Amendment with industrial and agricultural wastes reduces surface-water nutrient loss and storage of dissolved greenhouse gases in a subtropical paddy field

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Type: *Article*

Running head: *Industrial and agricultural wastes increases porewater nutrient concentration and reduces surface-water nutrient loss and storage of dissolved greenhouse gases*

23   ABSTRACT

24   Paddy fields are important ecosystems for supporting human life. They are frequently

25   fertilized more than necessary for providing high yields of rice (*Oryza sativa*), so

26   nutrients are lost by leaching into aquatic ecosystems, which become eutrophic. Rice

27   production is also an important source of greenhouse gases (GHGs). Mitigation of the

28   nutrient losses and GHG emissions from paddy fields is crucial both for the

29   sustainability of rice production and the reduction of adverse environmental effects. We

30   examined the effects of the application of biochar, steel slag, shell slag, gypsum slag

31   and silicate and calcium slag (produced from steel slag) on water nutrient

32   concentrations and dissolved GHGs in a paddy field in subtropical southeastern China,

33   one of the most important areas of rice production in the world. The concentrations of

34   total dissolved nitrogen (TN) and total dissolved phosphorus (TP) in the surface water

35   were lower in plots amended with shell slag than the control plots. Mean porewater

36   TN and TP concentrations, however, were higher, and the mean porewater dissolved

37   CO_2 concentration was 68% lower in the plots amended with silicate and calcium slag

38   than the control plots. Mean dissolved CH_4 concentrations were 92 and 70% lower in

39   the plots amended with gypsum slag and silicate and calcium slag, respectively. Mean

40   dissolved N_2O concentrations did not differ significantly among all plots. The

41   concentrations of dissolved CO_2 and CH_4 were correlated with their production and

42   emission. The concentration of dissolved CO_2 was negatively correlated with porewater

43   concentrations of NH_4^+, NO_2^-, NO_3^-, TN, TP and Cl^-. The concentration of dissolved

44   CH_4 was negatively correlated with porewater concentrations of NH_4^+, TN, TP,

45   dissolved organic carbon (DOC), SO_4^{2-} and Cl^-. The concentration of dissolved N_2O

46   was correlated positively with the concentrations of NO_2^-, NO_3^-, DOC and SO_4^{2-} and

47   negatively with the porewater concentration of NH_4^+. These results support the use of

48   these fertilizers alone or in combination for the mitigation of water nutrient losses and

49   GHG production in rice agriculture and will provide a scientific basis for continuing

50   the search for an easy, economical and optimum management of fertilization.

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1. Introduction

Rice (*Oryza sativa*) is the most important cereal crop globally, currently feeding over 50% of the population (Haque et al., 2015). Rice production, however, needs to increase by 40% by the end of 2030 to cope with the increasing demand by a growing population worldwide (FAO, 2009). The leaching of nutrients from agricultural activities, though, contributes to the eutrophication of aquatic ecosystems and approximately 20% of the total emissions of atmospheric greenhouse gases (GHGs) (Hütsch, 2001).

Eutrophication is a major environmental concern (Sunda and Cai, 2012; Sardans et al., 2012; Peñuelas et al., 2012, 2013), with large impacts on water quality and human health (Svirčev et al., 2014). The causes of the sharp increase in water eutrophication driven by increases in nitrogen (N) and phosphorus (P) pollution (Lewis et al., 2011; Sardans et al., 2012) include both point-source (Kiedrzyńska et al., 2014) and nonpoint-source (Vilches et al., 2014) pollution. Agricultural nonpoint-source pollution is the direct cause of 60-70% of the global pollution of rivers and lakes (Zhu, 2006). Methods to minimize these environmental impacts of agricultural activities must be continuously improved. The rates of fertilizer application continue to rise, so the potential risk of nutrient loss from paddy fields and the consequent eutrophication are also increasing (Savci, 2012). Strategies of agricultural management, e.g. water management (Díaz et al., 2012) or the application of straw (Wang et al., 2014a), biogas slurry (Guo et al., 2014) or biochar (Liu et al., 2015), are being investigated and developed to both reduce environmental risks and achieve sustainable rice production. Different studies, however, have come to different conclusions, so further research is clearly warranted.

