Parent material influences soil abiotic N$_2$O production from chemical oxidation of hydroxylamine

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Abstract. Hydroxylamine (NH$_2$OH) and nitrite (NO$_2^-$) represent pivotal nitrification intermediates that substantially govern soil abiotic N$_2$O production. Yet, the intricate factors influencing the abiotic formation of N$_2$O from chemical reactions involving NH$_2$OH and NO$_2^-$ remain uncertain. This study was designed to reveal the impacts of land use type and parent material on soil abiotic N$_2$O production in response to NH$_2$OH and NO$_2^-$ amendments. Our investigation revealed that land use type exerted no significant influence on abiotic production of N$_2$O with NH$_2$OH and NO$_2^-$ addition. Nevertheless, the parent material exhibited a notable ($P < 0.01$) effect on N$_2$O production intrigued by NH$_2$OH addition. Specifically, a markedly higher abiotic N$_2$O production from NH$_2$OH was observed in soils developed from Quaternary red clay than those derived from granite. Subsequent analysis demonstrated that the soils originating from Quaternary red clay displayed significantly higher manganese (Mn) content in comparison to those originating from granite. This finding consistently aligns with the close correlation between the abiotic N$_2$O production via chemical oxidation of NH$_2$OH and Mn content of soil. Furthermore, the site preference (SP) values for N$_2$O arising from NH$_2$OH and NO$_2^-$ addition were 25-30‰ and around 20‰, respectively, aligning with the expected ranges characterizing ammonia oxidation and chemodenitrification processes. Our findings provide valuable insight into the distinct influence of parent material on soil abiotic N$_2$O production via chemical oxidation of NH$_2$OH, contributing to a better understanding of the underlying mechanisms, and highlight the significance of soil factors in regulating abiotic N$_2$O production within soil ecosystems.
1 Introduction

Nitrous oxide (N\textsubscript{2}O) holds a pivotal position in the atmosphere, both as a long-lived greenhouse gas and a precursor to nitric oxide, contributing to the depletion of stratospheric ozone (IPCC, 2007). Agricultural soil ecosystems contributed to 52\% of anthropogenic N\textsubscript{2}O emissions due to the large input of nitrogen (N) fertilizers (Tian et al., 2020). Recent findings have revealed that N\textsubscript{2}O production in soil is influenced by both biotic and abiotic processes (Heil et al., 2016; Liu et al., 2019, 2018; Wei et al., 2022). Notably, abiotic processes may contribute to 29.3-37.7\% of global total N\textsubscript{2}O production (Wei et al., 2022). Hydroxylamine (NH\textsubscript{2}OH) and nitrite (NO\textsubscript{2}\textsuperscript{-}) emerge as critical N intermediates that significantly contribute to abiotic N\textsubscript{2}O production. However, the intricate factors influencing abiotic N\textsubscript{2}O production from these two intermediates were still under investigation.

Hydroxylamine and NO\textsubscript{2}\textsuperscript{-} are two crucial intermediates within N cycle (Heil et al., 2016). Hydroxylamine can be released into the extracellular environment by ammonia-oxidizing microorganisms (Liu et al., 2017), methane-oxidizing microorganisms (Versantvoort et al., 2020), heterotrophic nitrifiers (Stouthamer et al., 1997; Verstraete and Alexander, 1972) and dissimilatory nitrate reduction to ammonium microorganisms (Giblin et al., 2013; Hanson et al., 2013). Subsequently, NH\textsubscript{2}OH undergoes oxidation mediated by soil metal oxidants, such as manganese oxide (MnO\textsubscript{2}) and ferric ion (Fe\textsuperscript{3+}), leading to the formation of N\textsubscript{2}O. Additionally, NH\textsubscript{2}OH can undergo fixation by soil organic matter to form compounds known as oximes (Porter, 1969). Considerable accumulation of NO\textsubscript{2}\textsuperscript{-} has been observed during nitrification in soils due to the
uncoupling of ammonia and nitrite oxidation (Duan et al., 2020a; Tierling and Kuhlmann, 2018). Nitrite can also accumulate during the denitrification process in anaerobic conditions (Burns et al., 1996). Remarkably, this accumulated NO$_2^-$ undergoes chemical reactions with ferrous iron and soil organic matter, giving rise to the intriguing phenomenon known as chemodenitrification (Nelson and Bremner, 1970, Wei et al., 2020). And various chemical properties of soil, such as pH, Fe concentration and organic matter content, have been demonstrated to exert significant influences on chemodenitrification (Chalk and Smith, 2020).

