Review

Stable Isotopes in Greenhouse Gases from Soil: A Review of Theory and Application

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Abstract: Greenhouse gases emitted from soil play a crucial role in the atmospheric environment and global climate change. The theory and technique of detecting stable isotopes in the atmosphere has been widely used to an investigate greenhouse gases from soil. In this paper, we review the current literature on greenhouse gases emitted from soil, including carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O). We attempt to synthesize recent advances in the theory and application of stable isotopes in greenhouse gases from soil and discuss future research needs and directions.

Keywords: greenhouse gas; stable isotope; soil respiration; isotope fractionation

1. Introduction

Climate change impacts on human lives and environmental safety, and has received considerable attention all over the world over the past few decades. Greenhouse gas emissions, principally changes in atmospheric carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) concentrations, play an important role in global climate change, [1–3]. These greenhouse gases account for a lower proportion of the atmospheric composition than oxygen and nitrogen, but are important because they increase the energy input to the surface of the lower atmosphere by absorbing infrared radiation from the Earth's surface [4]. CO₂, CH₄, and N₂O are the three primary greenhouse gases exchanged between the soil and the atmosphere [5], contributing about 80% of the current global radiative forcing [6], and these greenhouse gas emissions can be further enhanced by the impact of natural emissions (e.g., volcanic and hydrothermal) and human activities (e.g., fossil fuel combustion and agricultural practice) [7,8].

Soil is a major source of greenhouse gases [9], where emissions of CO₂, CH₄, and N₂O related to soil account for 35%, 47%, and 53% of total annual CO₂, CH₄, and N₂O emissions, respectively, including industry, agriculture, and so on [10]. Reducing soil greenhouse gas emissions is an effective pathway for global climate change mitigation [11,12]. However, the amount of greenhouse gas emission from soils, which needs to be determined the contribution to global carbon (C) budgets, is still not clear [10,13]. Stable isotope technologies will be necessary to enhance the quantitative assessment of soil constituents and reduce uncertainty in estimating the source of C in the soil or atmosphere, and for assessing the different responses of soil and plants to environmental conditions. As one of the most powerful tools for understanding ecological and environmental processes, many stable isotope methods have been used to record environmental information and monitor the ecological process at different spatial and temporal scales, or address issues that are intractable using other methods [14]. The use of stable isotopes (¹²C and ¹³C, ¹⁴N and ¹⁵N, ¹⁶O and ¹⁸O) allows the identification of greenhouse gas components and drivers. Carbon isotopes are only a little fractionated in trophic chains and are therefore more suitable as a marker, whereas nitrogen (N) isotopes are considerably fractionated in

trophic chains, which makes them less convenient but allows their use as an integral index of many ecological processes [15,16]. Therefore, in this review, we will offer some insight into the greenhouse gases, including CO₂, CH₄, and N₂O, emitted from soil based on the perspective of stable isotopes, and integrate our knowledge on greenhouse gas exchange between the soil and atmosphere.

2. Theory of Stable Isotope Techniques

2.1. Stable Isotopic Compositions

Stable isotope ratios of elements in the C, N and O components of plants and the soil environment often record and integrate ecological information relating to: (1) the identity of the ecological cycle processes that formed those elements' components; (2) the turnover rates of those formed elements' components processes; and (3) the environmental factor response during the decomposition or formation of organic and inorganic matter [17]. Many biogeochemical processes are often accompanied by changes in the concentration ratio between the stable isotopes of the elements C, N, and O (e.g., $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^{18}\text{O}$, respectively) [18]. Using C, N, and O stable isotope ratios of CO₂, CH₄, and N₂O may be an effective way of tracing the sources of fugitive emissions from soil respiration. Furthermore, isotope measurements can help in the attribution and quantification of surface sources because the magnitude of isotopic fractionation associated with each production pathway may differ [19]. Multiple stable isotopes exist for most chemical elements, and stable isotope ratios are expressed, using the δ -notation in per mil (‰), as the deviation of the sample's isotope ratio from the respective isotope ratio of the reference material [20], where

