

Greenhouse Gases Formation and Emission

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Glossary

Biogeochemical cycles Natural pathways by which the chemical elements that are present in the organic matter are circulated through biological, geological, and chemical cycles in the biotic and abiotic Earth's compartments.

Global warming A rise in the Earth's standard atmospheric temperature that causes related changes in climate and that may result from the greenhouse gases effect.

Introduction

The rising temperature of earth, known as global warming (GW), is mainly the result of the rise of greenhouse gases (GHGs) concentration in the atmosphere since the beginning of the 20th century, mostly due to anthropogenic activities. Global warming, as we know, is one of the major threats to the environment because of the resulting climate change. Oxygen (O₂) and nitrogen (N₂) are the principal atmosphere gases at concentrations of 21% and 78%, respectively, nevertheless it is thought that they do not absorb or emit thermal radiation. Water vapor and less abundant gases, such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O), because of their long atmospheric lives and their relatively high thermal absorption capacities, are generally known as greenhouse gases. Besides water vapor that is not considered to be a cause of man-made global warming because it does not persist in the atmosphere for more than a few days, the most important greenhouse gas is CO₂, followed by CH₄ and N₂O which are the other most relevant contributors to GW. Hundred year global warming potential of methane, nitrous oxide and other GHGs is compared to CO₂ in terms of CO₂ equivalence (CO₂eq). This last is a simple way to normalize all greenhouse gases in a standard unit based on the radiative forcing of a unit of CO₂ over 100 years. For example 1 g of methane has a global warming potential 28 times higher than 1 g of CO₂ and so it is expressed as 28 g of CO₂eq. Biological and/or non-biological, as natural and anthropogenic processes are involved in GHG cycling (most carbon (C) and nitrogen (N) cycles).

Soils can be a source or a sink of CO₂, CH₄, and N₂O depending on the specific conditions. Natural soils are mainly a sink for natural GHGs and sequester as much C and N they emit, but due to human activities, mainly agriculture, soils can be mainly a source for GHGs. In fact, intensive agriculture, sustained by mineral fertilizer use, has contributed significantly to the elevation of atmospheric GHGs, including CO₂, CH₄, and N₂O. Rising GHG emissions usually lead to a decrease in soil C. Currently, soil organic C is twice that of all standing crop biomass, making it an extremely important player in the C cycle.

Anyhow, agronomic practices have the potential to reduce agricultural GHG emissions. Main management practices that impact GHG emissions and soil C content include various tillage practices, several N fertilization amounts and typologies (mineral, manure, or a combination of both), the use of cover crops, aeration, and water levels. Moreover, other agriculture GHGs sources are intensive livestock such as cattle intensive production systems and rice paddy fields. Furthermore deforestation, especially in tropical rainforest, adds more C to the atmosphere than cars and trucks traffic; the reason is that when trees are cut down or dead, they release their carbon content in the environment. Employing best agricultural management practices (BMPs), we can promote the sequestration of CO₂ plus N₂O and the preservation of soil C. Measuring soil C storage and GHG emissions and using them as metrics to evaluate BMPs are vital in understanding agriculture's role in this topic.

Carbon Greenhouse Gases

Carbon Dioxide (CO₂)

CO₂ is a colorless gas with a density about 50% higher than that of dry air. In the CO₂ molecule (molecular weight of 44 g mol⁻¹) carbon atom is covalently double bonded with two oxygen atoms, and it is naturally present in the earth's atmosphere. Because the oxygen of CO₂ molecule forms intermolecular hydrogen bonding with the hydrogen of water, CO₂ is soluble in water, and it occurs in groundwater, rivers and lakes, ice caps, glaciers, and seawater (CO₂ solubility in water is about 1.45 g L⁻¹ at 15°C) and in deposits of petroleum and natural gas too. CO₂ is odorless at usual concentrations, however its aqueous solution has, at high concentrations, a sharp and acidic odor and taste.