Generally, parent materials exert a significant impact on soil formation processes, leading to alteration in various soil physical and chemical properties, including soil pH and organic matter concentration (Miller and Donahue, 1990). Additionally, it has been documented that land use types and agricultural management practices, such as the application of inorganic N fertilizers and organic manure, have a marked influence on physical and chemical properties of soils (Zhang and Xu, 2005). For instance, the long-term utilization of mineral fertilizers in orchard soils is frequently associated with soil acidification (Guo et al., 2010; Yan et al., 2018). Consequently, it is reasonable to anticipate variations in abiotic N$_2$O production in soils derived from different parent materials and those under divergent land use types.

In our study, we conducted a laboratory incubation experiment to investigate the impacts of land use type and parent material on abiotic N$_2$O production through the addition of NH$_2$OH and NO$_2^-$. Gamma (γ) sterilization and site preference (SP) techniques were used to reveal the contribution of abiotic processes to N$_2$O production.
from different sources (Casciotti et al., 2010; Jung et al., 2014; Sutka et al., 2008, 2006).

Previous research has revealed that distinct SP values for N₂O produced through various microbial and chemical processes. Specifically, SP values for N₂O molecule yielded by purely cultured ammonia-oxidizing archaea (AOA) have been documented in the range of 13.1-34‰ (Jung et al., 2014), while ammonia-oxidizing bacteria (AOB) exhibit SP values spanning from 14.2‰ to 38.2‰ (Casciotti et al., 2010). Additionally, Sutka et al. (2008) found that fungal denitrification had SP values ranging from 22.8‰ to 40‰. In contrast, bacterial denitrification processes presented a low SP range, falling in the scope of -5.9-0.7‰ (Haslun et al., 2018; Lewicka-Szczebak et al., 2014; Sutka et al., 2006; Toyoda et al., 2005; Yamazaki et al., 2014). Furthermore, SP values of N₂O produced through chemical reactions has been identified spanning a wide range of 16.8-35.6‰ (Buchwald et al., 2016; Grabb et al., 2017; Heil et al., 2015, 2014; Jones et al., 2015). Notably, Duan et al. (2020a) reported that SP values of N₂O produced from chemical reactions involving NH₂OH and NO₂⁻, ranging from 27.4‰ and 36.5‰ in greenhouse vegetable soils. Nevertheless, the understanding of SP values stemming from abiotic N₂O production due to NH₂OH and NO₂⁻ addition in different soils remains limited. Therefore, in this study, we hypothesized that: 1) soil parent material and land use type could exert an influence on abiotic N₂O production from chemical reactions involving NH₂OH and NO₂⁻ due to the variations of soil physico-chemical properties; 2) SP values of N₂O molecule yielded from chemical oxidation of NH₂OH and NO₂⁻ chemodenitrification fall in the scope of abiotically-produced N₂O in previous studies.

2 Materials and methods
2.1 Sample collection and chemical analysis

Fifteen soils from five sites in mainland China (Fig. 1): Changsha (CS, 113°19′E, 28°33′N), Tongcheng (TC, 113°46′E, 29°13′N), Taoyuan (TY, 111°31′E, 29°14′N), Dangyang (DY, 111°48′E, 30°41′N) and Xianning (XN, 114°22′E, 30°0′N) were collected for this study, representing a range of land use types and parent materials. At each site, soils were collected from the top 20-cm layer. After removing litters and plant roots, soils were placed into sealed bags and transferred to the laboratory of Huazhong Agricultural University. Soils were naturally dried in a well-ventilated room, then passed through a 2-mm sieve and stored at room temperature.

