Role of chemical reactions in the nitrogenous trace gas emissions and nitrogen retention: A meta-analysis

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Abstract: Increasing evidence has been found that chemical reactions affect significantly the terrestrial nitrogen (N) cycle, which was previously assumed to be mainly dominated by biological processes. Due to the limitation of knowledge and analytical techniques, it is currently challenging to discern the contribution of biotic and abiotic processes to the terrestrial N cycle for geobiologists and biogeochemists alike. To better understand the role of abiotic reactions in the terrestrial N cycle, it is necessary to comprehend the chemical controls on nitrogenous trace gas emissions and N retention in soil under various environmental conditions. In this manuscript, we assess the role of abiotic reactions in nitrous oxide (N_2O) and nitric oxide (NO) emissions as well as N retention through a meta-analysis using all related peer-reviewed publications before August 2020. Results show that abiotic reactions contributed 29.3−37.7% and 44.0−57.0% to the total N_2O emission and N retention, representing 3.7−4.7 and 4.0−6.0 Tg yr^{-1} of global terrestrial N_2O emission and N retention, respectively. Much higher NO production was observed in sterilized soils than that in unsterilized treatments indicating the major contribution of chemical reactions to NO emission and rapid microbial reduction of NO to N_2O and N_2. Chemical hydroxylamine oxidation accounts for the largest abiotic contribution to N_2O emission, while chemical nitrite reduction and fixation represent for the largest contribution to abiotic NO production and soil N retention, respectively. Factors influencing the abiotic processes include pH, total organic carbon (TOC), total nitrogen (TN), the ratio of carbon to nitrogen (C/N), and transition metals. These results broadened our knowledge about the mechanisms involved in chemical N reactions and provided a simplified estimation about their contribution to nitrogenous trace gas emission and N retention, which is meaningful to further study interactions of biologically and chemically mediated reactions in biogeochemical N cycle.

Keywords: chemical reactions, nitrous oxide, nitric oxide, N retention, terrestrial N cycle

1 Introduction

Nitrogen (N) is a fundamental element in ecosystems that determines the function and structure of terrestrial ecosystems in a complex way. After the innovation of Habor-Bosch process, anthropogenic reactive N input into the environment increased by 125 Tg N yr^{-1} till 1990s compared with pre-industrial levels (Galloway et al., 2008; Gruber and Galloway, 2008), 9–10 Tg N yr^{-1} of which is immobilized in soil in terrestrial ecosystems (Zaehle, 2013), 12.52 Tg yr^{-1} and 10.99 Tg yr^{-1} of which is emitted into the atmosphere as nitrous oxide (N_2O) and nitric oxide (NO), respectively (Lee et al., 1997; Tian et al., 2015). Increased N retention have adversely affected terrestrial ecological functions by delaying the decomposition of organic matter (Dias et al., 2013), changing the biochemical composition of soil organic matter (SOM) (Gillespie et al., 2014), altering soil biota (Eisenlord and Zak, 2010), and modifying plant physiology (Langley and Megonigal, 2010). Elevated atmospheric N_2O is not only contributing about 6% to the global climate change but also acting as the currently most important ozone-depleting substance in the stratosphere (Ravishankara et al., 2009; WMO, 2019). While, NO acts as a catalyst for the production of atmospheric ozone, radicals, and nitric acid (HNO_3) in precipitation (Tadic et al., 2021). A better understanding of the complex biogeochemical N processes, as well as the influence of environmental factors, is mandatory to reduce the negative environmental effects of anthropogenic reactive N input.

In the last decades, biological processes were considered to dominant the biogeochemical N cycle, while an increasing number of studies have demonstrated that chemically mediated interactions play important rules in the formation of N_2O, NO, and soil organic N (SON) compounds in terrestrial ecosystems (Burge and Broadbent, 1961; Nõmmik, 1965; Nommik and Nilsson, 1963; Ostrom et al., 2016; Peters et al., 2014; Pilegaard, 2013; Schmidt-Rohr et al., 2004; Stevenson and Harrison, 1966; Stevenson and Swaby, 1964; Venterea, 2007; Wullstein and Gilmour, 1966). Ammonium (NH_4^+), hydroxylamine (NH_2OH), nitrite (NO_2^-), and nitrate (NO_3^-) are the four key reactive N intermediates from biological N transformations (Fig. 1), NH_4^+ and NO_3^-, ranging heterogeneously from a few to a thousand mg N kg^{-1} soil, are relatively stable with lower enthalpy of formation compared with NH_2OH and NO_2^- (Cruz et al., 2008), while NH_2OH and NO_2^- generally exit in a range of several μg N kg^{-1} soil to 1 mg N kg^{-1} soil in terrestrial ecosystems (Liu et al., 2014; Shen et al., 2003).

Nitrification and denitrification are the main microbial sources of NH_2OH and NO_2^- (Fig. 1), which are mediated by ubiquitous bacteria, archaea, and fungi, accounting for 0.5–5% of the total soil microbial biomass (Giles et al., 2012). Considerable release of NH_2OH into the environment from nitrifiers has been observed (Kits et al., 2019; Liu et al., 2017b). The acid dissociation constant (pK_a) of NH_2OH and NO_2^- is 5.94 and 3.27 at 298 K, respectively, therefore the decomposition of NH_2OH is favored by alkaline pH, while NO_2^- by acid pH (Politzer and Murray, 2008; Riordan et al., 2005). N_2O is the known main products of chemical NH_2OH oxidation by Fe(III), and manganese dioxide (MnO_2) at alkaline conditions (Fig. 1) (Bremner et al., 1980; Heil et al., 2015; Nelson, 1978). Moreover, the –NOH group of NH_2OH can substitute the oxygen atom of the abundant carbonyl groups (–C=O) in aldehydes, ketones, acetyl halides, lactams, and esters in SOM, to form aldoximes, ketoximes, and hydroxamic acids (Fig. 1), which lead to chemically mediated soil N retention (Politzer and Murray, 2008). By contrast, the chemical reduction of NO_2^- by transition metals and SOM lead to considerable production of N_2O, NO, and SON can be produced in soil (Fig. 1) (Jones et al., 2015; Nelson and Bremner, 1970; Stevenson and Harrison, 1966; Stevenson et al., 1970; Stevenson and Swaby, 1964; Wei et al., 2017b; Wullstein and Gilmour, 1966).

Amides and amines are the most abundant organic N species contributing more than 50% to SON (Thorn and Cox, 2009; Vairavamurthy and Wang, 2002), and their extracellular decomposition catalyzed by proteases can become the main source of free amino groups ($-NH_2$), accounting for 12–30% of SON (Bremner, 1957). Their microbial mineralization is one of the main source of NH_4^+ in soil. The fixation of $R-NH_2$, including glycine and cyanamide, as well as NH_4^+, has been observed in spruce humus (Chalk and Smith, 1983; Nõmmik, 1970), and anilides indole, pyrrole, pyridine, and amide could be the products of abiotic reactions of $R-NH_2$ with phenols (Burge and Broadbent, 1961; Schmidt-Rohr et al., 2004; Thorn and Mikita, 1992). The NO_3^- anion, produced through nitrification of NH_4^+, consists of one central N atom surrounded by three identically bonded oxygen atoms in a trigonal planar arrangement, which ensures its low enthalpy of formation (Fig. 1). However, Davidson et al. (2003) proposed that Fe(II) could reduce NO_3^- to NO_2^- through the so called “ferrous wheel” mechanism, which could further chemically react with SOM and transition metals, leading to nitrogenous gas emission and N retention (Zhu-Barker et al., 2015; Heil et al., 2016). Meanwhile, coupled oxidation of NH_4^+ and reduction of Fe(III) has been reported in anoxic wetland and paddy soils, during which NO_2^- or N_2 are formed (Clément et al., 2005; Shrestha et al., 2009; Yang et al., 2012), contributing significantly to soil N loss (Ding et al., 2014).

While the question still remains how much the above abiotic processes contribute to the total biogeochemical N cycle (Cleemput and Samater, 1996; Heil et al., 2015; Schmidt-Rohr et al., 2004; Thorn and Mikita, 2000; Vairavamurthy and Wang, 2002; Venterea, 2007; Wei et al., 2017a). To bridge this knowledge gap, we conduct a meta-analysis using all peer-reviewed publications of the last 55 years which explore the chemically mediated emissions of N_2O and NO, as well as soil N retention in this integrated manuscript.

2 Material and Method

2.1 Selection criteria and database for meta-analysis

Peer-reviewed publications (before August 2020) related to abiotic N_2O and NO emissions, as well as N retention in soil were selected from the databases Web of Science and Google Scholar using the keywords "abiotic nitrous oxide emission", "abiotic nitric oxide emission", "abiotic nitrogen retention", "abiotic ammonium reaction", "abiotic nitrite reaction", "abiotic hydroxylamine reaction", or "abiotic nitrate reaction", double searching was conducted by substituting “abiotic” with “chemical”. Searching results were refined by applying the following criteria to select studies finally used for the meta-analysis: 1) N_2O or NO emissions, or N retention was reported after application of a certain N species (NH_4^+, NH_2OH, NO_2^-, NO_3^-, or organic N compounds) in selected studies; 2) a certain approach, such as autoclaving, irradiation, chemical disinfection, or dissimilar reaction rates, was applied to discern abiotic reactions from biotic processes; 3) detailed experimental setup including sample size, monitoring time, N application rate, and soil conditions were reported to normalize chemical N emission or retention rate for meta-analysis; 4) data in selected studies had to be collected immediately after the application of N species till the end of the experiment. In total 478 studies at 80 locations were selected as shown in Fig.2, multiple observations of the same treatment over different time scales were averaged after normalized based on timescale, and observations of different treatments were regarded as individual studies. All the selected peer-reviewed publications that met the above requirements are listed in the Supporting Information (Data S1).

2.2 Performance of meta-analysis

The abiotic N transformation rate (*DR*) and the contribution of abiotic processes (*RR*) to N_2O emission, NO emission, and N retention after application of certain N species (NH_4^+, NH_2OH, NO_2^-, NO_3^-, or organic N compounds) were quantified as follows:

$$lnDR = \ln(R_a - R_{a0}) \qquad (1)$$

$$lnRR = \ln((R_a - R_{a0})/(R_t - R_{t0})) \qquad (2)$$

where R_a and R_{a0} stand for the chemical N transformation rate in sterilized treatments with and without N application, respectively; R_t and R_{t0} stand for the total N transformation rate in unsterilized treatments with and without N application, respectively; *R* was normalized as N_2O-N, NO-N, and SON-N formation of total applied N per hour (%(applied N) h^{-1}) to compare results in different studies where monitoring time scales and N application rate varied. R_{a0} and R_{t0} were used for background correction and assumed to be zero if no control treatment without N application was reported; the calculation is based on the assumption that process rates in sterilized soil are representative of abiotic process rates in live soil. Due to the limited availability of standard deviations of reported mean values in selected publications, a replication-based weighting method was used in this meta-analysis (Xia et al., 2018):

$$Weight = (n_a \times n_t)/(n_a + n_t) \qquad (3)$$

where n_a and n_t denote the replicate number of sterilized and unsterilized treatment, respectively.

