1 ***Detailed regional predictions of N_2O and NO emissions from a tropical highland***
2 ***rainforest***

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1 Abstract

Tropical forest soils are a significant source for the greenhouse gas N_2O as well as for NO, a precursor of tropospheric ozone. However, current estimates are uncertain due to the limited number of field measurements. Furthermore, there is considerable spatial and temporal variability of N_2O and NO emissions due to the variation of environmental conditions such as soil properties, vegetation characteristics and meteorology. In this study we used a process-based model (ForestDNDC-tropica) to estimate N_2O and NO emissions from tropical highland forest (Nyungwe) soils in southwestern Rwanda. To extend the model inputs to regional scale, ForestDNDC-tropica was linked to an exceptionally large legacy soil dataset. There was agreement between N_2O and NO measurements and the model predictions though the ForestDNDC-tropica resulted in considerable lower emissions for few sites. Low similarity was specifically found for acidic soil with high clay content and reduced metals, indicating that chemo-denitrification processes on acidic soils might be under-represented in the current ForestDNDC-tropica model. The results showed that soil bulk density and pH are the most influential factors driving spatial variations in soil N_2O and NO emissions for tropical forest soils. The area investigated (1113 km^2) was estimated to emit ca. 439 ± 50 t N_2O-N yr^{-1} (2.8-5.5 kg N_2O-N ha^{-1} yr^{-1}) and 244 ± 16 t NO-N yr^{-1} (0.8-5.1 kg N ha^{-1} yr^{-1}). Consistent with less detailed studies, we confirm that tropical highland rainforest soils are a major source of atmospheric N_2O and NO.

2   Introduction

Soils are both a source and a sink of gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). All these gases are potent greenhouse gases (GHG). In particular, N_2O is 298 times as potent as CO_2 and ranks third after CO_2 and CH_4 as a global warming agent (Meehl et al., 2007). In addition, NO emitted from soils acts as a precursor of tropospheric ozone, which contributes to the greenhouse effect as well (Delmas et al., 1997).

The concentrations of the atmospheric GHGs have accelerated during the past century, indicating an urgent need for process-based understanding of the factors influencing the exchange of these gases between the soil and atmosphere at a range of scales, as a route to developing effective mitigation strategies. Natural sources of atmospheric N_2O and NO are significant in the respective global budgets and include oceans and tropical forest soils. The importance of tropical forests as sink and source of carbon GHGs is relatively well known, but N_2O and NO fluxes from tropical forest soils are far less well characterized. On its own, tropical forest soils are identified as a major natural source for atmospheric N_2O (Matson et al., 1990; Bouwman et al., 1993; Mosier et al., 1998; Breuer et al., 2000; Kiese et al., 2002, 2003; Butterbach-Bahl et al., 2004; Werner et al., 2007b) and are responsible for an approximately 1.3 ± 0.3 Tg nitrogen (N) yr^{-1} (Werner et al., 2007a). Similarly, based on the few existing data, NO from tropical forest soils represent a significant source with estimates ranging from 1.1 to 3.0 Tg N yr^{-1} within the global atmospheric budget (Davidson and Kingerlee, 1997; Gut et al., 2002; Butterbach-Bahl et al., 2004). Further simulation results, using an N isotope coupled mechanistic biogeochemical model, showed that total gaseous losses, including N_2, from tropical rain forest soils in Hawaii contributed for ~26–48% of total N losses (Bai and Houlton, 2009).

Production of N_2O and NO in tropical forest soils is closely linked to the microbial processes of nitrification when ammonia is oxidized to nitrate in the presence of oxygen, and denitrification when nitrate used as an electron acceptor instead of oxygen, as well as chemical process of chemo-denitrification when nitrite react with metallic cations such as Fe (II) (e.g. Davidson et al., 2000; Serca et al., 1994; Butterbach-Bahl et al., 2004).

89   To characterize a scale N dynamics biogeochemical models, such as the DeNitrification-
90   DeComposition based models PnET-DNDC (Li et al., 2000; Stange et al., 2000; Butterbach-Bahl
91   et al., 2001), ForestDNDC-tropica (Werner at al., 2007a) and LandscapeDNDC (Haas et al.,
92   2012), simulate soil climate, litter decomposition and plant growth, in order to determine soil C
93   and N turnover and predict the soil-atmosphere exchange of GHGs. Irrespective of extensive
94   research on microbial nitrification and denitrification and their contribution to N_2O and NO
95   fluxes (e.g. Matson and Vitousek, 1990; Davidson et al., 2000; Butterbach-Bahl et al., 2004;
96   Lisboa et al., 2011; Rowlings et al., 2011) the magnitude of gaseous nitrogen (N) emissions for
97   global sources are still highly uncertain at all scales.

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99   Amongst others a high spatio-temporal variability in environmental factors is a reason for the
100 high uncertainty of current regional and global estimates of GHG emissions from soils, in
101 general (Kesik et al., 2005; Werner at al., 2007a). Moreover, for most regions little information
102 exists on the spatial heterogeneity and/or average values of physicochemical soil properties,
103 driving biogeochemical models. Currently, global estimations of N_2O emissions for tropical
104 forest rely mostly on the International Soil Reference and Information Center (ISRIC-WISE,
105 with focus on tropical and subtropical regions), which does not distinguish between agriculture
106 and natural land cover.

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108 The estimation of N_2O emission from tropical forest in such a global study is based on soil
109 properties, like OC, which are predominantly collected for agriculture soils that can be an
110 obvious source of bias. Furthermore, global studies do not explicitly differentiate highland from
111 lowland tropical forests, which strongly affects climate and soil properties. Given the uncertainty
112 associated with current estimations of N_2O and NO emissions from global tropical forests, which
113 rely on relatively few soil inventories from tropical forests, no reliable spatial explicit predictions
114 for N-trace gases are available for the tropical forests.
115 Given the importance of N-trace gases in the GHG balance of tropical forests there is an urgent
116 need to quantify the impact of the regional distribution of soil properties and vegetation
117 characteristics on the model estimates of these gases. To do so, emphasis should be put on using
118 regionally available legacy soil data to predict spatial N-trace gas emissions.

119 Legacy soil data is data collected during historical soil surveys e.g. for the purpose of soil
120 mapping are generally collected without any statistical criteria. Such legacy soil data can,
121 however, be valuable for biogeochemical models as it is the best and the only available data.
122 This also links to the wider discussion about uncertainty in biogeochemical models (Werner et
123 al. 2007a), which have recently highlighted the potential effort for improving spatial information
124 on soil and vegetation data from tropical forests.

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126 In this study we incorporate historical soil data to predict regional N_2O and NO emissions from
127 the mountainous tropical rainforest in Nyungwe national park, Rwanda, using the ForestDNDC-
128 tropica biogeochemical model (Werner et al., 2007a). Using these predictions we aim to answer
129 key questions such as: 1) what is the N_2O and NO source strength of a mountainous tropical
130 forest soil? 2) to what extend do these values differ from current estimates? 3) and how sensitive
131 is the ForestDNDC-tropica model to changes in driving (historical) input variables.

132 3 Material and methods

133 3.1 Site description

134 Nyungwe forest in southwestern Rwanda (2°17´S - 2°49´S / 29°03´E – 29°29´E, 1485-2950 m
135 asl, Fig. 1a) is one of the largest and best-preserved mountainous rainforests in Africa. The forest
136 occupies an area of about 100,000 ha dividing the Nile and the Congo river catchments. Overall
137 temperatures vary between 8 and 29 degrees and yearly rainfall ranges from 1308 to 2071 mm
138 yr^{-1}, with the rainy season lasting from September until May. The forest contains various
139 ecosystems ranging from dense forest, bamboo groves to marshes, and contains approximately
140 1105 plant species, as well as high biodiversity of fauna. (Graham et al., 1995; Masozera and
141 Alavalapati, 2004; Plumptre et al., 2007) The vegetation is characterized by *Entandrophragma*
142 *excelsum, Parinari excelsa, Prunus Africana and Octotea usambarensis* (Van Ranst et al., 1997).

143 3.2 Model description

144 Model description DeNitrification-DeComposition (DNDC) models (Li et al., 1992) have been
145 developed for simulating ecosystem C and N-cycling and associated emission of trace gases. In
146 particular, the ForestDNDC-tropica model includes sub-models that simulate soil climate, litter
147 decomposition, plant growth and biogeochemical processes contributing to trace gases emissions

148　in order to determine soil C and N turnover and predict the soil-atmosphere exchange of GHG

149　from tropical forest soil.

150　In the soil climate sub-model, daily climate data is used to calculate soil temperature, moisture

151　and oxygen profiles. This is done by considering soil properties (texture), and plant and

152　microbial turnover processes of C and N. Forest growth is calculated depending on temperature,

153　water and nitrogen availability. Litter production, water and nitrogen demand of plants and root

154　respiration is linked with the soil and the decomposition sub-model. N-trace gas production,

155　consumption and emission are calculated within the sub-models nitrification and denitrification.

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157　In general, these simulations are carried out by considering soil properties such as texture, OC

158　and N content, mineral soil pH and bulk density (BD), vegetation parameters (aboveground

159　biomass, wood mass, leaf mass and floor mass) and climate data (daily precipitation, minimum

160　and maximum temperature). A detailed description of the above mentioned input parameters is

161　given in subsequent sections. In the present study, no modifications of the model were performed

162　and the model set-up remained unchanged as compared to the Werner et al. (2007a) study. A

163　more detailed description for the ForestDNDC-tropica model is given in Werner et al. (2007a).

164　***3.3　Model input data***

165　3.3.1　Soil data

166　We used the soil profile database of Rwanda produced based on a national soil surveys (1981 -

167　1993). The soil database gives a full description of ~2000 soil profiles covering the Rwandan

168　territory (Imerzoukene and Van Ranst, 2002; Verdoodt and Van Ranst, 2006a; Verdoodt and

169　Van Ranst, 2006b). Topsoil (0-30 cm) data of sand, silt, clay, gravel, organic carbon (OC), total

170　nitrogen (TN), mineral soil pH, and litter layer pH for our study area was extracted from the

171　database. We selected 147 soil profiles located within the Nyungwe forest. Summary statistics

172　for all selected soil properties are shown in Table 1. Missing values for TN (30% of the selected

173　profiles) were estimated by regression equation which was based on a statistical analysis of the

174　complete datasets: TN = 0.0994×OC 0.7178 (R^2=0.74, p<0.05). Since soil bulk density values

175　are largely missing in the original survey, bulk density was derived using specific pedo-transfer

176　functions (PTF) for tropical highland forest soils (Gharahi Ghehi et al., 2012b).

