United States Department of Agriculture
Agricultural Marketing Service | National Organic Program
Document Cover Sheet
https://www.ams.usda.gov/rules-regulations/organic/petitioned-substances

Document Type:

☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

Carbon Dioxide

Crops

Identification of Petitioned Substance

Chemical Names:
CO_2; carbon dioxide; carbonic acid anhydride; carbonic anhydride; dioxomethane; methanedione

Other Name:
carbonic acid gas; dry ice

Trade Names:
CO_2; carbon dioxide

CAS Number:
124-38-9

Other Codes:
EC number: 204-696-9
NIOSH RTECS number: FF6400000
UNII: 142M471B3J
EPA PC code: 016601

Summary of Petitioned Use

Carbon dioxide was petitioned in 2020 for inclusion on the National List of Allowed and Prohibited Substances, hereafter referred to as the National List, for use as a plant or soil amendment. This full scope technical report serves to provide the National Organic Standards Board (NOSB) with technical information to support the review of the petition to add carbon dioxide to 7 CFR 205.601(j). This report focuses on uses of carbon dioxide in organic crop production as a plant or soil amendment. In addition to the evaluation questions included in the report template, the NOSB Crops Subcommittee requested a focus question:

Describe the use frequency and application rates of all application methods, including in greenhouses and others.

The same petition requested the addition of carbon dioxide to 7 CFR 205.601(a) of the National List for use as an algicide, disinfectant, and sanitizer, including uses in irrigation systems, to acidify irrigation water (Eco2Mix, Inc., 2020). Sources of irrigation water tend to be alkaline in some areas, which may inhibit plant nutrient uptake and lead to the formation of mineral scale in equipment (NOP, 2014b). In 2022, the NOSB recommended to the National Organic Program (NOP) to add carbon dioxide to § 205.601(a), but at the time of this writing the NOP has not taken regulatory action (NOSB, 2022). The NOSB made their recommendation without a technical report. The NOSB has requested this technical report to address the sections of the petition requesting the addition of carbon dioxide to § 205.601(j), as a plant or soil amendment, before making a second recommendation (NOSB, 2022).

This report explores the use of gaseous carbon dioxide in indoor crop production as an atmospheric enrichment substance, as well as the fertilization and soil amending effects resulting from dissolved carbon dioxide in irrigation water. Although the petition does not specifically discuss the use of carbon dioxide for atmospheric enrichment in greenhouses, this is the most prevalent use of the material in agriculture. For the sake of thoroughness and in response to the NOSB's requested focus question, this report describes all potential uses of carbon dioxide including gaseous, dissolved for use as a soil amendment, and as a pH adjuster in irrigation systems.

Characterization of Petitioned Substance

Composition of the Substance:
Carbon dioxide is composed of one carbon atom and two oxygen atoms with the molecular formula CO_2 (National Center for Biotechnology Information, 2023). Each oxygen atom is bonded to the central carbon atom with double covalent bonds in a linear configuration (National Research Council (US), 2001; Patnaik, 2003). See Figure 1 for a visual representation of the molecule.

Figure 1: Molecular structure of CO_2

Throughout this report, carbon dioxide will be referred to as CO_2.

Source or Origin of the Substance:

CO_2 results from the oxidation of carbon and occurs ubiquitously in the environment and throughout the solar system (National Center for Biotechnology Information, 2023; Patnaik, 2003). Currently, the average carbon dioxide concentration in Earth's atmosphere is approximately 420 parts per million (ppm), or 0.042%, but has been steadily increasing since the beginning of the industrial revolution (NOAA, 2022).

Carbon dioxide forms from a variety of different chemical and biological processes, including (National Center for Biotechnology Information, 2023; Patnaik, 2003):

- respiration by microbes, fungi, and animals
- the combustion or decomposition of carbon-based substances, and
- volcanic eruptions or other geological processes

Volcanic processes release just 1% compared to the amount of carbon dioxide released by humans (Steen, 2006). Though the annual carbon dioxide output of volcanoes is highly variable, on average humans emit as much carbon dioxide in 2-3 days as volcanic processes emit in one year (Gerlach, 2011). Plants utilize carbon dioxide in photosynthesis and rely on the substance for their survival (National Center for Biotechnology Information, 2023; Patnaik, 2003).

CO_2 is the end product of all combustion processes, chemical (as in the burning or thermal decomposition of organic matter), and biological (as in digestion of carbohydrates for energy) (Aresta et al., 2013). Commercial production of CO_2 occurs by several different methods, including burning carbon-based fuel, reactions between acids and bicarbonate salts, extraction from exhaust gases resulting from a variety of industries, alcohol production, beer fermentation, and direct extraction from wells (Chapel & Mariz, 1999; Steen, 2006). See *Evaluation Question* #2 for detailed manufacturing information.

Properties of the Substance:

At normal atmospheric pressures and temperatures, CO_2 occurs as a mostly odorless, colorless, and tasteless gas. It is denser than air. CO_2 is the most often cited and recognized greenhouse gas and the largest contributing factor to global climate change (National Center for Biotechnology Information, 2023; Patnaik, 2003).

CO_2 is moderately soluble in water. Solubility increases with increasing pressure and decreases with increasing temperature (Patnaik, 2003). When dissolved, CO_2 forms small amounts of carbonic acid (H_2CO_3) in solution and is defined as a weak acid in this form (Häring (Ed.), 2007; National Center for Biotechnology Information, 2023). No matter the temperature, CO_2 will never exist as a liquid at atmospheric pressure, but will solidify into dry ice upon cooling (Patnaik, 2003). Dry ice directly sublimes back to gas with increasing temperature (Patnaik, 2003; Scott et al., 2009). By controlling pressure, however, CO_2 is easily converted into a liquid which is the most common commercial form (Häring (Ed.), 2007). See Figure 2 for a visual representation of the phase changes for CO_2 based on relative temperature and pressure.

CO_2 is very stable in the atmosphere, and typically requires significant energy input to react or break down due to it being fully oxidized (National Research Council (US), 2001; Steen, 2006).

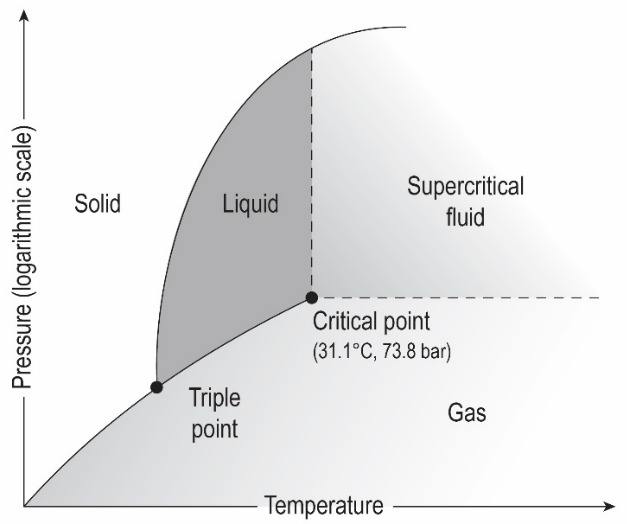

Figure 2: Phase changes in CO2. Adapted from Bauer et al. (2013)

Table 1 describes some chemical and physical properties of CO_2 at atmospheric temperature and pressure (ATP).

Table 1: Chemical and physical properties of CO_2

Property	Value
Physical State and Appearance	Gas
Odor	Odorless
Taste	Tasteless
Color	Colorless; white as frozen solid
Molecular Weight (g/mol)	44.009
Density (g/L)	1.799
pH	3.7
Solubility (mL/100 mL water, 20°C)	88 (increases with pressure)
Boiling Point (°C)	-78.464 (sublimes)
Melting Point (°C)	n/a; sublimes directly to gas from solid at ATP
Critical Temperature (°C)	31
Vapor Pressure (atm)	56.5
Stability	Stable
Reactivity	Metal dusts may ignite in CO_2 atmosphere. Forms carbonic acid in water.

Sources: (National Center for Biotechnology Information, 2023; Patnaik, 2003)

CO_2 plays an essential role in the process known as the carbonic acid system, which largely governs the pH of soils and aquatic environments (Drever, 1997). In contact with water, a proportion of CO_2 dissolves until equilibrium is reached between CO_2, bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and carbonic acid (H_2CO_3) (Drever, 1997). A greater proportion of CO_2 shifts the equilibrium to the formation of carbonic acid resulting in lower pH (Drever, 1997). Greater carbonate concentration shifts the equilibrium in the other direction, resulting in higher pH (Drever, 1997). Due to the high ratio of carbonates in many surface environments (such as calcium carbonate limestone), the pH of irrigation water is often elevated (greater than 7) (Albano et al., 2017). Below a pH of 6, the majority of the inorganic carbon species are in the form of solvated CO_2 (molecular CO_2 surrounded by water molecules) or carbonic acid (Drever, 1997). The acidic hydrogen ions contributed by carbonic acid work to neutralize alkalinity and lower pH, but they also react with carbonates to produce alkaline bicarbonate ions. This leads to a buffered system, meaning that it resists a precipitous drop in pH and becomes relatively stable (Drever, 1997). Figure 3 illustrates the relation of inorganic carbon species concentrations to pH.

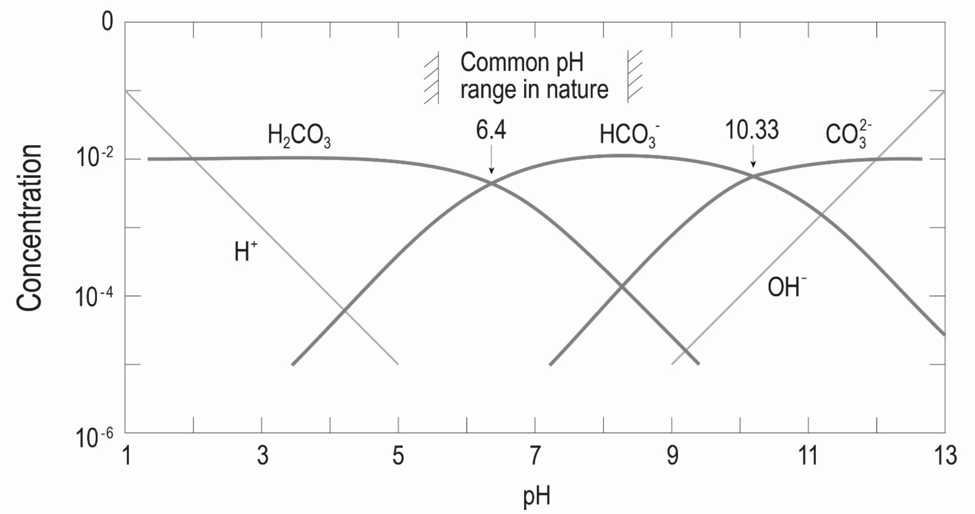

Figure 3: Concentration of carbonate species as a function of pH, assuming the concentration of dissolved CO_2 is 10^{-2} at 25°C. The units are considered irrelevant, and the assumption is that the CO_2 will be almost wholly carbonic acid (H_2CO_3) at acidic pH. At pH 6.4, carbonic acid and bicarbonate (HCO_3^-) concentrations are roughly equal. At pH 10.33, bicarbonate and carbonate (CO_3^{2-}) concentrations are roughly equal. Adapted from Drever (1997).

Specific Uses of the Substance:

Atmospheric adjustment in indoor production

Greenhouse farmers frequently employ gaseous CO_2 to reach optimal atmospheric levels for plant growth.

Ambient air contains 350-450 ppm CO_2, while the optimal concentration of CO_2 for plant growth in a greenhouse environment is 800-1000 ppm (Poudel & Dunn, 2017; Thomson et al., 2022; Wang et al., 2022). As plants grow, they metabolize CO_2 in the air of the greenhouse, depleting it (Wang et al., 2022). Plants consume CO_2 at greater rates during midday, resulting in daytime concentrations of typically just 100-250 ppm (Jin et al., 2009; Thomson et al., 2022). Due to design, exchange of air between the inside and outside of a greenhouse is limited in order to regulate the internal temperature of the building (Wang et al., 2022). To allow indoor CO_2 levels to increase back to outdoor concentration, venting is required, which simultaneously impacts the controlled temperatures in the greenhouse (Thomson et al., 2022). Ventilation alone cannot maintain constant CO_2 concentrations within the greenhouse at a level comparable to that outside the greenhouse, however (Wang et al., 2022). Natural turnover of air by venting may help to moderate CO_2 levels during warm months, but venting is usually not practical during colder periods or in colder regions, and supplementation by other methods may be advisable (Poudel & Dunn, 2017; Thomson et al., 2022; Wang et al., 2022).

CO_2 replenishment and enrichment in greenhouse settings may involve one or more of the following (Poudel & Dunn, 2017; Thomson et al., 2022):

- Combustion of biomass and injection of flue gas
- Use of natural gas or propane burners
- Injection of commercial gas from compressed tanks
- Controlled decomposition, fermentation, or composting
- Chemical neutralization reactions

CO_2 can be a limiting nutrient for plants in a greenhouse (Wang et al., 2022). C_3 plants like tomatoes and cucumbers are especially sensitive to CO_2 concentrations, and they generally show the greatest response to enrichment when compared to the other plant types (Ahammed & Yu, 2023; Wang et al., 2022). However, some studies involving perennial grasses have shown that CO_2 enrichment yields greater biomass increases in some C_4 plants with very long lifespans, but only after several years of growth, while long-lived C_3 plants stop responding to the enrichment over time (Ahammed & Yu, 2023).[1] Since

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[1] Examples of common agricultural C_4 plants include corn, sorghum, sugarcane, and millet.

most studies are conducted on short timescales, the consensus that C_3 plants respond more dramatically to elevated CO_2 may be skewed (Ahammed & Yu, 2023). See Inset 1 for a brief introduction to C_3, C_4, and CAM plant types and their respective metabolic pathways.

Increasing CO_2 beyond ambient air concentration (up to approximately 1000 ppm) can increase yields and increase the content of some nutrients in leafy, fruit, and root vegetables 10-60% (Wang et al., 2022). Therefore, supplemental sources of CO_2 are used for enrichment (Wang et al., 2022).

Enrichment does not always need to occur constantly because carbon assimilation by plants is highest in the morning (Wang et al., 2022). However, plants vary in their responses to periodic CO_2 enrichment. Some plants may yield more edible biomass under periodic enrichment, while others (such as cotton, wheat, chrysanthemums, soybeans, tomatoes, wheat, and rice) may grow better with constant enrichment (Kimball, 2016; Wang et al., 2022). In a meta-analysis of the available literature on open air CO_2 enrichment, Kimball (2016) states that definitive experiments need to be designed to identify those plants that may respond more positively to pulsed, or periodic, CO_2 enrichment.

Producers may enrich CO_2 at 1000-1200 ppm in order to increase yield and cause plants to mature earlier (Ampim et al., 2022). Ampim et al. (2022) found such levels to increase red lettuce yield by 30%, while also increasing levels of some nutritive compounds, such as flavonoids, caffeic acid, and sugars. However, CO_2 enrichment negatively affected the growth of lettuce inoculated with arbuscular mycorrhizal fungi. Elevated levels of CO_2 caused these fungi-inoculated lettuce plants to consume more sugars for shoot growth and to promote mycorrhizal colonization instead of leaf production. CO_2 enrichment does not universally improve nutrient levels in crops. In tomatoes for example, elevated CO_2 levels can cause a decrease in crude protein, vitamin C, organic acids, and fat (Ampim et al., 2022).

Enrichment with gaseous CO_2 may be expensive for producers. The combination of potential CO_2 sources such as boilers, gas burners, purified CO_2 tanks, and the associated heating and exhaust gas infrastructure may exceed roughly $200,000 a year for 10 acres of greenhouse space in the European market (Ahammed & Yu, 2023). A large proportion of this cost is attributed to fuel costs for necessary heating. While it may be more economical to introduce dissolved CO_2 in a liquid amendment to the root zone, this method is far less efficient and requires extreme care and control of all other factors, including CO_2 concentration, light irradiance level, temperature, pH, and salinity level (Ahammed & Yu, 2023).

Beginning in the 1980s, the U.S. Department of Energy (DOE) began conducting experiments in a variety of biomes around the country to help understand the long-term consequences of anthropogenic CO_2 emissions on plant growth, soils, and the carbon cycle in general. The experiments ranged from small CO_2-enriched chambers over ground cover plants, to CO_2 fumigation of entire stands of open-air hardwood forest. U.S. DOE published the summarized results of the studies in 2020 in the U.S. Department of Energy Free-Air CO_2 Enrichment Experiments: FACE Results, Lessons, and Legacy report (US DOE, 2020). Though the data collected is largely focused on environmental impact, some experiments focused on effects of CO_2-enrichment (550 ppm) on various agriculturally important plants. Table 2 summarizes some crop yield responses observed in the studies (Kimball, 2016; US DOE, 2020).

Table 2: Forage and food crop responses to elevated CO_2 concentration (550 ppm) observed in Free-Air CO_2 Enrichment (FACE) studies.