The meta-analysis was conducted with MetaWin 2.1 (Rosenberg, Adams & Gurevitch, 2000), in which a bootstrapping of 4,999 iterations was used to generate mean effect sizes and 95% confidence intervals (CIs). Abiotic processes were considered to contribute significantly to the N cycle if 95% CIs were higher than zero, while categorical variables were regarded significantly different from each other in case their 95% CIs did not overlap. According to the availability of related studies, lnRR and lnDR were performed with all reactive N species, NH_2OH, and NO_2^- for N_2O emission, all reactive N species for NO emission, all reactive N species and NH_4^+ for N retention. Spearman correlation analysis was conducted to explore the linear correlations of lnRR and lnDR with TN, TOC, C/N, pH, and the contents of manganese (Mn) and iron (Fe). Furthermore, total nitrogen (TN), total organic carbon (TOC), the ratio of carbon to nitrogen (C/N), land use type, and soil pH were regarded as category factors by dividing them into three ranges (<3, 3−10, and >10 mg kg^{-1} for TN; <3, 3−20, and >20 % for TOC; <13, 13−20, and >20 for C/N; <5, 5−7, and >7 for soil pH; cropland, forest, and grassland for land use type) to study their effects on the biotic and abiotic reactions in the meta-analysis.

2.3 Net effect of abiotic processes in N cycle

The net effects of abiotic reactions in global terrestrial NO and N_2O emissions, as well as N retention, were estimated as follows:

$$N_{abiotic} = N_{total} \times RR \qquad (4)$$

where N_{total} denotes global terrestrial N_2O emission (12.52 Tg yr^{-1}; (Tian et al., 2015)), NO emission (10.99 Tg yr^{-1}; (Lee et al., 1997)), and N retention (10 Tg yr^{-1}; (Galloway et al., 2008; Zaehle, 2013)). *RR* is the average contribution of abiotic reactions to total N_2O emission, NO emission, and N retention obtained from our meta-analysis.

3 Results

3.1 the role of abiotic processes in N_2O emission

The meta-analysis of lnRR of N_2O emission was conducted based on 109 studies, among which 53 and 43 studies focused on abiotic N_2O emission derived from NO_2^- and NH_2OH, respectively. Results showed that abiotic processes contributed on average 33.2% to total N_2O emissions, when the reactive N intermediates NO_2^-, NO_3^-, and NH_2OH were considered (Fig. 3a), which represents about 3.7-4.7 Tg yr^{-1} of global terrestrial N_2O emission. The application of NH_2OH to sterilized soils led to the highest abiotic N_2O production rate of 0.6 %(applied N) h^{-1} (Fig. 3d), as well as the largest (50%) abiotic contribution to the total N_2O emission (Fig. 3a). The chemical N_2O production rates from NO_2^- and NO_3^- were 2–3 magnitudes lower compared with that of NH_2OH (Fig. 3d), while their chemical reactions accounted for 22–27% less of the total N_2O emission than that of NH_2OH (Fig. 3a). Across all studies, the highest abiotic N_2O production rate occurred under environmental conditions of TN >10 mg kg^{-1}, TOC >20 %, C/N >20, and pH <5 (Fig. 3d), while the lowest abiotic contribution to the total N_2O emission occurred at conditions of 3−10 mg kg^{-1} TN, 3−20% TOC, 13−20 C/N, and pH >7 (Fig. 3a). The land use type did not alter significantly the contribution of abiotic processes to terrestrial N_2O emission (Fig. 3).

In treatments with NH_2OH application, abiotic N_2O production rate was significantly ($p < 0.05$) higher if TN was <3 mg kg^{-1}, TOC <3%, and C/N <13 compared with higher levels of TN, TOC, and C/N (Fig. 3e). The lowest NH_2OH-related abiotic N_2O production rate, as well as abiotic N_2O contribution, was found at pH <5. However no significant differences of abiotic N_2O contribution were observed among different TN, TOC, C/N, and pH levels (Fig. 3b). Spearman correlation analysis revealed a significant positive correlation of pH ($p < 0.01$), but negative correlation of TOC ($p < 0.05$), TN ($p < 0.01$), and C/N ($p < 0.01$) with abiotic NH_2OH-derived N_2O production rate in soil (Table 1). Similarly, Mn content was significantly ($p < 0.01$) positively correlated with NH_2OH-derived abiotic N_2O production rate, but not with abiotic N_2O contribution (Table 1).

On the contrary to NH_2OH, the highest abiotic N_2O production rate of NO_2^- was observed under environmental conditions of TN >10 mg kg^{-1}, TOC >20%, and C/N >20 (Fig. 3f). In contrast, chemical reactions contributed the least to the total NO_2^--derived N_2O emission when TN was between 3−10 mg kg^{-1}, TOC between 3−20%, and C/N between 13−20 (Fig. 3c). Regardless of the significantly higher NO_2^--derived chemical N_2O production rate at pH <5, there was no significant difference of abiotic N_2O contribution among pH levels of <5, 5−7, and >7 (Fig. 3c and f). According to Spearman correlation analysis, TN and TOC contents were significantly ($p < 0.01$) positively correlated with the abiotic N_2O production rate of NO_2^- (Table 1).

As the mostly important N_2O-precursors, NO_2^- and NH_2OH behaved completely differently to the changes of environmental conditions. Chemical N_2O production rate of NO_2^- increased linearly with increasing ln(TOC) and ln(TN), as well as decreasing ln(Mn). On the contrary, ln*DR* of NH_2OH-derived abiotic N_2O emission decreased linearly corresponding to increasing ln(TOC), ln(TN), and decreasing ln(Mn) (Fig. S1). The ln*DR* of abiotic N_2O production was positively linearly ($p < 0.01$) correlated with ln(pH) when NH_2OH, but not NO_2^-, acted as N_2O precursor (Fig. S1). However, except for the positive ($p < 0.05$) linear correlation of ln(pH) with ln*RR* of NO_2^--derived N_2O emission, no other significant correlation was observed between environmental conditions and ln*RR* of N_2O emission, neither after NO_2^- application nor after NH_2OH application (Table 1, Fig. 4).

3.2 the role of abiotic processes in NO emission

The meta-analysis of the contribution of chemical reactions to the total NO emission and abiotic NO production rate was conducted based on 26 and 58 studies, respectively, most of which focused on the NO_2^--related chemical NO production. Unexpectedly high contribution (82−149%) of abiotic reactions to the total NO emission was found because of the much higher NO emission in sterilized soils than that in unsterilized treatments (Fig. 5a), and 9.0-16.3 Tg yr^{-1} of global terrestrial NO emission was attributed to abiotic reactions according to Eq. 4. Similar to N_2O, the lowest contribution of chemical reactions to total NO emission occurred at intermediate ranges of TN (3−10 mg kg^{-1}), TOC (3−20 %), C/N (13−20), and pH (5−7) (Fig. 5a). Among all the studied reactive N intermediates, chemical decomposition of NO_2^- represented the fastest abiotic NO production rate, which was two orders of magnitude higher than for the other N intermediates (Fig. 5b). The overall abiotic NO production rate was about 2.4−3.5 ×10^{-3} %(applied N) h^{-1}, and was lowest at the lowest TN (<3 mg kg^{-1}), TOC (<3 %) and C/N (<13) levels, and the highest pH (>7) range (Fig. 5b).

According to the Spearman correlation analysis, pH was significantly ($p < 0.01$) negatively correlated with abiotic NO production rate (ln*DR*), but positively ($p < 0.05$) correlated with abiotic contribution to total NO emissions (ln*RR*) (Table 1). After natural logarithm transformation, the abiotic NO emission rate was positively linearly correlated with ln(TOC) ($p < 0.05$), ln(TN) ($p < 0.01$), ln(Fe) ($p < 0.01$), and ln(Mn) ($p < 0.01$), while negatively correlated with ln(pH) ($p < 0.01$) (Fig. S3). By contrast, ln*RR* of abiotic NO contribution was also significantly ($p < 0.05$) linearly correlated with ln(TOC), ln(TN), ln(pH), and ln(Mn) (Fig. 6).

3.3 the role of abiotic processes in N retention

According to the meta-analysis of the available 113 studies, abiotic processes contributed on average 44−57% to total N retention, standing for about 4.4–5.7 Tg yr^{-1} of global N retention. The abiotic contribution to N retention highly depended on the N precursors, increasing in the order: NO_2^- > NO_3^- > NH_4^+ (Fig. 7a). The lowest abiotic contribution to N retention was found for the TN range of 3−10 mg kg^{-1}, but differences were not significant among the three levels of TOC, C/N, and pH (Fig. 7a). When NH_4^+ acted as the precursor of N retention alone, the abiotic contribution to N retention averaged at 25−36 % (Fig. 7b), and ln*RR* was significantly ($p < 0.05$) positively correlated to ln(TOC) and ln(TN), but negatively ($p < 0.01$) to ln(pH) (Fig. 8). When NO_3^- acted as the reactive N intermediate alone, the average abiotic contribution to the total N retention was around 66 %, and ln*RR* was significantly ($p < 0.05$) positively correlated to ln(TOC) and ln(TN) (Fig. 8). Even though NO_2^- contributed the highest share to abiotic N retention, ln*RR* of NO_2^--derived N retention was neither significantly correlated to C/N, TOC, TN, pH, nor to their natural logarithm transformed values (Table 1 and Fig. 8).

The average abiotic N retention rate was 0.8−1.0 %(applied N) h^{-1} based on the 251 studies, in which NH_4^+, NH_2OH, NO_2^-, and NO_3^- acted as precursors, and the abiotic N retention of NO_3^-, followed by NH_2OH, turned out to be the fastest among all the four common reactive N intermediates (Fig. 8c). Environmental conditions including TN, TOC, C/N, and pH affected largely the abiotic N retention rate, which turned out to be the highest at TN >10 mg kg^{-1}, TOC >20 %, C/N >20, and pH <5 (Fig. 8c). In addition, a significant ($p < 0.01$) linear correlation was found between ln*DR* of abiotic N retention and ln(C/N), ln(TOC), ln(TN), and ln(pH) (Fig. S4). The land use type did not change significantly the contribution of chemical reactions to total terrestrial N retention, but abiotic N retention rate was significantly higher in forest than that in cropland and grassland (Fig. 7).

4 Discussion

4.1 Abiotic N_2O emission

Chemical reactions of NO_2^- and NH_2OH are currently the mostly studied abiotic N_2O sources, while the attribution of chemical reduction of NO_3^- to N_2O has been explored only in a few studies (Fig. 3). Biological production of NO_2^- is regulated by nitrification and denitrification, while its microbially mediated consumption is catalyzed by nitrite reductase (NiR) and hydrazine synthase (HZS) during denitrification, nitrifier denitrification, and anaerobic ammonia oxidation (anammox), respectively (Fig. 1). Therefore, nitrifiers, denitrifiers, and anammox compete with transition metals and SOM for NO_2^- in terrestrial systems (Heil et al., 2016).

Transition metals and SOM are among the most important reactants with NO_2^- to form N_2O in chemical and microbial-mediated N-nitrosation reactions (Liu et al., 2017a; Spott et al., 2011; Van Cleemput and Baert, 1983; Wei et al., 2020). Compared with SOM, the reduction rate of NO_2^- by transition metals is much faster, and no catalyst is required for the reaction (Guerbois et al., 2014; Van Cleemput and Baert, 1983; Wullstein and Gilmour, 1966). Contents of TN and TOC were significantly ($p < 0.01$) positively correlated with the $\ln DR$ of NO_2^--derived abiotic N_2O emission, and the $\ln RR$ of chemical reduction of NO_2^- to the total N_2O emission was significantly ($p < 0.05$) positively correlated with Fe content (Table 1). Based on ^{15}N tracer modelling, Müller et al. (2014) found that N_2O production associated with the reactions of NO_2^- with SON accounted for about 54% of total N_2O emission in terrestrial ecosystems.