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178   3.3.2 Weather data

179   No long-term meteorological data from the forest were available and therefore daily weather data

180   for the years 1981-1993 from the nearest three climatological weather stations at an altitude of

181   ~2000 m and an average distance to the forest of < 5 km were used (Minagri and CTB/BTS,

182   1993a, 1993b). In addition to past thirteen years climate data, we used more recent years (2007-

183   2008) data measured at the Uwinka climate station (2°28´43.3´´S, 29°12´00´´E, 2465m asl)

184   located within the Nyungwe forest which has been established on 2007. The climatological data

185   used, consisted of daily precipitation and daily minimum and maximum temperatures.

186   Daily weather data were spatially interpolated for the forest using the Thiessen polygon approach

187   in GIS (geographic information system) (ESRI ArcMap 9.3 software). The mean annual

188   temperature and precipitation (1981-1993) for the climate polygons were 16.8 °C and 1458 mm,

189   respectively. For the northern region of the Nyungwe forest, decreased amounts in annual

190   precipitation and higher values of mean annual temperature have been observed. The average

191   annual mean temperature and precipitation (2007-2008) at Uwinka climate station is 14.5 °C and

192   1824.7 mm, respectively. The rainfall during the recent years was slightly higher than the

193   average rainfall observed in most of the years during the period 1981-1993. In the rainy seasons

194   of the years 2007-2008, monthly rainfall was approximately more than 150 mm and higher than

195   during the years 1981-1993 (Fig. 2).

196   3.3.3 Vegetation data

197   We used the Lund-Potsdam-Jena General Ecosystem Simulator (LPJ-GUESS (Smith et al.,

198   2001)) to derive a regional distribution of aboveground biomass estimates for Nyungwe forest.

199   The LPJ-GUESS is an object-oriented, modular framework for modeling the dynamics of

200   ecosystem structure and functioning at scales from plot to global scales, and at varying levels of

201   process detail. The LPJ-GUESS model simulates vegetation dynamics and structure based on

202   the tropical evergreen plant function type (PFT), which represent individual physiological,

203   morphological and bioclimatic (Smith et al., 2001; Sitch et al., 2003). Taking time series of

204   climate data (as mentioned above) and, given constraints of latitude, topography, and Nyungwe

205   soil characteristics (as mentioned above), as input, the LPJ-GUESS model dynamically

206   computed spatially explicit transient vegetation composition in terms of plant functional types,

207   and their associated carbon and water budgets. Aboveground biomass (wood, leaf and floor

208 mass) was extracted from the output of the LPJ-GUESS model and used as input drivers for

209 ForestDNDC-tropica. The fine root mass was estimated as $0.7\times$ leaf mass (Kiese et al., 2005;

210 Werner et al., 2007a). The spatial distribution of the simulated aboveground biomass is shown in

211 Fig. 1b. The simulated aboveground biomass for the Nyungwe forest (ranging from 74 to 400 t C

212 ha^{-1}) were in similar magnitude to those reported by Werner et al. (2007a) (100-225 t C ha^{-1} for

213 tropical rainforest soils for eastern Africa). Furthermore, our simulated aboveground biomass up

214 to 400 t C ha^{-1} were of similar magnitude as the reported aboveground biomass of ~500 t C ha^{-1}

215 for the northern part of the Nyungwe forest (Nsabimana, 2009).

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217 *3.4   Model runs*

218 In order to predict N_2O and NO emission from Nyungwe forest, soil, climate and vegetation data

219 were integrated into a GIS database covering Nyungwe forest, with a spatial resolution of 0.025°

220 $\times$ 0.025°. Many tropical forests are faced with a lack of soil data, thus requiring the generation of

221 parameter maps based on rather limited datasets. The Inverse Distance Weighting (IDW)

222 technique (Myers, 1993), a weighted average interpolator, was used for preparing the spatial

223 distribution of model input parameters for grid cells where no observational data were available.

224 We used a conservative linear weights function of 1 to interpolate the values. An IDW approach

225 was preferred over kriging techniques because little spatial auto-correlation was observed for the

226 selected properties. An example of the spatial distribution of the aboveground biomass and

227 selected soil characteristics is shown in Fig. 1. Since many existing soil datasets for natural

228 forested ecosystems comprise generally less than 30% of the size compared to our dataset

229 (ISRIC-WISE global soil profile data set; Nsabimana et al., 2008; Kiese et al., 2008; Werner at

230 al., 2007a), we are argue that the spatial map of model input parameters (Fig. 1) is the best

231 possible estimate of the spatial patterns of the topsoil property in tropical forested ecosystems at

232 such a scale today.

233

234 All input data was formatted in ForestDNDC-tropica compatible formats. Finally, ForestDNDC-

235 tropica was run in a daily time-step for the years 1981-1993 and 2007-2008 on this final

236 vegetation and soil dataset. The model was run 🗨a two years simulation period, using the first

237 year as spin-up period in order to allow model internal C and N pools to equilibrate. The

238   estimated N_2O emissions are converted to CO_2 equivalents for comparison with other GHG
239   emissions. We used N_2O 100-year global warming potential (GWP=310).

240   *3.5   Model validation with measured N-trace gases fluxes*

241   To validate the ForestDNDC-tropica model output, N$_2$O and NO emission data for soils of the
242   Nyungwe tropical forest by Gharahi Ghehi et al. (2012a) were used. The latter study carried out
243   a medium-term incubation experiment with soils from 31 locations within the Nyungwe forest.
244   Since the incubation data covered three water filled pore space levels (50, 70 and 90% WFPS), a
245   weighted mean WFPS average was used here for comparing soil incubation results and model
246   simulations. On the basis of the laboratory simulated WFPS we calculated a weighted mean
247   average of N_2O and NO emissions for each individual location (percent time at 40-60%, 60-80%
248   and 80-100% WFPS) using simulated WFPS values by ForestDNDC-tropica to extrapolate the
249   incubation data. The extrapolated incubation N_2O and NO data were calculated using the
250   following formula:

$$EI = \frac{\left[(X_{meas})_{50\%WFPS} \times \sum day_{mod40-60\%WFPS}\right] + \left[(X_{meas})_{70\%WFPS} \times \sum day_{mod60-80\%WFPS}\right] + \left[(X_{meas})_{70\%WFPS} \times \sum day_{mod80-100\%WFPS}\right]}{\sum day_{mod40-100\%WFPS}}$$

251

252   where EI is extrapolated incubation N_2O or NO data , x_{meas} is the laboratory measured N_2O or
253   NO value, $\sum day_{mod}$ is sum of day of year of simulated WFPS values at 40-60%, 60-80% and 80-
254   100% by ForestDNDC-tropica.

255

256   To further evaluate the model, the Friend beta sensitivity index (β) (Friend et al., 1993) was
257   computed to assess the influence of individual model parameters on model output on a regional
258   scale (e.g., Butterbach-Bahl et al., 2004). Different model parameters were varied one-at-a-time
259   over their plausible range while keeping the others at their nominal value. We used the climate
260   data of the year 1993 and calculated variation of simulated average N_2O emissions in response to
261   changes in plus-minus 1 for pH, and plus-minus 25% for BD and in plus-minus 50% for other
262   input parameters.
263   Sensitivity index is than defined as:

$$\beta = \frac{\dfrac{[N_2O]_1 - [N_2O]_0}{[N_2O]_0}}{\dfrac{P_1 - P_0}{P_0}}$$

264   where P_1 and P_0 are the individual input parameter that increased and decreased, respectively;

265   and the β index is calculated from the resulting change in N_2O emissions ($P_0 \rightarrow [N_2O]_0$ or $P_1 \rightarrow$

266    $[N_2O]_1$). The deviation of the β value from zero would imply a proportional to the sensitivity of a

267   given parameter and the sign of β indicates the direction of correlation (a negative or positive

268   correlation) (Kiese et al., 2005; Werner et al., 2007a). We reported the average β values for all

269   147 data locations in the historical data set.

3.6   Change in historical soil data

271   The soil properties have been obtained at least three decades ago and may have changed in time

272   due to logging activities; so changes of historical soil data over time can affect the overall

273   uncertainty of GHG inventories. The possibility of changes of historical soil data over time was

274   shown by selecting 29 locations out of the 147 sites in the Nyungwe forest, for which a soil

275   sampling was performed by Gharahi Ghehi et al. (2012a) during September 2009. We carried out

276   a comparative analysis of simulated values N_2O and NO using current with past input soil

277   properties to test whether changes of historical soil data would significantly affect model

278   outcome.

4   Resu

4.1   Modeled N_2O and NO emissions

281   The simulated N_2O emission for Nyungwe forest for the period 1981-1993 range from 2.8 to 5.5

282   kg N ha^{-1} yr^{-1}, with an average of 3.8 ± 0.52 kg N ha^{-1} yr^{-1}. The emission rates for the period

283   2007-2008 vary between 2.2 and 4.7 kg N_2O-N ha^{-1} yr^{-1}, with an average value of 3.7 ± 0.40

284   N_2O-N ha^{-1} yr^{-1}. The highest N_2O emissions (4-5.5 kg N ha^{-1} yr^{-1}) are simulated in regions with a

285   relatively high clay (>30%) or OC (>4%) content, namely north - northeast and south of the

286   Nyungwe forest (Fig. 3). Lower emissions are estimated for the eastern part of the forest, an area

287   with predominantly sandy soils. Total emissions from the entire Nyungwe forest are estimated at

288   373-504 t N_2O-N yr^{-1} (mean = 439 ± 50 t NO-N yr^{-1}) for the period 1981-1993 and 384 t N_2O-N

289   yr^{-1} and 489 t N_2O-N yr^{-1} for 2007 and 2008, respectively (Fig. 4).

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291   The magnitude of simulated NO emission ranges from 0.8 to 5.1 kg N ha^{-1} yr^{-1} for 1981-1993

292   periods, with an average of 2.0 ± 0.8 kg N ha^{-1} yr^{-1}. The emission rates for the period 2007-

293   2008 range from 2.5 to 5.0 kg NO-N ha^{-1} yr^{-1}, with an average value of 3.8 ± 0.4 kg NO-N ha^{-1}

294   yr^{-1}. Significantly lower NO emissions (0.8-2.0 ha^{-1} yr^{-1}) are seen in the center and towards the

295   south of the forest, regions with high soil pH (pH>4) or a relatively high OC (>4%) content (Fig.

