Carbon Dioxide in Limestone Caves and its Effect on Cavers

There are increasingly frequent reports of 'foul air' – an excess of carbon dioxide and reduced oxygen – in caves. Garry K. Smith describes the problem and how to deal with it.

This article is a condensed version of previously-published papers by Garry K. Smith of the Newcastle and Hunter Valley Speleological Society, Australia. Although written from his Australian perspective, the problem of CO_2 build-up is increasingly being seen in UK caves.

A list of UK further reading is given at the end of the article.

Introduction

Foul air, sometimes called 'bad air', is an atmosphere which has a noticeable, abnormal physiological effect on humans. In limestone caves, foul air can be described as air containing more than 0.5% carbon dioxide (CO_2) and/or less than 18% oxygen (O_2) by volume. As a comparison, normal air contains approximately 0.03% CO_2 and 21% O_2 by volume. There are isolated caves that contain other gases such as methane, ammonia, hydrogen sulphide or carbon monoxide, but these gases are generally rare in limestone caves. Although not a significant problem in the majority of caves around the world, those containing foul air may become death traps for cavers not familiar with the signs and symptoms of the gases involved.

An elevated CO_2 concentration is usually the most life-threatening foul-air scenario found within limestone caves. This colourless, odourless and non-combustible gas is the body's regulator of the breathing function. In industry the maximum safe working level recommended for an 8-hour working day is 0.5% (5000 ppm by volume; Australian regulations). A concentration of 10% or greater can cause respiratory paralysis and death within a few minutes.

To the novice caver, their first encounter with foul air is often a frightening experience. Typically there is no smell or visual sign and the first physiological effects are increased pulse and breathing rates. Higher concentrations of CO_2 lead to clumsiness, severe headaches, dizziness and even death. Experienced foul-air cavers may notice a dry acidic taste in their mouth, but the average caver may not notice this effect.

How CO_2 Gets Into Caves

CO_2 enters caves by several methods, each of which has a bearing on the gas ratio composition of the cave atmosphere and its variation from that of the above-ground atmosphere. The two main methods by which CO_2 gets into caves are:

- CO_2 is absorbed by the ground water as it passes through surface soil containing high concentrations of the gas, due to the decay of vegetation. This water percolates through the rock strata and enters the cave system, usually taking part in the calcite deposition cycle. In this instance the addition of extra CO_2 to the cave atmosphere displaces O_2 and nitrogen (N_2).

- CO_2 may be a by-product of organic and micro-organism metabolism or respiration by fauna such as bats or humans. The oxygen concentration is simply reduced in proportion to the increase in CO_2, while the N_2 concentration stays constant.

Even though carbon dioxide is 1.57 times as dense as nitrogen and 1.38 times as dense as oxygen, it will have a tendency to disperse in an isolated volume of air owing to gaseous diffusion. In other words a mixture of gases will not separate into layers of different-density gas if they are left for a long time in a still chamber.

Foul air is often encountered in pockets at the lower sections of deep caves where there are no active streams and air movement is minimal. Notwithstanding the comments made above about mixing, frequently there appears to be a definite boundary between good air and foul air, with a noticeable elevation in CO_2 concentration in the latter. In caves containing foul air, on numerous occasions I have experienced these invisible boundaries within a transition zone of less than one metre. Often there isn't a gradual transition in air quality as one might expect if dispersion of the gases were occurring at a relatively fast rate.

A possible explanation of the high concentration of CO_2 in some deep caves with a relatively still atmosphere is that CO_2 is being produced metabolically or entering the cave via ground water at a greater rate than the gas can diffuse into the cave atmosphere, thus settling at the bottom of the cave because it is a relatively dense gas (Smith, G. K., 1997a).

This build-up of CO_2 is more prevalent in deep caves, but it can also be found in some shallow caves with a vertical range of less than 10 metres. A very still cave atmosphere may allow CO_2 to sink to (or remain at its origin in) the deepest part of the cave where it displaces O_2 and N_2, thus allowing CO_2 to build up at the lowest point. An example of this would be Suicide Hole Cave at Crawney Pass, New South Wales, which has a vertical range of approximately six metres and contains a high concentration of CO_2 in the bottom two metres of cave passages. The CO_2 can be attributed to metabolic processes in a large number of fine tree roots in a passage just above the foul air.