The production of NH_2OH is controlled by the ammonia monooxygenase (AMO) activity, while its consumption is regulated by microbial oxidation and various chemical reactions (Liu et al., 2017c). In a series of batch experiments, N_2O production rate of chemical NH_2OH oxidation tended to be 1−3 orders of magnitude higher than that of biological processes (Harper et al., 2015). Even though environmental factors significantly affect the chemical N_2O emission rate of NH_2OH (Table 1, Fig. 3), they also regulate the microbial NH_2OH production and consumption (Ermel et al., 2018). As a consequence of the bidirectional regulation, the apparent contribution of abiotic NH_2OH oxidation to the total N_2O emission was not significantly influenced by environmental factors (Table 1, Fig. 3). Alkaline pH strongly promotes the self-decomposition of NH_2OH to form N_2O (Heil et al., 2016), which explains the significant ($p < 0.01$) positive correlation of pH with the $\ln DR$ of NH_2OH-derived abiotic N_2O production (Table 1).

4.2 Abiotic NO emission

Nitrite is the direct precursor in both microbial and chemical NO production processes (Islam et al., 2008; Medinets et al., 2015; Riordan et al., 2005), and reduction of NO by nitric oxide reductase (NOR) represents the main NO sink (Pilegaard, 2013). Much higher NO emission in sterilized treatments than that in unsterilized ones was reported in many studies (Duan et al., 2020; Homyak et al., 2017;

Wang et al., 2019; Wei et al., 2017a), which resulted in a *RR* of NO emission much higher than 100% (Fig. 5a). In microbial pathways, NO is released as a by-product from denitrification (Heil et al., 2016), and microbial NO emission is slowed down when NO is rapidly reduced by NOR to N_2O and N_2 (Pilegaard, 2013). By contrast, chemically produced NO in sterilized soils is directly emitted into the atmosphere due to the lack of active NOR. The much higher *RR* of NO emission than 100% indicates that microbial reactions play as very likely a sink of NO especially in situations where NOR is highly active.

The role of chemical NO_2^- conversion in NO production was first considered in a process-oriented model in forest soils (Li et al., 2000), and the meta-analysis in this study revealed that chemical decomposition of NO_2^- represented the highest abiotic NO production rate (Fig. 5). Transition metals, namely elements with partially filled *d*-orbitals, or which can form cations with partially filled *d*-orbitals according to IUPAC (1997), have very dynamic valence with a shape-shifting nature. They include iron (Fe), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), cobalt (Co), and molybdenum (Mo), among which Fe (7−550 g kg^{-1}) and Mn (20−3000 mg kg^{-1}) are the most abundant ones in soil and they are generally thought to play a more important role in biogeochemical N cycle than others (Lindsay, 1979). The redox potentials (E_h) of Fe(III)/Fe(II) (+0.771 V) (Li et al., 2019) and Mn(IV)/Mn(III) (+2.01 V) (Yamaguchi and Sawyer, 1985) are much higher than that of NO_3^-/NO_2^- (+0.42 V) and NO_2^-/NO (+0.375 V) (Berks et al., 1995). Therefore, the chemical reduction of NO_3^- and NO_2^- to NO by Fe and Mn complexes, indicated by the significant ($p < 0.01$) correlation of chemical production rate of NO with the contents of Fe and Mn in soil (Fig. S3), occurred most likely in combination with other redox pairs.

Except for NO_2^- reduction by transition metals, the chemical reaction of NO_2^- with SOM accounts for the other main chemical NO source. Our finding that TOC content was significantly positively correlated with the abiotic production NO rate (Figs. S3) is in agreement with previous studies (Fitzhugh et al., 2003; Opuwariboi and Odu, 1975). In this regard, the quality of SOM plays a more important role than quantity, e.g., the chemical NO production rate of NO_2^- with SOM fractions decreased largely in the order: humin > humic acid > fulvic acid (Wei et al., 2017a). By contrast, higher abundance and activity of microbial NO_2^- reducers are in line with higher TOC content, which was negatively correlated with ln*RR* of NO emissions (Fig. 6) due to the large promotion of biotic NO production (Fig. S4).

4.3 Abiotic N retention

By contrast to the microbial N retention, chemical N retention pathways involve various reactions of NH_4^+, NO_2^-, and NO_3^-, among which the chemical immobilization of NO_2^- represented the highest abiotic contribution to total N retention (Fig. 7). Despite the argument that the chemical reduction rate of NO_3^- is too slow to make a difference in the N cycle (Colman et al., 2007, 2008), it has been found that microbially mediated oxidation of Fe(II) and reduction of NO_3^- are commonly co-occuring under various environmental conditions (Chakraborty and Picardal, 2013; Muehe et al., 2009; Straub et al., 1996), resulting in abiotic NO_3^- immobilization in organic N compounds (Corre et al., 2007; Dail et al., 2001; Torres-Canabate et al., 2008).

The fixation of NH_4^+ by mineral clay particles or SOM was first observed decades ago. When NH_4^+ penetrates the interlayers of clay minerals, it sheds its hydration water shell and enters the lattice voids, leading to physical NH_4^+ fixation (Kittrick, 1966; Nõmmik, 1965). Except physical NH_4^+ fixation, it was demonstrated that NH_4^+ can also be chemically fixed into SON through reactions with SOM, especially at alkaline pH and in the presence of oxygen (Broadbent, 1960; Nommik and Nilsson, 1963).

Formation of organic N compounds was also found for the abiotic reactions of HNO_2 with SOM components. For example, 7-hydroxy-6-methoxy-1,2(4*H*)-benzoxazin-4-one was produced in the chemical reaction of HNO_2 with ferulic acid (Rousseau and Rosazza, 1998), nitrosophenol, *p*-diazoquinone, and *o*-diazoquinone in the case of phenol (Kikugawa and Kato, 1988), nitrosonaphthol and nitronaphthol in the case of naphthol (Azhar et al., 1989), nitroso and heterocyclic compounds in the case of humic and fulvic acids (Thorn and Mikita, 2000). Heterocyclic and nitro-aromatic compounds are common organic N compounds resulting from abiotic reactions, and they have received increasing interest in the last years due to their resistance to decomposition (Leinweber et al., 2009). Heterocyclic compounds like pyrroles and pyridines, pyrazines, nitriles, and imines have been detected in various natural humic substances (Thorn and Cox, 2009), and the content of heterocyclic N was found to increase during humification (Abe et al., 2005). Gillespie et al. (2009) also found that nitro-aromatic compounds do exist in the rhizosphere of pea, accompanied by a decrease of aromatic C compounds. This suggest that the long-term N retention could be caused by the increase of heterocyclic and nitro-aromatic N compounds from chemical N immobilization in soil (Thorn and Cox, 2009).

Higher TOC content provides more active sites for N intermediates, hence TOC content was significantly ($p < 0.01$) positively correlated with the abiotic N retention (Fig. S5), which is in agreement with previous studies (Fitzhugh et al., 2003; Opuwariboi and Odu, 1975). On the one hand, higher pH reduces the reactivity of NO_2^- (Corre et al., 2007; Fitzhugh et al., 2003), on the other hand, it also inhibits the solubility of most transition metals and decreases the activity of SOM electrophilic functional groups including –C=O, –OH, and –COOH (Stevenson, 1995). In line with these mechanisms, our meta-analysis revealed a significant negative linear correlation of ln(pH) with ln*DR* of abiotic N retention (Table 1).

4.4 the role of abiotic processes in the terrestrial N cycle

Sterilization of environmental samples is generally applied to distinguish the N gas emission or N retention from chemical reactions, however, its influence on soil properties and structure cannot be avoided. Chemical reactions are generally regarded to be much faster compared with biological processes, the approach of time difference, i.e. the difference between short-term (10−30 min) and long-term (more than 6 h) N transformation processes, is sometimes used to estimate the contribution of abiotic processes (Corre et al., 2007; Wang et al., 2019). Highly energetic irradiation destroys microbial enzymes and cell components, while high-pressure steam autoclaving damages microbial cell membranes and proteins; and both processes decrease soil aggregation, increase dissolved organic matter (DOM) content, and decrease the aromaticity and polycondensation of DOM (Berns et al., 2008; Buessecker et al., 2019). Cell lysis occurs during chloroform fumigation, but enzyme activities are less inhibited (Blankinship et al., 2014). On the opposite side, chemical inhibitors generally efficiently inhibit the activities of microbial enzymes, but also change the soil chemistry at the same time (Buessecker et al., 2019). Azide, for example, can react with DOM and pyrite, lowering the reducing capacity of the microcosm, and form N_2O and NO with soil-derived NO_2^- (Hendrix et al., 2019).

The chemical N retention rate estimated based on the time difference approach was about two orders of magnitude higher than that of other sterilization techniques, while the lowest abiotic N retention and N_2O production rates were observed in irradiated samples (Fig. 9). No soil disturbance occurs when the time difference approach was applied, but the existence of biological processes in the short term, which might be much faster rather than negligible, could account for the overestimation of abiotic N retention rate (Kizewski et al., 2019; Zhu and Wang, 2011). Even though irradiation increased DOM content, the chemical reactivity of DOM could be slightly inhibited due to the decrease of aromaticity of DOM (Berns et al., 2008), while the influence of chemical inhibitors on abiotic reactions highly depends on their interactions with SOM and transition metals, which explains their differences in abiotic reaction rates (Fig. 9). Estimated on the basis of our meta-analysis results, abiotic reactions account for approximately 3.7−4.7, 9.0−16.3, 4.0−6.0 Tg yr^{-1} of global terrestrial N_2O emission, NO emission, and N retention, respectively. However, we have to keep in mind these results were calculated based on the simplified calculation (Equation 4), uncertainties can be caused by different sterilization techniques, land use types, soil conditions. More research data at various environmental conditions are needed to develop a more sophisticated model for a more precise estimation of abiotic reactions in global N cycle.

To gain complete understanding of the role of chemical reactions in the biogeochemical N cycle, efforts have to be made to disentangle biotic and abiotic processes in terrestrial ecosystems. Empirically derived rate laws have been applied to quantify abiotic N transformation processes without disturbance of local soil conditions (Liu et al., 2019; Stanton et al., 2018). Stanton et al. (2018) suggested that N_2O production from chemical reduction of NO by Fe(II) followed a rate law of $d[N_2O]/dt = 7.2\times10^{-5}[Fe(II)]^{0.3}[NO]^1$, sustaining an N_2O flux of 100−200 Tg N yr^{-1} across an oceanwide oxycline for the Proterozoic era (2.5−0.5 billion years before present). A first order fitting ($d[N_2O]/dt = k[NH_2OH]^{0.9}[MnO_2]^{0.3}$) was also reported to model the kinetics of NH_2OH oxidation by Mn(IV) oxides (Cavazos et al., 2018). By contrast, Liu et al. (2019) also reported that the kinetics of NO_3^- and NO_2^- reduction by Fe(II) with or without microbial mediation was well fitted with a pseudo-first-order model to quantify the N_2O and NO production from these reactions. One of the major drawbacks of these models is that the pH effect and the mineral formation on the redox interaction surface were not considered, despite their significant influence on reaction kinetics (Chen et al., 2020).