Basic soil physicochemical properties were analyzed before the incubation. Briefly, the metallic elements were determined with inductively coupled plasma optical emission spectrometry (Agilent 5110 ICP-OES, Agilent, USA). Total carbon (C) and N contents were analyzed with an elemental analyzer (FlashSmart 11206125, Thermo Scientific Inc., USA). Ammonium ($\text{NH}_4^+$) and nitrate ($\text{NO}_3^-$) were extracted with 1 M KCl (dry soil: solution = 1:10 w/w) and shaken for 24 h and determined with ion chromatography (Thermo Scientific, USA). Soil pH was measured with a pH probe after shaking soil with 1 M KCl (dry soil: solution = 1:10 w/w). Dissolved organic C (DOC) content was analyzed with acid-base titration method, while dissolved organic N (DON) content was calculated by total dissolved N (determined by ultraviolet spectrophotometer) minus dissolved inorganic N ($\text{NH}_4^+$ and $\text{NO}_3^-$). The detailed information of soil chemical properties is shown in Table 1.
2.2 Soil sterilization

Half of the soils were irradiated under 20 kGy ($^{60}$Co) at Huada Biological Technology, Guangzhou, China. After that, the soils were rewetted with sterilized deionized water to reach around 40% water-holding capacity (WHC), and then incubated for 72 h at 28 °C. The sterilized soils (1.0 g) were used to check irradiation efficiency by plating the soil slurries (soil : water = 1:1) on sterilized R2A medium, incubating for 72 h, 28 °C. Neither bacteria nor fungi was observed, demonstrating that the irradiation process was successful.

2.3 Amendment of NH$_2$OH and NO$_2^-$ solutions

Sterilized and non-sterilized soils (0.5 g) were weighed into 12-ml gas chromatography (GC) vials (labco, England). Then, sterilized deionized water was added to bring the soil moisture to 40% WHC. Vials were then incubated for 72 h at room temperature (25 ± 1 °C). After that, NH$_2$OH and NaNO$_2$ solution were filtered through 0.22-μm filters and added to the vials to bring the soil to 60% soil WHC. Then, the vials were sealed tightly and incubated for 7 h at 25 °C. The added NH$_2$OH and NO$_2^-$ concentration were 5 mg N kg$^{-1}$ soil and 50 mg N kg$^{-1}$ soil, respectively. The concentration of added NO$_2^-$ mimicked the maximum level that can achieve after N fertilizer application; as for the concentration of NH$_2$OH added, 10-times smaller than amended NO$_2^-$ and much higher than its natural content, the relatively high dose is beneficial for producing significant amount of N$_2$O and for further study of SP determination. At the end of incubation, 20 ml 99.9% N$_2$ was injected to the vials and then 20-ml headspace gas was collected from
the vials. N$_2$O concentration in the headspace gas was analyzed by using an Agilent 7890A Gas Chromatograph.

Conversion rates of added NH$_2$OH and NO$_2^-$ to N$_2$O were also calculated to predict the relative role of NH$_2$OH and NO$_2^-$ in N$_2$O production, which were calculated by the following equations:

$$\frac{[N_2O-N, NH_2OH] - [N_2O-N, \text{control}]}{[NH_2OH-N]} \quad (1)$$

$$\frac{[N_2O-N, NO_2^-] - [N_2O-N, \text{control}]}{[NO_2^--N]} \quad (2)$$

where [N$_2$O-N, NH$_2$OH] is the concentration of N$_2$O-N derived from NH$_2$OH amendment; [N$_2$O-N, control] the concentration of N$_2$O-N derived from the control and [N$_2$O-N, NO$_2^-$] the concentration of N$_2$O-N derived from NO$_2^-$ amendment; [NH$_2$OH-N] and [NO$_2^-$-N] represent the concentration of added NH$_2$OH and NO$_2^-$, respectively.

