Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Geologic Storage of Carbon Dioxide with Monitoring and Verification

Volume 2

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Geologic Storage of Carbon Dioxide with Monitoring and Verification

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Chapter 26

HUMAN HEALTH AND ECOLOGICAL EFFECTS OF CARBON DIOXIDE EXPOSURE

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ABSTRACT

Understanding of human health and ecosystem impacts from exposure to elevated concentrations of CO_2 in air, soils and water is needed to assess the consequences of leakage from geologic storage projects. This chapter places CO_2 storage in the context of the global carbon cycle, reviews information on human health effects and ecosystem impacts from exposure to high concentrations of CO_2, and reviews industrial uses of CO_2 and describes the regulations put in place to protect workers and the public. This information provides the foundation for understanding and assessing risks of leakage from geological storage projects.

INTRODUCTION

To begin a risk assessment of geologic storage, we must first understand both the context for evaluating CO_2 exposures as well as the human health and environmental impacts of exposure to elevated concentrations of CO_2. Fortunately, there is a large amount of information to draw on in this regard. Carbon dioxide was one of the first gases identified, and it remains widely used in industry. Regulations are well developed for using CO_2 in occupational and industrial settings and for storing and transporting it. Moreover, the central role that CO_2 plays in living systems and ecosystem processes has motivated the development of an enormous knowledge base from which to begin this assessment.

We begin this chapter by placing CO_2 storage in the context of the global carbon cycle. We then summarize what is known about the basic physiology of CO_2 and how exposure to elevated concentrations leads to human and ecological risks. A review of industrial sources, uses, and accidents follows, and finally, we summarize current regulations and monitoring approaches for occupational and industrial exposures to CO_2.

CO_2 STORAGE IN THE CONTEXT OF THE GLOBAL CARBON CYCLE

Carbon dioxide is ubiquitous in the natural world. It undergoes an endless cycle of exchange among the atmosphere, living systems, soil, rocks, and water. Volcanic outgassing, the respiration of living things from humans to microbes, mineral weathering, and the combustion or decomposition of organic materials all release CO_2 into the atmosphere. Atmospheric CO_2 is then cycled back into plants, the oceans, and minerals through photosynthesis, dissolution, precipitation, and other chemical processes. Biotic and abiotic processes of the carbon cycle on land, in the atmosphere, and in the sea are connected through the atmospheric reservoir of CO_2.

Figure 1 illustrates the primary compartments of the global carbon cycle and the fluxes between them. The atmosphere contains approximately 755,000 Mt of carbon (Mt C), the terrestrial biosphere 1,960,000 Mt C and the oceans 38,100,000 Mt C. Carbon dioxide from the atmosphere is converted into biological matter by photosynthesis. The process, called primary production, converts approximately 60,000 Mt C (225,000 MMT CO_2) into biomass each year. This flux is balanced by a nearly equal flux of CO_2 back into the atmosphere, resulting from the respiration of living organisms and the decomposition of organic matter. Differences between these two competing fluxes determine whether the terrestrial biosphere is a net source or sink of CO_2. Carbon dioxide also dissolves in surface, ground, and ocean water, mostly as bicarbonate (HCO_3^-; $CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$), and in shallow tropical waters, it precipitates out as carbonate rocks such as limestone ($CaCO_3$; $2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H_2O + CO_2$). Annually, approximately 90,000 Mt C are exchanged between the ocean and the atmosphere. These quantities provide a context for evaluating the 6000 Mt C that is currently generated from fossil fuel combustion and the fraction of that amount that may be stored in geological formations in the future.

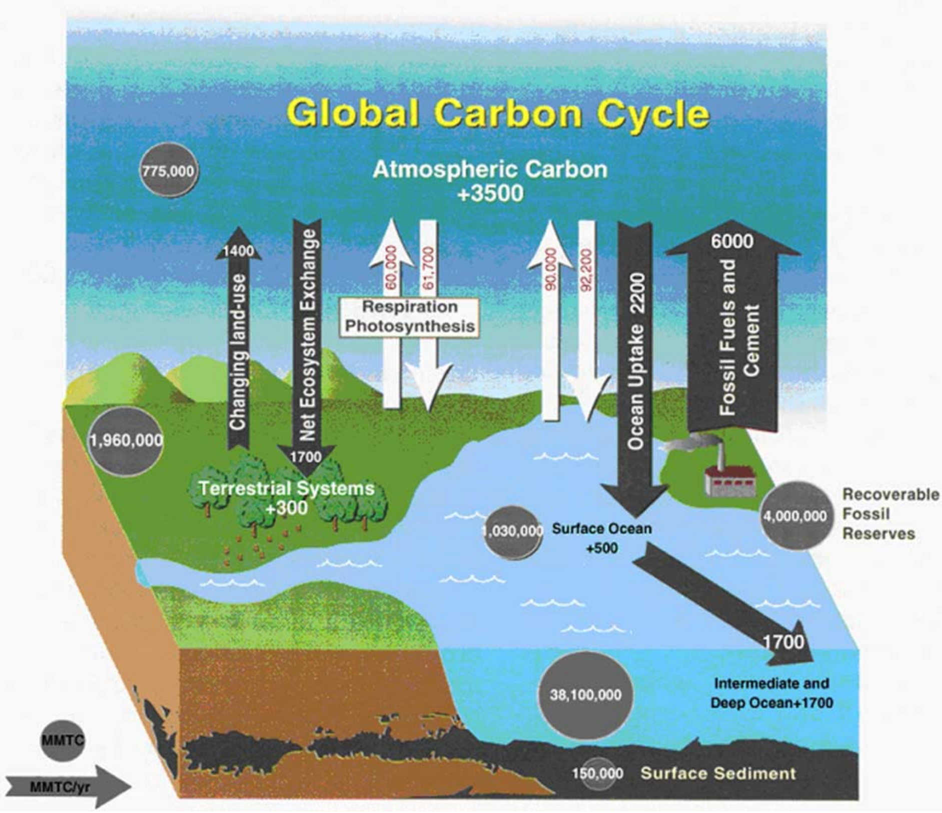

Figure 1: Global biogeochemical carbon cycle. Includes human influence from fossil fuel combustion and changing land-use patterns. Black arrows indicate net fluxes and white arrows indicate gross fluxes. Annual net additions are shown as + numbers, and pool sizes (circles) are shown in gray. All quantities are in million metric tonnes Carbon, MMTC, and all fluxes are in MMTC/yr (modified from US DOE, 1999).

The quantities of CO_2 that might be stored may also be put in the context of other known carbon reservoirs, as well as industrial and natural emissions. Figure 2a and b tabulate many of the known carbon reservoirs and fluxes, and compare them to the carbon storage goals identified by the US DOE. The current US DOE target for global annual storage capacity by 2025 is 1000 Mt C/yr [1]. As shown in Figure 2b, this is nearly equal to (for example) the US annual petroleum consumption or global annual natural gas consumption in 1998. The US DOE goal for global carbon storage capacity in 2050 is 4000 Mt C/yr, which is comparable to the total US natural gas reserves as assessed in 1998. While these comparisons point to the very large

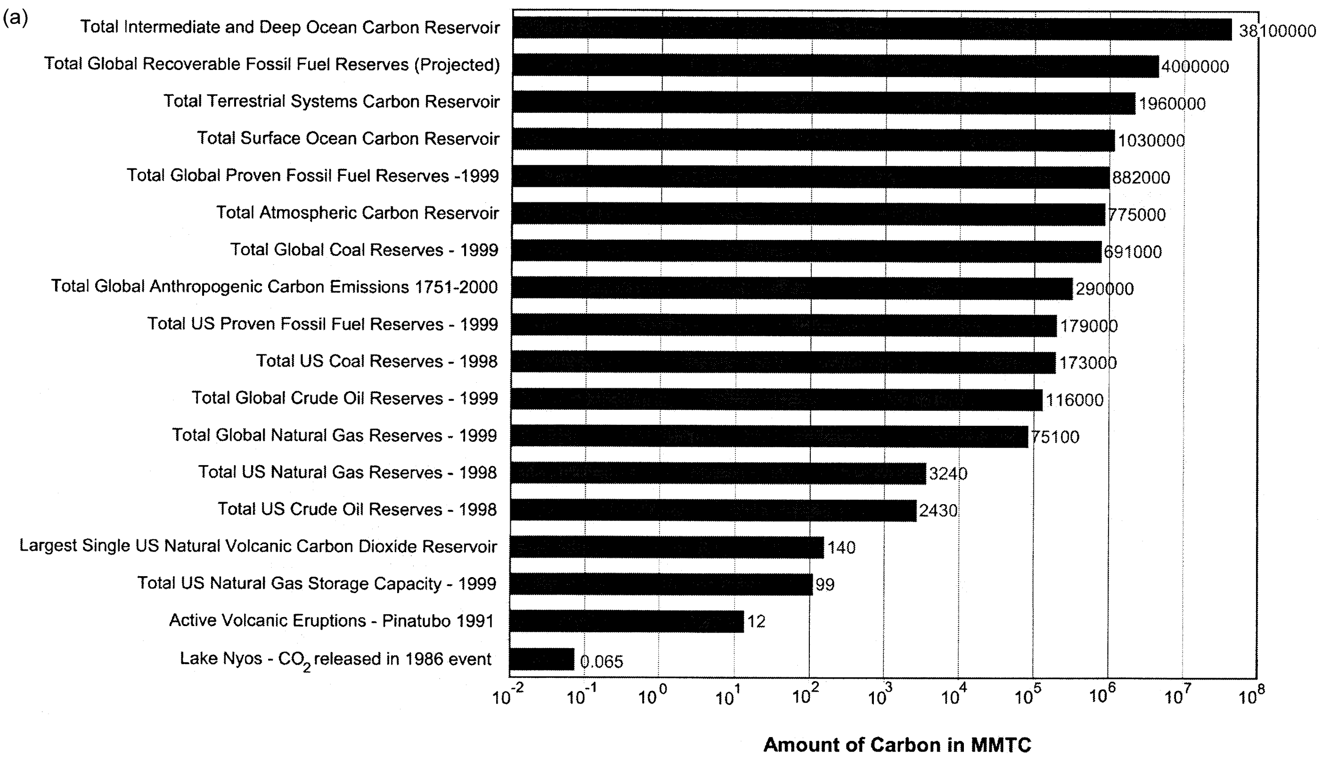

Figure 2: (a) Comparison of carbon reservoirs and one-time events. Data tables, references, and conversions can be found in Ref. [77]. Estimates are order of magnitude only and may include small conversion discrepancies due to independent rounding. (b) Comparison of carbon fluxes and target sequestration rates. Estimates are order of magnitude only and may include small conversion discrepancies due to independent rounding.

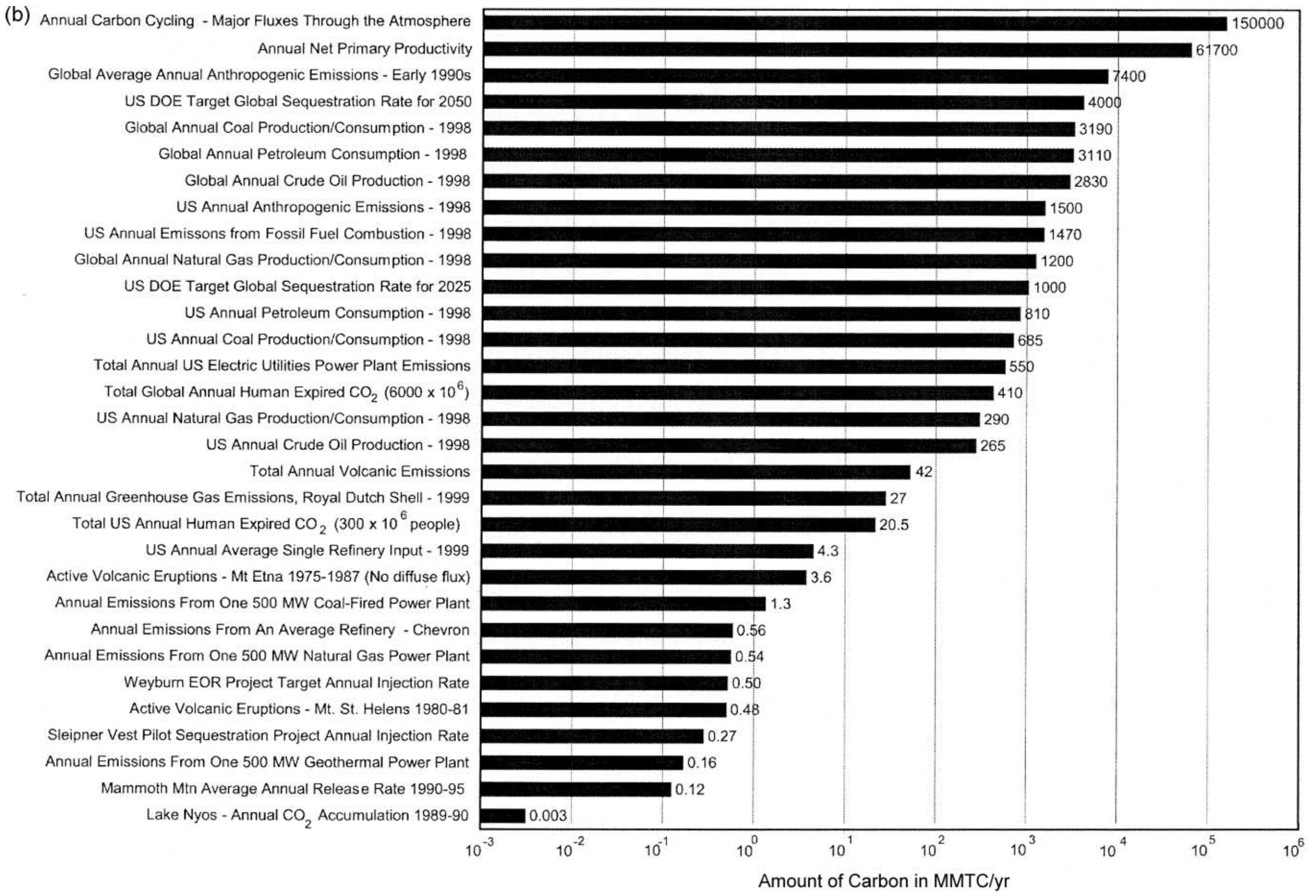

Figure 2: Continued.

quantities of CO_2 that may be stored, they are still small in comparison to the 90,000 MMTC/yr exchanged annually between the atmosphere and ocean and the 60,000 MMTC/yr exchanged between the atmosphere and the terrestrial biosphere. On the other hand, Figure 2b illustrates that the storage target is large compared to the global volcanic emissions of 42 Mt C/yr.