296   3). The simulated total NO emission for 1981-1993 ranged from 207 to 255 t NO-N yr^{-1} (mean =

297   244 ± 16 t NO-N yr^{-1}) and 489 t NO-N yr^{-1} and 384 t NO-N yr^{-1} for 2007 and 2008, respectively

298   (Fig. 4). The total soil NO emission in the year 1981-1993 was lower than in 2007-2008. These

299   figures demonstrate that large discrepancy in climate data resulted in as much a two-fold increase

300   in NO emission over recent years. However, model predictions that soil NO emissions are higher

301   in wetter (2007-2008) as compared to dryer years (1981-1993) are in contrast to laboratory

302   findings, were NO emissions decreased with increasing soil moisture.

303   *4.2   Model validation with measured N-trace gases fluxes*

304   For the 31 sites simulated mean N_2O and NO emissions were generally < 15 g N₂O-N ha^{-1} d^{-1}.

305   Although most of the laboratory N_2O and NO agreed well with simulated data, a few sites

306   showed measurements that were three to four times higher (Fig. 5).

307   The high measured N_2O and NO emission values of > 15 g N ha^{-1} d^{-1} (Fig. 5) in laboratory study

308   of Gharahi Ghehi et al. (2012a) were somewhat surprising. They pointed out that chemo-

309   denitrification might be an important production pathway due to high free iron concentration in

310   these acidic soils.

311

312   Overall, the simulated N_2O and NO data showed an underestimation of the emission by

313   ForestDNDC-tropica. Correlation analysis between measured and simulated N_2O and NO fluxes

314   yielded non-significant correlations of r=0.24, p>0.05 and r=0.16, p>0.05, respectively.

315   However, when excluding high emission values (emissions > 15 g N_2O-N ha^{-1} d^{-1}) from the

316   laboratory data sets, we observed a significant correlation between measured and simulated

317   values of N_2O (r = 0.42, p<0.05) and NO (r = 0.51, p<0.05) fluxes (Fig. 5).

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319 Figure ⬜ illustrates the parameters included in the sensitivity analysis by varying the individual

320 parameters by ± 1 for pH, $\pm 25\%$ for BD and $\pm 50\%$ for other input parameters. This simple

321 model sensitivity test was previously used in several modeling studies, for example Butterbach-

322 Bahl et al. (2004), Kiese et al. (2005), and Werner et al. (2007a). Overall, soil BD and pH were

323 the most sensitive parameters for both N_2O and NO emissions. The observed sensitivity of N_2O

324 emission rates for the Nyungwe forest was comparable to other published N_2O simulation data

325 for tropical rain forest ecosystems using the same model. Kiese et al. (2005) and Werner et al.

326 (2007a) reported a pronounced sensitivity of N_2O emission rate to changes in pH and BD in

327 tropical forest ecosystems in Australia and global tropical forests, respectively. The sensitivity of

328 N_2O and NO emissions on leaf mass, temperature, rainfall, OC and clay content variability were

329 lower as compared to changes in soil pH and BD.

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331 Overall, the calculated β-values in this study were lower as compared to those in the Kiese et al.

332 (2005) and Werner et al. (2007a), e.g. a β-value of 2.5 for pH in Werner et al. (2007a) compared

333 to 0.67 in our study. These lower β-values probably come from the smaller range of possibly

334 values due to the restricted simulation region. For example Werner et al. (2007a) selected 1000

335 simulated grid cells out of a global dataset to assess model sensitivity, whereas we determined

336 the sensitivity of modeled N_2O and NO emissions on variations in input parameters by selecting

337 all 147 locations sites in the Nyungwe forest.

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339 ### *4.3   Change in historical soil data* 💬

340 The soil properties have been obtained at least three decades ago and may have changed in time

341 due to logging activities; so changes of historical soil data over time can affect the overall

342 uncertainty of GHG inventories. The possibility of changes of historical soil data over time was

343 shown by selecting 29 locations out of the 147 sites in the Nyungwe forest, for which a soil

344 sampling was performed by Gharahi Ghehi et al. (2012a) during September 2009. We carried out

345 a comparative analysis of simulated values N_2O and NO using current with past input soil

346 properties to test whether changes of historical soil data would significantly affect model

347 outcome.

5   Discussion

5.1   N₂O and NO emissions

To the best of our knowledge simulated and N_2O and NO emission from the Nyungwe forest represents the first explicit regional N_2O and NO emission inventory for a tropical forest on the African continent. The estimated annual average N_2O emission from Nyungwe forest (~3.8 kg N ha^{-1} yr^{-1}) is in line with simulated annual N_2O emissions from tropical rainforest soils for eastern Africa (~3.5 kg N ha^{-1} yr^{-1}) by Werner et al. (2007a).

On average the entire Nyungwe forest emits 439 t of N_2O-N and 244 t of NO-N per year (1981-1993) and ~384-489 t N_2O -N and ~489-384 t NO-N for period 2007-2008. Werner et al. (2007a) estimated the N_2O source strength of tropical forest soils of Africa (assuming a total rainforest area of 3.055×10^6 km^2) to be 344,000 t N_2O yr^{-1}, which is equivalent to 113 t for our area. The latter number is significantly lower than our mean estimate of 439 t N_2O-N yr^{-1} (1981-1993). This discrepancy may be due to two principal factors. First, Werner et al. (2007a) used the soil profile data from the ISRIC-WISE soil database and linked these to the global FAO soil map, whereas we used 147 soil data inside the tropical forest (Rwanda database). Specifically with regard to soil OC contents our database comes up with higher values as compared to the Werner et al. (2007a) study, as in the latter study soil OC contents of the most prominent soil classes in Africa was 1.38% (our database: average of 5.5%). Second, there are also differences in simulated years and origins of climate data.

The average model estimates in our study for N_2O (3.8 kg N ha^{-1} yr^{-1}) and NO (2.0 kg N ha^{-1} yr^{-1}) for the Nyungwe forest are also supported by field measurements from other studies. On average, the mean annual N_2O emission from tropical forest in Australia and southwest China was 1-3 kg N ha^{-1} yr^{-1} (Kiese et al., 2005; Werner et al., 2007a). Higher N_2O emissions (2.6 kg N ha^{-1} yr^{-1}) for forests in Kenya were reported by Werner et al. (2007b). In general, measurement of N_2O fluxes from tropical mountain forests range between 0.01 and 3.75 kg N ha^{-1} yr^{-1} (Breuer et al., 2000; Ishizuka et al., 2005; Holtgrieve et al., 2006; Purbopuspito et al., 2006; Köhler et al., 2009) and between 0.03 and 0.4 kg ha^{-1} yr^{-1} for NO (based on only one study of Davidson and Kingerlee, 1997). However, NO emissions up to 3 kg ha^{-1} (for a period of 3 months and not for one year) were reported for rain forests in Queensland, Australia at the onset of the rainy season

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379   (Butterbach-Bahl et al., 2004). Compared to other published NO emission data for other tropical

380   rain forest ecosystems, the simulated NO emissions of up to 5 kg ha^{-1} yr^{-1} at the Nyungwe forest

381   were high. This can be the effect of low soil pH values as ForestDNDC-tropica considers a

382   chemo-denitrification algorithm for pH values lower than 4 as co-process of NO production only

383   (pH<4 cover ~ 92% of the total forest area).

384   *5.2   Model and model parameter uncertainty*

385   Werner et al. (2007a) and Butterbach-Bahl et al. (2004) pointed out that spatial variations in

386   regional N_2O and NO emissions were mainly resulting from differences in the spatial distribution

387   of soil and climate characteristics. For example, the two-fold increase of total annual NO

388   emission for 2007-2008 years (384-489 t NO-N yr^{-1}) compared to 1981-1993 years (244 ± 16 t

389   NO-N yr^{-1}) indicates that large discrepancy in climate data play a major role in the N dynamics.

390

391   The different rainfall pattern between 1981-1993 and 2007-2008 periods within the study area

392   might be related to shifts in weather patterns due to adjacent land use/land cover change

393   (LULCC) as an important climate forcing (Mahmood et al., 2010) or altitude difference of

394   almost 500 m between the old stations and the Uwinka station which explains at least the

395   differences in temperature. There is also a known but not well-documented gradual decrease in

396   rainfall from west to east, and since two of the old stations are located east of the forest they are

397   likely underestimating the precipitation in the forest.

398

399   The high NO emissions simulated during wetter years could be a consequence of the rapid

400   mineralization of litter accumulated during the dry period. Specifically at the onset of the rainy

401   season (six months) the effect of the rainfall events on surface litter decomposition is direct and

402   more pronounced as compared to decomposition dynamics of root litter and organic matter in the

403   mineral soil. Our high NO emissions simulated during wetter years most likely are the result of

404   higher NO production in the surface litter layer. Though NO production was also simulated in

405   these years in the mineral soil, this contributed only little to total emissions, since NO

406   consumption in the mineral layer was increasing at the time. We emphasize that the simulated

407   responses of high NO emissions to the rainfall events are in agreement with observation by

408   Butterbach-Bahl et al. (2004). They observed that wetting events at the onset of the rainy season

409   resulted in peak NO emissions cumulating to several kg of NO-N within a few weeks.

410   For our N_2O emissions such a clear effect between wetter and dryer years is not visible, since

411   N_2O production in the model occurs mainly in the mineral layer. Again, increased soil moisture

412   will increase anaerobiosis and simulate further conversion of N_2O to N_2, so that total emissions

413   are less affected.

414

415   The variation in simulated N_2O and NO emissions in the Nyungwe forest also reflected the

416   texture and soil physico-chemical properties. For instance, N_2O emissions exceeding 4 kg ha^{-1} yr^{-1}

417   were found in the northwestern part of the forest, which is characterized by high clay and OC

418   contents and low pH (<4). Several authors (Nömmik (1956), Weier and Gillam, 1986; Granli and

419   Bockman, 1994) have shown that low pH decreases the activity of the N_2O-reductase, thereby

420   increasing production of N_2O, rather than N_2 from denitrification. For nitrification, it has also

421   been demonstrated that low pH <or= 4 values favor N_2O production (Sitaula and Bakken, 1993;

422   Martikainen and De Boer, 1993; Kesik et al., 2006). All this is in agreement with field

423   observations of N_2O emissions for different tropical lowland forest sites in Australia by Kiese

424   and Butterbach-Bahl (2002) which revealed that low pH was a crucial factor driving high N_2O

425   emissions.