GHGs are produced by microorganisms and stored in porewater. Knowing the amount of GHG dissolved in porewater is therefore very important for evaluating the

79   potential emission of GHGs (Jahangir et al., 2012; Pighini et al., 2015). N input

80   (Jahangir et al., 2012), water chemistry (Whitfield et al., 2011) and salinity (Teixeira et

81   al., 2013) are dependent on the dissolved concentrations of CO_2, CH_4 and N_2O. The

82   relationships of porewater properties and dissolved GHGs with alternative crop

83   amendments, however, have been little studied but would provide valuable information

84   for improving the agricultural management to mitigate GHG emission.

85   Some studies have reported increases in rice production by the application of steel

86   slag (Wang et al., 2014b; 2015), increasing the resistance against diseases (Ning et al.,

87   2014) and increasing greenhouse gas emissions (Wang et al., 2014b; 2015). No data,

88   however, are available for the effects of the application of steel slag or other urban-

89   industrial wastes on dissolved GHGs and the dynamics of surface or porewater nutrients

90   in rice croplands. Moreover, industrial and agricultural wastes are far less commonly

91   applied in subtropical than temperate regions (Furukawa and Inubushi, 2002; Ali et al.,

92   2008; Wang et al., 2014b). A better understanding of the effects of industrial and

93   agricultural waste on paddy fields and the GHG dynamics of subtropical paddy fields

94   is thus needed.

95   Sixty percent of the Chinese population depends on rice-based food (Zhu, 2006).

96   The leaching of nutrients from rice croplands, however, accounts for 60-70% of the

97   freshwater eutrophication in China (Zhu, 2006). Sixty to 65, 50-60 and 30-40% of the

98   N, P and potassium applied in fertilizers, respectively, are drained and leached from

99   paddy fields to freshwater (Cheng and Li, 2007). Ninety percent of the paddy fields in

100 China are in subtropical regions, such as the provinces of Fujian, Jiangxi and Hunan.

101 The development of valid and reliable methods for increasing soil fertility, reducing

102 nutrient loss and sustaining rice productivity in Chinese paddy fields in subtropical

103   regions is therefore important. We hypothesised that the amendment with biochar, steel

104   slag, shell and gypsum slag, and a silicate and calcium fertilizer can improve soil

105   fertility and prevent leaching losses by increasing the soil nutrient retention capacity as

106   a result of the high adsorption capacity of these compounds. Moreover, their high

107   contents of Fe^{3+} and SO_4^{2-} can make them to act as electron acceptors thus reducing

108   the formation of CH_4 and N_2O and their potential effect on soil pH can lead to the

109   precipitation of CO2 as carbonates. We aimed to test these hypotheses by measuring

110   the effects on nutrients and greenhouse gas emissions in soil porewater and surface

111   water after the application of various waste materials (biochar, steel slag, shell slag,

112   gypsum slag and a silicate and calcium fertilizer produced from steel slag) to

113   experimental paddy fields.

114   We aimed to: (1) determine the response of dissolved CO_2, CH_4 and N_2O to the

115   application of various industrial and agricultural wastes in a paddy fields, and (2) assess

116   the impacts of the applications on the availability of nutrients in soil porewater and (3)

117   their loss to surface-water.

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126   **2. Materials and methods**

127   *2.1. Study site*

128   Our study was conducted at the Wufeng Agronomy Field of the Fujian Academy of

129   Agricultural Sciences in Fujian province, southeastern China (26.1°N, 119.3°E) (Fig.

130   1), during the early rice crop (16 April – 16 July) in 2014. The proportions of sand, silt

131   and clay particles in the top 15 cm of the soil, which was poorly drained, were 28, 60

132   and 12%, respectively. This soil layer had a bulk density of 1.1 g cm^{-3}, pH of 6.5,

133   organic carbon content of 18.1 g kg^{-1}, total N (TN) content of 1.2 g kg^{-1} and total P (TP)

134   content of 1.1 g kg^{-1}. The water level was maintained at 5-7 cm above the soil surface

135   throughout the growing season by an automatic water-level controller, during the final

136   tiller period crop was dried during one week and thereafter wet and dry alternation

137   management was used. Finally the paddy field was last drained one week before the

138   harvest.