$$\delta^{13}\text{C}, \delta^{15}\text{N} \text{ and } \delta^{18}\text{O} = [(R_{\text{SAMPLE}} - R_{\text{STANDARD}}) / R_{\text{STANDARD}}] \times 1000$$

where $R_{\text{SAMPLE}} = {}^{13}\text{C}/{}^{12}\text{C}$, ${}^{15}\text{N}/{}^{14}\text{N}$, or ${}^{18}\text{O}/{}^{16}\text{O}$ of the sample and $R_{\text{STANDARD}} = {}^{13}\text{C}/{}^{12}\text{C}$ of the PDB standard (0.0112372), Air-N₂ for N (0.003676) or Vienna Standard Mean Ocean Water (V-SMOW) for O [21].

All plants discriminate against ${}^{13}\text{C}$ during photosynthesis but the extent of this discrimination is a function of the photosynthetic pathway type [22–24]. Terrestrial plants can be divided into two types of plants, C₃ and C₄, depending on the type of photosynthetic pathway [25]. Terrestrial plants that utilize the C₃ (Calvin cycle) pathway have $\delta^{13}\text{C}$ values ranging from approximately −35‰ to −20‰, plants that utilize the C₄ (Hatch–Slack) photosynthesis pathway have higher $\delta^{13}\text{C}$ values ranging from about −19‰ to −9‰, and the average $\delta^{13}\text{C}$ values of C₃ and C₄ plants are approximately −27‰ and −13‰, respectively [26,27]. Soil microbial and bacterial decomposition is one of the most important sources of greenhouse gases, using stable isotopes to trace soil nitrification and denitrification processes [28]. Therefore, the source of greenhouse gas components in the soil and atmosphere can be easily traced by using stable isotopes in the process of the ecosystem C cycle.

2.2. Soil CO₂, CH₄ and N₂O Stable Isotope Signatures

CO₂. The total emission of CO₂ from soils is one of the most important fluxes in the terrestrial ecosystem C cycle, controlling global C budgets and the ecological balance [29]. Soil C sequestration is also an effective method of reducing the atmospheric concentration of greenhouse gases, defined as the process of removing C from the atmosphere and depositing it in a reservoir (Figure 1) [30,31]. There are two different ways to exchange C between the soil and atmosphere, including direct and indirect exchange. First, the direct exchange of atmospheric greenhouse gases transforms these gases into soil inorganic carbon (SIC) compounds, and soil C is absorbed by roots and discharged directly into the atmosphere through plants. Second, in the indirect exchange of atmospheric CO₂, atmospheric CO₂ is incorporated into plant tissue through the photosynthetic process, and subsequently, part of the plant biomass is indirectly sequestered as soil organic carbon (SOC) during decomposition processes [1]. SOC is decomposed by microorganisms to form CO₂, which is returned to the atmosphere [32]. CO₂ is produced in the soil through a series of microbial processes and residual soil organic matter (SOM)

enriches ^{13}C . CO_2 is continuously transported to the overlying atmosphere via molecular diffusion and enriches ^{12}C [33]. However, the CO_2 emitted by the soil is not all derived from the decomposition of SOM, due to the soil C cycle being a complex and slow process, and other soil C sources, including C pools in the soil, heterotrophic or autotrophic organisms, root respiration, and turnover rates of C pools [26]. Therefore, using the information provided by the soil, it is still difficult to determine whether the soil is a C source or a C sink for atmospheric CO_2 . Previous research has reported the $\delta^{13}\text{CO}_2$ (the isotope ratio of CO_2) values of C_3 plants varied between -23‰ and -40‰ , and C_4 plants varied between -9‰ and -19‰ [34]. Drewer et al. [35] estimated that the $\delta^{13}\text{CO}_2$ values of *Miscanthus* (C_4 plants) ranged from -9‰ to -11‰ , and the farmland ranged from -22‰ to -29‰ after one year of *Miscanthus* removal. Pendall and King [36] found that the decomposition rate of SOM is high and the $\delta^{13}\text{C}$ values are low in the initial stage of topsoil C sequestration, and high $\delta^{13}\text{C}$ values were observed in subsoils. In addition, the subsoil isotope values were generally higher than the topsoil in CO_2 respiration. They suggested that microbial activity first consumes fresh residue in the topsoil, resulting in ^{13}C depletion, and ^{13}C enrichment of the subsoil.

