



1 **Parent material influences soil abiotic N<sub>2</sub>O production**  
2 **from chemical oxidation of hydroxylamine**

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9



10 **Abstract.** Hydroxylamine (NH<sub>2</sub>OH) and nitrite (NO<sub>2</sub><sup>-</sup>) represent pivotal nitrification  
11 intermediates that substantially govern soil abiotic N<sub>2</sub>O production. Yet, the intricate  
12 factors influencing the abiotic formation of N<sub>2</sub>O from chemical reactions involving  
13 NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> remain uncertain. This study was designed to reveal the impacts of  
14 land use type and parent material on soil abiotic N<sub>2</sub>O production in response to NH<sub>2</sub>OH  
15 and NO<sub>2</sub><sup>-</sup> amendments. Our investigation revealed that land use type exerted no  
16 significant influence on abiotic production of N<sub>2</sub>O with NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> addition.  
17 Nevertheless, the parent material exhibited a notable ( $P < 0.01$ ) effect on N<sub>2</sub>O  
18 production intrigued by NH<sub>2</sub>OH addition. Specifically, a markedly higher abiotic N<sub>2</sub>O  
19 production from NH<sub>2</sub>OH was observed in soils developed from Quaternary red clay  
20 than those derived from granite. Subsequent analysis demonstrated that the soils  
21 originating from Quaternary red clay displayed significantly higher manganese (Mn)  
22 content in comparison to those originating from granite. This finding consistently aligns  
23 with the close correlation between the abiotic N<sub>2</sub>O production via chemical oxidation  
24 of NH<sub>2</sub>OH and Mn content of soil. Furthermore, the site preference (SP) values for N<sub>2</sub>O  
25 arising from NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> addition were 25-30‰ and around 20‰, respectively,  
26 aligning with the expected ranges characterizing ammonia oxidation and  
27 chemodenitrification processes. Our findings provide valuable insight into the distinct  
28 influence of parent material on soil abiotic N<sub>2</sub>O production via chemical oxidation of  
29 NH<sub>2</sub>OH, contributing to a better understanding of the underlying mechanisms, and  
30 highlight the significance of soil factors in regulating abiotic N<sub>2</sub>O production within  
31 soil ecosystems.



## 32 **1 Introduction**

33 Nitrous oxide (N<sub>2</sub>O) holds a pivotal position in the atmosphere, both as a long-lived  
34 greenhouse gas and a precursor to nitric oxide, contributing to the depletion of  
35 stratospheric ozone (IPCC, 2007). Agricultural soil ecosystems contributed to 52% of  
36 anthropogenic N<sub>2</sub>O emissions due to the large input of nitrogen (N) fertilizers (Tian et  
37 al., 2020). Recent findings have revealed that N<sub>2</sub>O production in soil is influenced by  
38 both biotic and abiotic processes (Heil et al., 2016; Liu et al., 2019, 2018; Wei et al.,  
39 2022). Notably, abiotic processes may contribute to 29.3-37.7% of global total N<sub>2</sub>O  
40 production (Wei et al., 2022). Hydroxylamine (NH<sub>2</sub>OH) and nitrite (NO<sub>2</sub><sup>-</sup>) emerge as  
41 critical N intermediates that significantly contribute to abiotic N<sub>2</sub>O production.  
42 However, the intricate factors influencing abiotic N<sub>2</sub>O production from these two  
43 intermediates were still under investigation.

44 Hydroxylamine and NO<sub>2</sub><sup>-</sup> are two crucial intermediates within N cycle (Heil et al.,  
45 2016). Hydroxylamine can be released into the extracellular environment by ammonia-  
46 oxidizing microorganisms (Liu et al., 2017), methane-oxidizing microorganisms  
47 (Versantvoort et al., 2020), heterotrophic nitrifiers (Stouthamer et al., 1997; Verstraete  
48 and Alexander, 1972) and dissimilatory nitrate reduction to ammonium microorganisms  
49 (Giblin et al., 2013; Hanson et al., 2013). Subsequently, NH<sub>2</sub>OH undergoes oxidation  
50 mediated by soil metal oxidants, such as manganese oxide (MnO<sub>2</sub>) and ferric ion (Fe<sup>3+</sup>),  
51 leading to the formation of N<sub>2</sub>O. Additionally, NH<sub>2</sub>OH can undergo fixation by soil  
52 organic matter to form compounds known as oximes (Porter, 1969). Considerable  
53 accumulation of NO<sub>2</sub><sup>-</sup> has been observed during nitrification in soils due to the



54 uncoupling of ammonia and nitrite oxidation (Duan et al., 2020a; Tierling and  
55 Kuhlmann, 2018). Nitrite can also accumulate during the denitrification process in  
56 anaerobic conditions (Burns et al., 1996). Remarkably, this accumulated  $\text{NO}_2^-$   
57 undergoes chemical reactions with ferrous iron and soil organic matter, giving rise to  
58 the intriguing phenomenon known as chemodenitrification (Nelson and Bremner, 1970,  
59 Wei et al., 2020). And various chemical properties of soil, such as pH, Fe concentration  
60 and organic matter content, have been demonstrated to exert significant influences on  
61 chemodenitrification (Chalk and Smith, 2020).