139   We tested five experimental treatments: amendments with biochar, steel slag, shell

140   slag, gypsum slag and silicate and calcium slag (produced from steel slag; *hereafter*

141   *silicate-calcium slag*). The main characteristics of the waste amendments are described

142   by Wang et al. (2016, submitted). We established three replicate plots (10 × 10 m) for

143   each treatment and an untreated control in which the rice seedlings (cv. Hesheng 10)

144   were inserted in the soil to a depth of 5 cm with a spacing of 14 × 28 cm using a rice

145   transplanter.

146   All control and treatment plots received the same water and fertilizer management.

147   The field was plowed to a depth of 15 cm with a moldboard plow and leveled two days

148 before rice transplantation. Mineral fertilizers were applied using standard practices for

149 rice crops in southern China, with three splits of complete (N-P_2O_5-K_2O=16-16-16%;

150 Keda Fertilizer Co., Ltd.) and urea (46% N) fertilizers in both the control and treated

151 plots. A basal fertilizer was applied one day before transplantation at rates of 42 kg N

152 ha^{-1}, 40 kg P_2O_5 ha^{-1} and 40 kg K_2O ha^{-1}. The second application was broadcasted

153 during the tiller initiation stage (seven days after transplanting (DAT)) at rates of 35 kg

154 N ha^{-1}, 20 kg P_2O_5 ha^{-1} and 20 kg K_2O ha^{-1} and the third application was broadcasted

155 during the panicle initiation stage (56 DAT) at rates of 18 kg N ha^{-1}, 10 kg P_2O_5 ha^{-1}

156 and 10 kg K_2O ha^{-1}.

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158 *2.2. Collection of surface water and soil porewater*

159 Surface water and porewater were sampled *in situ* once a week from 16 April to 16 July

160 2014. Samples of surface water were collected using a 50-ml plastic syringe equipped

161 with a 3-way stopcock. Three specially designed PVC tubes (5.0 cm inner diameter)

162 were installed to a depth of 15 cm in each plot. Porewater samples were collected using

163 50-ml syringes and then separated into two parts: about 10 ml were injected into pre-

164 evacuated 20-ml vials, and the remainder 40 ml was injected into 100-ml sample vials.

165 The samples of both surface water and porewater were stored in a cool insulated box in

166 the field until transported to the laboratory where they were stored at -20 °C until the

167 analysis of the nutrients and GHGs.

168

169 *2.3. Measurement and calculation of dissolved CO_2, CH_4 and N_2O*

170 The sample vials were thawed at room temperature and then vigorously shaken for 5

171 min to equilibrate the CH_4 concentrations between the water and the headspace. Gas

172 samples were collected from the headspace of the vials and analyzed for CO_2, CH_4 and

173 N_2O concentrations by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-

174 2014, Kyoto, Japan).

175   The concentrations (C) of CO_2, CH_4 and N_2O dissolved in the water were

176 calculated by (Ding et al., 2003):

$$C = \frac{Gh \cdot Vh}{22.4 \cdot Vp}$$

177

178 where Gh is the CO_2, CH_4 and N_2O concentration ($\mu l\ l^{-1}$) in the air samples from the

179 vials, Vh is the volume of air in the vial (ml) and Vp is the volume of the water in the

180 vial (ml).

181

182 *2.4. Measurement of nutrient concentrations in the surface water and porewater*

183 The concentrations of NH_4^+, NO_2^-, NO_3^-, TN and TP in the surface water and porewater

184 were determined using a sequence flow analyzer (San^{++}, SKALAR Corporation

185 production, Breda, The Netherlands), the concentration of dissolved organic carbon

186 (DOC) was determined using a TOC Analyzer (TOC-V CPH, Shimadzu Corporation,

187 Kyoto, Japan) and SO_4^{2-} and Cl^- concentrations were determined by ICS2100 ion

188 chromatography (American Dionex Production, Sunnyvale, USA).