426

427   The high NO emissions were found in the center and towards the north and northeastern of the

428   forest, which are growing on soil characterized by low soil pH and relatively high OC or high

429   clay contents. Moreover, all in the study of Serca et al. (1994) the combined influence of low pH

430   and high OC was used to estimate the NO production potential of forest soils in the Mayombe

431   forest.

432

433   Furthermore, Gharahi Ghehi et al. (2012a) suggest that high N_2O and NO emissions for some

434   sites in the Nyungwe forest are possibly due to chemo-denitrification processes. Chemo-

435   denitrification is thought to occur when nitrite (NO_2^-) in acid soils reacts with organic

436   components to produce NO and N_2O (Bremner, 1997). Under acidic conditions chemo-

437   denitrification may be a significant source of NO, N_2O, N_2 when NO_2^- is reduced to NO, N_2O or

438   N_2 with Fe (II) as an electron donor (Van Cleemput and Baert, 1984; Cooper et al., 2003).

439 We have evidence of chemical pathways for NO ~~and N₂O~~ production in the Nyungwe forest soils

440 (see supplementary material for detailed description). Our laboratory experiment argues that

441 abiotic denitrification can be an important source of ~~N₂O and~~ NO under certain circumstances,

442 i.e. low pH and present of reduced inorganic compounds (e.g. Fe (II)).

443 In the present version of ForestDNDC-tropica NO and N_2O is mainly simulated via microbial

444 nitrification and dentrification pathways. Although chemo-denitrification has been included in

445 ForestDNDC-tropica (soil pH < 4) our study suggests that rates of chemo-denitrification for NO

446 production in tropical soils may still be underestimated and that it is likely to be necessary to

447 introduce such a mechanism for N_2O as well.

448

449 In addition to pH, bulk density has a significant influence on N_2O and NO emissions. Increasing

450 bulk density increases the anaerobic zone and increasing the probability for saturated moisture

451 conditions following rainfall. This triggers denitrification and N_2O emissions and decreases NO

452 emissions (Stange et al., 2000; Kiese et al., 2005). Therefore, in order to further improve N_2O

453 and NO emissions from tropical forest, improved spatial maps of soil pH and bulk density are

454 needed. In general, soil BD measurements have rarely been made in soil surveys. However, it

455 has been shown that organic content can be used as a sole predictor of topsoil BD in tropical

456 forest soils (Gharahi Ghehi et al., 2012b).

457 ### *5.3   N₂O and NO emissions: an integrated approach*

458 Although uncertainties remain in our model results we are confident that, given the available

459 driving data, the results give us a good insight into the spatial and temporal variability in N_2O

460 and NO emissions. A comparative analysis of current with past TN, pH, clay and OC content

461 values for a select subset of 29 locations (see Gharahi Ghehi et al., 2012a) displayed significant

462 differences for all soil driving information but the clay values (p>0.05). This data shows that soil

463 properties have changed over the last three decades.

464 The probable reasons for these changes in the Nuyngwe forest based on personal communication

465 (G. Wallin, August 2012) and several field observations (P. Boeckx, 2005-2012) could be the

466 following:

467 i) forest fires in eastern part of the forest in 1999, ii) traditionally more disturbances occurs in the

468 eastern part, although locally some mining and logging activities have been done in the west as

469   well and iii) disturbance caused by people normally have occurred where the forest have been

470   accessible, thus in the same areas where the most extensive soil sampling has been carried out.

471   We acknowledge that these changes could affect our estimates of N_2O and NO. However, soil

472   structural properties free of anthropogenic disturbance are in general more stable and change

473   little over time.

474   On a regional to global scale, N_2O emission from e.g. grassland in West/East Africa regions is

475   estimated to be 15.0 Mt CO_2 equivalents (Stehfest and Bouwman, 2006). Considering our small

476   study area (1113 km^2) our estimate with a range of 0.19-0.25 Mt CO_2 equivalents (373-505 t

477   N_2O-N = 0.19-0.25 Mt CO_2) for 1981-2008 confirms the potential importance of tropical forests

478   as a major source of atmospheric N_2O on a regional, national and even global scale.

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6   Conclusion

Although, there is still a considerable uncertainty associated with our emission estimates, our results are providing a first spatial explicit predictions of N_2O and NO for tropical forest at this scale. The results are in line with other studies, confirming substantial N_2O and NO emissions from tropical forests, thereby suggesting that N_2O and NO losses play a major role in the N cycle of tropical forests. Though there are still several limitations (e.g. clustering of legacy data; chemo-denitrification only considered for NO but not for N_2O) our results show that state of the art process-based models in combination with site-specific (historical) input data can be used to improve tropical N_2O and NO emission estimates.

Temporal variability has shown to be sensitive to known processes such as changes in precipitation. Our study further corroborates the notion that soil BD content and pH are the most influential factors driving spatial variations in soil NO and N_2O emissions for tropical forest soils and should therefore receive priority is monitoring campaigns.

However, some abiotic processes that contribute to, but not completely integrate, into our N trace gas modelling effort were found. In particular, chemo-denitrification processes on acidic soils seem to be under represented in the current ForestDNDC-tropica model.

Scaling N_2O values from the Nyungwe forest in CO_2 equivalents and comparing them to CO_2 emission equivalents from grassland in West/East Africa indicates that the GHG contribution of N_2O (and NO) emissions from tropical highland rainforest cannot be understated.

527

Supporting information Available

Details on the chemo-denitrification process and reported abiotic NO and N_2O fluxes from

Nyungwe forest soil.

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Table 1. Summary statistics for topsoil (0-30 cm) clay, silt, sand, gravel, organic carbon (OC), total nitrogen (TN), pH-soil, bulk density (BD) and pH-litter: mean, minimum (min), median, 25 and 75 percentile, maximum (max.), standard deviation (SD) and coefficient of variation (CV)