The Effects on Humans

The effects of increased levels of CO_2 and decreased levels of O_2 on humans are shown in ***Tables 1 and 2***; but as each person's body has a slightly different reaction and tolerance to stressful situations, the symptoms shown are general. However, nobody is immune to the dangers posed by CO_2.

Exposure to between 1 and 2% CO_2 for some hours will result in acidosis, even if there is no lack of oxygen. Acidaemia will result and secondary mechanisms are initiated by the body's homeostatic processes in an attempt to prevent drastic changes in pH and to return the pH towards normal.

Prolonged breathing of air containing around 2% CO_2 or higher will disturb bodily function by causing the tissue fluids to become too acidic. This will result in loss of energy and feeling run down even after leaving the cave. It may take up to several days in a good environment for the body metabolism to return to normal.

Health and Safety rules cite 0.5% CO_2 as the 'threshold limit value time weighted average'. This is the concentration to which a person may be exposed, eight hours a day, five days a week, without harm. The *Laboratory Safety Manual* (1992), quotes that a concentration of 5% CO_2 and above is "immediately dangerous to life and health". It also says that this is the concentration which will cause irreversible physiological effects after 30 minutes' exposure. (Section 24, pp4-5, 'Oxygen-Deficient Atmosphere').

One must be mindful that the sight of bats in a cave does not necessarily mean that the atmosphere is suitable for humans. On several occasions I have experienced laboured breathing in caves containing bats, where a simple butane cigarette lighter failed to ignite and a struck match head only fizzed before going out. The bats seemed to be unaffected by the low O_2 and high CO_2 content of the atmosphere. These observations are echoed by Hamilton-Smith (1972) who states that

CO_2	Effect
0.03%	Nothing happens, as this is the normal carbon dioxide concentration in air
0.5%	Lung ventilation increases by 5%. This is the maximum safe working level recommended for an eight-hour working day in industry (Australian Standard)
1.0%	Symptoms may begin to occur, such as feeling hot and clammy, lack of attention to details, fatigue, anxiety, clumsiness and loss of energy, which is commonly first noticed as a weakness in the knees ('jelly legs')
2.0%	Lung ventilation increases by 50%, headache after several hours' exposure. Accumulation of carbon dioxide in the body after prolonged breathing of air containing around 2% or more will disturb body function by causing the tissue fluids to become too acidic. This will result in loss of energy and feeling run down even after leaving the cave. It may take the person up to several days in a good environment for the body metabolism to return to normal
3.0%	Lung ventilation increases by 100%, panting after exertion. Symptoms may include headaches, dizziness and possible vision disturbance, such as seeing speckled stars
5–10%	Violent panting and fatigue to the point of exhaustion merely from respiration, & severe headache. Prolonged exposure to 5% could result in irreversible effects on health. Prolonged exposure to > 6% could result in unconsciousness and death
10–15%	Intolerable panting, severe headaches and rapid exhaustion. Exposure for a few minutes will result in unconsciousness and suffocation without warning
25–30%	Extremely high concentrations will cause coma and convulsions within one minute of exposure. Certain death

Table 1 – The effects of elevated levels of CO_2.

O_2	Symptoms
21–14%	First perceptible signs, with increased rate and volume of breathing, accelerated pulse rate and diminished ability to maintain attention
14–10%	Consciousness continues, but judgement becomes faulty. Rapid fatigue following exertion. Emotions affected, in particular ill temper is easily aroused
10–6%	Can cause nausea and vomiting. Loss of ability to perform any vigorous movement or even move at all. Often the victim may not be aware that anything is wrong until collapsing and being unable to walk or crawl. Even if resuscitation is possible, there may be permanent brain damage
below 6%	Gasping breath. Convulsive movements may occur. Breathing stops, but heart may continue beating for a few minutes – ultimately death

Table 2 – The effects of low levels of oxygen.

"…the Bent-winged Bat is able to tolerate higher concentrations of gas (CO_2) than that acceptable to human beings".