2.4 Analysis of $^{15}$N site preference of N$_2$O

To further explore the pathways of N$_2$O generation, the isotope experiment was performed. Soil (0.5 g) was weighed into a 12-ml labco vial followed by the addition of NH$_2$OH and NO$_2^-$ solution, and then the vial was sealed tightly. The vials were incubated at 25 °C for 7 hours and 20 ml headspace gas was collected following the same steps mentioned above, to determine the $^{15}$N site preference of N$_2$O by using an isotope ratio mass spectrometer (Toyoda and Yoshida, 1999). $^{15}$N$^{\text{bulk}}$ and $^{15}$N$^{\text{a}}$ were monitored, $^{15}$N$^{\beta}$ could be calculated by the following equations:

$$\Delta^{15}N^{\beta} = \delta^{15}N^{\text{bulk}} - \delta^{15}N^{\text{a}} \quad (3)$$

Site preference is defined as
SP = δ^{15}N^α - δ^{15}N^β  \hspace{1cm} (4)

2.5 Statistical analysis

Analysis of variance (ANOVA) was performed for analyzing the differences in N$_2$O emissions among non-sterile and γ-irradiated samples. Tukey’s post-hoc tests were utilized to identify significant differences at $P < 0.05$. The ANOVA also evaluated the percentage of total variance explained by land use types and parent materials. Spearman correlation analysis was performed to find relationship between N$_2$O emissions and possible variables. All the statistical analyses were conducted in R (version 4.0.3, R Foundation for Statistical Computing, Vienna, Austria).

3 Results

3.1 Effects of parent material and land use on soil physicochemical properties

Parent material had significant ($P < 0.05$) effects on several soil properties, including soil texture composition, DOC content, NO$_3^-$ content, Mn and Fe contents (Table 2, Fig. 2). Soils developed from late Pleistocene sediment have the largest amount of silt and clay content, as well as NO$_3^-$ and Fe contents among all the parent materials. Soils developed from granite showed a characteristic of the largest proportion of sand and the least Fe content among all the parent materials. The Mn content in soils from Quaternary red earth was significantly ($P < 0.05$) higher than that from granite and late Pleistocene sediment.

For land use type, the most affected properties were silt content, soil pH, TC, TN and
NH₄⁺ content (Table 2). Forest soil had the least TC and TN content, and lowest pH among all the land use types. Tea fields had the largest NH₄⁺ content, and paddy soil showed the highest pH and the largest TC and TN among all the land use types.

3.2 Effects of parent material and land use type on N₂O production with NH₂OH and NO₂⁻ addition

Parent material had a significant ($P < 0.05$) influence on N₂O production from soils amended with NH₂OH (Fig. 3a, 4a). Soils developed from Quaternary red clay and late Pleistocene sediment have relatively higher N₂O production (0.77-4.76 mg N kg⁻¹ soil and 1.97-2.11 mg N kg⁻¹ soil, respectively) with NH₂OH addition than those developed from granite (0.16-1.07 mg N kg⁻¹ soil). In the treatments with NO₂⁻ addition, N₂O production from different parent materials were in the range of 0.18-0.82 mg N kg⁻¹ soil and showed insignificant difference (Fig. 3b, 4b). Land use type showed little influence on N₂O emissions among the 15 soils with NH₂OH and NO₂⁻ addition (Fig. 4). Average N₂O production from the five land use types were in an approximate range (0.98-2.28 mg N kg⁻¹ soil and 0.39-0.50 mg N kg⁻¹ soil, respectively) with NH₂OH and NO₂⁻ addition.

The conversion ratios of NH₂OH to N₂O in soils from Quaternary red clay (50.9%) was significantly larger than that from late Pleistocene sediment (27.7%), and granite (7.2%) (Table 3). Around 90% of NH₂OH to N₂O came from abiotic processes in soils from Quaternary red clay, while the ratios were around 69% for soils from late Pleistocene sediment and granite. The effect of land use types on the conversion ratios
of NH$_2$OH to N$_2$O was not significant, with ratios ranging from 16.5% to 34.6%. The conversion ratios of NO$_2^-$ to N$_2$O was much smaller than that of NH$_2$OH to N$_2$O, with ratios ranging from 0.93% to 11.6%. Neither parent material nor land use types affected the conversion ratios of NO$_2^-$ to N$_2$O. Most (68.4-98%) of N$_2$O with NO$_2^-$ addition came from abiotic processes.