Among the greenhouse gases, CO₂, as presented in the introduction paragraph is the reference gas with a global warming potential of 1, lower than all other greenhouse gases. However it contributes > 60% to GW due to its huge emission amount. The concentration of CO₂ in the atmosphere has increased from approximately 277 parts per million (ppm) in 1750, at the beginning

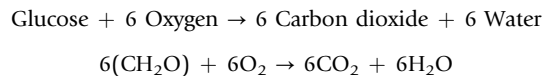
of the Industrial Era, to 402.8 ± 0.1 ppm in 2016. The increase of atmospheric CO₂ above the preindustrial levels was primarily caused by the release from deforestation and other land-use change activities. While emissions from the burning of fossil fuels started before the Industrial Era, they only became the dominant source of anthropogenic emissions to the atmosphere from around 1920 and their relative share has continued to increase until present.

Sources of atmospheric CO₂ include volcanoes activities, the combustion and decay of organic matter, respiration of aerobic (oxygen-using) organisms; extraction and burning of fossil fuels, clearing of lands, and production of cement and steel and so on by human activities.

These sources are at least partially balanced by a set of physical, chemical, or biological processes, called “sinks,” that tend to remove CO₂ from the atmosphere. The main C sink are plants that through the photosynthesis process grab CO₂ from atmosphere.

Plant life is a fundamental natural sink. In the oceans, marine life can absorb dissolved CO₂, and some marine organisms even use CO₂ to build skeletons and other structures made of calcium carbonate (CaCO₃).

Organic matter respiration, operated by heterotrophic organisms, is the most important path through which the CO₂, photosynthetically fixed as glucose, comes back to the atmosphere:



This organic matter degradation occurs in both soils (primarily in the rooting zone) and oceans (within the surface mixed layer). Organic matter respiration and CO₂ release in the atmosphere are controlled in part by the composition of the organic matter and the environmental factors (e.g., temperature, soil moisture, and soil porosity, texture/mineralogy).

In total, more than twice as much C is stockpiled in the world's soil than in the vegetation or atmosphere combined. Considering all the C stored in soil, soil organic carbon (SOC) makes up about 50% of all soil organic matter (SOM).

About a third of the soil organic C occurs in forests, another third is in grasslands and savannas, and the rest is in wetlands, croplands, and other biomes. SOM is composed by soil microorganisms communities (mainly bacteria and fungi), plant and animal tissues, fecal material, and products derived from their decomposition. Soil CO₂ flux is primarily the result of a combination of microbial decomposition of SOM and plant root respiration. The main drivers of soil CO₂ flux are soil temperature, soil moisture, and substrate C availability. Temperature affects CO₂ flux by speeding up the rate of microbial decomposition when soils are warm and water is not a limiting factor. Although rising temperatures cause an increase in CO₂ flux rate from soils, in some parts of the world there are no clear trends of decreasing soil carbon with increasing mean annual temperature. This is due, partly, to competing processes within the system, such as SOC rising due to increased primary productivity that principally occurs through the photosynthesis process (better water and nutrient availability), and SOC decreasing by increased respiration processes. While in the short-term, warming depletes SOC, in the long-term, C losses by accelerated microbial respiration may be equalized by increases in C inputs to the soil tied to increased net primary production, as well as any acceleration of soil physico-chemical “stabilization” reactions. Additionally, changes in microbial community composition or declines in the temperature sensitivity decomposition processes may reduce the response of microbial respiration to increasing temperature over time (i.e., thermal acclimation cold soil and air temperatures have the opposite effect on CO₂ flux rate, causing it to slow down). Even though slowed, soil microorganisms maintain both catabolic (CO₂ production) and anabolic processes (biomass synthesis) under frozen conditions. Because of this, gaseous exchange between the atmosphere and soil does not stop even under frozen soil, resulting in the accumulation of CO₂ during winter and its release into the atmosphere during spring thaw events. Another dominant factor controlling the net exchange of GHGs is soil moisture, which can vary dramatically over time and space. The production and transport of GHGs in soil is strongly affected by changes in soil moisture through diel 24-h period cycles, wet-up and dry-down events, management practices, seasonal patterns, and interannual variation in climate. Overall, when water is limiting, plant and microbial availability increase with soil moisture, thereby increasing soil CO₂ flux directly by alleviating plant and microbial desiccation stress and indirectly by increasing substrate availability (via higher rates of plant growth, photosynthesis, belowground C allocation by root exudate) and microbial access to substrate for example, increase C diffusion through soil water. Finally, respiration generally increases with C availability. Plant respiration is largely dependent on C from current photosynthetic activity and, under non-limiting soil temperatures and moisture availabilities, microbial respiration increases with labile C availability. Thus, soils with high organic matter inputs and stocks, like those found near the equator, means greater C substrate availability, which is synonymous with greater flux. Depth and placement of soil carbon is yet another factor to consider when attempting to make precise conclusions about CO₂ flux. For example, in agroecosystems, the bulk of SOM is within the top 10 cm of the soil surface.

