Organically fertilized tea plantation stimulates N_2O emissions and lowers NO fluxes in subtropical China

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12   **Abstract**

13   Tea plantations are rapidly expanding in China and other countries in the tropical and subtropical

14   zones, but so far there are very few studies including direct measurements on nitrogenous gases

15   fluxes from tea plantations. On the basis of 2-year field measurements from 2012 to 2014, we

16   provided an insight into the assessment of annual nitrous oxide (N_2O) and nitric oxide (NO) fluxes

17   from Chinese subtropical tea plantations under three practices of conventional urea application,

18   alternative oilcake incorporation and no nitrogen fertilization. Clearly, the N_2O and NO fluxes

19   exhibited large intra- and inter-annual variations, and furthermore their temporal variability could

20   be well described by a combination of soil environmental factors including soil mineral N,

21   water-filled pore space and temperature, based on a revised "hole-in-the-pipe" model. Averaged

22   over 2-year study, annual background N_2O and NO emissions were approximately 4.0 and 1.6 kg

23   N ha^{-1} yr^{-1}, respectively. Compared to no nitrogen fertilization, both urea and oilcake application

24   significantly stimulated annual N_2O and NO emissions, amounting to 14.4-32.7 kg N_2O-N ha^{-1} yr^{-1}

25   and at least 12.3-19.4 kg NO-N ha^{-1} yr^{-1}, respectively. In comparison with conventional urea

26   treatment, on average, the application of organic fertilizer significantly increased N_2O emission by

27   71% but decreased NO emission by 22%. Although the magnitude of N_2O and NO fluxes was

28   substantially influenced by N source, the annual direct emission factors of fertilizer N were

29   estimated to be 2.8-5.9%, 2.7-4.0% and 6.8-9.1% for N_2O, NO and N_2O+NO, respectively, which

30   are significantly higher than those defaults for global upland croplands. This indicated that the

31   rarely determined N_2O and NO formation appeared to be a significant pathway in the nitrogen

32   cycle of tea plantations, which are a potential source of national nitrogenous gases inventory.

33   Keywords：nitrous oxide, nitric oxide, tea plantation, nitrogen fertilizer, emission factor

1 Introduction

Nitrous oxide (N_2O) and nitric oxide (NO) are two of the most important anthropogenic nitrogen compounds emitted to the atmosphere, which are directly or indirectly involved in global warming and atmospheric chemistry (Williams et al., 1992; IPCC, 2013). It is well accepted that human activities strongly influence the source of N_2O and NO, as nitrogen fertilizer applied in agriculture is now the vital source of inorganic/organic nitrogen substrate for nitrification and denitrification processes, leading to increased N_2O and NO emissions (McElroy and Wang, 2005; Galloway et al., 2008). Recently anthropogenic emissions from the application of nitrogenous fertilizers in agriculture were estimated to be 1.7-4.8 Tg N yr^{-1} for N_2O and 3.7 Tg N yr^{-1} for NO, accounting for approximately 60% and 10% of the total global estimates, respectively (IPCC, 2013). However, one should admit that a dearth of direct measurements of nitrogenous gases fluxes in some agricultural areas makes these estimates highly uncertain, and it also results in the projection and mitigation of agricultural N_2O and NO emissions posing considerable challenges (Davidson and Kingerlee, 1997; Reay et al., 2012), although the measurements of these emissions have been made for many decades. Taking as an example, Stehfest and Bouwman (2006) summarized information from 1008 N_2O and 189 NO emission measurements in agricultural fields worldwide, and indicated that the representation of number of measurements in tropical and subtropical climates was only 13-14% and 23-28% for N_2O and NO, respectively. As suggested by Reay et al. (2012), therefore, a central aim of future study on e.g., N_2O emissions from agricultural systems should be to increase the coverage encompassing various agricultural land-use/cover types and climates as well as management practices.

Tea is one of the three most common beverages (i.e., coffee, tea and cocoa) worldwide, and tea crops are widely planted in the tropical and subtropical regions (Xue et al., 2013). China is the world's largest tea producing country, and its tea plantation area had reached 1.85 million ha in 2009, contributing approximately 52% to the world total (Han et al., 2013a). Besides, tea is a leaf harvested crop, and nitrogen is the most important nutrient for increasing the content of free amino acids, an index of the quality of tea leaves (Tokuda and Hayatsu, 2004). For improving the yield and quality of tea leaves, therefore, large amounts of nitrogen fertilizer are increasingly applied by tea farmers. For instance, the application rates of nitrogen fertilizer to tea plantations have been as

63   high as 450-1200 kg N ha^{-1} yr^{-1}, which significantly surpasses the recommended rate of 250-375

64   kg N ha^{-1} yr^{-1} for high tea yields (Tokuda and Hayatsu, 2004; Hirono and Nonaka, 2012; Fu et al.,

65   2012; Zhu et al., 2014). Not surprisingly, such high nitrogen inputs can easily induce excess

66   residual nitrogen and acidification of soil, both influence the nitrogen cycle of tea fields in which a

67   great deal of nitrogenous gases are produced (Jumadi et al., 2008; Zhu et al., 2014) . It was

68   reported that the N$_2$O emissions from tea fields were greatly higher than those from other upland

69   fields (Jumadi et al., 2005; Han et al., 2013a). Akiyama et al. (2006) analyzed data on N$_2$O

70   emissions from 36 sites with 246 measurements in Japanese agricultural fields and reported that

71   the mean fertilizer-induced emission factor of N$_2$O in tea fields was much higher as compared to

72   other upland fields and paddy fields. Nevertheless, there are still very few data available on N$_2$O

73   emissions from Chinese tea plantations (Fu et al., 2012; Li et al., 2013; Han et al., 2013a).

74   Meanwhile, tea plantations to which large amounts of nitrogen fertilizer have been added are also

75   probably one of the important sources of NO. So far, however, no study is available for NO fluxes

76   from tea fields worldwide, which hinders the development of the sound NO emission inventory

77   (Huang and Li, 2014).

78   As tea production in China has intensified to meet market demands over the past decades, public

79   concerns over the negative impacts of conventional synthetic nitrogen fertilizers application in tea

80   plantations on human health and environmental quality have also increased (Pimentel et al., 2005;

81   Han et al., 2013b). These concerns have led to increased grower interest in organically fertilized

82   tea plantations, and by 2011 approximately 45,000 ha of tea fields were under organic fertilization

83   in China (Han et al., 2013b). Furthermore, the conversion of conventional synthetic nitrogen

84   fertilization to organic fertilizer practice in tea plantations has been identified as a feasible

85   measure in the aspects of promoting soil carbon sequestration and ameliorating soil pH (Han et al.,

86   2013b; Wang et al., 2014). On the other hand, organic fertilization systems have been shown to

87   substantially affect N$_2$O emissions compared with conventional management practices, but the

88   influence can be either stimulatory (Akiyama and Tsuruta, 2003a, b; Syväsalo et al., 2006) or

89   marginal and even inhibitory (Akiyama and Tsuruta, 2003b; Burger et al., 2005; Petersen et al.,

90   2006; Kramer et al., 2006). Although these studies have demonstrated organic fertilizer practices

91   may improve soil quality and influence nitrogenous gases fluxes in some agricultural systems, no

92 study has specifically compared N_2O and NO emissions in response to organic and synthetic

93 nitrogen fertilizer application in tea plantations to our knowledge.