189

190 *2.5. Measurement of GHG emissions*

191 Static closed chambers were used to measure CO_2, CH_4 and N_2O emissions during the

192 study period. we deployed three replicate chambers in each treatment and the chambers

193 and sampling are described in detail by Wang et al. (2015). Gas flux was measured

194 weekly in all chambers. Gas samples were collected from the chamber headspace using

195 a 100-ml plastic syringe with a three-way stopcock 0, 15 and 30 min after deployment

196 of the upper compartment. The samples were immediately transferred to 100-ml air-

197 evacuated aluminum-foil bags (Delin Gas Packaging Co., Ltd., Dalian, China), sealed

198 with butyl rubber septa and transported to the laboratory. The CO_2, CH_4 and N_2O

199 concentrations were measured by gas chromatography (Shimadzu GC-2010 and

200 Shimadzu GC-2014, Kyoto, Japan). The GHG fluxes were calculated by the change of

201 concentrations over time (Wang et al., 2015).

202

203 *2.6. Measurement of soil GHG production*

204 Gas production was measured weekly in all chambers. CO_2, CH_4 and N_2O production

205 in the top 15 cm of soil was determined by anaerobic incubation (Wang et al. 2010).

206 Ten grams of fresh soil were placed into 120-ml incubation bottles, and 20 ml (two

207 volumes of water on a w/v soil/water basis) of distilled water were added. The bottles

208 were sealed with rubber stoppers. The bottles were purged with N_2 for 3 min to replace

209 the headspace oxygen (O_2) and were then incubated at room temperature for 5 d. Two

210 milliliters of gas were extracted by a syringe from the headspaces at 1, 3 and 5 d. CO_2,

211 CH_4 and N_2O concentrations were measured by gas chromatography (Shimadzu GC-

212 2010 and Shimadzu GC-2014, Kyoto, Japan). GHG production was calculated by the

213 change of concentration over time (Wang et al., 2015).

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2.7. Statistical analysis

The difference in the nutrient concentrations of the surface water and porewater and in the dissolved CO_2, CH_4 and N_2O concentrations among the treatments and controls were tested for statistical significance by repeated-measures analyses of variance (RM-ANOVAs). The relationships between dissolved GHG emissions and porewater properties were determined by Pearson correlation analysis. These statistical analyses were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA).

We also performed multivariate statistical analyses. We determined the overall differences in the changes of the porewater N fractions (dissolved NH_4^+, NO_3^- and NO_2^-), organic carbon (SOC) and CO_2, CH_4 and N_2O concentrations among the control and treated soils using general discriminant analysis (GDA), including the component of the variance due to the different sampling dates as an independent categorical variable. Discriminant analyses consist of a supervised statistical algorithm that derives an optimal separation between groups established a priori by maximizing between-group variance while minimizing within-group variance (Raamsdonk et al., 2001). GDA is thus an adequate tool for identifying the variables most responsible for the differences among groups while controlling the component of the variance due to other categorical variables. The GDA was performed using Statistica 6.0 (StatSoft, Inc., Tulsa, USA).

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236 **3. Results**

237 *3.1. Surface-water nutrient concentrations*

238 Surface-water concentrations of NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^- varied

239 significantly among the treatments and sampling dates ($P<0.01$, Tables 1 and S1). The

240 temporal variations of mean NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^-

241 concentrations in the control and treatment plots are shown in Fig. 2. Mean values of

242 all sampling days of NH_4^+ concentrations in the plots amended with the steel, shell and

243 silicate-calcium slags were 24, 21 and 33% lower, respectively, than those in the

244 controls ($P<0.05$, Tables 1 and S1). Mean values of all sampling days of NO_2^-

245 concentrations in the plots amended with steel slag, biochar, shell slag, gypsum slag

246 and silicate-calcium slag were 48, 27, 36, 43 and 39% lower, respectively, than those in

247 the controls ($P<0.05$). Mean values of all sampling days of NO_3^- concentrations in the

248 plots amended with the steel, shell, gypsum and silicate-calcium slags were 67, 75, 70

249 and 75% lower, respectively, than those in the controls ($P<0.05$). Mean values of all