From a risk-assessment perspective, a more useful comparison may be the quantity of CO_2 associated with an individual storage project. Each facility is anticipated to store 0.25–10 Mt C/yr. For example, the Sleipner storage project in the North Sea currently injects 1 Mt CO_2 or 0.27 MMTC (1 tonne carbon = 3.667 tonnes CO_2) into the Utsira Formation beneath the sea floor. While this is small in comparison to the reservoirs and fluxes mentioned thus far, it is twice the annual release of CO_2 at Mammoth Mountain in California between 1990 and 1995, where over 100 acres of trees were killed by the natural release of magmatic CO_2. The 1986 Lake Nyos event in Cameroon released 0.24 MMT CO_2 (0.07 MMTC), approximately one quarter of the annual amount stored annual at Sleipner. This natural CO_2 release led to 1746 people and many animals being killed, up to 14 km away and 24 h after the initial event. However, a significantly larger release in 1991 from an eruption at Mt Pinatubo ejected 11.5 Mt C in one massive event, but the gas dispersed high in the atmosphere and did not pose a direct hazard.

In addition to providing a context for evaluating the magnitude of CO_2 that may be stored, these comparisons illustrate the important point that the risk associated with CO_2 storage depends much more on effective dispersion than the total quantity of CO_2 released. A small leak may pose significant risk to exposed humans, animals, or ecosystems if it becomes concentrated. Conversely, a very large release, even over a short period of time can have little effect if it is discharged high above the ground surface and dispersed by wind. It also points out the fact that large releases from a storage project could result in a significant hazard if confirmed to a small area.

GENERAL PHYSIOLOGY OF CARBON DIOXIDE

Understanding the general physiology of CO_2 provides a context for evaluating the environmental health impacts of CO_2 releases. Carbon dioxide is an important biological compound because it is the ultimate source of carbon for all life. Organic chemistry, the chemistry of biological compounds, is the study of carbon chemistry. Also, the biological cycling of carbon between photosynthesis and cellular respiration is a major portion of the global carbon cycle and is mediated through atmospheric CO_2 [2].

Primary producers, such as plants and photosynthetic microbes, use energy from sunlight, water, and CO_2 absorbed from the atmosphere to generate all of their organic constituents. The primary product of carbon fixation or photosynthesis is the carbohydrate glucose. A simple empirical formula for carbohydrates is CH_2O. Photosynthesis uses energy (E), CO_2, and water (H_2O) to make carbohydrates (CH_2O) and oxygen (O_2). In the evolution of the biosphere, this process generated virtually all of the oxygen in the atmosphere and remains central to the world around us.

$$\text{Photosynthesis} = CO_2 + H_2O + E \rightarrow CH_2O + O_2$$
$$\text{Respiration} = CH_2O + O_2 \rightarrow CO_2 + H_2O + E; \quad E \rightarrow \text{ATP}$$

Cellular respiration is the controlled reverse of photosynthesis, and the two together are integral to the flow of energy and carbon through the biosphere, as shown in Figure 3. Respiration, as depicted in Figure 4, is the combustion or oxidation of carbohydrates coupled to gas exchange and to reactions that produce ATP (adenosine tri-phosphate), the chemical energy currency of life. ATP is the primary form of energy used by most life for biosynthesis, metabolism, and movement. Some plants and microorganisms can produce every organic compound they need from glucose as a carbon skeleton starting material and energy source. The biosynthetic pathways retained in animals are relatively limited, so animals must consume organic material to obtain energy in the form of glucose and diverse raw starting materials. The processes of photosynthesis in primary producers and respiration, which is nearly universal among all forms of life, are of ancient origin and highly conserved through evolution. The few exceptions are chemoautotrophic bacteria. They survive on alternative abiotic energy sources and are typically thermophiles (heat-lovers), thiophiles (sulfur-lovers), or obligate anaerobes (oxygen-haters, e.g. methanogens) [3].

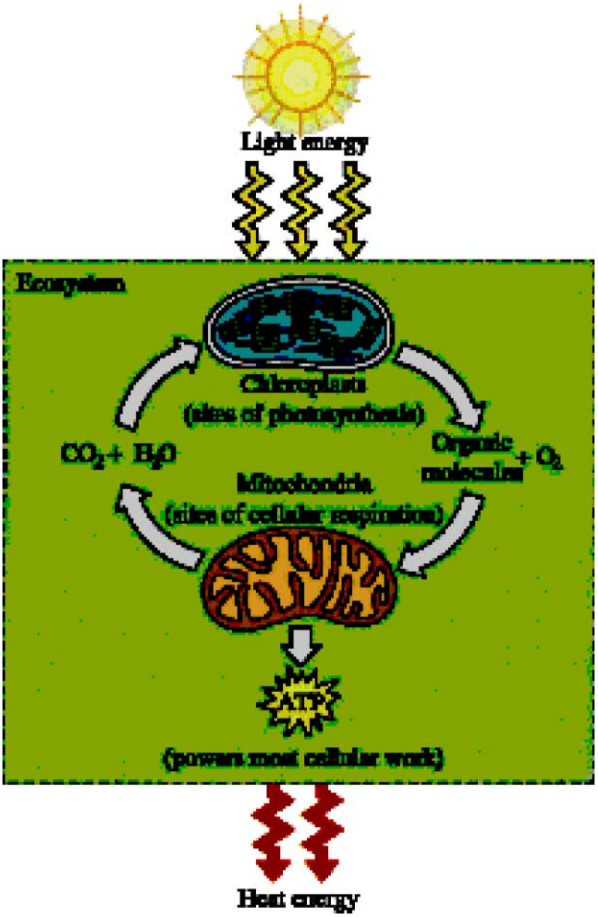

Figure 3: Fundamental biological carbon and energy cycles involving photosynthesis and respiration (Campbell et al. [4]).

HUMAN PHYSIOLOGY OF CARBON DIOXIDE: NORMAL AND HAZARDOUS EXPOSURE

Human Physiology of Carbon Dioxide

In humans, like the vast majority of organisms, cellular respiration consumes O_2 and generates CO_2. Breathing is the process by which we obtain oxygen from air and remove CO_2 from our bodies. Figure 5 illustrates how the coupling between the circulatory system and the respiratory systems transports O_2 to cells throughout our bodies and removes respired CO_2. Air breathed into the lungs contains 21% O_2 and 0.04% CO_2, and exhaled air is 16% O_2 and 3.5% CO_2 on average, though it can exceed 5% CO_2 during strenuous exercise.

Blood returns from the periphery through the right side of the heart to the lungs and contains 5% O_2 and 6% CO_2. Carbon dioxide diffuses out of the blood and into the lungs, and O_2 diffuses in the opposite direction, from the lungs to the blood. Blood leaving the lungs has 5% CO_2 and 14% O_2 and travels through the left

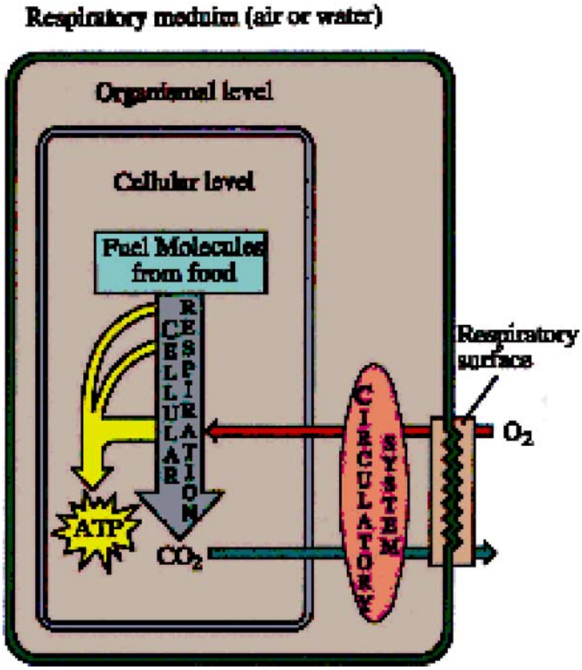

Figure 4: The role of gas exchange and respiration in bioenergetics. Illustration depicts the coupling of gas exchange and cellular respiration via the respiratory and circulatory systems (Campbell et al. [4]).

side of the heart, then on to the periphery. Oxygenated blood flows through capillaries surrounded by extracellular fluid. Oxygen is pulled out of the blood and into the cells because of its constant consumption by cellular respiration which maintains the low concentration within the cells, generally less than 5% O_2. The concentration of CO_2 in the blood, 5%, is lower than in the cells, where respiration produces CO_2, so CO_2 is absorbed into the blood and transported to the lungs [4].

Carbon dioxide is involved in several physiological functions aside from cellular respiration and bioenergetics. It is the primary regulator of breathing in coordination with two regions of the brain, the pons and the medulla. Most CO_2 is transported in red blood cells in its dissolved, hydrated form of bicarbonate (HCO_3^-). When CO_2 dissolves in the blood, it increases H^+ concentration or decreases pH, and humans are very sensitive to changes in pH. The concentrations of CO_2, electrolytes, and total weak acids determine blood pH [5], which is normally 7.4, and Van de Ven et al. [6] considered a pH drop of -0.04 to indicate acute metabolic acidosis. The relationship between CO_2 and pH is the most likely basis for CO_2 toxicity. The medulla monitors CO_2 levels in the blood by measuring subtle changes in pH, and lowered pH stimulates the need to breathe. Sensors in the aorta and carotid bodies detect blood oxygen, but oxygen levels only affect breathing when dangerously low, as at altitude. Via its role in acid–base and electrolyte balance, bicarbonate is involved in other processes including bone buffering and renal regulation [7–10].

Hyperventilation leads to hypocapnea or alkalosis, which is low blood CO_2 and high pH. Extreme stress and anxiety causes rapid breathing, which quickly lowers blood CO_2 levels and increases blood pH. The initial symptoms of hypoxia and feeling out-of-breath are indistinguishable from alkalosis. The breathing control center does not tell the body to breathe when blood pH is elevated, as long as there is sufficient oxygen. In a paradoxical, reinforcing reaction, one panics even more and continues taking rapid, deep breaths that keep

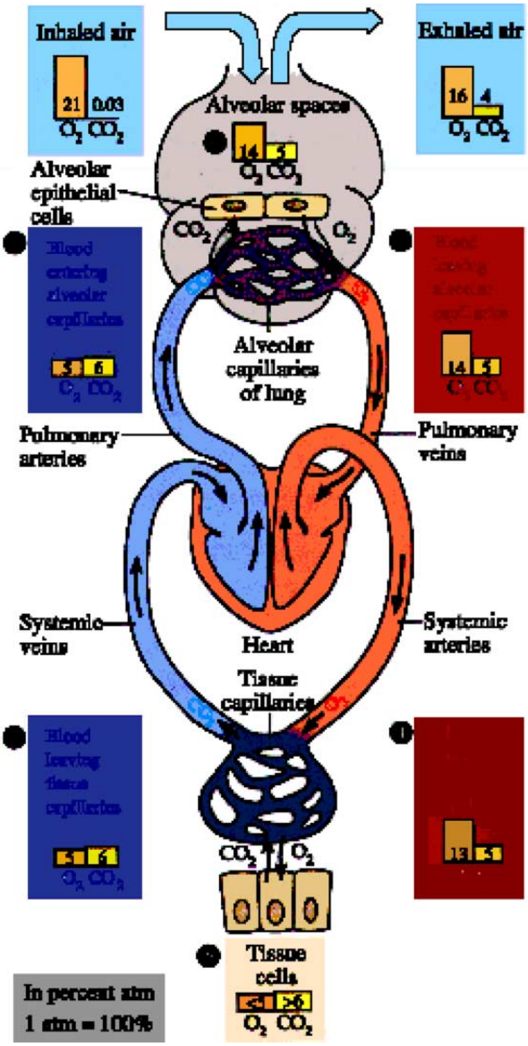

Figure 5: Gas exchange and variation in respiratory gas concentration along the coupled respiratory and circulatory systems (Campbell et al. [4]).

blood pH elevated. One feels dizzy and out-of-breath, which further exacerbates the feelings of anxiety and panic. Taking slow, normal breaths or rebreathing exhaled air from a paper bag allows blood CO_2 levels to increase and return the control of breathing to the normal mechanism. This happens in any case after the person loses consciousness and the body's autonomic systems take over. At high altitude, hyperventilation is more serious because low CO_2 reduces the drive to breathe, while reduced partial pressures of oxygen require more vigorous breathing. For pilots to avoid losing consciousness, supplied oxygen is necessary and often contains added CO_2 to augment the physiological drive to breathe [11,12].