Isotopic signatures have been widely used for process identification and source partitioning. Differences of ^{15}N fractionation factor ($\varepsilon^{15}N$) of abiotic and biotic NO_3^- reduction were found in laboratory studies, while $\varepsilon^{15}N$ of abiotic NO_2^- reduction was not significantly different from that of biotic NO_2^- reduction (Buchwald et al., 2016; Margalef-Marti et al., 2020; Margalef-Marti et al., 2019). The ^{15}N site preference (SP) of N_2O was regarded as an efficient tool to partition N_2O sources (Toyoda and Yoshida, 1999). Although significant differences of N_2O SP values were found between biological processes, e.g. nitrification and denitrification (Toyoda et al., 2017), the SP of N_2O from abiotic oxidation of NH_2OH (34–36 ‰) is overlapping with that of biotic nitrification (Heil et al., 2014). Furthermore, the SP value of N_2O varied largely in reactions of NO_2^- with lignin derivatives, and this variation was affected by both pH and the structure of the organic substances (Wei et al., 2019; Wei et al., 2017b). It has also been reported that N_2O sources were biased when SP was used for N_2O source partitioning without considering N_2O production from abiotic NO_2^-–SOM reactions (Wei et al., 2017a). Notably, the isotopic signatures of N_2O from abiotic NO_2^- reactions are undistinguishable from the other N_2O pathways, such as NH_2OH oxidation, fungal denitrification, nitrifier denitrification, and bacterial denitrification (Ostrom et al., 2016; Peters et al., 2014; Wei et al., 2017b), which limits greatly the use of current N_2O source partitioning tools.

The diverse microbially and chemically mediated reactions make it challenging to quantify the biotic and abiotic contribution to the biogeochemical N cycle: i) Chemical and microbial electron transfer processes support but also compete with each other. Microbial processes are not only sources of reactive N intermediates but also compete with chemical reactions for these intermediates. ii) The microbial and chemical electron transfer rates are both highly affected by environmental conditions (redox potential, pH, radicals, etc.). Nevertheless, knowledge is currently limited about their integrated interactions on microbially and chemically mediated biogeochemical N transformations. iii) Different sterilization techniques disturb soil properties, and depending on whether the changes of soil properties lead to up- or downregulation of the chemical reaction rates, the contribution of chemical reactions to the biogeochemical N cycle could be either overestimated or underestimated. iv) Research is scarce in terms of basic reaction rates, isotopic signatures, and environmental influences of microbially and chemically mediated reactions and their interplay in terrestrial ecosystems. Future studies should emphasize the relative contributions of chemical and enzymatically catalyzed processes in the biogeochemical N cycle. Except traditional control experiments using sterile techniques, alternatives such as modelling and advanced isotopic techniques, e.g. clumped isotopic techniques, should be included in future experimental approaches to distinguish abiotic reactions from biotic processes.

5 Conclusions

Soil microbes act as main drivers of the N flow in soils, during which reactive N intermediates, such as NH_4^+, NO_2^-, NH_2OH, NO_3^-, amino acids, and amino sugars, are released to terrestrial ecosystems. Transition metals, phenols, humus, and organic radicals are chemically highly reactive to these N intermediates. Various abiotic reactions occur once these reactive compounds get in contact with each other, leading to abiotic N gas emission and soil N retention. This meta-analysis has demonstrated that these abiotic reactions of reactive N-intermediates, derived from biotic processes, play an important role in the terrestrial N cycle: abiotic reactions account for approximately 3.7−4.7 and 4.0−6.0 Tg yr^{-1} of global terrestrial N_2O emission and N retention, respectively.

Although traditional control experiments with sterilized soil can help to discern chemically mediated N transformations, it fails to discern the potential interplay of biotic and abiotic processes, e.g. NH_2OH production from microbial NH_4^+ oxidation with AMO, followed by both/either chemical NH_2OH oxidation by Fe(III) and/or microbial NH_2OH oxidation by HAO. Current standard experimental approaches should be adapted by integrating sterilized and unsterilized control design, modelling, and isotopic techniques. Further kinetic, isotopic, and modelling studies of involved biotic and abiotic reactions would provide biogeochemists with tools for a better understanding of the complex interplay of biologically and chemically mediated reactions in the biogeochemical N cycle.

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Table 1. Spearman correlation of environmental conditions with the contribution of chemical reactions to total N_2O emission, NO emission, and N retention (lnRR), as well as abiotic N_2O production, NO production, and N retention rates (lnDR).

	N_2O						NO		N retention								
	all N species		NH_2OH		NO_2^-		all N species		all N species		NH_4^+		NO_2^-		NO_3^-		Others
	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR	lnRR	lnDR
TOC	-0.056	-0.013	**-0.351***	0.042	**0.360****	-0.108	**0.366****	**-0.470****	**0.484****	0.071	**0.308****	**0.314***	**0.729****	-0.085	**0.809****	0.405	**0.819****
TN	**0.203***	-0.043	**-0.457****	0.006	**0.327****	-0.170	**0.331***	**-0.476****	**0.383****	0.087	0.110	**0.364***	**0.705****	-0.314	**0.623****	0.422	**0.805****
C/N	0.050	0.073	**-0.410****	0.120	0.090	-0.075	0.212	-0.348	**0.362****	-0.002	**0.322****	0.188	**0.376****	-0.042	**0.749****	0.030	**0.780****
pH	0.065	0.085	**0.441****	0.000	0.003	0.119	**-0.506****	**0.442***	**-0.389****	-0.096	**-0.248***	**-0.388***	**-0.782****	0.156	**-0.851****	-0.218	**0.413****
Fe	-0.107	-0.064	0.112	-0.212	0.225	**0.482***	0.053	0.188	–	–	–	–	–	–	–	–	–
Mn	**0.370****	0.023	**0.497****	-0.119	**-0.461***	0.242	**0.675****	-0.324	–	–	–	–	–	–	–	–	–

Note:

* $p < 0.05$;

$^{**}p < 0.01$

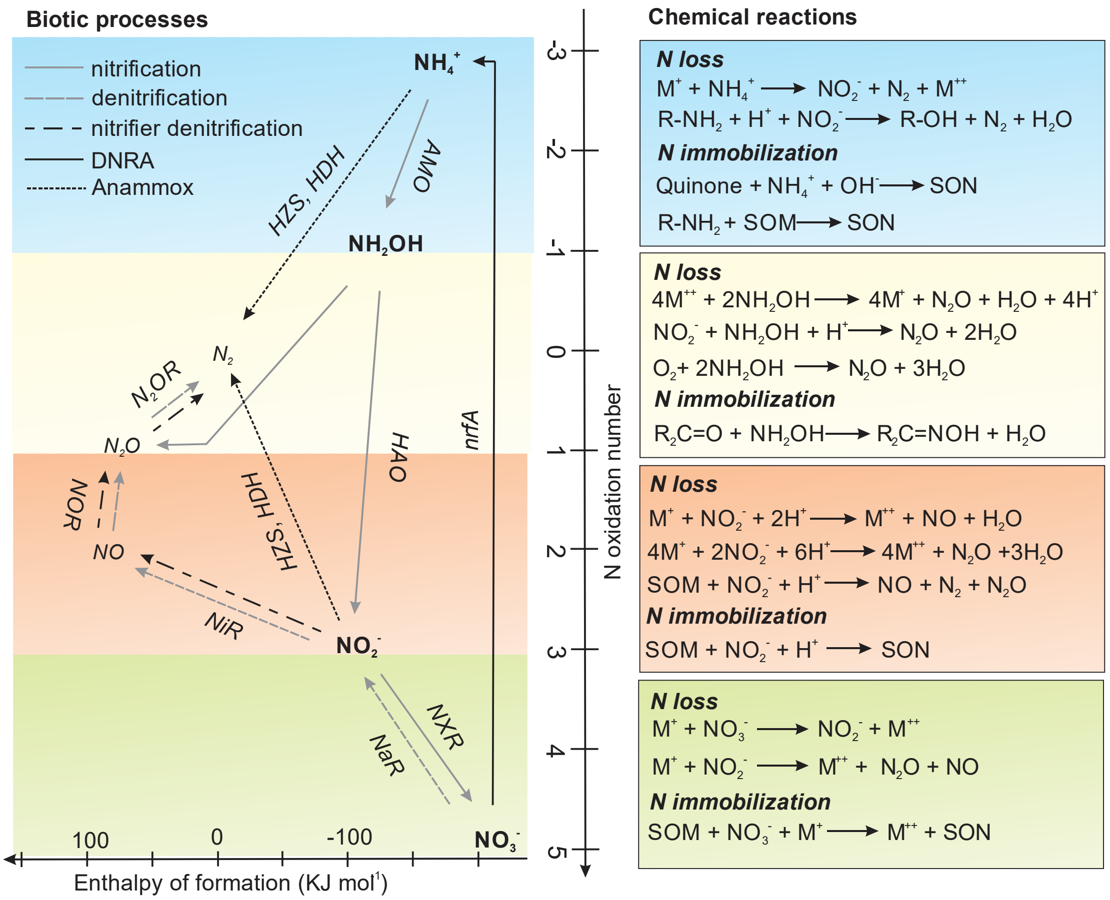

Fig. 1. Microbial processes and associated chemical reactions within the biogeochemical N cycle in soil, listed according to the N oxidation number of involved N species. Microbial nitrification, denitrification, nitrifier denitrification, anaerobic ammonia oxidation (Anammox) and dissimilatory nitrate reduction to ammonium (DNRA) are shown on the left-hand side, which are catalyzed by ammonia monooxygenase (AMO), hydroxylamine oxidoreductase (HAO), nitrite oxidoreductase (NXR), nitrate reductase (NaR), nitrite reductase (NiR), nitric oxide reductase (NOR), nitrous oxide reductase (N_2OR), hydrazine synthase (HZS), and hydrazine dehydrogenase (HDH), and nitrite reductase (nrfA). Reactive N intermediates in soil produced from microbial processes mainly involve free amino-compounds ($R\text{-}NH_2$), ammonium (NH_4^+), hydroxylamine (NH_2OH), nitrite (NO_2^-), and nitrate (NO_3^-), their chemical reactions with soil organic matter (SOM), transition metals (M^+/M^{++}; mainly iron and manganese), and oxygen (O_2) are shown on the right-hand side. Enthalpy of formation of N species at 298 K.

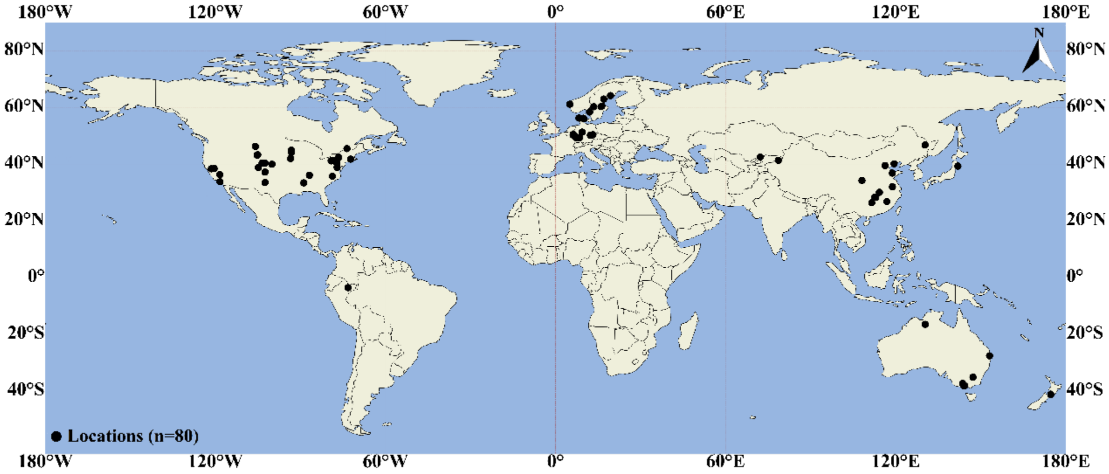

Fig. 2. Location of study sites included in the mate-analysis.