250 sampling days of TN concentrations in the plots amended with the steel and shell slags

251 were 29 and 32% lower, respectively, than those in the controls ($P<0.05$). Mean values

252 of all sampling days of TP concentrations in the plots amended with the shell slag were

253 68% lower than those in the controls ($P<0.05$) (Table 1). Mean values of all sampling

254 days of SO_4^{2-} concentrations in the plots amended with the gypsum and silicate-calcium

255 slags were 25 times higher and 29% higher, respectively, than those in the controls

256 ($P<0.05$, Tables 1, S1 and S2). Mean values of all sampling days of Cl^- concentrations

257 in the plots amended with the biochar, gypsum slag and silicate-calcium slags were 26

258 and 43%, 310% higher, respectively, than those in the controls ($P<0.05$, Tables 1 and

259 S1).

260

261 *3.2. Porewater nutrient concentrations*

262 Porewater NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^- concentrations varied

263 significantly among the treatments and sampling dates ($P<0.01$, Tables 1 and S3). The

264 temporal variations of mean NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^-

265 concentrations in the control and treatment plots are shown in Table S4. Mean values

266 of all sampling days of NH_4^+ concentrations in the plots amended with biochar were

267 26% lower than those in the controls ($P<0.05$, Tables 1, S3 and S4). Mean values of all

268 sampling days of NO_3^- concentrations in the plots amended with the gypsum and

269 silicate-calcium slags were 58 and 81% higher, respectively, than those in the controls

270 ($P<0.05$). Mean values of all sampling days of TN concentrations in the plots amended

271 with the steel, shell slag, gypsum and silicate-calcium slags were 25, 29, 35 and 48%

272 higher, respectively, than those in the controls ($P<0.05$). Mean values of all sampling

273 days of TP concentrations in the plots amended with the silicate-calcium slag were 95%

274 higher than those in the controls ($P<0.05$). Mean values of all sampling days of DOC

275 concentrations in the plots amended with the biochar were 22% higher than those in the

276 controls ($P<0.05$). Mean values of all sampling days of SO_4^{2-} concentrations in the plots

277 amended with the gypsum and silicate-calcium slags were 25 times higher and 52%

278 higher, respectively, than those in the controls ($P<0.05$, Fig. 3, Tables 1, S3 and S4).

279 Mean values of all sampling days of Cl^- concentrations in the plots amended with the

280 biochar, gypsum and silicate-calcium slags were 21, 27 and 149% higher, respectively,

281 than those in the controls ($P<0.05$). The soil pH in the control plots (6.07 ±0.04) was

282 lower ($P<0.05$) than soil pH in the plots amended with steel slag, biochar, shell slag,

283 gypsum slag and silicate-calcium slag (6.31 ± 0.02, 6.33 ± 0.02, 6.30 ± 0.02, 6.16 ±

284 0.03 and 6.81 ± 0.03, respectively).

285

286 *3.3. Porewater dissolved CO_2, CH_4 and N_2O concentrations*

287 Porewater dissolved CO_2, CH_4 and N_2O concentrations varied significantly among the

288 treatments and sampling dates ($P<0.01$, Tables 1 and S5). The temporal variations of

289 mean CO_2, CH_4 and N_2O concentrations in the control and treatment plots are shown in

290 Table S6. Mean values of all sampling days of CO_2 concentrations in the plots amended

291 with the silicate-calcium slag were 68% lower than those in the controls ($P<0.05$)

292 (Table 1). Mean values of all sampling days of CH_4 concentrations in the plots amended

293 with the gypsum and silicate-calcium slags were 92 and 70% lower, respectively, than

294 those in the controls ($P<0.05$) (Table 1). Mean values of all sampling days of N_2O

295 concentrations did not differ significantly among the amended and control plots (Table

296 1).

