OPINION

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Widespread production of nonmicrobial greenhouse gases in soils

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Abstract

Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are the three most important greenhouse gases (GHGs), and all show large uncertainties in their atmospheric budgets. Soils of natural and managed ecosystems play an extremely important role in modulating their atmospheric abundance. Mechanisms underlying the exchange of these GHGs at the soil–atmosphere interface are often assumed to be exclusively microbe-mediated (M-GHGs). We argue that it is a widespread phenomenon for soil systems to produce GHGs through nonmicrobial pathways (NM-GHGs) based on a review of the available evidence accumulated over the past half century. We find that five categories of mechanistic process, including photodegradation, thermal degradation, reactive oxidative species (ROS) oxidation, extracellular oxidative metabolism (EXOMET), and inorganic chemical reactions, can be identified as accounting for their production. These pathways are intricately coupled among themselves and with M-GHGs production and are subject to strong influences from regional and global change agents including, among others, climate warming, solar radiation, and alterations of atmospheric components. Preliminary estimates have suggested that NM-GHGs could play key roles in contributing to budgets of GHGs in the arid regions, whereas their global importance would be enhanced with accelerated global environmental changes. Therefore, more research should be undertaken, with a differentiation between NM-GHGs and M-GHGs, to further elucidate the underlying mechanisms, to investigate the impacts of various global change agents, and to quantify their contributions to regional and global GHGs budgets. These efforts will contribute to a more complete understanding of global carbon and nitrogen cycling and a reduction in the uncertainty of carbon-climate feedbacks in the Earth system.

KEYWORDS
carbon cycling, extracellular oxidative metabolism, greenhouse gas, nitrous oxide, nonmicrobial, photodegradation, soil organic matter, thermal degradation

1 | INTRODUCTION

The atmospheric abundance of CO_2, CH_4, and N_2O has been continuously increasing since the industrial revolution in 1,750, reaching a concentration of 404.7 ppm, 1852.3 and 324.2 ppb in 2016, respectively (Dlugokencky & Tans, 2016). In addition to their importance in the Earth's radiative forcing, these gases play key roles in atmospheric chemistry. CH_4 is the most abundant organic trace gas in the atmosphere and contributes to tropospheric ozone dynamics, while N_2O is the largest stratospheric O_3-depleting substance and is projected to remain so for the remainder of this century (Myhre et al., 2013). However, there still exist uncertainties regarding production

mechanisms and magnitudes from terrestrial ecosystems, and these uncertainties restrict precise quantification of their contributions to the atmospheric budget (Ciais et al., 2013; Kirschke et al., 2013; Saunois et al., 2016; Tian et al., 2016). Nevertheless, soil–atmosphere exchanges of CO_2, CH_4, and N_2O are recognized as significantly contributing to their atmospheric balances (Paustian et al., 2016). Natural sources of these gases from terrestrial ecosystems are studied and discussed with an assumption of microbe-mediated activities (M-GHGs; e.g., Bradford et al., 2016; Mooney, Vitousek, & Matson, 1987). However, accumulating evidence shows that nonmicrobial processes can also produce GHGs (NM-GHGs). This paper offers a review of knowledge about NM-GHGs from the land surface (soil and plant detritus) to introduce their discovery, to summarize the underpinning mechanisms, to examine the influences from global change, and to discuss their implications. We expect this synthesis paper to bring more attention to NM-GHGs production in soils from the biogeochemistry, ecology, and atmospheric science communities, and also to build a sense in the mind of researchers from other fields and even the public that GHGs exchanges between the atmosphere and land surface are not merely limited to the traditional microbial activities.

The underlying processes responsible for the production and/or consumption of M-GHGs are well understood and extensively reviewed. CO_2 is produced through heterotrophic respiration by soil microorganisms during plant residues and soil organic matter decomposition, although soil fauna could also make contributions (Schlesinger & Andrews, 2000). CO_2 emissions during plant residues and soil organic matter decomposition represent the largest single source from terrestrial ecosystems to the atmosphere (Schlesinger & Andrews, 2000). CH_4 is produced under anaerobic conditions through methanogenesis and consumed under both aerobic and anaerobic conditions by methanotrophs (Chan & Parkin, 2001; Tate, 2015) and anaerobic oxidizers (Gauthier, Bradley, & Simek, 2015), respectively. Well-aerated upland soils represent the only terrestrial sink of atmospheric CH_4 (Ciais et al., 2013). The N_2O production to date involves three identified microbe-mediated pathways: nitrification, coupled nitrification and denitrification, and nitrifier denitrification (Huang et al., 2014; Van Groenigen et al., 2015; Wrage, Velthof, Van Beusichem, & Oenema, 2001). Soil N_2O consumption resulting from, e.g., nondenitrifying populations with a broad range of metabolisms and habitats should not be neglected (Sanford et al., 2012). Agricultural soils plus soils of natural ecosystems form the largest source to the atmospheric burden (Ciais et al., 2013).