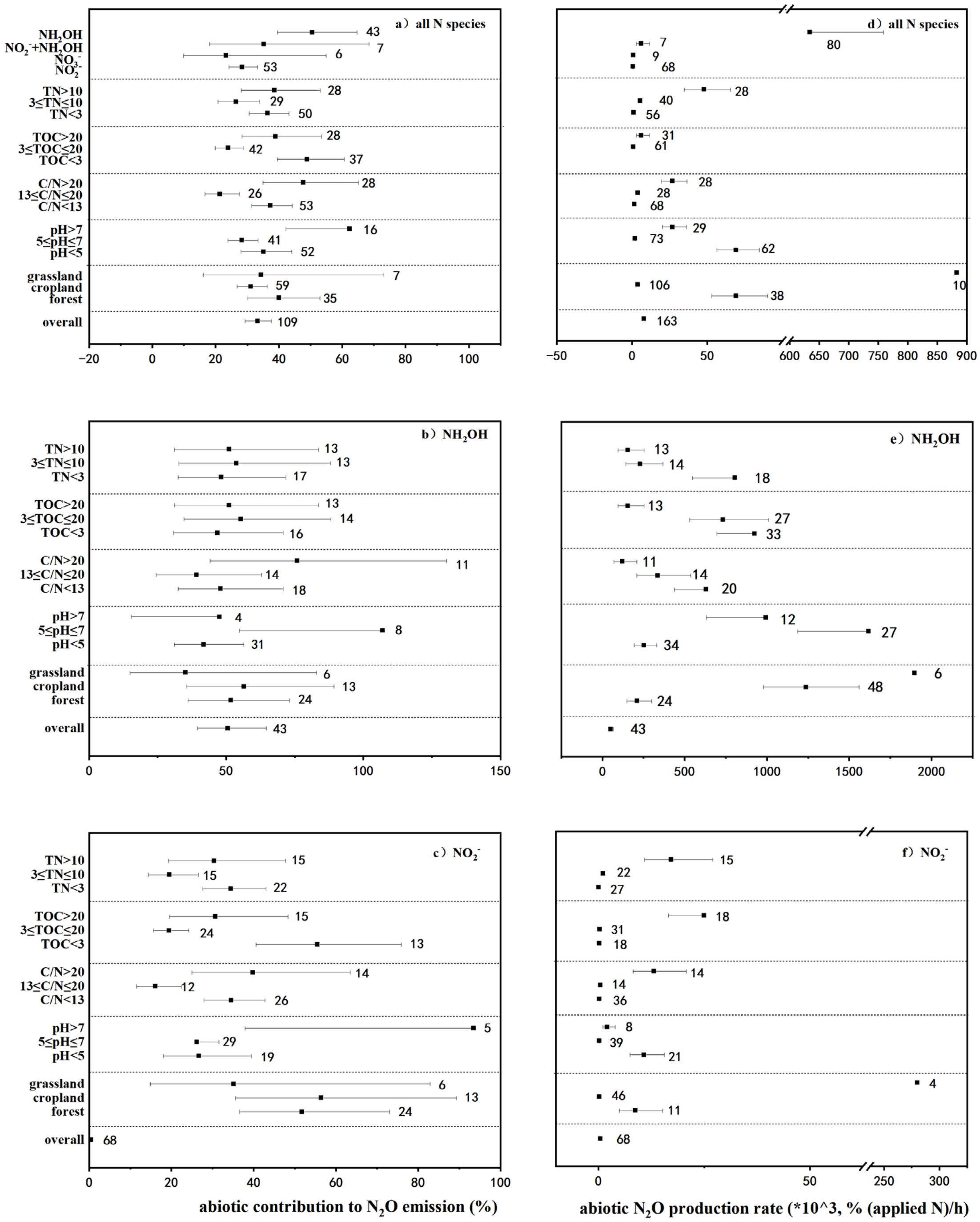

Fig. 3. The contribution of abiotic reactions of NO_2^-, NO_3^-, and NH_2OH (a), NH_2OH alone (b), and NO_2^- alone (c) to the total N_2O emission, as well as the abiotic N_2O production rate of NO_2^-, NO_3^-, and NH_2OH (d), NH_2OH alone (e), and NO_2^- alone (f). Numbers on the right side indicate the experimental studies used for the meta-analysis. TN, total nitrogen (mg kg^{-1}); TOC, total organic carbon (%); C/N, the ratio of carbon to nitrogen.

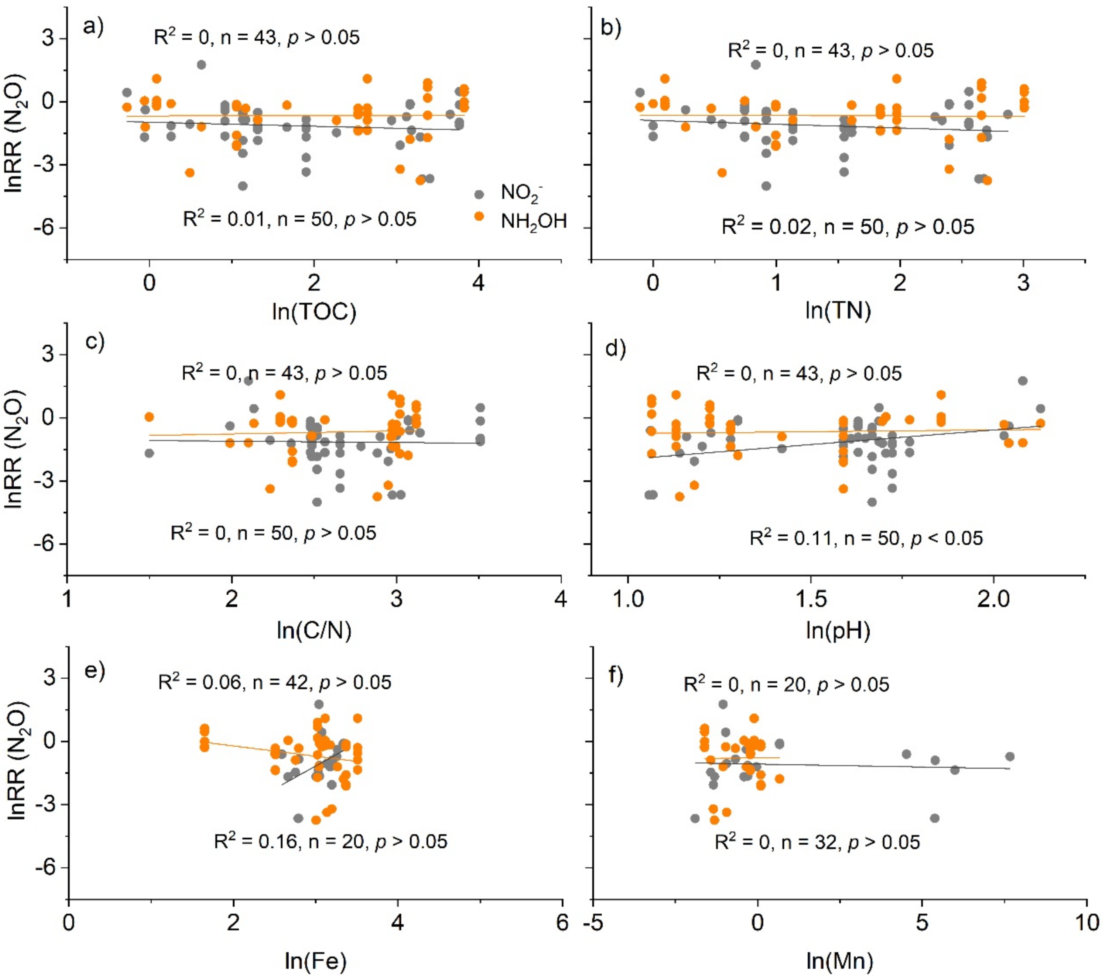

Fig. 4. Correlation of lnRR of abiotic N_2O emission with natural logarithm transformed total organic carbon (ln(TOC), a), total nitrogen (ln(TN), b), the ratio of carbon to nitrogen (ln(C/N), c), soil pH (ln(pH), d), Fe content (ln(Fe), e), and Mn content (ln(Mn), f).

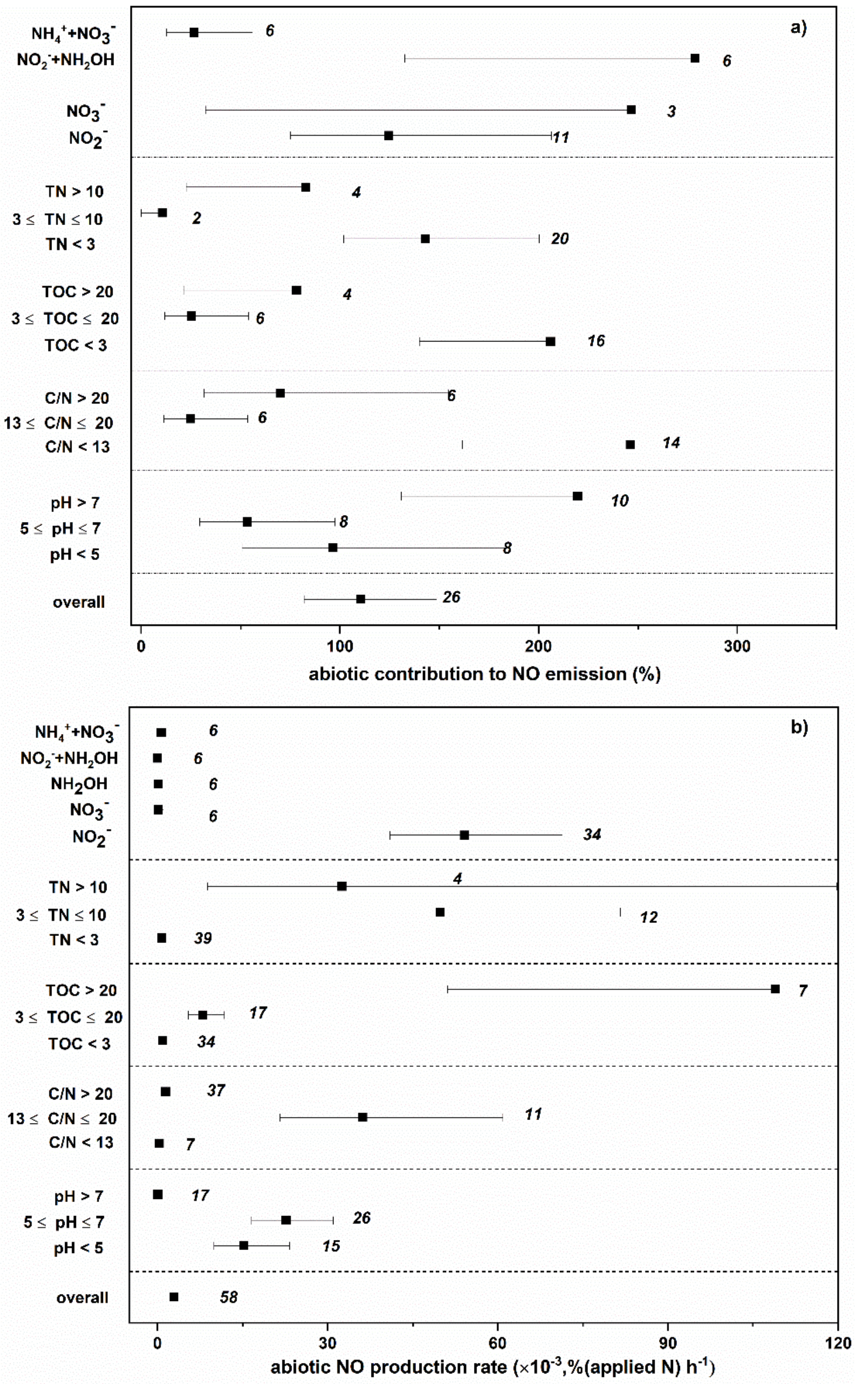

Fig. 5. The contribution of abiotic reactions to the total NO emission (a) and the abiotic NO production rate (b). Numbers on the right side indicate the experimental studies used for the meta-analysis. TN, total nitrogen (mg kg^{-1}); TOC, total organic carbon (%); C/N, the ratio of carbon to nitrogen.