| Parameter	n	Mean	Min	25 per.	Median	75 per.	Max.	SD	CV
Mineral topsoil									
Clay (%)	144	34	2.0	23.0	36.0	44.0	71.0	14.2	0.4
Sand (%)	144	43	9.0	32.0	40.0	53.0	86.0	17.2	0.4
Silt (%)	144	23	5.0	15.0	20.0	28.0	61.0	12.2	0.5
Gravel (vol.%)	144	1.8	0.0	0.0	0.0	0.0	47.0	6.1	3.4
OC (%)	147	5.5	0.3	3.6	5.3	7.0	15.1	2.5	0.5
TN (%)	101	0.3	0.1	0.2	0.3	0.4	0.6	0.1	0.3
pH-soil (-)	147	3.8	3.0	3.5	3.7	4.0	5.4	0.4	0.1
BD (g/cm3)	147	0.92	0.80	0.94	0.94	1.02	1.28	0.13	0.14
Litter layer									
pH-litter (-)	129	4.1	3.0	3.6	3.9	4.4	7.5	0.8	0.2
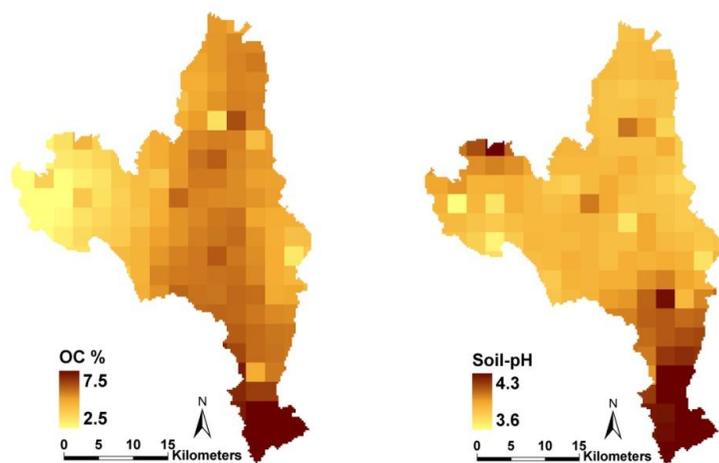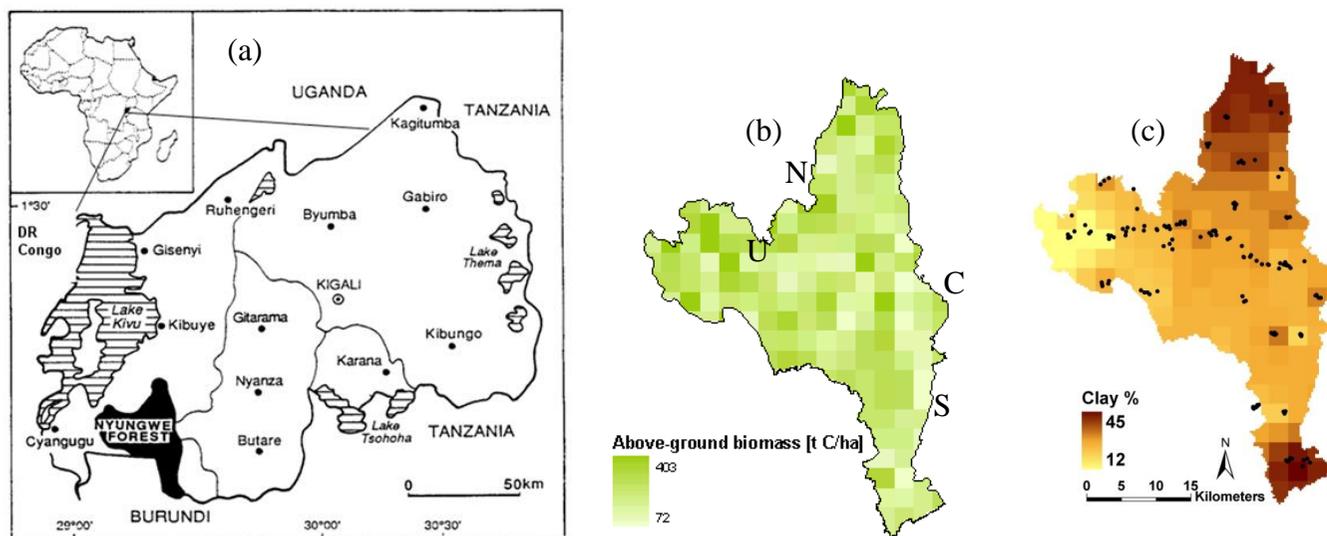
Figure 1. Location of the Nyungwe forest in southwestern Rwanda (a), Spatial distribution of some selected model input parameters; above-ground biomass (b), soil clay content and location of 147 legacy soil profiles (black bullets) (c), soil organic carbon (OC) (d) and soil pH (e). Location of three climate stations around the forest are shown by letter (N=north, C=Center, S=south); the recent climate station in the Nyungwe forest is shown by a U (b)
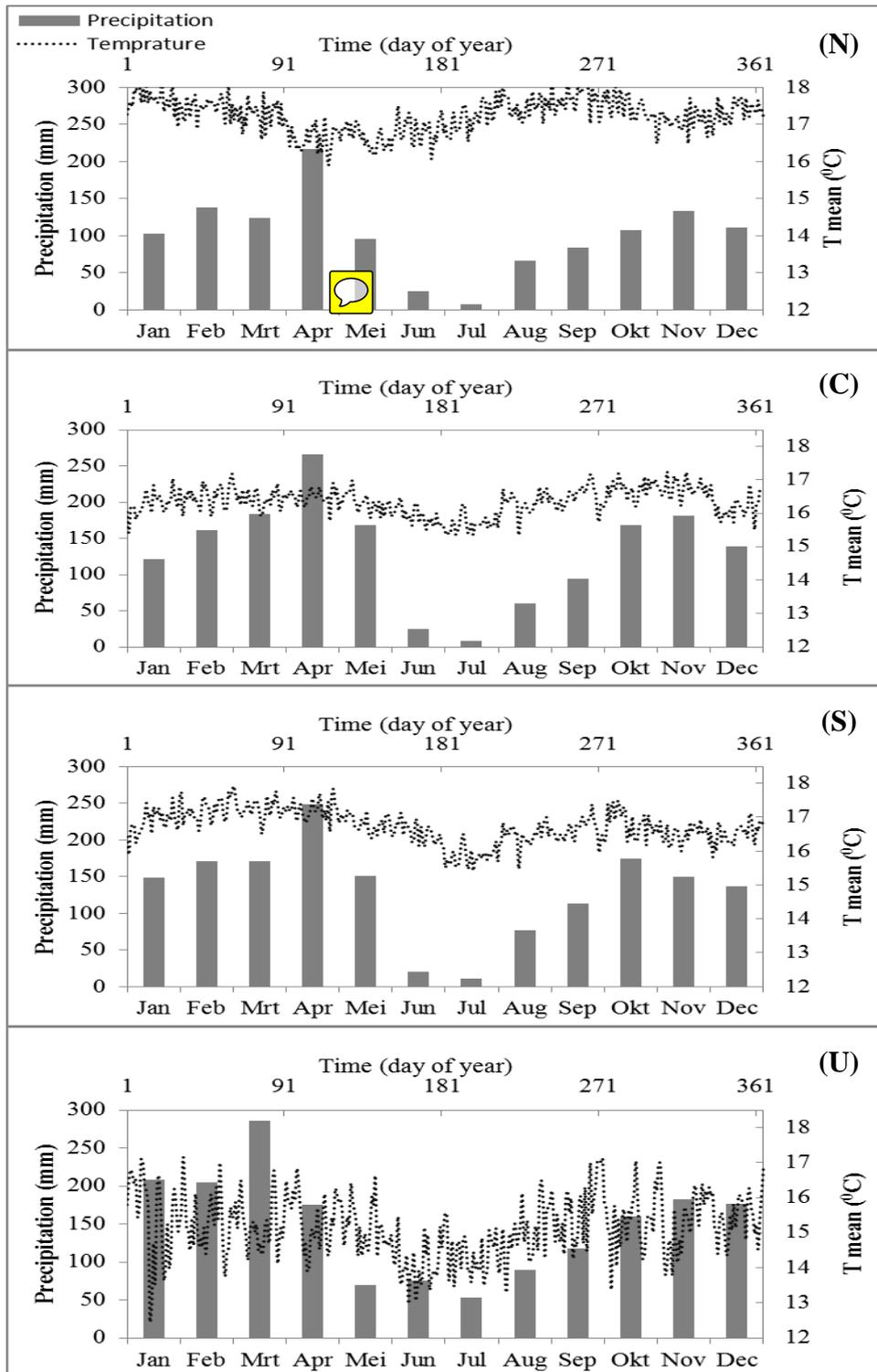
Figure 2. Seasonal variation of climate parameters expressed as daily means (Temprature) and mounly means (Precipitation) from the three climate stations (from 1981 to 1993) north (N), Center (C), south (S), and the recent (2007 to 2008) climate data at Uwinka (U) in the Nyungwe forest increasing soil moisture.
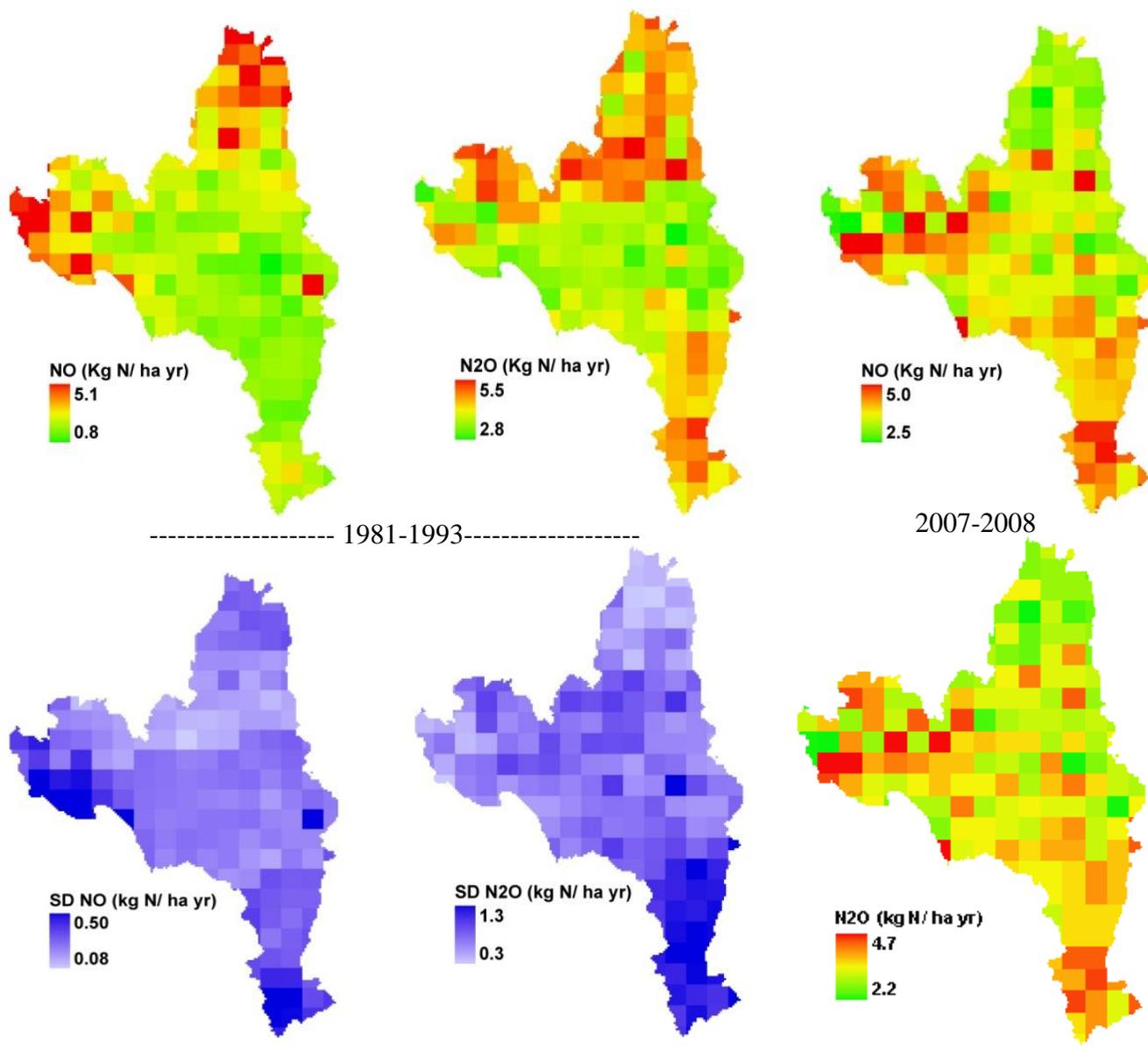
-------------------- 1981-1993-------------------   2007-2008