Figure 1. Processes of soil greenhouse gas emissions (modified from Rastogi et al. [3]). O, oxidation; M, methanogenesis; N/D, nitrification and denitrification.

CH_4 . Rice fields are one of the most important anthropogenic emission sources of atmospheric CH_4 and contribute about 11%–13% of the total global emissions [37–39]. Rice fields play a key role in the increase of atmospheric CH_4 concentration and proper management can result in the soil acting as a C sink [40,41]. Stable isotope fractionation happens in the production, oxidation, and transport of CH_4 emission processes: (1) the preferential consumption of $^{12}\text{CH}_4$ by methanotrophic bacteria for CH_4 production; (2) the $^{12}\text{CH}_4$ is utilized faster than $^{13}\text{CH}_4$ by methanotrophic bacteria for CH_4 oxidation, and the enrichment of ^{13}C in the residual CH_4 ; (3) $^{13}\text{CH}_4$ is transported significantly slower than $^{12}\text{CH}_4$, leading to an isotope ratio difference [42–44]. Zhang et al. [37] observed the changes in the processes of CH_4 emission and the $\delta^{13}\text{C}$ value from fields and via paddy plants during the rice season in China (Figure 2). The rice growing season lasts about 113 days, and the CH_4 emission changed significantly over different periods. The CH_4 flux value with different days (D) appeared in the following order: $\text{D50} > \text{D70} > \text{D88} > \text{D20} > \text{D108}$. However, $\delta^{13}\text{C}$ had the opposite trend in CH_4 flux, with the highest and lowest values appearing on D108 (-68.7‰) and D50 (-61.5‰), respectively. It is most noticeable that there was a significant negative correlation between CH_4 emissions and the $\delta^{13}\text{C}$ value. Similar $\delta^{13}\text{C}$ values and patterns of variation were also observed in previous studies (Table 1). The change of

$\delta^{13}\text{C}$ occurs in the CH_4 emission processes, including production, oxidation and transport. The ^{13}C is enriched at the beginning of the season. Subsequently, a rapid depletion in ^{13}C occurs and reaches the lowest value, being mostly depleted in ^{13}C in the middle of the season. During the late period of the season, ^{13}C becomes enriched again.

Table 1. Overview of $\delta^{13}\text{C}$ values of CH_4 emissions in different countries from rice fields ^a.

Location	Seasonal Coverage	$\delta^{13}\text{CH}_4$ (‰)	Reference
Japan	throughout the season	−68 to −48	Uzaki et al., 1991 [45]
Japan	throughout the season	−72 to −56	Tyler et al., 1994 [46]
China	throughout the season	−71 to −52	Bergamaschi, 1997 [47]
	throughout the season	−71 to −58	
America	throughout the season	−66 to −61	Chanton et al., 1997 [48]
America	throughout the season	−58 to −53	Tyler et al., 1997 [49]
America	throughout the season	−63 to −46	Bilek et al., 1999 [42]
	throughout the season	−62 to −48	
Italy	throughout the season	−67 to −47	Marik et al., 2002 [50]
	throughout the season	−65 to −53	
Italy	throughout the season	−73 to −58	Krüger and Frenzel, 2003 [51]
Germany	throughout the season	−68 to −61	Conrad and Klose, 2005 [52]
China	throughout the season	−71 to −47	Zhang et al., 2012 [53]
China	throughout the season	−61 to −59	Zhang et al., 2014 [54]

^a Adapted from the study of Marik et al. [50] and Zhang et al. [53].