297

298 *3.4. Relationships of the porewater dissolved CO_2, CH_4 and N_2O concentrations with*

299 *the nutrient concentrations*

300 The dissolved CO_2 concentration was significantly and negatively correlated with

301 porewater NH_4^+, NO_2^-, NO_3^-, TN, TP and Cl^- concentrations (Table 2). The dissolved

302   CH$_4$ concentration was negatively correlated with porewater NH$_4^+$, TN, TP, DOC, SO$_4^{2-}$

303   and Cl$^-$ concentrations. The dissolved N$_2$O concentration was correlated positively with

304   porewater NO$_2^-$, NO$_3^-$, DOC and SO$_4^{2-}$ concentrations and negatively with porewater

305   NH$_4^+$ concentration.

306

307   *3.5. Relationship among porewater dissolved CO$_2$, CH$_4$ and N$_2$O and GHG production*

308   *and emission*

309   The dissolved CO$_2$ concentration was positively correlated with dissolved CH$_4$ and N$_2$O

310   concentrations (Table 2), but the dissolved CH$_4$ and N$_2$O concentrations were not

311   significantly correlated. The dissolved CO$_2$ concentration was positively correlated

312   with CO$_2$ production and emission (Table 3). The dissolved CH$_4$ concentration was

313   positively correlated with CH$_4$ production and emission (Table 3). The dissolved N$_2$O

314   concentration was positively correlated with N$_2$O production but was not significantly

315   correlated with N$_2$O emission (Table 3).

316

317   *3.6. GDA analysis*

318   Soil porewater CO$_2$, SO$_4^{2-}$, Cl$^-$, TN and NH$_4^+$ concentrations significantly separated

319   the soil samples in the GDA (Table S7). The high SO$_4^{2-}$ concentrations in the plots

320   amended with gypsum slag and the Cl$^-$ concentrations in the plots amended with the

321   silicate-calcium slag were the most important differences in porewater concentrations

322   (Fig. 2, Table S8). The overall differences were similar among the control plots and the

323   plots amended with the biochar and the steel and shell slags.

4. Discussion

324

325 The results showed that the industrial and agricultural wastes applied to the surface soil

326 acted as reservoirssources of nutrients for the soil and as a filter to prevent the loss of

327 nutrients from the soil to the surface water of these paddy fields. Less nutrients were

328 lost from soil porewater to surface water so nutrient concentrations increased in

329 porewater and decreased in surface water. Total soil N and P and soil dissolved NO_3^-

330 increased in soils amended with the industrial and agricultural wastes. This study also

331 provides evidence that biochar and steel, shell and silicate-calcium slags enhanced

332 carbon sequestration by paddy fields soils, improved soil fertility, increased rice yields

333 and mitigated GHG emission.

334

335 4.1. *Treatment effects on surface-water nutrient concentrations*

336 The application of the waste amendments, except the silicate-calcium slag, decreased

337 the nutrient concentrations in the surface water, especially for the steel and shell slags.

338 These two amendments decreased N concentrations in the surface water, and the shell

339 slag also decreased the concentrations of P in the surface water. Previous studies

340 reported that slag filters in blast furnaces could remove N and P from waste-

341 stabilization pond effluents (Hamdan and Mara, 2013; 2014) and also that steel slag

342 amendment could decrease N and P nutrient concentrations in the surface water in

343 subtropical paddy fields (Zeng et al., 2012). These amendments can remove N and P in

344 several ways. They are porous and provide more nutrient adsorption sites, which

345 promotes the sorption of nutrients and decreases their release to the surface water

346 (Agyei et al., 2002; He et al., 2013). The amendments were also alkaline substances, so

347 their application increases the soil pH. The soil pH in the plots amended with steel slag,

348 biochar, shell slag, gypsum slag and silicate-calcium slag were higher than in control

349 plots and similar to those reported in a previous study using similar amendments such

350 as lime and gypsum (Zambrosi et al., 2007).Higher pHs of soil and soil water promote

351 the reaction of basic ions such as Ca^{2+}, Fe^{2+} and Mg^{2+} with OH^- in aqueous solutions,

352 and the products then precipitate. These reactions liberate the sites of electric charge on

353 the surfaces of soil particles and applied waste substances, thereby allowing the

354 adsorption of other nutrient ions such as NO_3^-, NH_4^+ or soluble phosphate ions (Ye et

355 al., 2006), as has been observed after amendments with industrial and agricultural

356 wastes in previous studies (Agyei et al., 2002; Kostantinos et al., 2006; Ali et al., 2008).

