Dear Editor,

Thank you for considering the revision of our manuscript "**Phosphorus addition mitigates N_2O and CH_4 emissions in N-saturated subtropical forest, SW China**" by Yu et al., for publication in Biogeosciences.

As suggested by the reviewers, we have reanalyzed our whole dataset with linear mixed effects models using R, and documented the details of statistical approaches in the last section of M&M. The discussion of treatment effects is now based on plot means instead of subplot measurement. Consequently, the presentation of our data in the Results and Figures has been changed. Also, we have made required revisions according to reviewers' comments in the main text. More details regarding the revision (changes referred to the line numbers in the revised manuscript) can be found below. Also, the main manuscript marked with change (in red text) is supplemented in the end of this cover letter.

We thank you again for your effort and time spent on our manuscript.

Best regards,

Longfei Yu on behalf of all coauthors

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Interactive comment on "Phosphorus addition mitigates N_2O and CH_4 emissions in N-saturated subtropical forest, SW China" by Longfei Yu et al.

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Referee #1

General comments:

Yu and co-authors present an interesting dataset of nitrous oxide (N2O) and methane (CH4) flux, nitrate (NO3-) concentration and other ancillary measurements from a forest ecosystem P-addition experiment conducted in a N-saturated (N-deposition is about 40 to 65 kg ha-1 yr-1) secondary Masson pine-dominated forest at TieShanPing (TSP), Chongqing, SW China (developed after a clear cut about 50 years ago) over a period of 18 months. After a single dose of P (applied as solid NaH2PO4*2H2O at a rate of 79.5 kg P ha-1) was added, Yu and co-authors found out that both N2O and CH4 emissions and NO3- concentrations in soil water decreased following P-addition during the 18-months period. They speculate that P-addition may have stimulated mineral N uptake by P-limited plants or microbes leading to decreased NO3- concentrations and N2O emissions. Concomitantly, decreasing mineral N concentrations may have relieved N inhibition of microbial CH4 oxidation leading to decreased CH4 emissions. Spatial and temporal dynamics of nutrient imbalances and their effects on biogeochemistry in forest ecosystems are very complex and difficult to decipher but important to understand in order to predict impacts of global change processes on trace gas fluxes in forest ecosystems. The results from Yu and co-authors are very interesting and valuable. Nutrient-addition experiments in whole forest ecosystems are very difficult to conduct but their results are often much more realistic than countless laboratory experiments trying to mimic whole ecosystem conditions.

R 1.0: We thank referee #1 for the appraisal and valuable comments intended to improve the presentation of the data. We have responded below to the comments.

However, I have major concerns and recommend a reanalysis of the dataset:

1) I would suggest to reanalyze the whole dataset using linear mixed effects models (Koehler et al. 2009 and Jones et al. 2016) to account for repeated measurements (monthly measurements over 1.5 years) and for within-group variance of a stratification (block-design of the study) which has not been done so far.

R 1.1: We agree with the referee that Linear Mixed Effects Models would be better to capture within-group variances, even though the overall result may not differ substantially. In the revision, we will document the details of our statistical tests for different parameters, and present our final outcomes with reanalyzed results.

2) Please take into account that all of your replicates in your plot are pseudo-replicates because they depend on one single block (which is your true replicate). In total you have three independent samples for the P-addition plots and three independent reference samples. Consequently, the dataset and figures should be reanalyzed and presented appropriately. If the blocks are so heterogenous you may show

patterns in different blocks or outliers but your whole discussion should focus on significant results of the reanalyzed dataset based on plot means and not subplots.

R 1.2: We agree with the referee's suggestions and will change the manuscript accordingly.

3) I doubt that chronic N deposition alone has transformed TSP soils to a regional hotspot for N2O and CH4 emissions. You have not measured that. Changes in soil bulk density/soil compaction following a clear-cut about 50 years ago may be even more important. Water-filled pore space or gravimetric water content in soils are major controllers of N2O and CH4 production. These variables are almost always measured in soil trace gas flux studies and highly depend on soil bulk density which has also not been measured or is not presented in the manuscript. Since there was a clear-cut at the TSP site about 50 years ago and the soil type at this site is a Haplic Acrisol, where clay translocation processes in mineral horizons form clay-enriched horizons. Such a soil is prone to soil compaction. Especially in these clay-enriched horizons soil compaction may lead to increased bulk densities, may promote oxygen limitation and therefore increase rates of microbial denitrification and methanogenesis that eventually may lead to net CH4 and N2O emissions from this forest site. It would be great if authors could provide data about soil bulk densities, soil properties in general and soil water content variables.

R 1.3: N saturation, indicated by significant nitrate leaching from soils, has been previously confirmed at TSP, (Chen and Mulder, 2007; Huang et al., 2015; Zhu et al., 2013b). Accordingly, annual N_2O fluxes previously observed at TSP were among the highest fluxes reported in literature (Zhu et al., 2013b). Chronic N deposition does not only increase soil N availability, but also contributes to soil acidification (Huang et al., 2016), which is believed to facilitate large N_2O emission factors (N_2O flux: total N input) (Liu et al., 2014). Therefore, based on the previous findings, our study mainly addresses the P-addition effect on GHG emissions at TSP.

We also agree with the referee that edaphic factors, specific to Haplic Acrisols, play a role in the N_2O and CH_4 emissions in TSP. Though WFPS was not directly monitored throughout our observation, the range of WFPS and its effect on N_2O emissions in TSP have been well presented and studied by Zhu et al (2013b). The clear cut of the forests in the 1950s may affect the edaphic conditions in clay-rich horizon in soil, but not likely for the organic top horizon, where microbial activities such as denitrification were found to be strongest (Zhu et al., 2013a). In the revision, we will provide a better description of the soil properties for TSP referring to detailed data from previous studies (Sørbotten, 2011; Wang et al., 2007; Zhu et al., 2013b).

Minor comments:

Line 28 to 30: Nutrient imbalances in forest ecosystems and their effects on greenhouse gas emissions are very complex and shift in space and time. The present study analyzed effects of a single dose of P fertilizer on trace gas fluxes in an approximately 50-years old secondary forest over a period of 18 moths. It is simply too daring to extrapolate results from this special forest site to acid forest soils in general. Please do not speculate so much.

R 1.4: Our results have potential implications for other N-saturated subtropical forests, despite that further tests are needed. We will rephrase our conclusions and largely confine them to our site.

Line 127: change to: "In each block, plots were randomly assigned to a reference (Ref) and a P treatment."

R 1.5: Agreed

Line 164-165: How often and when did you measure trace gas fluxes? Did you take water samples (NH4+ and NO3- concentrations) at the same time? A different sampling time may explain the lack of correlation between N2O emissions and NO3- concentrations.

R 1.6: Gas flux measurements were conducted monthly in the warm season and bi-monthly in the cold seasons. Soil water samples were retrieved on the same day the gas fluxes were measured and analyzed for NO_3^- and NH_4^+. A lack of correlation between N_2O emissions and NO_3^- concentrations has been observed in other studies at TSP, e.g. by Zhu et al. (2013), who attributed this finding the non-limiting NO_3^- concentrations in the well-drained hillslope soils.

Line 251-254: Why do you use different units (μg N m-2 hr-1; kg N ha-1 yr-1) for the same variable?

We will revise the units, but stick to μg N_2O-N m^{-2} h^{-1} for instantaneous fluxes (e.g. Figs. 2 and 5) and kg N_2O-N ha^{-1} yr^{-1} for cumulative fluxes, as common in the GHG literature.

Line 282: change to atmospheric

R 1.7: ok

Line 362: Your study does not demonstrate that chronically high N deposition has transformed TSP soil to a regional hotspot for N2O and CH4 emissions. You have not measured that.

R 1.8: This has been discussed in R 1.3 and previously demonstrated by Zhu et al. (2013b).

Figures: Please provide information about sample size and if you use SD or SE in all of your figures.

R 1.9: ok

Reference: Jones et al. (2016) Biogeosciences, 13, 4151–4165 Koehler et al. (2009) Global Change Biology, 15, 2049 -2066

Referee #2

General comments The authors reported en experiment of P addition (79 kg P ha-1 yr-1, applied as NaH2PO4 powder) to an N saturated, Masson pine-dominated forest at TieShanPing (TSP), Chongqing, SW China for a period of 18 months. In the experiment, they measured soil fluxes of N2O and CH4, soil chemistry and plant growth. They found that P addition significantly decreased soil N2O emissions and turned the soil from CH4 emissions into a net sink. The experiment is appropriate. Data interpretation was logical and supported their conclusion. The study is for a type of ecosystem (subtropical, high ambient N deposition, N-saturated forest soil) for which such information is lacking. Their findings are interesting, can help us understand the interaction effect of N and P on greenhouse gas emission and also have implication for the forest management (such as P fertilization). In addition, the manuscript is also well organized and well written. I have only some minor concerns which I would like to discuss with the authors or maybe helpful for improving the manuscript, please see details below.

R 2.0: We thank referee #2 for the positive feedback. The comments are addressed point by point below.

Specific comments

1) P7, Line117. "annual N deposition at TSP measured in throughfall varies between 40-65 kg ha-1". What is the N deposition in precipitation there? Because N deposition in throughfall may be affected by difference in species, structure etc. of the forest, N deposition in precipitation is better data for comparing different forests.

R 2.1: The bulk deposition at TSP is in a range of 20 to 30 kg N ha^{-1} yr^{-1} (Chen and Mulder, 2007). We will add this to our site description.

2) P9, L165. Please give the locations (in the center of the plot?) where you measured the gas emission in the plots.

R 2.2: Chambers for flux measurements were deployed next to the lysimeters, which were randomly distributed near the center in each of the 20m * 20 m plots, at least 3 meters away from the border.

3) P9, L165-167. "to investigate the immediate effect of P addition on ..... (7, 10 and 12 May) after the P application." Did you show these results in the result or discussion section? If not, please delete it.

R 2.3: Yes, the data were shown in Fig. S6 and result section (line 228). Other studies have reported stimulation of N_2O emission by P addition, presumably due to microbial response in soil (Mori et al., 2013; Wang et al., 2014). Hence, we included the short-term data for comparison.