94 In this paper, we present the results of a 2-year field study in which N_2O and NO fluxes were

95 measured simultaneously in Chinese subtropical tea plantations under three practices of

96 conventional urea application, alternative organic fertilizer incorporation and no nitrogen

97 fertilization. The main objectives of the present study were to characterize and quantify annual

98 N_2O and NO fluxes and their direct emission factors across different years, and to evaluate the

99 effect of organic fertilizer management on N_2O and NO fluxes as well as to clarify the underlying

100 mechanisms and factors regulating these fluxes from tea plantations.

101 **2 Materials and methods**

102 **2.1 Site description and field treatments**

103 Field measurements were carried out in a tea planting farm (32°07′22″N, 110°43′11″E, approx.

104 441 m above sea level) of the Agricultural Bureau of Fangxian, Hubei Province, China. The region

105 is characterized by a northern subtropical monsoon climate with cool and dry winters as well as

106 warm and humid summers. From 2003 to 2011, the mean annual precipitation and air temperature

107 for this site were 914 mm and 14.2 °C, respectively. Before the campaign of tea cultivations, all

108 fields in this area had been cultivated with rice-fallow or rice-oilseed rape rotation cropping

109 system. The tea plants in the experimental field were transplanted in March 2008, thereafter it has

110 been continuously cultivated with regular synthetic nitrogen fertilizers and irrigation additions

111 according to common regional management practice. The topsoil (0-15 cm) of the experimental

112 site is of a loamy texture with (mean ± SE, n=12) 12.7±0.1% clay (<0.002 mm), 39.3±0.5% silt

113 (0.002-0.02 mm), and 48.0±0.6% sand (0.02-2 mm). Other important soil physiochemical

114 properties include organic carbon content of 13.6±0.2 g kg^{-1}, total nitrogen content of 1.5±0.1 g

115 kg^{-1}, pH of 5.0±0.1, and bulk density of 1.25±0.03 g cm^{-3}.

116 Our field study was performed over the course of two consecutive years from September 2012 to

117 October 2014. As shown in Table 1, three experimental treatments were set up on the tea (T) field

118 with approximately 4-year-old plantation: one with additions of urea (UN) that is the local

119 farmer's conventional and common practice for this region, another with applications of organic

120   fertilizer (OM) that is likely to be used alternative practice in the future for this region, and the

121   final treatment with no synthetic nitrogen fertilizers or organic fertilizers (NN) application. These

122   fertilizer treatments were arranged in a randomized complete block design with four replicates,

123   resulting in a total of 12 plots (each with an area of 8 m × 8 m). For the TUN plots, urea was

124   applied at the common rate of 450 kg N ha^{-1} yr^{-1} in two splits (one third of annual nitrogen inputs

125   as basal fertilization in the autumn time, two thirds as topdressing in the spring time). With respect

126   to TOM, organic fertilizer was applied at rates and times in accordance with TUN (Table 1). The

127   form of fertilizer applied in TOM was oilcake, which is a typical organic fertilizer in tea

128   cultivations of China and other countries like Japan. This organic fertilizer contained 7.1% N and

129   had a C:N ratio of 6.1. In addition, all treatments received equal amounts of phosphorous and

130   potassium (i.e., 225 kg P_2O_5 ha^{-1} yr^{-1} and 225 kg K_2O ha^{-1} yr^{-1}) in terms of fertilizer

131   recommendations by local farmers. On each replicated plot, the width of the canopy of tea plants

132   was approximately 0.5 m, and the distance of inter-row space between the canopies was about 0.4

133   m. All of the fertilizers were applied as band application in the inter-row space between canopies

134   with widths of approximately 0.2 m, and then incorporated into soils with a depth of

135   approximately 0.1 m, which is the conventional practice in tea cultivations. Due to the young

136   plantation age, the present tea plants did not receive any trimming during the experimental period,

137   and they also seldom experienced leaf harvest.

2.2 Measurements of N_2O and NO fluxes

139   The fluxes of N_2O and NO were in situ measured simultaneously using manually closed

140   chamber-based techniques (Zheng et al., 2008; Yao et al., 2009). As mentioned above, all

141   fertilizers were incorporated in the form of bands between the rows of tea plants, and the

142   remaining area was covered by canopy under which no fertilizer was applied. To better evaluate

143   gas fluxes from the tea field, a size of rectangular stainless-steel frame of 0.70 m × 0.90 m (width

144   × length) was set up in each replicated plot, which covered four tea plants and parts of spaces

145   between rows. That is, the frame covered the whole canopy area (i.e., 0.5 m in length) and

146   two-half of the fertilized inter-row spaces on both sides of tea canopy (i.e., 0.2 m in length each

147   side), representing the whole tea field landscape. To eliminate the possibility of influence on N_2O

148 and NO fluxes from the temporary installation of chamber bases (Matson et al., 1990), the frames

149 were inserted into the soil to a depth of 0.15 m one month before the start of flux measurements,

150 and they were maintained in place throughout the entire observation period, except when it was

151 removed for necessary farming practices (e.g., band fertilization). Besides, the sampling locations

152 were connected with boardwalks to prevent soil disturbance during the sampling period. In general,

153 flux measurements were conducted five times per week during the first week after each

154 fertilization event, and three times per week during the rest of time. Almost all of the gas sampling

155 was taken between 09:00 and 11:00 local standard time on each measuring day to minimize the

156 influence of diurnal temperature variation. Based on the size of frames and the height of tea plants,

157 insulated chambers with a bottom area of 0.70 m × 0.90 m and a height of 1.0 m were designed for

158 gas samplings. These chambers were wrapped with a layer of styrofoam and aluminum foil to

159 minimize temperature changes during the sampling period. Also, two circulating fans driven by

160 12V DC were installed inside the sampling chamber to facilitate mixing of chamber air and thus

161 inhibiting the formation of gas concentration gradients, and a hole of 2 cm diameter was fitted in

162 the top panel for equilibrating the pressure during the placement of them on the base frames. This

163 hole was embedded during the gas sampling using a pressure balance tube whose diameter and

164 length were determined according to the recommendation of Hutchinson and Mosier (1981). To

165 acquire the N_2O flux, five gas samples were withdrawn from the chamber headspace using 60 ml

166 polypropylene syringes fitted with three-way stopcocks at fixed intervals of 0, 10, 20, 30 and 40

167 min after covering. Within 3 h after collection, the N_2O concentrations of gas samples stored in

168 airtight syringes were directly analyzed in the laboratory established beside the experimental field,

169 using a gas chromatograph (GC, Agilent 7890A, Agilent Technologies, CA, USA) equipped with

170 an electron capture detector at 330 °C on the basis of $DN-CO_2$ method, as described in detail by

171 Zheng et al. (2008). The N_2O was separated by two stainless steel columns (both with an inner

172 diameter of 2 mm, one with a length of 1 m and the other with a length of 2 m) packed with

173 Porapak Q, 80/100 mesh at 55 °C isothermally. To ensure quality and stability assurance, the GC

174 system was inserted five standard N_2O samples with concentrations of 350 ppbv (the national

175 center for standard matters, Beijing, China) between every 10 unknown gas samples. Results of

176 GC analyses were accepted when five standard gas calibrations produced coefficient of variation

177   lower than 1%. The N_2O flux was determined by the linear or nonlinear change of gas

178   concentrations during the time of chamber closure, as described in detail by Wang et al. (2013). In

179   this study, the minimum detection limit of N_2O flux was approximately 2.6 μg N m^{-2} h^{-1}.