Because of this, temporal dynamics of CO₂ flux are more intimately related to air temperature than to soil temperature. Also, it is known that the respiration rates of many soils are strongly linked with the amount of carbon not intimately associated with minerals. Mineral soil occurs below the litter and organic layer, where soil carbon may be closely associated with mineral particles—accounting for over 60% of carbon in most forest soils, proposing that the decomposition/respiration rate of mineral soil carbon is relatively insensitive to temperature. This is because the carbon located here may be protected from microbial mineralization by stabilization mechanisms, such as occlusion in soil aggregates (physical protection) or interactions with mineral surfaces (chemical sorption to mineral surfaces).

Methane (CH₄)

CH₄ is the second most important greenhouse gas in volume after CO₂, contributing to global warming potential with 28 times more infrared radiative heating effect than CO₂ on a mole-per-mole basis at a 100 year time horizon. Its atmospheric concentration, due to human activity, has increased by a factor of 2.5 since preindustrial times, that is, from 722 ppb in 1750 to 1803 ppb in 2011. Furthermore, after almost one decade of stable CH₄ concentrations since the late 1990s, atmospheric measurements have shown a renewed concentration increase since 2006, probably tied to a rise in natural wetland and fossil fuel emissions.

Generally, CH₄ emissions in atmosphere can be due to both human activities or natural processes from biogenic, thermogenic or pyrogenic sources. Anthropogenic emissions account for 50%–65% of total emissions including coal mining, natural gas use, agriculture, wastewater and waste treatment.

Considering CH₄ budget for the decade of 2000–09 (bottom-up estimates) agriculture and waste sectors (rice, animals and waste) are the second contributors to biogenic CH₄ emissions (with values ranging from 187 to 224 Tg (CH₄) year⁻¹) after natural wetlands emissions that ranged from 177 to 284 Tg (CH₄) year⁻¹.

Soils play an important role in the CH₄ cycle because both methanogenesis (CH₄ production) and methanotrophy (CH₄ oxidation) take place in them. In view of this soils CH₄ fluxes are the net result of the CH₄ production by methanogenesis and CH₄ oxidation by methanotrophy processes.

Methane production

Methanogenesis is operated by strictly anaerobic bacteria which requires negative oxydo-reduction potentials ($E_h < -200$ mV). Methanogens belong to the domain Archaea which have a limited trophic spectrum comprised of a small number of simple substrates: H₂ + CO₂, acetate, formate, methylated compounds (methanol, methylamines, dimethylsulphur), and primary and secondary alcohols. This allows to distinguish five trophic groups of methanogens: hydrogenotrophs, formatotrophs, acetotrophs, methylotrophs, and alcoholotrophs. The two major pathways of CH₄ production in most environments where organic matter decomposition is significant are acetotrophy and CO₂ reduction by H₂.

The possible pathway for CH₄ emission from soil are: (i) diffusion of dissolved CH₄ along the concentration gradient, (ii) release of CH₄-containing gas bubbles (ebullition), and (iii) transport via the aerenchyma of vascular plants (plant-mediated transport).

The first process, diffusion, takes place because of the formation of a CH₄ concentration gradient from deeper soil layers, where the production of CH₄ is large, to the atmosphere, while oxidation of CH₄ occurs in upper layers. Diffusion is a slow process compared to the other two transport mechanisms, that is, ebullition and plant-mediated transport, but it is biogeochemically important because it extends the contact between CH₄ and methanotrophic bacteria in the upper aerobic layer, promoting CH₄ oxidation.