Human exposure to elevated levels of CO_2 can be hazardous either by (1) reducing the oxygen content of the ambient air and causing hypoxia or (2) through direct carbon dioxide toxicity. For example, the National

Institute of Occupational Safety and Health (NIOSH) confined-space-hazard classification system defines CO_2 as a nontoxic, inert gas that displaces oxygen. In most cases of hazardous CO_2 exposure, it is presumed to act as a simple asphyxiant, even though extensive research indicates that exposure to elevated concentrations of CO_2 has significant effects before oxygen dilution could be physiologically significant. Typically, the ambient oxygen concentration is 21%, and the normal range is from 19.5 to 23.5%. Below 17% O_2, hypoxia leads to weakened night vision, increased breathing rate and volume per breath, and increased heart rate. Declining muscle coordination, rapid fatigue, and intermittent respiration are observed between 14 and 16% O_2, in addition to increased volume per breath and accelerated heart rate. Nausea, vomiting, and unconsciousness occur between 6 and 10%. Below 6%, loss of consciousness is rapid, and death takes place within minutes [13].

Effects of Low-level and Chronic Exposure to CO_2

At exposure to slightly elevated concentrations of CO_2, such as in rebreathing masks on airplanes at high altitude, the effects of elevated CO_2 can be beneficial, but that changes rapidly when concentrations exceed a few percent. In the year 2000, the average concentration of CO_2 in the atmosphere was 370 ppm. Studies show the threshold for perceiving stale air is 800 ppm. Carbon dioxide is used to assess adequate ventilation in buildings, and standards are set to ensure indoor odor control and comfort. Sick building syndrome (SBS) is a broad suite of health problems and complaints associated with inadequately ventilated buildings. Research shows that CO_2 is a good proxy for SBS and sufficient ventilation. Carbon dioxide builds up in enclosed spaces where occupants respire it, but no causal connection between SBS and CO_2 is known at this time. No physiological compensation or adverse health effects have been noted at or below 1% CO_2, though no controlled studies of exposure to such low levels have been done yet for longer than 6 weeks. Most studies involved healthy young male subjects, especially in controlled atmospheres such as submarines. Carbon dioxide tolerance in highly susceptible subgroups such as children, the elderly, or people with respiratory deficiency has not been studied—except for some work on chronic acidosis resulting from respiratory impairments and the observation of decreased ventilatory response to CO_2 in infants who were developmentally exposed to cocaine [8,14–20].

Carbon dioxide acts as a respiratory stimulant above 1%, and chronic exposure to 1.5–3% CO_2 results in physiological adaptation without adverse consequences. The only lingering effects are increased alveolar dead space (alveoli are the microscopic air sacs in the lungs where gas exchange takes place) and decreased sensitivity to increased concentrations of CO_2 as measured by respiratory stimulation. Exposure to 1.5–3.0% CO_2 leads to hypercapnea (elevated levels of blood CO_2). Because of the direct relationship between dissolved blood CO_2 and pH, hypercapnea is synonymous with decreased blood pH or acidosis. The immediate reaction is increased breathing depth and rate (respiratory compensation). In response to chronic acidosis, the body compensates by bicarbonate reabsorbtion in the blood and through bone buffering and renal regulation. Increased urine production aids in excreting excess hydrogen ions (H^+) and bicarbonate. Calcium deposition may increase transiently, but the body eventually attains homeostatic compensation as long as the chronic level of CO_2 exposure does not exceed 3%.

Elevated CO_2 levels in the air or blood limit the capacity for exercise and require increased respiration and long-term metabolic compensation. Below 3%, no adverse effects appear aside from the awareness of increased breathing rate and effort, mild headache, and sweating. No deleterious long-term consequences have been observed for chronic exposure to 3% CO_2 or less, and all symptoms of short-term exposure to such levels have proven to be short lived and reversible [8,21,22].

Acute Exposure to Elevated Concentrations of CO_2

The most striking effect of CO_2 levels over 3% is the exponential increase in minute volume, the average volume breathed during 1 min. Minute volume increases from 7 L/min at 0.03% CO_2 to 8 L/min at 1%, 9 L/min at 2%, 11 L/min at 3%, 26 L/min at 5%, and 77 L/min at 10.4%. Volume per breath increases from 440 to 2500 ml during exposure to 10.4% CO_2.

Hearing loss and visual disturbances occur above 3% CO_2. Carbon dioxide also acts as a local vasodilator and a potent cerebral vasodilator. This may explain many of the symptoms associated with CO_2 toxicity, including narcosis, headache, and dizziness. Healthy young adults exposed to more than 3% CO_2 during exercise experience adverse symptoms, including labored breathing, headache, impaired vision, and mental confusion.

Exposure to 4–5% CO_2 for a few minutes leads to headache, dizziness, increased blood pressure, and uncomfortable dyspnea (difficulty breathing). Suppressed shivering is observed at 7.5% CO_2 for 15 min in 5 °C. Seven to 10% CO_2 for several minutes to an hour results in headache, increased heart rate, shortness of breath, dizziness, sweating, rapid breathing, and near or full unconsciousness. (The lowest published lethal concentration for humans, reported in 1933, was 9% CO_2 for 5 min—Vermont SIRI 2001.) Eye flickering, psychomotor excitation, myoclonic twitching, headache, dizziness, dyspnea, sweating, restlessness, and "fullness in head" were observed at 10% carbon dioxide. Dizziness, drowsiness, severe muscle twitching, and unconsciousness occur after one to several minutes' exposure to 10–15% CO_2. Above 15%, loss of consciousness occurs in less than 1 min. Narcosis, respiratory arrest, convulsions, coma and death due to depression of the central nervous system can take place rapidly with continued exposure. Death occurs within minutes at 30% CO_2 [8,21,22]. An interesting aside to the discussion of hazardous CO_2 exposure is the routine use of a single breath of 20–35% CO_2 to diagnose and treat panic disorder [23–26].

Figure 6 summarizes information about natural occurrences of carbon dioxide compared with physiologically relevant concentrations and thresholds at which human health effects become noticeable or significant (see a discussion of regulatory limits for occupational CO_2 exposure later in this chapter). Clearly, CO_2 is not toxic at parts per million or even low percentage levels, but someone enveloped in a cloud of highly concentrated CO_2 is in imminent danger. The risk of exposure to dangerous levels whenever CO_2 is concentrated in large amounts or under pressure must be considered in the context of geologic CO_2 storage for both surface facilities and leakage from geological formations. Fortunately, industry has long experience with CO_2 and routinely controls this hazard in settings such as breweries, beverage carbonation facilities, and enhanced oil recovery (EOR) operations—through engineering and procedural controls and monitoring. Although individual susceptibility to CO_2 is variable, general guidelines are straightforward and useful, especially in light of the precautionary principle used in setting occupational exposure limits.

ECOLOGICAL AND ENVIRONMENTAL IMPACTS OF CO_2 RELEASES

The environmental impacts of CO_2 releases are not well understood despite numerous natural and man-made examples and extensive physiological research. Nevertheless, a summary of the existing literature that is qualitatively relevant to the potential risks of geologic CO_2 storage is helpful. Respiratory physiology and pH control are the primary physiological mechanisms controlling responses of different forms of life to hazardous CO_2 exposures. Information on the response of animals and vegetation to elevated CO_2 and low levels of O_2 can be found in diverse locations, including physiology, respiratory physiology, comparative physiology, plant physiology, botany, food preservation, and aerospace literature. Human responses are useful models for other mammals, and for all air breathers and large terrestrial animals, because of the universal nature of respiration. The death of animals and people in similar areas from the plume of natural CO_2 released from Lake Nyos, Cameroon in 1986 supports this observation. Plants usually have a higher tolerance for CO_2 than mammals, as evidenced by the lack of broad vegetation die-off at Lake Nyos. A standard amount used to preserve food from insects, microbes, and fungi is 40% CO_2; at this amount, insects are incapacitated or killed and microbes and fungi either die or experience severely retarded growth rates. Comparative physiology reveals that gas exchange mechanisms and organs, respiratory medium, and pH and osmotic homeostatic regulation vary among organisms and according to the ecological niche inhabited. These factors determine tolerance to elevated CO_2. The physiological basis of CO_2 tolerance and ecosystem response will be reviewed by looking at respiration and gas exchange in simple organisms, animals, and plants.

Simple Organisms: Cellular Respiration, Homeostasis, Diffusion, and Increasing Complexity

Cellular respiration, especially the preliminary step called glycolysis, which does not require oxygen, is almost universal among organisms from the most simple to the most complex. Photosynthetic organisms store solar energy as the chemical energy of organic compounds by converting water and CO_2 to simple carbohydrates and oxygen. This provides the organic material consumed by all heterotrophic organisms. Oxidative respiration is the reverse—the harnessing of chemical energy via the breakdown of carbohydrates back to CO_2 and water. As a result, CO_2 is the primary metabolic waste product of all oxygen-consuming

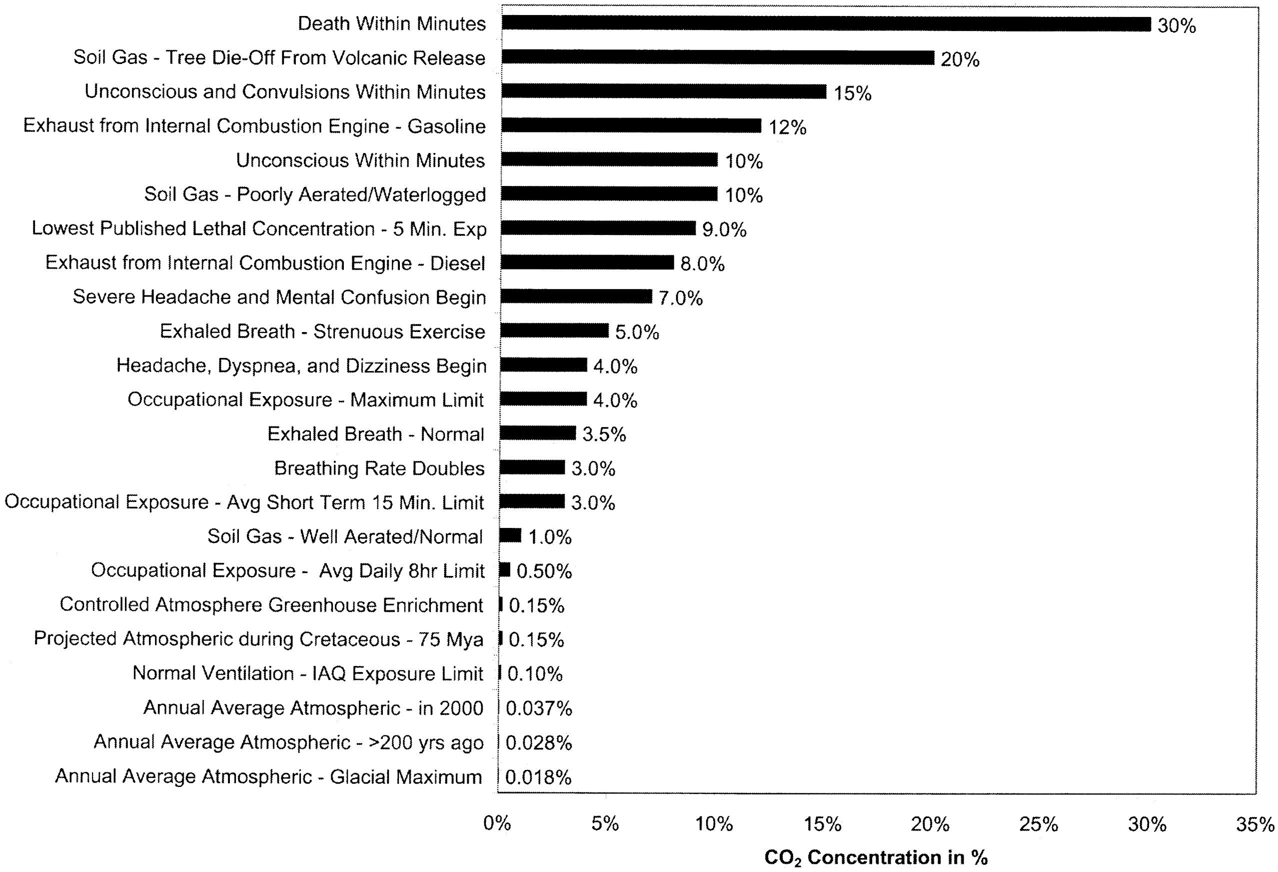

Figure 6: Comparison of ambient concentrations of CO_2 and risks of exposure. Data tables with references in Ref. [77].

organisms. Respiration requires regular gas exchange between an organism and its environment. Oxygen is required as the terminal electron acceptor in oxidative respiration and CO_2 must be eliminated. All single-celled organisms maintain some level of homeostasis, especially osmotic and pH, by controlling what passes through their cell membranes; but in the case of respiratory gases, diffusion is usually the operative, uncontrolled process. Microbes have adapted to virtually every environment that exists on Earth, and they use biochemical mechanisms to adjust to variable environmental conditions [29]. Some microbes can survive in virtually 100% CO_2 as long as trace amounts of O_2 are available. The suspension of metabolism under extreme desiccating conditions is an analogous survival mechanism. As a result of variation in environmental conditions and such adaptive capabilities, only a qualitative generalization is useful about the level of CO_2 that is toxic to microbes or bacteria. Although the range is broad and CO_2 concentrations below 10% kill some simple organisms, in general 50% CO_2 has a significant inhibitory if not lethal effect [27,28].

