping and gases may be exiting the ground.

Field measurements are necessary to identify point sources and gas response to atmospheric conditions but are not as accurate as laboratory analyses. If the source is to be identified, grab samples are required.



Figure 1. Dräger MultiWarn II



Figure 2. Borehole monitoring with sampling wand

Grab Samples

Grab samples of the gases should be obtained for molecular analyses in the laboratory. Gas samples for laboratory analysis can be collected in a variety of commercially available containers, including glass sampling bulbs, sampling bags, vacutainers, and various glass bottles.

Grab samples should be obtained at the entry points identified during field testing of the site (Figure 3). If a room is unsafe to enter, the sample should be taken from the atmosphere. Sample wands with an aspirator or pump are necessary to take point source samples (Figure 4). 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. Gas analyses in the laboratory are generally conducted by gas chromatography.

Detector tubes will provide only field quality sample results and are not recommended for detailed investigations where quantitative data are required. Detector tubes must be selected for each particular gas to be tested, often requiring trial and error sampling.



Figure 3. Rock ledge entry points.



Figure 4. Aspirator pump and Tedlar bag

Laboratory Analysis

Molecular analysis provides quantitative analysis of a grab sample. Molecular analyses are fundamental to attempt to identify the source of gases. Results for molecular analyses combined with other aspects of a site specific investigation may be sufficient to interpret the source of the gases. Molecular analysis for blasting investigations should include N₂, O₂, CO₂, CO, CH₄, H₂, and Ar.

Due to other environmental processes in the subsurface, molecular analyses alone may not always be sufficient 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 sources may occur, it is advisable to conduct analysis for carbon and hydrogen isotopes. Isotopes are different forms of the same element. For example, the origin and source of stray CH₄ can be determined through isotopic analysis of carbon (¹²C, ¹³C, and ¹⁴C), and hydrogen (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 the source to be distinguished⁵.

Molecular and isotopic analyses combined with a site specific investigation generally provide a definitive answer regarding the source of carbon based gases.

Source Determination - Molecular Analysis

Different gas sources often exhibit different ratios of gases and isotopic signatures. Results of the molecular analysis can be compared to normal atmospheric conditions as shown in Table 1. The ratio of components is often useful in determining the source of gas. If the gas constituents and ratios between a source and problem area are similar, then further investigation of that source is warranted. From Table 1, the residence gas most closely resembles the Backfill 1 gas.

The data in Table 1 are not all from the same site but are useful in illustrating the typical characteristics of gases whose origins are different. Each source will be discussed separately.

Gas	Air	Blasting – Borehole	Backfill 1 with Limestone	Backfill 2	Landfill	Abandoned Mine	Residence
N ₂	78.09%	89.29%	81.09%	78.00%	3.70%	87.77%	80.35%
O ₂	20.95%	5.78%	7.29%	19.30%	0.8%	0.30%	9.82%
Ar	0.93%	1.07%	0.96%	0.93%		1.05%	0.96%
CO ₂	0.03%	3.86%	10.65%	1.43%	47.0%	8.96%	8.86%
CO	0%	0.0023%			0.1%	0%	
CH ₄	0%	0.0003%	0.013%	0.0087%	47.4%	1.88%	0.15%

Table 1. Gas samples from various sources.

Blasting Gases: As discussed earlier, blasting generates elemental nitrogen, CO₂, and water. If the detonation is not ideal, the blast emits CO and nitrogen oxides. If N₂, CO₂, and CO components of the samples are elevated, the gases may be linked to blasting. Without elevated levels of all three, the gases are unlikely to be related to blasting.

Backfill Gases: Reclaimed surface mines can be a source of CH₄ and CO₂. Often trees and other organics materials are buried. Degradation of this organic material generates both CH₄ and CO₂. The primary precursor of carbon in organic material is CO₂ from the atmosphere. Occasionally, calcium carbonate (CaCO₃) is added to the backfill of surface mines to treat acid drainage. When the acidic waters contact the limestone, CO₂ is produced. An atmosphere from this backfill would be rich in CO₂.

Landfill Gases: CO₂ and CH₄ generated in landfills are microbial in origin. Occasionally, CO₂ and CH₄ from an active landfill may migrate undetected outside of the landfill perimeter. Unpermitted, pre-regulation landfills may also represent CH₄ sources with the potential for migration to other areas. When these gases are detected, the CH₄ component presents a much larger hazard than the CO₂.

Abandoned Mine Gases: Gases produced from abandoned mines may be microbial, thermogenic, or mixed in origin. Abandoned underground coal mines are CO₂ and CH₄ sources with the potential for migration to areas of lower pressure. In the absence of a mine fire, CO should not be present. Fluctuating barometric conditions often drive the migration of CO₂ and CH₄ from shallow abandoned coal mines. Pressure is reduced at the soil/atmosphere interface under falling barometric conditions, resulting in soil outgassing.