4) P11, Line 195 Statistical analyses. In the Experimental Design, the author showed that three blocks were established and two plots in each block in the study forest. In each block, plots were assigned randomly to a reference (Ref) and a P treatment. Did you try One-way Repeated-Measures ANOVA to exam the treatment effect for the emission of CH4 and N2O, due to measuring the gas repeatedly.

R 2.4: We have used repeated measures ANOVA to compare the fluxes of CH_4 and N_2O as well as DIN concentrations among all our plots (Ref-1, Ref-2, Ref-3, P-1, P-2 and P-3). These six plots were compared as independent groups instead of three Ref plots as a group and three plots as the other. If we use N_2O fluxes as an example, our results showed that in blocks 2 and 3, ref-2 and ref-3 were significantly larger than P-2 and P-3, respectively. Indeed, we believe and appreciate the suggestion from referee #1, that Linear Mixed Effects Models are better for interpreting treatment effects in our study. In the revision, we will reanalyze our dataset and anchor our discussion within the outcome of a Mixed Effect Model. For comparing parameters for tree-growth and soil properties (single observations only), one-way ANOVA is used (as in the original manuscript).

5) P19, L362-363. "Overall, our study demonstrates that chronically high N deposition has transformed TSP soils to a regional hotspot for N2O and CH4 emission." It is not clear for me. Could you explain it?

R 2.5: For details, please refer to R 1.3 and R1.8.

6) P25, L565-568, "Zhang et al., 2014. Responses of nitrous oxide emissions to nitrogen and phosphorus

....." has been published in Biogeosciences, please replace Biogeosciences Discuss.

R 2.6: Thanks. We will change it in the new version of manuscript.

7) P27, L585, Table 1. How did you get n=6? Did you mixed samples in each plot?

R 2.7: Before P application, we sampled the soil (for background properties) three times within each plot. Since there was no treatment yet, we combined two plots in the same block for presentation of the data.

8) P28, L591, Table 2. The yearly variation for some data is big. For example, PAL in the ref plots was 5.4 in Aug. 2013, but was 13.4 in Aug. 2015. Do you have any explanation for it?

R 2.8: Every half year, we sampled soil in triplicates from each plot randomly. Significant spatial heterogeneity is common in surface soils in 20*20 m^2 plots, as the litterfall may directly affect surface soil composition.

Referee #3

This paper report the effects of P addition on leachate chemistry and gas exchange of N2O and CH4 in a high N deposition forest of the warm and humid part of China. The results are interesting and the paper easy to read. However, the statistical treatment is not ideal, since the repeated nature of the measurements seems not to have been considered in the model tests. I see this problem is well addressed by the other reviewers. This needs to be addressed although it will not change the outcome and major conclusions.

R 3.0: We thank referee #3 for the constructive and detailed suggestions. Regarding the statistical methods, we will reanalyze the dataset with Linear Mixed Effects Model as proposed by referee #1, so as to improve and justify the interpretation of our results. Please refer to our response to referee #1 for more details on statistical analyses.

Below is my mainly minor comments listed by line number

70: 'and'= 'but'

R 3.1: Ok.

71: delete: 'even'

R 3.2: Ok.

123: spell out what means PAl here at first appearance.

R 3.3: P_{AL} means "ammonium lactate-extractable P, a common method to determine plant available P". We will modify it in the revised manuscript.

126: 5-m buffer is a bit narrow, but cannot be changed

R 3.4: The designs of plot size and buffering strip were made with reference to Zheng et al. (2016) and Martinson et al. (2013). In line 126, the "5-m buffer strip separated the two plots in each block" actually means that 5-m buffer was included for each plot, thus resulting in 10-m distance between the borders of two neighboring plots. To avoid confusion, we will modify this sentence in the new version.

127: 'ad' = 'at' 130: '.... in the TSP soil.' 141: 'Within each plot, three ceramic....'

R 3.5: We appreciate and accept the linguistic corrections from referee #3. Changes will be made in the revision.

145: 'winter' = 'dormant' or 'dormant and dry'?

R 3.6: The "winter season" mainly refers to the "dormant and dry season". We will rephrase it accordingly.

200: should be repeated ANOVA of some kind. It seems to me that the statistical analysis is not optimal.

R 3.7: Please refer to R2.4 for details.

206: check the subscript on P

R 3.8: We will check through and unify all the subscripts to "P_{AL}".

290: I am not in favor of discussing degrees of N-saturation; I would instead say 'DHSRB is less N-rich with lower inorganic N availability than TSP'

R 3.9: We agree with it in general, but we will just use "less nitrate-leaching" to describe DHSRB in comparison to TSP.

303: 'frequently' = 'shortly'

R 3.10: We assume that it refers to "frequently" in line 301 instead. We agree that "shortly" is more accurate.

306: delete 'TSP' here, implied in nearby

R 3.11: Thanks for the suggestion. We will delete "TSP".

312-318: inhibition by NH4 cannot explain emission only lower uptake rates; so delete or reformulate

R 3.12: We are aware that the inhibition by ammonium affects gross methane uptake and not directly net emissions. However, the observed mean CH_4 exchange rates (emission or uptake) at our TSP site was significantly smaller than reported in other subtropical forests from South China (Fang et al., 2009; Zhang et al., 2008) **(Figs. 5 and 6). Therefore, it is reasonable to suggest that the inhibition of methane uptake by ammonium may have contributed to reverse net methane uptake to emission during "hotspots or hot moments" (Megonigal and Guenther, 2008) of methane production.**

330: like line 290; reformulate

R 3.13: Changes will be made as presented in R3.9.

328-334: I would suggest that both reason (and others as well) may have contributed

R 3.14: As presented in the introduction section (line 91-93), "whether P addition affects the methanotrophic community in soils directly or alleviates the NH_4^+-inhibition effect on CH_4 oxidation through enhanced N uptake" remains under debate (Veraart et al., 2015). In our case, we only have evidence for reduction in nitrate availability from soil water, supporting the "indirect" mechanism.

351-353: I do not understand this; what is the 'tree biomass estimates' doing here?

R 3.15: Other studies have documented that P limitation may restrict tree growth in Masson pine forests (Wang et al., 2007). Our hypothesis was that P addition may enhance tree growth and thus N uptake. As discussed in our manuscript, the tree biomass estimates show that no such effect occurred within two years after P addition

353-356: Why not, this should be simple and not much effort?

R 3.16: From the previous long-term study conducted at TSP forest (Huang et al., 2015), we have learned that the abundance of ground vegetation species is highly variable from year to year. This makes the evaluation of ground vegetation biomass really uncertain in a two-year scale (our study). In the long-term experiment, we have planned to include the measurements of ground vegetation.

436-38: something wrong in this ref 587: add 'lactate' 589, 594+595 add these lines to the table legend

R 3.17: We thank referee #3's efforts on our manuscript. We will revise the maunscript according to the reviewer's suggestions.

Details of revision:

Line 4: "Department of Environmental Sciences" changed to "Faculty of Environmental Sciences and Natural Resource Management".

Line 17: "soil chemistry" to "soil N and P"

Line 28-30: "Our study suggests that P fertilization of N-saturated, subtropical forest soils could mitigate GHG emissions in addition to alleviate nutrient imbalances and reduce losses of nitrogen through NO_3^- leaching and N_2O emission." changed to "Our study indicates that P fertilization of N-saturated, subtropical forest soils mitigates N_2O and CH_4 emissions, in addition to alleviating nutrient imbalances and reducing losses of N through NO_3^- leaching."

Line 68-69: Add "on N_2O emissions" after "(3 to 5 years)"

Line 71: Delete "even".

Line 83: Delete "other"

Line 101-102: Delete "ambient" and delete "ii) to test whether P affects N cycling in a highly N-saturated forest and"

Line 109-110: "Having a monsoonal climate, TSP has a mean annual precipitation" to "TSP has a monsoonal climate, with mean annual precipitation"

Line 112: "The soil is a loamy yellow mountain soil" changed to "Soils are predominantly well-drained, loamy yellow mountain soil"

Line 115-117: Add "The soil bulk density of the O/A horizon (~5 cm) is about 0.75 g cm^{-3}. Soil water-filled pore space (10 cm) at TSP hilltop generally ranges from 50 to 70% (annual mean ~ 60%; Zhu et al., 2013b)."

Line 119-120: Add "while the annual bulk N deposition is from 20 to 30 kg ha^{-1} (Chen and Mulder, 2007)".

Line 122: Add "decreased" before "abundance"

Line 125: Change "P_{Al}" to "ammonium lactate-extractable P".

Line 128: Change "near a hilltop" to "well-drained soils of"

Line 129-130: Change "A 5-m buffer strip separated the two plots in each block. In each block, plots were assigned ad random to a Reference and a P treatment" to "Adjacent plots were separated by at least 10-m buffer zone. In each block, plots were randomly assigned to a Reference and a P treatment".

Line 138: "Together with the addition of phosphate, the P-treated plots also received 59.0 kg ha^{-1} of sodium (Na)."changed to "The addition of $NaH_2PO_4{\cdot}2H_2O$ at the P-treated plots also resulted in an input of 59.0 kg ha^{-1} of sodium (Na)."

Line 144: Change "triplicates of" to "three".

Line 145: Add "near plot centre" after "at 5-cm and 20-cm soils".

Line 148: Change "in the winter season" to "in the dry and dormant season".

Line 167: Delete "in micro-plots"

Line 198-213: Linear mixed effect models have been applied to analyze time-series data, to account for both repeated measurements and within-group variance of a stratification variable (block design). The fixed effect (treatment by P or not) is then tested by analysis of variance. The whole dataset has been reanalyzed with more appropriate statistical methods using R. The most important details are added to the text.

Line 216: "P_{AL}" to "P_{Al}".

Results Section: The descriptions of differences in mean NO_3^- concentrations, N_2O and CH_4 fluxes among three blocks are now removed (Line 223-224; Line 236-237; Line 246-248).