Plant type and crop	Yield responses
Ryegrass	• 10% increase under sufficient nitrogen and water • no increase under limited nitrogen
Wheat, rice, and barley	• approximately 19% increase under sufficient nitrogen and water • 16% increase under limited nitrogen • 22% increase under limited water
Soybean, pea, peanut, and common bean	• average 16% increase
Sorghum and maize	• slight decrease under sufficient nitrogen and water • 30% increase under limited water conditions

Plant type and crop	**Yield responses**
Potato tuber	approximately 27% increase
Sugar beet	approximately 9% increase under sufficient nitrogen 15% increase under limited nitrogen
Clover	24% increase at both sufficient and limited nitrogen
Cotton (full boll)	38% increase at sufficient nitrogen and water slightly higher than 38% increase under limited water
Cotton (lint only)	approximately 55% increase
Grape	approximately 28% increase
Coffee	approximately 13% increase

All plants do not photosynthesize in the same way and plants utilize CO_2 in different ways to produce their food. Three different types of plants are defined by the three different biochemical pathways responsible for photosynthesis. These three plant types are known as C_3, C_4, and CAM (or crassulacean acid metabolism) and each type primarily fixes CO_2 differently from the air.

C_3 plants are the most common and have the simplest CO_2 fixation process of the three. C_3 plants utilize CO_2 to form two 3-carbon compounds in the chloroplast, hence they are referred to as C_3. C_4 plants incorporate the CO_2 into a 4-carbon compound first, but via a more complex pathway. The 4-carbon compound is enzymatically transformed, and a carboxyl group is released (decarboxylation), liberating CO_2 and leading to localized high concentrations. The plant then utilizes CO_2 in a manner similar to the C_3 pathway.

Unlike with C_3 and C_4 plants, CAM plants uptake gaseous CO_2 predominately at night, closing their stomata during the day to conserve water. This CO_2 is stored in cell vacuoles overnight and converted into a 4-carbon compound that is released the next day. Upon release, the compound is decarboxylated, releasing the CO_2 for use in the same endpoints of the C_3 and C_4 plant pathways.

In the simplest terms, C_4 and CAM plants evolved a method to compartmentalize, concentrate, and store CO_2 for more efficient usage while conserving water. The concentration of CO_2 in C_4 plant tissues (1500 ppm or more) is typically higher than ambient outdoor concentration (350-450 ppm) and higher than that found in C_3 plants (260-290 ppm). In CAM plants, the CO_2 concentration is dramatically higher (5000 ppm or more) than in C_4 plants. From an energy expenditure standpoint, C_4 plants are most efficient at utilizing CO_2, CAM plants are next, and C_3 plants are the least efficient. However, in the midst of increasing atmospheric CO_2 levels, the efficiency of the C_3 pathway is expected to increase with it. Similarly, C_3 plants react more positively to elevated CO_2 concentrations in indoor production facilities.

Examples of the abundant C_3 plant group include the majority of agricultural crops like cereal grains, legumes, trees, and many grasses and leafy greens. C_4 plants are far rarer in agricultural settings, especially greenhouses, and include sugarcane, corn, and sorghum. Rarely, CAM plants are grown agriculturally; most CAM plants are adapted to hot climates and include cacti, pineapples, and orchids.

Of the 150 most cultivated edible agricultural species, only 10 are defined as C_4 plants and two are defined as CAM plants (prickly pear cactus and pineapple). However, despite the fact that few CAM plants are grown agriculturally and the majority (8 of 10) of the most damaging agricultural weeds are C_4 plants, CAM plants actually exist in greater numbers than C_4 plants from a species perspective.

Inset 1: C_3, C_4, and CAM plants and their utilization of CO_2.

Sources: ***(Nobel, 1991; Rogers et al., 1997)***

Dissolved in irrigation water

Crop producers may dissolve CO_2 in irrigation water by injecting it into irrigation lines, though available literature suggests this practice is rarer than atmospheric enrichment and less research has been devoted to it. According to the petition (Eco2Mix, Inc., 2020) and the available literature on the topic, producers may choose to apply CO_2-enriched irrigation water for two primary reasons:

- As a carbon source for photosynthetic processes or for secondary indirect plant/soil amendment effects
- As a pH reducing agent to adjust the growing medium for plants (soil environment or hydroponic system) or to help dissolve limescale in equipment resulting from water with high alkalinity

In a literature comparison, Enoch and Oleson (1993) explored historical studies on CO_2-enriched irrigation water dating back to the 1800s. The authors state that significant research was conducted on the topic of enriching water with CO_2 throughout the 1800s and into the early 20th century, but this work was not consulted in later experiments conducted following World War II and into the latter part of the century. Their paper on the topic was included in the 2020 petition to add CO_2 to the National List. The literature review for this technical report found little published modern research on this topic compared to CO_2's use as an atmospheric amendment for indoor crop production. Enoch and Oleson (1993) reported a 2.9% crop yield increase in their statistical analysis of the available published and unpublished literature regarding irrigating crops with CO_2-enriched water. The authors also reported atmospheric CO_2 in greenhouse tests at slightly elevated levels above control environments, indicating CO_2 escapes from the water (Enoch & Olesen, 1993). The benefits of CO_2-enriched irrigation water may partially just be a result of this unintended atmospheric addition (Cramer et al., 2001; Enoch & Olesen, 1993).

Enoch and Oleson (1993) hypothesize that the modest 2.9% yield increases seen in their literature analysis of studies exploring CO_2-enriched water were not the result of increased carbon uptake through roots. Instead, elevated soil CO_2 derived from enriched water led to positive impacts to nitrifying bacteria, thus resulting in greater available nitrogen for plants (Enoch & Olesen, 1993). Additionally, they hypothesize that the pH reduction resulting from carbonic acid in the CO_2-enriched water leads to greater dissolution of mineral nutrients, freeing them for plant use (Enoch & Olesen, 1993). The authors also found studies indicating that CO_2 may mimic plant hormones like ethylene, but later studies indicate that elevated CO_2 increases or alters plant hormone production rather than acting itself as a hormone (Ahammed & Yu, 2023; Gamage et al., 2018; Seneweera et al., 2003).

Other researchers have explored how nutrient availability is affected by pH and alkalinity reduction of irrigation water. Albano et al. (2017) observed an increase in concentrations of soil dissolved calcium, manganese, and zinc when irrigating with alkaline well water adjusted with sulfuric acid to pH 6.4, and further increases in plant available nutrients after adjustment to pH 4.8. Morgan and Graham (2019) reported the same dissolved nutrient increases, along with magnesium, in soil adjusted to pH below 6 using sulfuric acid. Xiang et al. (2009) reported an increase in rice leaf concentrations of zinc, phosphorus, potassium, sulfur, aluminum, and copper after soil acidification.

Compared to the available research into the pH adjustment of irrigation water with strong mineral acids like sulfuric, nitric, and phosphoric acids, studies involving CO_2 injection as an acidifier are rare (Branco et al., 2007; Lampreave et al., 2022). The majority of the literature dates back to the 1980s-90s; more modern agricultural science journals contain limited data. In a recent study, Lampreave et al. (2022) showed that irrigating grapes grown in calcareous (alkaline) soils with water containing 400 ppm CO_2 improved the availability of nutrients and reduced the incidence of chlorosis due to iron deficiency. The authors suggest this could reduce the use of synthetic iron chelate inputs like iron EDTA in European vineyards (Lampreave et al., 2022).

Two relatively modern studies were located from Brazil that required translation from the original Portuguese. Branco et al. (2007) found that CO_2-enriched irrigation water does not affect the absorption of nitrogen by tomatoes; Kano et al. (2013) reported greater concentrations of manganese and zinc in plant tissues when irrigating melon with CO_2-enriched water. Mauney and Hendrix (1988) reported the same zinc and manganese uptake increase when using CO_2-enriched water on cotton in an older study.[2] Other studies from the same general time period indicate no plant tissue nutrient concentration differences following irrigation with CO_2-enriched water in cucumber and tomato (Hartz & Holt, 1991) or in bell pepper (Storlie & Heckman, 1996).

The concentration of CO_2 in the root zone of plants is already generally over 10 times greater than in the atmosphere due to plant respiration and microbiological activity (Ahammed & Yu, 2023; Shimono et al.,

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[2] The authors also demonstrated that none of the carbon fixed by photosynthesis came from the CO_2-enriched irrigation water treatment using carbon isotope analysis methods (Mauney & Hendrix, 1988).

2019). The proportion of CO_2 absorbed through roots for use in photosynthetic processes is less than 1% and CO_2-enriched water is generally impractical for this use (Cramer et al., 2001; Enoch & Olesen, 1993; Ford et al., 2007; Mauney & Hendrix, 1988). Cramer et al. (2001) tested CO_2-enriched water as well as gaseous fumigation of CO_2 to the root zone of greenhouse tomatoes, and determined that any quality or yield increases were not economically significant.

CO_2 may also be used as an alternative to citric acid or sulfur burners to prevent clogging in irrigation lines due to limescale deposition or algae, particularly in drip emitters (NOSB, 2022). Acidification of irrigation water can prevent mineral or algal buildup in equipment, and this use has already been discussed by the NOSB and recommended as an allowed use in organic production (NOSB, 2022).

Other uses

CO_2 may be used in insecticidal post-harvest applications in controlled atmosphere storage of agricultural commodities and is exempt from the requirement of a tolerance by the EPA at 40 CFR 180.1049 for this use.

CO_2 has numerous non-agricultural uses including, but not limited to (Grand View Research, 2022; Patnaik, 2003):

- Beverage carbonation.
- In food packaging as air replacement.
- Food chilling and freezing.
- Various medical and surgical applications, including pharmaceutical production.
- Chemical, fuel, and building material manufacture.
- Crude oil recovery processes.
- In aerosol propellants.
- In fire control products.
- As shielding gas for welding.
- As an extractant of organic compounds (when used as a supercritical fluid).

The chemical industry uses a significant amount of CO_2 (about 200 million metric tons, MMT, per year) as a precursor in the production of fertilizers, carbonate chemicals, fuels, and medicines, but this amount is dwarfed by total human emissions into the atmosphere (nearly 38 billion metric tons per year and increasing) (Aresta et al., 2013; Crippa et al., 2022). Significant research is being conducted to repurpose emitted CO_2 (spent carbon) into products (working carbon) (Aresta et al., 2013).

<u>Approved Legal Uses of the Substance:</u>

Synthetic CO_2 is included on the USDA NOP National List of Allowed and Prohibited Substances at 7 CFR 205.605(b)(10) without limiting annotation as an allowed ingredient in processed products labeled as “organic” or “made with organic (specified ingredients or food group(s)).”

CO_2 is exempt from the requirement of a tolerance when used as an insecticide after harvest in modified atmospheres for stored insect control on food commodities at 40 CFR 180.1049. CO_2 is also exempt from the requirement of a tolerance when used as an inert propellant in pre- or post-harvest pesticide formulations, and when applied to animals in pesticide formulations at 40 CFR 180.910 and § 180.930, respectively. It is classified as List 4A, a minimal risk inert ingredient, in the obsolete 2004 EPA List 4 (US EPA, 2004), permitting it as an inert ingredient in pesticides used in organic crop and livestock production by 7 CFR 205.601(m)(1) and § 205.603(e)(1). EPA-registered labels describe many uses, including as an insect fumigant for trucks, trailers, silos, ships, and railroad cars; for invasive carp deterrence or for injection under ice in waterways as a lethal control for nuisance species; as an insecticide, acaricide, and rodenticide for burrowing pests in agricultural environments; and for indoor residential insect control (bed bugs and cockroaches) (EPA, 2016).

CO_2 is classified as "Generally Recognized as Safe" (GRAS) by the U.S. Food and Drug Administration (FDA) at 21 CFR 184.1240, with no limitations for food use other than good manufacturing practices as a leavening agent, processing aid, propellant, and aerating agent.

Action of the Substance:

CO_2 affects plant growth in myriad ways. In the most general terms, CO_2 increases photosynthesis rates, thereby increasing growth and yield. It also stimulates root growth and earlier flowering, reduces bud abortion, improves stem strength, increases flower size, alters nutrient uptake rates, affects the colonization of symbiotic and pathogenic microbial species on plant roots, and alters overall plant shape (Albano et al., 2017; Gamage et al., 2018; Ontario Ministry of Agriculture, Food and Rural Affairs, 2002; Rogers et al., 1997; Seneweera et al., 2003).

Significant research is underway to predict how plants will react to increasing atmospheric CO_2 as a result of anthropogenic emissions. See the comprehensive reference list contained in the U.S. DOE Free-Air CO_2 Enrichment report for further information about completed or ongoing studies (US DOE, 2020). While these data are only indirectly related to purposeful air enrichment in indoor production facilities, the research can be useful here to describe the mode of action of CO_2 in plant growth.

Role in photosynthesis

Photosynthesis is catalyzed by the enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase, typically referred to by the abbreviation "Rubisco" (Gamage et al., 2018). Rubisco reacts with CO_2 or oxygen (O_2) depending on the ratio between the two gases; at higher CO_2 levels, photosynthesis is favored and at higher O_2 levels, photorespiration is favored. Photorespiration essentially wastes the potential energy involved in the photosynthesis process. At atmospheric CO_2 levels, the efficiency of carboxylation by Rubisco (the mechanism by which plants convert energy through photosynthesis) is low. Increasing the CO_2 concentration thereby promotes the efficiency of photosynthesis and the ability of plants to convert light energy into chemical energy. Photosynthesis approximately doubles when CO_2 concentrations are doubled (Gamage et al., 2018).

Plants are always in a CO_2-deficient state without supplementation because they absorb more CO_2 during photosynthesis than they emit during photorespiration (Poudel & Dunn, 2017). Photosynthetic processes do not infinitely increase with increasing CO_2 levels, however. Since photosynthesis requires CO_2 and light to proceed, plants may reach a CO_2 saturation point where they cannot photosynthesize any more under given light conditions (Poudel & Dunn, 2017). Plants may also adapt to elevated CO_2 levels in a phenomenon known as "photosynthetic acclimation," during which the positive response to elevated CO_2 becomes less pronounced over time (Ahammed & Yu, 2023; Gamage et al., 2018). Photosynthetic acclimation is a complex system that is not fully resolved, but is likely the result of a nitrogen assimilation suppression mechanism at elevated CO_2 levels, and is apparent in determinate plant varieties (Ahammed & Yu, 2023; Gamage et al., 2018). CO_2 also induces toxicity in plants at concentrations above approximately 1,800 ppm (Poudel & Dunn, 2017).

Effects on other cellular processes

Stomata, the pores in plant tissues that regulate the exchange of gases between the atmosphere and plant cells, are affected by CO_2 concentration (Ahammed & Yu, 2023; Gamage et al., 2018; Z. Xu et al., 2016). In general, elevated CO_2 levels lower the stomatal conductance, or the rate at which gases are exchanged, thereby reducing the rate at which CO_2 is absorbed (Z. Xu et al., 2016). This works against the photosynthetic increase described above. However, the reduction in stomatal conductance also leads to conservation of water in plant tissue, reducing water loss due to evapotranspiration and benefiting plant growth through increased water use efficiency (Rogers et al., 1997; Z. Xu et al., 2016). As a result, CO_2 enrichment may help mitigate drought conditions or minimize their effects (Ahammed & Yu, 2023; US DOE, 2020).

The reduction in evapotranspiration also works to reduce the cooling effect on leaves resulting from evaporation, leading to local temperature increases near plant canopies (Kimball, 2016). The processes by which stomata are affected by elevated CO_2 are numerous and biologically complex, involving gene expression, ion concentration in various plant cell types, hormonal alterations, enzyme activation, and protein repression (Ahammed & Yu, 2023; Gamage et al., 2018; Z. Xu et al., 2016).

Increased photosynthesis leads to increased sugar production and increased transport of sugars for the development of new tissue (Gamage et al., 2018). Certain enzymes that regulate sugar production and transport also increase under elevated CO_2 levels, which prevents photosynthesis-inhibiting starches from building up in leaf tissue. The same increase in carbohydrate sugar production leads to lower nitrogen concentration in some plant parts. While the precise mechanism at work here is not fully understood, the most likely explanation is a reduction in nitrate assimilation, or the process by which plants convert nitrate into ammonia and ultimately organic nitrogen compounds. Plants under elevated CO_2 levels exhibit increased carbon to nitrogen ratio in tissue as a result (Gamage et al., 2018).

Increased carbon to nitrogen ratio in elevated CO_2 environments may explain the observed trend of young plants undergoing a burst of rapid growth, followed by slower growth after becoming established (Gamage et al., 2018). Due to rapid growth improvements following CO_2 supplementation, plants utilize a larger volume of nutrients and may exhibit deficiencies, particularly of nitrogen, or micronutrients like zinc, iron, or boron (Gamage et al., 2018; Poudel & Dunn, 2017). Soil fertilization may then be required to sustain increased growth rates initiated by CO_2 supplementation (Poudel & Dunn, 2017).

Elevated CO_2 results in a general increase in cell wall division and a shortening of the overall duration of cell division, enhancing early growth (Gamage et al., 2018). The genes encoding for cell wall loosening enzymes are up-regulated, allowing more rapid tissue growth (Gamage et al., 2018). Plant hormones like ethylene, auxins, gibberellins, and cytokinins also appear to increase, contributing to accelerated cell division, bud development, and earlier flowering (Gamage et al., 2018; Seneweera et al., 2003). These growth pattern effects combine to alter plant morphology under elevated CO_2 (Gamage et al., 2018; Seneweera et al., 2003). Leaf number, thickness, area, and overall plant canopy size often increase (Gamage et al., 2018). One study found the number of rice grains per head substantially increased under elevated CO_2 (Seneweera et al., 2003). The report also noted observations of increased branching in trees (Seneweera et al., 2003).