Figure 2. The relationship between CH_4 and $\delta^{13}\text{C}$ in time evolution mode (a) and the correlation between them (b) (from Zhang et al. [37]).

N_2O . N_2O is a potent greenhouse gas, and its content in the atmosphere affects the recovery of the ozone layer and contributes to about 6% of the global greenhouse effect [55,56]. Among the sources of anthropogenic N_2O emissions, roughly 58% are related to agricultural production systems [57]. According to the IPCC (Intergovernmental Panel on Climate Change) [13], soil ecosystems are the most important source of global N_2O emissions, representing about 65% of the total amount of N_2O emitted into the atmosphere, especially, farmland N fertilizer, which accounts for the largest proportion. An important source of N_2O in soils is related to microbiological processes: bacterial nitrification (N_2O as a byproduct) and denitrification (N_2O as an intermediate product) [28,58]. Nitrification includes autotrophic nitrification (microbes use CO_2 as a C source) and heterotrophic nitrification (microorganisms use organic carbon as a C source), and the heterotrophic nitrification substrate is organic nitrogen or inorganic nitrogen. N_2O production in soil during autotrophic nitrification is traditionally considered to be minor in comparison with denitrification [59]. Nitrification is a multistep process, involving the continuous oxidation of ammonia (NH_3) under aerobic conditions: $\text{NH}_3 \rightarrow \text{NH}_2\text{OH} \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^-$, and denitrification is a series of processes involving a

successive reduction of nitrate under anaerobic conditions: $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$ [60–62]. The atmospheric concentration of N_2O has been growing exponentially, mainly due to the growing food demand of the human population and increased use of chemical fertilizers, especially the use of nitrogen-based fertilizers, stimulating soil microbial nitrification and denitrification [63]. Stable isotopes have become a useful research tool for N_2O production processes, for inferring the sources, production and consumption processes, and better estimating the atmosphere N_2O budget [62]. The stable isotope ratio of N_2O quantifies the contribution of denitrification to N_2O flux and provides the basis for determining the proportion of N_2O derived from aerobic nitrifying versus anaerobic denitrifying bacteria [64]. The $\delta^{15}\text{N}$ composition is considered to be a relative contribution of nitrification and denitrification to the soil N_2O emission. Previous research estimates of the ^{15}N isotope effect (ϵ) (product–substrate) for N_2O production by the soil denitrification process vary from -10‰ to -45‰ [65–68]. Snider et al. [69] reported that for the upland and wetland temperate forest soils' stable isotopic composition of $\delta^{15}\text{N}\text{-N}_2\text{O}$ by denitrification under different moisture and temperature conditions, the wetland soil exhibited consistently larger N_2O production rates compared to upland soils, and the ^{15}N isotope effect ranged from -20‰ to -29‰ .