Figure 3. Average annual (1981-1993; 2007 and 2008) predicted NO and N_2O emissions from the Nyungwe forest soil; and standard deviation (SD) indicating inter-annual variability of NO and N_2O fluxes
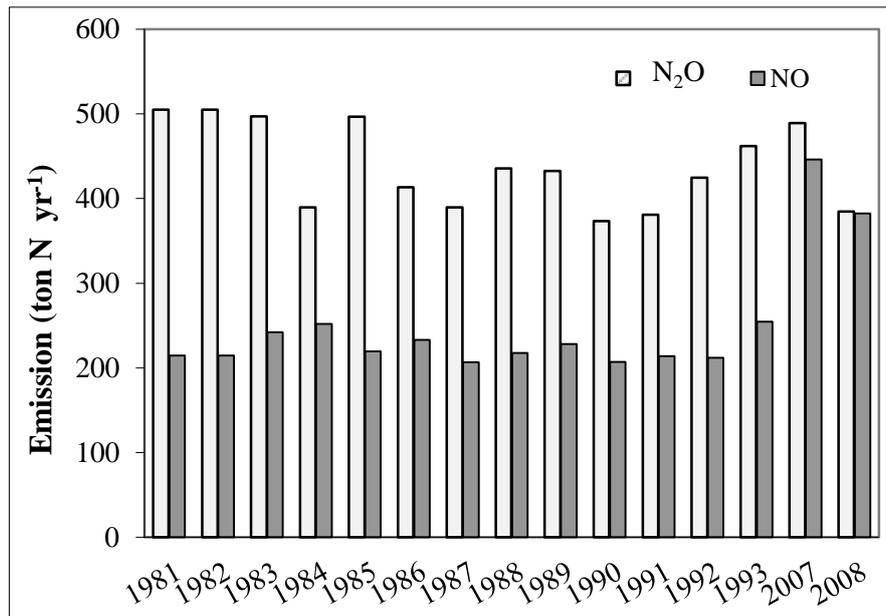
Figure 4. Annual variation of total predicted N_2O and NO emissions from the Nyungwe forest soils for the years 1981-1993, 2007-2008
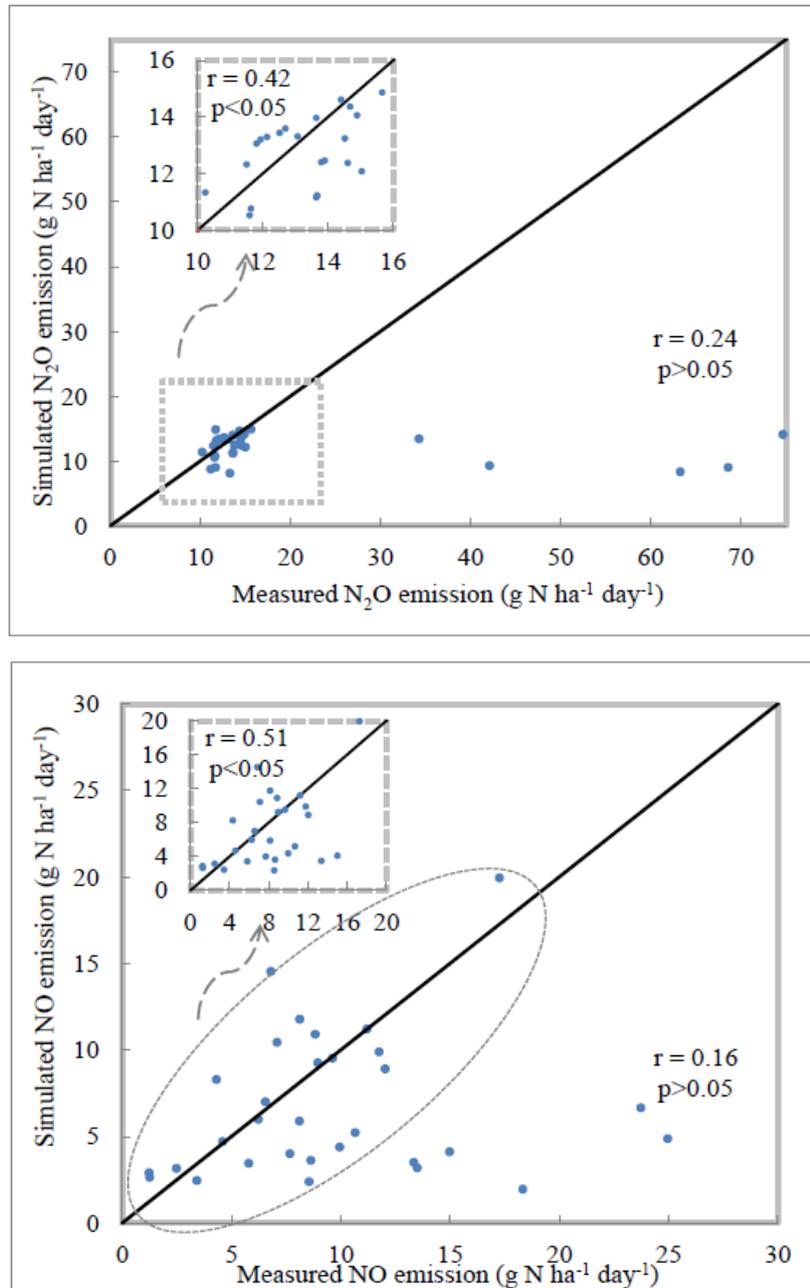
Figure 5. Comparision of simulated and measured mean N_2O and NO emission for 31 sites in the Nyungwe forest
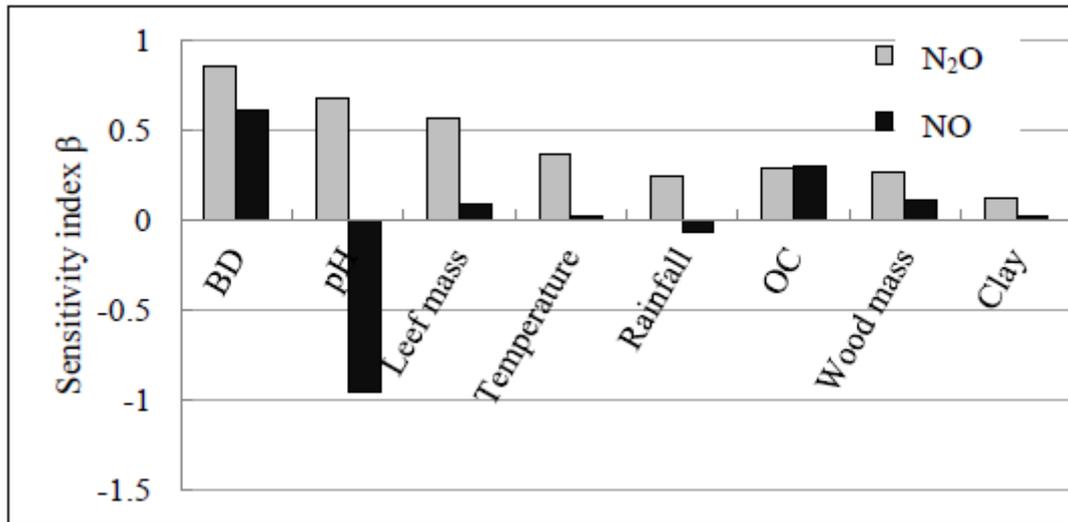
Figure 6. Model sensitivity for changes of individual input parameters (plus minus 1 for pH, plus minus 25% for bulk density (BD) and plus minus 50% for other driving parameters) on N_2O and NO emissions
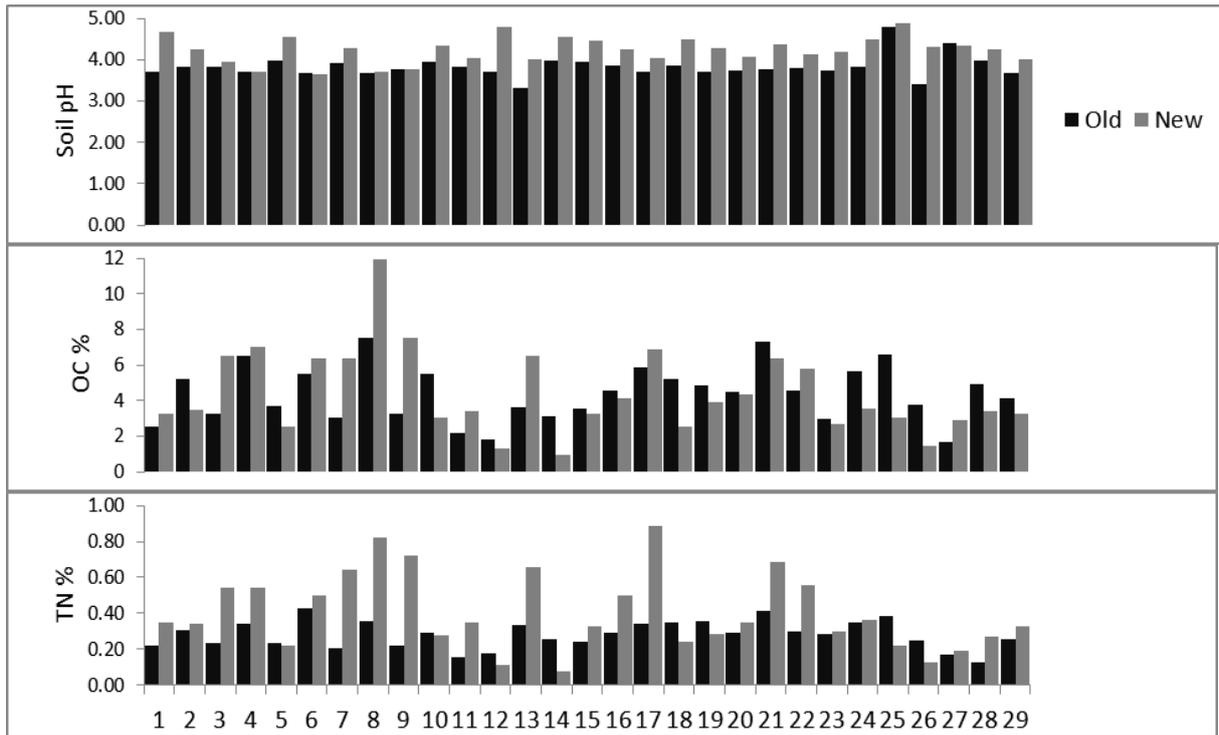
Figure 7. Temporal variation of clay, organic carbon (OC), total nitrogen (TN) and pH values for 29 locations in the Nyungwe forest; 'Old' and 'New' indicate soil surveys in 1980's and 2009, respectively

Supplemental material

Abiotic-denitrification in tropical highland rainforest soils

Tropical rainforest soils are often characterized by high concentrations of crystalline reactive Iron (Fe) and fluctuating redox conditions, which are likely to support Fe reduction coupled to anaerobic ammonium oxidation (Feammox) (Yangh et al., 2012) or chemo-denitrification (Van Cleemput and Baert, 1984). Luther et al. (1997) pointed out that high Fe concentrations and pH values below 6.8 provide conditions under which Feammox based produce N_2 production could take place. Furthermore, chemo-denitrification can occur in Fe-rich and moderately acidic soils, reducing NO_2^- (nitrite) to NO (nitric oxide), N_2O (nitrous oxide), or N_2 (di-nitrogen) through self-decomposition of nitrous acid or in reaction with metallic cations such as Fe (II) (Van Cleemput and Baert, 1984).

We performed a preliminary experiment to assess if abiotic denitrification could occur in tropical mountain forest soils of the Nyungwe national park. We focused on the acidic soils of the Nyungwe forest to test if chemo-denitrification plays a role for NO and N_2O production in addition to microbial processes.

Laboratory experiment

We selected seven soil samples from a dataset of 31 soil samples from the Nyungwe forest for which NO and N_2O production potentials have been determined previously (Gharahi Ghehi et al., 2012). These 7 samples cover different organic carbon content, pH and Fe levels (Table S1).

Mercuric chloride ($HgCl_2$) was used as the sterilizing agent because among sterilization techniques (i.e., autoclaving, fumigation), $HgCl_2$ results in minimal changes in chemical and physical soil properties, with no significant effects on nutrient concentrations (Trevors, 1996; Wolf et al., 1989). The rate of $HgCl_2$ addition of 3000 mg $HgCl_2$ kg^{-1} soil was in the range recommended by Wolf and Skipper (1994) (500-20000 mg kg^{-1} of dry soil) to achieve effective inhibition of microbial metabolism. In addition, Trevors (1996) pointed out that generally, a concentration of 500 mg $HgCl_2$ kg^{-1} dry soil is satisfactory.