See Figures 4 and 5 for diagrammatical summaries of plant growth effects resulting from elevated atmospheric CO_2 levels.

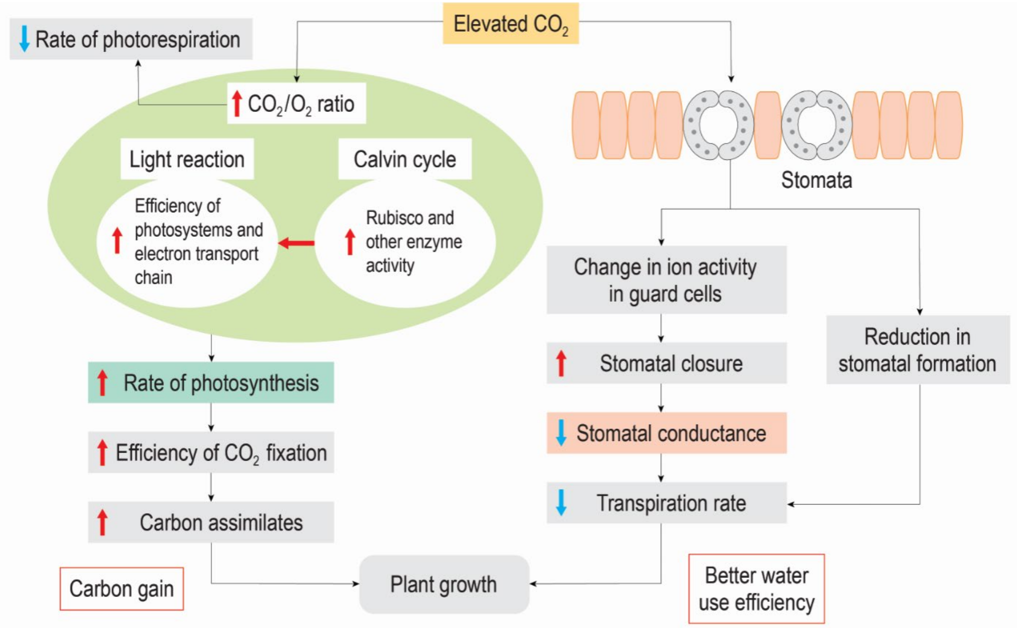

Figure 4: Effect of elevated CO_2 on photosynthesis and stomatal conductance on plant growth. The green oval represents a chloroplast, and the orange rectangles represent guard cells. Adapted from Gamage et al. (2018).

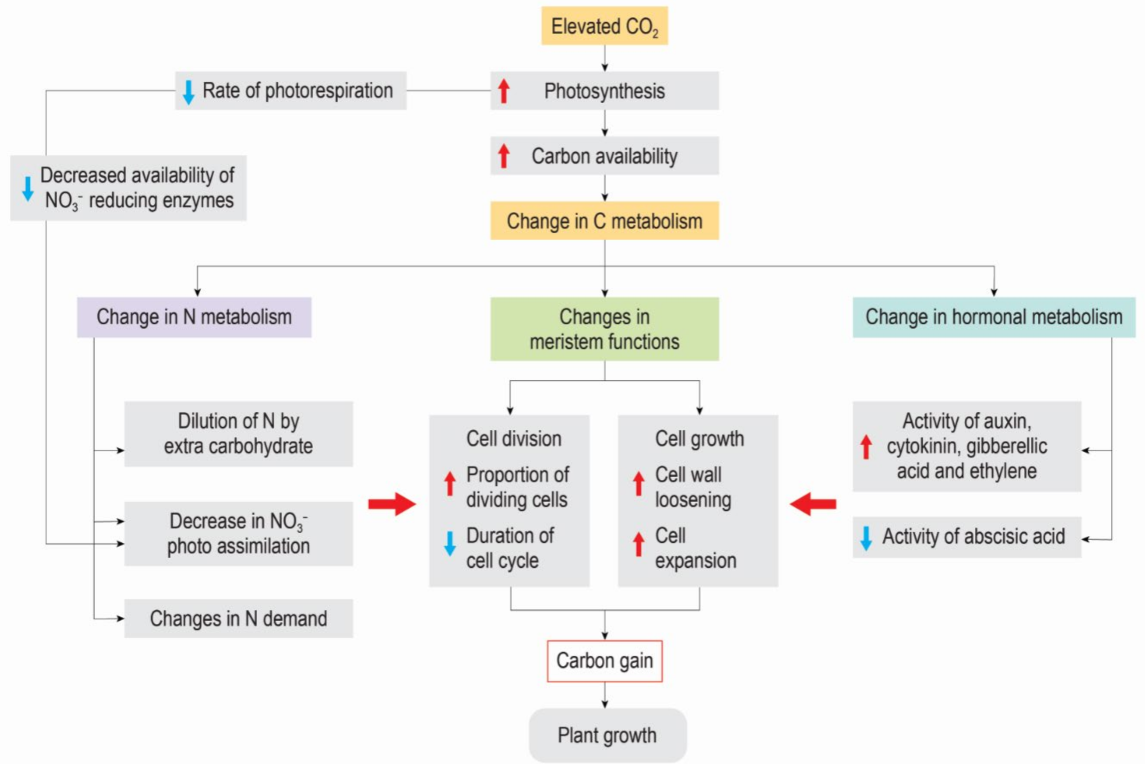

Figure 5: Effect of elevated CO_2 on other cellular processes and plant growth. Adapted from Gamage et al. (2018).

As discussed under *Specific Uses of the Substance* above, CO_2-enriched irrigation water may also be applied, and the beneficial effects to plant growth are largely unrelated to photosynthesis. The small percentage (<1%) of the total CO_2 absorbed by roots and ultimately used in photosynthetic processes may actually be a secondary indirect CO_2 utilization (Shimono et al., 2019). At low soil pH (5.6-6.1), CO_2 may move into the plant xylem, but it is rapidly respired back to the atmosphere, where some may actually be reabsorbed for use in photosynthesis (Ford et al., 2007; Shimono et al., 2019). However, plant roots also have the ability to absorb bicarbonate ion, HCO_3^-, through their roots and use it similarly to CO_2 (He et al., 2007). Bicarbonate ion is more favored between a pH range of 6.36-10.33. The pH of the system is the determining factor in the predominant available carbonate type, and questions remain about how this complex system may affect plant growth (Ahammed & Yu, 2023).

The equilibria between CO_2, carbonate ion, bicarbonate ion, and carbonic acid in a liquid continually shift depending on environmental factors (Adamczyk et al., 2009; Drever, 1997). At normal atmospheric temperatures and pressures, a solution of these dissolved ions reaches a slightly acidic pH of approximately 5.7. This is kept mostly stable (buffered) by equilibrium forces even after further acid addition, unlike with strong mineral acids (Adamczyk et al., 2009). See *Properties of the Substance* above for a more detailed description of the complex carbonic acid cycle.

As described above, plants may experience a lull in photosynthesis at midday, when both temperature and light are at a maximum, as a result of stomata closure. He et al. (2007) showed that uptake of root zone CO_2 or bicarbonate ion may activate in lettuce during this lull, further illustrating the complexity of all of the factors that may contribute to plant growth in varying CO_2 environments.

<u>Combinations of the Substance:</u>

CO_2 tends to be a by-product of other processes rather than a component. Composting, fermentation, digestion, and combustion all result in the emission of CO_2 rather than utilization. As a precursor in the production of other substances, CO_2 is used in too many capacities to list here.

As a stable compound, inert stabilizers, solvents, or preservatives are not needed to facilitate CO_2 storage in gaseous or cryogenic liquid form. Bulk CO_2 storage tanks are typically constructed of steel and insulated with polyurethane foam behind a vapor barrier (Air Products and Chemicals, 2014).

CO_2 is used in the production of carbonate and bicarbonate salts, many of which appear on the National List. The manufacturing processes for various synthetic carbonates appearing on the National List are summarized below (NOP, 2014a, 2023a; Patnaik, 2003):

- Sodium carbonate peroxyhydrate at 7 CFR 205.601(a)(8) for use as an algicide, disinfectant, and sanitizer, including irrigation system cleaning systems: produced by combining sodium carbonate with hydrogen peroxide. The reactant sodium carbonate can be prepared using the Solvay Process, in which calcium carbonate is thermally decomposed, liberating CO_2, which is subsequently reacted with ammonia and sodium chloride to form sodium bicarbonate. Ultimately, sodium bicarbonate is calcined to produce sodium carbonate.
- Ammonium carbonate at 7 CFR 205.601(e)(1) for use as an insecticide (including acaricides or mite control) and at 7 CFR 205.605(b)(4) for use as a leavening agent: produced by passing CO_2 gas through dissolved ammonia.
- Potassium bicarbonate at 7 CFR 205.601(i)(9) for use as a plant disease control: produced by passing CO_2 gas through a solution of concentrated potassium carbonate.
- Carbonates of zinc, copper, iron, manganese, molybdenum, selenium, and cobalt at 7 CFR 205.601(j)(7)(ii) for use as plant micronutrients: often produced by reacting sodium carbonate (itself prepared with CO_2) with other metal salts.
- Ammonium bicarbonate at 7 CFR 205.605(b)(5) for use as a leavening agent: produced by passing CO_2 gas through dissolved ammonia.
- Potassium carbonate at 7 CFR 205.605(b)(24): produced by passing CO_2 gas through a solution of potassium hydroxide.

Only one of the EPA registered CO_2 products on the Pesticide Product Label System (PPLS) website explicitly lists another ingredient. The product, Propoxide 892 (EPA reg. no. 47870-3), lists, in addition to CO_2, propylene oxide as an active ingredient (EPA, 2016). It is not feasible or legal for anyone to use this fumigant product as a plant or soil amendment because propylene oxide is an acute toxin.

Status

Historic Use:

Commercial technology has existed since at least the late 1980's for CO_2-enrichment in irrigation water (Kuckens, 1989); however, only a small number of companies produce the equipment (such as Carborain from Technica Entwicklungsgesellschaft mbH & Co. KG; CO_2 GRO Inc.; and Eco2Mix). We found limited literature describing its use.

As a stand-alone gas, it is used in conventional greenhouse production (Esmeijer, 1999).

Irrigation water use

According to Enoch & Oleson (1993), the first experiments testing the effects of CO_2-enriched water on plant development was in 1866 by Birner & Lucanus. In their review, Enoch & Oleson describe dozens of papers, covering roughly 125 years of research into the effects and possible mechanisms of CO_2-enriched irrigation water affecting plant growth. While we were able to find research papers about the *experimental* use of CO_2-enriched water, we found no non-promotional articles documenting the practice of enriching irrigation water with CO_2, such as by university extension centers.

We identified three companies that produced CO_2-enriched irrigation water equipment. All three were marketed differently.

The oldest product found, Carborain, was granted a U.S. patent in 1989 (Kuckens, 1989). Currently, marketing for this product primarily focuses on preventing calcium scale deposits on leaves and fruit, but also makes the following statements (Technica Entwicklungsgesellschaft, 2014):

- prevents limescale on irrigation equipment.
- safe for plants due to CO_2 creating a weak acid.
- improves nutrient absorption.
- functions as an adjuvant for plant protective agents.

Marketing for CO2 GRO Inc. equipment indicates that it is intended as an alternative to CO_2 gas enrichment in protected (indoor) production (CO2 GRO Inc., n.d.). Additionally, they indicate the CO_2 enriched water produced by their products serves as a plant protection agent (CO2 GRO Inc., n.d.).

Eco2Mix (a product made by the petitioner) is marketed for water pH control, replacing the use of mineral acids (Eco2Mix, Inc., n.d.).

Gaseous greenhouse use

Researchers have investigated the effects of CO_2 on plant growth in closed containers and greenhouses since at least 1902 (Wittwer & Robb, 1964). Despite the existence of studies demonstrating large increases in yields (such as doubling and tripling yield of tomatoes and cucumbers), CO_2 enrichment in greenhouses was still not widely adopted by the mid-1960s (Wittwer & Robb, 1964). However, by the early 1970s, greenhouse enrichment had begun to be used by commercial growers (Enoch et al., 1976; Poudel & Dunn, 2017; Slack & Calvert, 1972). In the mid-1980s, CO_2 enrichment in greenhouses was common (Schapendonk & Gaastra, 1984; Tjosvold, 2018). According to Esmeijer (1999), in 1995, 80% of greenhouse horticulture businesses used supplemental CO_2.[3]

Organic Foods Production Act (OFPA), USDA Final Rule:

CO_2 is not mentioned in OFPA.

USDA organic regulations do not currently allow producers to enrich (fertilize) crops with synthetic CO_2. Only nonsynthetic sources of CO_2 are currently allowed for CO_2 enrichment (such as from composted straw; see *Evaluation Question #12*).

CO_2 can be used as an inert ingredient in pesticide formulations per 7 CFR 205.601(m). This regulation allows materials (such as CO_2) that appear on 2004 EPA List 4 to be used as inert ingredients.

In production and handling, CO_2 can be used as a synthetic, nonagricultural ingredient, in both organic and made with organic products per 7 CFR 205.605(b)(10). The allowance at § 205.605 includes uses as a post-harvest substance in the handling of raw agricultural products and facility pest management, as described in Guidance NOP 5023 (NOP, 2016a).

International Acceptance:

CO_2 is most commonly allowed as a pest control material, as a food additive, and for atmospheric modification in storage facilities under international standards (detailed below). Canadian standards allow its use in soil and greenhouse applications as well.

Canadian General Standards Board Permitted Substances List

CO_2 is allowed in crop production as well as processing and handling under the Canadian Organic Standards per CAN/CGSB 32.311-2020.

In organic crop production, it is allowed for enrichment, storage treatment, and pest control per the Permitted Substances List (PSL) Table 4.2.

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[3] While ambiguous, we assume that Esmeijer was speaking about greenhouse production in the Netherlands, not globally.

CO_2 is allowed in organic processing and handling for a variety of uses:

- as a food additive with the following restriction: *carbonation of wine and mead is prohibited* (PSL Table 6.3).
- as a processing aid (PSL Table 6.5).
- as a food-grade cleaner, disinfectant, and sanitizer, permitted without a mandatory removal event (PSL Table 7.3).
- as a facility pest management substance with the following restriction: *for controlled atmosphere storage and for storage pest control* (PSL Table 8.2).
- as a post-harvest handling substance with the following restriction: *for controlled atmosphere storage* (PSL Table 8.3).

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)

CO_2 is allowed in crop production as well as processing and handling under the guidelines in CODEX GL 32-1999.

As a pesticide in organic crop production, CO_2 is allowed with the following restriction: *need recognized by certification body or authority* (Annex 2 Table 2).

In organic processing and handling, CO_2 (INS 290) is allowed as a handling ingredient and processing aid for food of plant or animal origin (Annex 2, Table 3 & Table 4).

European Union (EU) Regulation, EU No. 2018/848 and 2021/1165

CO_2 is allowed for a variety of uses in crop production as well as processing and handling under the European Union organic standards per EC No. 2021/1165:

- as a plant protectant in organic crop production (Annex I, 4, 225A).
- as a food additive and processing aid:
  - in products of plant and animal origin (Annex V, Part A, Section A1 & A2).
  - for pH regulation in yeast production (Annex V, Part C).
  - for "the production and conservation of organic grapevine products of the wine sector" (Annex V, Part D).

Japan Agricultural Standard (JAS) for Organic Production

Under the Japanese Agricultural Standards, CO_2 is allowed in crop production, processing and handling, feed production, and livestock production.

As a fumigant and post-harvest applied substance, CO_2 is allowed per the Japanese Agricultural Standard for Organic Products of Plant Origin per Public Notice of the Ministry of Agriculture, Forestry and Fisheries No. 1605 of October 27, 2005:

- As a fumigant, with the following restriction: *Limited to the use in storage facilities* (Appended Table 2).
- "For maintenance and improvement of the quality of plant products" (Appended Table 5).

As a food additive and facility pest management substance in food production, CO_2 is allowed per the Japanese Agricultural Standard for Organic Processed Foods per Joint Public Notice No. 18 of the Ministry of Finance and the Ministry of Agriculture, Forestry and Fisheries of September 1, 2022, Appended Table 1 & 2.

Similarly, CO_2 is allowed as a facility pest management substance per the Japanese Agricultural Standards for Organic Feed per Ministry of Agriculture, Forestry and Fisheries Notification No. 1607 of October 27, 2005, Appended Table 2.

CO_2 is allowed in organic livestock production as a fumigant in storage facilities per the Japanese Agricultural Standard for Organic Livestock Products per Public Notice of the Ministry of Agriculture, Forestry and Fisheries No. 1608 of October 27, 2005, Appended Table 2.

IFOAM – Organics International

CO_2 is allowed in organic crop production as well as processing and handling under the IFOAM Norms.

As a crop protectant and growth regulator in organic crop production, CO_2 is allowed with the following restriction: *shall not be the result of burning fuel solely to produce carbon dioxide; allowed only as a by-product of other processes* (IFOAM, Appendix 3).

As a food additive and production aid (including for use in the production of flavoring agents), CO_2 is allowed per IFOAM Appendix 4–Table 1.

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

<u>Evaluation Question #1:</u> Indicate which category in OFPA that the substance falls under: (A) Does the substance contain an active ingredient in any of the following categories: copper and sulfur compounds, toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed, vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?