Fungi are not simple organisms from an evolutionary perspective, but their respiratory gas exchange is controlled by diffusion as opposed to more complex, specialized systems. As with insects and microbes, the majority of information on the tolerance of fungus to elevated CO_2 comes from food-preservation literature. This source biases our understanding toward the amount and duration of exposure at which virtually nothing survives as opposed to defining the minimum level at which the most sensitive are harmed. Temperature, relative humidity, oxygen concentration, and CO_2 concentration all have significant effects on the growth of fungi. Significant inhibition of growth and the germination of spores were observed at 15–25% CO_2 for two types of fungi. At 30% CO_2, no measurable growth was observed, and 50% CO_2 prevented the germination of spores [30,31].

Animals: Comparative Physiology and Active Bulk Gas Exchange in Water and Air

To summarize the effects of elevated CO_2 on animals, a brief review of respiration in complex organisms is required. The transition from water to air as the respiratory medium, the transition to terrestrial habitation, and increasing metabolic rates that could ultimately support flight dominate the evolutionary history of respiration. Aqueous, soil, terrestrial, and aerial environments offer distinct respiratory challenges. Also, respiration encompasses two interrelated yet distinct processes, the procurement of oxygen and the elimination of carbon dioxide.

The oldest form of respiration is simple diffusion in water. Water is relatively dense and viscous compared to air, so gas exchange using water is inherently less efficient because of the energy required to move it. Oxygen is more difficult to obtain because it is poorly soluble, and CO_2 is relatively easy to eliminate because it is highly soluble. Paleoclimatic evidence suggests that 70 million years ago, previous climates were typically much warmer, biological productivity was much higher, and consequently tropical swamps were widespread. These conditions are thought to be one of the main driving forces behind the evolution of air breathing because such waters have little O_2 and very high levels of CO_2. The end product of organic matter decay in such reducing environments is predominantly methane, with 60% methane, 30% CO_2, and 10% hydrogen, carbon monoxide and ethylene typical of carbohydrate-rich decomposition (refer to references in Maina [32]). Studies of the physiology of inhabitants of high CO_2 aquatic or marine environments such as Lake Nyos were not found, but the preponderance of lungfish in the Amazon Basin is suggestive of the relationship between swampy conditions and air breathing [10,32,33].

Terrestrial habitation requires two major adaptations. The first is to minimize water loss, and the second is to increase metabolism to meet the demands of terrestrial mobility. Supporting and moving the entire body weight without the buoyancy of water is energy intensive. Fortunately, air is a much more efficient medium for delivering oxygen, in contrast to aqueous breathing, but CO_2 disposal becomes difficult. The CO_2 carrying capacity of water is high, especially when bicarbonate is included. The limiting factor, then, is the exchange rate at the respiratory interface. Developing or co-opting the enzyme carbonic anhydrase solves this problem, because it catalyzes the bi-directional conversion of CO_2 to bicarbonate and back again, and accelerates the reaction rate in the range of a millionfold [4,32].

Ambient O_2, CO_2, and pH are determining factors for what types of organisms inhabit a given environment. A rapid or significant change in any of these conditions would cause biological stress, and the type of respiratory organ tells us much about an organism's normal environment and its ability to adapt or survive.

Aquatic and marine animals use skin diffusive respiration, the gill, the water lung, or the placenta. The transport of respiratory gases in the circulatory system, the diffusion of gases between the blood and the cells, and the placenta in utero are the connection of humans with water as a respiratory medium. Gills are considered either simple or complex, and they are involved in many different processes, including respiration, feeding, ammonia excretion, locomotion, and the regulation of osmotic pressure, acid–base balance, and some hormones. Because of the extensive buffering capacity of the oceans, pH varies little in marine environments, but the concentrations of O_2 and CO_2 can be dynamic. This is especially true in enclosed or stagnant bodies of water where mixing is not thorough. Lakes that are stably stratified by salinity or temperature contrasts are particularly susceptible to variations in respiratory gas concentrations. In contrast, freshwater does not have much buffering capacity, so CO_2 released into freshwater could change pH significantly. The dearth of macrofauna in or near geothermal efflux or soda springs suggests that CO_2 leakage may have significant localized impacts. The effects of such change would depend upon the natural variability of pH in that specific environment and an organism's physiological ability to adapt.

Typically, a change in pH of a few tenths would be a significant stressor, if not fatal. However, the impact of CO_2 released into a body of water depends upon the amount and rate of release, the water body's buffering capacity, and its mixing dynamics. Studies of the natural CO_2 release at Mammoth Mountain, California, indicated that large amounts of CO_2 were dispersed through the groundwater system and released quickly upon exposure to the atmosphere. In fact, no evidence of a high CO_2 flux remained in water even a few hundred meters downstream of the source (Kennedy, 2001, personal communication). Evidence from fish kills and swamps suggests that O_2 is the key respiratory gas among aquatic and marine organisms instead of CO_2, except to the extent that CO_2 could affect environmental pH [32,33].

The transition from water to air breathing and from aquatic to terrestrial habitat involved bimodal breathing, the combination of an air-breathing lung with remnant gills or skin diffusive respiration. Some current bimodal breathers are exclusively aquatic (e.g. lungfish), some are primarily terrestrial (e.g. land crabs), and some live in both worlds (e.g. amphibians). Most bimodal breathers are amphibians, gastropod molluscs, crustaceans, or lungfish. Such animals obtain most of their oxygen via their lungs and eliminate most CO_2 through the skin or gills, effectively separating these processes; but they often have multiple modes of breathing available, depending upon the respiratory medium and medium of immersion. No studies were found that specifically addressed the tolerance of bimodal breathers to elevated CO_2 concentrations.

Food preservation research has shown that insects have much higher tolerance to CO_2 than vertebrates. Mortality data for the rusty grain beetle compiled by Mann et al. [34] varies from 15% CO_2 for 42 days to 100% CO_2 for 2 days. Table 1 shows a subset of recommended CO_2 concentrations and exposure time. Even after hours to days of exposure to high CO_2, many insects can recover. Other insects' tolerances have been measured, and 35% CO_2 is the minimum concentration needed for effective control of all but a few unusually CO_2 tolerant species [35]. Another common trend is decreasing mortality with increasing CO_2 concentrations above 85% [36,37]. Zhou et al. [38,39] are investigating the precise mechanisms of elevated CO_2 effects on insects.

TABLE 1

CONCENTRATIONS OF CO_2 AND THE DURATION REQUIRED FOR EFFECTIVE CONTROL OF THE RUSTY GRAIN BEETLE (VIRTUALLY 100% KILLED)

CO_2 concentration (%)	**Exposure time (days)**
15+	42
40	8–13
60	3–4
80	3
100	2

Mann et al. [34].

Information on CO_2 tolerance was not compiled for each type of animal, but some further studies on burrowing animals and soil invertebrates were found.

Fossorial animals, more commonly called burrowers, live within soils, where environmental conditions are extremely variable. Even though soils are extremely heterogeneous, CO_2 in the soil atmosphere normally increases with depth along a diffusion gradient. Diffusion is the primary transport mechanism for O_2 into the soil air and for CO_2 out to the atmosphere, and diffusion limits respiration in the soil environment because respiration itself is a constant source of CO_2. In well-aerated soils, the CO_2 concentration can remain below 1% at 1 m depth; but in poorly aerated, waterlogged soils, CO_2 levels can exceed 10%. In fact, the major controls on O_2 and CO_2 levels in soils are the amount of respiration, the moisture level, and the specific soil chemistry [32,40–42].

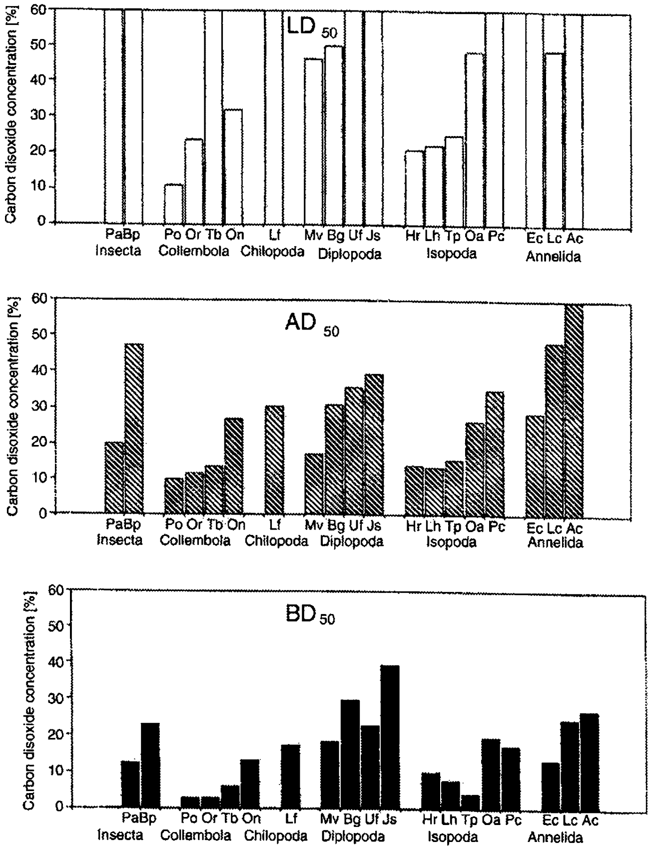

Figure 7: Response of 19 species of soil invertebrate to elevated levels of CO_2. The concentrations of CO_2 at which behavioral reactions (BD50), constant paralysis (AD50), or mortality (LD50) appeared in 50% of animals. Species abbreviations are shown in Table 2. LD50 was higher than 60% CO_2 for some species, but the range in this figure is limited to 60% (reproduced from Sustr and Simek [43]).

The response of soil invertebrates to CO_2 shows inter- and intra-species variation and depends upon their ecomorphological niche. The results of the study by Sustr and Simek [43] are shown in Figure 7. Behavioral changes in half of the observed individuals for a given species occurred between 2 and 39% CO_2 in the ambient soil air, with the majority of species affected by 20%. Paralysis in half of observed individuals was apparent between 10 and 59% CO_2. Half of the species were paralyzed by 30%, and all but one were paralyzed by 50%. Carbon dioxide levels from 11 to 50% were lethal for half of the species investigated. The effects of CO_2 depend upon temperature, humidity, and oxygen concentration, but (according to previous research) the dilution of oxygen in soil environments at high CO_2 levels is not significant. Breathing mechanism had an obvious effect, with gills and skin-diffusive respiration being more sensitive to CO_2 levels than tracheal and pseudotracheal respiratory mechanisms or skin breathing earthworms with closed circulatory systems. Biochemical mechanisms also appeared significant based upon the range in sensitivity of springtails (Collembola), a group using skin diffusive respiration [43] (Table 2).

TABLE 2
SPECIES ABBREVIATIONS AND DESCRIPTIONS MODIFIED FROM SUSTR AND SIMEK [43]

Species		**Abbreviation**	**Notes on age, habitat, and ecomorphological type**
Insecta (Insects)	*Pyrrhocoris apterus*	Pa	Adults, soil surface
	Bibio pomonae	Bp	Larvae, litter
Collembola (Springtails)	*Pogonognatellus flavescens*		Epigeic (surface) species
	Orchesella flavescens	Or	Atmobiotic species
	Tetrodontophora bielanensis	Tb	Hemiedaphic species (part-time soil dweller)
	Onychiurus cf. ambulans	On	Euedaphic species (soil dweller)
Chilopoda (Centipedes)	*Lithobius forficatus*	Lf	Litter
Diplopoda (Millipedes)	*Melogona voigti*	Mv	Litter
	Blaniulus guttulatus	Bg	Litter
	Unciger foetidus	Uf	Litter
	Julus scandinavius	Js	Litter
Isopoda (Pill bugs)	*Hyloniscus riparius*	Hr	Litter, hygrophilous (water/moisture loving)
	Trichoniscus pussillus	Tp	Litter, hygrophilous
	Oniscus asellus	Oa	Litter, hygrophilous
	Porcellium collicolla	Pc	Litter
Enchytraeidae (Potworms)	*Enchytraeus crypticus*	Ec	Litter
Lumbricidae (Earthworms)	*Lumbricus castaneus*	Lc	Epigeic species
	Aporrectodea caliginosa	Ac	Endogeic (subsurface) species

Another group of insects analogous to soil dwellers are beetles and fly larvae that are specially adapted to living in dung pats. Microbial activity in fresh pats is substantial, so the dung air may have O_2 concentrations below 1%, CO_2 concentrations from 20 to 30%, and methane concentrations from 30 to 50%. The dung insects generally could adapt to 20% CO_2, and some larvae remained visibly unaffected up to 43% CO_2. Yet tolerance varies greatly, and some surface-dwelling insects are paralyzed by 8% CO_2 [41].

Burrowers have the highest CO_2 tolerance among vertebrates because soil air often contains high levels of CO_2. Most burrowers inhabit open tunnels and spend only part of their time underground. Such animals include gophers, many rodents, and some birds. The CO_2 content of their respective burrows have been measured as high as 4, 2, and 9%. Concentrations of CO_2 as high as 13.5% have been found in the dens of hibernating mammals (see references in Maina [32]).