### 3.3 Effects of soil factors on N$_2$O production with NH$_2$OH and NO$_2^-$ addition

In non-sterile samples, N$_2$O production was positively ($P < 0.05$) correlated to soil Fe and Mn content with NH$_2$OH addition, whereas N$_2$O production was negatively ($P < 0.05$) correlated to soil Fe content and pH with NO$_2^-$ addition (Fig. 5). In γ-irradiated samples, N$_2$O production was positively ($P < 0.05$) correlated to soil Mn content with NH$_2$OH addition. However, soil Fe content did not affect N$_2$O production significantly in γ-irradiated samples with NO$_2^-$ addition (Fig. 5). Conversely, N$_2$O production was negatively ($P < 0.05$) correlated to soil pH with NO$_2^-$ addition, but correlated to soil DON positively ($P < 0.05$) (Fig. 5).

### 3.4 Site specific $^{15}$N isotopic signatures of N$_2$O

Soils named DY1, CS1, TC3, TC5 were used for stable isotopic signature determination. The SP values of N$_2$O ranged from 26.8‰ to 28.4‰ with NH$_2$OH addition in non-sterile soils, which fell in the scope of SP values from nitrification (Fig. 6). The SP value of N$_2$O ranged from 18.2‰ to 21.6‰ with NO$_2^-$ addition in non-sterile soils, which fell in the scope of SP values from chemodenitrification (Fig. 6). γ sterilization had no effect on the SP values of N$_2$O with NH$_2$OH addition, with SP value ranged
from 24.5‰ to 28.9‰. Nevertheless, γ sterilization had significant ($P < 0.05$) effects on the SP values of N$_2$O with NO$_2^-$ addition, with SP value ranged from 20‰ to 22.7‰. The δ$^{18}$O-N$_2$O values ranged from 31.7‰ to 34‰ with NO$_2^-$ addition in non-sterile soils, which also fell in the scope of values derived from denitrification. Nevertheless, the δ$^{18}$O-N$_2$O value ranged from 5.7‰ to 15.6‰ with NH$_2$OH addition in non-sterile soils, which was much lower than the values observed in nitrification.

4 Discussion

Parent materials and land use types may have significant influences on soil basic physicochemical properties. During soil formation, changes occur in soil physical and chemical properties, such as soil pH and organic matter concentration (Alfaro et al., 2017; Angst et al., 2018). Moreover, the mineralogy of parent material can interact with soil management practices, including land use types and long-term fertilization, thereby influencing basic soil properties (Stone et al., 2015; Sun et al., 2016). In this study, parent materials had a significant influence on soil texture. Quaternary red clay and late Pleistocene sediment resulted in fine-textured soil while granite led to coarse-textured soil, which was similar to previous studies (Deng et al., 2015; Hu et al., 2003). In addition, significant differences in Mn and Fe contents across parent materials were observed. Soils developed from Quaternary red clay had the highest Mn content while soils generated from granite had the lowest Mn and Fe contents, which was consistent with earlier studies (Blume and Schwertmann, 1969; Bromfield et al., 1983). For total C and total N as well as NH$_4^+$-N content, land use types explained more variance than
parent materials which was consistent with the study of Zhang et al. (2018). However, we observed significant difference in soil pH across land use types, which was not aligned with previous studies (Lauber et al., 2008; Zhang et al., 2018).

The conversion rates of NH$_2$OH to N$_2$O in the sterilized acidic soils ranged from 3.7% to 84.8% (data not shown), most of the results were fallen in the scope of earlier reports. Bremner et al. (1980) reported that NH$_3$OH addition increased N$_2$O production in sterilized soils, with conversion rates of NH$_2$OH to N$_2$O varied from 34% to 80%.

Recently, Liu et al. (2019) revealed the conversion rates of NH$_2$OH to N$_2$O fell in the scope of 73-93%. Interestingly, we observed that parent material had significant effects on N$_2$O production from NH$_2$OH addition. Soils developed from Quaternary red clay had the highest N$_2$O production and late Pleistocene sediment the second largest, while granite led to the lowest N$_2$O yield. This was mainly attributed to the much higher Mn content in Quaternary red clay and high concentration of Fe in late Pleistocene sediment than granite. Furthermore, Spearman correlation coefficients suggested that the conversion rates of NH$_2$OH to N$_2$O were positively correlated to Mn and Fe content in soils (Fig. 5), which were consistent with the results shown by Bremner et al. (1980) and Liu et al. (2019).