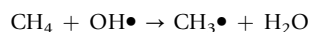
The second process, ebullition, takes place when CH₄ production is large. Gas bubbles are formed and emigrate to the surface. As this process is fast, CH₄ oxidation is absent or negligible.

The third process, plant mediated transport, takes place through an internal system of continuous air spaces named aerenchyma, a structure which is developed by vascular plants to adapt to flooded environments. The basic function of this structure is to transport the O₂ necessary for root respiration and cell division in submerged organs, but it is also used for CH₄ transportation from the rhizosphere to the atmosphere, bypassing the aerobic, CH₄-oxidizing layers. This process involves two major mechanisms: molecular diffusion and bulk flow. The gradient of CH₄ concentration formed inside the aerenchyma conduits is the driving force for CH₄ diffusion from the peat root zone to the aerial parts of the plant. The other plant-mediated transport mechanism, bulk transportation, involves the migration of CH₄ along the plant, also through the aerenchyma structure, from the leaves to the rhizome and back to the atmosphere through old leaves or horizontal rhizomes connected to other shoots. The driving force for this process is a pressure gradient generated by differences in temperature or water vapor pressure between the internal air spaces in plants and the surrounding atmosphere. This is a very efficient and rapid mechanism of CH₄ transportation and, in consequence, it is responsible for most of CH₄ emissions (>95%) to the atmosphere from rice paddies.

The factors controlling CH₄ production in soil are anaerobic conditions and redox potential, electron acceptors, substrate availability, temperature, diffusion, water availability and water table, soil pH and salinity, fertilizer and manure additions and amendments, trace metals, competitive inhibition, vegetation, plant species and cultivars, and elevated CO₂ concentrations.

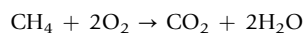
Methane oxidation

The major fraction of CH₄ emitted in the atmosphere is submitted to oxidation. Oxidation by OH radicals represent the main sink of atmospheric CH₄ (around 90% of the global CH₄ sink) and it takes place mostly in the troposphere according to the reaction:



The remaining sink is thought to be split roughly equally between the stratosphere (removal by OH and O¹[D]) and biological consumption in near-surface soils. Uptake of methane occurs via oxidation by specialized aerobic bacteria, methanotrophs, although CH₄ oxidation can be also monitored in anaerobic conditions.

The aerobic methane oxidation, operated by methanotrophs, can be summarized as follow:

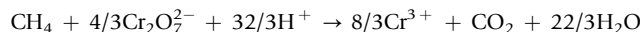
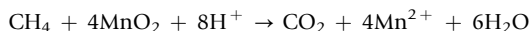
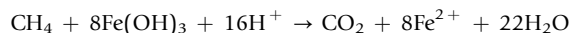


Aerobic methanotrophic bacteria can be classified in three groups (type I, II, and X) considering morphological features, membrane structures, guanine and cytosine content, phospholipid fatty acids composition and various other physiological characteristics.

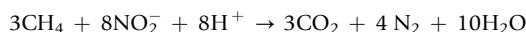
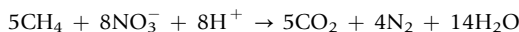
Several mechanisms have been offered to explain anaerobic CH₄ oxidation. First, sulfate-driven anaerobic methane oxidation:



Other electron acceptors such as oxides of iron, manganese and chrome, could also oxidize methane anaerobically as below reported:



Another proposed CH₄ oxidation process is the anaerobic oxidation of methane coupled to denitrification with CO₂ release as below summarized:



Biological anaerobic CH₄ oxidation is done by a consortium of anaerobic archaea in association with anaerobic bacteria.

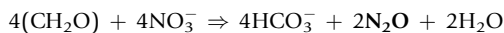
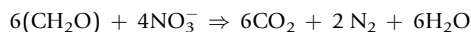
Optimal conditions for most of methanotrophs have been found in environments with near neutral pH, temperature in the mesophilic range (ca. 25°C) and low salinity.