CO_2 does not contain an active ingredient in any of the categories listed in (A) above. However, the substance is listed on 2004 EPA List 4A (US EPA, 2015), and was not revoked under NOP 5008, *Guidance: Reassessed Inert Ingredients* (NOP, 2011). As an insecticide, "carbon dioxide is exempted from the requirement of a tolerance when used after harvest in modified atmospheres for stored insect control on food commodities" per 40 CFR 180.1049.

<u>Evaluation Question #2:</u> Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Several different methods are utilized to manufacture or capture CO_2 since it is the end result of so many chemical and biological processes. The most prominent processes used are fuel combustion, as a by-product of hydrogen and ammonia production, and fermentation (Price, 2015).

Combustion of hydrocarbon fuel and chemical decomposition

Combustion-derived CO_2 is manufactured both specifically for capture and as a recovered by-product of other industrial processes including power generation, steam boilers, cement manufacture, and lime kilns (Chapel & Mariz, 1999; Steen, 2006). This is known as flue gas recovery. The majority of flue gas recovery is the result of natural gas methane combustion, but some comes from the combustion of fuel oils or coal (Chapel & Mariz, 1999; Steen, 2006). Monoethanolamine (MEA) solutions typically absorb and capture the CO_2 for recovery in scrubbers (Chapel & Mariz, 1999).

The combustion of natural gas results in CO_2 and water vapor, represented in Equation 1 (Patnaik, 2003):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$

Calcium oxide is one of the principal components of cement. The calcination of calcium carbonate limestone in kilns results in calcium oxide lime and CO_2, represented by Equation 2, which spontaneously occurs at temperatures above approximately 900°C (Kumar et al., 2007):

$$CaCO_3 + heat \rightarrow CaO + CO_2 \tag{2}$$

Lime kilns use fossil fuels to reach calcination temperatures. CO_2 results from the combustion of fuels as well as the calcium carbonate decomposition reaction.

Synthesis gas

Large volumes of CO_2 are produced as a by-product of synthesis gas (syngas) production (El-Nagar & Ghanem, 2019; Schneider et al., 2020). Syngas is used as a raw material in many chemical and fuel production processes as an alternative to directly refined compounds from crude oil, and can be prepared from biomass, carbon-based wastes, or fossil fuels (El-Nagar & Ghanem, 2019). In general, carbon-based feedstocks are "gasified" by exposure to heat without combustion in the presence of oxygen or steam, resulting in a mixture of different gases including carbon monoxide, hydrogen, CO_2, water, and methane (El-Nagar & Ghanem, 2019). The generalized reaction is (El-Nagar & Ghanem, 2019):

$$Biomass + O_2 \rightarrow CO + H_2 + CO_2 + H_2O + CH_4 \tag{3}$$

Syngas, a combustible mixture of different gases, may also be prepared from natural gas (Schneider et al., 2020). When exposed to pressurized steam and in contact with a catalyst, a hydrogen and carbon monoxide mixture (with lesser amounts of carbon dioxide) forms in a process known as steam reforming represented by Equations 4-6 (Anzelmo et al., 2018; Schneider et al., 2020):

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{4}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{5}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{6}$$

Since natural gas is mostly methane, Equations 4 and 5 produce the bulk of the hydrogen, the desired material in natural gas steam reforming, with CO_2 as a by-product (Anzelmo et al., 2018). The carbon monoxide is used downstream to produce more hydrogen and CO_2 in Equation 6 (Anzelmo et al., 2018).

Approximately half of the purified hydrogen resulting from syngas production is used in the Haber-Bosch process to manufacture ammonia through the following reaction (El-Nagar & Ghanem, 2019; Kyriakou et al., 2017; Schneider et al., 2020):

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{7}$$

The nitrogen in Equation 7 comes from the atmosphere and the hydrogen primarily from syngas (Patnaik, 2003; Van der Ham et al., 2014). Approximately 1.4% of all CO_2 emissions on a global scale result from this overall reaction system (Capdevila-Cortada, 2019), which also accounts for 1-1.4% of all energy usage on Earth (Capdevila-Cortada, 2019; Van der Ham et al., 2014).[4]

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[4] The enormous energy expenditure of the Haber-Bosch process is the result of the high temperatures and pressures required to break the triple chemical bond in atmospheric diatomic nitrogen, along with the sheer scale of ammonia produced with this method (Van der Ham et al., 2014).

Fermentation

CO_2 may be produced as a by-product of carbohydrate fermentation by yeast in the production of ethanol or alcoholic beverages (Patnaik, 2003; Steen, 2006). Equation 8 represents a simplified chemical reaction by which yeast consume glucose (or other fermentable sugars) yielding CO_2 gas and ethyl alcohol (ethanol):

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH \tag{8}$$

CO_2 is often suspended in foam during fermentation and must be passed through a separator (Steen, 2006). The gas then enters a scrubber to remove alcohols and ketones, resulting in CO_2 with a purity as high as 99.998% (Steen, 2006).

Natural CO_2 wells

During natural gas and oil exploration, deposits of nearly pure (98%) CO_2 are often encountered that may be exploited (Allis et al., 2001). The process for extraction is generally similar to natural gas extraction, achieved by drilling and pumping to the surface (Allis et al., 2001). In the United States, the majority of economically viable natural CO_2 wells are associated with already existing petroleum or methane operations in Colorado, Wyoming, New Mexico, Texas, and Utah, but one of the most substantial sources in Mississippi primarily produces CO_2 alone (Eppink et al., 2014).

Onsite production

Producers may initiate chemical reactions between acids and carbonate salts onsite to generate CO_2 (Poudel & Dunn, 2017). Dripping acetic acid solutions onto baking soda or another carbonate material, for example, will produce CO_2 and water in a chemical decomposition reaction. In order to produce enough CO_2 to have an effect on plant growth, large amounts of reactants are required and the CO_2 concentration is exceedingly difficult to control, so this is not typically a practical method for growers (Poudel & Dunn, 2017).

Processing and transport

Depending on the source, CO_2 may require different levels of purification and processing (Häring (Ed.), 2007). Typically, CO_2 derived from hydrogen generation in syngas production, natural gas refining, acid neutralization and brewery operations require the least amount of secondary processing. CO_2 derived from flue gases, lime calcination kilns, and cement furnaces require significant purification steps. Impurities in the latter are numerous, but notable examples are highly toxic nitrogen and sulfur oxides, hydrogen cyanide, mercury, and heavy metal oxides (Häring (Ed.), 2007).

For low purity CO_2, adsorption purification is typically required to strip CO_2 from exhaust gases (Häring (Ed.), 2007). The gas mixture resulting from combustion enters a stripper consisting of a column most commonly filled with an amine solvent and water. MEA is a common choice, particularly for flue gas derived from fuel combustion or lime kilns, but certain alcohols may also be used. Gas enters the bottom of the stripper and CO_2 is absorbed by the solvent, forming a chemical bond. One example of this reaction (9), using MEA, appears here (Häring (Ed.), 2007):

$$C_2H_5ONH_2 + H_2O + CO_2 \leftrightarrow C_2H_5ONH_3^+ + HCO_3^- \tag{9}$$

Fresh solvent continuously enters the stripper from the top. The CO_2-enriched liquid is pumped from the bottom to the top of the stripper and heated by further solvent introduced below (Häring (Ed.), 2007). At higher temperatures, the temporary chemical bond breaks and CO_2 is liberated from the solvent. Solvent steam is recondensed by cool water for reuse (Häring (Ed.), 2007).

After collection, CO_2 is typically compressed, purified further using activated carbon beds, then cooled by water and refrigerants (Häring (Ed.), 2007). Residual water and other impurities may be removed by molecular sieves like zeolite or clay matrices, or by silica gel. Finally, the purified CO_2 gas is liquefied against evaporative refrigerants and stored as a liquid in pressurized refrigeration units. Various chemical and physical methods may be used for final purification in order to meet specific requirements for different industries (Häring (Ed.), 2007).

CO_2 is usually shipped to distributors on tanker trucks (Steen, 2006). In large-scale agricultural operations, CO_2 is often transferred directly from trucks to storage tanks on farms, but small-scale operations may purchase 20 to 50 pound tanks directly from distributors (Poudel & Dunn, 2017). In the case of gas derived from natural wells, the majority is transported by gas pipeline for use in oil recovery operations (Allis et al., 2001).

CO_2 may also be prepared as dry ice (Häring (Ed.), 2007). When pressurized CO_2 is released from its container into the atmosphere, a portion of the gas solidifies into “snow” through a process known as adiabatic cooling (Häring (Ed.), 2007). The snow can then be compressed into ice blocks or pellets and shipped in insulated boxes (Häring (Ed.), 2007). Some naturally high purity, well-derived CO_2 may be frozen into dry ice for transport (Allis et al., 2001). Dry ice gradually sublimes back into gas (Häring (Ed.), 2007).

Small-scale crop producers may use dry ice blocks for atmospheric enrichment rather than other CO_2 supplementation methods because it is inexpensive, it very slightly reduces the temperature of greenhouses, and is readily available (Poudel & Dunn, 2017). A one-pound dry ice block can supply CO_2 to a 100 m^2 area for a full day, for just a few dollars. However, the concentration of CO_2 is difficult to control (Poudel & Dunn, 2017).

Market statistics

CO_2 from ethanol production is the largest share of the CO_2 consumer market by dollar value, making up 33% of total sales revenue, closely followed by CO_2 from hydrogen production (including steam reforming) (Grand View Research, 2022). From an economic perspective, the market value of CO_2 used for agricultural applications is a small fraction compared to the food, medical, oil and gas, and rubber industries, which were responsible for approximately 80% of all market value of CO_2 in 2021. Of the remaining 20%, slightly less than half was spent on fire-fighting applications, with the remainder only classified as “other” in the market data obtained for this report (Grand View Research, 2022).

The market value for CO_2 does not necessarily correspond to the total usage of different sources. The International Energy Agency (IEA) (2019) state that the fertilizer industry uses 56% of all CO_2 produced in the manufacture of urea. Approximately 33% is used in the oil and gas industry, while the food and beverage industry uses just 6% (IEA, 2019). The remaining 4% is for “Other” uses, presumably including direct agricultural applications not related to fertilizer production. The disconnect between market value and total usage seems to be the result of regional and industry differences, and prices are often determined through market negotiations. According to IEA (2019), the price of one ton of CO_2 can range from 3 dollars per ton for CO_2 sourced from ammonia production waste under long-term sales contracts to greater than 400 dollars per ton for high-purity CO_2 used in certain specialty applications. There is also a seasonal component since fertilizer manufacturing is tied to the spring planting season, and beverage manufacturing increases in summer (IEA, 2019).

Given the ubiquity of excess CO_2 in the atmosphere and as a by-product of so many industrial processes, it is ironic that shortages of the gas became apparent in 2022 (Bettenhausen, 2022; Chappell, 2022; Popli, 2022). Due to necessary maintenance at ammonia plants, the shutdown of ethanol plants, contamination at a natural high-producing CO_2 well, and driver shortages, brewers and other food processing industries had difficulty sourcing CO_2. Some of the shortage was attributed to COVID-19 pandemic supply chain challenges with some level of resolution expected soon (Bettenhausen, 2022; Chappell, 2022; Popli, 2022).

<u>Evaluation Question #3:</u> Discuss whether the petitioned substance is formulated or manufactured by a chemical process or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)).
Although CO_2 production is ultimately a physical process of separating it from other substances, thus resulting in a nonsynthetic outcome when consulting NOP 5033-1: *Guidance: Decision Tree for Classification of Materials as Synthetic or Nonsynthetic* (2016b), the processes to manufacture the raw materials used in CO_2 production are often classified as synthetic. CO_2 derived from the combustion of fossil fuels is produced by burning biological matter (or rather fossilized biological matter), but the process for refining raw hydrocarbons into useful fuels like fuel oil, natural gas, or alkane fuels is typically considered to be a synthetic process. It is possible to produce CO_2 naturally (non-synthetically) using fermentation processes or extraction from natural CO_2 wells, but the prevalence and availability of different CO_2 production streams is difficult to define, is determined by regional industry and transport infrastructure, and by the nature of the commodified raw chemical material market because many streams may be combined. However, Eppink et al. (2014) state that 97% of all CO_2 directly extracted from natural wells is used in the process of enhanced oil recovery (EOR), in which CO_2 is injected into oil deposits to push oil to the wellbore.

Synthetic sources: hydrocarbon fuel combustion, syngas production, and chemical decomposition
Natural gas is extracted from oil wells (associated gas) or from gas wells (non-associated gas). Before entering a pipeline, the gas must be treated to meet certain purity requirements (Eser, 2020a). A mixture of temperature and pressure control separates liquids from gases; liquids are sent to an oil refinery and gas is further treated. Hydrogen sulfide and CO_2 are separated by treatment with synthetic amines, and the natural gas is further treated with activated carbon to remove mercury, and glycol to remove water. Finally, the gas stream is combined with an oil that absorbs other hydrocarbon impurities before entering a pipeline. It may also be compressed into a cold liquid for non-pipeline transport (Eser, 2020a).

In general, several streams of natural gas are combined and transported by pipeline to refineries, meaning the variable purity levels of each stream result in a mix requiring refinement (Zhang et al., 2017). Synthetic mercaptan is also added to commercial natural gas as an odorant to make leaks easier to identify.

Other hydrocarbon fuels may be recovered from natural gas processing, or produced directly from crude oil (Eser, 2020b). Crude oil is distilled into different weight fractions, which would typically be defined as a physical process. Some of the resulting fractions are then “cracked” using heat, pressure, steam, or chemical catalysts (Eser, 2020b). The processes that use chemical catalysts are synthetic according to the Decision Tree. Those that use heat, pressure, or steam may be considered physical processes and therefore nonsynthetic.

The production of synthesis gas is directly linked to natural gas refining processes, utilizing “cracking” and steam reforming on the gas stream to break methane into carbon monoxide, hydrogen, CO_2, and water (El-Nagar & Ghanem, 2019).

Generally, fossil fuel refining processes are considered synthetic when examined against the Decision Tree (NOP, 2016b). In the case of cracking, chemical changes occur that are not mediated by a biological process or heat. The commodified nature of fossil fuel derivatives often results in mixtures derived from different sources and refineries, so determining which sources might qualify as synthetic or nonsynthetic is not always achievable.

The production of calcium oxide used in cement manufacture is considered a synthetic chemical process as well, with CO_2 as a by-product. The thermal decomposition of carbonate rocks by calcination, resulting in alkaline earth oxides and CO_2, is specifically noted in NOP 5033-1 as a synthetic process (NOP, 2016b).

As described above, operators may also produce CO_2 onsite from carbonate materials and acids. The acid/base reaction that occurs results in a chemical change in the material. As a simple example, the reaction of limestone with vinegar containing acetic acid chemically transforms calcium carbonate and acetic acid into calcium acetate, CO_2, and water.

Nonsynthetic sources: fermentation and CO_2 gas wells

CO_2 derived from fermentation processes is typically relatively clean when compared to that produced from hydrocarbon combustion (Steen, 2006). The processing system may be as simple as skimming residual foam left over from the fermentation process, followed by a treatment with water to remove soluble alcohols and ketones. These recovery systems can produce CO_2 with an extremely high purity of 99.998%, without the use of additives or reactants besides water (Steen, 2006). Compression into liquid or dry ice are both physical processes involving only pressure control.

Due to the frequent association of natural CO_2 gas wells with natural gas and petroleum extraction operations, many facilities have proprietary processing and separation schemes for CO_2 refining operations (Eppink et al., 2014). Deposits may contain hydrogen sulfide that requires removal and repurposing into elemental sulfur, or helium, another valuable product. A small fraction of directly extracted CO_2 may enter the consumer market, since 97 percent is used in oil production (Eppink et al., 2014). The majority of the literature consulted for this report concerning natural CO_2 wells explores the reinjection of naturally occurring CO_2 to recover oil while simultaneously sequestering carbon underground.

<u>Evaluation Question #4:</u> Describe the persistence or concentration of the petitioned substance and/or its by-products in the environment (7 U.S.C. § 6518 (m) (2)).

CO_2 used in agriculture will largely be derived from fossil fuels, previously stored in the lithosphere (see *Evaluation Question* #2). The lithosphere is the largest reservoir by far of CO_2 on earth (see Table 3) (Mackenzie & Lerman, 2006; Topham et al., 2014). CO_2 used in irrigation water or for gaseous enrichment will re-enter the carbon cycle (see Figure 6), temporarily persisting or concentrating in one of the three other major reservoirs: the terrestrial biosphere, the hydrosphere (oceanic reservoir), or atmosphere (US DOE, 2008; Cawley, 2011; IPCC, 2021).

It is difficult to concretely identify the amount of CO_2 that is currently produced for irrigation water and greenhouse use. In part, this is due to a continuing rapid increase in greenhouse production. For an estimate of the amount of CO_2 that will re-enter the carbon cycle as a result of agricultural use, see the *Focus Question* at the end of this report.