Sterilization has affected the conversion rates of NH$_2$OH to N$_2$O significantly, with decrease of N$_2$O production after $\gamma$ sterilization. Moreover, SP values were found in the range from 25‰ to 29‰ in both sterilized and unsterilized soils (Fig. 6), which were similar with the results of Jung et al. (2014) that SP values of N$_2$O produced by AOA ranged from 13.1‰ to 34‰. However, Heil et al. (2015) demonstrated SP values of
34.1 ± 1.9‰ from a sterilized cropland soil with NH$_2$OH addition. In an earlier study, Heil et al. (2014) reported that the SP value of N$_2$O generated from chemical reactions with NH$_2$OH ranged from 33.9‰ to 35.6‰. Based on our findings, we inferred that N$_2$O produced from NH$_2$OH in acidic soils can be attributed to the combination of archaeal ammonia oxidation and abiotic reactions. However, further research is still necessary to fully elucidate factors influencing SP values in abiotic N$_2$O production pathways.

Regarding the conversion of NO$_2^-$ to N$_2$O, NO$_2^-$ addition increased N$_2$O production with conversion rates of 4.3% to 16.3%, which were in lined with the results of Venterea et al. (2003). Nevertheless, parent materials and land use types did not affect the conversion of NO$_2^-$ to N$_2$O significantly. Correlation analysis showed that the conversion rates of NO$_2^-$ to N$_2$O were negatively correlated to pH values and Mn content, and positively correlated to DON and C content (Fig. 5). Similar results were revealed by Liu et al. (2019) that soil properties, such as DOM, Fe, and Mn content, had strong effects on the contribution of NO$_2^-$ to N$_2$O formation. Moreover, significant difference of N$_2$O production following NO$_2^-$ addition was observed among non-sterile and sterilized acidic soils, which was probably due to the increased soil dissolved organic matter caused by γ sterilization (Berns et al., 2008). Nonetheless, SP values indicated that N$_2$O converted from NO$_2^-$ was produced mainly via abiotic pathways. Our results were in line with the results reported by Liu et al. (2019), who found irradiation of soil had little influence on N$_2$O production in strongly acidic forest soils following NO$_2^-$ addition.
In supporting, SP values of N₂O produced from soils amended with NO₂⁻ were found in the range of 18‰ to 23‰ (Fig. 6), which were consistent with the results reported by Jones et al. (2015), who revealed that SP values of N₂O formed via NO₂⁻ reduction by Fe (II) were in the range of 10.0-22‰. Similarly, Wei et al. (2017) reported that N₂O generated from NO₂⁻ reduction with soil organic matter fractions at pH of 3.4 had a SP value of 20.27-26.14‰. Whereas, Toyoda et al. (2005) found that N₂O produced via NO₂⁻ reduction with trimethylamine-borane had a constant SP of approximately 30‰. Moreover, higher SP values of N₂O abiotically produced were reported by Heil et al. (2014), which were in the range of 34-35‰. It seems like SP values of N₂O chemically produced are in the relatively high-value scopes. However, δ¹⁸O-N₂O values measured in this study were lower than previously reported results, implying that a weaker fractionation during chemical reactions with NH₂OH in both non-sterile and sterilized soils. In conclusion, SP values obtained from this experiment shed some light in abiotic N₂O production processes with application of NO₂⁻ and NH₂OH to the same soil.

5 Conclusions

Our findings underscore the significant influence of parent materials on soil physicochemical properties, particularly Mn contents, and its potential effect on abiotic pathways to N₂O production in acidic soils. Furthermore, the accumulation of NH₂OH and NO₂⁻ amplifies the role of abiotic mechanisms, with their influence tightly linked to specific physicochemical properties of the soil. SP values reveal the contribution of abiotic processes of NH₂OH and NO₂⁻ to N₂O production in the tested soils additionally.
Further investigation should focus on the effects of parent materials on the activity and abundance of microbial community and portion of biotic N₂O production to total N₂O production.