Table S1 Soil chemical characteristics, organic carbon (OC), Iron (Fe II& III), Nitrite-N (NO_2^--N), ammonium-N (NH_4^+-N) and Nitrate-N (NO_3^--N), for seven soil samples selected from a dataset of 31 soil samples from the Nyungwe forest

Soil sample	OC	Soil-pH	Fe (II)	Fe (III)	NO_2^--N	NH_4^+-N	NO_3^--N
	%		%	%	($\mu g\ g^{-1}$ soil)	($\mu g\ g^{-1}$ soil)	($\mu g\ g^{-1}$ soil)
1	3.9	4.47	0.13	0.44	0.0258	266.26	1.02
2	6.5	4.14	0.41	2.70	0.0338	216.76	14.93
3	1.0	3.98	0.31	4.55	0.0422	47.09	9.87
4	4.2	3.74	0.47	6.29	0.0546	160.51	16.10
5	6.6	3.85	0.33	2.04	0.0444	17.55	1.26
6	3.2	4.15	0.45	5.17	0.0336	25.05	5.23
7	4.2	3.40	0.46	6.05	0.0376	72.42	14.50

One day before the start of the experiment we first tested microbial activity with sterilization treatment ($HgCl_2$ sterilized) and four incubation times (1, 2, 5 and 24 h). Therefore, 25 g dry soil was added to two 1200 ml airtight sealed glass containers. Five milliliters of 15 mg $HgCl_2$ L^{-1} was added to the soil sample in a solution of deionized water and mix thoroughly into the soil. After 1, 2, 5 and 24 h, the headspace of the glass jar was sampled for dioxide carbon (CO_2) analyses both from live soil and Hg-treated soil. Addition of 3000 mg $HgCl_2$ kg^{-1} dry soil clearly eliminated CO_2 production (Fig. S1a, b). This indicates that the Hg-treatment was effective in eliminating the activity of soil microorganisms.
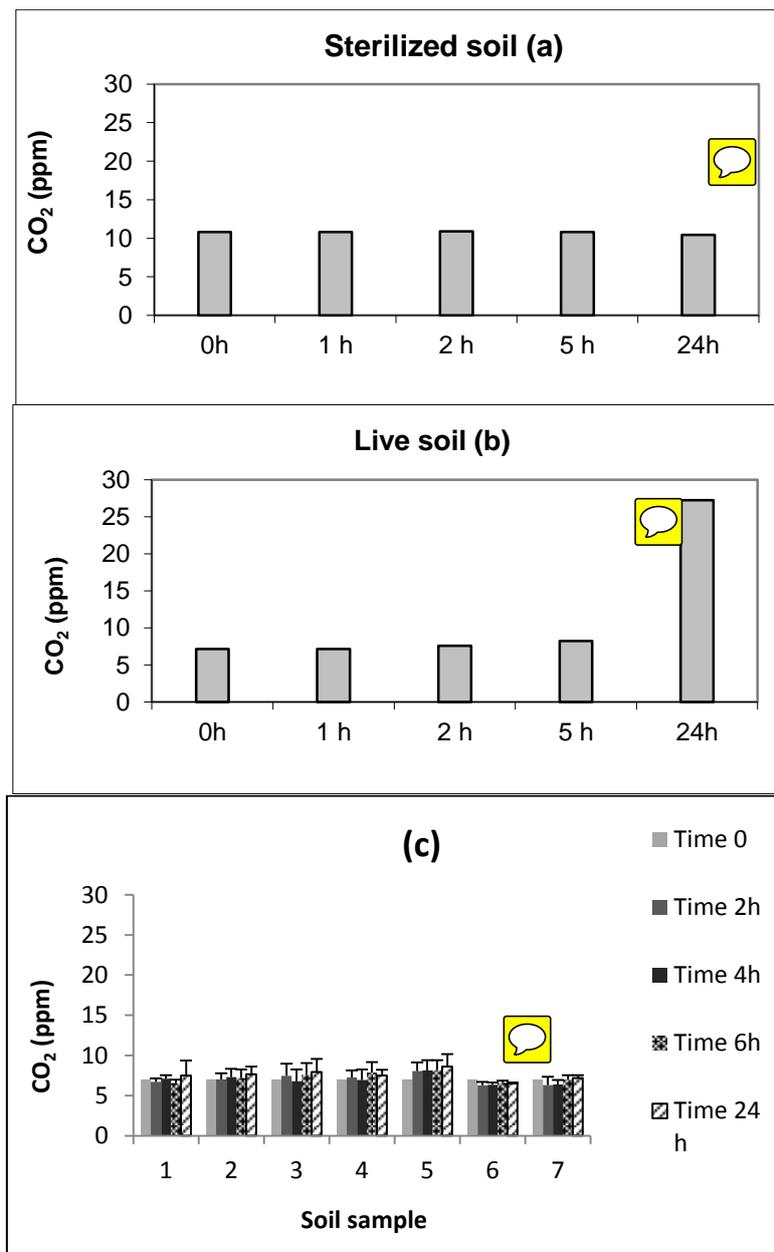
Fig. S1 Comparison of headspace carbon dioxide (CO_2) concentrations between $HgCl_2^-$ treated (a) and live soil (b) for 1, 2, 5 and 24 h after $HgCl_2$ addition; headspace CO_2 concentrations for $HgCl_2$-treated soils for the seven Nyungwe soil samples for each nitric oxide (NO) and nitrous oxide (N_2O) sampling time during the incubation (c), error bars are plus one standard deviation

All seven soil samples in three replicates were incubated at 70% water filled pore space (WFPS). We applied the same laboratory techniques that were used by Gharahi Ghehi et al. (2012) to measure soil N_2O and NO production. For each treatment 25 g dry soil was added to an incubation tube that was placed into an airtight sealed glass container with a volume of 1200 ml. Soils received 10 atom% $Na^{15}NO_2$ and 5 milliliters of 15 mg $HgCl_2$ L^{-1} . The rate of ^{15}N addition was equivalent to ~1 fold of the soil NO_2^- -N concentration in each soil sample (range 0.025-0.054 µg $^{15}NO_2^-$ -N g^{-1} soil). Immediately after addition of $^{15}NO_2^-$ -N -, the glass containers were closed. After 0, 2, 4, 6 and 24 h, NO concentration of the headspace was determined using an NO analyzer (CLD 77AM, Eco Physics, Switzerland) and immediately after the NO measurements, a 12 ml gas sample was withdrawn from the headspace for CO_2 and N_2O analyses. The stored gas vials was analyzed on a gas chromatograph (14B, Shimadzu, Japan) equipped with an electron capture detector, ECD) for CO_2 and N_2O detection. Following the sampling at 24 h, all glass contents were opened and 0.2 g of wet soil was sampled from each tube for analyzes of Fe (II) and Fe (III). The remaining soil was extracted in 50ml of 1M KCl for analysis of NO_2^- concentration and ^{15}N NO_2^-.

Soil Fe (II) was measured colorimetrically by dissolving 10 mg of soil sample in a solution of H_2SO_4 and HF in the presence of powdered orthophenantroline on a steam bath (Shapiro, 1960). Total Fe (Fe (II) + Fe (III)) was measured upon sodium dithionite extraction (Mehra and Jackson, 1960) and measured via optical emission spectrometer (Varian ICP-OES) (720 ES, Mulgrave VIC 3170, Australia). Soil ^{15}N as NO_2^- content were measured by trace gas (TG II) coupled to an isotope ratio mass spectrometer (TG-IRMS) (20–20, SerCon, Crewe, UK). Extractable NO_2^- concentrations was determined using copper-cadmium reduction on a Brann+Luebbe autoanalyser AA3.

Results

The negligible rates of CO_2 production in all seven Hg-treated soils over 24 h (Fig. S1c) showed that the Hg-treatment was effective in eliminating the activity of soil microorganisms. Twenty four hours after addition of ^{15}N-NO_2^-, no ^{15}N was observed in NO_2^- for all soils that received $^{15}NO_2^-$. Furthermore, Figure S2a shows that the large proportion of soil NO_2^- (added $^{15}NO_2^-$+ Soil NO_2^-) disappeared after 24 h of incubation.

Except two soil samples, N_2O concentrations showed no significant increase between the 0 and 2 h incubation time. Figure S2b also illustrates that N_2O concentrations from few sterilized soil samples have a significant increase after 24 h of incubation.

Multiple comparisons of all NO concentrations from all sterilized soil samples showed a significant increase between 0 and 2 h ($p<0.05$), and small increase observed in concentration thereafter (no significant differences between 2, 4, 6 and 24h) (Fig. S2b, c). Therefore, we used N_2O and NO emissions during a 2 h incubation time to calculate N-gas fluxes in $\mu g\ m^{-2}\ h^{-1}$ (Table S2). Follow up measurement of Fe (II) and Fe (III) showed no significant differences between 0 and 24 h of incubation time (Fig. S3). The results also showed that most of the Fe is in the oxidized form Fe (III).

Table S2 Nitrous oxide (N_2O) and nitric oxide (NO) flux rates calculated in $\mu g\ m^{-2}\ h^{-1}$