180   For each NO flux measurement, gas samples were collected from the same chamber that was used

181   for N_2O flux measurements (Yao et al., 2009). Before closing the chamber, approximately 2.5-3 L

182   gas sample from the headspace of each chamber was extracted into an evacuated bag made of inert

183   aluminum-coated plastic, and this measurement was regarded as time 0 min for NO analysis. After

184   40 min under chamber enclosure conditions (i.e., after finishing N_2O sample collections), another

185   headspace gas sample with the same volume was extracted from each chamber into another

186   evacuated bag. From these bag samples, NO concentrations were analyzed within 1 h by using a

187   model 42i chemiluminescence NO-NO_2-NO_x analyzer (Thermo Environmental Instruments Inc.,

188   USA). The NO_x analyzer instrument was calibrated monthly in the laboratory using a TE-146i

189   dilution-titration instrument (dynamic gas calibrator). A cylinder of standard gas of 50 ppmv NO

190   in N_2 (the national center for standard matters, Beijing, China) and a zero gas generator (Model

191   111 Zero Air Supply) were used for multipoint calibrating, spanning, and zeroing of the NO_x

192   analyzer. The NO flux was determined from the concentration at the end of the chamber enclosure

193   period by subtracting the concentration at time 0 min. It should be noted that although some

194   studies deriving N_2O and NO fluxes by employing either a simple linear regression method (e.g.,

195   Williams and Davidson, 1993; Kim and Kim, 2002; Zheng et al., 2003; Venterea et al., 2003; Li

196   and Wang et al., 2007; Pang et al., 2009; Zhao et al., 2015) or a nonlinear regression model (e.g.,

197   Valente et al., 1995; Kroon et al., 2008; Yao et al., 2010a; Wang et al., 2013) have been widely

198   adopted, it is clear that inappropriate application of a linear model to nonlinear data may seriously

199   underestimate the trace gas flux (Hutchinson and Livingston, 1993; Kutzbach et al., 2007). For

200   example, Kroon et al. (2008) suggested that on average, the N_2O emission estimates with the

201   linear regression method were 46% lower than the estimates with the exponential regression

202   method. Similarly, Mei et al. (2009) conducted a field intercomparison of NO flux measurements

203   with linear and nonlinear regression methods, and observed that the linear estimates of NO flux

204   were 26% lower on average relative to the nonlinear method. However, to date there has been

205   limited field comparison of these two methods to assess comparability of N_2O or NO fluxes

206   calculated by them. Based on our data sets of NO measured in wheat fields using the automatically

207   static translucent chamber-based system (the raw data from the case studies of Zheng et al., 2003

208   and Yao et al., 2010a), the NO fluxes were re-estimated using linear and nonlinear regression

209   methods. In order to better compare the two regression methods, a subset of data collected in the

210   evening time was used that satisfied the present conditions of static opaque chamber technique.

211   Finally, approximately 3489 pairs of observations were used for comparing the difference between

212   the two regression methods; and the results showed that the linear model underestimated the NO

213   fluxes by 3% to 59% (mean: 31%) at the 95% confidence interval, as compared to the nonlinear

214   method. Overall, these findings indicate that data sets of N_2O collected in this study are relatively

215   reliable, but the present method of linear accumulation assumption inevitably introduce an extent

216   of underestimation into the NO fluxes for cases with nonlinear accumulations. Therefore, it has to

217   be noted that the NO fluxes reported in this study represent the conservative magnitude for the

218   present tea plantations.

219   **2.3 Auxiliary measurements**

220   The air temperature inside the chamber headspace during the flux measurements was recorded

221   with a manual thermocouple thermometer (JM624, Tianjin, China). Air pressure and temperature

222   as well as daily precipitation were obtained from an automatic meteorological station set up on the

223   experimental farm. The air temperature measured in the chamber enclosures and air pressure

224   obtained from the meteorological station were directly utilized in the flux computations to

225   calculate the gas density during the sampling conditions by using the ideal gas law. Soil (5 cm)

226   temperature was automatically measured in 30 min intervals from the direct vicinity of the

227   chamber frames using a HOBO temperature sensor (Onset, USA). Soil water content (0-6 cm) was

228   recorded daily using a portable frequency domain reflectometry (FDR) probe (MPM-160, China).

229   Three replicate soil samples (0-10 cm) in each plot were collected at 1-2 week intervals using a 3

230   cm diameter gauge auger. Following the collection, the fresh samples were bulked into one

231   composite sample for each treatment, and then immediately extracted with 1 M KCl and 0.05 M

232   K_2SO_4 to determine the concentrations of soil mineral N (NH_4^+ and NO_3^-) and dissolved organic

233   carbon (DOC), respectively, both with a soil: solution ratio of 1:5. The NH_4^+, NO_3^- and DOC

234   concentrations were measured simultaneously with a continuous flow colorimetric analysis

235   instrument (San++, Skalar Analytical B.V., Netherlands).

236   **2.4 Statistical analysis**

237   Statistical analysis was conducted using the SPSS19.0 (SPSS China, Beijing, China). Before

238   variance component analysis, all data were tested for normal distribution using the Nonparametric

239   Tests approach, and the original data that failed the test were log transformed ($P = 0.01$-0.42). To

240   determine differences in nitrogenous gases fluxes and soil environmental variables among

241   treatments during the given pronounced flux-related event (e.g., fertilization events, growing

242   period), Linear Mixed Models for randomized complete block design were used with least

243   significant difference tests at $P < 0.05$ level. Differences in N_2O and NO emissions due to main

244   effects like fertilizer treatment, year, treatment $\times$ year and block $\times$ treatment as random effect were

245   analyzed using Linear Mixed Models, and the model was fitted using the restricted maximum

246   likelihood procedure. Multiple linear or non-linear regression analysis was applied to examine the

247   correlations between N_2O and NO fluxes and soil environmental factors.

248   **3 Results**

249   **3.1 Environmental variables**

250   Annual precipitation was 804 mm from mid September 2012 to the end of September 2013, 890

251   mm from the beginning of October 2013 to mid October 2014 (Fig. 1a); both values were smaller

252   than the multiyear average precipitation (914 mm). Apart from the precipitation, sprinkling

253   irrigation was applied four times per year depending on climatic conditions, amounting to 150 and

254   135 mm for the two years, respectively. Soil temperature showed comparable fluctuations with the

255   air temperature, ranging from -0.1 to 28.3 °C. The mean annual soil temperature was 14.9 and

256   14.6 °C for the 2012/2013 and 2013/2014, respectively (Fig. 1a), with no treatment impacts. Soil

257   water content expressed as WFPS (water-filled pore space) ranged from 20% to 80% during the

258   study period, which was mainly influenced by rainfall and irrigation events. The mean WFPS

259   across 2012 to 2014 were 49.1%, 49.7% and 48.6 % for TNN, TUN and TOM, respectively, with

260   no significant difference among them (Fig. 1b).

261　Soil NH_4^+ concentrations in TUN and TOM remarkably increased following the fertilizer

262　applications in March and October, and varied from 4.1 to 654 mg N kg^{-1}SDW (soil dry weight)

263　(Fig. 2a). The temporal patterns of NO_3^- concentrations were also affected by nitrogen applications,

264　ranging from 2.4 to 188 mg N kg^{-1}SDW, but the elevated peaks were observed slightly later than

265　the peaks for NH_4^+ (Fig. 2b), reflecting the occurrence of nitrification. In contrast, both NH_4^+ and

266　NO_3^- concentrations in TNN were relatively stable and always below 50 mg N kg^{-1}SDW. Clearly,

267　TUN and TOM significantly enhanced soil mineral N concentrations, compared to TNN ($P<0.05$).

268　During the study periods, soil NH_4^+ averaged 17, 138 and 113 mg N kg^{-1}SDW for TNN, TUN and

269　TOM in the first year (2012-2013), respectively; and mean NH_4^+ concentrations were 5.4, 172,

270　106 mg N kg^{-1}SDW for TNN, TUN and TOM in the second year (2013-2014), respectively (Fig.