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

72 In our study, we conducted a laboratory incubation experiment to investigate the  
73 impacts of land use type and parent material on abiotic  $\text{N}_2\text{O}$  production through the  
74 addition of  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$ . Gamma ( $\gamma$ ) sterilization and site preference (SP)  
75 techniques were used to reveal the contribution of abiotic processes to  $\text{N}_2\text{O}$  production



76 from different sources (Casciotti et al., 2010; Jung et al., 2014; Sutka et al., 2008, 2006).  
77 Previous research has revealed that distinct SP values for N<sub>2</sub>O produced through  
78 various microbial and chemical processes. Specifically, SP values for N<sub>2</sub>O molecule  
79 yielded by purely cultured ammonia-oxidizing archaea (AOA) have been documented  
80 in the range of 13.1-34‰ (Jung et al., 2014), while ammonia-oxidizing bacteria (AOB)  
81 exhibit SP values spanning from 14.2‰ to 38.2‰ (Casciotti et al., 2010). Additionally,  
82 Sutka et al. (2008) found that fungal denitrification had SP values ranging from 22.8‰  
83 to 40‰. In contrast, bacterial denitrification processes presented a low SP range, falling  
84 in the scope of -5.9-0.7‰ (Haslun et al., 2018; Lewicka-Szczebak et al., 2014; Sutka et  
85 al., 2006; Toyoda et al., 2005; Yamazaki et al., 2014). Furthermore, SP values of N<sub>2</sub>O  
86 produced through chemical reactions has been identified spanning a wide range of 16.8-  
87 35.6‰ (Buchwald et al., 2016; Grabb et al., 2017; Heil et al., 2015, 2014; Jones et al.,  
88 2015). Notably, Duan et al. (2020a) reported that SP values of N<sub>2</sub>O produced from  
89 chemical reactions involving NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup>, ranging from 27.4‰ and 36.5‰ in  
90 greenhouse vegetable soils. Nevertheless, the understanding of SP values stemming  
91 from abiotic N<sub>2</sub>O production due to NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> addition in different soils remains  
92 limited. Therefore, in this study, we hypothesized that: 1) soil parent material and land  
93 use type could exert an influence on abiotic N<sub>2</sub>O production from chemical reactions  
94 involving NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> due to the variations of soil physico-chemical properties;  
95 2) SP values of N<sub>2</sub>O molecule yielded from chemical oxidation of NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup>  
96 chemodenitrification fall in the scope of abiotically-produced N<sub>2</sub>O in previous studies.

## 97 **2 Materials and methods**



98 2.1 Sample collection and chemical analysis

99 Fifteen soils from five sites in mainland China (Fig. 1): Changsha (CS, 113°19'E,  
100 28°33'N), Tongcheng (TC, 113°46'E, 29°13'N), Taoyuan (TY, 111°31'E, 29°14'N),  
101 Danyang (DY, 111°48'E, 30°41'N) and Xianning (XN, 114°22'E, 30°0'N) were  
102 collected for this study, representing a range of land use types and parent materials. At  
103 each site, soils were collected from the top 20-cm layer. After removing litters and plant  
104 roots, soils were placed into sealed bags and transferred to the laboratory of Huazhong  
105 Agricultural University. Soils were naturally dried in a well-ventilated room, then  
106 passed through a 2-mm sieve and stored at room temperature.

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



119 2.2 Soil sterilization

120 Half of the soils were irradiated under 20 kGy ( $^{60}\text{Co}$ ) at Huada Biological Technology,  
121 Guangzhou, China. After that, the soils were rewetted with sterilized deionized water  
122 to reach around 40% water-holding capacity (WHC), and then incubated for 72 h at  
123 28 °C. The sterilized soils (1.0 g) were used to check irradiation efficiency by plating  
124 the soil slurries (soil : water = 1:1) on sterilized R2A medium, incubating for 72 h, 28 °C.  
125 Neither bacteria nor fungi was observed, demonstrating that the irradiation process was  
126 successful.

127 2.3 Amendment of  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  solutions

128 Sterilized and non-sterilized soils (0.5 g) were weighed into 12-ml gas chromatography  
129 (GC) vials (labco, England). Then, sterilized deionized water was added to bring the  
130 soil moisture to 40% WHC. Vials were then incubated for 72 h at room temperature (25  
131  $\pm 1$  °C). After that,  $\text{NH}_2\text{OH}$  and  $\text{NaNO}_2$  solution were filtered through 0.22- $\mu\text{m}$  filters  
132 and added to the vials to bring the soil to 60% soil WHC. Then, the vials were sealed  
133 tightly and incubated for 7 h at 25 °C. The added  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  concentration were  
134 5 mg N  $\text{kg}^{-1}$  soil and 50 mg N  $\text{kg}^{-1}$  soil, respectively. The concentration of added  $\text{NO}_2^-$   
135 mimicked the maximum level that can achieve after N fertilizer application; as for the  
136 concentration of  $\text{NH}_2\text{OH}$  added, 10-times smaller than amended  $\text{NO}_2^-$  and much higher  
137 than its natural content, the relatively high dose is beneficial for producing significant  
138 amount of  $\text{N}_2\text{O}$  and for further study of SP determination. At the end of incubation, 20  
139 ml 99.9%  $\text{N}_2$  was injected to the vials and then 20-ml headspace gas was collected from



140 the vials. N<sub>2</sub>O concentration in the headspace gas was analyzed by using an Agilent  
141 7890A Gas Chromatograph.