The Australian Standard (AS 2685-1986, p7), *Safe Working in Confined Space*, states that entry to confined space shall not be permitted if the oxygen level is below 18%. This standard was revised in 1995 and the minimum concentration raised to 19.5% by volume under normal atmospheric pressure, equivalent to a partial pressure of O_2 of 19.8kPa.

The indications are that very little difficulty is caused by short-term exposure to O_2/N_2 mixtures down to about 10% O_2; the problem is not the shortage of O_2 but the excess of CO_2.

Field (1992) states that the great majority of healthy people, whether young or old, would not be limited by their ventilatory function during physical exertion when breathing air at sea level containing 3.1% CO_2 and 15% O_2, but many, particularly the elderly, would experience mild to moderate breathlessness. In an atmosphere containing 4.3% CO_2 and 12.4% O_2, the average healthy person with a reasonable level of physical fitness would be capable of less than half the maximum physical exertion they could normally attain breathing normal air.

One should note that it is not simply just the O_2 volume percent which is important for human respiration, but the O_2 partial pressure. For instance the O_2 partial pressure decreases at higher altitude, while the O_2 volume percent remains constant. For example, the partial pressure of O_2 at an altitude of 2000 metres above sea level is 17.7kPa (177 millibar), which is equivalent to breathing air in which the concentration of O_2 has been reduced to 17.5%.

How the Body Eliminates CO_2

The human body under average conditions inhales air that contains approximately 21% oxygen and 0.03% carbon dioxide. The air breathed out of the lungs contains approximately 15 to 16.3% O_2 and about 4.5% CO_2, which is sufficient to revive a person using expired air resuscitation (EAR). A person at rest inhales and exhales approximately 6 litres of air per minute, but in times of stress this may increase to more than 100 litres/minute.

The CO_2 level in the blood is an important stimulus to respiration. Nerve receptors in the aorta, near the heart, and in the carotid arteries, which go to the head and neck, monitor changes in the CO_2 concentrations in the body. If the amount of CO_2 in the blood increases, both the rate and depth of breathing increase. Changes in oxygen levels are also monitored, but the receptors are not as sensitive to changes in oxygen as to changes in CO_2.

Data Logging: Electronic Detection of CO_2

SpeleoScene **52** (Sept-Dec 2002) reports that elevated levels of CO_2 have been detected recently in caves in Mendip, Forest of Dean and Derbyshire regions. The article suggests that the increase may be linked to changes in farming practices (e.g. the washing out of cow-sheds and the spraying of the resulting nitrogen-rich slurry on fields). CO_2 levels have been observed to change with the weather and the seasons, so there is clearly an interest in trying to correlate CO_2 levels with meteorological conditions and surface agricultural activity.

A sub-surface data-logger that monitored CO_2 levels at frequent intervals could probably provide some interesting data. However, this equipment is likely to be prohibitively expensive, even if largely home-built. CO_2 is not an easy gas to detect and the sensors are correspondingly expensive.

The problem is that CO_2 is not a very reactive gas and it cannot be further oxidised. For example, the fuel gases (e.g. CO, H_2, CH_4) can easily be detected by oxidising them on a hot electrode and detecting the change in resistance. Sensors that do this are available at low cost. And carbon monoxide (CO) can be detected at concentrations as low as 1ppm using a cheap sensor based on an electrolytic cell. But these methods cannot be used to detect CO_2. So how might we detect CO_2 and can we built a cheap home-made sensor to avoid having to buy commercial equipment?

From A-level chemistry, we know that bubbling CO_2 into lime water makes it turn milky, due to a suspension of $CaCO_3$. Could we devise a machine to pump the gas through water and then measure the cloudiness using a simple photocell? Probably not. As those of you who studied chemistry at A-level will recall, the milky solution disappears if you continue to bubble in CO_2 because the precipitate re-dissolves in the weakly acidic solution – not to mention the problems of accurately calibrating such a system for temperature variation.