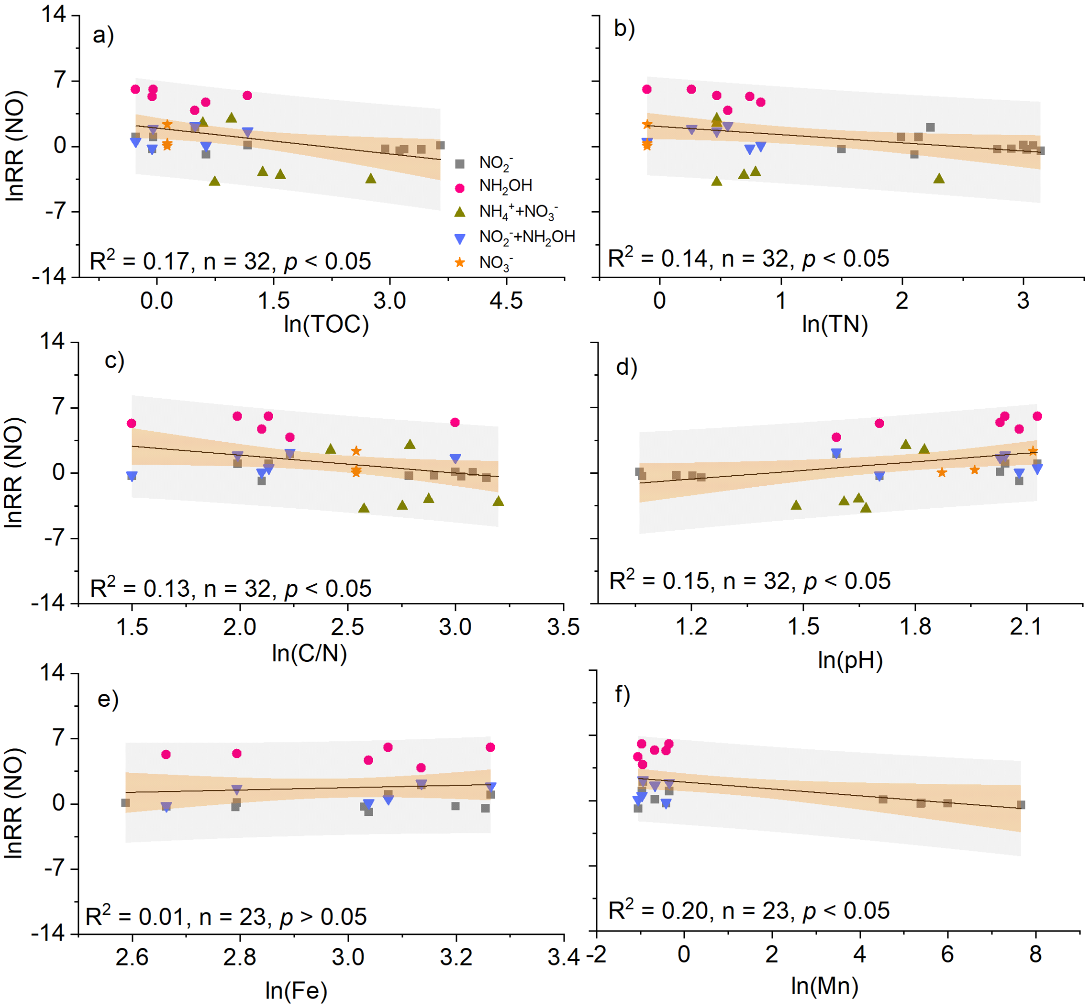

Fig. 6. Correlation of lnRR of abiotic NO contribution with natural logarithm transformed total organic carbon (ln(TOC), a), total nitrogen (ln(TN), b), the ratio of carbon to nitrogen (ln(C/N), c), soil pH (ln(pH), d), Fe content (ln(Fe), e), and Mn content (ln(Mn), f).

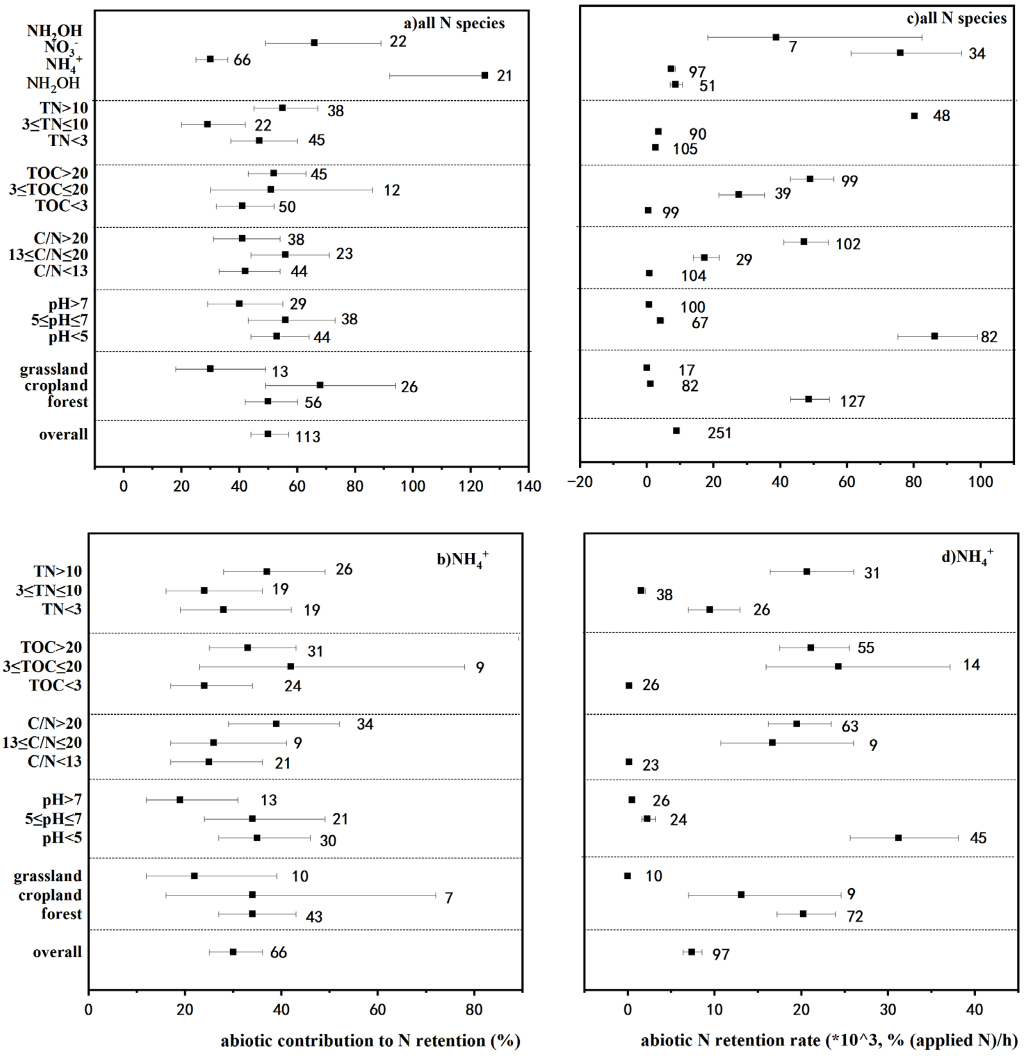

Fig. 7. The contribution of abiotic reactions of NH_4^+, NO_2^-, and NO_3^-(a), NH_4^+ alone (b) to the total N retention, as well as the abiotic N retention rate of NH_4^+, NO_2^-, NO_3^-, and NH_2OH (c), NH_4^+ alone (d). Numbers on the right side indicate the experimental studies used for the meta-analysis. TN, total nitrogen (mg kg^{-1}); TOC, total organic carbon (%); C/N, the ratio of carbon to nitrogen.

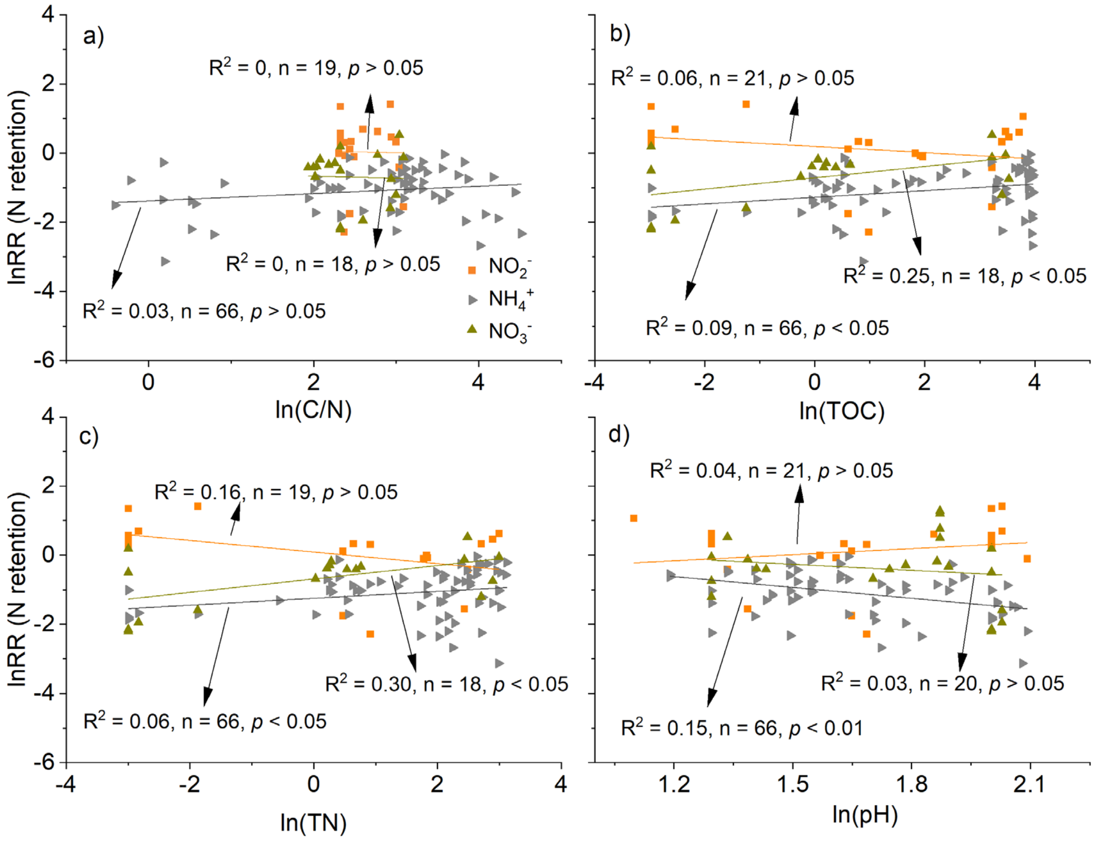

Fig. 8. Correlation of lnRR of abiotic N retention with natural logarithm transformed the ratio of carbon to nitrogen (ln(C/N), a), total organic carbon (ln(TOC), b), total nitrogen (ln(TN), c), and soil pH (ln(pH), d).