Increasing evidence has been showing that it is a widespread phenomenon for the terrestrial ecosystems to produce CO_2, CH_4, and N_2O via nonmicrobial processes from the land surface. Here, we use the term "nonmicrobial" rather than "abiotic" to depict these gases to, on the one hand, contrast directly with the traditional, extensively discussed "microbial" sources, and, on the other hand, to better indicate the scope of this review. Geological processes can also contribute to production and the efflux of soil GHGs (Rey, 2015), and NM-CH_4 and NM-N_2O can be produced from vegetation's physiological metabolisms as well (Keppler, Hamilton, Braß, &

Röckmann, 2006; Lenhart et al., 2015). These sources, however, are beyond the scope of this review. This paper centers on the nonmicrobial production and emission of GHGs from the biogeochemical processing of carbon and nitrogen in the whole soil systems (including plant residues) (Figure 1). Here, we find the mechanisms responsible for the nonmicrobial production of these three gases do not show big differences; overall, with organic and/or inorganic precursors NM-GHGs can be produced through photodegradation, thermal degradation, oxidation by reactive oxidation species (ROS), extracellular oxidative metabolism (EXOMET), and/or inorganic chemical reactions. It is noteworthy that EXOMET is regarded as one of the nonmicrobial pathways because of an absence of intracellular metabolic processes, although enzymes necessary for its functioning can be of microbial origin. These mechanistic processes are subject to influences from global environmental disturbances both directly and indirectly from altered vegetation activities. More importantly, NM-GHGs play an important role in influencing regional budgets of the dryland areas and are projected to become more significant globally, which may partially explain their large atmospheric budget uncertainties. Large knowledge gaps warrant more studies of this paradigm.

2 | DISCOVERY OF NM-GHGS

The idea of NM-CO_2 production from terrestrial ecosystems originated from studies of litter decomposition in arid and semiarid regions at the end of 1980s, when researchers found abiotic processes rather than only biotic processes also play a significant role in litter mass loss (Montaña, Ezcurra, Carrillo, & Delhoume, 1988; Moorhead & Reynolds, 1989). Not until 1999, however, were there direct measurements of CO_2 production from photodegradation of particular organic matter (POM) from plant detritus (Anesio, Tranvik, & Granéli, 1999). During this period, investigations into oceanic carbon cycling around 1990 to a great extent facilitated its finding. It was found that coastal ocean carbon budget could not reach a balance with only a biological carbon loss pathway. This budget imbalance eventually promoted the finding of photodegradation as a mechanistic process to close the budget (Miller, 1994; Mopper, 1989; Mopper et al., 1991). Subsequent studies found that terrestrial-derived dissolved organic matter (DOM) in water can be photodegraded into low molecular weight organic compounds, dissolved inorganic carbon (DIC), and other volatile compounds (e.g., carbon monoxide and carbonyl sulfides) (e.g., Miller & Zepp, 1995). By contrast, the studies in terrestrial ecosystems on photodegradation-derived NM-CO_2 production were seldom seen; rather, attention was still paid to litter mass loss (e.g., Austin & Vivanco, 2006; Moody et al., 2001). Only recently, works on direct measurements of NM-CO_2 production in soils begin to accumulate (e.g., Brandt, Bohnet, & King, 2009; Gliksman et al., 2017; Lee, Rahn, & Throop, 2012; Rutledge, Campbell, Baldocchi, & Schipper, 2010; Yanni, Suddick, & Six, 2015).

By contrast, the finding of CH_4 production via nonmicrobial pathways from land surface was much later compared with NM-
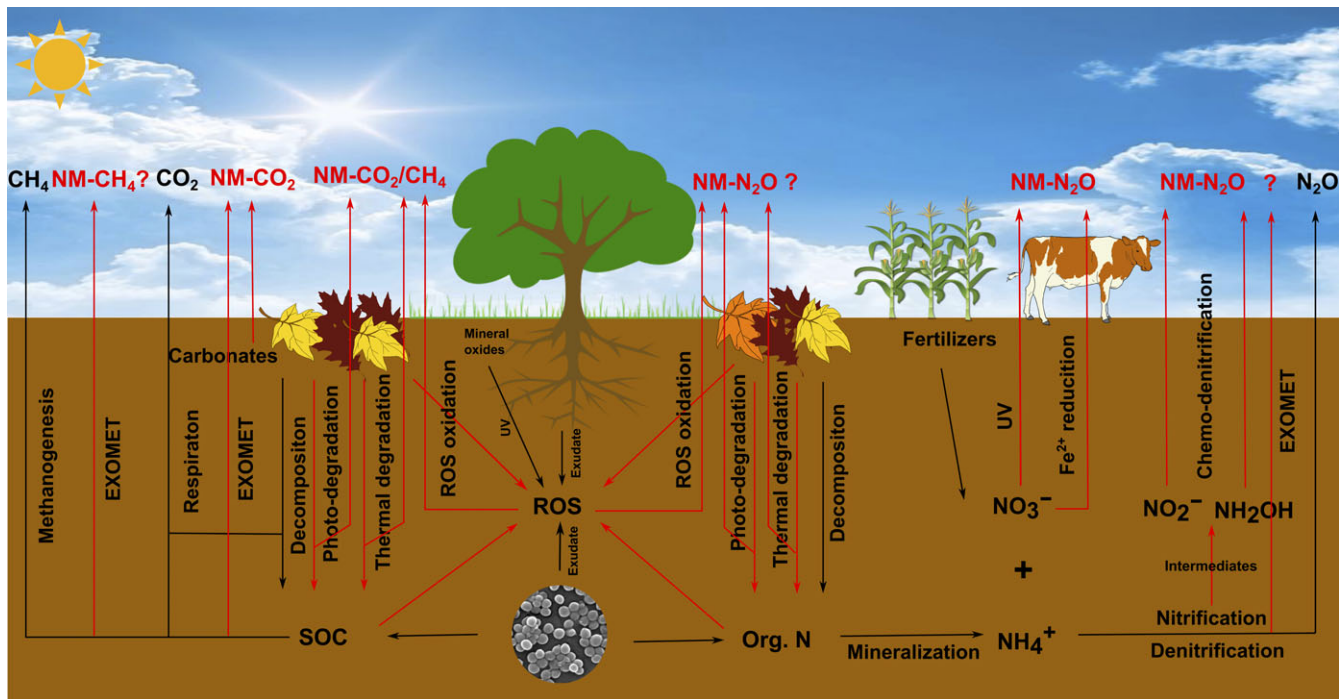
FIGURE 1 Schematic of processes responsible for NM-GHGs production from the land surface. Red and black lines denote the nonmicrobial and microbial pathways, respectively. The question mark indicates the pathways that still need to be substantiated. ROS, reactive oxidative species; SOC, soil organic carbon; EXOMET, extracellular oxidative metabolism [Colour figure can be viewed at wileyonlinelibrary.com]