142 Conversion rates of added NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O were also calculated to predict  
143 the relative role of NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> in N<sub>2</sub>O production, which were calculated by the  
144 following equations

$$145 \quad \frac{[\text{N}_2\text{O-N, NH}_2\text{OH}] - [\text{N}_2\text{O-N, control}]}{[\text{NH}_2\text{OH-N}]} \quad (1)$$

$$146 \quad \frac{[\text{N}_2\text{O-N, NO}_2^-] - [\text{N}_2\text{O-N, control}]}{[\text{NO}_2^-\text{-N}]} \quad (2)$$

147 where [N<sub>2</sub>O-N, NH<sub>2</sub>OH] is the concentration of N<sub>2</sub>O-N derived from NH<sub>2</sub>OH  
148 amendment; [N<sub>2</sub>O-N, control] the concentration of N<sub>2</sub>O-N derived from the control and  
149 [N<sub>2</sub>O-N, NO<sub>2</sub><sup>-</sup>] the concentration of N<sub>2</sub>O-N derived from NO<sub>2</sub><sup>-</sup> amendment; [NH<sub>2</sub>OH-  
150 N] and [NO<sub>2</sub><sup>-</sup>-N] represent the concentration of added NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup>, respectively.

#### 151 2.4 Analysis of <sup>15</sup>N site preference of N<sub>2</sub>O

152 To further explore the pathways of N<sub>2</sub>O generation, the isotope experiment was  
153 performed. Soil (0.5 g) was weighed into a 12-ml labco vial followed by the addition  
154 of NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> solution, and then the vial was sealed tightly. The vials were  
155 incubated at 25 °C for 7 hours and 20 ml headspace gas was collected following the  
156 same steps mentioned above, to determine the <sup>15</sup>N site preference of N<sub>2</sub>O by using an  
157 isotope ratio mass spectrometer (Toyoda and Yoshida, 1999). <sup>15</sup>N<sup>bulk</sup> and <sup>15</sup>N<sup>α</sup> were  
158 monitored, <sup>15</sup>N<sup>β</sup> could be calculated by the following equations

$$159 \quad \Delta^{15}\text{N}^\beta = {}^{15}\text{N}^{\text{bulk}} - \delta^{15}\text{N}^\alpha \quad (3)$$

160 Site preference is defined as





161 
$$SP = \delta^{15}N^{\alpha} - \delta^{15}N^{\beta} \quad (4)$$

## 162 2.5 Statistical analysis

163 Analysis of variance (ANOVA) was performed for analyzing the differences in N<sub>2</sub>O  
164 emissions among non-sterile and  $\gamma$ -irradiated samples. Tukey's post-hoc tests were  
165 utilized to identify significant differences at  $P < 0.05$ . The ANOVA also evaluated the  
166 percentage of total variance explained by land use types and parent materials. Spearman  
167 correlation analysis was performed to find relationship between N<sub>2</sub>O emissions and  
168 possible variables. All the statistical analyses were conducted in R (version 4.0.3, R  
169 Foundation for Statistical Computing, Vienna, Austria).

## 170 3 Results

### 171 3.1 Effects of parent material and land use on soil physicochemical properties

172 Parent material had significant ( $P < 0.05$ ) effects on several soil properties, including  
173 soil texture composition, DOC content, NO<sub>3</sub><sup>-</sup> content, Mn and Fe contents (Table 2, Fig.  
174 2). Soils developed from late Pleistocene sediment have the largest amount of silt and  
175 clay content, as well as NO<sub>3</sub><sup>-</sup> and Fe contents among all the parent materials. Soils  
176 developed from granite showed a characteristic of the largest proportion of sand and  
177 the least Fe content among all the parent materials. The Mn content in soils from  
178 Quaternary red earth was significantly ( $P < 0.05$ ) higher than that from granite and late  
179 Pleistocene sediment.

180 For land use type, the most affected properties were silt content, soil pH, TC, TN and



181  $\text{NH}_4^+$  content (Table 2). Forest soil had the least TC and TN content, and lowest pH  
182 among all the land use types. Tea fields had the largest  $\text{NH}_4^+$  content, and paddy soil  
183 showed the highest pH and the largest TC and TN among all the land use types.

### 184 3.2 Effects of parent material and land use type on $\text{N}_2\text{O}$ production with 185 $\text{NH}_2\text{OH}$ and $\text{NO}_2^-$ addition

186 Parent material had a significant ( $P < 0.05$ ) influence on  $\text{N}_2\text{O}$  production from soils  
187 amended with  $\text{NH}_2\text{OH}$  (Fig. 3a, 4a). Soils developed from Quaternary red clay and late  
188 Pleistocene sediment have relatively higher  $\text{N}_2\text{O}$  production ( $0.77\text{-}4.76 \text{ mg N kg}^{-1}$  soil  
189 and  $1.97\text{-}2.11 \text{ mg N kg}^{-1}$  soil, respectively) with  $\text{NH}_2\text{OH}$  addition than those developed  
190 from granite ( $0.16\text{-}1.07 \text{ mg N kg}^{-1}$  soil). In the treatments with  $\text{NO}_2^-$  addition,  $\text{N}_2\text{O}$   
191 production from different parent materials were in the range of  $0.18\text{-}0.82 \text{ mg N kg}^{-1}$  soil  
192 and showed insignificant difference (Fig. 3b, 4b). Land use type showed little influence  
193 on  $\text{N}_2\text{O}$  emissions among the 15 soils with  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  addition (Fig. 4). Average  
194  $\text{N}_2\text{O}$  production from the five land use types were in an approximate range ( $0.98\text{-}2.28$   
195  $\text{mg N kg}^{-1}$  soil and  $0.39\text{-}0.50 \text{ mg N kg}^{-1}$  soil, respectively) with  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$   
196 addition.