271　2a). Compared to TUN, TOM greatly decreased soil NH_4^+ concentrations during both studied

272　years, although this influence was not statistically significant for the first year. The mean NO_3^-

273　concentrations across 2012-2014 in TNN, TUN and TOM were around 5.7, 44 and 49 mg N

274　kg^{-1}SDW, respectively, with no significant difference between TUN and TOM for either year (Fig.

275　2b).

276　Over the whole study period, soil DOC concentrations ranged from 17 to 317 mg C kg^{-1}SDW in

277　TNN, from 10 to 488 mg C kg^{-1}SDW in TUN and from 20 to 559 mg C kg^{-1}SDW in TOM (Fig.

278　2c). The mean DOC concentrations across the both studied years were approximately 142, 146

279　and 179 mg C kg^{-1}SDW for TNN, TUN and TOM, respectively. Obviously, TOM significantly

280　increased mean soil DOC concentration compared to TNN and TUN ($P<0.05$), but there was no

281　significant difference between TUN and TNN.

282　**3.2 Annual N_2O and NO fluxes and their direct emission factors**

283　Seasonal pattern of N_2O fluxes was generally driven by temporal variation in air and soil

284　temperatures, which was relatively higher during the tea growing season from March to

285　September than in winter. The cumulative N_2O release from all treatments across the tea growing

286　season accounted for 54-86% of the annual emission. Meanwhile, the seasonal variability of N_2O

287　fluxes were also influenced by fertilization and rainfall/irrigation events (Fig. 3a). The N_2O fluxes

288　in TUN and TOM increased after each of the fertilizer applications, and then gradually decreased

289   to the levels comparable to those from TNN. Obviously, the N_2O emissions varied significantly

290   with fertilizer treatment and year. Across the investigated two years, annual N_2O emissions ranged

291   from 1.9 kg N ha^{-1} yr^{-1} for TNN to 32.7 kg N ha^{-1} yr^{-1} for TOM (Table 2). Compared to TNN, the

292   2-year mean N_2O emissions were remarkably increased by 345% and 660% for TUN and TOM,

293   respectively ($P<0.05$). In comparison with TUN, TOM significantly increased annual N_2O

294   emission by 71% on average ($P<0.05$). On the annual scale, the direct emission factors of N_2O

295   were an average of 3.1% and 5.9% for tea plantations under urea and organic fertilizer treatment,

296   respectively.

297   Clearly, the NO fluxes demonstrated a seasonal variability that was similar to the N_2O fluxes. That

298   is, they were higher from March to September and lower from December to March, and also

299   affected by fertilization and rainfall/irrigation events (Fig. 3b). Similar to N_2O, the NO emissions

300   were greatly influenced by fertilizer treatment and year. The annual NO emissions from all

301   treatments ranged from 0.4 to 19.4 kg N ha^{-1} yr^{-1} (Table 2), of which 53-77% was released during

302   the tea growing season. Compared to TNN, the fertilizer applications (TUN and TOM)

303   significantly increased annual NO emission by 8-11 times on average ($P<0.05$). In contrast to N_2O,

304   TOM significantly decreased annual NO emission by 22% relative to TUN ($P<0.05$). Averaging

305   across the two years, the direct emission factors of NO were 3.8% and 2.9% for TUN and TOM,

306   respectively. In addition, the N_2O+NO emissions were, on average, 5.6, 36.7 and 45.1 kg N ha^{-1}

307   yr^{-1} for TNN, TUN and TOM, respectively, indicating that alternative organic fertilization

308   significantly enhanced nitrogen oxide emissions (Table 2).

309   **3.3 Relationships of N_2O and NO fluxes with soil environmental factors**

310   Across the 2-year study period, stepwise multiple regression analysis showed that WFPS was the

311   key factor controlling N_2O and NO fluxes for both TUN and TOM. Furthermore, a nonlinear

312   response curve best described the decreases in molar ratios of NO to N_2O fluxes with increasing

313   WFPS (Fig. 4). However, variations in WFPS could explain only 22-30% of the variance in the

314   ratios, suggesting the importance of some other factors (e.g., soil mineral N and temperature) on

315   regulating these fluxes. To better evaluate the combined effects of soil environmental factors on

316   N_2O and NO fluxes, therefore, the revised "hole-in-the-pipe" model as described by Yao et al.

317 (2015) and Yan et al. (2015) was tested in this study. Over the entire study period, the analysis

318 results displayed that the temporal variations of N_2O and NO fluxes in TUN and TOM could be

319 well described by a combination of soil environmental factors, including soil mineral N, WFPS

320 and   temperature.   That   is,   for   TUN:

321 $Ln(N_2O+NO) = 0.30Ln(NH_4^+ + NO_3^-) + 2.53Ln(WFPS) - \dfrac{13.9}{RT_K}$, R^2=0.97, P<0.01; and

322 $Ln(N_2O+NO) = 0.17Ln(NH_4^+ + NO_3^-) + 2.68Ln(WFPS) - \dfrac{13.6}{RT_K}$, R^2=0.96, P<0.01 for

323 TOM; in which R and T_k are the molar gas constant (8.31 J mol^{-1} k^{-1}) and soil temperature in

324 Kelvin, respectively.

325 **4 Discussion**

326 **4.1 Intra- and inter-annual variations of N_2O and NO fluxes and related environmental**

327 **factors**

328 Currently, the existing studies on tea fields only focused on N_2O fluxes (Jumadi et al., 2005;

329 Akiyama et al., 2006; Gogoi and Baruah, 2011; Fu et al., 2012; Han et al., 2013a; Yamamoto et al.,

330 2014), and therefore they are not directly comparable to our present study. Our results

331 demonstrated annual characteristics of N_2O and NO fluxes simultaneously, which is important for

332 better understanding of how the climatic and environmental factors affecting soil nitrogen turnover

333 processes in tea plantations. Generally, the subtropical climate is characterized by the hot-humid

334 season from April through September and the cool-dry season from October through March every

335 year, leading to significant seasonal variations in soil environmental factors (Lin et al., 2010).

336 Driven by the seasonality of soil temperature, WFPS, NH_4^+ and NO_3^- contents, the N_2O and NO

337 fluxes showed large temporal variations (Skiba et al., 1998; Williams et al., 1999; Yan et al., 2015),

338 characterizing by significantly higher during the tea growing season than in winter in this study

339 (Fig. 3). The present result is in agreement with previous studies conducted in other agricultural

340 systems under the subtropical climate, such as in vegetable fields (Min et al., 2012; Yao et al.,

341 2015), paddy rice-upland crop rotation ecosystems (Yao et al., 2013) and orchard plantations (Lin

342 et al., 2010), highlighting the climatic controls on N_2O and NO fluxes. Furthermore, up to 97% of

343   the variance in N_2O and NO fluxes could be explained by the combined effects of soil temperature,

344   WFPS and mineral N content, indicating an essential role of the environmental factors on N_2O and

345   NO fluxes. Overall, the knowledge of temporal variations in N_2O and NO fluxes and their related

346   driving forces plays an important role for up-scaling nitrogenous gas fluxes to the regional and

347   global scale.