CO_2. The discovery of land surface NM-CH_4 production originated from the finding of aerobic CH_4 production from plant foliage in 2006 by Keppler et al. (2006). Since then, a series of studies have further confirmed that dry leaves can be a source of CH_4 under various environmental stressors including UV radiation, heating, and physical injury [see reviews by Bruhn, Møller, Mikkelsen, and Ambus (2012) and Wang, Chang, Chen, and Han (2013)]. This naturally inspired researchers to ponder whether soils can also produce NM-CH_4. Accordingly, Hurkuck, Althoff, Jungkunst, Jugold, and Keppler (2012) first reported with direct evidence NM-CH_4 production in aerobic soils. This finding is further confirmed by following studies (Gu et al., 2016; Jugold et al., 2012; Wang, Hou, Liu, & Wang, 2013).

In the context of extensive application of nitrogen fertilizers to meet food demand by a growing world population, investigations into the nitrogen transformations in agricultural systems led to the much earlier finding of NM-N_2O production in soils than that of NM-CO_2 and NM-CH_4. In the early 1960s, to explain observed N-deficits in soils that accumulated nitrite following addition of urea, Smith and Clark (1960) first observed N_2O emissions from soils via chemical reactions rather than by microbial activities. Clark (1962) proposed that nonenzymatic nitrite decomposition is associated with gaseous N loss, which is referred to as chemodenitrification. Following studies discovered more chemical reactions that are responsible for NM-N_2O and other trace gases (N_2 and NO) (Nelson & Bremner, 1970). These initial findings of NM-GHGs paved the way for further efforts toward a deep diving into this paradigm of soil GHGs

production in terms of mechanisms, regulating factors, and source strengths, as discussed immediately below.

3 | UNIFYING MECHANISMS

3.1 | Photodegradation

Photodegradation is a solar-induced process of organic material degradation that can result in a reduction in the molecular mass of organic compounds, an alteration of the capacity of absorbing light both in the ultraviolet and visible spectrum, and the formation of novel photoproducts, including, but not limited to, CO_2 and CH_4 (e.g., CO; Austin & Vivanco, 2006; Lee et al., 2012; Schade, Hofmann, & Crutzen, 1999; Figure 1). In essence, solar radiation supplies the necessary dissociation energy for the cleavage of functional groups in the organic compounds that act as precursors of NM-GHGs (Table 1). For example, the functional group of carboxyl, widely present in plant residues and soil organic matters, can be excited to form NM-CO_2 (Lee et al., 2012), whereas the functional groups including, e.g., methyl, methoxyl, and methyl sulfides, have been proved forming NM-CH_4 (Althoff et al., 2014; Keppler et al., 2008). N_2O is likely another product of photodegradation, which is strongly implied by results from Bruhn, Albert, Mikkelsen, and Ambus (2014) who observed UV-induced N_2O production from live plants.

Photodegradation-induced NM-GHGs production is subject to change from various environmental factors. First of all, wavelength is a primary regulating factor. Across the wide spectrum of solar

TABLE 1 Identified precursors (functional groups, organic and inorganic compounds, and inorganic ions) of NM-GHGs and corresponding mechanistic pathways

Gas	Precursor	Source	Mechanism	References
CO_2	Carboxyl (R-COO-)	Present in most organic compounds	Photo-/thermal degradation/ROS	Lee et al. (2012) and van Asperen et al. (2015)
	Carbonate ion (CO_3^{2-})	Silicates, dolomites	Carbonate precipitation	Rey (2015) and Soper et al. (2016)
	Glucose	Widely present in soil and plant residues	EXOMET	Kéraval et al. (2016)
CH_4	Methyl (-CH_3)	Alkane	Photo-/thermal degradation/ROS	Vigano et al. (2008), Keppler et al. (2008), Lee et al. (2012), Wang, Hou, et al. (2013), Wang, Chang, et al. (2013) and Althoff et al. (2014)
	Methoxyl (-OCH_3)	Lignin, pectin		
	Methyl sulfides (-SCH_3)	Methionine, dimethyl disulfide, dimethyl sulfoxide		
	N-containing compounds	Amide, Amine		
	Methylphosphinidene (CH_3P-)	Methylphosphonic acid		
N_2O	Nitrite (NO_2^-)	Intermediates of nitrification and denitrification	Chemodenitrification	Bremner et al. (1980), Bremner (1997), Samarkin et al. (2010) and Heil et al. (2016)
	Hydroxylamine (NH_2OH)			
	Nitrate (NO_3^-)	Fertilizer	Light-initiated reduction	Rubasinghege, Spak, Stanier, Carmichael, and Grassian (2011)