On the basis that many scientific instruments use technology that is years out of date, we could investigate some more esoteric methods. Could we build a device based on nuclear magnetic resonance (NMR)? NMR in liquid water can be demonstrated with simple electronic equipment but, unfortunately, this is not so for a gas (it is too rarefied) and, in any case, not for CO_2 because it is only the rare ^{13}C isotope that we could get to resonate.

One possible solution would be to measure O_2 depletion rather than CO_2 build-up. But oxygen sensors are expensive too, and for research into CO_2 this technique would not be experimentally sound.

It seems that any home-built CO_2 detector would have to be based on infrared absorption – just like commercial sensors. CO_2 absorbs strongly at 4.3μm. Obtaining an infrared emitter at this frequency is straightforward (anything 'hot' will do). An optical filter tuned to 4.3μm would have to be specially manufactured but the cost, spread over a number of units, would not be too great. We might need a similar filter tuned to a nearby frequency to allow us to make a ratiometric reading. The infrared detector is a slight problem because cheap passive-infrared detectors (as used in burglar alarms) usually use an 'unfavourable' arrangement of sensors. But there are a number of possible solutions to this problem.

All-in-all, though, the design work would be time-consuming. Perhaps the best option would be to keep an eye on the new solid-state gas sensors being developed by Ion Optics (**www.ion-optics.com**). These MEMS-based infrared gas sensors (MEMS = micro-electrical-mechanical systems) feature an emitter, filter and detector all on a single chip and promise an attractive low-cost solution to CO_2 sensing – if they eventually hit the market place.

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Exchange of the two gases takes place in the lungs by diffusion across the walls of the air sacs (alveoli). Oxygen from inspired air diffuses across the lining of the air sacs and enters the circulation, while CO_2 moves in the opposite direction. The gases are transported between the cells and the lungs by the circulation of the blood. A gas at high concentration (or partial pressure) will move to an area of relatively low concentration (or partial pressure), until an equilibrium is reached. This enables CO_2 in the body at a relatively high concentration to diffuse from the capillaries into the inhaled air in the lungs (Smith, G. K., 1993 & 1997b).

A Simple Test for Foul Air

In the majority of cases of foul air found in caves, the real danger is the CO_2 concentration, which is the main trigger for the human body to increase its breathing rate. Prolonged exposure to a concentration of just 6% CO_2 or more may be enough to cause suffocation. In the majority of cases, if a person in a cave has any of the symptoms of elevated carbon dioxide exposure, a simple 'naked flame test' will fail; but ***note that the flame test is not a reliable test to determine the actual CO_2 concentration***.

The naked flame test (see box) can be undertaken by igniting a match or butane cigarette lighter or carrying a lit candle into suspected foul air. If the flame is extinguished, foul air is present. Where possible a butane lighter should be used to reduce unpleasant fumes emitted from striking matches while testing air quality in the confines of a cave (Smith, G. K., 1997a).

Laboratory tests have proven that combustion of a match, candle or butane cigarette lighter will cease at a concentration of about 14.5 to 15% oxygen. In fact humans can survive in an atmosphere containing 10% oxygen, so when the flame test just fails, the atmosphere still contains enough oxygen to survive.

Dealing With High CO_2 Levels

A test should be made as soon as foul air is suspected, and if a naked-flame-test fails, then all members of the party should immediately exit the cave in an orderly manner without panicking. Inexperienced cavers in the group should be especially watched and guided to the entrance.

When undertaking vertical pitches in caves suspected of containing foul air the first person down should make thorough checks for CO_2. Besides carrying ascenders, a pre-rigged safety belay system set up in the abseil rope is a wise option in the event that the first person down may be overcome when suddenly descending into an area of high CO_2 concentration. Certainly a large knot tied in the end of the abseil rope before it is descended, is essential to the retrieval of an overcome person.