**Code availability.** The R codes used for (bio)statistical analyses are available upon request.


**Competing interests.** The contact author has declared that none of the authors has any competing interests.

**Acknowledgements.** This research was supported by Province natural science fund of Guangdong (2022A1515010786) to S. L. We sincerely appreciated the anonymous reviewers and editors for their critical and valuable comments to help improve this manuscript.

**References**


Liu, S., Schloter, M., and Brüggemann, N.: Accumulation of NO\textsubscript{3} during periods of drying stimulates soil N\textsubscript{2}O emissions during subsequent rewetting: Nitrite stimulates N\textsubscript{2}O emissions during rewetting, European Journal of Soil Science, 69, 936–946,


Toyoda, S. and Yoshida, N.: Determination of Nitrogen Isotopomers of Nitrous Oxide on a


Figure 1. The geographical locations of the five sampling sites: Dangyang (DY), Xianning (XN), Taoyuan (TY), Tongcheng (TC) and Changsha (CS).

Figure 2. Manganese (Mn), iron (Fe) contents and pH values of the fifteen soils. Capital and lowercase letters indicate significant difference in Fe and Mn contents, respectively. The difference in pH values is insignificant.
Figure 3. Net N2O production in fifteen soils with and without γ-sterilization after addition of NH2OH (a) and NO2- (b) by parent material. Asterisks indicate significantly (P < 0.05) higher values between non-sterile and γ-sterilized samples at one soil. Error bars represent standard deviation (SD, n = 3).
Figure 4. Emissions of N₂O from soils amended with NH₂OH (a) and NO₂⁻ (b), which were sorted by parent material and land use type. Capital and lowercase letters indicate significant difference among non-sterile and γ-sterilized soils, respectively. No letters indicate insignificant difference.
Figure 5. Spearman correlation coefficients between soil N₂O production from different amendments and soil properties after 7-hour incubation. One asterisk represents a significance under $P < 0.05$; two asterisks represent a significance under $P < 0.01$. 

https://doi.org/10.5194/egusphere-2023-2033
Preprint. Discussion started: 12 September 2023
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Figure 6. Relationships between the SP and δ18O values of N2O in non-sterile and γ-sterilized soils after NH2OH and NO2- addition. The selected soils are DY1, CS1, TC3, TC5. Parameter references are listed as follow: (Buchwald et al., 2016; Frame and Casciotti, 2010; Grabb et al., 2017b; Haslun et al., 2018; Heil et al., 2015, 2014; Jinuntuya-Nortman et al., 2008; Jones et al., 2013; Jung et al., 2014; Lewicka-Szczebak et al., 2014; Maeda et al., 2015; Ostrom et al., 2010; Rohe et al., 2017; Santoro et al., 2011; Sutka et al., 2008, 2006; Toyoda et al., 2005; Well and Flessa, 2009; Yamamoto, 2017; Yamazaki et al., 2014; Yang et al., 2014).
Table 1. Summary of soil properties in this study.