197 The conversion ratios of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  in soils from Quaternary red clay (50.9%)  
198 was significantly larger than that from late Pleistocene sediment (27.7%), and granite  
199 (7.2%) (Table 3). Around 90% of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  came from abiotic processes in soils  
200 from Quaternary red clay, while the ratios were around 69% for soils from late  
201 Pleistocene sediment and granite. The effect of land use types on the conversion ratios



202 of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  was not significant, with ratios ranging from 16.5% to 34.6%. The  
203 conversion ratios of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  was much smaller than that of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$ , with  
204 ratios ranging from 0.93% to 11.6%. Neither parent material nor land use types affected  
205 the conversion ratios of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$ . Most (68.4-98%) of  $\text{N}_2\text{O}$  with  $\text{NO}_2^-$  addition came  
206 from abiotic processes.

### 207 3.3 Effects of soil factors on $\text{N}_2\text{O}$ production with $\text{NH}_2\text{OH}$ and $\text{NO}_2^-$ addition

208 In non-sterile samples,  $\text{N}_2\text{O}$  production was positively ( $P < 0.05$ ) correlated to soil Fe  
209 and Mn content with  $\text{NH}_2\text{OH}$  addition, whereas  $\text{N}_2\text{O}$  production was negatively ( $P <$   
210  $0.05$ ) correlated to soil Fe content and pH with  $\text{NO}_2^-$  addition (Fig. 5).

211 In  $\gamma$ -irradiated samples,  $\text{N}_2\text{O}$  production was positively ( $P < 0.05$ ) correlated to soil  
212 Mn content with  $\text{NH}_2\text{OH}$  addition. However, soil Fe content did not affect  $\text{N}_2\text{O}$   
213 production significantly in  $\gamma$ -irradiated samples with  $\text{NO}_2^-$  addition (Fig. 5). Conversely,  
214  $\text{N}_2\text{O}$  production was negatively ( $P < 0.05$ ) correlated to soil pH with  $\text{NO}_2^-$  addition, but  
215 correlated to soil DON positively ( $P < 0.05$ ) (Fig. 5).

### 216 3.4 Site specific $^{15}\text{N}$ isotopic signatures of $\text{N}_2\text{O}$

217 Soils named DY1, CS1, TC3, TC5 were used for stable isotopic signature determination.  
218 The SP values of  $\text{N}_2\text{O}$  ranged from 26.8‰ to 28.4‰ with  $\text{NH}_2\text{OH}$  addition in non-  
219 sterile soils, which fell in the scope of SP values from nitrification (Fig. 6). The SP  
220 value of  $\text{N}_2\text{O}$  ranged from 18.2‰ to 21.6‰ with  $\text{NO}_2^-$  addition in non-sterile soils,  
221 which fell in the scope of SP values from chemodenitrification (Fig. 6).  $\gamma$  sterilization  
222 had no effect on the SP values of  $\text{N}_2\text{O}$  with  $\text{NH}_2\text{OH}$  addition, with SP value ranged



223 from 24.5‰ to 28.9‰. Nevertheless,  $\gamma$  sterilization had significant ( $P < 0.05$ ) effects  
224 on the SP values of  $\text{N}_2\text{O}$  with  $\text{NO}_2^-$  addition, with SP value ranged from 20‰ to 22.7‰.  
225 The  $\delta^{18}\text{O}\text{-N}_2\text{O}$  values ranged from 31.7‰ to 34‰ with  $\text{NO}_2^-$  addition in non-sterile  
226 soils, which also fell in the scope of values derived from denitrification. Nevertheless,  
227 the  $\delta^{18}\text{O}\text{-N}_2\text{O}$  value ranged from 5.7‰ to 15.6‰ with  $\text{NH}_2\text{OH}$  addition in non-sterile  
228 soils, which was much lower than the values observed in nitrification.

#### 229 **4 Discussion**

230 Parent materials and land use types may have significant influences on soil basic  
231 physicochemical properties. During soil formation, changes occur in soil physical and  
232 chemical properties, such as soil pH and organic matter concentration (Alfaro et al.,  
233 2017; Angst et al., 2018). Moreover, the mineralogy of parent material can interact with  
234 soil management practices, including land use types and long-term fertilization, thereby  
235 influencing basic soil properties (Stone et al., 2015; Sun et al., 2016). In this study,  
236 parent materials had a significant influence on soil texture. Quaternary red clay and late  
237 Pleistocene sediment resulted in fine-textured soil while granite led to coarse-textured  
238 soil, which was similar to previous studies (Deng et al., 2015; Hu et al., 2003). In  
239 addition, significant differences in Mn and Fe contents across parent materials were  
240 observed. Soils developed from Quaternary red clay had the highest Mn content while  
241 soils generated from granite had the lowest Mn and Fe contents, which was consistent  
242 with earlier studies (Blume and Schwertmann, 1969; Bromfield et al., 1983). For total  
243 C and total N as well as  $\text{NH}_4^+\text{-N}$  content, land use types explained more variance than



244 parent materials which was consistent with the study of Zhang et al. (2018). However,  
245 we observed significant difference in soil pH across land use types, which was not  
246 aligned with previous studies (Lauber et al., 2008; Zhang et al., 2018).

247 The conversion rates of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  in the sterilized acidic soils ranged from 3.7%  
248 to 84.8% (data not shown), most of the results were fallen in the scope of earlier reports.  
249 Bremner et al. (1980) reported that  $\text{NH}_2\text{OH}$  addition increased  $\text{N}_2\text{O}$  production in  
250 sterilized soils, with conversion rates of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  varied from 34% to 80%.  
251 Recently, Liu et al. (2019) revealed the conversion rates of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  fell in the  
252 scope of 73-93%. Interestingly, we observed that parent material had significant effects  
253 on  $\text{N}_2\text{O}$  production from  $\text{NH}_2\text{OH}$  addition. Soils developed from Quaternary red clay  
254 had the highest  $\text{N}_2\text{O}$  production and late Pleistocene sediment the second largest, while  
255 granite led to the lowest  $\text{N}_2\text{O}$  yield. This was mainly attributed to the much higher Mn  
256 content in Quaternary red clay and high concentration of Fe in late Pleistocene sediment  
257 than granite. Furthermore, Spearman correlation coefficients suggested that the  
258 conversion rates of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  were positively correlated to Mn and Fe content in  
259 soils (Fig. 5), which were consistent with the results shown by Bremner et al. (1980)  
260 and Liu et al. (2019).