Sources listed do not necessarily mean an exhaustive collection of all possible contributors.

radiation wavelengths reaching the Earth's surface, UV-B (280–315 nm) is the most effective wavelength band across the UV range (200–400 nm); recent studies show that visible light (blue and green wavelengths: 400–500 nm) are also of great importance (e.g., Austin, Méndez, & Ballaré, 2016; Brandt et al., 2009). In addition, radiation intensity is a key player in regulating the rate and magnitude of NM-GHGs production. For example, NM-CH_4 production rate is linearly increased with the radiation intensity (Jugold et al., 2012; Vigano, Van Weelden, Holzinger, Keppler, & Röckmann, 2008). Photodegradation is not limited to the aerobic conditions (photooxidation); rather, it can also function under anaerobic conditions. Both photodegraded CO_2 and CH_4 are measurable under aerobic (i.e., photooxidation) and anaerobic conditions (Lee et al., 2012). However, the release rate of CO_2 and CH_4 can be inhibited and stimulated by anoxia, respectively (Lee et al., 2012). This is because the presence of O_2 enables the CH_4 formed to be further oxidized to CO_2. In addition, moisture can also exert an impact. Water provides the hydrogen that can act as electron donors. For example, appropriate water can stimulate the photodegradation, as reported by Anesio et al. (1999). How moisture and its interactions with oxygen affect the photodegradation needs further investigations. Generally, it is likely that there is a tradeoff between oxygen level and water content. Therefore, too much water would probably suppress production, as with the thermal degradation (discussed below).

3.2 | Thermal degradation

With adequate thermal energy, thermal degradation is another pathway that is capable of dissociation of chemical bonds to form NM-GHGs from precursors (Table 1; Figure 1). This mechanism has been substantiated in both plant residues (Lee et al., 2012; Vigano et al.,

2008; Wang et al., 2011) and soils (Jugold et al., 2012; van Asperen et al., 2015; Wang, Hou, et al., 2013) for NM-CH_4 and/or NM-CO_2. Similar to photodegradation, NM-N_2O is likely to be produced during thermal degradation, but direct evidence is still not yet available.

Our discussion of the functioning temperature of this pathway is confined to a relatively low value that is lower than 100°C (well below the ignition point). The emission rate increases with temperature following an exponential function (Vigano et al., 2008; Wang, Hou, et al., 2013). However, the release rates are usually lower than those seen with photodegradation because the potential thermal energy at these temperatures is generally lower than the incident solar radiative energy (Lee et al., 2012). Identically, this mechanism functions in both aerobic and anaerobic environments. For instance, NM-CO_2 production from plant residues was detected under anaerobic conditions (Lee et al., 2012), and NM-CH_4 production and emission under anaerobic conditions from both plant residues and soils were also confirmed (Wang et al., 2011; Wang, Hou, et al., 2013). Because the CH_4 produced cannot be further oxidized to form CO_2 without O_2 as an oxidant, anoxia inhibits NM-CO_2 production (Lee et al., 2012). By contrast, the direction of the anoxia effects on NM-CH_4 is variable. Anoxia was observed to both inhibit (Lee et al., 2012; Wang, Hou, et al., 2013) and stimulate NM-CH_4 production from soils and plant residues (Fig. S1; Gu et al., 2016; Wang et al., 2011), perhaps because of differences in the composition and abundance of precursors. This hypothesis was tested by Wang et al. (2011), who found three categories of responses to anoxia from dried plant leaves of different species: enhanced, suppressed, and similar. In addition, as with photodegradation, moisture is another key regulating factor during thermal degradation. This is exemplified by the impacts of moisture on NM-CH_4 production from soils (Hurkuck et al., 2012; Wang, Hou, et al., 2013) and dried leaves (Fig. S1).

Water may significantly enhance or suppress CH_4 production depending on the tradeoff between its direct effect and indirect effect by regulating the oxygen conditions (Wang, Hou, et al., 2013). Apparently, more research is needed to elucidate impacts of these different environmental factors.

3.3 | ROSs oxidation

Reactive oxidative species can be produced in the entire soil system. Soil biological activities, including plant roots, bacteria, and fungi, can exude ROSs (Frahry & Schopfer, 1998; Kersten & Kirk, 1987). Further, the soil itself can also produce ROSs through photochemical reactions with certain mineral oxides (Georgiou et al., 2015; Moorhead & Callaghan, 1994). ROSs are highly oxidative (Apel & Hirt, 2004), capable of cleaving functional groups that can form NM-GHGs (Figure 1; Table 1). This mechanism has been demonstrated for both NM-CH_4 and NM-CO_2 production from both plant residues and soils. For example, hydroxyl radical (OH) produces NM-CH_4 from soils (Jugold et al., 2012; Wang, Hou, et al., 2013) and dry plant leaves (Althoff, Jugold, & Keppler, 2010; Wang et al., 2011). It is likely that ROSs can also excite the formation of NM-N_2O, as indicated by the N_2O production from oxidation of organic nitrogen (Stange, Spott, & Müller, 2009).