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<th>Clay (%)</th>
<th>Sand (%)</th>
<th>pH</th>
<th>TC (g/kg)</th>
<th>TN (g/kg)</th>
<th>DOC (mg/kg)</th>
<th>DON (mg/kg)</th>
<th>NH$_4^+$ (mg/kg)</th>
<th>NO$_3^-$ (mg/kg)</th>
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Table 2. One-way ANOVA ($P < 0.05$) of soil physicochemical properties including dissolved organic carbon (DOC), total carbon (TC), total nitrogen (TN), total ferric ion (Fe), total manganese (Mn), silt, clay and sand content, etc.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Silt (%)</th>
<th>Clay (%)</th>
<th>Sand (%)</th>
<th>pH</th>
<th>TC (g/kg)</th>
<th>TN (g/kg)</th>
<th>DOC (mg/kg)</th>
<th>DON (mg/kg)</th>
<th>NH$_4^+$ (mg/kg)</th>
<th>NO$_3^-$ (mg/kg)</th>
<th>Fe (g/kg)</th>
<th>Mn (g/kg)</th>
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</thead>
<tbody>
<tr>
<td>Quaternary red clay</td>
<td>37.59a</td>
<td>35.18b</td>
<td>27.23b</td>
<td>4.94a</td>
<td>9.87a</td>
<td>0.99a</td>
<td>15.24a</td>
<td>8.82b</td>
<td>10.12a</td>
<td>6.53b</td>
<td>30.80b</td>
<td>1.74a</td>
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<td>19.45b</td>
<td>27.18c</td>
<td>53.37a</td>
<td>5.04a</td>
<td>8.13a</td>
<td>0.69a</td>
<td>16.31a</td>
<td>10.39b</td>
<td>19.39a</td>
<td>5.81b</td>
<td>21.34c</td>
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<tr>
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<td>45.86a</td>
<td>45.62a</td>
<td>8.52c</td>
<td>4.86a</td>
<td>8.59a</td>
<td>0.97a</td>
<td>12.77a</td>
<td>19.33a</td>
<td>2.76a</td>
<td>17.60a</td>
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<td>31.13a</td>
<td>46.10a</td>
<td>4.88bc</td>
<td>9.68b</td>
<td>0.90bc</td>
<td>16.68a</td>
<td>15.47a</td>
<td>27.56a</td>
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<td>0.82bc</td>
<td>14.88a</td>
<td>12.84a</td>
<td>5.53b</td>
<td>9.90a</td>
<td>25.05a</td>
<td>0.61a</td>
</tr>
<tr>
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<td>34.84ab</td>
<td>37.50a</td>
<td>27.65a</td>
<td>4.69c</td>
<td>6.42b</td>
<td>0.64c</td>
<td>13.68a</td>
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<td>8.04ab</td>
<td>7.43a</td>
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<td>8.53a</td>
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<td>16.90ab</td>
<td>4.53a</td>
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</table>
Table 3. The conversion ratios (%) of NH$_2$OH and NO$_2^-$ to N$_2$O and the contribution ratios (%) of abiotic N$_2$O production to the total N$_2$O emission with NH$_2$OH and NO$_2^-$ addition.

<table>
<thead>
<tr>
<th></th>
<th>MH$_2$OH Conversion ratio (%)</th>
<th>Abiotic contribution (%)</th>
<th>NO$_2^-$ Conversion ratio (%)</th>
<th>Abiotic contribution (%)</th>
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<tr>
<td>Quaternary red clay</td>
<td>50.9 ± 26.1a</td>
<td>90.0 ± 16.4a</td>
<td>9.3 ± 4.0a</td>
<td>91.2 ± 21.2a</td>
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<tr>
<td>Granite</td>
<td>7.2 ± 3.1c</td>
<td>69.3 ± 25.7b</td>
<td>10.3 ± 5.0a</td>
<td>87.5 ± 15.2a</td>
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<tr>
<td>Late Pleistocene sediment</td>
<td>27.7 ± 4.4b</td>
<td>69.2 ± 15.4b</td>
<td>12.5 ± 1.2a</td>
<td>98.2 ± 4.1a</td>
</tr>
<tr>
<td>Tea field</td>
<td>28.9 ± 34.3a</td>
<td>76.6 ± 28.4ab</td>
<td>10.9 ± 6.2a</td>
<td>98.0 ± 27.1a</td>
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<tr>
<td>Fruit field</td>
<td>34.6 ± 23.0a</td>
<td>77.4 ± 20.8ab</td>
<td>9.7 ± 3.1a</td>
<td>95.6 ± 6.5a</td>
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<td>Forest soil</td>
<td>16.5 ± 12.2a</td>
<td>83.4 ± 19.5a</td>
<td>11.6 ± 3.0a</td>
<td>97.9 ± 3.7a</td>
</tr>
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<td>23.7 ±15.0a</td>
<td>54.1 ± 14.1b</td>
<td>8.8 ± 2.1a</td>
<td>68.4 ± 28.4b</td>
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<td>Paddy soil</td>
<td>39.7 ± 32.0a</td>
<td>91.6 ± 8.6a</td>
<td>8.1 ± 4.1a</td>
<td>85.9 ± 9.6ab</td>
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