261 Sterilization has affected the conversion rates of  $\text{NH}_2\text{OH}$  to  $\text{N}_2\text{O}$  significantly, with  
262 decrease of  $\text{N}_2\text{O}$  production after  $\gamma$  sterilization. Moreover, SP values were found in the  
263 range from 25‰ to 29‰ in both sterilized and unsterilized soils (Fig. 6), which were  
264 similar with the results of Jung et al. (2014) that SP values of  $\text{N}_2\text{O}$  produced by AOA  
265 ranged from 13.1‰ to 34‰. However, Heil et al. (2015) demonstrated SP values of



266  $34.1 \pm 1.9\%$  from a sterilized cropland soil with  $\text{NH}_2\text{OH}$  addition. In an earlier study,  
267 Heil et al, (2014) reported that the SP value of  $\text{N}_2\text{O}$  generated from chemical reactions  
268 with  $\text{NH}_2\text{OH}$  ranged from 33.9% to 35.6%. Based on our findings, we inferred that  
269  $\text{N}_2\text{O}$  produced from  $\text{NH}_2\text{OH}$  in acidic soils can be attributed to the combination of  
270 archaeal ammonia oxidation and abiotic reactions. However, further research is still  
271 necessary to fully elucidate factors influencing SP values in abiotic  $\text{N}_2\text{O}$  production  
272 pathways.

273 Regarding the conversion of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$ ,  $\text{NO}_2^-$  addition increased  $\text{N}_2\text{O}$  production  
274 with conversion rates of 4.3% to 16.3%, which were in lined with the results of Venterea  
275 et al. (2003). Nevertheless, parent materials and land use types did not affect the  
276 conversion of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  significantly. Correlation analysis showed that the  
277 conversion rates of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  were negatively correlated to pH values and Mn  
278 content, and positively correlated to DON and C content (Fig. 5). Similar results were  
279 revealed by Liu et al. (2019) that soil properties, such as DOM, Fe, and Mn content,  
280 had strong effects on the contribution of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  formation. Moreover, significant  
281 difference of  $\text{N}_2\text{O}$  production following  $\text{NO}_2^-$  addition was observed among non-sterile  
282 and sterilized acidic soils, which was probably due to the increased soil dissolved  
283 organic matter caused by  $\gamma$  sterilization (Berns et al., 2008). Nonetheless, SP values  
284 indicated that  $\text{N}_2\text{O}$  converted from  $\text{NO}_2^-$  was produced mainly via abiotic pathways.  
285 Our results were in line with the results reported by Liu et al. (2019), who found  
286 irradiation of soil had little influence on  $\text{N}_2\text{O}$  production in strongly acidic forest soils  
287 following  $\text{NO}_2^-$  addition.



288 In supporting, SP values of N<sub>2</sub>O produced from soils amended with NO<sub>2</sub><sup>-</sup> were found  
289 in the range of 18‰ to 23‰ (Fig. 6), which were consistent with the results reported  
290 by Jones et al. (2015), who revealed that SP values of N<sub>2</sub>O formed via NO<sub>2</sub><sup>-</sup> reduction  
291 by Fe (II) were in the range of 10.0-22‰. Similarly, Wei et al. (2017) reported that N<sub>2</sub>O  
292 generated from NO<sub>2</sub><sup>-</sup> reduction with soil organic matter fractions at pH of 3.4 had a SP  
293 value of 20.27-26.14‰. Whereas, Toyoda et al. (2005) found that N<sub>2</sub>O produced via  
294 NO<sub>2</sub><sup>-</sup> reduction with trimethylamine-borane had a constant SP of approximately 30‰.  
295 Moreover, higher SP values of N<sub>2</sub>O abiotically produced were reported by Heil et al.  
296 (2014), which were in the range of 34-35‰. It seems like SP values of N<sub>2</sub>O chemically  
297 produced are in the relatively high-value scopes. However, δ<sup>18</sup>O-N<sub>2</sub>O values measured  
298 in this study were lower than previously reported results, implying that a weaker  
299 fractionation during chemical reactions with NH<sub>2</sub>OH in both non-sterile and sterilized  
300 soils. In conclusion, SP values obtained from this experiment shed some light in abiotic  
301 N<sub>2</sub>O production processes with application of NO<sub>2</sub><sup>-</sup> and NH<sub>2</sub>OH to the same soil.

## 302 **5 Conclusions**

303 Our findings underscore the significant influence of parent materials on soil  
304 physicochemical properties, particularly Mn contents, and its potential effect on abiotic  
305 pathways to N<sub>2</sub>O production in acidic soils. Furthermore, the accumulation of NH<sub>2</sub>OH  
306 and NO<sub>2</sub><sup>-</sup> amplifies the role of abiotic mechanisms, with their influence tightly linked  
307 to specific physicochemical properties of the soil. SP values reveal the contribution of  
308 abiotic processes of NH<sub>2</sub>OH and NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>O production in the tested soils additionally.