357 The surface-water DOC concentrations also decreased slightly in the amended plots,

358 which is an important indication that industrial and agricultural waste can fix carbon,

359 and thus decrease the loss of DOC in the surface water. Conversely, the concentrations

360 of Ca^{2+}, Fe^{3+} and Mg^{2+} in the surface water increased in the amended plots, because the

361 amendments contained these ions (Agyei et al., 2002; He et al., 2013). The industrial

362 and agricultural wastes were rich in silicon, calcium and potassium, which are essential

363 nutrients for rice growth (Luo et al., 2002).

364

365 *4.2. Treatment effects on soil porewater nutrient concentrations*

366 The effects of the amendments on the soil porewater differed and were frequently

367 contrary to the effects on the surface water described above (Figs. 2 and 3). Porewater

368   NH_4^+, NO_2^-, NO_3^-, TN, TP, DOC, SO_4^{2-} and Cl^- concentrations varied significantly

369   among the treatments and sampling dates (Fig. 3). The biochar decreased the NH_4^+

370   concentration in the porewater, but most of the other amendments increased the

371   porewater nutrient concentrations, at least at some times during the growing season.

372   The steel, gypsum and silicate-calcium slags increased the porewater nutrient

373   concentrations the most. A previous study had reported that amendment with steel slag

374   increased N and P nutrient concentrations in the porewater of a subtropical paddy field

375   (Zeng et al., 2012).

376   The increase in soil pH associated with amendments with industrial and

377   agricultural wastes, such as steel slag, can increase P availability (Wang et al., 2014b;

378   2015) and hence rice production (Ali et al., 2009; 2012). The addition of silicate ions

379   (for amendments with steel and silicate-calcium slags) can also increase P availability

380   by displacing phosphate from ligand-exchange sites (Roy et al., 1971; Lee et al., 2004)

381   and/or decreasing phosphate sorption on soil colloids (Shariatmadari and Mermut,

382   1999). In our study, the increase in the N fraction in the porewater at some sampling

383   times may also have been caused by the actions of the above mechanisms on P. The

384   mean SO_4^{2-} concentrations in the porewater were significantly higher in the plots

385   amended with the gypsum and silicate-calcium slags than in the control plots. The

386   increases in sulfate may have had different causes with the different amendments. The

387   gypsum slag contains high levels of sulfate, and the silicate-calcium slag would increase

388   soil ferric concentrations relative to the control, which would inhibit the reduction of

389   sulfate in the soil solution (Lovley and Phillips, 1987), thereby increasing sulfate

390   concentrations in the porewater.

391

392   *4.3. Treatment effects on soil porewater dissolved GHG concentrations*

393   The dissolved CO_2 concentration varied during the growing season, increasing with

394   rice growth and temperature. Temperature plays an important role in controlling

395   dissolved CO_2 concentrations, due to its control of biological activity (Inglett et al.,

396   2012). The increase in dissolved CO_2 concentration may have been due to the

397   enhancement of soil microbial activity (Vogel et al., 2014) or to altered plant-root

398   respiration. Some amendments, such as the silicate-calcium slag, that contain higher

399   levels of Ca^{2+} can decrease dissolved CO_2 concentrations. These amendments would

400   increase the pH, facilitating the absorption of CO_2 by the carbonate-bicarbonate

401   buffer system (Gilfillan et al., 2009; Liu et al., 2011; Ma et al., 2013). Ca^{2+} can also

402   combine with CO_2 to form $CaCO_3$, which is deposited in the soil and decreases the

403   amount of dissolved CO_2 and thus CO_2 emission (Phillips et al., 2013).