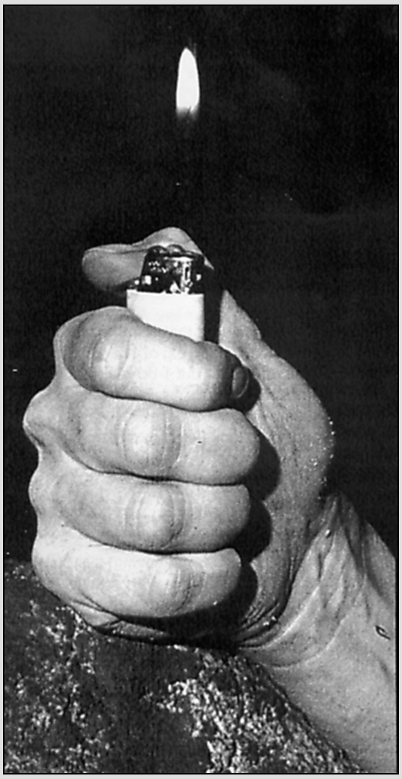
A safety belay should be mandatory on all pitches where a ladder is more than just a hand-hold. Cavers should only enter areas of foul air during special circumstances, such as search and rescue operations, exploration and scientific work. Under these circumstances special precautions should be taken to ensure the safety of the group.

The Naked Flame Test

Because an elevated CO_2 concentration in caves *usually* corresponds to depletion in O_2, cavers have for many years used the naked flame test to determine whether the atmosphere contained too much CO_2.

The naked flame test involves lighting a match or cigarette lighter in the cave air, or carrying a burning candle into a suspected foul air area, whereupon the flame would extinguish when a particular concentration was reached. This test has been widely accepted by cavers as a fairly accurate indication of CO_2 concentration.

I have I undertaken extensive testing in controlled atmospheres which has revealed that the Naked Flame Test is *not* a reliable test of CO_2 concentrations, other than to indicate that the cave atmosphere is most likely dangerous to human life. In fact the naked flame is only measuring the O_2 concentration and the CO_2 has such a small influence over combustion that it can be ignored within the concentration range found in caves.



This photo was taken in Grill Cave at Bungonia, NSW, Australia, where the interface of high CO_2 concentration is encountered and O_2 is close to 15%. A butane lighter was lit in good air and gradually lowered into the foul air. The 25mm flame stayed burning just above the oxygen-deficient interface. The photo shows that within the foul air there was insufficient O_2 to support the combustion of butane but, at 75mm higher, there *was* sufficient oxygen.

This phenomenon can not occur with solid fuels, such as matches and candles, as the heat from the flame is required to vaporise the volatile compounds.

Concluding Remarks

In the majority of cave atmospheres an elevated CO_2 concentration corresponds to a depletion of O_2. A high CO_2 concentration is the most life-threatening foul-air situation encountered underground.

Conversely, a life-threateningly-low concentration of O_2 is rarely encountered, but when the CO_2 is so high as to be dangerous to humans, there is generally not enough O_2 to support combustion.

The first physiological signs of high levels of CO_2 include increased heart and breathing rates, headache, clumsiness, fatigue, anxiety and loss of energy. If you or a member of your group experiences any of the common side-effects of CO_2 poisoning, you should carry out a simple flame test with a butane cigarette lighter. In the *majority* of cases, if a person has any of the symptoms characteristic of an elevated carbon dioxide concentration, a simple naked flame test will fail. If the butane (or match) fails to ignite, notify others in the party and vacate the cave in a safe manner. ***However, the flame test is not a fully-reliable test for CO_2 concentration.***

Carbon dioxide when treated with respect is no worse than the other dangers in caves. Despite the possible dangers, caving is still safer than driving a motor vehicle, which most of us take for granted. The best advice is 'If in doubt, get out'. ■

References

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Acknowledgements

This article is based on (Smith. Garry K., 1997b; 1999) as listed above, with the permission of the author. Versions of those two papers are available on-line at **www.wasg.iinet.net.au**. Click on the ASF tab.

Further Reading

In the UK, the Council of Southern Caving Clubs (CSCC) web site has a news item (16/11/02) on the closing of GB Cave due to high CO_2 levels. See **www.tuoni.demon.co.uk / cscc / CSCCnews.htm**. The site includes a short article by Tony Boycott on the dangers of CO_2 at **www.tuoni.demon.co.uk / cscc / CO2.htm**.

A longer article (unaccredited) appeared in the NCA's newsletter: *SpeleoScene* **52**.