The chemical species and abundance of ROSs are important in regulating the production and emission rate of NM-GHGs. Different species of ROSs have differing oxidative capacity (Apel & Hirt, 2004), and an increasing availability can enhance the magnitude of production. For instance, the increasing availability of hydrogen dioxide (H_2O_2) and hydroxyl radical (OH) strongly enhanced NM-CH_4 release from soils (Jugold et al., 2012; Wang, Hou, et al., 2013). Additionally, this pathway was observed to be affected by anoxia. Wang, Hou, et al. (2013) found that anoxia always stimulates NM-CH_4 production compared with oxic conditions from both peat and forest soils. This might be attributed to no further oxidation of CH_4 to form CO_2 with anoxia.

3.4 | Extracellular oxidative metabolism

Extracellular oxidative metabolism, first proposed by Maire et al. (2013), is another pathway responsible for NM-GHGs production (Figure 1). The complex metabolisms that were originally believed to be only maintained inside cells have been found able to fully function outside cells in soils as long as essential catalysts, in particular the endoenzymes stabilized by soil particles, exist (Kéraval et al., 2016; Maire et al., 2013). NM-CO_2 production has been demonstrated through this pathway. For example, glucose has been identified acting as a precursor of NM-CO_2 formed from the oxidation catalyzed by enzymes stabilized in soils and by soil mineral and metal catalysts (Kéraval et al., 2016; Table 1). It is postulated that this mechanism could also function for production of NM-N_2O and NM-CH_4, as a release of endoenzymes responsible for methanization and denitrification is highly possible from dead cells (Maire et al., 2013). However, direct experimental evidence is needed.

Obviously, the initiation of EXOMET mechanism is fundamentally contingent on the availability of catalysts including endoenzymes and some of soil minerals and metals, among which the endoenzymes are released from the cell lysis of dead microorganisms. Therefore, a variety of factors accounting for microbial death and release of endoenzymes including among others virus infection, predation, and environmental stresses like drought can influence the functioning of this mechanism (Maire et al., 2013). However, the performance of EXOMET could be further subject to influences from factors including soil minerals, organic matters, moisture, and pH. Overall, the stronger ability to stabilize enzymes resulting from, e.g., a higher content of clay particle and/or soil organic matter, may induce more NM-GHGs production. However, soil pH also plays an important role in the functioning of the enzymes. For example, Maire et al. (2013) found a relatively low activity of EXOMET when examining a soil with a high clay content but a low pH relative to the enzyme requirement of alkaline conditions. Additionally, oxygen conditions in soils may affect EXOMET as well, with anaerobic conditions suppressing the carbon oxidation and NM-CO_2 release rates but promoting NM-CH_4 and NM-N_2O production. It is noteworthy that these effects all came from very initial explorations, and more investigations are strongly encouraged to examine the impacts of these different factors and beyond.

3.5 | Inorganic chemistry reactions

The aforementioned four categories of mechanistic process in essence are confined to organic compounds as precursors. In fact, inorganic chemical reactions in soils can also account for production of NM-GHGs (Table 1; Figure 1). Evidence points to NM-CO_2 production and emissions with carbonate as a precursor which experiences weathering–precipitation reactions (Hannam et al., 2016; Rey, 2015; Roland et al., 2013; Soper, McCalley, Sparks, & Sparks, 2016). During dry periods of low biological activity, these reactions become more apparent (Rey, 2015). Moreover, a very recent study by Soper et al. (2016) for the first time proved that the diurnal emission pattern of NM-CO_2 via this pathway is strongly dependent on surface temperature, with the rates increasing with temperature.

Current findings see much more evidence for NM-N_2O production in soils. Three inorganic nitrogen precursors to date have been identified: nitrate ion (NO_3^-), nitrite (NO_2^-), and hydroxylamine (NH_2OH). The precursor NO_3^- in a form of ammonium nitrate in agricultural soils, usually from fertilizer applications, can form NM-N_2O via a radiation-initiated chemical reaction (Rubasinghege et al., 2011). Further, nitrate in soil pore space can be reduced by minerals containing Fe (2+) to form NM-N_2O (Samarkin et al., 2010). The other two precursors, NO_2^- and NH_2OH, are intermediates of microbial nitrification and denitrification. NM-N_2O produced from reactions initiated with NO_2^- is by a mechanism referred to as chemodenitrification in general [first proposed by Clark (1962)], which can reduce nitrite (NO_2^-) to form N_2O by means of coupled oxidation of metal (e.g., ferrous iron and manganese) or soil organic matter (e.g., humic acids) (Bremner, 1997; Samarkin et al., 2010;

Thorn & Mikita, 2000; Venterea, 2007). Another pathway of NM-N_2O production is via chemical decomposition of NH_2OH (Bremner, 1997; Bremner, Blackmer, & Waring, 1980; Heil, Vereecken, & Brüggemann, 2016). The mechanism initiated with NO_2^- is more responsible for NM-NO production, while the decomposition of NH_2OH is exclusively linked with NM-N_2O production. Hence, it was observed that NM-N_2O originated from chemical decomposition of NH_2OH greatly exceeded the production by chemodenitrification of NO_2^- (Bremner et al., 1980). NM-N_2O produced from these two pathways are influenced by factors including soil pH, organic matter content, and mineral content. For example, N_2O losses via chemodenitrification are most significant during nitrification in acidic soils (Bremner, 1997). More details concerning these effects can be referred to two recent reviews by Heil et al. (2016) and Zhu-Barker, Cavazos, Ostrom, Horwath, and Glass (2015).