348   On the other hand, our study clearly demonstrated that annual N_2O and NO emissions were

349   significantly affected by the factor of year (Fig. 3), even though the field management and soil

350   temperature were comparable across the two study years. A presumable reason for the pronounced

351   inter-annual variations of N_2O and NO fluxes was the difference in precipitation, particularly

352   rainfall distribution throughout a year. For example, the cumulative rainfall of 94 mm over a

353   period from 20th to 26th June, 2013 was received that brought soil water content changing from

354   25% to 64% WFPS on average (Fig. 1). As was also observed by our auxiliary measurements that

355   soil NH_4^+ and NO_3^- increased after rainfall events during this period (Fig. 2a-b), the

356   drying-rewetting event could enhance the availability of nitrogen substrate and stimulate microbial

357   activity (Davidson, 1992; Williams et al., 1992; Yao et al., 2010b), and thus, resulting in the

358   following elevated fluxes of N_2O and NO (Fig. 3a-b). Similarly, a number of studies also reported

359   that the large inter-annual variability in N_2O and NO fluxes were mainly influenced by the

360   difference in annual distribution of the precipitation (e.g., Akiyama and Tsuruta, 2003b; Yao et al.,

361   2013).

362   **4.2 Fertilizer type influencing annual N_2O and NO emissions**

363   As tea plantations displayed high N_2O production activities, they might be a major source of

364   nitrogenous gases in agricultural systems (Tokuda and Hayatsu, 2001, 2004; Zhu et al., 2014). Our

365   observations confirmed earlier findings, with annual N_2O emissions ranging from 14.4 to 32.7 kg

366   N ha^{-1} yr^{-1} and NO emissions from 12.3 to 19.4 kg N ha^{-1} yr^{-1} for the fertilized tea plantations

367   (Table 2). Generally, our annual N_2O emissions were within the range of the reported magnitudes

368   of 4.3-30.9 kg N ha^{-1} yr^{-1} for Chinese subtropical tea fields (Fu et al., 2012; Han et al., 2013a).

369   Based on the thorough review of Akiyama et al. (2006), annual N_2O emissions were presented

370   from 0.6 to 61.0 kg N ha^{-1} yr^{-1} for Japanese tea plantations, with a mean value of 24.3 kg N ha^{-1}

371   yr^{-1}. Obviously, the mean annual N$_2$O emission in our study (mean: 24.1±4.0 kg N ha^{-1} yr^{-1}) was

372   well consistent with the Japanese estimated value. In contrast, the magnitude of N$_2$O emissions

373   from the present tea plantations was much higher than that from the paddy rice-fallow cropping

374   systems in the same region (0.8-6.6 kg N ha^{-1} yr^{-1}, Yao et al., 2014). With respect to NO, this is the

375   first time reporting annual NO emission for tea plantations to our knowledge. On average, tea

376   plantations released at least 16.8 kg N ha^{-1} yr^{-1} NO into the atmosphere, which fell within the

377   range of 1.1-47.1 kg N ha^{-1} yr^{-1} for Chinese conventional vegetable fields under the subtropical

378   climate (e.g., Li and Wang, 2007; Mei et al., 2009; Deng et al., 2012; Yao et al., 2015). As these

379   authors acknowledged, their high NO emissions for vegetable fields were mainly attributed to

380   quite high nitrogen inputs, ranging from 317 to 1464 kg N ha^{-1} yr^{-1}. Nevertheless, our observed

381   annual NO emissions were relatively higher as compared to those estimates of 0.5-6.5 kg N ha^{-1}

382   yr^{-1} for rice-wheat cropping systems with nitrogen application rates of 150-375 kg N ha^{-1} yr^{-1}

383   (Zheng et al., 2003; Yao et al., 2013; Zhao et al., 2015) and of 4.0-6.9 kg N ha^{-1} yr^{-1} for forest

384   ecosystems (Li et al., 2007) in Chinese subtropical regions.

385   Although the fertilized tea plantations emitted large amounts of N$_2$O and NO, the magnitude of

386   these emissions was significantly influenced by the applied fertilizer type. That is, organically

387   fertilized tea plantation increased N$_2$O emission by 71% but decreased NO emission by 22%,

388   compared to conventional urea application (Table 2). Our stimulatory effect of organic fertilization

389   on N$_2$O emission and simultaneously inhibitory impact on NO emission supports the findings of

390   some previous studies (Thornton et al., 1998; Akiyama and Tsuruta, 2003a, b; Hayakawa et al.,

391   2009). However, other studies showed that organic fertilization may reduce N$_2$O emissions or that

392   emissions of N$_2$O and NO were not affected at all (Harrison et al., 1995; Akiyama and Tsuruta,

393   2003b; Vallejo et al., 2006; Yao et al., 2009). It was generally accepted that the NO to N$_2$O

394   emission ratio was used as a potential indicator for distinguishing between nitrification and

395   denitrification process (Anderson and Levine, 1986; Skiba et al., 1992; Harrison et al., 1995;

396   Williams et al., 1998). As calculated from the results of Table 2, the molar ratios of NO to N$_2$O

397   emissions were in the range of 1.8-2.5 for the TUN plots but < 1.0 in the TOM plots. This may

398   indicate that nitrification was probably the dominant process for N$_2$O and NO production in the

399   conventional urea treatment, while denitrification would be more dominant process in organic

400 fertilization, although both nitrification and denitrification could occur under the present soil

401 moisture conditions (i.e., 20%-80%WFPS) according to a conceptual model proposed by

402 Davidson (1991). Denitrifiers have a very high affinity for NO and tend to utilize it in preference

403 to N_2O as a substrate even in well-aerated soils (Conrad, 2002; Yamulki and Jarvis, 2002). It is

404 therefore to be expected the differences in N_2O and NO emission response between urea and

405 organic fertilizer treatment. This view was further supported by our observations on soil NH_4^+ and

406 DOC. It is well recognized that NH_4^+ enhanced NO fluxes since it affected nitrification, whereas

407 the addition of DOC generally diminished these fluxes by enhancing soil respiration and thereby

408 inducing the anaerobic conditions that favored the production of N_2O and the consumption of NO

409 through denitrification (Granli and Bockman, 1994; Vallejo et al., 2006; Meijide et al., 2007). In

410 this study, therefore, TOM with lower NH_4^+ and higher DOC, emitted more N_2O and less NO than

411 those of TUN. Alternatively, opposite trends observed for N_2O and NO emissions between TUN

412 and TOM was probably regulated by soil heterotrophic nitrification, the direct oxidation of organic

413 N to NO_3^- without passing through mineralization (Müller et al., 2004; Islam et al., 2007). It has

414 been identified that heterotrophic nitrification, especially for acidic soils with organic amendments,

415 plays an important role in soil nitrogen transformations, including the production and consumption

416 processes of NH_4^+ and NO_3^- as well as N_2O and NO (Dunfield and Knowles, 1998; Zhu et al.,

417 2011, 2014; Medinets et al., 2015). Hence, one can assume that given WFPS being comparable in

418 all treatments, heterotrophic nitrification was the most important process for consumption of NO

419 and production of N_2O in the organic fertilizer treatment, whereas autotrophic nitrification

420 dominated in urea application. Besides, it has been validated that soils receiving organic

421 amendments significantly reduce NO fluxes as a result of increased NO consumption via aerobic

422 co-oxidation reactions in heterotrophic bacteria (Baumgärtner et al., 1996; Dunfield and Knowles,

423 1998; Conrad, 2002). This assumption could be also supported by our measurements on soil NH_4^+

424 and NO_3^-. That is, TOM showed comparable even slightly higher NO_3^- relative to TUN, although

425 TUN demonstrated relatively high NH_4^+ due to the rapid release of urea hydrolysis (Fig. 2a-b).

426 This indicated that heterotrophic nitrification contributed substantially to the production of NO_3^- in

427 TOM, because the application of organic matter can enhance the direct oxidation of organic N to

428 NO_3^- via soil heterotrophic nitrification (Zhu et al., 2011, 2014). Overall, although our data

16

429 supported the above mentioned views, the exact reaction mechanisms were not determined

430 directly in the present study. Therefore, further detailed investigations are needed to provide a

431 complete assessment on the relative contribution of autotrophic nitrification, heterotrophic

432 nitrification and denitrification to N_2O and NO fluxes from tea plantations, based on new

433 approaches and techniques, e.g., ^{15}N tracing techniques (Müller et al., 2007).