309 Further investigation should focus on the effects of parent materials on the activity and  
310 abundance of microbial community and portion of biotic N<sub>2</sub>O production to total N<sub>2</sub>O  
311 production.

312

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

314

315 **Author contributions.** Shurong Liu: Conceptualization, Methodology, Supervision,  
316 Writing-Review & Editing. Suyun Li: Investigation, Data curation, Writing-Original Draft,  
317 Writing-Review & Editing, Visualization. Cai Gan: Resources, Investigation, Writing-Original  
318 Draft. Danni Cai: Investigation. Jiani Ma: Writing-Review and Editing.

319

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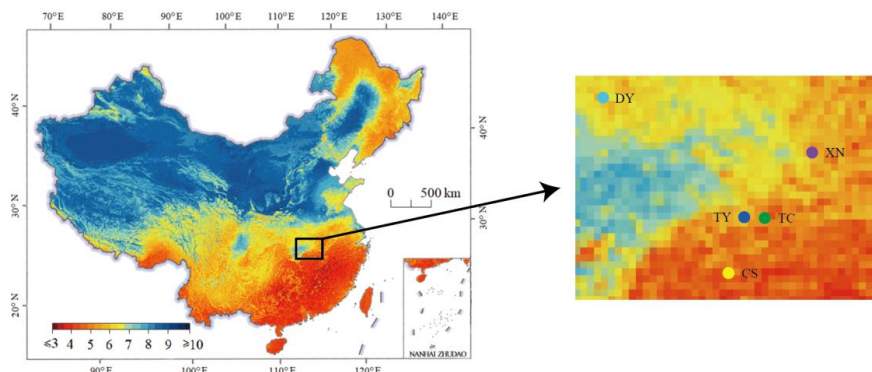
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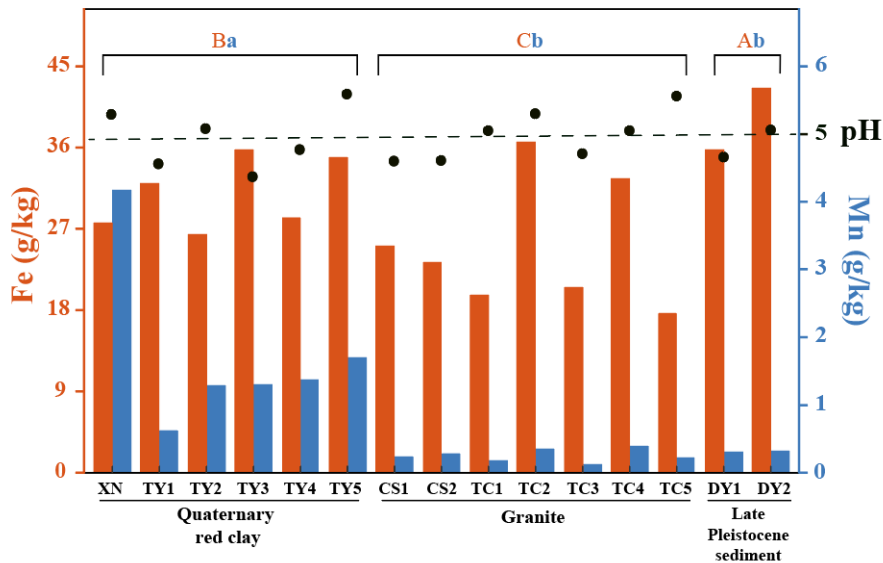
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501

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

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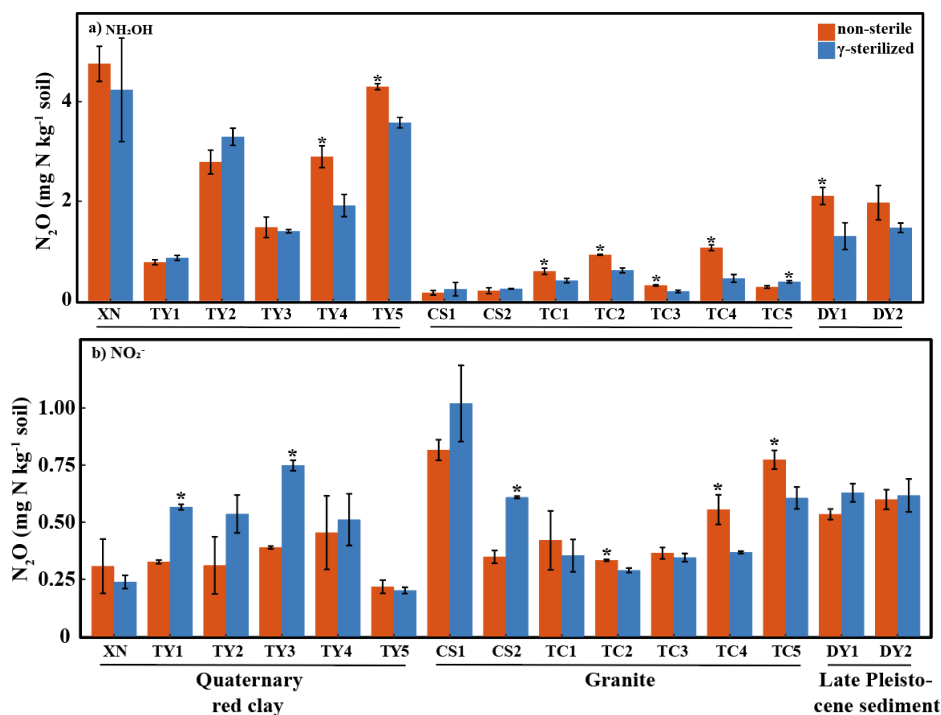