3.6 | Coupling with M-GHGS production

The different processes responsible for NM-GHGs production per se are not isolated (Figure 1). Solar UV radiation can result in ROS production in soils (Georgiou et al., 2015; Moorhead & Callaghan, 1994), both of which are able to initiate NM-GHGs production, as discussed above. In addition, the solar radiation change can result in land surface temperature change, which further alters the NM-GHGs production.

More importantly, the close couplings between NM-GHGs and M-GHGs production also exert significant influences on GHGs production (Figure 1). First, the intensity and rate of NM-GHGs production affect the processes responsible for M-GHGs production. This could be probably because plant residues and soil organic matter degradation by the nonmicrobial processes can facilitate the microbe-mediated decomposition, stimulating M-GHGs production. For example, photodegradation results in direct NM-CO_2 production and emissions from residues and soil organic matter, and it simultaneously facilitates CO_2 return to the atmosphere by enhancing the microbial decomposition via changing the chemistry of plant residues to more labile components (Foereid, Bellarby, Meier-Augenstein, & Kemp, 2010; Song, Peng, Jiang, Zhu, & Wang, 2013; Wang, Liu, Wang, & Chen, 2015). Photodegradation can also accelerate the microbe-mediated nitrogen mineralization and thus promote N_2O production (Foereid et al., 2010). This could also be true for NM-CH_4, although direct evidence is lacking. In turn, processes responsible for M-GHGs production can also influence NM-GHGs. This is best exemplified by NM-N_2O, which, via inorganic reactions, is closely linked with M-N_2O production. As mentioned above, two precursors of NM-N_2O—NO_2^- and NH_2OH—are intermediates of the nitrification process that are responsible for M-N_2O production. The nitrogen mineralization and nitrogen nitrification thus strongly influence the NM-N_2O production via the inorganic reaction route. Moreover, production of M-GHGs and that of NM-GHGs have a mutually competitive effect. This is exemplified by NM-CO_2 production via the EXOMET pathway, which strongly competes with cellular carbon mineralization for available substrates (Kéraval et al.,

2016). Therefore, to achieve a full understanding of NM-GHGs production it is essential to acquire a comprehensive understanding of both M-GHGs and NM-GHGs production and, in particular, their couplings.

4 | IMPACTS OF GLOBAL CHANGES ON NM-GHGS

Mechanisms and processes discussed above are strongly subject to influences from regional and global environmental changes that can alter the intensity and/or wavelength of solar UV radiation reaching the land surface, land surface temperature, and soil moisture and oxygen condition, as well as quantity and/or quality of plant residues and soil organic matter. These changes probably include among others stratospheric ozone (O_3) depletion, tropospheric O_3 pollution, nitrogen deposition, climate warming, precipitation regime shift, and herbivory, which could significantly influence NM-GHGs production and emissions from land surfaces in both direct and indirect pathways.

The direct impacts are straightforward but often poorly understood in terms of magnitude and pattern. One of the few relatively well-studied (but still far from enough) global change agents is solar UV radiation change. UV radiation variability is strongly contingent on the stratosphere O_3 level and also affected by climate change-related variables such as GHGs levels, cloud cover, and aerosols (Bornman et al., 2015; Erickson, Sulzberger, Zepp, & Austin, 2015; Williamson et al., 2014); for instance, stratospheric O_3 depletion can enable more intense solar UV radiation reaching the Earth's surface. By manually manipulating wavelength and/or intensity of ultraviolet radiation, impacts on NM-CH_4 and $-CO_2$ production were investigated (e.g., Vigano et al., 2008; Yanni et al., 2015). In addition, global climate change, especially ongoing climate warming, accompanying increased frequency and severity of fire plus enhanced radiation, is increasing the land surface temperature (Hartmann et al., 2013), directly stimulating NM-GHG production via the thermal degradation mechanism. However, direct observational evidence is still not yet available.

In addition to these direct effects, the possible indirect impacts are through affecting plant secondary metabolites, thus altering the quantity and in particular quality of plant residues and soil organic matter. These altered plant residues' chemistry and soil organic matter quality would fundamentally determine the amount and rate of NM-GHGs (especially CH_4 and CO_2) production and emissions by shaping the composition and abundance of different organic compounds (Table 1). Many studies have concluded that the stresses from those various global change agents, including among others solar UV radiation (Gehrke, Johanson, Callaghan, Chadwick, & Robinson, 1995), O_3 (Findlay, Carreiro, Krischik, & Jones, 1996), climate warming (Dillon, Wang, & Huey, 2010), and herbivory (Percy et al., 2002), can alter the organic constituents of plant residues and soil organic matters. However, currently there are no studies on the impacts of global changes on NM-GHGs production mediated by these

intermediate changes in terms of plant residues quality, although such influences on microbial decomposition have been extensively studied (e.g., Horner, Gosz, & Cates, 1988; Kainulainen, Holopainen, & Holopainen, 2003).

It is noteworthy that the close couplings between NM-GHGs and M-GHGs indicate that the altered decomposition of plant residues and soil organic matter responsible for M-GHGs production resulting from global change (e.g., climate warming; Crowther et al., 2016) would also largely affect the NM-GHGs production and emissions. Therefore, the impacts of global change, either direct or indirect, on the NM-GHGs are expected to become a fruitful research avenue in the face of ever-accelerated global environmental changes.