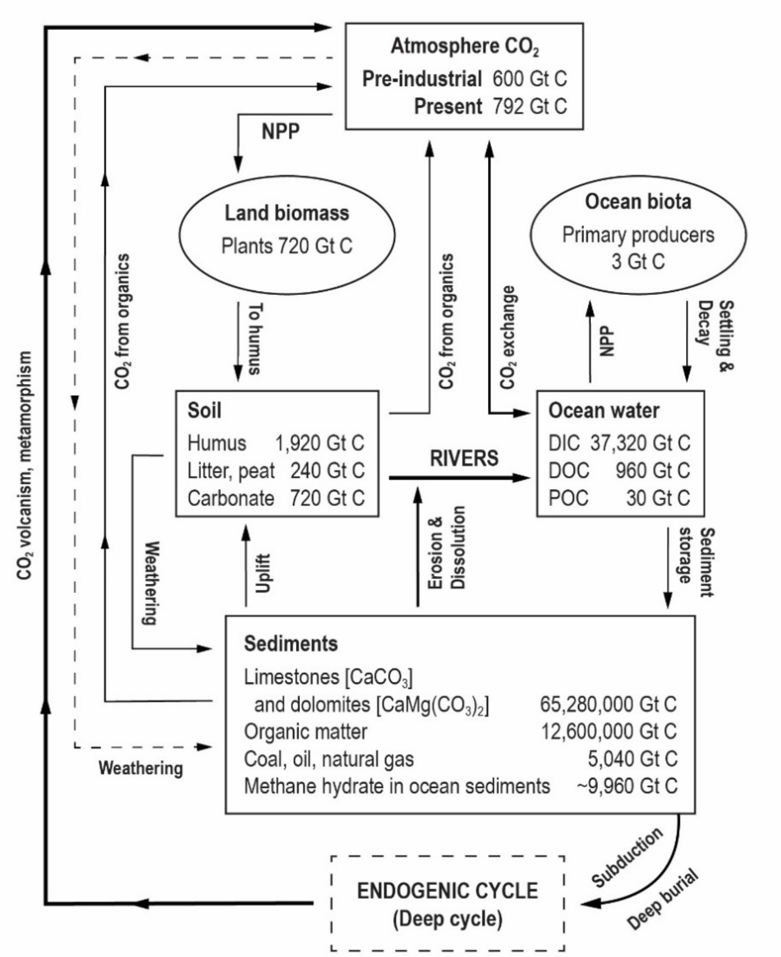

Figure 6: Global biogeochemical cycle of carbon. NPP is net primary production. DIC is dissolved inorganic carbon. DOC is dissolved organic carbon. POC particulate organic carbon. 1 gigaton C (Gt C) = 1 trillion kg. Adapted from Mackenzie & Lerman (2006).

Table 3: Estimate of the total mass of CO_2 (equivalent) in different systems on Earth. Data from Topham et al., 2014 and Bar-On et al., 2018.

System	Quantity (metric tons)	Notes
Lithosphere	5.5 X 10^{16}	Found in carbonate minerals, metals, and organic compounds in the earth's crust.
Atmosphere	2.3 X 10^{12}	Found as CO_2 gas.
Hydrosphere	1.4 X 10^{14}	Found as dissolved CO_2 gas, carbonates, hydrogencarbonates, and carbonic acid.
Biosphere (as global biomass)	*2.0 X10^{12}	*Reported as 5.5 X 10^{11} metric tons of carbon, not CO_2. Calculated using the atomic mass ratio of CO_2 to carbon (3.67) multiplied by 5.5 X 10^{11} metric tons of carbon.

CO_2 persistence/concentration background

Carbon is often found in oxidized forms at the Earth's surface, such as CO_2 gas or carbonate ions (Mackenzie & Lerman, 2006). Around 210 gigatons (Gt) of carbon is cycled through the biosphere each year (US DOE, 2008). CO_2 is a major part of the carbon cycle, being emitted and absorbed by natural processes (US EPA, 2022). Plant respiration and the decay of organic matter are the largest contributors of CO_2 to the atmosphere (Strawn et al., 2015). Around 120 Gt of carbon moves between the atmosphere and terrestrial biosphere due to processes such as photosynthesis and respiration, while 90 Gt moves between the ocean and the atmosphere (US DOE, 2008). The oceans and terrestrial biosphere serve as significant "sinks," or collection reservoirs for CO_2 that would otherwise exist in the atmosphere (Cawley, 2011; Jiang et al., 2019; Khatiwala et al., 2013; US DOE, 2008). The oceans absorb about 1.6 Gt of carbon per year more than they emit, while terrestrial systems (excluding human activity) absorb around 1.4 Gt more per year than they emit (Cawley, 2011).

The residence time for a molecule of CO_2 in the atmosphere is approximately five years (Cawley, 2011). However, CO_2 exists in an equilibrium, moving to and from different reservoirs. The rate at which CO_2 moves in all of the different reservoirs, especially surface and deep waters in the ocean, affects how quickly the entire system responds over the long term (Solomon et al., 2007). The time it takes CO_2 to reach equilibrium when there is some type of disturbance (such as an influx of CO_2 from burning fossil fuels) is therefore much longer than five years, with a variety of estimates from about 100 years (Cawley, 2011; Solomon et al., 2007) to potentially thousands of years (IPCC, 2021).

In the atmosphere

Gaseous CO_2 is relatively stable in the atmosphere, except when exposed to high temperature, certain reactive reagents, electricity, and to some degree, ultraviolet light (Mackenzie & Lerman, 2006; National Research Council (US), 2001; Topham et al., 2014). Other carbon compounds in the atmosphere, such as carbon monoxide (CO), methane (CH4), and hydrocarbons are ultimately oxidized to form CO_2 (Mackenzie & Lerman, 2006). CO_2 in the atmosphere regularly moves back and forth between terrestrial and ocean systems (Cawley, 2011; Jiang et al., 2019; Khatiwala et al., 2013; US DOE, 2008).

CO_2 concentrations in the atmosphere fluctuate throughout the year (Esmeijer, 1999). In winter months, CO_2 concentrations may be higher than in summer, when photosynthesis captures it at a higher rate (see Figure 7, below). In fall and winter, decay from fallen leaves (along with reduced photosynthesis) increase the flow of CO_2 to the atmosphere (US DOE, 2008).

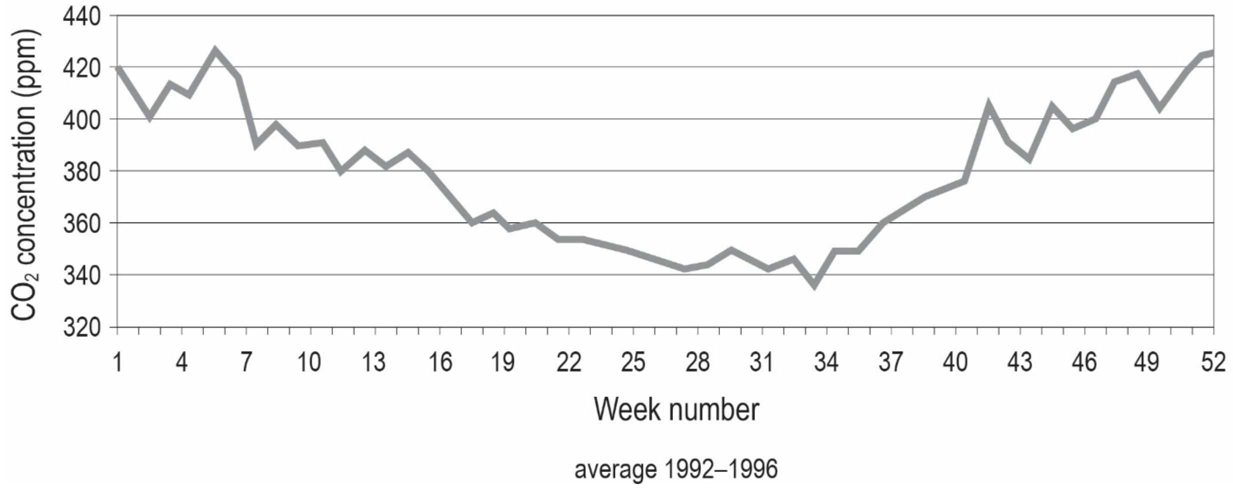

Figure 7: Average outside concentration of CO_2 per week between 1992–1996, measured in Naaldijk, Netherlands. Adapted from Esmeijer (1999).

In the oceans

When CO_2 in the atmosphere dissolves in surface waters of the ocean, some of it reacts to form HCO_3^- and CO_3^{2-} (Solomon et al., 2007). Collectively, these three materials (CO_2, HCO_3^- and CO_3^{2-}) are known as dissolved inorganic carbon (DIC). When DIC moves to colder parts of the ocean (found at high latitude), it sinks to deeper parts of the ocean. When deep ocean water moves to warmer parts of the ocean, it moves upwards, drawing DIC along with it. When phytoplankton photosynthesize, they take up some of the DIC, transforming it into dissolved organic carbon (DOC). Some of this is trapped in dead organisms, most of which are broken down by bacteria, reforming DIC. A small amount of DOC continues to sink into the ocean depths, where it is buried or re-suspended. These biotic and abiotic processes create a vertical gradient in the ocean, where deep water has higher levels of CO_2, and surface water has lower levels (Solomon et al., 2007).

In terrestrial systems

In terrestrial systems, about half of the CO_2 that is taken up during photosynthesis is respired immediately, where it returns to the atmosphere (US DOE, 2008). The rest becomes biomass, which feeds subsequent trophic levels. Some of the biomass, such as in woody plants and soil organic matter, can remain for thousands of years. Eventually, respiration processes return almost all of the carbon to the atmosphere (except for that which becomes fossilized) (US DOE, 2008).

Anthropogenic increase

From 1750 to 2020, atmospheric concentration of CO_2 has increased by 47.9% (US EPA, 2022). This increase comes primarily from anthropogenic combustion of fossil fuels (US EPA, 2022). One of the other contributors is land use changes, such as deforestation (IPCC, 2021). By 2007, human activity was contributing about 9 Gt of carbon annually to the global carbon cycle (US DOE, 2008).[5] As of 2019, CO_2 emissions due to fossil fuel use alone was approximately 9.9 Gt (IPCC, 2021).

For many decades, the proportion of anthropogenic CO_2 emissions accumulating in different reservoirs has remained constant, with (IPCC, 2021):

- 46% to the atmosphere
- 31% to terrestrial systems
- 23% to the oceans

<u>Evaluation Question #5:</u> Describe the toxicity and mode of action of the substance and of its breakdown products and any contaminants.

Plants

Elevating CO_2 can benefit plants, but soil composition, nutrient availability, plant species and plant genetics all influence the response (Dong et al., 2022; Enoch & Olesen, 1993). Generally speaking, increasing CO_2 up to 1200 ppm is beneficial to C_3 plants (Bugbee et al., 1994; Reuveni, 1997). However, increasing CO_2 beyond that can cause a decrease in plant growth and yield (Bugbee et al., 1994; Reuveni, 1997; Schwarz, 1999). For example, Schwarz (1999) found that plants in growth chambers showed symptoms of toxicity when subjected to 2000 ppm CO_2 (see Table 4), while control plants did not.

Schwarz (1999) found that elevating CO_2 to 2000 ppm caused some plant species to have reduced leaf area and increased leaf thickness. This is consistent with what several other researchers have found in a range of plants (Kovenock & Swann, 2018; Rogers et al., 1997). This response to increased CO_2 results in decreased photosynthetic efficiency (Kovenock & Swann, 2018; Rogers et al., 1997).

Table 4: Summary of CO_2 toxicity symptoms in shoots of various plant species after 4-6 days of CO_2 treatment (2000 ppm). Adapted from Schwarz, 1999.

Crop	Yellow stripes	Yellowing	Crumbling	Reduced leaf area	Delay in development	Recovery after treatment ended
Wheat	+	-	-	-	No	Fully
Maize	+	-	-	-	No	Fully
Bean	-	+	+	++	Yes	No
Bean + saline soil	-	++	++	++	Yes, very strong	No, collapse
Soybean	-	+	-	+	Yes	Partly
Tomato	-	+	+	+	Yes	Partly
Tomato + saline soil	-	+	+	+	Yes, very strong	No, collapse
Lettuce	-	+	-	++	Yes	Partly
Radish	-	-	-	-	Yes	Partly

+ = strong signs; ++ = very strong signs; - = no signs

Enoch & Olesen (1993) report that in early experiments, some plant injury occurred with CO_2 treatments. However, one of the mentioned experiments (Noyes, 1914) involved treating only two plants (one corn

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[5] Fossil fuel use contributed 7.6 gigatons of carbon.

plant, one tomato plant), with an unidentified quantity of CO_2. In experiments by Cannon & Free (1925), experimental concentrations of CO_2 in the root atmosphere between 25 to 75% caused root growth to slow or stop in some plants like *Covillea tridentate* and *Krameria canescens*, while other plants like *Mesembryanthemum aequilaterale* were relatively unaffected.

In contrast, while Schwarz (1999) noted toxicity symptoms in aerial plant parts, he found no symptoms in roots. Schwarz states that most reported toxic symptoms in the root environment are likely a result of the lack of oxygen, and not high CO_2 concentration.

The negative growth responses of plants at CO_2 concentrations over 1200 ppm is often attributed to its influence on ethylene production (Bugbee et al., 1994; Enoch & Olesen, 1993; Mathooko, 1996; Mathooko et al., 1998). CO_2 can affect the production of ethylene, in some cases inducing it, while in other cases suppressing it, depending on a variety of factors (Dhawan et al., 1981; Bugbee et al., 1994; Mathooko et al., 1998; Mathooko, 1996). Ethylene is a plant hormone involved with several physiological processes, including ripening, stress responses, senescence, and growth (Enoch & Olesen, 1993; Mathooko et al., 1998).

We found no information that specifically indicated that carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) ions, formed from the dissolution of CO_2 in water, are toxic to plants.

Microorganisms

At significantly elevated levels, CO_2 inhibits microbial growth, and this effect is amplified under pressure (Ballestra et al., 1996; Bertoloni et al., 2006).

Schulz et al. (2012) investigated the effects of CO_2 concentration from 50-100% in the gas-phase of a liquid medium on a representative sample of bacteria commonly found in terrestrial and freshwater systems: *Pseudomonas putida, Bacillus subtilis, Desulfovibrio vulgaris, and Thauera aromatica*. Generally speaking, the lag phase between when bacteria were added to glass tubes and when they began reproducing was significantly lengthened for those grown in the presence of CO_2 (50–100%). The researchers also found that the growth rate decreased as CO_2 concentration increased. The inhibitory effect of CO_2 on growth was the most pronounced for *P. putida*, an obligate aerobe. At 60% CO_2, *P. putida* showed severely inhibited growth (Schulz et al., 2012).

A few mechanisms have been proposed to explain the effect that CO_2 has on microorganisms. Sears & Eisenberg (1961) proposed that CO_2 decreases how miscible membranes are in water, and increases their electrical resistance. Ballestra et al. (1996) suggested that antimicrobial properties of CO_2 involved a complex mechanism, with CO_2 penetrating into the cell and forming anti-microbial compounds, damaging membranes, disrupting enzymatic activities, and decreasing pH. Jones & Greenfield (1982) proposed that CO_2 inhibits specific microbial metabolic processes. By increasing CO_2 concentration within the cell, the CO_2 equilibrium is disturbed, which inhibits metabolic chemical reactions that would normally produce *more* CO_2. The excess CO_2 already in the cell limits the reaction rates of processes that produce additional CO_2 during specific steps—essentially clogging these processes.

Animals

CO_2 can be toxic to animals, depending on its concentration. In a review of toxicology literature, Guais et al. (2011) found evidence that elevated levels of CO_2 caused a wide variety of toxic effects in mammals (see Table 5). Factors involved in causing these effects include CO_2's role in:

- lowering blood pH.
- control of breathing rate through interacting with chemoreceptors.
- vasodilation and vasoconstriction (including in the brain), depending on concentration.
- participating in biochemical reactions (along with HCO_3^-), for example that:
    - transport hydrogen ions in mitochondria.
    - produce cell membrane components.
    - produce glucose.
    - produce pyrimidine (used to form other substances such as RNA and DNA).

- other metabolic pathways.
- triggering the production of inflammation-related substances, such as cytokines, interleukins, and mucus glycoprotein.
- hormone secretion.

Table 5: Effects of elevated CO_2 on mammals. Data summarized from Guais (2011).

Animal	**Exposure type**	**[CO_2]**	**Effect type**	**Specific effect**
Guinea pig	Acute (1 hour)	15%	Respiratory acidosis[6]	Partial pressure of CO_2 ($PaCO_2$) increased to 17.8%.[7]
Guinea pig	Chronic (73 day)	15%	Respiratory acidosis	Initially (first day), animals show: • decline in extracellular and urine pH, and inorganic phosphorus plasma concentration. • increase in calcium plasma concentration and urine inorganic phosphorus. Later: • extracellular pH returns to normal. • plasma calcium remains high. • inorganic phosphorus remains low. • renal calcification after 48 hours.
Rat	Chronic (11 days)	10–15%	Respiratory acidosis	$PaCO_2$ increases to 15-22%.
Human	Acute	5%–20%	Metabolic	At 5%, doubles rate of glycolysis and cellular respiration. At 20%, depresses cellular respiration (no further effect on glycolysis).
Guinea pig	Chronic	1.5–3%	Metabolic	At 1.5%, weight loss for 25 days, then begin to regain weight after. At 3%, weight loss for 35 days.
Guinea pig	Chronic (7 days)	15%	Metabolic	Transient increase in metabolic enzymes, which return to normal after 3-7 days (depending on the enzyme).
Guinea pig and rat	Chronic (7 days)	3%	Metabolic	Depletion of glycogen vacuoles, and an increase in fat vacuoles. This is likely due in part to acidosis causing a repression in fat metabolism. CO_2 exposure can also increase fat synthesis in the liver.
Monkey	Acute	5–10%	Pulmonary	Respiratory rate doubles when exposed to 5% CO_2, and death occurs at 10%.
Guinea pig	Chronic	1–15%	Pulmonary	At 1%: changes to lung cells (alveolar pneumocytes), including enlargement (hyperplasia). At 3-15%: malformations in lung tissue (hyaline membranes), loss of surfactants in alveoli, edema, decreased gas exchange and lung collapse (atelectasis).
Mouse	Chronic (2 weeks)	8%	Pulmonary	Abnormal lung development in young mice, no effect on adult mice.
Dog and monkey	Acute	10%	Cardiovascular	Increases heart rate due to changes in blood pH.
Guinea pig	Chronic	15%	Neuroendocrine	Stimulates adrenal glands.
Rat and guinea pig	Chronic	5–15%	Reproductive	At 5-10%, causes reversible damage to testes. At 15%, decreases sperm formation in rats and guinea pigs.