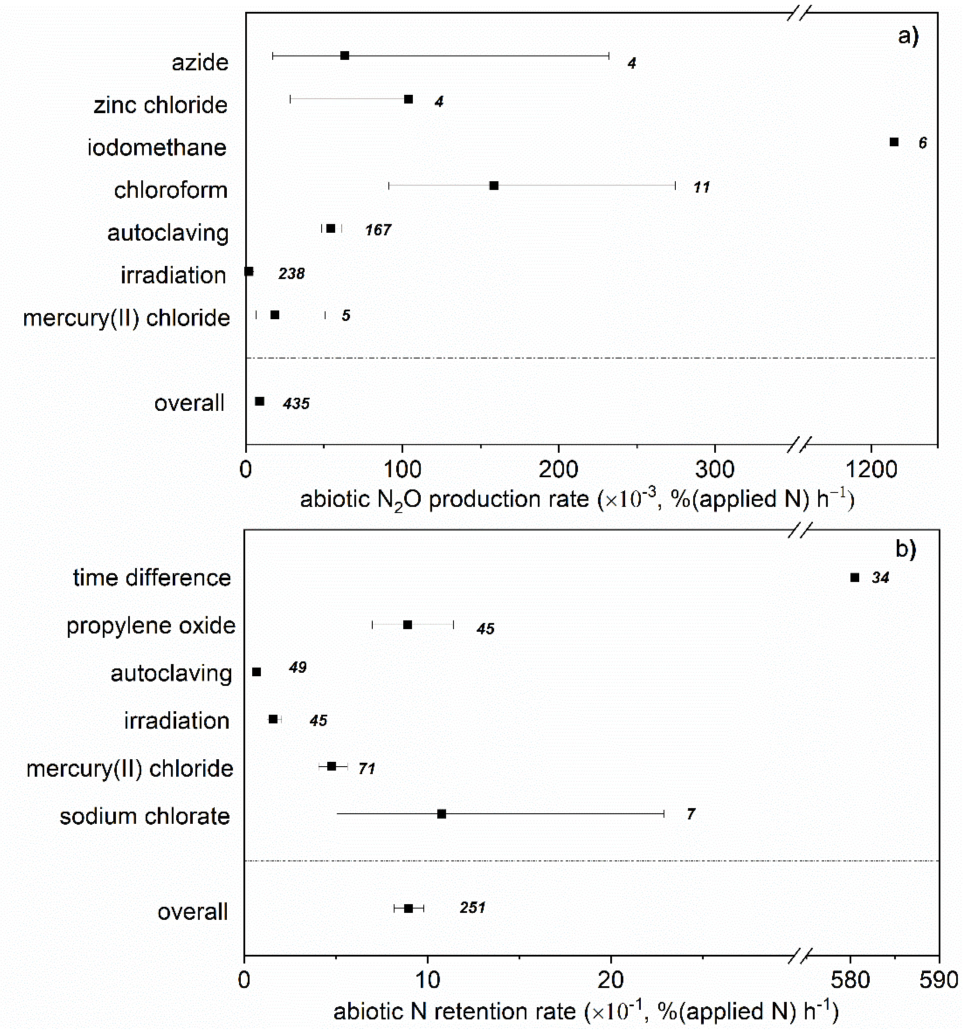

Fig. 9. Effects of sterilization techniques on abiotic N_2O production rate (a) and N retention rate (b). Numbers on the right side indicate the experimental studies used for the meta-analysis.

Data S1. References of all datasets included in this meta-analysis

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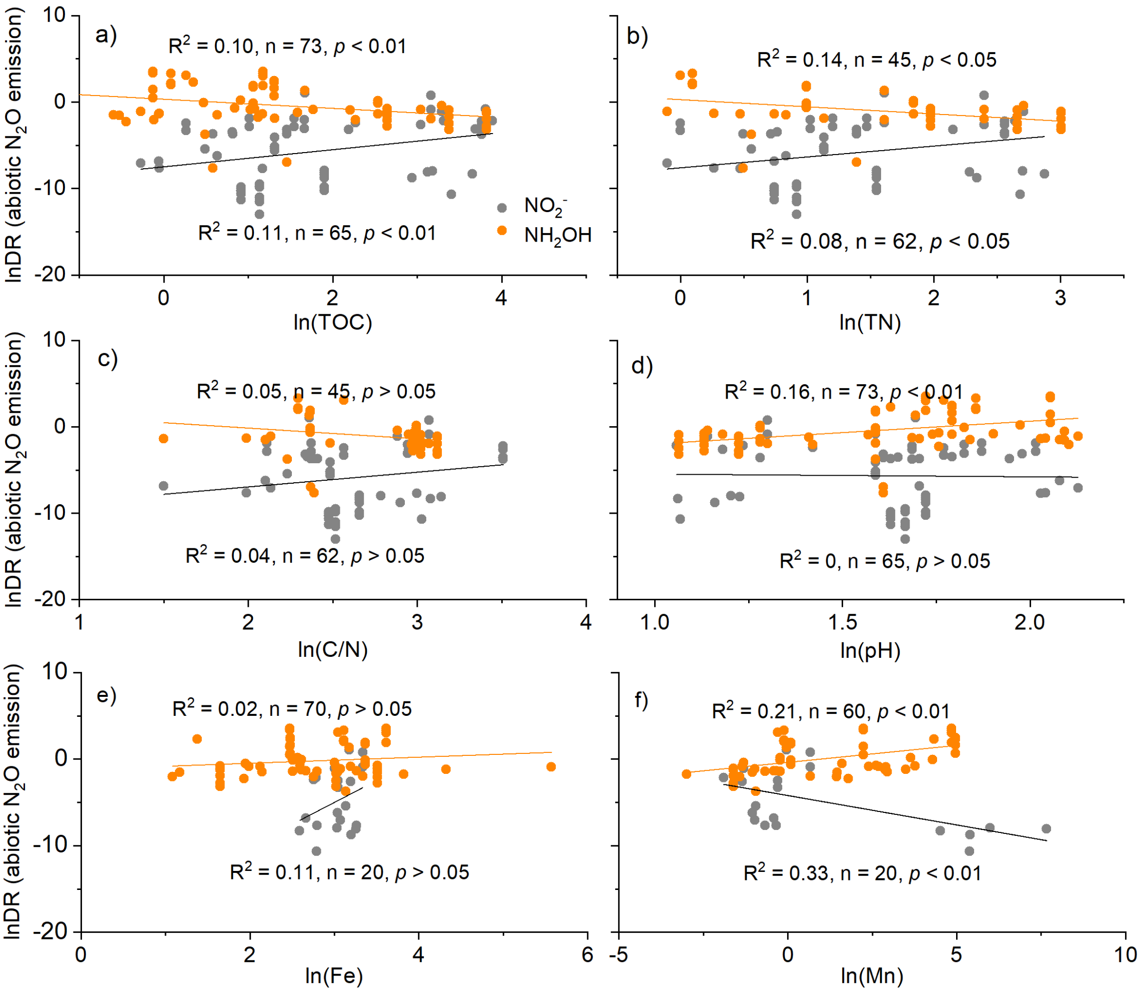

Fig. S1. Correlation of lnDR of abiotic N_2O emission with natural logarithm transformed total organic carbon (ln(TOC), a), total nitrogen (ln(TN), b), the ratio of carbon to nitrogen (ln(C/N), c), soil pH (ln(pH), d), Fe content (ln(Fe), e), and Mn content (ln(Mn), d).

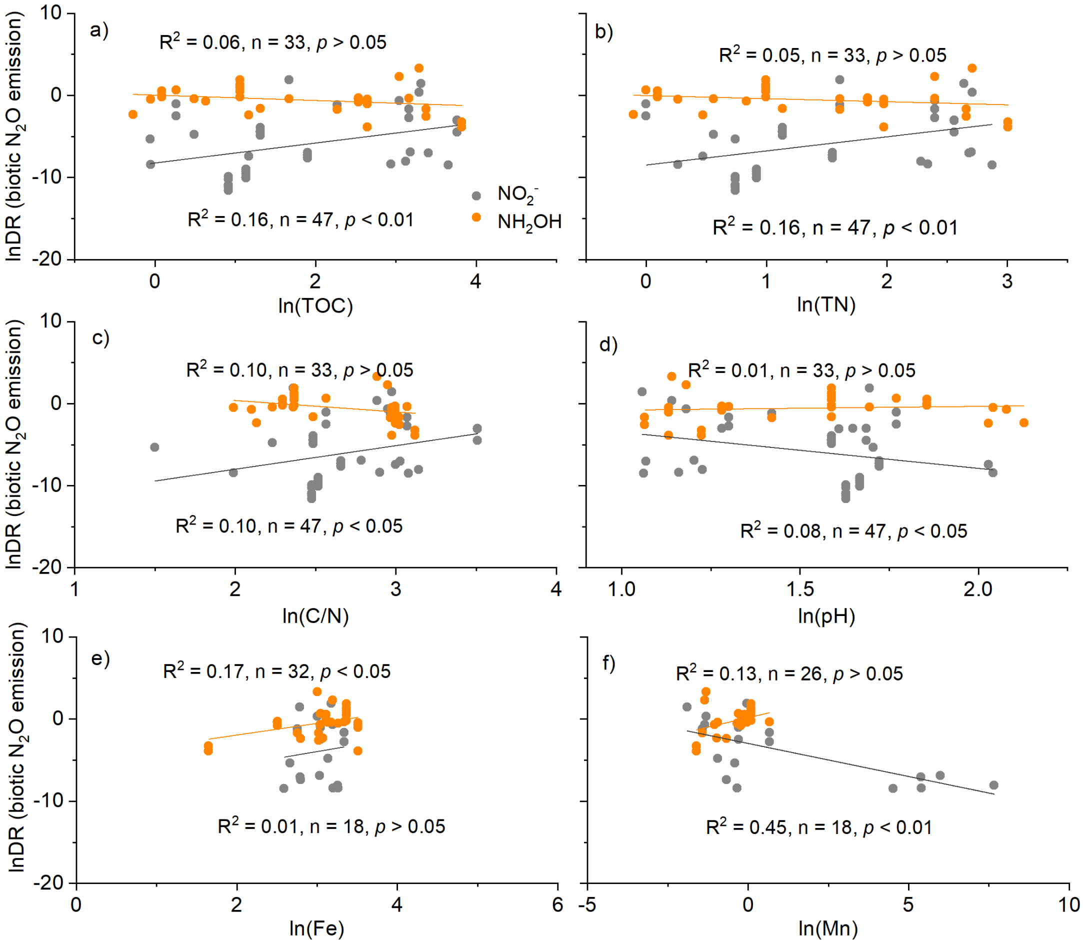

Fig. S2. Correlation of lnDR of biotic N_2O emission with natural logarithm transformed total organic carbon (ln(TOC), a), total nitrogen (ln(TN), b), the ratio of carbon to nitrogen (ln(C/N), c), soil pH (ln(pH), d), Fe content (ln(Fe), e), and Mn content (ln(Mn), f).