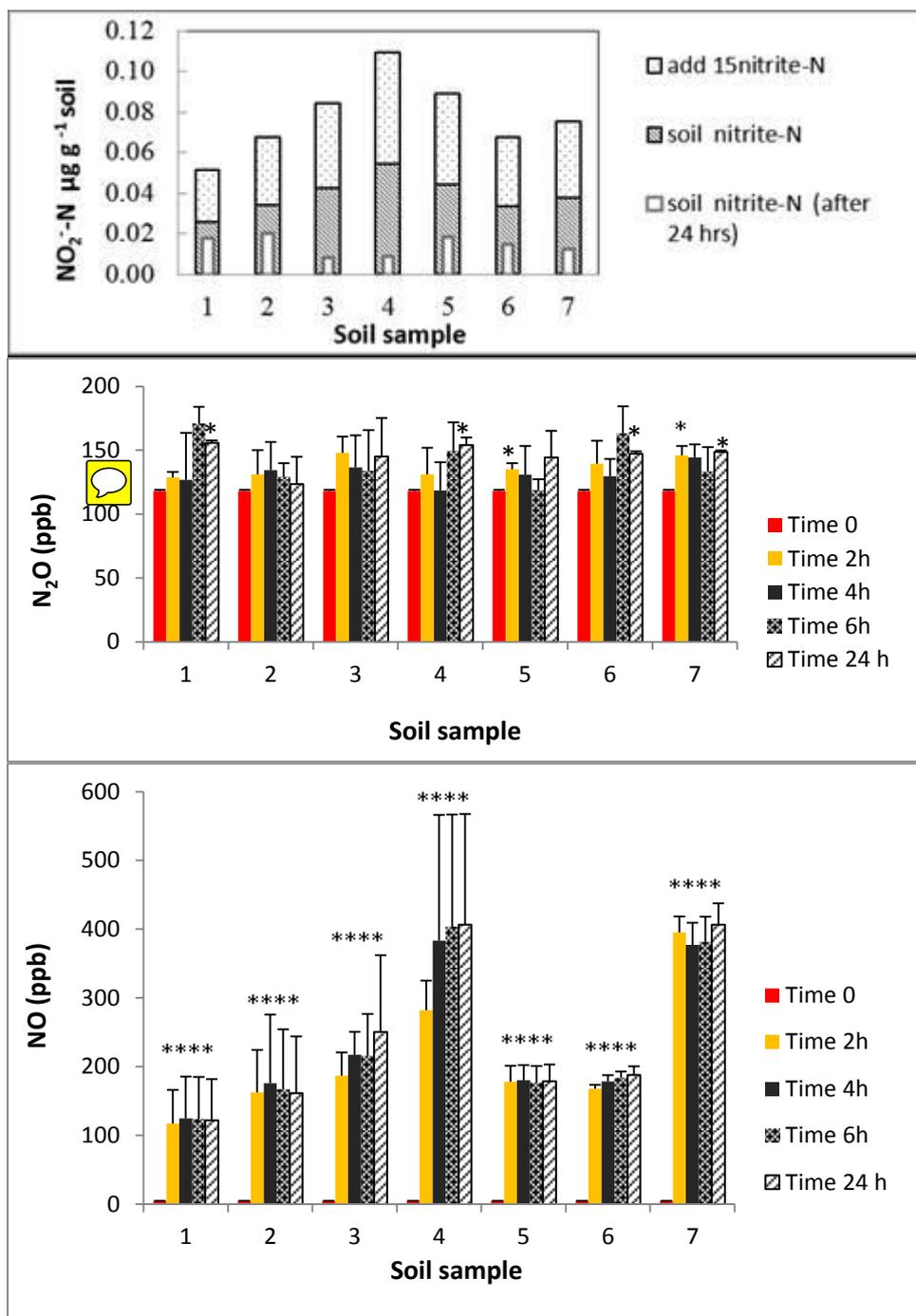| Soil sample	$\mu g\ N_2O$-N $m^{-2}\ h$	μg NO-N $m^{-2}\ h$
1	8.75 ± 3.54	67.62 ± 29.05
2	10.77 ± 15.75	95.11 ± 36.66
3	24.71 ± 10.66	110.24 ± 20.69
4	20.63 ± 3.37	149.64 ± 26.28
5	13.97 ± 4.08	104.04 ± 13.90
6	17.88 ± 14.97	98.86 ± 2.39
7	23.14 ± 5.02	235.97 ± 14.62

Fig. S2 Nitrite (NO_2^-) concentration in soil before incubation and after 24 hours of incubation among seven soil samples (a); nitrous oxide (N_2O) and nitric oxide (NO) concentration in the headspace of the glass jar for each sampling time for the seven Nyungwe soil samples (a,b); error bars are plus mines one standard deviation, significant deference from 0 h time have been indicated by a star
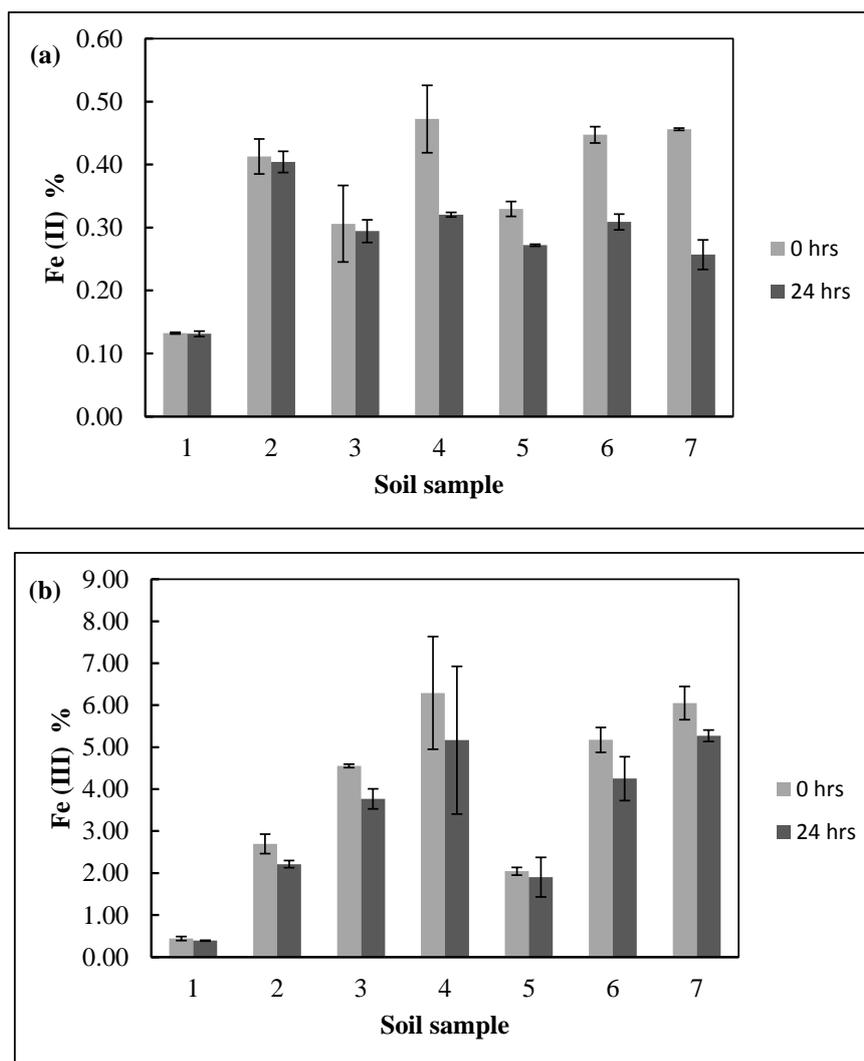
Fig. S3 Extractable Fe (II) and Fe (III) concentrations before and after 24 hours of incubation. error bars are plus mines one standard deviation

As a result, we acknowledge that consumption of all added ^{15}N-NO$_2^-$ and concurrent N$_2$O and NO emissions from the Nyungwe forest soils are possibly due to abiotic processes, such as chemo-denitrification.

Nitrite is known to react readily and abiotically with Fe (II). Ammonium (NH$_4^+$) can follow a similar fate if it is first oxidised to NO$_2^-$. So, abiotic NO and N$_2$O production is thought to occur in all our soil samples with pH around 4 or <4 as follows:

First, oxidation of soil NH$_4^+$ coupled to reduction of Fe (III) (Feammox, Yang et al., 2012), may provide a source of Fe (II) and NO$_2^-$. Second, by reaction of Fe (II) with NO$_2^-$, Fe (III) and NO, N$_2$O or N$_2$ can be formed (Fig. S4) (Van Cleemput and Baert, 1984; Van Cleemput

and Samater 1996). However, we note that NH_4^+ concentration in all seven soil samples were high due to long storage (~2 years) for dry soil samples (Table S1).

Moreover, Davidson et al. (2003) pointed out that Nitrate (NO_3^-) can abiotically reduced to NO_2^- via reduced inorganic components (e.g. Fe (II)). So we speculate that this reaction pathway wherby Fe (II) reduces NO_3^- to NO_2^- most likely play a role in producing NO/N_2O through abiotic processes (see NO_3^- concentration for seven soil samples in Table S1).
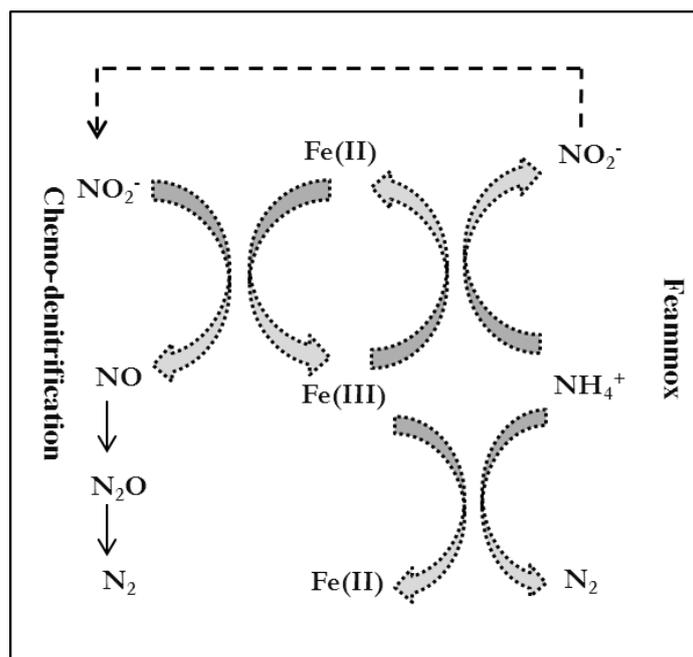

Fig. S4 Chemo-denitrification and Feammox pathway for nitric oxide (NO), nitrous oxide (N_2O) and di-nitrogen (N_2) production

Furthermore, the variation in abiotic N_2O emissions was significantly positively correlated with Fe (III) ($r = 0.85$, $p < 0.05$). N_2O emissions also correlated negatively with pH and positively with Fe (II) but not significant. NO emissions was negatively, significantly correlated with pH ($r = 0.92$, $p < 0.05$). The correlation was also positive with Fe (II) and Fe (III) but not significant. These results are supportive to other studies which were showing abiotically produce soil NO (and N_2O) is thermodynamically favorable at acidic soil with reduced metals.

To summarize, based on our results the abiotic NO (and N_2O) production is a very fast (< 2 h) process, which can be a major pathway responsible for production NO (and N_2O) in the Nyungwe forest soils. Furthermore, we point out that a mixed abiotic-biotic pathway of N_2O production may be also accrued in soils. An abiotic pathway in which, NO_2^- is reduced to NO

followed by the biotic reduction of NO to N_2O. However, we do not have evidence for the contribution of the abiotically produced NO to microbially produced N_2O from our experiment.

In addition, since no ^{15}N-NO and $^{15}N_2O$ could be measured (concentrations < detection limit) in our experiment, there was no evidence to determine if NO_2^- is source of NO or N_2O emissions.

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