Line 232: Add "values of" before "up"

Line 259: Add "of N_2O emission rates" after "range"

Line 262: Delete "up to"

Line 266: Change "High" to "Large"

Line 277: Change "The" to ", which attributed the", delete "was attributed to"

Line 278: Change "due to" to "as a consequence of"

Line 284: Delete "(DHSBR)"

Line 292: Change "DHSBR" to "Dinghushan"; same applied to **Line 299 and 301**

Line 293: "which is not strongly different from that" to "which is similar to the N deposition at our site"

Line 292-295: "By contrast, the DHSBR site in South China receives 36 kg of atomospheric N ha^{-1} yr^{-1}, which is only slightly smaller than the N deposition at our site (Huang et al., 2015), and showed larger N_2O emission rate than the Ecuadorian site (~ 0.88 kg N ha^{-1} yr^{-1} in the reference plot; Zheng et al., 2016)." changed to "By contrast, the Dinghushan site in South China receives 28 kg N ha^{-1} yr^{-1} through wet inorganic N deposition (Zheng et al., 2016), which is similar to the

N deposition at our site (Chen and Mulder, 2007b; Huang et al., 2015). They also observed larger N_2O emission rates (~ 0.88 kg N ha^{-1} yr^{-1} in the Reference plots) than in the Ecuadorian site."

Line 301: Change "less N-saturated" to "less N-rich".

Line 312: Change "frequently" to "shortly".

Line 317: "TSP" deleted.

Line 320: Change "for South Chinese forest soils" to "for well-drained, forest soils in South Chinese forest"

Line 321-325: Change "As CH_4 fluxes at our sites were not significantly correlated with climatic factors (Fig. S4c and d), CH_4 emissions cannot be explained by (transient) wet conditions." to "Since aerated upland soils typically provide favourable conditions for microbial CH_4 uptake (Le Mer and Roger, 2010), the net emission observed in our sites is unlikely due to enhanced production, but rather by supressed consumption."

Line 329: Change "our" to "the TSP"

Line 341: Add "soil water loss due to"

Line 341-342: Change "the high degree of N saturation" to "the strong N enrichment".

Line 343: Change "the" to "direct"

Line 344: Change "the methane monooxygenase enzyme (Veldkamp et al., 2013), rather than a direct P-stimulation" to "methane monooxygenase (Veldkamp et al., 2013), rather than to P-stimulation"

Line 352: "the toxicity threshold" to "toxicity"

Line 352-354: Change "The frequent precipitation in the humid forest of this study (Yu et al., 2016), both prior and following the addition of $NaH_2PO_4.2H_2O$ (Fig. 2), efficiently diluted and leached Na^+, thus minimizing toxic effects." to "Frequent precipitation at TSP (Yu et al., 2016), both prior and following the addition of $NaH_2PO_4.2H_2O$ (Fig. 2), apparently diluted and leached Na^+, thus preventing toxic effects."

Line 357-358: Add "which represent a major decline in mobile anions in the P-treated soils"

Line 363-364: Add "increase in tree growth, due to"

L**ine 375-376:** "our study demonstrates that chronically high N deposition has transformed TSP soils to a regional hotspot for N_2O and CH_4 emission" changed to "our study suggests that N-saturated TSP soils act as a regional hotspot for N_2O and CH_4 emissions".

Line 605: Add “lactate”.

Figs. 1, 4, 6, S3 and S6: More appropriate statistics have been used to compare the data for the Reference and P treatments. Data used in the box whisker plots are now derived from the averages of subplot triplicates.

Added references

Chen, X. Y. and Mulder, J.: Atmospheric deposition of nitrogen at five subtropical forested sites in South China., Sci. Total Environ., 378(3), 317–30, doi:10.1016/j.scitotenv.2007.02.028, 2007.

Koehler, B., Corre, M. D., Veldkamp, E., Wullaert, H. and Wright, S. J.: Immediate and long-term nitrogen oxide emissions from tropical forest soils exposed to elevated nitrogen input, Glob. Chang. Biol., 15(8), 2049–2066, doi:10.1111/j.1365-2486.2008.01826.x, 2009.

R Core Team: A language and environment for statistical computing. R Foundation for statistical computing, 2015; Vienna, Austria, 2016.

Main Manuscript marked with change_ bg-2016-470

Phosphorus addition mitigates N_2O and CH_4 emissions in N-saturated subtropical forest, SW China

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Article type: Research Article

Abstract

Chronically elevated nitrogen (N) deposition has led to severe nutrient imbalance in forest soils. Particularly in tropical and subtropical forest ecosystems, increasing N loading has aggravated phosphorus (P) limitation of biomass production, and has resulted in elevated emissions of nitrous oxide (N_2O) and reduced uptake of methane (CH_4), both of which are important greenhouse gases. Yet, the interactions of N and P and their effects on GHG emissions remain understudied. Here, we report N_2O and CH_4 emissions together with soil N and P data for a period of 18 months following P addition (79 kg P ha^{-1} yr^{-1}, applied as NaH_2PO_4 powder) to an N-saturated, Masson pine-dominated forest at TieShanPing (TSP), Chongqing, SW China. We observed a significant decline both in NO_3^- concentrations in soil water (at 5- and 20-cm depths) and in N_2O emissions, the latter by 3 kg N ha^{-1} yr^{-1}. We hypothesize that enhanced N uptake by plants and soil microbes in response to P addition, results in less available NO_3^- for denitrification. By contrast to most other forest ecosystems, TSP is a net source of CH_4. As for N_2O, P addition significantly decreased CH_4 emissions, turning the soil into a net sink. Based on our observation and previous studies in South America and China, we believe that P addition relieves N-inhibition of CH_4 oxidation. Within the 1.5 years after P addition, no significant increase of forest growth was observed at TSP, but we cannot exclude that understory vegetation increased. Our study indicates that P fertilization of N-saturated, subtropical forest soils mitigates N_2O and CH_4 emissions, in addition to alleviating nutrient imbalances and reducing losses of N through NO_3^- leaching.

Key Word: N_2O and CH_4 emission, N saturation, Phosphate fertilization, soil CH_4 uptake, acid forest soil.

1 Introduction

Anthropogenic activities have transformed the terrestrial biosphere into a net source of CH_4, N_2O and CO_2, leading to increased radiative forcing (Montzka et al., 2011; Tian et al., 2016). During the last decade, atmospheric concentrations of CO_2, CH_4, N_2O have increased at rates of 1.9 ppm yr^{-1}, 4.8 and 0.8 ppb yr^{-1}, respectively (Hartmann et al., 2013). In China, the exponential increase of reactive nitrogen (N) input into the biosphere since the 1970s has likely led to more carbon (C) being sequestered in the biosphere (Cui et al., 2013; Shi et al., 2015). However, enhanced emissions of N_2O and CH_4 due to chronic N pollution potentially offset the cooling effect by C sequestration (Liu and Greaver, 2009; Tian et al., 2011).

Microbial nitrification and denitrification in soils account for about 60% of N_2O emissions globally (Ciais et al., 2013; Hu et al., 2015). Although, microbial activity is often restricted in low pH soils of unproductive forests, surprisingly large N_2O emissions have been reported from acid, upland forest soils in South China (Zhu et al., 2013b). Reported average N_2O fluxes in humid, subtropical forests range from 2.0 to 5.4 kg ha^{-1} yr^{-1} (Fang et al., 2009; Tang et al., 2006; Zhu et al., 2013b), which by far exceeds global averages for temperate or tropical forest ecosystems (Werner et al., 2007; Zhuang et al., 2012). This has been attributed to frequently shifting aeration conditions during monsoonal summers, promoting both nitrification and denitrification (Zhu et al., 2013b) and to large soil NO_3^- concentrations due to efficient cycling of deposited N in acid subtropical soils (Yu et al., 2016).

Chronically elevated rates of N deposition (30-65 kg ha^{-1} yr^{-1}; Xu et al., 2015) have resulted in strong nutrient imbalances in southern Chinese forests, aggravating phosphorus (P) limitation (Du et al., 2016). Phosphorous deficiency in N-saturated forests restricts forest growth and thus

constrains its capability to retain N (Huang et al., 2015; Li et al., 2016), resulting in ample amounts of mineral N (NH_4^+ and NO_3^-) being present in the soil solution. Accordingly, Hall & Matson (1999) observed larger N_2O emission in P-limited than in N-limited tropical forests after one year of repeated N addition. Likewise, previous N manipulation studies in forests of South China reported pronounced stimulation of N_2O emissions by N addition (Chen et al., 2016; Wang et al., 2014; Zheng et al., 2016), supporting the idea that P limitation causes forests to be more susceptible to N saturation and N_2O-N loss. In an N-limited tropical montane forest in southern Ecuador, P addition alone (10 kg P ha^{-1} yr^{-1}) had no effect on N_2O emissions during the first two years. However, N_2O emission was smaller when P was added together with N (50 kg N ha^{-1} yr^{-1}) than in treatments with N addition alone (Martinson et al., 2013). After continued fertilization for three years, also P addition alone reduced N_2O emissions at these sites (Müller et al., 2015). In tropical China, with high N deposition (~ 36 kg ha^{-1} yr^{-1}; Mo et al., 2008), P addition (150 kg P ha^{-1} yr^{-1}) to an old-growth forest revealed a similar pattern, with no initial effect on N_2O emissions (0-2 years) but a significant longer term effect (3 to 5 years) on N_2O emissions (Chen et al., 2016; Zheng et al., 2016). In a secondary tropical forests in South China, Wang et al. (2014) found no effect on N_2O emissions of P alone (100 kg P ha^{-1} yr^{-1}), and in treatments combining P with N (100 kg N ha^{-1} yr^{-1}), N_2O emissions ~~even~~ increased during the wet season. Meanwhile, they observed a significant increase in soil microbial biomass after P addition, which is in line with previous findings in tropical forest soils of South China (Liu et al., 2012). Thus, they attributed the stimulating effect of P addition on N_2O emissions to the larger nitrification and denitrification potential of the increased soil microbial biomass. This was also proposed by Mori et al. (2014), based on results from a short-term incubation study with P addition, excluding plant roots.