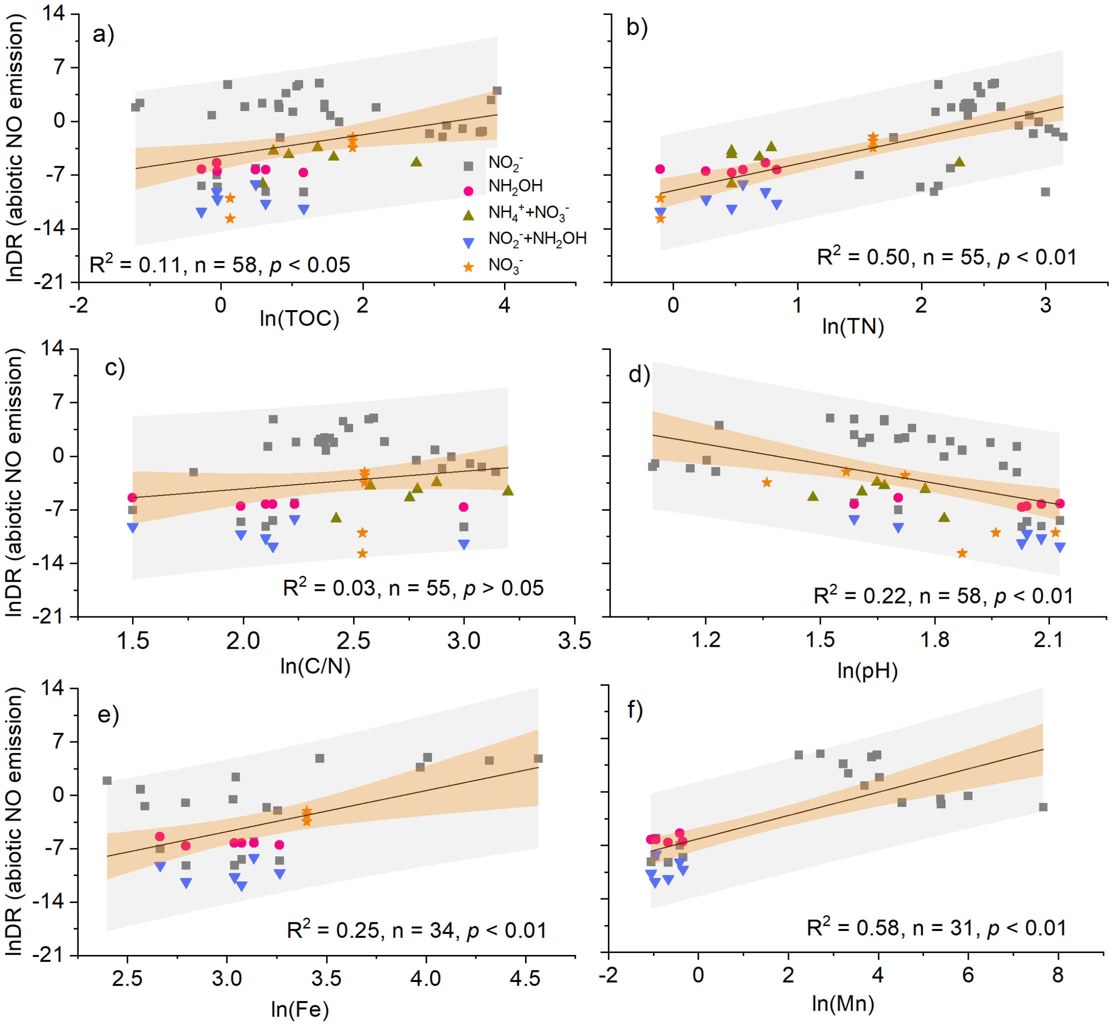

Fig. S3. Correlation of lnDR of abiotic NO emission with natural logarithm transformed total organic carbon (ln(TOC), a), total nitrogen (ln(TN), b), the ratio of carbon to nitrogen (ln(C/N), c), soil pH (ln(pH), d), Fe content (ln(Fe), e), and Mn content (ln(Mn), d).

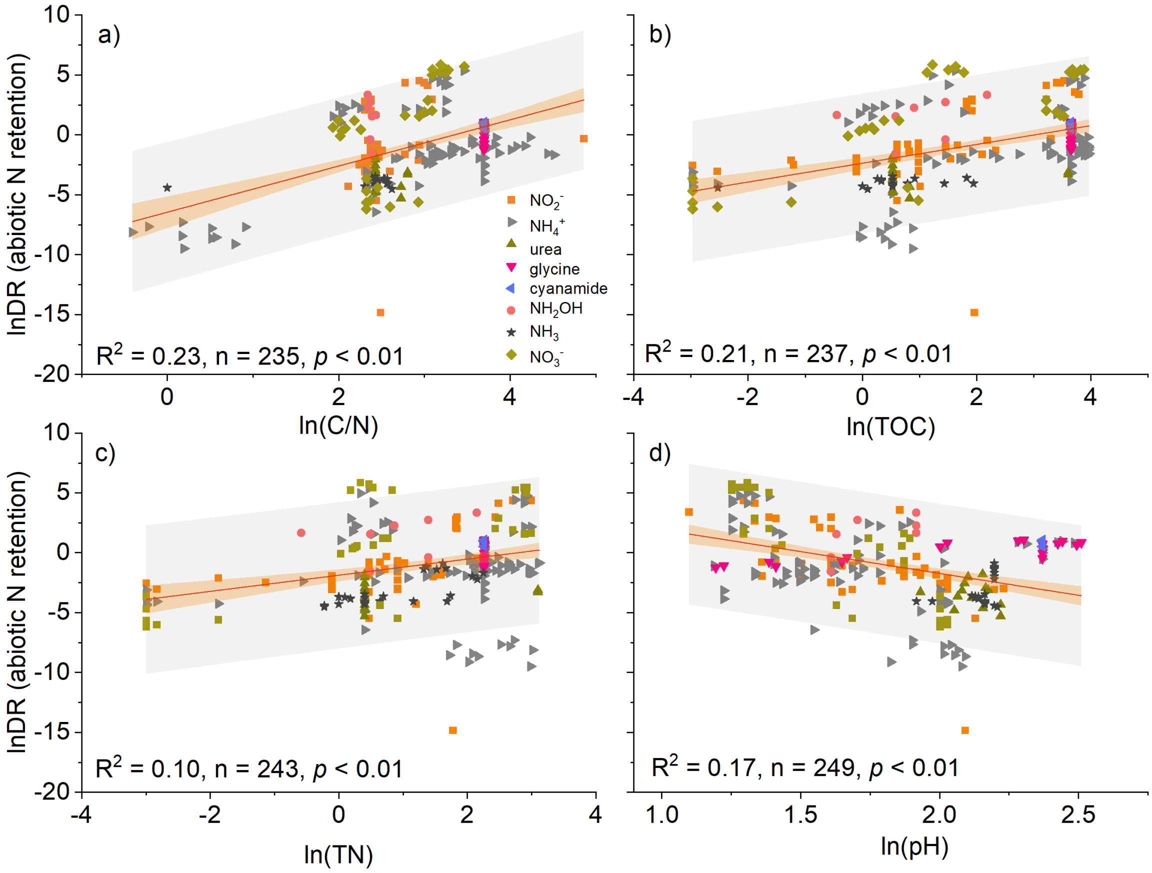

Fig. S4. Correlation of lnDR of abiotic N retention with natural logarithm transformed the ratio of carbon to nitrogen (ln(C/N), a), total organic carbon (ln(TOC), b), total nitrogen (ln(TN), c), and soil pH (ln(pH), d).

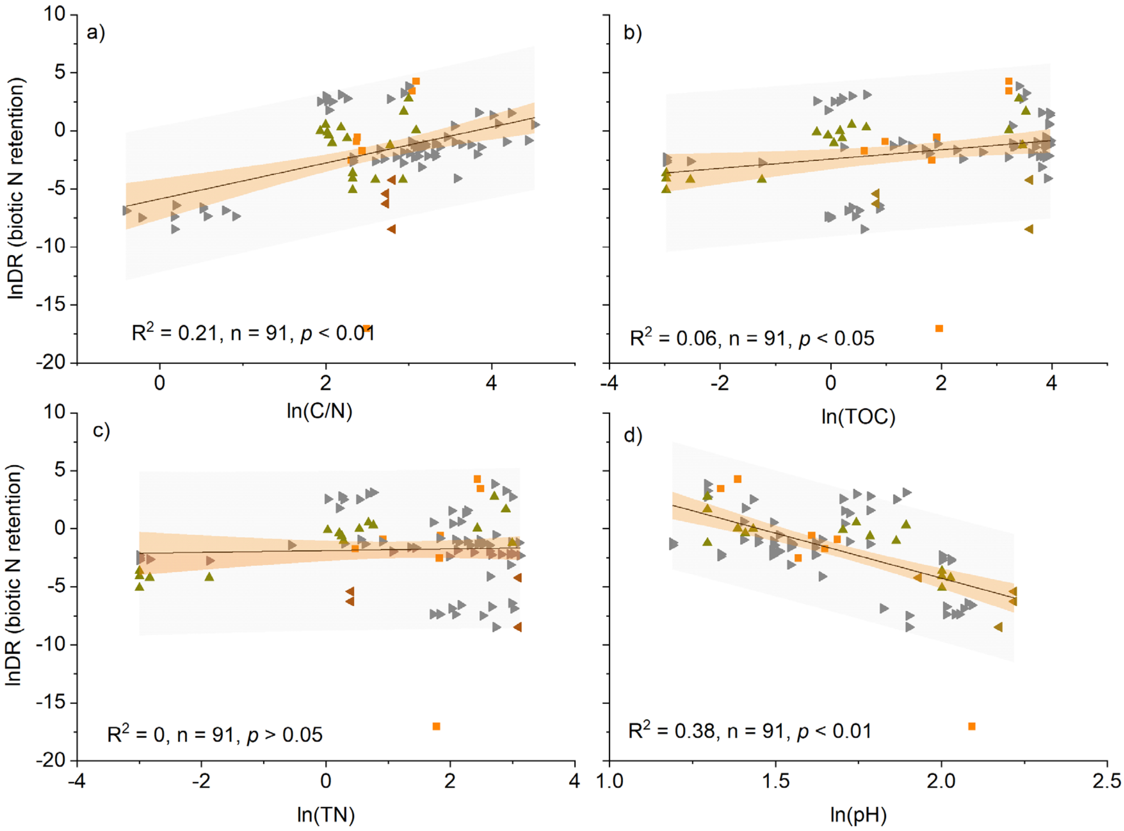

Fig. S5. Correlation of lnDR of biotic N retention with natural logarithm transformed the ratio of carbon to nitrogen (ln(C/N), a), total organic carbon (ln(TOC), b), total nitrogen (ln(TN), c), and soil pH (ln(pH), d).

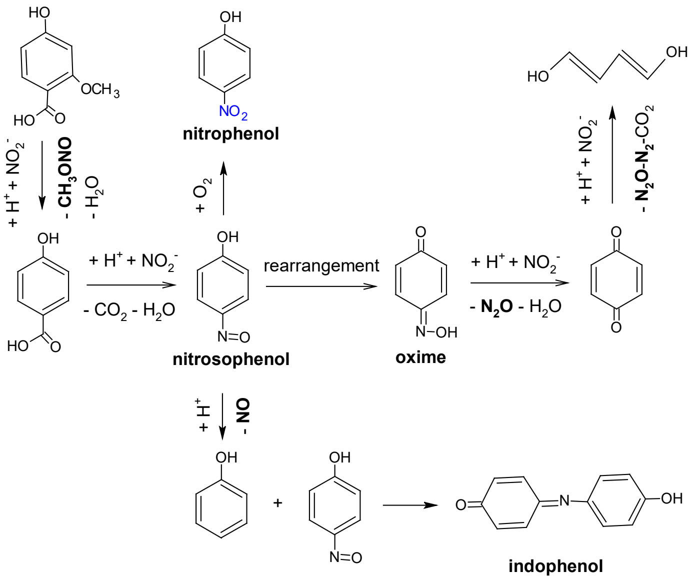

Fig. S6. Proposed pathways involved in the chemical reaction of nitrite (NO_2^-) with 4-hydroxy-3-methoxybenzoic acid under acidic conditions.