Among the major classes of terrestrial vertebrates—reptilia, mammalia, and aves—the lung takes on several forms. Reptilian lungs are morphologically the most diverse, but they are also the least efficient. Aerobic capacity in reptiles is a fraction of that in mammals. In contrast, anaerobic capacity and tolerance for hypoxia is greater. As a result, reptiles are probably more tolerant to elevated CO_2 than mammals. Turtles are specially adapted to hypoxia via depressed metabolism. They can withstand complete anoxia for days or even months and a decrease in brain pH to 6.4. The diaphragm affects the complete functional separation of the thoracic and abdominal cavities in mammals and is a unique characteristic. The homogeneity of form and function of the mammalian lung is another striking feature: all are tidally (rhythmically) ventilated, dead-end sacs. The lungs of bats are proportionally much larger in order to sustain flight and increased aerobic capacity, yet bats are aerobically inefficient relative to birds. The lung airsac system of birds is closest to the multicameral reptilian lung. There is remarkable morphological and functional homogeneity among bird lungs, as with mammals, but the lung airsac is a highly efficient gas exchanger. The airsac changes volume by only 1–2% per breath, but it allows a constant unidirectional flow of air through the lungs. Along with several other structural and functional characteristics (including countercurrent exchange), the avian lung is unquestionably the most efficient vertebrate gas exchange system known. Birds can sustain increases in aerobic capacity by a factor of 20–30, while elite human athletes can manage similar increases for a few minutes at most. Birds are uniquely tolerant to low-pressure oxygen deficiency and low CO_2 from flying at altitude and sustaining high-energy output. Specific references to the tolerance of birds to elevated CO_2 were not found.

Effects of Elevated CO_2 Concentrations on Plants

At slightly enriched levels (500–800 ppm) over atmospheric background (370 ppm), carbon dioxide usually stimulates growth in plants, depending on the mechanism of introducing CO_2 into the photosynthetic or Calvin cycle—C3, C4, or CAM (crassulacean acid metabolism). The majority of plants are C3, like trees, and first make a three-carbon acid when fixing CO_2. As part of adapting to arid conditions, the need to minimize water loss during hot, dry days, and perhaps low levels of CO_2, C4 and CAM plants such as grasses and succulents first make four-carbon acids. C4 plants separate CO_2 uptake and fixation spatially by segregating the processes in different cell types, and CAM plants separate uptake and fixation temporally by absorbing CO_2 at night and fixing it during the day [44]. The experimental increase of ambient CO_2, called free air CO_2 enrichment (FACE), initially causes proportional increased growth in C3 plants, followed by a tapering down to slightly elevated growth rates above unenriched levels. It also increases water-use efficiency and changes carbon allocation among tissue types. The growth rate of C4 and CAM plants is not limited by CO_2 availability as it is for C3 plants. As a result, the response of C4 and CAM plants is usually more complex and of lesser magnitude, so no simple generalization can be made about the effects of FACE [45]. Enhanced growth of plants in controlled-atmosphere greenhouses with enriched CO_2, optimally between 1000 and 2000 ppm, is the result of elevated CO_2 in conjunction with elevated temperature, plentiful water, and intensive fertilization [46]. Individual plants adapt easily to small changes in ambient CO_2, perhaps changing the allocation of biomass among roots, stems, and leaves, but over decades to centuries, plant species composition may change at the ecosystem level, generally in favor of C3 plants, with a consequent change in ecosystem composition and type. Research is underway to investigate the response of all aspects of ecology and the environment to elevated CO_2, projected temperature increases, and alterations to the hydrologic cycle (see articles in Refs. [45,47–52]).

The range and effects of high levels of CO_2 on plants, between FACE and lethal levels, are not clearly delineated. The precise mechanisms of tree kill in events like the outgassing from Mammoth Mountain, California, are poorly understood. The most likely cause is suppression of root-zone respiration via hypoxia, hypercapnia, or acidification of the soil environment. Long-term exposure over weeks or months to 20% or more CO_2 in soil gas led to dead zones where no macroscopic flora survived. The distribution of effects relative to CO_2 concentration suggests that 20–30% is a critical threshold for plants and ecosystems in general. Although some plants will die quickly from severe hypoxia, the lack of vegetation killed by the natural release of CO_2 at Lake Nyos indicates that plants generally have a much higher tolerance than animals to extremely high, short-lived exposures.

Concluding Remarks Regarding Ecosystem Exposure to Elevated Levels of CO_2

In future, a more thorough review of comparative, plant, and ecosystem physiology relating to hypoxia, hypercapnea, pH tolerance, and biochemical mechanisms of homeostasis may prove fruitful. In fact, modeling of ecosystem response to various scenarios of CO_2 release will require rigorous, quantitatively defined thresholds or probability distributions correlating CO_2 concentrations with specific impacts. Human tolerance provides a convenient rule of thumb for environmental CO_2 exposure limits, based on this review of physiology.

With regard to geologic storage, subsurface CO_2 storage and leakage may lead to the dissolution of minerals, the mobilization of metals in the aqueous phase, and the potential concentration of organic compounds in supercritical CO_2 due to its solvent properties [53–55]. The rates, likelihood, and potential significance of these processes (if any) are not well known. The risks associated with these types of processes are not addressed here.

Carbon dioxide outgassing near geothermal vents, fumaroles, and soda springs may provide an opportunity for research on the environmental effects of a range of concentrations and duration of exposure. The scarcity of macrofauna in such high CO_2 environments may be indicative of the physiological stress caused by elevated CO_2. However, the presence of other gases such as H_2S in some cases may make it difficult to draw quantitative conclusions about the effects of elevated CO_2 concentrations from such an evaluation.

More importantly, while there has been a great deal of research about the ecological effects of slightly elevated concentration of CO_2 and on the high concentrations that are known to create a lethal response, there is little research about short or long-term exposure to intermediate concentrations of CO_2. (For example, what would be the ecological consequence of prolonged exposure to 3–5% CO_2?) Soil gas and biological surveys near natural CO_2 surface releases and above underground reservoirs would be useful to address issues such as these.

INDUSTRIAL SOURCES AND USES OF CO_2

The risk-assessment process for CO_2 can also be informed by a review of industrial sources and uses, safety issues and procedures, and accidents. Carbon dioxide was one of the first chemicals identified, and it has diverse uses. Table 3 is a summary of US emissions and sinks of CO_2 in 1998. Fossil fuel combustion generated 1468.2 million metric tonnes of carbon equivalents (Mt CE). All other industrial processes utilized and ultimately emitted 18.4 Mt CE. In addition to being a by-product of fossil fuel combustion, CO_2 is a by-product of pH control/acid neutralization, cement manufacture, and the chemical production of lime, ammonia, ethyl alcohol, hydrogen, ethylene oxide, and synthetic natural gas.

Yet CO_2 is also a commodity with diverse applications. The main sources of CO_2 for industrial use are natural reservoirs, the by-product of chemical manufacture, and separation from crude oil or natural gas. Manufacturing carbonates, urea, and methanol use CO_2 as a reactant. Carbon dioxide is used to carbonate beverages, and when produced by yeast, it is the leavening agent in baking and the by-product of fermentation in the manufacture of alcoholic beverages. We use it to preserve food and extinguish fires. Under regulations for the humane slaughter of livestock, we anesthetize and kill animals with it. The oil industry, in a process called EOR, pumps CO_2 into hydrocarbon reservoirs to aid in the secondary and tertiary recovery of oil and gas. In EOR, carbon dioxide can form an immiscible mixture with the reservoir oil, thus making it easier to extract it from the reservoir. When it dissolves in the crude oil, it causes a decrease in the fluid viscosity and density. This drive to increase volume maintains reservoir pressure and increases the proportion of original-oil-in-place recovered. Enriched levels of CO_2 in greenhouses enhance the growth of plants, and dry ice and liquid CO_2 are used as refrigerants. Carbon dioxide is also used as a pressurizing agent and a supercritical solvent. A list of applications provided by Airgas is listed in Table 4 [8,56–59].

For 1999, an industry research group called Freedonia reported the shipment of 1.81 Mt C of liquid carbon dioxide (1 Mt C = 3.67 million metric tonnes of CO_2) through the merchant market and 1.87 Mt C (6.86 Mt CO_2) total production, including on-site captive consumption. Another Freedonia CO_2 industry study from 1991 estimated that 20% of CO_2 sold on the merchant market came from natural reservoirs and 80% from captured emissions. The EPA's emissions estimate of 0.4 MMTC comes from assigning 80% of the 1.87 Mt C to emissions accounted for elsewhere and only the 20% derived from natural reservoirs uniquely to carbon dioxide consumption. Total EOR demand in 1999 according to Freedonia was 1.79 Mt C

TABLE 3
U.S. SOURCES OF CO_2 IN 1998

Source	**Amount in 1998**
Fossil fuel combustion	1468.2
Industrial processes	18.4
Cement manufacture	10.7
Lime manufacture	3.7
Limestone and dolomite use	2.4
Soda ash manufacture and consumption	1.2
Carbon dioxide consumption[a]	0.4
Iron and steel production[b]	23.9
Ammonia manufacture[b]	6.3
Ferroalloy production[b]	0.5
Aluminum production[b]	1.6
Natural gas flaring	3.9
Waste combustion	3.5
Land use change and forestry (sink)	(210.8)
International bunker fuels	31.3
Total emissions	1494.0
Net emissions (sources and sinks)	1283.2

Emissions and sinks in MMTC (US EPA [59]).

[a] Includes food processing, chemical production, carbonating beverages, and EOR. Primary sources include natural reservoirs, chemical manufacture, and separation from crude oil and natural gas.

[b] Emissions from these processes are primarily due to energy consumption and are included in the total for fossil fuel combustion.

TABLE 4
COMMON INDUSTRIAL USES OF CO_2

Beverage carbonation	The characteristic tingle and fizz of carbonated beverages results from the interaction of CO_2 and H_2O molecules in beverage solutions
Fire protection	CO_2 is widely used in fire extinguishers for both hand held and fixed systems. It is also used in "blanketing" to displace oxygen to prevent combustion. A major advantage of CO_2 is its cleanliness
Enhanced recovery of petroleum products	CO_2 is used in various processes of oil and natural gas well stimulation to enhance productivity
Molded product deflashing	Molded products, especially rubber compounds, often have undesirable flashings where mold sections were joined. CO_2 is used to cool and embrittle the flashings in preparation of mechanical removal, saving the high cost of hand trimming and buffing
pH control of waste water	One of the critical aspects of effluent disposal is its degree of alkalinity. CO_2 is one of the safest, cleanest and most economical means of reducing the pH of waste water
Foam expansion	The use of CO_2 as an expanding agent in polyurethane foams eliminates the use of volatile organic compounds and chlorofluorocarbons to provide a safe, low cost alternative to these harmful chemicals

(*continued*)

TABLE 4
CONTINUED

Shielded arc welding	CO_2 vapor is used to displace oxygen at the point of contact in arc welding. Speed, efficiency, quality and cost factors have stimulated wide use of this application in the Welding Industry
Low temperature grinding	CO_2 is added to heat sensitive materials in grinding operations for heat removal to prevent product softening or melting
Aerosol propellant	CO_2 is a cost effective alternative pressure medium in many non-water based aerosol products, eliminating the use of hazardous solvents and chlorofluorocarbons
Recarbonation of potable water	As a result of typical municipal potable water softening operations, the pH level of the water is raised which results in a chemically unstable water condition. The application of CO_2 (recarbonation) establishes a chemical balance and minimizes mineral deposits in the water distribution system
Purging and inerting	Fuel tanks, pipelines and other containers with explosive or combustible vapors must be purged prior to some types of maintenance and/or change in usage. CO_2 is an effective method for purging vessels of many unwanted vapors
Foundry core hardening	As an alternative to the conventional process of baking foundry cores, CO_2 is used in conjunction with a treated (silica) sand to form high quality cores resulting in time and energy savings
Chemical reactant	CO_2 is used in the production of various carbonate compounds, in controlling pH and in many other processes involving chemical reactions
IQf freezing	Cooling and freezing operations are integrated into high-speed production lines with CO_2 tunnel and spiral freezers. Advantages include reduction of cold storage space, bacteria retardation, greater refrigeration efficiency, enhanced product quality and more efficient space utilization
Shrink fitting	Machined metal products such as bushings, collars and seats which require a "tight fit" can be easily assembled by cooling with dry ice
Refrigeration in mixing and blending	CO_2 injection reduces heat buildup induced by blade friction in mixing and blending of meat products and firms it in preparation of the forming process. Semi-automatic operation reduces manpower and minimizes space requirements
Low-temperature testing	CO_2 is used as a refrigerant for testing products by simulating ambient temperatures down to -109.8F. CO_2 is easily stored, readily available and can be piped for automatic operation
Pest control in stored grain	Fumigating coffee, tea, tobacco and grains with CO_2 has been successful in controlling insects in storage. CO_2 provides a safe, clean alternative to environmentally hazardous fumigants
Greenhouse atmosphere enrichment	CO_2 is an essential raw material used by green plants in photosynthesis. Increasing the amount of CO_2 available to plants can greatly increase plant growth and yields
In-transit refrigeration of processed foods	Perishable processed foods can be refrigerated with CO_2 during processing, enabling direct loading onto trucks and sustained safe temperatures during mechanical refrigeration temperature pull-down. Valuable freezer space is conserved and risk of spoilage is minimized. CO_2 can also be used in limited applications as the sole refrigerant
In-flight food refrigeration	CO_2 in its solid form (dry ice) is used to refrigerate In-flight Modules by the Airline Industry. Alternative methods are not as reliable or cost effective
Non-destructive cleaning	CO_2 cleaning utilizes dry ice to remove contaminants from most surfaces, greatly reducing waste products and the need for chemical solvents, sand, water and other media
Modified atmosphere packaging	Packaging perishable food products with CO_2 greatly extends the product shelf life by limiting the growth of aerobic microorganisms. Other benefits include reduced development of rancidity and odors, and better color retention

(6.56 Mt CO_2), of which 5.3% or 0.09 Mt C (0.35 Mt CO_2) was supplied by the merchant market. The remaining 1.70 Mt C (6.21 Mt CO_2) was supplied via pipeline from natural reservoirs, separated from crude oil or natural gas, or recycled in existing EOR projects. Combining Freedonia's estimates for liquid CO_2 sold on the merchant market with the EOR estimates yields a total of 3.56 MMTC (13.1 MMT CO_2) utilized in 1999. The summary report on industrial gases for 1999 from the Department of Commerce (DOC) estimates total production of 3.25 MMTC (11.9 MMT CO_2). The difference of 0.31 MMTC (1.2 MMT CO_2) between the numbers from Freedonia and the DOC can be ascribed to uncertainty in the estimates of CO_2 separated from crude oil and natural gas or recycled within existing EOR projects. The proportion of CO_2 that comes from natural reservoirs versus recycled or separated from crude oil and natural gas has not been evaluated [59,60–62].