5 | REGIONAL AND GLOBAL IMPLICATIONS OF NM-GHGS

Current available evidence strongly indicates that these sources could be important in determining the regional GHGs budget, although it remains uncertain concerning the extent to which NM-GHGs can exactly contribute to their atmospheric abundances. Across dryland ecosystems, in particular the arid and semiarid areas, which are usually of high radiation intensity, severe water limitation, and sparse vegetation cover (Schimel, 2010), NM-GHGs production and emissions play an important role in the carbon and nitrogen cycling. The carbon cycle has been substantiated being largely affected by photodegradation through stimulating plant residues and soil organic matter decomposition (Austin & Vivanco, 2006; Foereid, Rivero, Primo, & Ortiz, 2011). Similarly, the nitrogen balance has also been proved to be largely affected by nonmicrobial processes (McCalley & Sparks, 2009). A big portion of the carbon and nitrogen returns to the atmosphere in the form of trace gases originated from nonmicrobial processes. For example, direct measurements of CO_2 flux show that the percentage comprised by NM-CO_2 is even as high as 60% (Table 2). As for upland ecosystems where soils generally act as a sink of atmospheric CH_4, they may act as sources by producing relatively large amounts of NM-CH_4 (Table 2). No estimates on NM-N_2O yet exist up to date.

Although currently limited estimates suggest a much less important role globally compared with regional impacts (Table 2), there is a great possibility that NM-GHGs have been nontrivial and will become increasingly important. First, the current estimates are confined to only some of the mechanistic processes (mostly photodegradation and thermal degradation; Table 2). The extent to which the other processes (e.g., ROS oxidation, EXOMET, and inorganic reactions) can contribute to NM-GHGs emissions is still without an estimate at all. For example, NM-CO_2 produced via inorganic reactions from carbonates is potentially large because a third of global soil carbon stock belongs to inorganic carbon (Schlesinger, 1982; Soper et al., 2016). NM-N_2O originated from soil fertilizer application around the world is unknown as well, which, however, is expected

to have a large annual flux considering the huge amount of fertilizer applied around the world (Rubasinghege et al., 2011).

Second, the fact is that NM-GHGs are a widespread phenomenon across biomes around the world. Austin et al. (2016) show that photodegradation is globally important in driving the carbon cycle. In addition, as suggested by Wang, Chang, et al. (2013), NM-CH_4 production is a widespread phenomenon. Even if most of the current reports, especially on CH_4 and CO_2 production, are located in dryland (arid and semiarid) regions, the dryland area, however, is projected to increase substantially to more than 50% of the land surface (Huang, Yu, Guan, Wang, & Guo, 2015), where the agricultural activities will further intensify to meet food demand (Hazell & Wood, 2008); the woody encroachment will accelerate (Stevens, Lehmann, Murphy, & Durigan, 2017); and the vegetation is experiencing a greening trend (Piao, Friedlingstein, Ciais, Zhou, & Chen, 2006). These changes would further increase NM-GHGs releases because of an increase in fertilizer application especially in developing countries (Rubasinghege et al., 2011) and an increase in the proportion of woody plant residues (Lee et al., 2012).

In particular, accelerated global environmental changes are likely to further enhance the NM-GHGs emissions. Among those changes, climate change would probably exert the most significant impacts. Global temperature is projected to continue to rise (Hartmann et al., 2013). In particular, there would likely be increasing frequency and intensity of extreme climate events, such as severe drought and heat waves, around the world (Seneviratne et al., 2012). In addition, the global mean UV-B radiation at the Earth's surface is projected to enhance in this century (Williamson et al., 2014). These global changes would be likely to enlarge their magnitude of occurrence in terms of both direct and indirect pathways as discussed above.

6 | PROSPECTS

To clarify the contributions of NM-GHGs to regional and global GHGs budget and hence their roles in altering the atmospheric radiative forcing and tropospheric chemistry, their production and emissions require more extensive research to elucidate the mechanistic details and to characterize their spatial–temporal heterogeneity patterns in terms of flux magnitude. Following research directions are suggested to achieve these objectives.

First, underlying mechanisms and the regulation by environmental factors need to be further untangled. This includes uncovering more precursors in the plant residues and soils, either functional groups of organic compounds or inorganic substances, and even new possible mechanistic pathways. The abundance and distribution of precursors embedded in the complex soil matrix with an extremely high heterogeneity is equally important. This has been demonstrated by the study on aggregate-level NM-CH_4 production by Wang, Hou, et al. (2013) which showed apparent heterogeneity across aggregates of different sizes, suggesting that pools of soil organic matter with differences in quality and quantity presenting different production capacity. Therefore, following studies should further examine