2.3. Environmental Factors Affect the Isotope Signal of Soil Greenhouse Gases

2.3.1. Temperature and Precipitation

The formation of SOM is mainly derived from plant litter and rhizomes, and the isotope ratio values of SOM records information on vegetation and soil C cycle processes, where plant and soil $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signals are closely related. The positive relationship between soil $\delta^{13}\text{C}$ and plant $\delta^{13}\text{C}$ revealed that plant litter and rhizomes may be sources of SOM [70]. The distribution of plants is mostly determined by climate, such as the C_3 plant, which dominates in the high latitude tundra and grassland, while C_4 plants are often distributed in high light intensity and semiarid environments, and crassulacean acid metabolism (CAM) plants are only present in desert ecosystems [71]. Climatic factors control the growth and survival of plants and influence the isotopic signature of ecosystem respiration. Zhang et al. [72] recognized that the $\delta^{13}\text{C}$ of soil CO_2 emissions was negatively correlated with temperature after farmland was afforested in central China. According to Vitória et al. [73], precipitation and $\delta^{15}\text{N}$ values are negatively correlated until the point of soil waterlogging. Lee et al. [71] suggested that changes of $\delta^{13}\text{C}$ in SOM obviously follow those of the plant zone in arid and semiarid central East Asia. The climate in central East Asia is mainly controlled by northern moisture, especially precipitation. Although temperature plays an important role in plant growth, the latter has not been caused by the higher temperature, but by the higher precipitation, in the central East Asia region. In addition, besides temperature and precipitation, parameters that influence the isotopic composition of soils include the plant photosynthetic efficiency, sunlight duration, altitude, and concentration of atmospheric CO_2 [74]. Knowledge of the response of soil greenhouse gas production, transport, emissions, and sequestration pathways to environmental conditions affords the potential for controlling global warming by, for example, control of the timing and scale of land use change, and mitigating changes in the regional microclimate.

2.3.2. Soil Physical Factors

The physical and chemical properties of soil are mainly affected by land use changes, which affect soil aggregate formation and stimulate soil microbial community repeated processing. For example, the conversion of degraded farmland to vegetation usually increases inputs of fresh organic matter and rhizome exudates, which in turn can change the underground soil structure and eventually affect the stable isotope ratio of soil [75]. Soil texture (coarse and fine particle size) is one of the most important controls of $\delta^{13}\text{C}$. Wynn and Bird [76] reported that the $<63\text{ }\mu\text{m}$ (percent of mineral particles) fraction is more ^{13}C enriched than bulk soil, and the $>63\text{ }\mu\text{m}$ fractions are more ^{13}C depleted in Australia. Koch and Fox [77] investigated the relationship between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values and soil depth changes after

grazing exclusion on the central Californian coast, and found that the $\delta^{13}\text{C}$ values did not change with depth and there was an increase in $\delta^{15}\text{N}$ values with depth in the fine soil. However, this conclusion is inconsistent with the results of previous studies [36], which may be due to significant differences in the soil respiration rates and subsurface soil structure for various vegetation types.

2.3.3. Soil Microbial Process

Soil microorganism metabolic processes are responsible for driving the belowground biogeochemical cycling of elements in the terrestrial biosphere [78]. However, soil microorganism communities' growth and activities are often limited by environmental change, and they are more sensitive to changes in temperature and precipitation [76]. Microbial growth also depends on resource availability, for instance, the input of SOM is closely associated with aboveground plant types. Plants further affect the microbial community composition and function by affecting available soil aggregate, nutrients, temperature, and moisture [79]. For instance, previous research indicated that the $\delta^{13}\text{C}$ of soil CO_2 emissions was positively correlated with the $\delta^{13}\text{C}$ of microbial biomass and negatively correlated with soil temperature [70,71]. Namely, the contribution of soil microbes to soil greenhouse gas production and emissions changes seasonally. Hornibrook et al. [80], based on a trace of $\delta^{13}\text{CH}_4$ in temperate zone wetlands, confirmed that microbial methanogenics obtained by the acetate fermentation pathway are more predominant in certain anoxic, organic-rich soils. Morse and Bernhardt [81] also noted that hypoxia provides the ideal low oxygen conditions conducive to microbial N_2O production by using ^{15}N tracers from nitrification and denitrification. Therefore, an anaerobic environment may be one of the most important conditions in the process of the soil microbial production of greenhouse gases.

3. Stable Isotope Application

3.1. Stable Isotope Tracer

Generally, stable isotope fractionation is achieved through the transition from one phase to another by organic and inorganic compounds, and the long-term dynamics of the ecosystem are reconstructed using stable isotope ratio differences [18]. Stable isotopes can record information on changes in greenhouse gas production, transport, and emissions by isotope fractionation during the soil ecosystem process [82]. Stable isotopes in greenhouse gas from soil are considered a promising option for tracking the source of atmospheric greenhouse gases [17]. The stable isotope is a potentially powerful tool for studying exchange processes of greenhouse gases between the soil and atmosphere. Isotopes can be used as evidence of CO_2 , CH_4 , and N_2O production and oxidation [83], organic matter and inorganic matter accumulation [84], and environmental conditions affecting the fractionation during greenhouse gas generation [85]. Stable isotopes have been widely used in biological processes in ecosystems over the past few decades, and we have a clear understanding of the mechanisms of isotopic fractionation.