434 **4.3 Background N_2O and NO emissions and direct emission factors of fertilizer N**

435 Although background N_2O and NO emissions occurring in the zero-N control have been

436 recognized as a major component for developing national emission inventory of nitrogenous gases

437 (Zheng et al., 2004; Huang and Li, 2014), direct measurements on background emissions,

438 especially measurements covering an entire year for tea plantations have been rare (Akiyama et al.,

439 2006). In our study, the mean annual background emissions were 4.0 kg N ha^{-1} yr^{-1} for N_2O and at

440 least 1.6 kg N ha^{-1} yr^{-1} for NO, respectively (Table 2). Our background N_2O emission is

441 comparable to the preliminary estimate of 3.66-4.24 kg N ha^{-1} yr^{-1} for Japanese tea fields

442 (Akiyama et al., 2006), but it is relatively lower than the reported value of 7.1 kg N ha^{-1} yr^{-1} for

443 another tea field in the Chinese subtropical region (Fu et al., 2012). Nevertheless, these

444 background N_2O emissions revealed by present and previous studies in tea plantations are

445 generally higher than those estimates for cereal grain croplands (ranging from 0.1 to 3.67 kg N

446 ha^{-1} yr^{-1}, with a mean of 1.35 kg N ha^{-1} yr^{-1}, Gu et al., 2007) and vegetable fields (1.1-2.7 kg N

447 ha^{-1} yr^{-1}, Wang et al., 2011; Liu et al., 2013) in China, or the recommended default value of 1 kg N

448 ha^{-1} yr^{-1} by IPCC (IPCC, 2006). Similarly, our mean background NO emission from tea

449 plantations is greater relative to cereal grain croplands (0.2-0.9 kg N ha^{-1} yr^{-1}, Yao et al., 2013; Yan

450 et al., 2015) and vegetable fields (0.2-0.8 kg N ha^{-1} yr^{-1}, Yao et al., 2015) in China. These

451 comparisons highlight the characteristic of high background N_2O and NO emissions from tea

452 plantations, which is probably due to long-term heavy nitrogen fertilization and subsequent soil

453 acidification (Tokuda and Hayatsu, 2004; Yamamoto et al., 2014). Soil acidity appears to be an

454 important factor in affecting biotic and abiotic processes and consequently promoting nitrogen

455 losses, such as enhancing N_2O production ratios from nitrification and depressing the conversion

456 of N_2O to N_2 in denitrification (Zhu et al., 2011) as well as inducing chemodenitrification for NO

457   production (Venterea et al., 2003; Medinets et al., 2015). It should, however, be noted that with

458   limited data available from tea plantations of the world and consequently the high uncertainties of

459   meta-analytic results, caution should be exercised in the interpretation of the differences in

460   background emissions of N_2O and NO between the current and previous studies.

461   In this study, the mean annual emission factor of NO for TUN was 3.8%, which was substantially

462   higher than those estimated for Chinese rice fields (0.04%) and uplands (0.67%) (Huang and Li,

463   2014), or the average value of 0.7% for global upland croplands (Bouwman et al., 2002; Yan et al.,

464   2005). The NO emissions from TUN were greatly reduced by practicing TOM, giving emission

465   factor of 2.9% (Table 2). Although the NO emission factors were lower for TOM relative to TUN,

466   TOM could not be proposed as a preferred management option for tea plantations because it

467   emitted much higher N_2O or N_2O+NO. The N_2O emission factors obtained on this study site (i.e.,

468   3.1% for TUN and 5.9% for TOM) were considerably higher than those estimated for Japanese tea

469   fields (2.8%, Akiyama et al., 2006) and another Chinese subtropical tea field (1.9-2.2%, Fu et al.,

470   2012), or the IPCC default value of 1% for global upland croplands (IPCC, 2006). These results

471   corroborated the assertion that tea plantations were an important source of atmospheric N_2O in

472   tropical and subtropical regions, and furthermore they extended the earlier findings by

473   demonstrating the characteristic of high NO and N_2O+NO emissions from tea plantations.

474   It is noteworthy that although our investigated tea plantations represent the major and typical

475   tea-planting types in Chinese subtropical regions, the obtained background and direct emission

476   factors of N_2O and NO could not be simply extrapolated to a regional scale due to the limited site

477   results (e.g., only four chamber-spatial measurements for each treatment) and the characteristics of

478   high spatial variability of nitrogenous gases fluxes (e.g., Li et al., 2013). A more holistic approach

479   for regional estimates of N_2O and NO emissions from tea plantations should be based on

480   meta-analysis of published nitrogenous gases fluxes to obtain representative background and

481   direct emission factors or on the basis of biogeochemical modeling validated by regional field data,

482   as suggested methodologies by IPCC (IPCC, 2006).

483   **5 Conclusions**

484   Based on two-year field measurements, this study provided an integrated evaluation on N_2O and

485 NO emissions in response to no nitrogen fertilization, conventional urea and alternative oilcake

486 application in Chinese subtropical tea plantations. Clearly, both N_2O and NO emissions varied

487 substantially within a year and between different years, which was chiefly driven by the

488 fertilization events and the distribution and size of rain events. Soil water-filled pore space,

489 temperature and mineral nitrogen content appeared to be the major factors regulating the

490 seasonality of N_2O and NO fluxes, and their correlation could be well presented by a revised

491 "hole-in-the-pipe" model. Compared to no nitrogen fertilization, the application of urea and

492 organic fertilizer to tea plantations stimulated annual N_2O and NO emissions. On average, the

493 organic fertilizer induced emission factor of N_2O (i.e., 5.9%) was significantly higher than the

494 urea-induced emission factor of 3.1%; however, the urea-induced emission factor of NO (i.e.,

495 3.8%) was significantly higher than the organic fertilizer induced emission factor of 2.9%. In total,

496 the substitution of conventional urea by organic fertilizer in tea plantations significantly increased

497 N_2O+NO emissions, and this stimulation effect should be taken into account in designing and

498 evaluating soil carbon sequestration strategy of organic fertilization.   Although the magnitude of

499 N_2O and NO emissions was significantly influenced by the applied fertilizer type, annual emission

500 factors of N_2O and NO induced by either urea or organic fertilizer application were all

501 substantially higher than those defaults for global upland croplands, indicating tea plantations may

502 contribute substantially to total N_2O and NO emissions from croplands in China. The results from

503 this study, however, may not necessarily indicate the feasible fertilizer management option in the

504 tea plantations, as a result of only presenting two nitrogen-trace gas species (i.e., N_2O and NO).

505 Therefore, when we finally provide a complete evaluation of nitrogen fertilizer practice in tea

506 plantations from an integrated agronomic and environmental point of view, future field

507 measurements are necessary to include the climatically and environmentally important carbon-

508 and nitrogen- trace gas fluxes (i.e., CH_4, CO_2, NO, N_2O and NH_3) as well as plant qualities and

509 yields.