79 As the sole biogenic sink for CH_4, upland soils play an important role in balancing terrestrial
80 CH_4 emissions (Ciais et al., 2013; Dutaur and Verchot, 2007). Atmospheric CH_4 uptake in soil is
81 mediated by the activity of methanotrophic bacteria, which oxidize CH_4 to CO_2 to gain energy
82 for growth. Well-drained forest and grassland soils are dominated by yet uncultured, high-
83 affinity methanotrophs residing in the upper soil layers (Le Mer and Roger, 2010). In addition to
84 edaphic factors (pH and nutrients), ~~other~~ parameters affecting the diffusion of CH_4 into the soil
85 (soil structure, moisture, temperature) are believed to be the major controllers for CH_4 uptake
86 (Smith et al., 2003). A number of studies have shown that excess N affects CH_4 fluxes in forest
87 soils (Liu and Greaver, 2009; Veldkamp et al., 2013; Zhang et al., 2008b). In general, N addition
88 promotes CH_4 uptake in N-limited soils by enhancing growth and activity of methanotrophs,
89 whereas excessive N input and N saturation inhibit CH_4 oxidation on an enzymatic level
90 (Aronson and Helliker, 2010; Bodelier and Laanbroek, 2004). P addition experiments in N-
91 enriched soils have shown positive effects on CH_4 uptake (Mori et al., 2013a; Zhang et al., 2011),
92 but the underlying mechanisms, i.e. whether P addition affects the methanotrophic community in
93 soils directly or alleviates the N-inhibition effect on CH_4 oxidation through enhanced N uptake
94 (Mori et al., 2013b; Veraart et al., 2015), remain unresolved.

95 Subtropical forests in South China show strong signs of N saturation, with exceedingly high
96 NO_3^- concentrations in soil water (Larssen et al., 2011; Zhu et al., 2013b). Little is known about
97 how P addition affects N cycling and N_2O emission in these acidic, nutrient-poor soils. Likewise,
98 the importance of increased mineral N concentrations for soil-atmosphere exchange of CH_4, and
99 how this is affected by P fertilization remain to be elucidated for soils of the subtropics. Here, we
100 assessed N_2O and CH_4 fluxes in an N-saturated subtropical forest in SW China under ambient N
101 deposition and studied the effects of P addition on emission rates, nutrient availability and tree

growth. The objectives were i) to quantify ~~ambient~~ N_2O and CH_4 emissions, ii) ~~to test whether P affects N cycling in a highly N saturated forest and iii)~~ to investigate the effect of P addition on N_2O and CH_4 emission.

105 # 2 Materials and Methods

106 ## 2.1 Site description

107 The study site "TieShanPing" (TSP) is a 16.2 ha subtropical forest (29° 380 N, 106° 410 E; 450
108 m a.s.l.), about 25 km northeast of Chongqing, SW China. TSP is a naturally regenerated,
109 secondary mixed coniferous-broadleaf forest, which developed after clear cutting in 1962
110 (Larssen et al., 2011). The forest stand is dominated by Masson pine (*Pinus massoniana*) and has
111 a density of about 800 stems ha^{-1} (Huang et al., 2015). TSP has a monsoonal climate, with mean
112 annual precipitation of 1028 mm, and a mean annual temperature of 18.2 ^{o}C (Chen and Mulder,
113 2007a). Most of the precipitation (> 70%) occurs during summer periods (April to September).
114 Soils are predominantly well-drained, loamy yellow mountain soil, classified as Haplic Acrisol
115 (WRB 2014), with a thin O horizon (< 2 cm). In the O/A horizon, soil pH is around 3.7, and the
116 mean C/N and N/P ratios are 17 and 16, respectively. In the AB horizon, which has a slightly
117 higher pH, mean C/N is well above 20. The soil bulk density of the O/A horizon (~ 5 cm) is
118 about 0.75 g cm^{-3}. Soil water-filled pore space (10 cm) at TSP hilltop generally ranges from 50
119 to 70% (mean ~ 60%; Zhu et al., 2013b). More details on soil properties are given in Table 1.

120 Annual N deposition at TSP measured in throughfall varies between 40 and 65 kg ha^{-1}
121 (dominated by NH_4^+; Yu et al., 2016), while the annual bulk N deposition is from 20 to 30 kg ha^{-1}
122 (Chen and Mulder, 2007b). According to regional data, annual P deposition via throughfall is <
123 0.40 kg ha^{-1} (Du et al., 2016). Strong soil acidification at TSP has resulted in severe decline in
124 forest growth (Li et al., 2014; Wang et al., 2007), and in decreased abundance and diversity of
125 ground vegetation (Huang et al., 2015). Pronounced N saturation with strong NO_3^- leaching from
126 the top soil has aggravated P deficiency (Huang et al., 2015). The total P content in the O/A

127 horizon is ~ 300 mg kg^{-1}, while ammonium lactate-extractable P is smaller than 5 mg kg^{-1} (Table
128 1).

129 **2.2 Experimental Design**

130 Three blocks, each having two 20 m * 20 m plots, were established on well drained soils of a
131 gently sloping hillside. Adjacent plots were separated by at least 10-m buffer zone. In each block,
132 plots were randomly assigned to a Reference and a P treatment. On 4 May 2014, a single dose of
133 P fertilizer was applied as solid $NaH_2PO_4 \cdot 2H_2O$, at a rate of 79.5 kg P ha^{-1}. The amount of P
134 added was estimated from P adsorption isotherms (Supplementary Materials, Table S1 and
135 Figure S1), to ensure significantly increase in soil available P. To apply P fertilizer evenly, we
136 divided each plot into a 5 m * 5 m grid and broadcasted the powdered fertilizer by hand in each
137 grid cell. The P dose applied at TSP was intermediate as compared to the 10 kg P ha^{-1} yr^{-1}
138 applied by Müller et al. (2015) to a mountain forest in Ecuador and the 150 kg P ha^{-1} yr^{-1} applied
139 by Zheng et al. (2016) to a subtropical forest in South China.

140 The addition of $NaH_2PO_4 \cdot 2H_2O$ at the P-treated plots also resulted in an input of 59.0 kg ha^{-1} of
141 sodium (Na). One month after the fertilizer application, Na^+ concentrations in soil water of the P
142 treatments were about 5 mg L^{-1} at 5-cm depth and 3 mg L^{-1} at 20-cm depth (Table S2). Although
143 somewhat larger than in the reference plots, the Na^+ concentration in soil water of the P
144 treatments are unlikely to have exerted a strong negative impact on plant and microbial activities.

145 **2.3 Sample collection and analyses**

146 Within each plot, three ceramic lysimeters (P80; Staatliche Porzellanmanufaktur, Berlin) were
147 installed at 5- and 20-cm soils near the plot centre in August 2013. To obtain water samples,

350-ml glass bottles with rubber stoppers were pre-evacuated, using a paddle pump, and connected to the lysimeters for overnight sampling. Between November 2013 and October 2015, we sampled soil pore water bi-monthly in the dry and dormant season and monthly during the growing season. All water samples were kept frozen during storage and transport. Concentrations of NH_4^+, NO_3^-, potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) in soil water were measured at the Research Center for Eco-Environmental Sciences (RCEES), Chinese Academy of Sciences, Beijing, using ion chromatography (DX-120 for cations and DX-500 for anions).

In August 2013, soils from the O/A (0-3 cm), AB (3-8 cm) and B (8-20 cm) horizons were sampled near the lysimeters for soil analysis. Total P and plant-available P contents were monitored in samples collected from the O/A horizons every six months, starting two days before P addition. Soil samples were kept cold (< 4 ^oC) during transport and storage. Before analysis, soil samples were air dried and sieved (2 mm). Soil pH was measured in soil suspensions (10 g dry soil and 50 ml deionized water) using a pH meter (PHB-4, Leici, China). Total soil C and N contents were determined on dried and milled samples, using a LECO elemental analyzer (TruSpec$^@$CHN, USA). To measure total P, 1 g dry soil was digested with 5 ml of 6 M H_2SO_4 (Singh et al., 2005) and measured as ortho-phosphate by the molybdenum blue method (Murphy and Riley, 1962). Ammonium lactate (0.01 M)-extractable P and H_2O-extractable P (P_{Al} and P_{H2O}, respectively) were measured as ortho-phosphate after extraction (1.5 g dry soil in 50 ml solution) (Singh et al., 2005). Ammonium oxalate (0.2 M)-extractable Fe, Al and P were measured by inductive coupled plasma (7500; Agilent) after extraction (1.5 g dry soil in 50 ml solution).

From August 2013 onwards, we measured N_2O and CH_4 emissions in triplicate ~~in micro-plots~~ close to the lysimeters, using static chambers (Zhu et al., 2013b). To investigate the immediate

171 effect of P addition on N_2O emissions, we sampled the gas emissions once before (2 May) and
172 three times (7, 10 and 12 May) after the P application. Gas samples (20 ml) were taken 1, 5, 15
173 and 30 minutes after chamber deployment and injected into pre-evacuated glass vials (12 ml)
174 crimp-sealed with butyl septa (Chromacol, UK), maintaining overpressure to avoid
175 contamination during sample transport. Mixing ratios of N_2O and CH_4 were analyzed using a gas
176 chromatograph (Model 7890A, Agilent, US) at RCEES, equipped with an ECD for detection of
177 N_2O (at 375 ^oC with 25 ml min^{-1} Ar/CH_4 as make up gas), a FID for CH_4 (250 ^oC; 20 ml min^{-1}
178 N_2 as make-up gas) and a TCD for CO_2. Exchange rates between soil and atmosphere
179 (emission/uptake) were calculated from measured concentration change in the chambers over
180 time, applying linear or polynomial fits to the concentration data. Cumulative N_2O emissions
181 over time were estimated by linear interpolation between measurement dates (Zhu et al., 2013b).

182 From October 2013 onwards, litterfall was collected during the first week of every month in five
183 replicates per plot. Litterfall collectors were made of 1 m^2 nylon nets (1 mm mesh size), held in
184 place by four wooden poles 0.8 m above the ground. Fresh litter was dried at 65^oC. In early
185 November 2013 and 2014 (at the end of the growing season), we collected current-year pine
186 needles from several branches of three trees in each plot. The collected needles were dried at
187 65 ^oC and the dry weight of 500 needles was determined. A subsample was dried at 80 ^oC and
188 finely milled prior to chemical analysis at the Chinese Academy of Forestry. Total C and N were
189 measured using an elemental analyzer (FLASH 2000; Thermo Scientific; USA). The contents of
190 K, Ca, Mg and P in the needles were determined by ICP-AES (IRIS Intrepid II; Thermo
191 Scientific; USA) after digesting 0.25 g dry weight samples with 5 ml of ultra-pure nitric acid. In
192 November 2013, and 2014, and in February of 2015, we measured the height and the diameter at
193 breast height (DBH) of 6 to 10 Masson pines (only those with DBH > 5 cm) at each plot. These

194 data were used to estimate the standing biomass of Masson pines based on standard allometric
195 equations (Li et al., 2011; Zeng et al., 2008).