TABLE 2 A compilation of estimates of local, regional, and global NM-GHG fluxes

Gas	Spatial scale	Source	Mechanism	Flux	% Of total GHG	Reference
CO_2	Theix, France	Soil	EXOMET	27 mg $C–CO_2$ kg^{-1}	48	Maire et al. (2013)
	Ponta Grossa, Brazil	Soil	EXOMET	26 mg $C–CO_2$ kg^{-1}	16	Maire et al. (2013)
	Chihuahuan Desert, USA	Plant residue	Photodegradation	4–15 g CO_2 m^{-2} $year^{-1}$	3	Brandt et al. (2009)
	Ione, California, USA	Plant residue/soil	Photodegradation	59 g CO_2 m^{-2} $year^{-1}$	60[c]	Rutledge et al. (2010)
	Torehape, New Zealand	Soil	Photodegradation	125–242 g CO_2 m^{-2} $year^{-1}$	13–25	Rutledge et al. (2010)
	Global	Plant residue	Photodegradation	NA	1	Foereid et al. (2011)
	Global	Plant residue	Photodegradation	84–253 Tg CO_2 $year^{-1}$	0.11–0.34	Lee et al. (2012)
	Global	Plant residue	Thermal degradation	11–33 Tg CO_2 $year^{-1}$	0.01–0.04	Lee et al. (2012)
CH_4	IMGERS, China[a]	Soil	Thermal degradation	15–53 μg m^{-2} $year^{-1}$	0.01–0.10	Gu et al. (2016)
	Global	Plant residue	Photodegradation	1–7 Tg CH_4 $year^{-1}$	0.48–3.33	Keppler et al. (2006)
	Global	Plant residue	Photodegradation	0.24–0.73 Tg CH_4 $year^{-1}$	0.11–0.34	Lee et al. (2012)
	Global	Plant residue	Thermal degradation	0.06–0.17 Tg CH_4 $year^{-1}$	0.03–0.08	Lee et al. (2012)
N_2O	USA	Agricultural soil	Inorganic reaction[b]	5,322 t N_2O $year^{-1}$	3[d]	Rubasinghege et al. (2011)

[a]IMGERS: Inner Mongolia Grassland Ecosystem Research Station, Chinese Academy of Sciences, China.
[b]This N_2O is produced from ammonium nitrate via radiation-initiated reactions.
[c]This number shows the dry season percentage.
[d]This percentage is based on the total anthropogenic N_2O emissions from USA. All the other percentages (CO_2 and CH_4) are based on natural sources.

the NM-GHGs production in relation to precursor heterogeneity resulting from soil physical, chemical, and biological heterogeneities. Moreover, an elucidation of the impacts of various global change agents alone and together on NM-GHGs production and emissions in terms of magnitude and spatiotemporal patterns is an urgent need. However, it is noteworthy that NM-GHGs and M-GHGs are likely to obey to different set of rules. This is especially evident for EXOMET-derived NM-CO_2. In contrast to soil microorganisms, EXO-MET-carrying enzymes have few physiological constraints and are resistant to high temperature and pressure, thus responding distinctively to environmental factors (Kéraval et al., 2016; Maire et al., 2013). Therefore, NM-GHGs and M-GHGs must be investigated separately when studying the impacts of these factors, e.g., climate warming.

However, how to differentiate these nonmicrobial sources from the traditional microbe-mediated production and emissions is a big challenge. In particular, the couplings between processes responsible for M- and NM-GHGs production make the distinction particularly difficult. Stable isotopic information, widely used in biogeochemistry research in partitioning sources (e.g., Whitman & Lehmann, 2015), could be a powerful means to distinguish NM-GHGs from M-GHGs. Microbial and nonmicrobial CO_2, CH_4, and N_2O are all isotopically distinguishable (Heil et al., 2014; Rey, 2015; Wang, Chang, et al., 2013). For instance, the recent study by Soper et al. (2016) confirmed carbonate-derived NM-CO_2 using Keeling plot by measuring the ^{13}C abundance. A bigger challenge arises when further differentiating among nonmicrobial pathways producing the same NM-GHG in the same soil system. However, current efforts remain insufficient in partitioning these GHGs sources of differing mechanisms, particularly in the field. Only when these two broad categories of sources are distinguished can the magnitude of NM-GHGs emission be truly quantified.

A third priority is for land surface or Earth System models to incorporate these processes responsible for NM-GHGs production. Currently, only rare works have tried to simulate these processes in global carbon and nitrogen cycling models (e.g., Foereid et al., 2011). Ignoring these processes further adds uncertainties into the regional and global carbon and nitrogen cycling predicted by the current biogeochemical models (Austin & Vivanco, 2006). With an increasing understanding of the underlying processes and regulating factors, algorithms accounting for NM-GHGs production and emissions could be developed, validated, and incorporated into the land surface models to better understand and predict the large spatiotemporal variability.

7 | CONCLUSIONS

In contrast to the traditional recognition of microbe-mediated GHGs exchange at the soil–atmosphere interface, a paradigm of NM-GHGs production and emissions from the soil systems is arguably developed based on the current available evidence of CO_2, CH_4, and N_2O production via nonmicrobial pathways. Currently, five categories of mechanistic process, including photodegradation, thermal degradation, ROS oxidation, EXOMET, and inorganic chemical reactions, have been identified being able to contribute to their production. These pathways are tightly coupled per se and with processes responsible for M-GHGs. NM-GHGs from soils could play an important role in regional GHGs budgets, in particular the arid regions. More studies should be conducted to understand the mechanistic details and factors at play, which should be distinguished from the traditional M-GHGs production when studying impacts of the various global change agents. It would be fruitful to further investigate the NM-GHGs production and emissions across large spatial and

temporal scales, which will help us completely understand global carbon and nitrogen cycling processes. This may reduce the current large uncertainty of global atmospheric budgets of these gases and increase the reliability of prediction on carbon-climate feedbacks.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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