Industry experience with CO_2 also provides insights into the safety concerns of any geologic storage project. Refineries process large quantities of hydrocarbons, on average 4.3 Mt CE per refinery in the US during 1999. According to the Texas Natural Resources Conservation Commission, one large refinery in Harris County, TX, vented 5.4 Mt CO_2 in 1998 [63], yet that CO_2 posed no immediate human health or environmental hazard because it dispersed from high smokestacks. Chevron Research and Technology Corporation's Health, Environment and Safety Group estimates that an average refinery emits 5600 tonnes CO_2/day or 2 Mt CO_2/yr (Chevron, 2001, personal communication). Shell, one of the largest international energy companies, estimated their total annual global emissions in 1999 to be 90 Mt of CO_2 alone or 27 Mt CE including other greenhouse gases [64]. CO_2 pipelines are mostly associated with EOR, and their accident record is available through the Office of Pipeline Safety (OPS) in the Department of Transportation (DOT). Eight accidents are on record for CO_2 pipelines from 1968 to 2000: three in 1994, one in 1995, three in 1996, and one in 1997. There were no injuries and no fatalities. A failed weld caused one and corrosion caused another. Three were failures of control or relief equipment, and two more resulted from other failed components. Outside force caused the other one [65].

Catastrophic pipeline failures are considered unlikely and the environmental consequences of a massive CO_2 pipeline rupture are expected to be minimal because of engineering controls. One attempt to model the impacts of rupture was reported by Kruse and Tekiela [66]. Typically, the main procedural controls are maintenance routines and visual inspections via plane, truck, or walking the line. If odorants and colorants are used, they render small leaks easier to detect. Vegetation that has been killed or that is visibly under stress is used to locate leaks in natural gas pipelines, especially where they are underground. In addition to manufacturing standards for the pipeline materials, automatic pressure control valves are placed regularly along the length of pipelines in the case of catastrophic ruptures. The safety control valves shut down the flow of gas if the pressure in the pipeline exits a preset range. The pressure drop of a large leak or rupture would trip the shut-off valves, so only the gas between two safety control valves could vent to the atmosphere. The spacing of such control devices is set according to regulations and safety considerations depending upon proximity to human residences.

The EPA published a review of the risks of CO_2 as a fire suppressant. Carbon dioxide is used in 20% of fire protection applications, and it is common in large industrial systems. The EPA report included a summary of 51 incidents that occurred between 1975 and 2000. These involved a total of 72 deaths and 145 injuries. In a characteristic incident at Idaho National Engineering and Environmental Laboratory, an accidental release during the maintenance of an electrical system resulted in one fatality and 12 injuries. The sudden discharge filled an enclosed space with 2.5 tonnes of CO_2 and created an atmosphere with approximately 50% CO_2 and 10.5% O_2.

Engineering controls and procedures set by the DOT, National Fire Protection Association (NFPA), American National Standards Institute (ANSI), Compressed Gas Association (CGA), American Society of Mechanical Engineers (ASME), and Occupational Safety and Health Administration (OSHA) are used to ensure the safety of refineries, pipelines, fire suppression systems, and any transportation of CO_2 whether it is pressurized, cryogenic, solid, liquid, or gas [67–69].

The cumulative experience of industry suggests two conclusions. First, carbon dioxide is a familiar and integral part of our everyday lives that is generally regarded as safe; and second, concentrated CO_2 in confined spaces poses a significant but well-known hazard that falls within standard industry practice, engineering controls, and safety procedures. The environmental consequences of CO_2 separation facilities and pipelines are the same as such facilities used for other purposes. Geologic carbon storage does not pose any new or uncertain hazards in its surface facilities.

CARBON DIOXIDE REGULATIONS

Regulations for CO_2 have been promulgated by a number of organizations for a variety of purposes. These guidelines roughly reflect our collective experience with, understanding of, and attitude toward CO_2 and provide further context for risk assessment. We discuss the regulations briefly and summarize them in Tables 5 and 6.

Occupational Health Standards for Carbon Dioxide

The OSHA in the Department of Labor (DOL) sets the most directly relevant regulations regarding CO_2. The NIOSH in the Center for Disease Control and Prevention (CDC) is part of the Public Health Service (PHS) in the Department of Health and Human Services (DHHS) and recommends exposure limits. These agencies regulate CO_2 as an occupational air contaminant. The general permissible exposure limit (PEL) set by OSHA is a time-weighted average (TWA) of 5000 parts per million by volume (ppm) (0.5%) for an 8-h work day and a 40-h workweek. The NIOSH recommended exposure limit (REL) is a 10-h/day and 40-h/week TWA of 5000 ppm, a 15-min TWA short-term exposure limit (STEL) of 30,000 ppm (3%), and 40,000 ppm (4%) as the level immediately dangerous to life and health (IDLH). All IDLH atmospheres require the use of respiratory protection equipment. The *Occupational Health Guideline for Carbon Dioxide*, published jointly by OSHA and NIOSH, is included as Appendix 7, and the NIOSH *Pocket Guide to Chemical Hazards* entry for CO_2 is attached as Appendix 8 [8,21,69–71].

The American Conference of Governmental Industrial Hygienists (ACGIH) is the source of OSHA standards for construction and recommends a 5000 ppm TWA threshold limit value (TLV) and a 30,000 ppm TWA-STEL. ACGIH and NIOSH criteria documents are the core sources of occupational exposure limits through their own research and references to primary literature. The limit for CO_2 in surface and underground metal and nonmetal mines set by the Mine Safety and Health Administration (MSHA) in DOL is referenced to the ACGIH as well [8,22,69].

The DOT regulates carbon dioxide through the Federal Aviation Administration (FAA) as an air contaminant and as a surrogate for adequate ventilation in cabin air (5000 ppm CO_2) [14,69].

Ventilation and Indoor Air Quality

The FAA uses the criteria for occupational exposure to CO_2 to set its ventilation rates, but that is unusual. General building ventilation and indoor air-quality requirements are set by American National Standards Institute (ANSI)/ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) Standard 62-1999 at 700 ppm above ambient outdoor CO_2 levels, or about 1000 ppm CO_2 for HVAC (Heating, Ventilating and Air-Conditioning) industrial ventilation systems. This standard was set using comfort and odor control criteria. HVAC systems often monitor CO_2 concentration as a general proxy for indoor air quality because it is the primary contaminant produced by occupants. Ventilation rates that keep CO_2 levels below 1000 ppm are proven to reduce SBS, complaints such as irritated eyes, nose, and throat; headache, coughing, nausea, and dizziness [15,18–20].

Confined Space Hazard and Fire Suppressant

NIOSH is the single best source of information on confined space hazards, and OSHA is the regulatory body with oversight responsibility. OSHA establishes labeling, warning, and training requirements for confined space hazards like CO_2. In occupational settings such as silos, manure pits, breweries, and ship holds, CO_2 is recognized as a serious inert gas danger that creates oxygen-deficient atmospheres. Other OSHA regulations control the use of CO_2 as a fire suppressant and require a discharge alarm, time to exit before discharge, and employee training about the hazards associated with the use of CO_2 to fight fires. Many of the OSHA rules regarding fire protection come from the National Fire Prevention Association (NFPA) [13,68,69,71–75]. The Emergency Management Institute of the Federal Emergency Management Agency (FEMA), professional and academic emergency management programs, and underground utilities organizations are additional sources of regulations, information, and training regarding confined space hazards.

Breathing Gas, Respiratory Protection, and Controlled, Self-Contained Atmospheres

Academic medical researchers and governmental aviation and aerospace organizations such as NASA and the US Naval Medical Research Institute have investigated the physiology of CO_2 and the engineering controls needed to sustain humans in controlled and self-contained environments. The compressed-breathing-gas CO_2 limit for OSHA/CGA Grade D breathing air used in respiratory protection and Self Contained Underwater Breathing Apparatus (SCUBA) equipment is 1000 ppm. Through the Coast Guard, the DOT establishes a limit for CO_2 at 1000 ppm in SCUBA breathing gas for commercial diving.

NIOSH and PHS also regulate the CO_2 content of breathing gas for self-contained breathing apparatus (SCBA) and supplied air respirators. These limits are the same CGA standard of 1000 ppm, but also mandate maximum inspired CO_2 content for rebreathed air while using an SCBA (as shown in Table 5). Because humans at rest exhale 3.5% CO_2 on average, some exhaled air in the mask of an SCBA is rebreathed. The equipment design must ensure that the average CO_2 content of inhaled air does not exceed the tolerances listed in Table 5 [58,69,76].

TABLE 5
MAXIMUM ALLOWED PERCENTAGE OF CO_2 IN MIXED SUPPLIED/ REBREATHED AIR FROM SCBA APPARATUS

Service Time (h)	**Maximum allowed CO_2 content in %**
< 1/2	2.5
1	2.0
2	1.5
3	1.0
4	1.0

US GPO, 2000-42 CFR 84.97.

Food Additive and Medical Gas

The DHHS sets rules for or defines uses of CO_2 as a general food additive, a leavening agent, a diagnostic indicator of severe disorders associated with changes in body acid–base balance, and as a medical gas. As long as CO_2 is manufactured in accordance with current good manufacturing practices (CGMP) as defined in 21 CFR sections 210–211, it is generally recognized as safe (GRAS) as a food additive. The CO_2 limit for medical gas is 500 ppm, as set by the CGA, United States Pharmacopeia (USP), and the National Formulary (NF).

Chemical Safety, Hazard Communication, and Hazard Response

Information on the hazards of CO_2 and recommended responses to its release are available through the OSHA-mandated Material Safety Data Sheets (MSDS) produced by manufacturers. Other sources about hazards include FEMA's Hazardous Material Guide, the DOT's Emergency Response Guide, toxicological information from the Registry of Toxic Effects of Chemical Substances (RTECS), and the International Chemical Safety Card (ICSC). The International Programme on Chemical Safety is a joint project of the United Nations Environmental Programme (UNEP), the World Health Organization (WHO), and the International Labour Office (ILO) that produces the ICSCs.

The response to CO_2 releases or hazards is the same as for any IDLH atmosphere. First, rescuers must wear respiratory protection. Victims are removed to a well-ventilated area and provided with supplementary oxygen if available. Aggressive ventilation and release to the atmosphere disperse the CO_2.

Transportation

Most regulations regarding CO_2 by the DOT refer to engineering controls on equipment used to transport CO_2 (such as tanks and pipelines) and include the OPS. The CGA, ANSI, ASME, and NFPA are other good sources of information and regulations pertaining to the transport of carbon dioxide by various means.

Toxic and Hazardous Substances: Where CO_2 is Not Regulated

The regulations that do not include carbon dioxide are equally interesting. As with any substance, the dose makes the poison. Even oxygen is toxic at high concentrations, so while CO_2 is a physiologically active gas and lethal above 15– 30%, it is not regarded as a toxic substance for regulatory purposes because it has no known toxicological effects (such as causing cancer, impairing the immune system, or causing birth defects). The EPA enforces the Clean Air Act by regulating ambient outdoor air-quality contaminants, and carbon dioxide is not included. The EPA does not set a limit for the amount of CO_2 allowed in food, as it does for other pesticides. Carbon dioxide is not suspected of any harmful effects in small concentrations (ppm), so the National Toxicology Program (NTP) has not studied it yet. None of the following organizations lists or studies CO_2 as a toxic substance: the Agency for Toxic Substances and Disease Registry (ATSDR) or NIOSH in the CDC, the National Institute of Environmental Health Science (NIEHS) in the National Institutes of Health (NIH), the National Center for Toxicological Research (NCTR) in the FDA, or the EPA. Nor do the following regulations identify or regulate CO_2 as a toxic or hazardous material: the Federal Insecticide, Fungicide, and Rodenticide Act of 1972 (FIFRA), the Resource Conservation and Recovery Act of 1976 (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund), and the Superfund Amendments and Reauthorization Act of 1986 (SARA). Only the inventory list for the Toxic Substances Control Act of 1976 (TSCA), the NIOSH confined-space hazard classification system, and FEMA's hazardous materials guide treat CO_2 as a hazardous substance to the extent that any concentrated or pressurized gas poses a danger. In all cases, it is included in the least hazardous category.

Summary of Regulations Related to CO_2

Table 6 is a summary of established exposure limits, and Table 7 is a list of the majority of regulations from the Code of Federal Regulations that pertain to CO_2.