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Table 1. Field management of synthetic and organic nitrogen fertilizers for tea plantations under

774   different treatments during the period of 2012-2014

	Nitrogen application rate (kg N ha^{-1})			Application date
	TNN	TUN	TOM[*]	
Basal fertilization	0	Urea (150)	Oilcake (150)	8 Oct (2012) 6 Oct (2013)
Topdressing	0	Urea (300)	Oilcake (300)	18 Feb (2013) 1 Mar (2014)
Total	0	450	450	

775   [*] The fertilizer of oilcake contained 7.1% N and had a C:N ratio of 6.1

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780 **Table 2.** Annual cumulative emissions of nitrous oxide (N_2O, in kg N ha^{-1} yr^{-1}), nitric oxide (NO,

781   in kg N ha^{-1} yr^{-1}) and N_2O plus NO (in kg N ha^{-1} yr^{-1}) as well as their respective direct emission

782   factors (EF_d, in %) for tea plantations under different fertilizer treatments during the period of

783   2012-2014

Year	Treatment[b]	N_2O[c]	EF_{d-N_2O}	NO[c]	EF_{d-NO}	N_2O+NO[c]	EF_{d-N_2O+NO}
2012-2013	TNN	6.2±0.3a		2.8±0.5a		9.0±0.4a	
	TUN	21.1±2.5b	3.3±0.5	19.4±0.3b	3.7±0.1	40.6±2.6b	7.0±0.6
	TOM	32.7±0.7c	5.9±0.2	17.0±0.4c	3.2±0.1	49.8±1.0c	9.1±0.2
2013-2014	TNN	1.9±0.1a		0.4±0.1a		2.3±0.2a	
	TUN	14.4±2.6b	2.8±0.6	18.3±0.5b	4.0±0.1	32.8±2.2b	6.8±0.5
	TOM	28.1±1.3c	5.8±0.3	12.3±1.1c	2.7±0.3	40.5±2.3c	8.5±0.5
2012-2014[a]	TNN	4.0 ± 0.1a		1.6±0.2a		5.6±0.2a	
	TUN	17.8±2.5b	3.1±0.6	18.9±0.4b	3.8±0.1	36.7±2.4b	6.9±0.5
	TOM	30.4±0.9c	5.9±0.2	14.7±0.6c	2.9±0.1	45.1±1.4c	8.8±0.3

784 Data shown are means ± standard errors of 4-spatial replicates. [a] Mean values of the two

785 investigated years. [b] TNN, no nitrogen fertilizer application; TUN, the common practice with urea

786 application rate of 450 kg N ha^{-1} yr^{-1}; and TOM, the alternative practice with organic fertilizer

787 application rate of 450 kg N ha^{-1} yr^{-1}. [c] Different letters within the same column indicate

788 significant differences among treatments in each year at $P < 0.05$ level.

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793 **Figure captions**

794 **Figure 1.** The temporal changes of (a) air and soil (5 cm) temperatures, daily precipitation and

795 irrigation, and (b) soil water content expressed as WFPS (water-filled pore space) at a depth of 0-6

796 cm for all the fertilizer treatments (i.e., the common practice with urea application (TUN), the

797 alternative practice with organic fertilizer application (TOM), and no nitrogen fertilizer application

798 (TNN)) in tea plantations during the period from September 2012 to October 2014.

799 **Figure 2.** Seasonal changes of the soil (a) ammonium (NH_4^+), (b) nitrate (NO_3^-), and (c) dissolved

800 organic carbon (DOC) concentrations (mean ± standard error) for all the fertilizer treatments ((i.e.,

801 the common practice with urea application (TUN), the alternative practice with organic fertilizer

802 application (TOM), and no nitrogen fertilizer application (TNN)) in tea plantations during the

803 period from September 2012 to October 2014. SDW is the abbreviation of soil dry weight.

804 **Figure 3.** Seasonal changes of (a) nitrous oxide (N_2O), and (b) nitric oxide (NO) fluxes (mean ±

805 standard error) for all the fertilizer treatments ((i.e., the common practice with urea application

806 (TUN), the alternative practice with organic fertilizer application (TOM), and no nitrogen fertilizer

807 application (TNN)) in tea plantations during the period from September 2012 to October 2014.

808 The downward arrows denote the time of fertilization.

809 **Figure 4.** Effect of soil water content (expressed as WFPS, water-filled pore space) on the molar

810 ratios of nitric oxide (NO) to nitrous oxide (N_2O) fluxes in the fertilized treatments (i.e., the

811 common practice with urea application (TUN), and the alternative practice with organic fertilizer