In the coal and gas fields, different gas sources generally exhibit different ratios of CH₄, C₂+ hydrocarbons (propane, butane, etc.), and isotopic signatures. The ratio of C₂+ hydrocarbons is

often useful to determine if the gas is microbial or thermogenic in origin. High concentrations of C₂+ hydrocarbons are an indication that the gas is thermogenic in origin. However, the absence or low concentrations of C₂+ hydrocarbons do not indicate the gas is microbial in origin⁹. This is due to other processes that may affect the composition of the gas during migration such as fractionation, i.e. removal or impediment of the heavier hydrocarbons as gas migrates through the soil column, or bacterial oxidation, the consumption or conversion of the C₂+ hydrocarbons. When combined with other elements of an investigation, stable carbon and hydrogen isotopic analyses provide powerful analytical tools to distinguish microbial and thermogenic hydrocarbon gas sources and stable carbon isotope analysis of stray CO₂ also yield data to determine if the source is organic or inorganic in origin¹⁰.

Source Determination – Isotopic Analysis

Stable carbon isotope geochemistry provides a valuable analytical tool to determine the origin of stray CO or CO₂. Isotopes are atoms whose nuclei contain the same number of protons but a different number of neutrons. Stable isotopes are not subject to radioactive decay. Their abundance in nature is controlled by other biological and physical processes, such as photosynthesis in the case of stable isotopes of carbon (¹²C and ¹³C). Sedimentary carbonates and organic matter possess discrete stable isotopic characteristics because of the operation of two different reaction mechanisms⁸.

1. Isotope equilibrium exchange reactions within the inorganic carbon system lead to an enrichment of ¹³C in carbonate rocks.
2. Kinetic isotope effects during photosynthesis concentrate ¹²C in organic matter.

¹³C/¹²C values are expressed in parts per thousand or per mil (o/oo). The standard is the internationally recognized PDB reference standard for carbon. This standard is from a cretaceous marine fossil, *Belemnitella Americana* from the PDB formation in South Carolina. The PDB standard has been assigned a value of 0 per mil. Negative numbers signify enrichment in the lighter isotope (¹²C) relative to the standard whereas positive numbers signify the carbon is enriched in the heavy isotope. Atmospheric CO₂ has a value of -8 per mil.

Isotopic analyses allow differentiation between microbial, thermogenic and organic and inorganic sources of carbon based gases. For example, CH₄ from a coalbed will often have a different stable carbon isotopic composition when compared to CH₄ from an active or abandoned gas well.

Stray CO₂ can also be traced to its source through isotopic analysis. CO₂ derived from an inorganic source (limestone) is typically enriched in the heavier isotope (¹³C). Whereas, CO₂ derived from an organic source (degradation of organic matter) will be enriched in the lighter isotope of carbon (¹²C). In blasting the carbon source is diesel fuel (CH₂) and is expected to be enriched in the lighter isotope of carbon. When the lighter isotope is predominant and the source is still uncertain (microbial or thermogenic), ¹⁴C analyses can provide the final clue.

Where microbial gas is suspected as the potential source, ¹⁴C analyses provide definitive results. Recently formed gases, such as landfill gases, are enriched in ¹⁴C, and are readily distinguished from thermogenic sources⁹. Thermogenic CH₂ was formed from organic materials that are

millions or hundreds of millions of years old and does not contain any detectable ^{14}C . Stray gas derived from diesel fuel will have no ^{14}C activity.

Summary

Carbon based gases, carbon monoxide and carbon dioxide, are produced in the detonation of explosives. Historically gases have been documented to travel through the ground up to 500 feet from the blast site. When these gases enter confined places where either workers or the public occupy the space, they may become overcome by gas. As blasting occurs in close proximity to work place confined spaces, like manholes, workers should be trained on the physiological signs of gases prior to blasting and during blasting. Testing of the work areas should also be conducted prior to entry. When blasting near public places, like homes, public education on the physiological signs of gases are best conducted during preblast surveys. On some occasions the blaster may be wise to offer commonly available in-home gas detection devices to the occupant. The aerial extent of concern should be tied to the local geology and subterranean man-made features.

If carbon gases are identified at any time, they may be attributed to blasting activities in the vicinity. Initial gas sampling consists of taking field samples to identify dangerous environments and ensuring the safety of the public. If CO or CO₂ concentrations exceed 9 ppm or 0.5%, respectively, a detailed investigation is recommended.

Detailed investigations include continuous monitoring and the collection and analysis of gas samples. Continuous monitoring provides a time history of gas concentrations that may relate to nearby activities or environmental changes such as barometric pressure swings. Clues of the driving mechanism may be found. Laboratory analysis of gas samples will provide detailed information on the molecular composition of the stray gas and nearby potential sources. When compared to each other, the source may become obvious. However if the molecular results prove inconclusive, isotopic analyses can be conducted to more clearly identify the gas source.

Site specific investigations combined with molecular and isotopic analyses and knowledge of the relative amounts of basic gases common in mine backfills, landfills, blasts, and abandoned mines, provide a comprehensive approach to identify the source of a stray gas.

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