196 Daily average air temperature and sum of precipitation were monitored by a weather station
197 (WeatherHawk 232, USA) placed on the roof at the local forest bureau, in about 1 km distance
198 from the sampling site (Yu et al., 2016).

199 **2.4 Statistical analyses**

200 Statistical analyses were performed using R version 3.3.1 (R Core Team, 2016). All data were
201 tested for normality (Kolmogorov-Smirnov's test) and homoscedasticity (Levene's test) before
202 further analysis. If not normally distributed, the data were normalized by logarithmic
203 transformation. Considering heterogeneity among blocks, temporal variabilities of NO_3^-
204 concentrations, N_2O and CH_4 fluxes were presented separately for each block. For time series
205 data, we used linear mixed-effect (LME) models, to account for both repeated measurements and
206 within-group variance of a stratification variable (block design). LME models were applied to
207 test the effects of P addition on soil N_2O and CH_4 fluxes, NH_4^+, NO_3^-, K^+, Ca^{2+} and Mg^{2+}
208 concentrations in soil water, as well as litterfall (Koehler et al., 2009; Müller et al., 2015). The
209 analysis was based on data for plot means (the average of 3 subplot replicates) from three blocks.
210 In LME models, treatments (Reference or P addition) were considered fixed effects, while
211 sampling time and plots were treated as random effects. We then assessed the significance of
212 fixed effects through analysis of variance for LME models. One-way analysis of variance
213 (ANOVA, Turkey post-hoc test) was conducted to examine the treatment effects on soil pH,
214 nutrient contents in organic matter, and data of tree growth. Significance levels were set to $p <$
215 0.05, if not specified otherwise.

3 Results

3.1 Nutrient concentrations in soil and soil water

Addition of P resulted in a significant increase in soil P content in the O/A horizon, both as P_{Al} and total P (Table 2). However, after 15 months, only P_{Al} indicated an enhanced P status, while total soil P did not differ significantly from background values at the reference sites. P addition had no significant effect on soil pH, or soil C and N content. The NO_3^- concentration in soil water collected at 5 cm depth varied seasonally, with significantly greater values (30-40 mg N L^{-1}) towards the start of the growing season in 2015 (April, Fig. S2), but not in 2014, likely due to dilution by abundant precipitation in February to March 2014. Addition of P resulted in significantly smaller NO_3^- concentrations in soil water at both 5- and 20-cm depths (Fig. 1b). In general, the concentration of NH_4^+ in soil water was small (< 0.5 mg L^{-1}) and not affected by P addition (Fig. 1a). At both depths, mean soil water concentrations of Mg^{2+} and Ca^{2+} were significantly smaller in the P-treated than the reference plots, and the sum of charge of dissolved base cations declined significantly in response to P addition (Fig. S3).

3.2 N_2O and CH_4 fluxes: effects of P addition

During the experimental period, N_2O fluxes varied seasonally (Fig. 2), showing a significant relationship with daily precipitation (Fig. S4a), but not with daily mean temperature (Fig. S4b). In the Reference plots, mean N_2O fluxes were generally below 50 μg N m^{-2} hr^{-1} in the dry, cool season, but reached values of up to 600 μg N m^{-2} hr^{-1} in the growing season (Fig. 2). Cumulative N_2O emissions were estimated with seasonally averaged fluxes, and they differed greatly among the three blocks (Fig. 3). The greatest annual N_2O emission was observed in the Reference plot (7.9 kg N ha^{-1}) of block 2. Mean N_2O fluxes during the 1.5 years after P addition were

238 significantly smaller in the P treatment than in the Reference (Fig. 4). The P addition resulted in
239 a decrease in cumulative N_2O emission by about 3 kg N ha^{-1} yr^{-1} on average, which is a 50%
240 reduction (Fig. 3). No immediate effects (within days) of P addition on N_2O emission was
241 observed (Fig. S5).

242 CH_4 fluxes varied greatly between blocks (Fig. 5). Net-emission of CH_4 was observed in summer
243 2013 (~ 80 μg C m^{-2} hr^{-1}) in blocks 1 and 2, whereas block 3 showed CH_4 uptake. From spring
244 2014 until October 2015, CH_4 fluxes were less variable in all blocks, with values fluctuating
245 around zero. A longer period of net-emission was observed in block 3 during the dry season
246 2014. The fluxes did not correlate with either precipitation or air temperature (Fig. S5c&d). In
247 the 1.5 years following P addition, mean CH_4 fluxes indicated net CH_4 emission (~ +3.8 μg C m^{-2}
248 hr^{-1}) in the Reference, whereas net CH_4 uptake (~ -6.5 μg C m^{-2} hr^{-1}) was observed in the P
249 treatment (Fig. 6). The suppressing effect of P addition on CH_4 emission was in accordance with
250 what was found for NO_3^- concentration and N_2O emission.

251 **3.3 The effect of P addition on tree growth**

252 Throughout the 2-year experimental period, we observed no change in tree biomass (138 t ha^{-1})
253 in response to P addition (Table S3). Likewise, there was no effect of P treatment on the 500-
254 needle weight (13 g on average). Between the two samplings in 2013 and 2014, we found
255 differences in chemical composition of the pine needles, but this effect was not linked to P
256 addition. Also, the C/N and N/P ratios of the needles (40 and 16, respectively) were hardly
257 affected by P addition. Monthly litterfall varied seasonally in both Reference and P treatment
258 (Fig. S6), but no significant difference was found between the two treatments.

4 Discussion

Background N_2O emission rates in the Reference plots were relatively large (Fig. 2), with mean values close to 100 μg N m^{-2} hr^{-1} (Fig. 4). This is within the range of N_2O emission rates previously reported for well-drained hillslope soils at TSP (Zhu et al., 2013b), but greater than the rates reported for other forests in South China. For instance, N_2O emission rates averaged to 37 μg N m^{-2} hr^{-1} in unmanaged sites at Dinghushan (Fang et al., 2009; Tang et al., 2006) and up to 50 μg N m^{-2} hr^{-1} in N-fertilized sites (Zhang et al., 2008a). TSP Reference plots emitted on average 5.3 kg N ha^{-1} yr^{-1} (Fig. 3), which is about 10% of the annual N deposition (50 kg ha^{-1} yr^{-1}) (Huang et al., 2015). These fluxes are well above average fluxes reported for tropical rainforests (Werner et al., 2007). Large N_2O emissions at TSP are likely due to the ~~high~~ large N deposition rates (Huang et al., 2015), as suggested by the similar trends indicated by data from a wide range of ecosystems (Liu et al., 2009). Also, warm-humid conditions during monsoonal summers may stimulate N_2O emissions (Ju et al., 2011), as monsoonal rainstorms triggered peak fluxes (Pan et al., 2003). The positive correlation between precipitation and N_2O emission peaks (Fig. S4a) may indicate the importance of denitrification as the dominant N_2O source. This is supported by recent ^{15}N tracing experiments at TSP (Zhu et al., 2013a).

Addition of P caused a significant decline in soil mineral N (predominantly NO_3^-; Fig. 2), particularly during summers, when NO_3^- concentrations were relatively high (Fig. S2). At the same time, annual N_2O emissions decreased by more than 50% (Figs. 3 and 4). These findings are consistent with a number of previous studies (Baral et al., 2014; Hall and Matson, 1999; Mori et al., 2014), which attributed the reduction of N_2O emissions in P-treated soils decreased mineral N content, most likely ~~due to~~ as a consequence of stimulated plant uptake and/or

281 microbial assimilation. It is noteworthy that there was no significant correlation between N_2O
282 emission rates and soil water NO_3^- concentration in our study (Figs. 2 and S2), suggesting that
283 the suppressing effect of P on N_2O emissions was indirect, probably by affecting the competition
284 for mineral N between plant roots and microbes (Zhu et al., 2016). In contrast to our 1.5-year
285 study, P-addition experiments in South Ecuador (Martinson et al., 2013) and South China (at
286 Dinghushan Biosphere Reserve ~~(DHSBR)~~ (Zheng et al., 2016) found no effect of a single P
287 addition on N_2O emission during the first two years after application. However, significant
288 reduction in N_2O emission was observed after three to five years with continuous P addition,
289 both at the Ecuadorian and the Chinese site (Chen et al., 2016; Müller et al., 2015). For the
290 montane forest site in Ecuador, the observed delay in N_2O emission response to P addition may
291 be explained by the moderate amount of P added (10 kg P ha^{-1} yr^{-1}; Martinson et al., 2013).
292 Moreover, the experiments were conducted in a forest with low ambient N deposition (~ 10 kg N
293 ha^{-1} yr^{-1}) and N_2O fluxes (~ 0.36 kg N ha^{-1} yr^{-1} in the Reference plots) (Martinson et al., 2013;
294 Müller et al., 2015). By contrast, the ~~(DHSBR)~~ Dinghushan site in South China receives 28 kg N
295 ha^{-1} yr^{-1} through wet inorganic N deposition (Zheng et al., 2016), which is ~~not strongly different~~
296 ~~from that~~ similar to the N deposition at our site (Chen and Mulder, 2007b; Huang et al., 2015).
297 They also observed larger N_2O emission rates (~ 0.88 kg N ha^{-1} yr^{-1} in the Reference plots) than
298 in the Ecuadorian site. However, forests do not always display a straightforward relationship
299 between N deposition and N_2O emissions. Manipulation experiments in the European NITREX
300 project, for instance, revealed a much stronger correlation of N_2O emissions with soil NO_3^-
301 leaching than with N deposition (Gundersen et al., 2012). Indeed, KCl-extractable mineral N at
302 the ~~(DHSBR)~~ Dinghushan site (~ 40 mg kg^{-1}; Zheng et al., 2016) is several-fold smaller than at
303 our site (> 100 mg kg^{-1}; Zhu et al., 2013b), indicating that ~~(DHSBR)~~ Dinghushan is less ~~N-~~

~~saturated~~ N-rich than TSP. This suggests that the response of N_2O emission to P addition might depend on the N status of the soil. The fact that numerous studies found apparent suppression of N_2O emission in short-term experiments (< 2 years) in N + P treatments, but not in treatments with P alone, supports this idea (Müller et al., 2015; Zhang et al., 2014b; Zheng et al., 2016).