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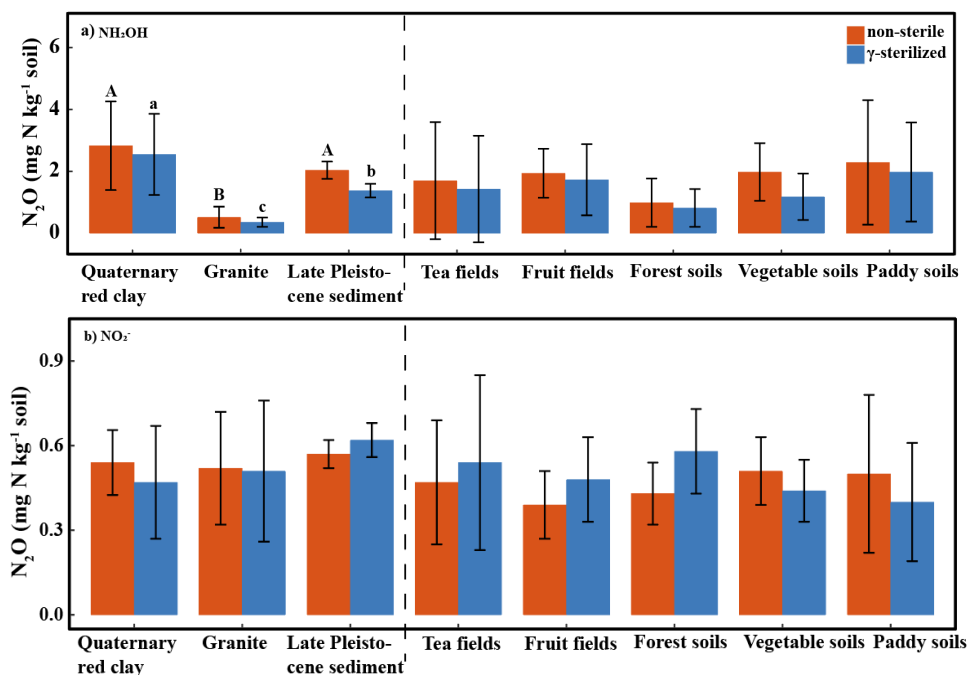
506 **Figure 2.** Manganese (Mn), iron (Fe) contents and pH values of the fifteen soils. Capital and  
 507 lowercase letters indicate significant difference in Fe and Mn contents, respectively. The  
 508 difference in pH values is insignificant.

509

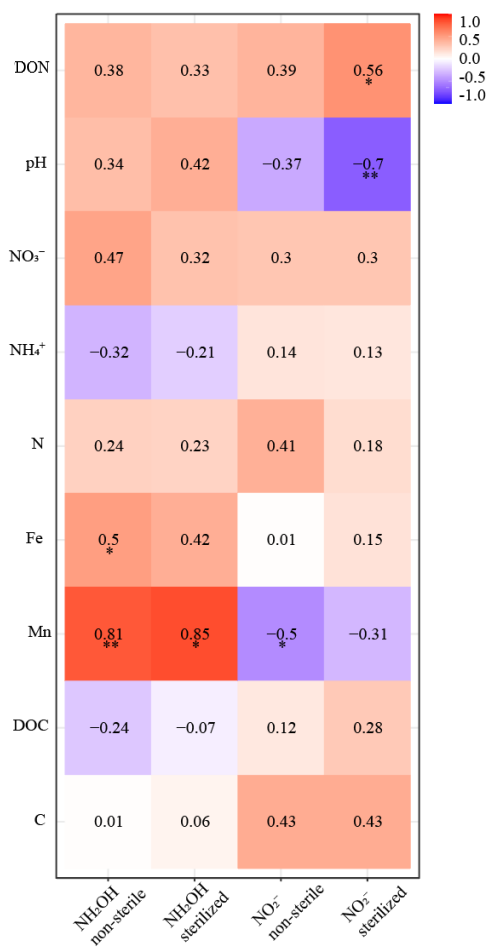
510



511 **Figure 3.** Net N<sub>2</sub>O production in fifteen soils with and without γ sterilization after addition  
 512 of NH<sub>2</sub>OH (a) and NO<sub>2</sub><sup>-</sup> (b) by parent material. Asterisks indicate significantly (*P* < 0.05)  
 513 higher values between non-sterile and γ-sterilized samples at one soil. Error bars represent  
 514 standard deviation (SD, n = 3).  
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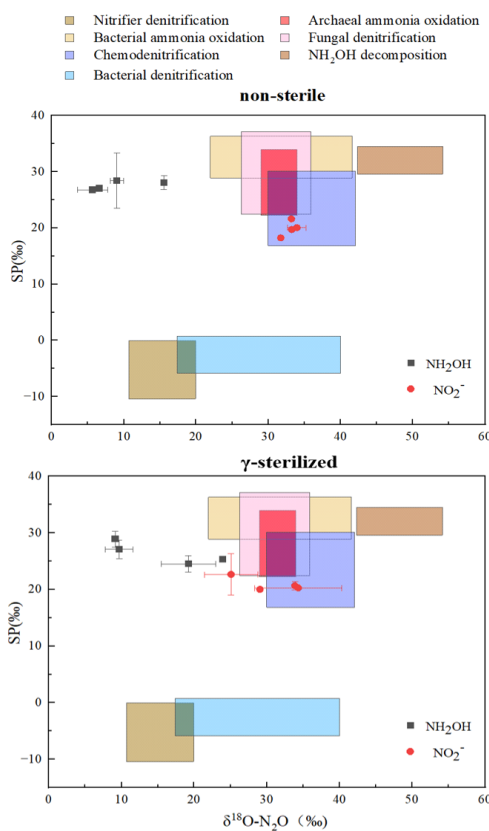


516  
517 **Figure 4.** Emissions of N<sub>2</sub>O from soils amended with NH<sub>2</sub>OH (a) and NO<sub>2</sub><sup>-</sup> (b), which were  
518 sorted by parent material and land use type. Capital and lowercase letters indicate significant  
519 difference among non-sterile and γ-sterilized soils, respectively. No letters indicate  
520 insignificant difference.  
521



**Figure 5.** Spearman correlation coefficients between soil N<sub>2</sub>O 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  $P < 0.01$ .