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[6] Lowered blood pH

[7] CO_2 freely diffuses from lung tissue into the bloodstream, resulting in an increase in the partial pressure of CO_2 ($PaCO_2$) (Guais et al., 2011). When $PaCO_2$ is elevated to a certain point, it causes a pH change in the blood (acidosis). The body responds by adding buffers (bicarbonate) to blood plasma to return pH to normal. Later, the body may excrete carbonic acid, and reabsorb more bicarbonate. The upper limit for normal is 6.75% $PaCO_2$ (Guais et al., 2011).

Animal	Exposure type	[CO_2]	Effect type	Specific effect
Rats and rabbits	Acute	6–13%	Developmental	At 6% for 24 hours during pregnancy, causes cardiac and skeletal malformations in rat pups. At 10%, causes abnormal eye development (retinopathy of prematurity) in rat pups. At 10-13% during pregnancy, rabbit pups develop vertebral malformations.

CO_2 is also toxic to invertebrates, and has been investigated as a tool to control a variety of species, including (Gunasekaran & Rajendran, 2005; Nielson et al., 2012):

- Asian clams.
- zebra mussels.
- New Zealand mudsnails.
- drugstore beetle.
- cigarette beetle.
- rust red flour beetle.
- confused flour beetle.
- Indian meal moth.
- German cockroach.

At high concentrations (35-90%) for prolonged periods of time (24-96 hours), it is 100% lethal to drugstore beetle (*Stegobium paniceum*) and cigarette beetle (*Lasioderma serricorne*) (Gunasekaran & Rajendran, 2005). The time and concentrations required for 100% mortality varied by life stage, with adults being more susceptible than eggs and larvae. At sub-lethal concentrations and exposure times, CO_2 can affect reproduction and developmental processes in insects, reducing successful progeny (Gunasekaran & Rajendran, 2005).

In a study of marine benthic invertebrates and fish, Lee et al. (2016) found that invertebrates varied in their tolerance to elevated CO_2 (1-30%). Intertidal organisms such as benthic copepods and clams were more resistant to elevated levels of CO_2, while sub-tidal species brittle starfish and medaka were more sensitive (Lee et al., 2016).

<u>Evaluation Question #6:</u> Describe any environmental contamination that could result from the petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).
Anthropogenic contributions of CO_2 continue to exceed what oceans and terrestrial systems can absorb; CO_2 is therefore increasing in the atmosphere. In the atmosphere, CO_2 absorbs longwave radiation coming from the earth's surface, causing warming known as "the greenhouse effect" (Topham et al., 2014; US EPA, 2022). This is the primary driver of climate change (Solomon et al., 2007; IPCC, 2021).

Generally speaking, any use of CO_2 that originated from a lithospheric source (e.g., fossil fuels), regardless of whether it is used "properly" or not, will ultimately add CO_2 to the other reservoirs – the atmosphere, the hydrosphere, and the biosphere (Esmeijer, 1999; Topham et al., 2014; US DOE, 2008; US EPA, 2022). Two other sources of CO_2 are hydrogen production and ammonia production (as a by-product), both of which ultimately rely on hydrocarbon feedstocks (Topham et al., 2014).

Agricultural activities contribute a variety of greenhouse gases (GHG) to the atmosphere, including CO_2 and methane (US EPA, 2022). Using CO_2 to enrich plants in greenhouses, or to adjust the pH of water, even if initially absorbed by water, plants, and soil, will eventually become distributed between the atmosphere, the oceans, and terrestrial systems (Esmeijer, 1999). However, passing CO_2 that is already produced from another process through a greenhouse or a water system does not necessarily *increase* the level of environmental contamination, nor does it reduce it in a significant way.

Production of CO_2 from carbonaceous fuels can also produce harmful gasses like NO_x, SO_2, and CO (Wang et al., 2022). Greenhouse operators sometimes burn fuel to heat their greenhouses and return waste CO_2 to the greenhouse for atmosphere enrichment. However, the need to replace fuel burning for heat from clean energy sources such as solar and geothermal means that CO_2 collected from heating processes may, by necessity, become used less frequently in the future (Wang et al., 2022).

The efficiency by which a greenhouse can convert supplied CO_2 into plant photosynthesis products can be measured by the CO_2-use efficiency, or "CUE" (Wang et al., 2022). A CUE of 100% would mean that all of the supplied CO_2 is converted by plant photosynthesis. Greenhouses usually have a CUE of less than 60%, meaning that over 40% of the CO_2 that is added is released into the atmosphere without being ever incorporated into plant biomass (Wang et al., 2022).

According to Ntinas (2020), GHG emissions from greenhouse vegetable production is a central issue in northern Europe, and these systems contribute to climate change. Similarly, Esmeijer (1999) notes that greenhouse horticulture shares responsibility for the rising CO_2 levels in the atmosphere. Fewer GHG emissions are produced transporting field-grown tomatoes from warm to cold climates, compared to growing tomatoes in heated greenhouses (Ntinas et al., 2020). Using renewable energy to heat greenhouses would improve their carbon footprint; but it would also mean that in order to achieve the same level of enrichment, CO_2 from another source (likely fossil-fuel based) would still be used.

Evaluation Question #7: Describe any known chemical interactions between the petitioned substance and other substances used in organic crop or livestock production or handling. Describe any environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).

At normal temperatures, CO_2 does not break down into simpler compounds, and it is not very reactive (Topham et al., 2014). While unlikely to be an issue in organic crop production, CO_2 can react with hydrogen gas to form carbon monoxide (CO). It can also react with ammonia to form ammonium carbamate, which when dehydrated then forms urea (Topham et al., 2014).

A selection of Safety Data Sheets note that CO_2 (Airgas, 2018; Millipore Sigma, 2021; Praxair Inc., 2015):

- is stable.
- does not produce hazardous decomposition products.
- does not polymerize under normal conditions of storage and use.
- does not have specific data available for conditions to avoid, except high temperatures or electrical discharges.
- does not have specific data for incompatible materials, except in combination with temperatures over 1000°F.

According to the New Jersey Department of Health (2016), CO_2 is not compatible with a variety of materials, most (but not all) of which are unlikely to be used in organic crop production. Exceptions to this are strong bases like sodium or potassium hydroxide that could exist in other crop inputs, and hydrogen peroxide that could be used in an algicide, disinfectant, or irrigation system cleaning product. Even so, mixing CO_2 with sodium hydroxide forms sodium carbonate (washing soda), a substance allowed at 7 CFR 205.605. The reaction of CO_2 with hydrogen peroxide forms peroxymonocarbonate (HCO_4^-, an oxidant similar to hydrogen peroxide but more reactive), but this reaction happens slowly and is unlikely to be of significant concern in organic crop production (Radi, 2022; Salvitti et al., 2023).

Using acids (such as carbonic acid) to lower pH to 6.0-6.8 in some circumstances can improve the bioavailability of some nutrients, such as iron, zinc, boron, and manganese (Inamuddin et al., 2021; Brautigan et al., 2014). However, in wet environments or where large amounts of irrigation are used, lowering pH can also potentially lead to cations leaching from the soil (NRCS, 2011). For more information on the role of pH in crop production see the 2023 NOP technical report *Sulfurous Acid* (NOP, 2023b).

Evaluation Question #8: Describe any effects of the petitioned substance on biological or chemical interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).

Effects on organisms

For information on the toxicity of CO_2 to plants, microbes, and animals, see *Evaluation Question #5* (above). In summary: at low concentrations (up to about 1200 ppm), CO_2 is generally safe and has low toxicity, and can have substantial beneficial effects to plants. However, at moderate concentrations (1200 ppm to several percent, depending on duration and tolerance of a given species) CO_2 can cause toxic effects in plants and animals. At high levels (>~50%), it can be toxic to microorganisms as well.

For information on the benefits of CO_2 to plants, see *Specific Uses of the Substance*, above. CO_2 is the primary substrate for photosynthesis, and can be a limiting reagent, especially in C_3 plants (see *Inset 1: C_3, C_4, and CAM plants and their utilization of* CO_2). Increasing CO_2 concentration to a point (up to about 1200 ppm) can make photosynthesis more efficient, resulting in higher plant growth and yield (Enoch & Olesen, 1993; Rogers et al., 1997). Other positive responses have been documented as well, such as improved rooting of plant cuttings, and increases in root dry weight in some species (Rogers et al., 1997). In some cases, plants acclimate to the increased CO_2, and photosynthetic rates fall back to rates of "normal" CO_2 concentrations, though this is somewhat unusual (Rogers et al., 1997).

Effects on soil

In water, a small amount of CO_2 (~0.1–0.3%) dissolves to form a weak acid, carbonic acid, which can also produce bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) at varying proportions depending on pH (Lerman & Mackenzie, 2018; Topham et al., 2014). This weak acid plays a key role in weathering, increasing the rate at which certain minerals and rocks dissolve and others precipitate, therefore affecting soil chemistry (Lerman & Mackenzie, 2018; Topham et al., 2014). For example, this action temporarily increases the concentration of cations like calcium in the soil (Strawn et al., 2015). In wet environments, or those with prolonged irrigation cycles with acidified water (such as from CO_2), these solubilized cations can be leached entirely from the soil (Strawn et al., 2015; Enoch & Olesen, 1993). In arid environments, bicarbonate (which is more soluble than carbonate and is present at a lower pH) and calcium are leached into lower layers (horizons) of soil (Strawn et al., 2015). Buildup of these substances leads to the formation of a cemented horizon (hardpan) that is difficult for plant roots and water to penetrate (Strawn et al., 2015).

However, using CO_2 to acidify water can improve water characteristics. In general, high alkalinity and high pH reduce water's ability to infiltrate deeply into the soil, reflecting a property known as hydraulic conductivity (Ali et al., 2019). Adjusting alkaline water to a pH of approximately 6 has been shown to reduce the loss of hydraulic conductivity (Ali et al., 2019), which can be achieved by feeding CO_2, or another acidic material like gypsum, sulfuric acid, or sulfur, into the water source.

Effects on denitrification

In anaerobic conditions, specific bacteria (e.g., *Pseudomonas* spp., *Acromobacter* spp., *Paracoccus* spp., and *Thiobacillus denitrificans*) reduce nitrate ($NO3^-$) and nitrite ($NO2^-$) to nitric oxide (NO), nitrous oxide (N_2O), and nitrogen gas (N_2) (Gowariker et al., 2008; Wei et al., 2015). Crop producers can expect to lose 3–62% of the nitrogen applied to the soil, due to denitrification processes (Gowariker et al., 2008). The rate of denitrification is influenced by (Gowariker et al., 2008):

- the amount (and type) of organic matter present
- moisture content
- aeration
- soil pH and temperature
- concentration and form of inorganic nitrogen (ammonium vs. nitrate)

The denitrification process occurs within bacterial cells, sequentially reducing nitrogen compounds in an electron transport chain process (Wan et al., 2016). Electron transport chains are biochemical processes involving several steps. Electrons are passed to a series of cellular components, providing the energy to create an electrochemical gradient across a membrane (due to more protons existing on one side of a membrane than the other) (Clark et al., 2020). This gradient drives another specific chemical reaction, usually to generate adenosine triphosphate (ATP), a universal energy-carrying molecule. Blocking any step in the chain can disrupt the process. Denitrification uses many of the same basic cellular components as aerobic respiration (with a few differences as well), except that nitrogen is used as the electron acceptor instead of oxygen (Chen & Strous, 2013).

Researchers have found that increasing environmental CO_2 concentrations can affect denitrification rates, but with varying responses (Wan et al., 2016). For example, in one study, increased CO_2 was associated with decreased denitrification, while in another, it was associated with an increase in denitrification. These varying results could be due to indirect effects that CO_2 has on the environment and denitrification processes, such as altering pH, displacing oxygen, and serving as a carbon source. However, CO_2 also acts directly on bacterial cells, disrupting components of the electron transport chain and decreasing denitrification (Wan et al., 2016).

Using the denitrifying bacteria *Paracoccus denitrificans* in a lab experiment, Wan et al. (2016) found a strong decrease in denitrification at even the lowest treatment level of 1000 ppm CO_2 (see Figure 8, below). They found that the strong, concentration-dependent effect of CO_2 on denitrification was caused by damage to bacterial membranes, and disruption of the electron transport chain (Wan et al., 2016).

While at first, the decrease in denitrification might appear to be a positive effect of CO_2, Wan et al. (2016) found that nitrous oxide and nitrite production *increased* (see Figure 9, below). Instead of the bacteria completely reducing nitrate to nitrogen gas, they produced more intermediate products (like nitrous oxide). Unlike nitrogen gas, nitrous oxide is an important greenhouse gas, nearly 300 times more powerful than CO_2 (US EPA, 2022).

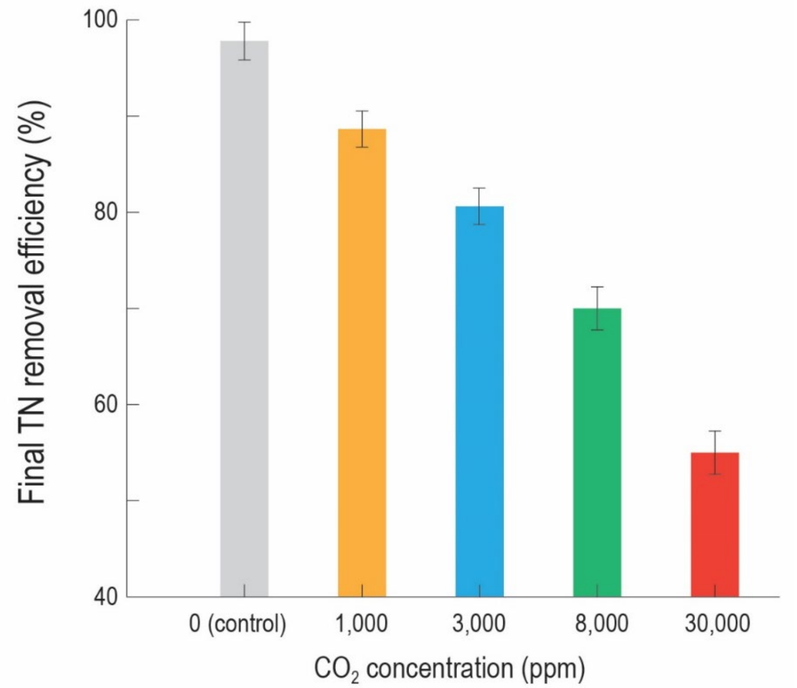

Figure 8: Total nitrogen removal efficiency during denitrification by *Paracoccus denitrificans* under different CO_2 treatments. Adapted from Wan et al. (2016).

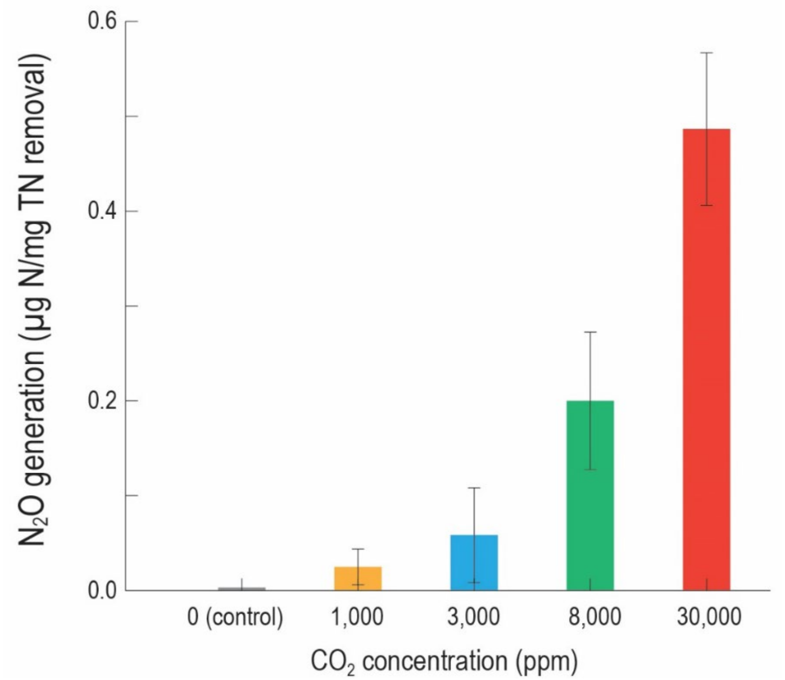

Figure 9: Nitrous oxide generation by *Paracoccus denitrificans* under different CO_2 treatments. Adapted from Wan et al. (2016).