Other studies have observed increased N_2O emissions upon P addition (Mori et al., 2013c; Wang et al., 2014). In an *Acacia mangium* plantation, fertilized with P, Mori et al. (2013b&c) found that N_2O emissions were stimulated in the short-term but reduced in the long-term. While suppression of N_2O emission by P has been attributed to increased plant N uptake (Mori et al., 2014), increased N_2O emission are generally explained by enhanced microbial biomass (Liu et al., 2012) and denitrification activity (Ehlers et al., 2010; He and Dijkstra, 2015). N_2O emissions measured ~~frequently~~ shortly after P addition at our site in May 2014 were not different from fluxes in untreated reference plots (Fig. S5). This may indicate that plant uptake at TSP is more important for the effect of P addition on N_2O emissions than changes in microbial activity, which are expected to occur more rapidly.

The Reference plots at TSP showed net CH_4 emission for extended periods of the year (Figs. 5 and 6). Also, long-term CH_4 fluxes sampled between 2012 and 2014 on ~~TSP~~ hillslopes near-by (Fig. S7; Zhu et al., unpublished data) showed net CH_4 emission. This is in contrast to the generally reported CH_4 sink function of forested upland soils (Ciais et al., 2013; Dutaur and Verchot, 2007). For example, CH_4 uptake rates reported for well-drained, forest soils in South Chinese forest range from 30 to 60 μg C m^{-2} hr^{-1} (Fang et al., 2009; Tang et al., 2006; Zhang et al., 2014a). Since aerated upland soils typically provide favourable conditions for microbial CH_4 uptake (Le Mer and Roger, 2010), the net emission observed in our sites is unlikely due to enhanced production, but rather by supressed consumption. One reason for the net CH_4 emission

327 at TSP could be inhibition of CH_4 oxidation by NH_4^+, as reported previously (Bodelier and
328 Laanbroek, 2004; Zhang et al., 2014a). The concentration of NH_4^+ in the soil water was rather
329 small (< 0.5 g $L^{-1;}$ Fig. 1), which does not preclude, however, that NH_4^+ availability from the soil
330 exchangeable pool is high. Zhu et al. (2013b) found extraordinarily high KCL-extractable NH_4^+
331 in TSP surface soils, likely reflecting the large atmogenic NH_4^+ input at ~~our~~ the TSP site (Huang
332 et al., 2015).

333 P addition had a significant impact on CH_4 fluxes, changing the soil from a net source to a net
334 sink on an annual basis (Fig. 6). However, the uptake rates of CH_4 in the P treatments remained
335 smaller than those reported for forest soils in tropical China (Tang et al., 2006; Zhang et al.,
336 2008b). The stimulating effect of P addition on CH_4 uptake is consistent with previous studies
337 (Mori et al., 2013a, 2013b; Zhang et al., 2011), and has been attributed to lessening the NH_4^+
338 inhibition of methane oxidation. Unfortunately, we did not measure KCl-extractable NH_4^+ in our
339 study, but a decline of available NH_4^+, which is the substrate for nitrification, is likely as NO_3^-
340 concentrations in soil water were significantly smaller with in the P-treatments (Fig. 1). P
341 addition may also result in a change of the taxonomic composition of the methane oxidizing
342 community (Mori et al., 2013a; Veraart et al., 2015). Alternatively, CH_4 oxidation may be
343 stimulated by increased CH_4 diffusion into the soil, due to enhanced root growth and increased
344 soil water loss due to transpiration in P-amended plots (Zhang et al., 2011). Given the ~~high~~
345 ~~degree of N saturation~~ strong N enrichment of TSP forest (Huang et al., 2015), it is likely that the
346 reason for the observed reduction in CH_4 emissions in response to P fertilization is due to
347 alleviating ~~the~~ direct NH_4^+ inhibition of methane monooxygenase (Veldkamp et al., 2013), rather
348 than to P-stimulation of methanotrophic activity (Veraart et al., 2015).

Shortly after fertilizer application, we observed a modest, albeit significant increase of Na^+ concentration in soil water (Table S2). Other studies have documented the potential toxicity of excess Na^+ in soil water to plant and microbial activities (Rengasamy et al., 2003; Wong et al., 2008). However, the occurrence of Na^+ toxicity at the treated plots, affecting N turnover processes, is unlikely, as Na^+ concentrations in soil water, within one month after application (Table S2), did not exceed 5 mg L^{-1}, far smaller than the values commonly assumed to indicate toxicity (40 to 100 mg L^{-1}) (Bernstein 1975). Frequent precipitation at TSP (Yu et al., 2016), both prior and following the addition of $NaH_2PO_4.2H_2O$ (Fig. 2), apparently diluted and leached Na^+, thus preventing toxic effects.

P application significantly increased plant-available P in the P-limited TSP soil (Table 2). Meanwhile, concentrations of leachable base cations (K^+, Mg^{2+}, Ca^{2+}) in soil water decreased (Fig. S3), as expected from the reduction of NO_3^- concentrations in the P-treatments, which represent a major decline in mobile anions in the P-treated soils (Mochoge and Beese, 1986). We observed no sign of stimulated forest growth or increased N uptake by plants within the relatively short period of our study (Table S3 and Fig. S6), making it difficult to link the observed reduction in mineral N in the soil solution (Fig. 1) to plant growth. When interpreting the observed P effect on NO_3^- concentrations in soil water, several aspects need to be considered. Firstly, two years of observation may be too short to detect any significant increase in tree growth, due to NO_3^- uptake by plants, given the commonly large variabilities in tree biomass estimates (Alvarez-Clare et al., 2013; Huang et al., 2015). Secondly, a significant proportion of the added P, and of excess N, may have been assimilated by the understory biomass, which was not assessed in this study. Previously, understory vegetation has been reported to quickly respond to P addition (Fraterrigo et al., 2011). Thirdly, as long-term N saturation and

372 acidification at TSP have reduced forest health (Lu et al., 2010; Wang et al., 2007), we may not
373 expect immediate response of forest growth to P addition. Large needle N/P ratios (17-22, Table
374 S3) indicated that P limitation for tree growth was not relieved 1.5 years after P addition (Li et al.,
375 2016). Therefore, enhanced N uptake by understory growth and/or soil microbial biomass may
376 have been the main mechanisms responsible for observed NO_3^- decline in the P-treated soil (Hall
377 & Matson 1999).

378 Overall, our study suggests that N-saturated TSP soils act as a regional hotspot for N_2O and CH_4
379 emissions. Within the short experimental period of 1.5 years, P fertilization was shown to
380 significantly decrease NO_3^- concentrations in soil water and to reduce both N_2O and CH_4
381 emissions. These findings provide a promising starting point for improving forest management
382 towards GHG abatement targets, taking into account the P and N status of subtropical soils in the
383 region.

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606

607 **Table 1** Background soil properties of the experimental plots at Tieshanping (TSP). Values are
608 means and standard deviations in parenthesis (n = 6). Soils were sampled in August 2013.

	Soil Layer	pH	Total C g kg^{-1}	Total N g kg^{-1}	Total P mg kg^{-1}	C/N	N/P
Block 1	O/A (0-3 cm)	3.7 (0.1)	80.7 (32.3)	4.8 (1.7)	308 (57)	17.0 (2.5)	15.5 (5.7)
	AB (3-8 cm)	3.8 (0.0)	23.9 (9.3)	1.3 (0.6)	-*	20.0 (3.0)	-
	B (8-20 cm)	3.9 (0.2)	8.6 (1.2)	< 0.05	-	-	-
Block 2	O/A (0-3 cm)	3.6 (0.1)	77.6 (13.4)	4.7 (0.8)	297 (44)	16.7 (1.3)	15.7 (2.8)
	AB (3-8 cm)	3.7 (0.1)	20.2 (5.3)	1.0 (0.3)	-	21.4 (3.3)	-
	B (8-20 cm)	3.9 (0.1)	7.1 (1.6)	< 0.05	-	-	-
Block 3	O/A (0-3 cm)	3.6 (0.1)	67.0 (15.5)	3.8 (0.8)	223 (45)	17.4 (0.6)	17.2 (3.7)
	AB (3-8 cm)	3.6 (0.1)	21.0 (7.9)	1.1 (0.5)	-	24.5 (4.6)	-
	B (8-20 cm)	3.8 (0.1)	7.2 (1.5)	< 0.05	-	-	-

	Soil Layer	P_{H2O} mg kg^{-1}	P_{Al} mg kg^{-1}	Al_{ox} mg kg^{-1}	Fe_{ox} mg kg^{-1}	P_{ox} mg kg^{-1}	P_{ox} / (Al_{ox} + Fe_{ox})
Block 1	O/A (0-3 cm)	< 5.0	5.8 (1.4)	1700 (513)	1933 (350)	85.8 (22.6)	0.025 (0.008)
	AB (3-8 cm)	< 5.0	2.1 (0.6)	1217 (243)	1692 (493)	47.1 (22.0)	0.016 (0.007)
	B (8-20 cm)	< 5.0	< 1.0	1083 (90)	1158 (249)	29.3 (28.6)	0.012 (0.011)
Block 2	O/A (0-3 cm)	< 5.0	5.9 (1.0)	1500 (238)	1792 (215)	79.2 (21.5)	0.024 (0.007)
	AB (3-8 cm)	< 5.0	1.6 (0.4)	925 (149)	1517 (320)	37.2 (10.7)	0.016 (0.006)
	B (8-20 cm)	< 5.0	< 1.0	892 (209)	1033 (413)	16.1 (10.5)	0.009 (0.007)
Block 3	O/A (0-3 cm)	< 5.0	4.1 (0.9)	1367 (180)	1667 (168)	50.7 (10.9)	0.017 (0.003)
	AB (3-8 cm)	< 5.0	4.4 (4.0)	1075 (128)	1350 (150)	24.8 (8.3)	0.010 (0.002)
	B (8-20 cm)	< 5.0	< 1.0	992 (130)	875 (138)	8.0 (2.0)	0.004 (0.001)