3.2. Application of Stable Isotopes in a Soil System

Ecosystem respiration partitioning. Ecosystem C exchange flux is the result of C uptake during the daytime by net photosynthesis and C losses by net respiration [86]. Photosynthesis can sequester 55% of the C in terrestrial ecosystems per year, and soil respiration accounts for approximately 69% of the total ecological respiration [87]. The total ecological respiration is a composite flux, including plant respiration (leaves and canopy) and soil respiration (autotrophic respiration and heterotrophic respiration) [88]. Partitioning total ecological respiration into plant (leaves and canopy) and soil respiration is important for evaluating the relative contribution of plants and soils to C sinks and presenting an accurate quantification of plant–soil–climate interactions. Because photosynthesis changes isotopic fractionation, plant and soil respiration have different CO_2 isotope signatures [89–92], and using $^{13}\text{C}\text{--CO}_2$ and $^{18}\text{O}\text{--CO}_2$ measurements, combined with C eddy flux and concentration measurements, for the partitioning may be a good option [88,90]. Isoflux-based isotopic flux partitioning (IFP) can potentially be used to conduct the partitioning for separate soil respiration from ecological respiration [86].

In addition, isotope ratio infrared spectroscopy (IRIS) and isotope ratio mass spectrometry (IRMS) also provide an effective method for measuring trends in the isotopic compositions of plant respiration and soil respiration [93]. Stable isotopes make up for the shortcomings of eddy covariance techniques that cannot separate ecological respiration components. As a tracer, stable isotopes provide a unique method for discriminating plant respiration and soil respiration in total ecological respiration.

Soil respiration component. The soil C cycle is strongly linked to plant metabolism (e.g., recent production of plant litter) and soil microbial activity. Soil produces CO₂ primarily through rhizosphere respiration and microbial respiration (e.g., autotrophic and heterotrophic respiration). Although the eddy covariance technique and micrometeorological techniques can achieve total CO₂ efflux, it is difficult to determine CO₂ from different sources, especially CO₂ produced by the rhizosphere and microbial respiration [26]. This is also one of the main challenges facing current ecosystem C cycle research. Stable isotope technology is an alternative method of measuring CO₂ that reduces soil and plant disturbances. Pulsed or continuous labeling of plants and soil using stable isotopes can accurately distinguish between CO₂ produced by the rhizosphere and microbial respiration. Generally, the rhizosphere and microbial respiration processes are often accompanied by changes in the concentration ratio between the stable isotopes of the element C [18]. This carbon stable isotope ratio difference can be used to quantify and distinguish between rhizosphere and microbial respiration. It is advantageous to distinguish soil respiration components in the short term. However, ¹³C may deplete rapidly and the isotope signatures of organic matter become similar to labeled plants over time [94]. Therefore, it is necessary to repeat the labeling of stable isotopes of soil and plants over a relatively long period of soil respiration.