**Figure 6.** Relationships between the SF and  $\delta^{18}\text{O}$  values of  $\text{N}_2\text{O}$  in non-sterile and  $\gamma$ -sterilized soils after  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  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.

Parent material	Land use	Soils	Silt (%)	Clay (%)	Sand (%)	pH	TC (g/kg)	TN (g/kg)	DOC (mg/kg)	DON (mg/kg)	NH <sub>4</sub> <sup>+</sup> (mg/kg)	NO <sub>3</sub> <sup>-</sup> (mg/kg)
Quaternary red clay	Tea	XN	9.9	33.13	56.97	5.29	9.64	1.043	13.43	9.91	3.41	9.17
	Tea	TY1	37.08	34.47	28.45	4.56	12.31	0.931	17.92	7.07	8.33	3.61
	Fruit	TY2	52.51	31.88	15.61	5.08	8.77	0.97	14.86	9.08	5.88	5.88
	Forest	TY3	40.43	40.87	18.7	4.37	11.13	0.97	16.62	11.59	18.52	6.89
	Vegetable	TY4	51.87	33.9	14.23	4.77	8.96	1.022	15.35	7.64	5.71	7.65
Pleistocene sediment	Paddy	TY5	43.48	35.33	21.2	5.59	8.2	1.022	13.24	7.64	18.85	5.99
	Tea	CS1	35.54	31.7	32.76	4.6	12.24	1.204	24.38	40.98	89.29	13.83
	Forest	CS2	21.32	26.96	51.73	4.61	3.26	0.255	13.28	5.05	4.06	3.94
	Tea	TC1	23.22	26.47	50.32	5.05	4.58	0.413	10.99	3.92	9.2	2.56
	Fruit	TC2	4.59	19.19	76.22	5.3	3.45	0.399	16.9	5.12	8.72	3.63
Granite	Forest	TC3	30.64	22.54	46.81	4.71	1.25	0.207	12.15	3.06	3.9	5
	Vegetable	TC4	35.13	33.5	31.37	5.05	11.74	1.166	13.51	8.33	5.66	8.66
	Paddy	TC5	6.85	29.92	63.23	5.56	20.78	1.876	22.97	6.27	14.94	3.07
	Fruit	DY1	48.49	39.71	11.79	4.66	8.91	0.999	12.86	24.3	1.98	20.19
	Forest	DY2	43.23	51.52	5.25	5.06	8.27	0.939	12.67	14.36	3.54	15



553 **Table 2.** One-way ANOVA ( $P < 0.05$ ) of soil physicochemical properties including dissolved organic carbon (DOC), total carbon (TC), total nitrogen (TN),  
 554 total ferric iron (Fe), total manganese (Mn), silt, clay and sand content, etc..

Variables	Silt (%)	Clay (%)	Sand (%)	pH	TC (g/kg)	TN (g/kg)	DOC (mg/kg)	DON (mg/kg)	NH <sub>4</sub> <sup>+</sup> (mg/kg)	NO <sub>3</sub> <sup>-</sup> (mg/kg)	Fe (g/kg)	Mn (g/kg)
<b>Quate rmary red clay</b>	37.59a	35.18b	27.23b	4.94a	9.87a	0.99a	15.24a	8.82b	10.12a	6.53b	30.80b	1.74a
<b>Granite</b>	19.45b	27.18c	53.37a	5.04a	8.13a	0.69a	16.31a	10.39b	19.39a	5.81b	21.34c	0.25b
<b>Late Pleistocene sediment</b>	45.86a	45.62a	8.52c	4.86a	8.59a	0.97a	12.77a	19.33a	2.76a	17.60a	39.80a	0.26b
<b>Tea field</b>	22.78b	31.13a	46.10a	4.88bc	9.68b	0.90bc	16.68a	15.47a	27.56a	7.29a	26.08a	1.30a
<b>Fruit field</b>	33.03ab	30.06a	36.91a	5.01b	7.31a	0.82bc	14.88a	12.84a	5.53b	9.90a	25.05a	0.61a
<b>Forest soil</b>	34.84ab	37.50a	27.65a	4.69c	6.42b	0.64c	13.68a	7.94a	8.04ab	7.43a	29.43a	0.52a
<b>Vegetable soil</b>	41.82a	33.66a	24.52a	5.13b	10.07b	1.09ab	14.43a	8.96a	5.10b	8.53a	29.51a	0.80a
<b>Paddy soil</b>	25.16ab	32.62a	42.21a	5.58a	14.49a	1.45a	18.10a	6.95a	16.90ab	4.53a	26.29a	0.95a



556 **Table 3.** The conversion ratios (%) of  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  and the contribution ratios (%)  
 557 of abiotic  $\text{N}_2\text{O}$  production to the total  $\text{N}_2\text{O}$  emission with  $\text{NH}_2\text{OH}$  and  $\text{NO}_2^-$  addition.

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

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