Increased toxicity of copper and pesticides

Dissolving CO_2 in water decreases pH, which can increase the toxic effects of copper on the marine polychaeta (segmented worm), *Arenicola marina* (Campbell et al., 2014). Cryer et al. (2022) estimated that a decrease of 0.3 pH units in the ocean will double the proportion of dissolved copper, Cu^{2+}, the most bioavailable form of the metal. This level of acidification is predicted to occur before the end of this century due to anthropogenic contributions to atmospheric and oceanic CO_2 (Campbell et al., 2014; Cryer et al., 2022). In a lab experiment, CO_2 appeared to work synergistically with copper, reducing calcification and respiration rate in the coral *Stylophora pistillata* (Cryer et al., 2022). Copper can be naturally occurring but is also used as a pesticide. See the 2022 NOP technical report *Copper Products (Fixed Coppers and Copper Sulfate)* for more information (NOP, 2022).

According to Enoch & Oleson (1993), CO_2 can affect the activity of pesticides like chlorpyrifos, metolachlor, fenamiphos, and EPTC (s-ethyl dipropylthiocarbamate) on nitrifying bacteria. When CO_2 concentrations are below or above optimal concentrations for nitrifying bacteria, these pesticides can inhibit nitrification (Enoch & Olesen, 1993).[8] Nitrification, the reverse process of denitrification, is an aerobic process of converting nitrogenous wastes into ammonium (NH_4^+) and then subsequently nitrite (NO_2^-) and nitrate (NO_3^-) (Clark et al., 2020; Muck et al., 2019). However, these synthetic pesticides are not allowed for use in organic agriculture.

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).

Besides independent researchers, numerous government and international organizations now study the effects of global warming on humans and the environment, including:

- U.S. Department of Energy
- U.S. Environmental Protection Agency
- National Oceanic and Atmospheric Administration
- Intergovernmental Panel on Climate Change

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[8] Maximum nitrification occurs between 5 and 29 ml CO_2/L (5000–29,000 ppm) (Enoch & Olesen, 1993)

Researchers produce a staggering amount of information that is not possible to synthesize into this report, except to say that any activities that generate excess CO_2 contribute to an ecological problem that has overwhelming proportions.

Human activities that generate CO_2 directly disrupt the global equilibrium of greenhouse gases, contributing to global warming, climate change, and ocean acidification (IPCC, 2021; Solomon et al., 2007). It is now widely known that these changes negatively affect many existing species, including humans. According to the U.S. EPA and the Intergovernmental Panel on Climate Change (IPCC), climate change affects health, the environment, and the economy (US EPA, 2021; Portner et al., 2022):

- increasing the frequency, intensity, and duration of heat waves, which pose health risks to the young and elderly.
- worsening air and water quality.
- increasing the spread of diseases.
- altering the frequency and intensity of extreme weather events.
- raising sea level, threatening coastal communities and ecosystems.
- changing patterns of rainfall, affecting water supply and hydroelectric energy.
- ecosystem changes, including changes in the geographic ranges of plant and animal species, timing of reproduction and migration.
- increasing disruptions to society, property damage, and economic damage due to heat waves, drought, fire, and floods.

Increases in atmospheric CO_2 do not only affect terrestrial systems. While the oceans have served as a crucial buffer to atmospheric CO_2 increase, this has led to ocean acidification (Khatiwala et al., 2013). This can negatively affect marine organisms. According to the IPCC (Portner et al., 2022) human-caused climate change has caused:

- widespread and rapid changes in the atmosphere, ocean, cryosphere, and biosphere.
- sea level increase of 0.2 m between 1901 and 2018.
- an increase in the *rate* of sea level rise, from 1.3 mm/yr. between 1901-1971, to an increase of 3.7 mm/yr. between 2006-2018.
- damage and irreversible loss in a variety of ecosystems, including in the oceans.
- hundreds of local losses of species on land and in the oceans.
- ocean warming and acidification, which have adversely affected food production from fisheries.

Despite the global danger of increasing CO_2, in some circumstances, it can be used for agriculture without adding harm to the environment. If the CO_2 were produced as a by-product of another activity *and* would otherwise have been disposed of into the atmosphere anyway, producers could pass it through an agricultural system without causing any additional increase in CO_2. However, using recycled CO_2 does not actually reduce emissions over the long term, because eventually this CO_2 is still returned to the atmosphere when crops decay or are digested and respired by organisms (Esmeijer, 1999). If done correctly, it could offer increased crop yields in specific scenarios without causing more harm than would have otherwise occurred if it were simply released into the atmosphere. There is still some potential that CO_2, even if used at relatively moderate concentrations, could cause an increase in even more potent greenhouse gases in the soil (see *Evaluation Question #8*, above). CO_2 has the potential to inhibit denitrification processes, leading to increased nitrous oxide emissions.

Applying CO_2 at higher than optimum levels could cause toxicity to a wide variety of organisms (see *Evaluation Question #5*). This situation is unlikely, however, because it would also begin to exert negative growth effects on crops, thus defeating the purpose of its use.

Evaluation Question #10: Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

No obvious short-term symptoms of toxicity occur when CO_2 concentrations are below 3% (30,000 ppm) (Price, 2015). Exposure to atmospheres containing 2% CO_2 for several hours increases blood pressure, produces acute headache, and increases the rate and labor of breathing. Above 3%, serious breathing difficulties follow. At 6%, sensory impairment may occur after a few minutes of exposure. Exposure to CO_2 at 9-10% concentration causes unconsciousness in as little as 5 minutes. Between 15 and 20% atmospheric concentration, loss of consciousness and muscle spasms begin, and above 20%, convulsions and death can occur within minutes. CO_2 acts as an asphyxiant (a suffocating agent) and many of the symptoms associated with CO_2 exposure are linked to oxygen deprivation (Price, 2015).

CO_2 can also be defined as a toxicant since it induces unconsciousness, respiratory failure, inflammation, and sensory impairment (Guais et al., 2011; Permentier et al., 2017). The classification of CO_2 as a toxicant is supported by the tendency of victims to lose consciousness within seconds of exposure to 30% atmospheres, rather than gradually suffocating or leaving the area (Permentier et al., 2017). Guais et al. (2011) describe multiple toxic effects of CO_2 observed in animal studies, including inflammatory effects to the lungs, cardiovascular system, and bladder, reproductive or birth defects, and cancers. Most of the severe and irreversible effects follow long-term exposure (generally weeks to months) to excessive CO_2 concentrations, far higher than would be encountered in most work environments.

No definitive toxic CO_2 level exists because tolerance among individuals is variable (Permentier et al., 2017). Tolerance appears to decrease with age, and smokers tend to develop greater tolerance as a result of frequent exposure (Permentier et al., 2017).

Instances of CO_2 poisoning are exceedingly rare events (Price, 2015). The concentrations found in nature, in typical industrial settings, or used in greenhouses, are far lower than any of the concern levels listed above and are not a threat to human health (Price, 2015). Adverse effects generally begin following exposure to 1% or greater CO_2, while background atmospheric levels are approximately 0.04% and enriched greenhouse atmospheres are approximately 0.1%. Confined areas like mines, silos, or fermentation chambers, for example, may be environments where CO_2 concentrations can surpass 1%, sometimes significantly (Price, 2015).

Historically, some poisoning events have been reported, often related to small enclosed spaces containing large amounts of materials in a state of fermentation or decomposition (Price, 2015). The Occupational Safety and Health Administration (OSHA) estimates approximately 90 deaths per year related to confinement in enclosed spaces, two thirds of which are rescuers attempting to retrieve others (Permentier et al., 2017). One well-publicized natural asphyxiation event occurred in Cameroon in 1986, when massive amounts of CO_2 were released from a volcanic lake, leading to the deaths of 1,700 people (Price, 2015; Scott et al., 2009). Several suicide cases are recorded each year related to dry ice confined with a victim in a small space, such as a car (Permentier et al., 2017).

Dry ice must be handled with extreme care due to its low temperature, and can cause severe burns or frostbite upon superficial contact with skin, sometimes leading to blistering or even tissue death (FSIS Environmental Safety and Health Group, n.d.; Scott et al., 2009). Direct contact with CO_2 emitted from compressed cylinders may provoke similar freeze burn effects (FSIS Environmental Safety and Health Group, n.d.).

The current OSHA Permissible Exposure Limit (PEL) for 8-hour exposure to gaseous CO_2 is 5,000 ppm, or 0.5% (OSHA, 2022).

A secondary, indirect effect of CO_2 enrichment that may have repercussions for human health is an increase in the use of pesticides (Rogers et al., 1997). Since increased CO_2 concentrations in the air or the soil leads to increases in plant growth and altered nutrient balance, rhizodeposition[9] would be expected to increase as well (Rogers et al., 1997). Elevated CO_2 and increased rhizodeposition might lead to increased microbial activity in the rhizosphere from beneficial as well as pathogenic organisms (Rogers et al., 1997). Producers may be inclined to apply more pesticides in response (Rogers et al., 1997). Pesticides are known to pose myriad health risks to applicators, and their residues in food and water can expose the general public to a range of toxins (Damalas & Eleftherohorinos, 2011).

Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

There is no substitute for gaseous CO_2 in plant biology. It is an essential component of the photosynthesis process. *Evaluation Question #12* describes several practices resulting in nonsynthetic CO_2 which may be used for atmospheric enrichment.

The petition to add synthetic CO_2 to the National List as a crop or soil amendment covers a number of different applications with distinct purposes, as described earlier in *Specific Uses of the Substance*. One of those is soil pH reduction. The only readily available nonsynthetic acid currently allowed to reduce the pH of irrigation water in organic production is citric acid, though the quantities needed and expense are vastly larger than with synthetic mineral acids like sulfuric, nitric, and phosphoric (Evans, 2014; University of Minnesota Extension, 2022). While some other nonsynthetic acids exist, it seems doubtful that they would be readily available in large enough quantities, at reasonable prices, to reduce the pH of irrigation water, and none of the extension services or papers consulted for this report mention any.

Soil pH can be reduced indirectly, without the use of acids. Synthetic elemental sulfur, permitted by the National List at 7 CFR 205.601(j)(2), and gypsum, available as an allowed nonsynthetic material, both works gradually to reduce soil pH. Elemental sulfur is also used in the production of sulfurous acid, permitted as a plant or soil amendment by the National List at § 205.601(j)(11) when produced on-farm.

While gypsum ($CaSO_4$) is not itself acidic, it can work in alkaline soils to reduce pH when sodium is also present (Brautigan et al., 2014). The calcium in gypsum displaces sodium in sodium carbonate (Na_2CO_3) to precipitate calcium carbonate due to solubility differences between the materials (calcium carbonate is less soluble than sodium carbonate) (Brautigan et al., 2014). The concentration of soluble carbonates is thereby reduced and pH decreases, though by a more modest margin than direct acid application (Brautigan et al., 2014). However, the starting pH value is critical when applying gypsum, which only has an effect at pH 8.4 and above; gypsum will have no pH reducing effect when the soil is pH 4.5-8.4 (Franzen et al., 2006). There also appears to be a complementary pH-reducing effect between gypsum application and the type of plant grown in the soil, likely the result of the specific plant's root system's ability to transport gypsum deeper into the soil (Brautigan et al., 2014; Jarwal et al., 2001). Canola and chickpea rotations have been shown to be more effective at lowering soil pH than wheat and safflower rotation when combined with gypsum, for example (Brautigan et al., 2014; Jarwal et al., 2001).

The application of sugars, such as glucose or molasses, may also indirectly reduce pH, despite not being acidic substances (Brautigan et al., 2014). Sugars serve as food for microbial populations in the soil that exude organic acids. The result is temporary since the sugars are consumed completely by microbial populations in as little as two months, after which pH begins to rise again (Brautigan et al., 2014).

Following direct application or suspension in irrigation water, elemental sulfur is oxidized by *Thiobacillus* spp. in the soil (Tabak et al., 2020). These bacteria exude sulfuric acid as hydrogen and sulfate ions (Sibbett, 1995; Tabak et al., 2020). In alkaline soils rich in carbonates, the pH change is typically negligible because of the sheer volume of carbonates that resist neutralization (Tabak et al., 2020). However, pH reduction may be more dramatic in soils without much carbonate (Tabak et al., 2020). Non-calcareous soils rich in clay and organic matter exhibit slow pH reduction, a property known as the buffering

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[9] Rhizodeposition is the process by which plants release organic and inorganic material back to the soil through the roots, including root cells, secretions, nutrient ions, and nitrogen and carbon compounds (Wichern et al., 2008).

capacity, following application of elemental sulfur (Tabak et al., 2020). The acidifying effect of sulfur can help to alleviate micronutrient deficiencies by the same acidification mechanism discussed elsewhere in this report (Tabak et al., 2020).

There is currently a lack of available academic and experimental data regarding the efficacy of sulfurous acid in comparison to other pH reducers used on soil or in irrigation water (H Zia et al., 2006). While sulfurous acid is not available commercially due to its instability, sulfurous acid generators are on the market for use on-site (NOP, 2014b; OMRI, 2021). These systems work by burning (oxidizing) elemental sulfur, producing sulfur dioxide gas (NOP, 2014b). The captured sulfur dioxide is then dissolved in irrigation water that passes through the chamber, forming hydrogen sulfite, also known as sulfurous acid, and the water is sprayed through irrigation equipment (NOP, 2014b). Although research is scant regarding the pH reducing effects of sulfurous acid on soil, at least one study has demonstrated that using sulfurous acid generators reduces sodium carbonate levels in saline irrigation water used in rice paddies (H Zia et al., 2006).

<u>Evaluation Question #12:</u> Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

As a carbon nutrient source, the use of dissolved CO_2 is generally impractical as discussed in *Specific Uses of the Substance* and *Action of the Substance* above. General soil management practices including the application of organic matter, and exposure to ambient air concentrations is sufficient in comparison.

There are several methods to increase CO_2 concentration within indoor crop production facilities, where CO_2 is a by-product of biological processes. All of these methods are based on harnessing gas emitted from organic decomposition.

Controlled fermentation

In small greenhouses, it may be beneficial to ferment sugars with yeast in buckets to increase indoor CO_2 concentrations (Poudel & Dunn, 2017). This method introduces difficulties in controlling CO_2 levels and can produce unpleasant odors (Poudel & Dunn, 2017). This method also may not be practical for all operations. Approximately 1 kg of sugar will produce 0.5 kg of CO_2 upon full fermentation (Poudel & Dunn, 2017). In a 100 m^2 (approximately 1,075 ft^2) greenhouse, it is estimated that approximately 0.5 kg of CO_2 would be needed per hour to maintain CO_2 levels at 1300 ppm (Ontario Ministry of Agriculture, Food and Rural Affairs, 2002). CO_2 generators fueled by propane or natural gas can produce approximately 3.7 kg of CO_2 per hour, by contrast (Poudel & Dunn, 2017). However, the resulting ethanol produced from sugar fermentation could later be used as fuel for more combustion-based CO_2 generation (Poudel & Dunn, 2017).

In-vessel composting

In an analysis of available literature, Thomson et al. (2022) concluded that repurposing the ample CO_2 produced from onsite composting operations would be comparable in price to generating it by natural gas or propane combustion. The researchers saw significant opportunities for compost-based CO_2 generation systems by utilizing in-vessel composting of crop waste within grow buildings. They do concede that little research has been devoted to the topic, and other challenges may be factors, including undesirable buildup of odors, methane, ethylene, ammonia, or other gases from compost systems that may cause plant damage in enclosed environments (Thomson et al., 2022).

Some studies have evaluated CRAM (crop residues and animal manure) composting systems to increase CO_2 levels in greenhouses. Jin et al. (2009) explored CRAM systems inside greenhouses as a supplemental CO_2 source. The researchers composted a mixture of rice straw crop residue and pig manure, inoculated with fungal species, and found that CO_2 levels were more than double the levels in control greenhouses after eight days, reaching as high as 1000-1500 ppm in the morning. Increased CO_2 persisted for two weeks, and vegetable yields increased significantly compared to the control. Karim et al. (2020) devised similar trials using manure and wheat straw inoculated with fungus in indoor CRAM systems and had comparable success, measuring CO_2 concentrations between 1000-1500 ppm. Jin et al. (2009) found that the average yield increases over three sites were: celery (270%); leaf lettuce (257%); stem lettuce (87%);

oily sow-thistle (140%); and Chinese cabbage (227%). Karim et al. (2020) also recorded dramatic yield increases for cherry tomato, measuring an increase of 500 kg/hectare. Vitamin C and total soluble sugar content was also elevated while nitrate was decreased in the vegetables grown in greenhouses utilizing the CRAM composting method in both studies (Jin et al., 2009; Karim et al., 2020).

Compost feedstocks determine the levels of CO_2 emitted during the indoor composting process (Thomson et al., 2022). Bean dregs from tofu production have been shown to be particularly effective at increasing CO_2 emissions when added as supplemental feedstocks in CRAM systems, but also lead to loss of nitrogen as emitted ammonia and NO_x gases (Thomson et al., 2022; Yang et al., 2020). However, the combination of bean dregs with biochar increases CO_2 emissions while preventing nitrogen loss in the final compost product, while also reducing emissions of the potent greenhouse gases methane and nitrous oxide (Yang et al., 2020). The addition of porous mineral feedstocks such as clays, zeolite, and diatomite have resulted in similar CO_2 increases combined with emission reductions of more harmful greenhouse gases (Thomson et al., 2022).