Nitrogen Greenhouse Gases

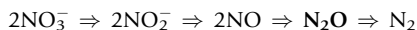
Nitrous Oxide (N₂O)

The N₂O is one of the most important greenhouse gases with a global warming potential, an index of the total energy added to the climate system by a component in question relative to that added by CO₂, for a time horizon of 100 years of 298 CO_{2(eq)}. N₂O is also capable of ozone depletion with negative impact on world life due to the lower capability to shield negative fraction of solar radiation (UV). The concentration of N₂O in the atmosphere increased at a rate of 0.73 ± 0.03 ppb year⁻¹ over the last three decades, mostly caused by nitrification and denitrification reactions of reactive nitrogen in soils and in the ocean.

The major source of N₂O in the atmosphere is heterotrophic denitrification, that is, reduction of nitrate to nitrogen gas under anoxic conditions:



It is generally agreed that during heterotrophic denitrification, nitrate is reduced to nitrite, which is followed by a stepwise reduction to nitric oxide, nitrous oxide, and finally nitrogen gas as below schematized:



This reaction is irreversible and occurs in the presence of available organic substrate mainly under anoxic or anaerobic conditions, where NO₃⁻ nitrogen is used as an electron acceptor in place of oxygen. Nitrate is the first inorganic compound which used by bacteria as electron acceptor after dissolved oxygen depletion from the water-soil system. Denitrification starts at redox potential values of about +220 mV. Environmental factors known to influence denitrification rates include the absence of O₂, redox potential, soil moisture, temperature, pH value, presence of denitrifiers, soil type, organic matter, nitrate concentration and the presence of overlying water.

Facultative heterotrophic anaerobic bacteria are the main actors of heterotrophic denitrification. Most denitrifying bacteria are chemoheterotrophs. They obtain energy solely through chemical reactions and use organic compounds both as electron donors and as a source of cellular carbon. Denitrifying bacteria are aerobes that substitute nitrate for oxygen as the terminal electron acceptor when there is little or no O₂ available. The genera *Bacillus*, *Micrococcus*, and *Pseudomonas* are probably the most important in soils; *Pseudomonas*, *Aeromonas*, and *Vibrio* in the aquatic environment.

The quantity of N₂O evolved during denitrification depends upon the amount of nitrogen denitrified and the ratio of N₂ to N₂O produced. The ratio is also affected by aeration, pH, temperature and nitrate to ammonia ratio in the denitrifying system. If the pH is below 4.5, the denitrification rate is relatively slow and only N₂O is produced. At pH > 5, N₂ is the main end product of denitrification. It has also been shown that certain amount of N₂O is formed during nitrification, however, it is difficult to distinguish between nitrification and denitrification as sources of N₂O.

Ozone (O₃)

O₃ is a short-lived trace gas that either originates in the stratosphere or is produced in situ by precursor gases (monoxide (CO), CH₄, and non-CH₄ hydrocarbons in the presence of nitrogen oxides (NO_x)) and sunlight. It is a bluish gas with a pungent smell,

dipolar and electrophilic molecule capable of very selective reactions, present in the air at concentrations of 0.01–0.05 ppm. In the atmosphere the presence of the O₃ is crucial for any life because it prevents shortwave solar UV radiation in the UVB (λ 280–315 nm) and UVC (λ 200–280 nm) from penetrating the atmosphere and reaching the Earth's surface. On the other hand O₃ exert a greenhouse effect increasing the global warming. As reported by the Intergovernmental Panel on Climate Change in the fifth assessment report: emissions of carbon monoxide and volatile organic compounds, a not well-defined group of hydrocarbons, lead to production of ozone on short time scales. By affecting OH and thereby the levels of CH₄ they also initiate a positive long-term ozone effect. The effects via ozone and CH₄ cause warming, and the additional effects via interactions with aerosols and via the O₃–CO₂ link further increase the warming effect.

See also: Ecological Data Analysis and Modelling: Carbon Biogeochemical Cycle and Consequences of Climate Changes. Ecological Processes: Decomposition and Mineralization. Global Change Ecology: Microbial Cycles; Emergence of Climate Change Ecology; Global Negative Emission Land Use Scenarios and Their Ecological Implications. Human Ecology and Sustainability: Carbon Footprint

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