609 P_{H2O} = Water-extractable P, P_{Al} = Ammonium lactate-extractable P,

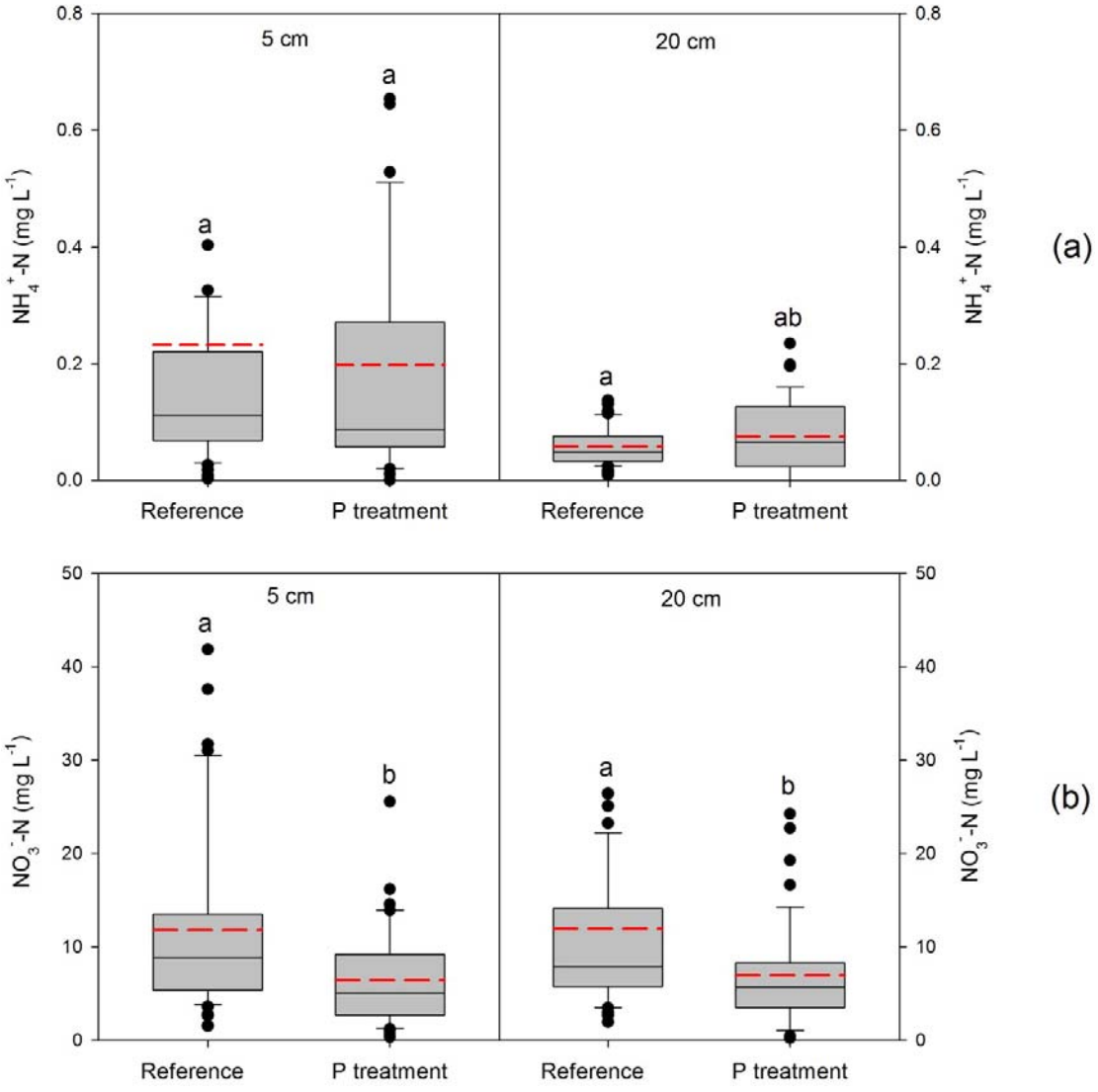
610 Al_{ox} = Oxalate extractable Al, Fe_{ox} = Oxalate extractable Fe, P_{ox} = Oxalate extractable P.

611 * Data not available

612 **Table 2** Soil pH, C, N and P contents in the O/A horizon (0-3 cm) in the References (Ref) and P
613 treatments. Values are means and standard deviations in parenthesis (n = 9). P addition was
614 conducted on 14/05/04, after the first two sampling dates.

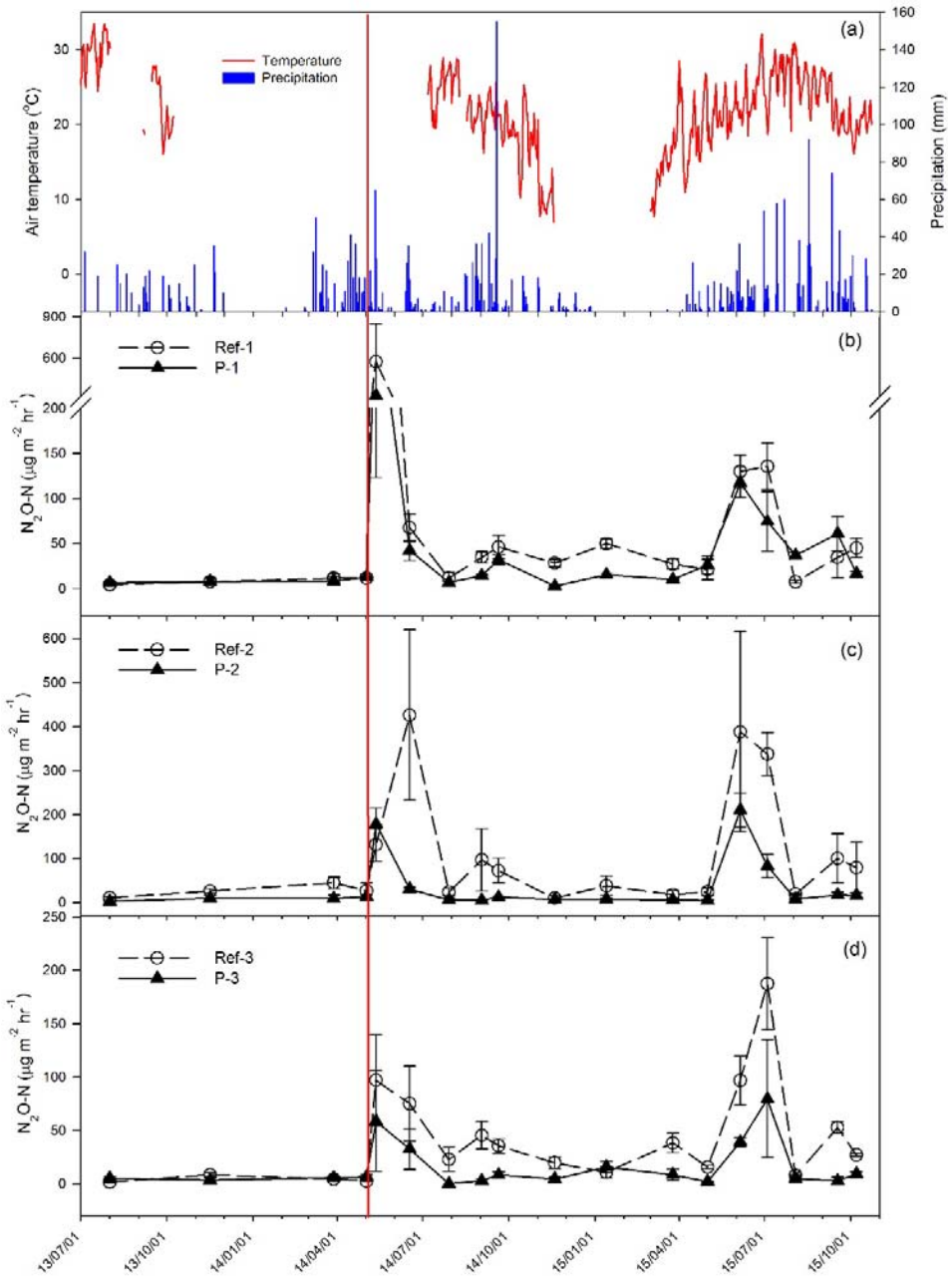
		pH	Total C	Total N	C/N	P_{Al}	Total P
			g kg^{-1}	g kg^{-1}		mg kg^{-1}	mg kg^{-1}
13/08/02	Ref	3.7 (0.1)^{bc†}	8.3 (2.3)^{ab}	0.5 (0.1)^{bcd}	16.9 (1.1)^{bcd}	5.4 (1.4)^{c}	292 (46)^{bc}
	P	3.6 (0.1)^{c}	6.7 (2.0)^{b}	0.4 (0.1)^{bd}	17.1 (2.1)^{bc}	5.1 (1.3)^{c}	260 (70)^{c}
14/05/02	Ref	3.7 (0.1)^{abc}	12.2 (4.2)^{a}	0.9 (0.3)^{a}	13.7 (1.5)^{e}	19.0 (8.0)^{c}	336 (65)^{bc}
	P	3.8 (0.2)^{abc}	9.0 (3.5)^{ab}	0.7 (0.2)^{abc}	14.2 (2.8)^{de}	13.7 (5.2)^{c}	270 (72)^{bc}
14/05/10	Ref	3.8 (0.1)^{abc}	9.9 (2.1)^{ab}	0.7 (0.2)^{ab}	14.0 (0.7)^{e}	15.4 (7.0)^{c}	304 (49)^{bc}
	P	3.9 (0.3)^{ab}	8.0 (1.9)^{ab}	0.6 (0.1)^{bcd}	14.3 (1.3)^{cde}	174 (114)^{a}	572 (242)^{a}
14/12/02	Ref	3.8 (0.1)^{abc}	10.5 (3.6)^{ab}	0.7 (0.3)^{ab}	14.5 (1.3)^{cde}	14.2 (7.4)^{c}	328 (102)^{bc}
	P	3.9 (0.2)^{abc}	9.5 (2.1)^{ab}	0.7 (0.1)^{abc}	14.0 (0.8)^{e}	66 (24)^{ab}	442 (106)^{ab}
15/08/02	Ref	3.9 (0.2)^{ab}	8.3 (2.2)^{ab}	0.4 (0.1)^{cd}	20.5 (2.5)^{a}	13.4 (6.2)^{c}	291 (61)^{bc}
	P	4.0 (0.2)^{a}	6.5 (1.9)^{b}	0.3 (0.1)^{d}	19.7 (2.2)^{ab}	57 (36)^{ab}	383 (136)^{bc}

615 † Different letters indicate significant differences ($p < 0.05$).