Water treatment for alkaline irrigation water

Options are limited in reducing the alkalinity and pH of irrigation water apart from neutralization with acids. The simplest alternatives involve growing crops in environments suited to their production and utilizing clean, neutral irrigation water, but this is not always feasible or possible.

Soluble salts in irrigation water may be the cause of high alkalinity, and many producers use reverse osmosis systems to remove them, though these systems may be expensive (Texas A&M University, n.d.; University of Massachusetts Amherst, 2015). Reverse osmosis systems work by utilizing pressure to force salty water through a membrane, leaving salts on one side and purified water on the other (Will & Faust, 2015). In situations where a water source is extremely high in soluble salts, reverse osmosis may be useful, but also introduces risks of micronutrient deficiency since these are also removed (Texas A&M University, n.d.).

Modest and temporary pH reductions can be achieved through the cultivation of specific cover crop legumes like alfalfa, fava bean, vetch, and lupine (Brautigan et al., 2014; R. K. Xu et al., 2002; Yan et al., 1996). Plant roots may secrete acidic hydrogen ions as they grow, but once the plants are removed, the pH tends to rise back to previous levels within months (Brautigan et al., 2014; Yan et al., 1996). However, retaining the crop stubble prolongs the pH reduction effect (R. K. Xu et al., 2002).

Brautigan et al. (2014) found that the application of a combination of earthworms and horse manure significantly lowered soil pH, but did not attribute it to the acidity of their castings. Instead, they concluded that the worms dragged manure deeper into the soil profile. While manure tends to have an alkaline pH, the authors attributed the pH reduction to the release of acids by the worms as they digested the manure, the secretion of acids by microbes digesting the manure, and by the decomposing corpses of worms (Brautigan et al., 2014).

Requested NOSB Discussion Topic

Focus Question: Describe the use frequency and application rates of all application methods, including in greenhouses and others.

Greenhouse atmosphere enrichment

Quantifying optimal application rates and use frequency for greenhouse CO_2 enrichment is difficult because so many factors must be considered in indoor production systems, including construction materials, climate, available energy sources, growth substrate, water supply, nutrient supply, and labor (Hemming et al., 2008; Vanthoor, 2011). Particularly in Western Europe, several software systems are available to help automate the control of these factors (Hemming et al., 2008).

In cooler climates, supplemental CO_2 is most often utilized from fall to early spring since vents tend to be closed for temperature control during cold periods (Poudel & Dunn, 2017). Many commercial operators use computers combined with gas analyzer instruments to automate supplementation (Hemming et al., 2008; Ontario Ministry of Agriculture, Food and Rural Affairs, 2002). The Ontario Ministry of Agriculture (2002) provides a mathematical formula for sustaining CO_2 levels of 1300 ppm during the day:

> *A typical greenhouse with a 2.4 m gutter has an approximate air volume of 400* m^3*/100* m^2 *floor area. To increase the level from 300–1,300 ppm requires the addition of 1,000 ppm or 0.1%* CO_2*. This requires 0.40* m^3 *or 0.75 kg of* CO_2 *per 100* m^2 *of greenhouse floor space. Add this amount before sunrise because photosynthetic activity is usually the greatest early in the day. After a level of 1,300 ppm is achieved, it must be maintained…Leaks in the greenhouse allow a continuous infiltration of outside air, which contains only 340 ppm* CO_2*. An average value for infiltration in a glass house would be one air change per hour. To compensate for this dilution, approximately 0.37 kg* CO_2*/100* m^2 *must be added to maintain the desired level of 1,300 ppm* CO_2*.*

Note that this recommendation is from 2002, when outdoor CO_2 levels were lower than today. Additionally, since these recommendations were based on the climate of Ontario, Canada, we can expect significant variation from other growing regions. However, we can provide very rough estimates of *maximum* application rates in the United States using these guidelines if we make a few basic assumptions. If we assume that *all* greenhouse acreage in the United States sustains daytime CO_2 concentrations in greenhouses at 1300 ppm, and that *all* producers use natural gas burners to produce the CO_2, we can calculate maximum usage rates and maximum natural gas consumption resulting from it. Using the most recent data from the USDA NASS 2017 census of agriculture (2019) detailed below, and statistics provided by the U.S. Energy Information Administration (2022) we could conclude that in this hypothetical scenario:

- U.S. greenhouse producers would use a maximum of approximately 129,000 kg of CO_2 per day to maintain 1300 ppm CO_2.
- 129,000 kg of CO_2 can be produced from approximately 71,800 cubic meters of natural gas (also equivalent to 71,800 liters of propane).
- The U.S. population currently uses approximately 6.5 cubic meters of natural gas per capita, per day.
- The maximum amount of natural gas usage for all greenhouse acreage CO_2-enrichment is equal to the usage of approximately 11,000 people per day.
- Maximum application of CO_2 to greenhouses equals approximately 0.008% of the natural gas used in electricity generation in the U.S. per day.

Gas burners also serve the second purpose of heating the indoor space, and it is important to note that fuel used primarily for heating is not included in these calculations.

Interest in the utilization of repurposed CO_2 in industrial agricultural greenhouses has increased recently, partly for yield enhancement, but also as part of a mitigation strategy for reducing greenhouse gas emissions (IEA, 2019). The global leader in CO_2 consumption for agricultural greenhouse use is the Netherlands, estimated to use 5-6.3 million metric tons (MMT) annually (IEA, 2019). However, it is estimated that only 0.5 MMT comes from repurposed external sources, with the remainder being generated onsite from burning natural gas, meaning that the effect on greenhouse gas emissions is a net increase (IEA, 2019). In the Netherlands, the horticultural industry (where greenhouses are used extensively) was responsible for emitting 8.0 MMT of CO_2 in 1996, 12% more than at the end of the previous decade (Esmeijer, 1999).

Furthermore, only 10-20% of CO_2 pumped into greenhouses is absorbed by plants, with the remainder vented outside to control humidity (Esmeijer, 1999; IEA, 2019). The IEA (2019) states that greenhouse use has a low potential as a carbon capture climate change mitigation strategy because biological storage is exceedingly temporary. The carbon utilized in biological processes is ultimately eaten and digested, decomposes, is composted, or is used in the production of other products and fuels, all of which release the CO_2 back to the atmosphere following combustion or decomposition (Esmeijer, 1999; IEA, 2019).

In 2017, there were 10,849 greenhouse farms in the U.S producing vegetables and fresh cut herbs (USDA NASS, 2019). The area under greenhouse production for vegetables and fresh cut herbs was 112,564,105 square feet, or 2,584 acres. Sales from these farms was $748 million. Tomatoes were the most common crop grown, accounting for 56% of greenhouse area (63,929,576 square feet, or 1,468 acres) (USDA NASS, 2019).

At the same time, there were 846 farms in the U.S. producing greenhouse fruits and berries (USDA NASS, 2019). The area under greenhouse production for greenhouse fruits and berries was 11,708,439 square feet, or 269 acres. Sales from these farms was $25 million (USDA NASS, 2019).

States with the most area in greenhouse production for vegetables and fresh cut herbs include (USDA NASS, 2019):

- California: 35.2 million ft^2 (808 acres)
- Texas: 7.4 million ft^2 (170 acres)
- New York: 5.4 million ft^2 (124 acres)
- Ohio: 5.0 million ft^2 (115 acres)
- Pennsylvania: 4.1 million ft^2 (94 acres)
- Maine: 3.4 million ft^2 (78 acres)

States with the most area in greenhouse production for fruits and berries include (USDA NASS, 2019):

- California: 6.3 million ft^2 (145 acres)
- Florida: 1.8 million ft^2 (41 acres)
- Oregon: 0.7 million ft^2 (16 acres)
- Michigan: 0.3 million ft^2 (7 acres)

In Canada, there were estimated to be 2,978 greenhouses in operation in 2015, with a total area of 256,153,124 square feet, or 5,880 acres (Alberta Government, 2018). Greater than half of that area was in the province of Ontario alone, covering an area of 150,908,226 square feet, or 3,464 acres (Alberta Government, 2018). Not all greenhouse area is used in vegetable production (Alberta Government, 2018). In 2019, the harvested area of greenhouse vegetables in Canada was 189,592,249 square feet, or 4,352 acres over 838 operations (Agriculture and Agri-Food Canada (AAFC), 2020). The 2019 values for the top-producing Canadian provinces by harvested area of greenhouse vegetable production are (Agriculture and Agri-Food Canada (AAFC), 2020):

- Ontario: 133.4 million ft^2 (3,062 acres)
- British Columbia: 32.6 million ft^2 (748 acres)
- Quebec: 13.7 million ft^2 (315 acres)
- Alberta: 8.0 million ft^2 (184 acres)

The majority of greenhouse vegetables grown in Canada are by far tomatoes, cucumbers, and peppers (Agriculture and Agri-Food Canada (AAFC), 2020; Alberta Government, 2018). Of the vegetables exported (by volume and value), greater than 99% are sold in the United States (Agriculture and Agri-Food Canada (AAFC), 2020).

Irrigation water acidification

The optimal frequency and application rates for irrigation water acidifiers, including CO_2, are similarly difficult to quantify. Factors affecting the amount of necessary acidifier to reach a certain pH and alkalinity include the alkalinity of the water, the crop, the acid dissociation constant of the acidifier, soil or substrate pH and alkalinity, and container size (Whipker et al., 1996). Each growing environment necessitates different adjustments to reach optimal conditions. Many universities agricultural extension services offer calculators to help growers determine sufficient volumes of acidifiers to use, but these typically only focus on nitric, sulfuric, phosphoric, and sometimes citric acids.

Some of the CO_2 from enriched water escapes into the surrounding air (Enoch & Olesen, 1993). In greenhouses, examples described by Enoch & Olesen show an increase up to 800 ppm over normal atmospheric concentrations.[10] Some of this may be absorbed by plants, but greenhouses with similar levels supplied in gaseous form are known sources for emitting CO_2 (Esmeijer, 1999).

Relation to total CO_2 emissions

Anthropogenic emissions of CO_2 come from a variety of sources (see Figure 10, below), with the largest sources relating to transportation, electric power generation, and industrial usage (US EPA, 2022). Within agricultural activities, which in the U.S. cause approximately 10% of all emissions, the EPA does not mention CO_2 enrichment of irrigation water or greenhouse atmosphere. Outside of agricultural values, the EPA estimates that in 2020, the emissions from captured CO_2 (such as might be used to produce bottled CO_2 for greenhouse use) were 5.0 MMT.[11] At the same time, natural gas systems overall (such as might be burned for greenhouse use) contributed 35.4 MMT of CO_2 (US EPA, 2022). Greenhouse and field use of captured CO_2 and natural gas burner systems are only some of the many uses that would fall under the EPA's metrics.

For comparison, agricultural soil management (such as applying fertilizer, irrigation, drainage, tillage and other practices that produce N_2O) contributes the most agricultural emissions, with 345 MMT of CO_2 equivalent produced in 2020 (see Figure 11, below); however many of these emissions are actually other gases such as N_2O and CH_4 (US EPA, 2022).

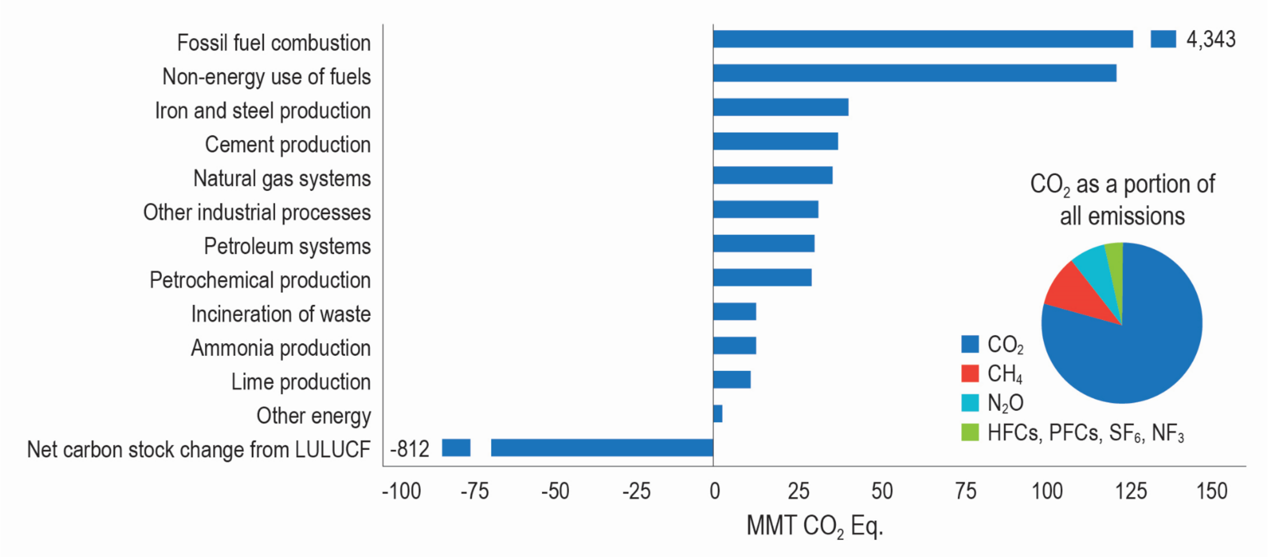

Figure 10: 2020 Sources of U.S. CO_2 emissions in millions of metric tons equivalent (MMT CO_2 Eq.). LULUCF (land use, land-use change, and forestry) represents the negative emission (CO_2 removal) resulting from carbon storage in forests, croplands, wetlands, grasslands, and settlements. Adapted from U.S. EPA (2022).

Note: MMT CO_2 Eq. represents the combination of all greenhouse gases and their global warming potential (GWP), adjusted to the equivalent GWP of CO_2. Emissions from aluminum production, carbide production, CO_2 consumption, ferroalloy production, lead production, magnesium production, other process uses of carbonates, phosphoric acid production, soda ash, titanium dioxide, urea consumption, and zinc production are included in "Other industrial processes." Emissions from abandoned oil and gas wells and coal mining are included in "Other energy." In the pie graph, CO_2 represents 78.8% of emissions. The other greenhouse gases represented in the pie graph are CH_4 (methane), N_2O (nitrous oxide), HFCs (hydrofluorocarbons), PFCs (perfluorocarbons), SF_6 (sulfur hexafluoride), and NF_3 (nitrogen trifluoride).

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[10] We were not able to evaluate the papers referenced by Enoch & Oleson ourselves due to language barriers and lack of availability for these resources, which were older and not found in contemporary databases.

[11] The EPA notes that this category of CO_2 includes a variety of commercial applications, including food processing, chemical production, carbonated beverage production, and refrigeration (US EPA, 2022).

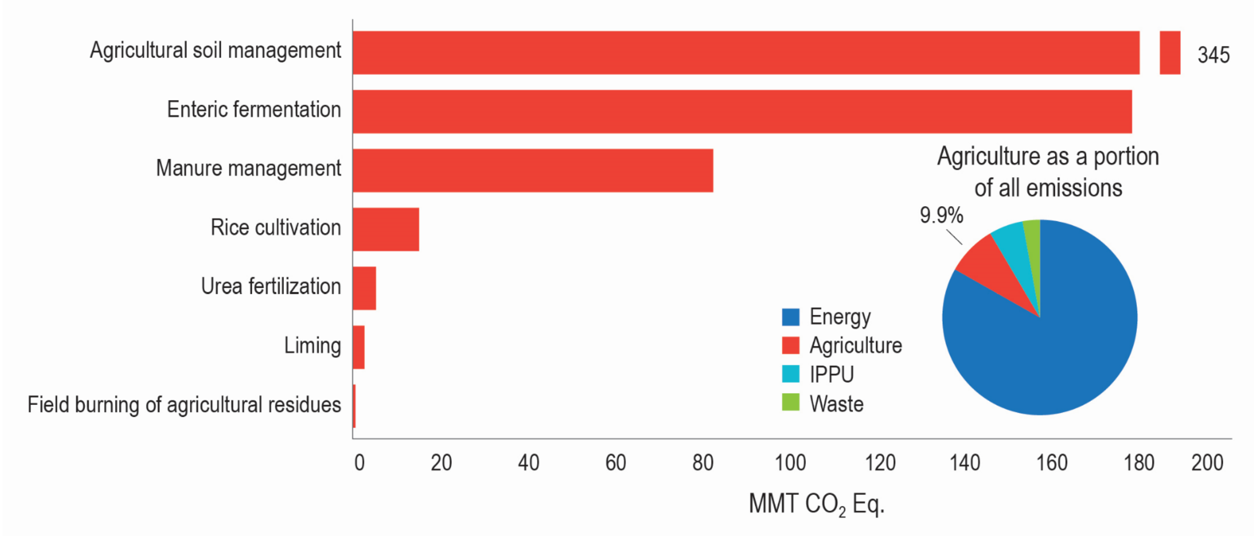

Figure 11: 2020 Agriculture sector U.S. greenhouse gas emission sources in MMT CO_2 Eq. Adapted from U.S. EPA (2022).

Note: Enteric fermentation is the process that occurs in the stomachs of cows, sheep, and goats, where microbes digest food and produce methane. IPPU stands for Industrial Processes and Product Use and includes emissions from non-energy related material processing and manufacturing.

Report Authorship

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All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.

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