Rhizosphere process. The rhizosphere process is one of the most important pathways for CH₄ emissions and the CH₄ produced by the soil is transported to the atmosphere by entering the roots of the plant [95]. CH₄ production in soil is very sensitive to changes in rhizosphere oxygen concentration, and CH₄ emissions change with the seasons. Therefore, an accurate understanding of the soil CH₄ nutrient community structure and its activity is of great significance for the exploration of CH₄ production and emission processes [96]. Methanogen requires strict anaerobic conditions, and rice fields are an important source of methane emissions. The phospholipid fatty acid-stable isotope probing (PLFA-SIP) methodology has been widely used in the tracking of rhizosphere microbial community structure changes [78]. The plant rhizosphere is closely related to soil C sequestration, which also depends on photosynthesis intensity, and rhizosphere microorganisms have different absorption characteristics for photosynthesis production [97]. Therefore, continuous pulse labeling of rice using ¹³C–CO₂ is used to track bacteria that affect the production of CH₄ by the rhizosphere microbial community. In addition, the microbial community is primarily regulated by nutrient availability in the soil and roots [98]. N addition and nutrient use efficiency are important factors affecting rhizosphere microbial activity [99]. Changes in stable isotope ratios (δ¹⁵N) can reflect soil N availability and plant nutrient use efficiency due to differences in the N fixation capacity of microbes and plant roots.

Rhizosphere priming effects. Plant leaves and root litter are the main sources of SOM, providing a labile substrate for soil microbial decomposition. The addition of organic matter causes rapid changes in the SOM turnover rate in the short term, and this change generally occurs in the rhizosphere (rhizosphere priming effects) [100]. Root exudates accelerate the decomposition of organic matter by increasing microbial activity, releasing more inorganic nitrogen, and thereby forming a priming effect [101,102]. Namely, there is a positive feedback relationship between SOM and the rhizosphere [103], and the effectiveness of SOM decomposition depends on microbial biomass mediated conversion [104]. Through the continuous and repeated labeling of plants with ¹³C-depleted CO₂ and ¹⁵N-enriched soil, we can differentiate root N sequestration and microbial nitrogen sequestration effectiveness, and root-derived CO₂ from SOM-derived CO₂ [105]. The difference in stable isotope ratios clarifies the relative importance of microbes, SOM, and roots to rhizosphere priming effects [106]. In addition, the rhizosphere priming effect may be affected by changes in abiotic factors in the soil environment (e.g., elevated CO₂, soil type, and temperature) [107–110]. Abiotic factors further influence the rate and

intensity of rhizosphere priming effects by affecting biological factors [108]. The rhizosphere priming effect is a complex multi-factor correlation process, and the stable isotope continuous labeling method is essential for estimating the contribution of CO₂ emissions from individual sources [26].

Figure 3. Overview of processes determining the stable isotope signals of greenhouse gas from soil.

4. Future Research for Soil Greenhouse Gas Emissions

This review may provide a bridge to determine the strength of coupling between soil greenhouse gas emissions and atmosphere change, by tracking the gas exchange processes of terrestrial ecosystems with stable isotope signatures (Figure 3). The production, transport, and emission of greenhouse gases in the soil is a complex chemical and microbiological process, which is affected by temperature, precipitation, soil moisture, soil properties, soil erosion, and manual management. In addition, the feedback effect of vegetation types on soil C and N sequestration is not clear, due to the complexity of the vegetation community composition and succession [111]. Isotopic monitoring of soil C and N fractionations, as well as greenhouse gas tracking, has been widely applied over most of the soil–atmospheric gas cycle. However, we still need to consider the interaction of soil temporal–spatial changes, microbial species distribution and tectonically active areas [112,113]. Therefore, at least three issues have been proposed that need to be focused on in future studies, including: (1) addressing the fact that the time-lag response of stable isotope signals to environmental changes during soil–atmosphere C exchange is rarely studied; (2) estimating the greenhouse gas from soil evolved by the rhizosphere priming effect, especially the separation of rhizosphere SOM and N fertilizer in farmland, where

using C and N isotope labeling may be the best option; (3) exploring the relationship between changes in rhizosphere priming effects and N use efficiency (N competition between tree species and microorganisms); and (4) based on greenhouse gas exchange of soil ^{13}C measurements, determining whether the plant C sink capacity is the determinant of the soil C sink. The deeply derived gasses composition could affect soil gas composition in tectonically active areas, and our review focuses only on earth's surface. Therefore, we need to discuss deeply derived gasses further.

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