TABLE 6
SUMMARY OF INFORMATION REGULATORY LIMITS FOR EXPOSURE TO CO_2

Organization	Regulation type	Regulation limit
OSHA	Occupational	5000 ppm TWA PEL; 30,000 ppm TWA STEL
NIOSH	Occupational	5000 ppm TWA REL; 30,000 ppm TWA STEL; 40,000 ppm IDLH
ACGIH	Occupational	5000 ppm TWA TLV; 30,000 ppm TWA STEL
ASHRAE	Ventilation	1000 ppm
OSHA/NIOSH/CGA/ USP/NF	Compressed breathing gas for respiratory protection SCBA and SBA	1000 ppm
OSHA/CGA/Coast Guard	SCUBA breathing gas	1000 ppm
FDA/CGA/USP/NF	Medical gas	500 ppm

CONCLUSIONS

Carbon dioxide is generally regarded as safe and non-toxic, inert gas. It is an essential part of the fundamental biological processes of all living things. It does not cause cancer, affect development, or suppress the immune system in humans. CO_2 is a physiologically active gas that is integral to both respiration and acid–base balance in all life. However, exposure to elevated concentrations of CO_2 can lead

TABLE 7
CODE OF FEDERAL REGULATIONS (CFRS) RELATING TO CARBON DIOXIDE

CFR	Government branch	Regulated as	Description	Regulation (limit/max)
9 CFR 313.5	FSIS, DOA	Anaesthetic and asphyxiant	Humane slaughter of livestock	XX
14 CFR 25.831	FAA, DOT	Ventilation air contaminant	In airplane cabins	5000 ppm (0.5%) by volume
21 CFR 137.180, 137.185, 137.270	FDA, DHHS	Leavening agent	In self-rising cereal flours	Must exceed 5000 (0.5%)
21 CFR 184.1240	FDA, DHHS	Direct food substance	GRAS—generally recognized as safe	GRAS
21 CFR 201.161	FDA, DHHS	Medical drug	Exempt from labeling requirements of 21 CFR 201.100	Exempt from labeling
21 CFR 210-211	FDA, DHHS	Medical gas	Current good manufacturing practices (CGMP)	CGMP
21 CFR 582.1240	FDA, DHHS	General purpose food additive	GRAS—generally recognized as safe	GRAS
21 CFR 862.1160	FDA, DHHS	Clinical chemistry test system	Diagnostic of blood acid–base imbalance	XX
29 CFR 1910.134	OSHA, DOL	Compressed breathing gas	In respiratory protection equipment CGA and USP	CGA breathing air Grade D—1000 ppm (0.1%)
29 CFR 1910.146	OSHA, DOL	Confined space hazard	General environmental controls	Permit required to enter
29 CFR 1910.155-1910.165 Subpart L	OSHA, DOL	Fire suppressant and confined space hazard	Required engineering controls on fire-fighting systems and equipment, employee training, and respiratory protection—NFPA	XX

29 CFR 1910.430	OSHA, DOL	Compressed breathing gas	Commercial diving operations—SCUBA	1000 ppm (0.1%)
29 CFR 1910.1000 Table Z-1	OSHA, DOL	Air contaminant	General occupational exposure limits	5000 ppm (0.5%) TWA PEL
29 CFR 1915.1000 Table Z	OSHA, DOL	Air contaminant	Exposure limits for shipyard employment	5000 ppm (0.5%) TWA PEL
29 CFR 1926.55	OSHA, DOL	Air contaminant	Exposure limits for construction	ACGIH: 5000 ppm (0.5%) TWA TLV
30 CFR 56.5001	MSHA, DOL	Air contaminant	Exposure limits for surface mines	ACGIH: 5000 ppm (0.5%) TWA TLV
30 CFR 57.5001	MSHA, DOL	Air contaminant	Exposure limits for underground mines	ACGIH: 5000 ppm (0.5%) TWA TLV
40 CFR 180.1049	EPA	Pesticide, insecticide	Tolerance for pesticide chemical in food	Exempt from tolerance
42 CFR 84.79	NIOSH, PHS, DHHS	Compressed breathing gas	SCBA	USP/NF, CGA: 1000 ppm (0.1%)
42 CFR 84.97	NIOSH, PHS, DHHS	Inspired air from SCBA	Test of inspired air in SCBA—control of rebreathing	> 30 min./2.5%; 1 h/2.0%; 2 h/1.5%; 3 h/1.0%; 4 h/1.0%
42 CFR 84.141	NIOSH, PHS, DHHS	Compressed breathing gas	Supplied air respirators	CGA: 1000 ppm (0.1%)
46 CFR 197.340	Coast Guard, DOT	Compressed breathing gas	Commercial diving operations—SCUBA	1000 ppm (0.1%)
49 CFR 100-180	DOT	Transportation material	General transportation requirements	
49 CFR 190-199	OPS, DOT	Gas or hazardous liquid	Engineering safety controls on pipelines	

to adverse consequences, including death. The effects of exposure to CO_2 depend on the concentration and duration of exposure.

Ambient atmospheric concentrations of CO_2 are currently about 370 ppm. Humans can tolerate increased concentrations with virtually no physiological effects for exposures that are up to 1% CO_2 (10,000 ppm). For concentrations of up to 3%, physiological adaptation occurs without adverse consequences. A significant effect on respiratory rate and some discomfort occurs at concentrations between 3 and 5%. Above 5%, physical and mental ability is impaired and loss of consciousness can occur. Severe symptoms, including rapid loss of consciousness, and possible coma or death result from prolonged exposure above 10%. Experiments conducted on a submarine crew exposed to up to 3% CO_2 for many weeks and short-term exposures to even higher concentrations have shown that all effects except for prolonged coma, consequences of prolonged hypoxia (lack of oxygen), and death are reversible. Loss of consciousness occurs within several breaths and death is imminent at concentrations above 25–30%. Deaths from catastrophic releases of CO_2 are known from industrial accidents and natural disasters.

The potential for lethal or otherwise harmful exposure depends on the nature of the release rather than on the concentration of CO_2 or the size of the release. In particular, since CO_2 is denser than air, hazardous situations arise when large amounts of CO_2 accumulate in low-lying, confined, or poorly ventilated spaces. Releases, even large ones, that are quickly dissipated in the atmosphere, such as those that occur during explosive volcanic releases or from tall industrial stacks, do not pose a hazard.

Evidence for the effects of exposure to elevated concentrations of CO_2 on natural resources and ecosystems comes from many sources, including volcanic releases, soda springs, comparative, respiratory and fundamental physiology, free-air CO_2 enrichment studies, food preservation literature, and space science research. Among the major classes of terrestrial vertebrates, respiratory physiology and mechanisms for acid–base balance (pH regulation) vary widely, so tolerance to CO_2 exposure varies as well. Tolerance for CO_2 also correlates to ecological niche suggesting evolutionary adaptation to environmental conditions. Plants, insects, and soil-dwelling organisms have higher tolerance to CO_2 than most other forms of life. In spite of these differences, all air-breathing animals including humans have similar respiratory physiology and therefore broadly similar tolerance to CO_2, and prolonged exposure to high CO_2 levels, above 20–30%, will kill virtually all forms of life except some microbes, invertebrates, fungi, and insects. Some microbes can survive in a pure CO_2 atmosphere as long as trace amounts of oxygen are available. However, the identity and physiology of microorganisms dwelling in deep geologic formations is largely unknown, so the effects of CO_2 on them are uncertain.

Ecosystem impacts from exposure to elevated concentrations of CO_2 are poorly understood. Plants in general are even more tolerant than invertebrates to elevated CO_2, so any small-scale, short-term gas leaks would have minimal impacts. Persistent leaks, however, could suppress respiration in the root zone or result in soil acidification, and catastrophic releases could certainly kill vegetation as well as animals. Most of the controlled experiments have focused on the moderate increases in CO_2 concentrations that are expected to occur due to atmospheric buildup of CO_2 from the continued use of fossil fuels or that stimulate plant productivity in greenhouses. The studies have shown that moderate increases in CO_2 concentrations stimulate plant growth, while decreasing the loss of water through transpiration. At the other end of the scale, tree kills associated with soil gas concentrations in the range of 20–30% CO_2 have been observed at Mammoth Mountain, California, where volcanic outgassing of CO_2 has been occurring since at least 1990. Little information is available in the intermediate range of 2–30%. In addition, information on the tolerance of aquatic ecosystems to short-term, catastrophic releases was not found during this literature search and may need to be researched.

Carbon dioxide is used in a wide variety of industries: from chemical manufacture to beverage carbonation and brewing, from EOR to refrigeration, and from fire suppression to inert-atmosphere food preservation. Sources of CO_2 include natural reservoirs, separation from crude oil and natural gas, and as a waste product of industrial processes (chemical manufacture), combustion processes (energy production), and biological respiration (brewing). Because of its extensive use and production, the hazards of CO_2 are well known and routinely managed. Engineering and procedural controls are well established for dealing with the hazards of compressed and cryogenic CO_2. Nevertheless, the hazards of CO_2 are significant as fatalities from fire-suppression system malfunctions and confined-space accidents attest.

CO_2 is regulated by Federal and State authorities for many different purposes, including occupational safety and health, ventilation and indoor air quality, confined-space hazard and fire suppression, as a respiratory gas and food additive, for animal anesthesia and the humane slaughter of livestock, transportation and most recently, as a greenhouse gas (UNFCCC). Federal occupational safety and health regulations set three limits:

- 0.5% or 5000 ppm for an average 8-h day or 40-h week,
- 3% or 30,000 ppm for an average short-term 15-min exposure limit,
- 4% or 40,000 ppm for the maximum instantaneous exposure limit above which is considered IDLH.

Most industrial and safety regulations for CO_2 focus on engineering controls and specifications for transportation, storage containers, and pipelines.

In addition to understanding when and how CO_2 is regulated for industrial and occupational settings, it is important also to know that CO_2 is not regulated, studied, or suspected as a toxic substance by the following federal agencies or regulations, including: Clean Air Act 1970, 1990, Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) 1972, Resource Conservation and Recovery Act (RCRA) 1976, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) 1980, Superfund Amendments and Reauthorization Act (SARA) 1986, NTP, ATSDR or the NIOSH within the CDC, NIEHS in the NIH, and the NCTR in the FDA. Only the inventory list for the TSCA of 1976, the NIOSH confined space hazard classification system, and FEMA's hazardous materials guide treat CO_2 as a hazardous substance to the extent that any concentrated or pressurized gas poses a danger.

In conclusion, the key poorly understood health, safety, and environmental concerns surrounding geologic storage of CO_2 relate to the potential for unanticipated leakage. Such releases could be associated with surface facilities, injection wells, or natural, geological "containers" and may be small-scale diffuse leaks or large catastrophic incidents. Long industrial experience with CO_2 and gases in general shows that the risks from industrial storage facilities are manageable using standard engineering controls and procedures. Serious accidents have occurred but the incidents described were preventable and experience teaches us how to operate these facilities even more safely. On the other hand, our understanding of and ability to predict CO_2 releases and their characteristics in any given geologic and geographic setting is far more challenging. Certainly there are many sites, such as oil and gas reservoirs where the probability of leakage is very low. However, brine formations, which generally are not well characterized and do not have cap rocks or seals that have stood the test of time, will require significant effort to evaluate potential risks, and these risks must be taken seriously.

To date, the majority of the thought process regarding the risks of CO_2 geologic storage has revolved around human health risks. This study raises the issue that, if leakage occurs, ecosystem risks may also be significant, particularly for soil dwelling or ground hugging organisms. In addition, acidification of soils in the vicinity of surface leaks may also harm plants. Similarly, persistent low-level leakage could affect aquatic ecosystems by lowering the pH, especially in stagnant or stably stratified waters.

REFERENCES

1. USDOE, Carbon Sequestration Research and Development, National Technical Information Service, Springfield, VA, 1999, www.ornl.gov/carbon_sequestration/.
2. N.E. Tolbert, J. Preiss (Eds.), Regulation of Atmospheric CO_2 and O_2 by Photosynthetic Carbon Metabolism, Oxford University Press, New York, NY, 1994.
3. S.E. Humphris, T.A. Zierenberg, L.S. Mullioneaux, R.E. Thompson, Geophysical Monograph 91: Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions, American Geophysical Union, Washington, DC, 1995.