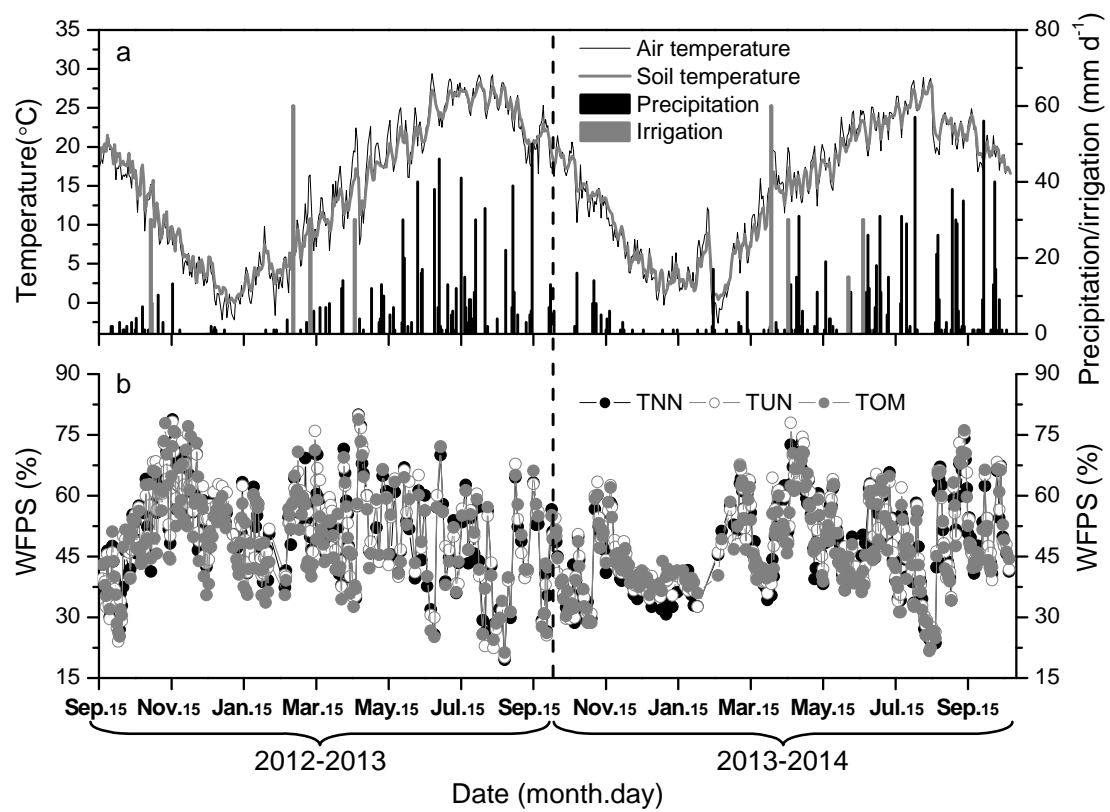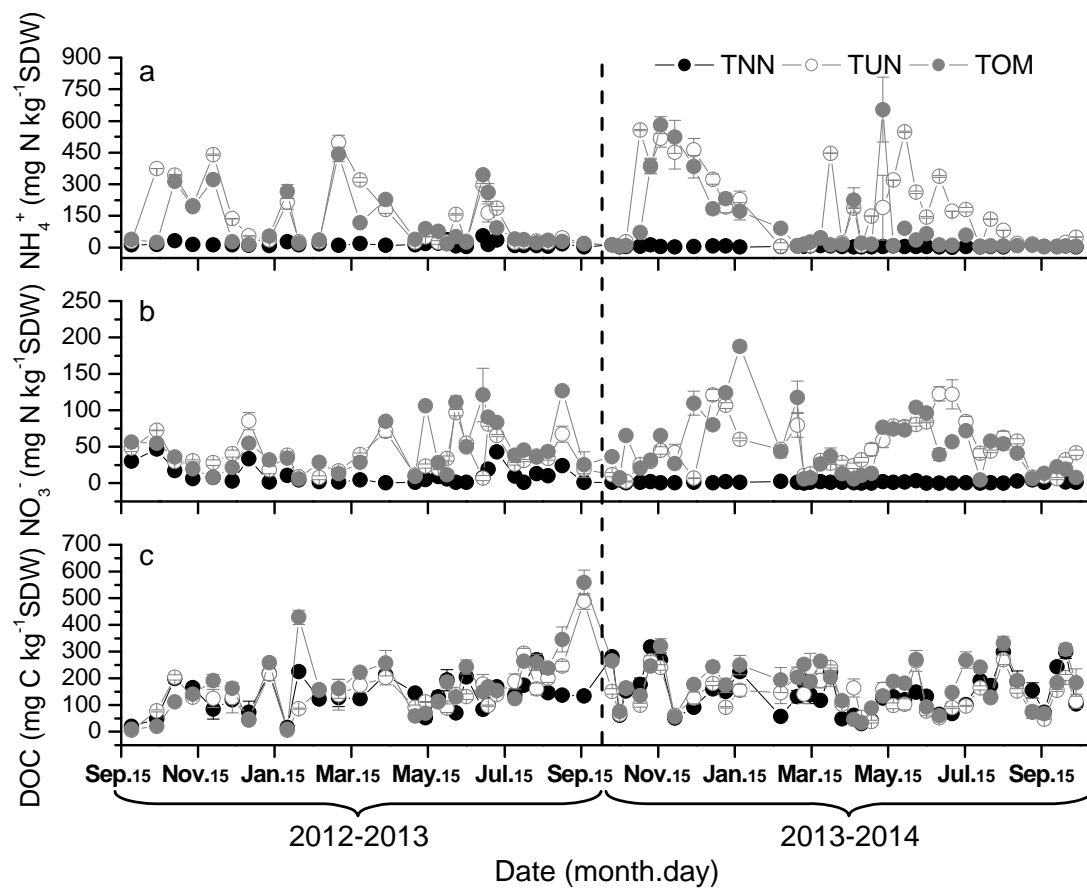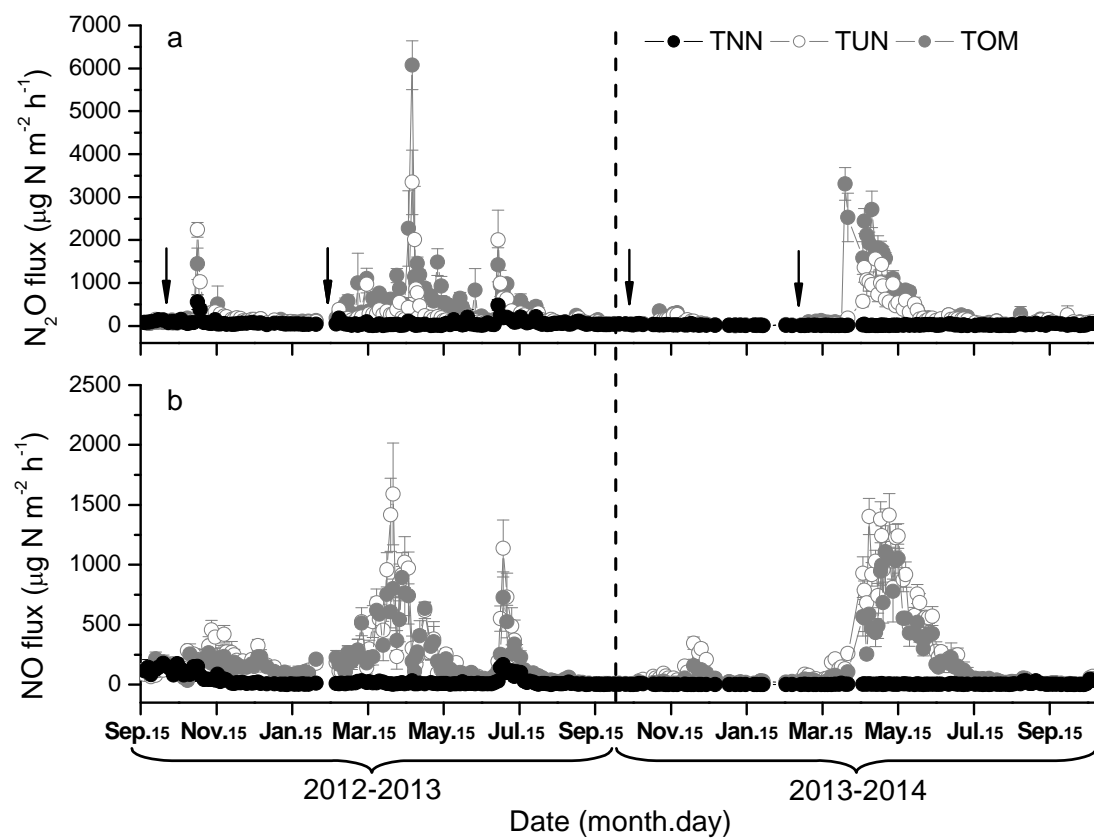812 application (TOM)) across the 2-year study period.
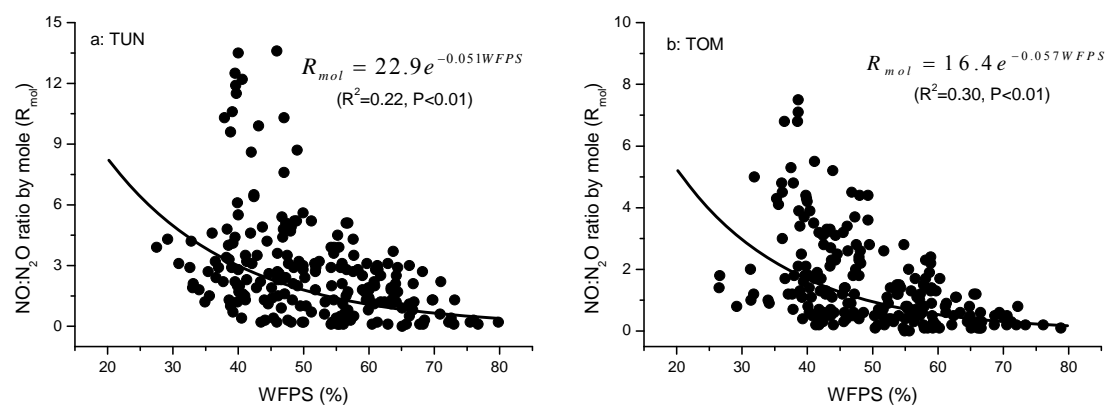
Figure 1.

Figure 2.

Figure 3.

Figure 4.

$$R_{mol} = 22.9 e^{-0.051 WFPS}$$
$$(R^2=0.22, P<0.01)$$

$$R_{mol} = 16.4 e^{-0.057 WFPS}$$
$$(R^2=0.30, P<0.01)$$

a: TUN

b: TOM