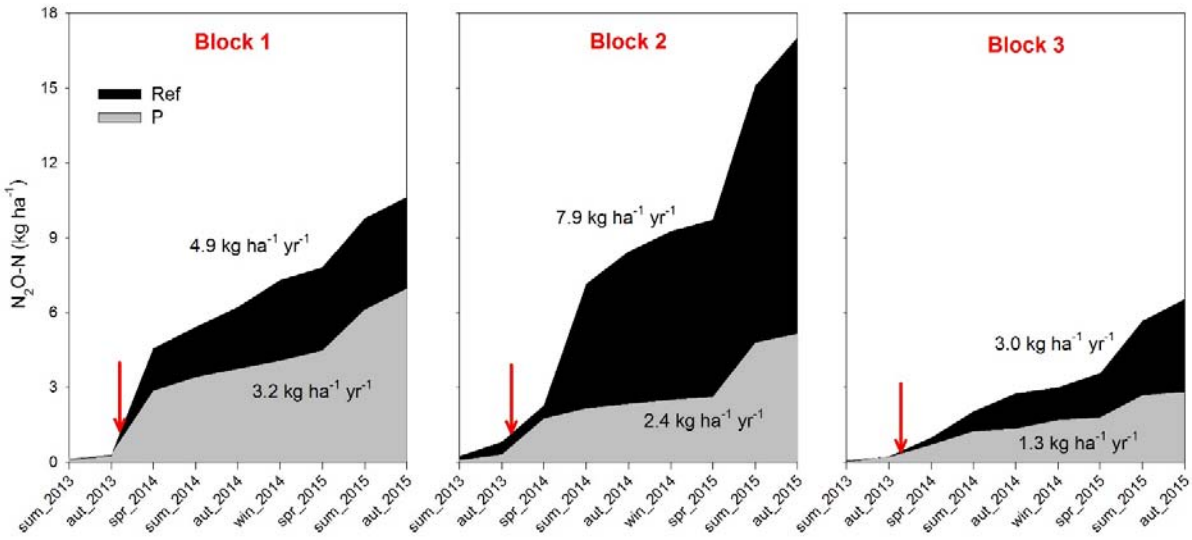
616

617 **Fig. 1** Box whisker plots of NH_4^+ (a) and NO_3^- (b) concentration in soil water at 5- and 20-cm
618 depths in the References and P treatments, throughout 1.5 years after the P addition; red dashed
619 lines indicate mean values; different letters indicate significant differences ($p < 0.05$).



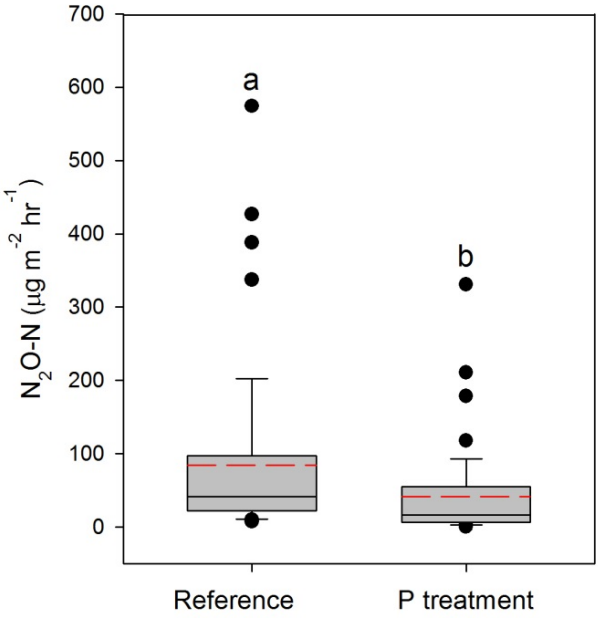
620

621 **Fig. 2** Daily mean air temperature and precipitation (a), and monthly mean N_2O fluxes (±SE) in
622 the References (Ref) and P treatments in each of the three blocks (b-d); the red vertical line gives
623 the date of P addition (4 May, 2014).



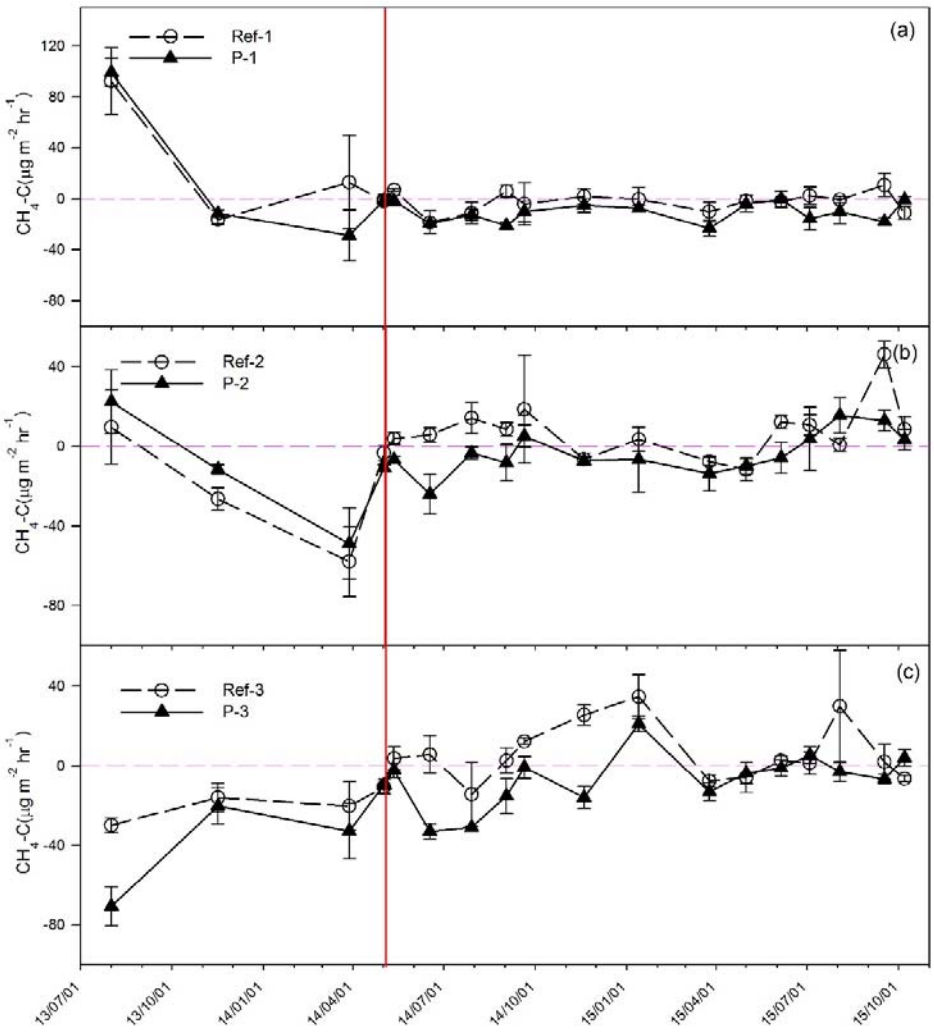
624

625 **Fig. 3** Cumulative N_2O emissions for three blocks in the References (Ref) and P treatments from
626 summer 2013 to autumn 2015; the red arrows refer to the date of P addition (4 May, 2014).



627

628 **Fig. 4** Box whisker plots for N_2O fluxes in the Reference and P treatment throughout 1.5 years
629 after the P addition; red dashed lines indicate mean values; different letters indicate significant
630 difference ($p < 0.05$).



631

632 **Fig. 5** Monthly mean CH_4 fluxes (±SE) in the References (Ref) and P treatments for three blocks
633 (a-c); the horizontal broken line indicates zero flux the red vertical line refers to the date of P
634 addition.

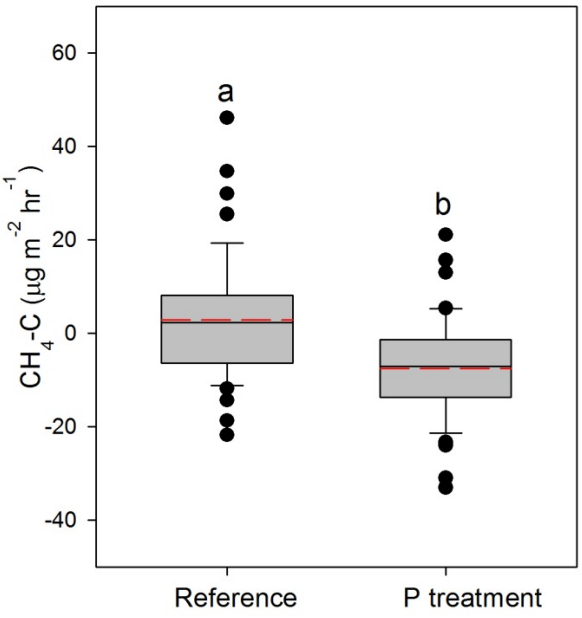


Fig. 6 Box whisker plots of CH_4 fluxes in the Reference and P treatment throughout 1.5 years after the P addition; red dash lines indicate mean values; the different letters indicate significant difference ($p < 0.05$).