4. N.A. Campbell, L.G. Mitchell, J.B. Reece, Biology, fifth ed., Benjamin/Cummings, Menlo Park, CA, 1999, plus earlier Publishing editions.
5. J.A. Kellum, Determinants of blood pH in health and disease, *Crit. Care* **4** (1) (2000) 6–14.
6. M.J.T. Van de Ven, W.N.J.M. Colier, M.C. van der Sluijs, B. Oeseburg, H. Folgering, Ventilatory response in metabolic acidosis and cerebral blood volume in humans, *Respir. Physiol.* **124** (2001) 105–115.
7. J.D. Jones, Comparative Physiology of Respiration, *Special Topics in Biology Series*, Edward Arnold Publishers, London, 1972.
8. NIOSH (National Institute of Occupational Safety and Health), Criteria for a Recommended Standard. Occupational Exposure to Carbon Dioxide, NIOSH Publication No. 76-194, US GPO, Washington, DC, 1976, www.cdc.gov/niosh/, www.gpo.gov.
9. N. Heisler, Interactions between gas exchange, metabolism, and ion transport in animals: an overview, *Can. J. Zool.* **67** (1989) 2923–2935.
10. F.N. White, Carbon dioxide homeostasis, in: S.C. Wood (Ed.), *Lung Biology in Health and Disease, Comparative Pulmonary Physiology—Current Concepts*, Vol. 39, Marcel Dekker, New York, NY, 1989, pp. 439–466.
11. Naval Aerospace Medical Institute (NAMI), United States Naval Flight Surgeon's Manual, third ed., 1991, http://www.vnh.org/FSManual/fsm91.html.
12. USAF (United States Air Force), USAF Flight Surgeon's Guide, online ed., 2001, http://wwwsam.brooks.af.mil/ram/fsr-web/fsr-default.htm.
13. NIOSH, Criteria for a Recommended Standard. *Working in Confined Spaces*, NIOSH Publication No. 80-106, US GPO, Washington, DC, 1979, www.cdc.gov/niosh/, www.gpo.gov.
14. NRC (National Research Council) Committee on Airliner Cabin Air Quality, The Airliner Cabin Environment: Air Quality and Safety, National Academy Press, Washington, DC, 1986, www.nap.edu.
15. USEPA and NIOSH, Building Air Quality: A Guide for Building Owners and Facility Managers, US GPO, Washington, DC, 1991.
16. USEPA, Indoor Air Pollution: An Introduction for Health Professionals, US GPO Publication No. 1994-523-217/81322, USEPA, Washington, DC, 1994, www.epa.gov/iaq/pubs/hpguide.html.
17. J.L. Gingras, A. Muelenaer, L.B. Dalley, K.J. O'Donnell, Prenatal cocaine exposure alters postnatal hypoxic arousal responses and hypercarbic ventilatory responses but not pneumocardiograms in prenatally cocaine-exposed term infants, *Pediatric Pulmonol.* **18** (1) (1994) 13–20.
18. OSHA (Occupational Safety and Health Administration), Indoor Air Quality, Federal Register # 59: 15968-16039, US GPO, Washington, DC, 1994, www.cdc.gov/niosh/, www.gpo.gov.
19. NIOSH, NIOSH Facts—Indoor Environmental Quality (IEQ), Document No. 705002, US GPO, Pittsburgh, PA, 1997, www.cdc.gov/niosh/, www.gpo.gov.
20. ASHRAE Standards Committee, ANSI/ASHRAE Standard 62-1999: Ventilation for Acceptable Indoor Air Quality, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Atlanta, GA, 1999, www.ashrae.org.
21. NIOSH (Occupational Health Guidelines for Chemical Hazards), Occupational Health Guidelines for Chemical Hazards, NIOSH Publication No. 81-123, US GPO, Washington, DC, 1981, www.cdc.gov/niosh/, www.gpo.gov.
22. ACGIH (American Conference of Governmental Industrial Hygienists), Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices (1994–1995), ACGIH, Cincinnati, OH, 1994.
23. W. Coryell, Hypersensitivity to carbon dioxide as a disease-specific trait marker, *Biol. Psychiatry* **41** (1997) 259–263.
24. J.P. Forsyth, C.W. Lejuez, C. Finlay, Anxiogenic effects of repeated administrations of 20% CO_2-enriched air: stability within sessions and habituation across time, *J. Behav. Therapy Exp. Psychiatry* **31** (2000) 103–121.
25. W. Coryell, A. Fyer, D. Pine, J. Martinez, S. Arndt, Aberrant respiratory sensitivity to CO_2 as a trait of familial panic disorder, *Biol. Psychiatry* **49** (2001) 582–587.
26. D. Koszycki, J. Bradwejn, Anxiety sensitivity does not predict fearful responding to 35% carbon dioxide in patients with panic disorder, *Psychiatry Res.* **101** (2001) 137–143.
27. M. McIntyre, B. McNeil, Dissolved carbon dioxide effects on morphology, growth, and citrate production in *Aspergillus niger* A60, *Enzyme Microb. Technol.* **20** (1997) 135–142.

28. M.H.J. Bennik, W. Vorstman, E.J. Smid, L.G.M. Gorris, The influence of oxygen and carbon dioxide on the growth of prevalent *Enterobacteriaceae* and *Pseudomonas* species isolated from fresh and controlled-atmosphere-stored vegetables, *Food Microbiol.* **15** (1998) 459–469.
29. J.K. Frederickson, T.C. Onstott, Microbes deep inside the Earth, Earth from the Inside Out, Scientfic American, New York, NY, 2000, pp. 10–15.
30. I. Haasum, P.V. Nielsen, Preincubation of *Penicillium commune* Conidia under modified atmosphere conditions: influence on growth potential as determined by an impedimetric method, *J. Stored Prod. Res.* **32** (4) (1996) 329–337.
31. S. Tian, Q. Fan, Y. Xu, Y. Wang, A. Jiang, Evaluation of the use of high CO_2 concentrations and cold storage to control *Monilinia fructicola* on sweet cherries, *Postharvest Biol. Technol.* **22** (2001) 53–60.
32. J.N. Maina, Zoophysiology Vol. 37: The Gas Exchangers—Structure, Function, and Evolution of the Respiratory Processes, Springer, Berlin, 1998.
33. S.K. Hamilton, S.J. Sippel, J.M. Melack, Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil, *Biogeochemistry* **30** (1995) 115–141.
34. D.D. Mann, D.S. Jayas, N.D.G. White, W.E. Muir, Mortality of adult *Cryptolestes ferrugineus* (Stephens) exposed to changing CO_2 concentrations, *J. Stored Prod. Res* **35** (1999) 385–395.
35. P.C. Annis, R. Morton, The acute mortality effects of carbon dioxide on various life stages of *Sitophilus oryzae*, *J. Stored Prod. Res.* **33** (2) (1997) 115–123.
36. E.C.W. Leong, S.H. Ho, Effects of carbon dioxide on the mortality of *Liposcelis bostrychophila* Bad. and *Liposcelis entomophila* (End.) (Psocoptera: Liposcelididae), *J. Stored Prod. Res.* **31** (3) (1995) 185–190.
37. G.N. Mbata, C. Reichmuth, The comparative effectiveness of different modified atmospheres for the disinfestation of Bambarra groundnuts, *Vigna Subterranea* (L.) Verde, infested by *Callosobruchus subinnotatus* (Pic) (Coleoptera: Bruchidae), *J. Stored Prod. Res.* **32** (1) (1996) 45–51.
38. S. Zhou, R.S. Criddle, E.J. Mitcham, Metabolic response of *Platynota stultana* pupae to controlled atmospheres and its relation to insect mortality response, *J. Insect Physiol.* **46** (2000) 1375–1385.
39. S. Zhou, R.S. Criddle, E.J. Mitcham, Metabolic response of *Platynota stultana* pupae during and after extended exposure to elevated CO_2 and reduced O_2 atmospheres, *J. Insect Physiol.* **47** (2001) 401–409.
40. R.G. Amundson, E.A. Davidson, Carbon dioxide and nitrogenous gases in the soil atmosphere, *J. Geochem. Expl.* **38** (1990) 13–41.
41. P. Holter, Tolerance of dung insects to low oxygen and high carbon dioxide concentrations, *Eur. J. Soil Biol.* **30** (4) (1994) 187–193.
42. J. Pinol, J.M. Alcaniz, F. Roda, Carbon dioxide efflux and pCO_2 in soils of three Quercus ilex montane forests, *Biogeochemistry* **30** (1995) 191–215.
43. V. Sustr, M. Simek, Behavioural responses to and lethal effects of elevated carbon dioxide concentration in soil invertebrates, *Eur. J. Soil Biol.* **32** (3) (1996) 149–155.
44. H. Mohr, P. Schopfer, Plant Physiology, Springer, New York, NY, 1995, translated by G. Lawlor and D.W. Lawlor.
45. D.M. Orcutt, E.T. Nilsen, *Physiology of Plants Under Stress*, Wiley, New York, NY, 2000, 683pp.
46. J.W. Mastalerz, The Greenhouse Environment, Wiley, New York, NY, 1977, 629pp.
47. M.C. Press, J.D. Scholes, M.G. Barker (Eds.), *Physiological Plant Ecology*, British Ecological Society/Blackwell, Malden, MA, 1999.
48. IPCC, IPCC Second Assessment Report: Climate Change 1995, Cambridge University Press, Cambridge, 1996.
49. IPCC, IPCC Third Assessment Report: Climate Change 2001, Cambridge University Press, Cambridge, 2001.
50. M.H., Jones, P.S., Curtis, (eds.), Bibliography on CO_2 Effects on Vegetation and Ecosystems: 1990–1999 Literature, ORNL/CDIAC-129, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, 2000. http://cdiac.esd.ornl.gov/epubs/cdiac/cdiac129/cdiac129.html.
51. CDIAC http://cdiac.esd.ornl.gov/, Oak Ridge National Laboratory, www.ornl.gov/, US Department of Energy, Oak Ridge, TN, 2001a.
52. CDIAC, Free Air CO_2 Enrichment (FACE), Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, TN, 2001, http://cdiac.esd.ornl.gov/programs/FACE/face.html.
53. J.A. Hyatt, Liquid and supercritical carbon dioxide as organic solvents, *J. Org. Chem.* **49** (26) (1984) 5097–5101.

54. J. Pawliszyn, N. Alexandrou, Indirect supercritical fluid extraction of organics from water matrix samples, *Water Pollut. Res. J. Can.* **24** (2) (1989) 207–214.
55. W.D. Spall, K.E. Laintz, A survey on the use of supercritical carbon dioxide as a cleaning solvent, in: J. McHardy, S.P. Sawan (Eds.), *Supercritical Fluid Cleaning*, Noyes Publishing, Westwood, NJ, 1998, pp. 162–194.
56. IEAGHG, Carbon Dioxide Utilization, 1995, www.ieagreen.org.uk/.
57. CGA, G6: Carbon dioxide, fifth ed., CGA, Arlington, VA, 1997, www.cganet.com.
58. Airgas, Inc., Applications of CO_2, www.airgas.com/carbonic/applications.htm, 2001.
59. USEPA, Carbon Dioxide as a Fire Suppressant: Examining the Risks, US GPO, Washington, DC, 2000, www.epa.gov/ozone/title6/snap/co2report.html.
60. Freedonia Group, Carbon Dioxide, Business Research Report B286, Freedonia Group, Inc., Cleveland, OH, 1991, 46pp.
61. Freedonia Group, Report 1345: Industrial Gases to 2004, Freedonia Group, Inc, Cleveland, OH, 2000.
62. USDOC (United States Department of Commerce), Current Industrial Reports—1998, Economics and Statistics Administration, Bureau of the Census, 1999.
63. Texas Natural Resources Conservation Commission (TNRCC), Point Source Emissions database, 2001, www.tnrcc.state.tx.us.
64. Shell, Royal Dutch, web site, http://www.shell.com/royal-en/content/0,5028,25544-51037,00.html, 2001.
65. USDOE, Annual Energy Report 1999, Energy Information Administration, US DOE, Washington, DC, 2000, DOE/EIA-0384(99)www.eia.doe.gov/aer/contents.html, www.eia.doe.gov/pub/pdf/multi.fuel/038499.pdf.
66. H. Kruse, M. Tekiela, Calculating the consequences of a CO_2-pipeline rupture, *Energy Convers. Manage.* **37** (6–8) (1996) 1013–1018.
67. USDOE, Type A Accident Investigation Board Report of the July 28, 1998 Fatality and Multiple Injuries Resulting From Release of Carbon Dioxide at Building 648, Test Reactor Area, Idaho National Engineering and Environmental Laboratory, 1998, www.id.doe.gov/doeid/foia/archive.htm, www.id.doe.gov/doeid/foia/tra-accident.htm.
68. USEPA, An Annotated Summary of Climate Change Related Resources, National Service Center for Environmental Publications, Cincinnati, OH, 2000.
69. US GPO (United States Government Printing Office), Code of Federal Regulations, US GPO, Washington, DC, 2000, www.access.gpo.gov.
70. NIOSH, Documentation for Immediately Dangerous to Life and Health Concentrations, NTIS Publication No. PB-94-195047, National Technical Information Service, Springfield, VA, 1994, www.cdc.gov/niosh/, www.ntis.gov.
71. NIOSH, NIOSH Pocket Guide to Chemical Hazards, NIOSH Publication No. 97-140, National Technical Information Service, Springfield, VA, 1997, www.cdc.gov/niosh/, www.gpo.gov.
72. NIOSH, Worker Deaths in Confined Spaces: A Summary of NIOSH Surveillance and Investigative Findings, NIOSH Publication No. 94-103, Publications Dissemination, DSDTT, NIOSH, Cinncinnati, OH, 1994.
73. CGA, P-14: Accident Prevention in Oxygen-Rich and Oxygen-Deficient Atmospheres, CGA, Arlington, VA, 1992, www.cganet.com.
74. CGA, SB-2: Oxygen Deficient Atmospheres, CGA, Arlington, VA, 1992, www.cganet.com.
75. CGA, SB-15: Safety Bulletin—Avoiding Hazards in Confined Work Spaces During Maintenance, Construction, and Similar Activities, CGA, Arlington, VA, 1998, www.cganet.com.
76. CGA (Compressed Gas Association, Inc.), G7: Compressed Air for Human Respiration, fourth ed., CGA, Arlington, VA, 1990, www.cganet.com.
77. S.M. Benson, R. Hepple, J. Apps, C.-F. Tsang, M. Lippman, Lessons learned from natural and industrial analogues for storage of carbon dioxide in deep geologic formations, Lawrence Berkeley National Laboratory Report, LBL-51170, Berkeley, CA, 2002.