404   The dissolved CH_4 concentration also varied during the growing season (Table

405   3). The concentration was lowest after rice transplantation and during the drainage

406   of the paddy field when the soil was not strictly anaerobic, which decreased the

407   population of methanogenic archaea (Minamikawa et al., 2014). Dissolved CH_4

408   concentrations were also generally lowered by the waste amendments, especially by

409   the gypsum and silicate-calcium slags. These decreases were consistent with their role

410   as electron acceptors, which can inhibit CH_4 production by competing with CO_2 as an

411   electron acceptor, thus reducing the dissolved CH_4 concentration. The lower

412   concentrations in our study may have been due to one or more of several processes:

413   (1) both Fe^{3+} and SO_4^{2-} are alternative electron acceptors preferentially used by

414   microbes, so their presence would decrease the amount of CH_4 produced by

415   methanogenic bacteria (Gauci et al., 2008; Ali et al., 2013), (2) competition with

416   methanogens for C substrates (Sakthivel et al., 2012) and/or (3) an increase in redox

417   potential (Ali et al., 2008, 2009).

418   The dissolved N_2O concentration also varied during the growing season and was

419   correlated with N_2O and CH_4 production (Table 2). The dissolved N_2O concentration

420   did not immediately increase after the application of the N fertilizer to all treatments

421   plots, perhaps because the nitrogenous fertilizer contained mostly NH_4^+ rather than

422   NO_3^-, and NH_4^+ was the most common form of N in our paddy fields soils. Most of the

423   fertilizer was applied before rice transplantation and during the tillering period when

424   the soil was an anaerobic environment caused by flooding the paddy fields soil

425   surface. The production of N_2O in anaerobic environments is mainly due to

426   denitrification (NO_3^- is the main substrate for denitrification). The NO_3^- concentration,

427   however, was very low, so the denitrification of NO_3^- reduction should have been very

428   slow. The rice also grew quickly after the tillering stage, so photosynthesis increased,

429   producing more O_2. This O_2 would then be transported and released to the soil, where

430   it could promote nitrification and denitrification, which could in turn produce more

431   N_2O using the NH_4^+ substrates from the accumulated nitrogenous fertilizer (Rochette

432   et al., 2010). Finally, the dissolved N_2O concentration increased with N_2O production

433   (Table 2), and the porewater N_2O concentrations did not differ significantly among the

434 amended and control plots.

435

436 **5. Conclusions**

437

438 1.Our results showed that the applications of biochar and steel, shell and silicate-

439 calcium slags were associated with a decrease of the concentrations of dissolved GHGs.

440

441 2. The industrial and agricultural wastes applied to the surface soil acted as reservoirs/

442 sources of nutrients for the soil and as a filter to prevent the loss of nutrients from the

443 soil to the surface water in these paddy fields. In particular total soil N and P and soil

444 dissolved NO_3^- increased in soils amended with the industrial and agriculture wastes.

445

446 3. Industrial and agricultural wastes generally represent very low-cost materials,

447 which facilitates their use on a large scale. They thus should be considered as good

448 alternatives to the excessive use of industrial fertilizers in order to achieve a more

449 sustainable agriculture by mitigating nutrient and GHG emissions from rice production

459   **Conflicts of Interest**

460   The authors declare no conflicts of interest.

461

462   **References**

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Tables

Table1. The annual means (± S.E.) of the different studied variables in different treatments plots. Different letters indicate significant differences among treatments ($P<0.05$) for each variable.

Variables	Control	Steel slag	Biochar	Shell slag	Gypsum slag	Si-Ca slag
Surface-water properties (mg l^{-1})						
[NH$_4^+$]	1.71±0.34ab	1.30±0.35ac	1.45±0.33a	1.34±0.27ac	1.87±0.58a	1.15±0.17ac
[NO$_2^-$]	0.15±0.03a	0.08±0.02b	0.11±0.02b	0.10±0.03b	0.09±0.02b	0.09±0.01b
[NO$_3^-$]	1.06±0.43a	0.35±0.13b	0.47±0.17ab	0.26±0.07b	0.32±0.10b	0.26±0.09b
[TN]	4.69±0.93a	3.31±0.62b	3.64±0.57ab	3.18±0.48b	3.76±0.74ab	3.77±0.63ab
[TP]	0.19±0.06ab	0.08±0.02b	0.09±0.02b	0.06±0.01bc	0.11±0.05b	0.26±0.04a
[DOC]	38.04±7.69a	23.75±4.09b	22.46±3.29b	23.46±3.40b	22.19±2.72b	27.40±3.72ab
[SO$_4^{2-}$]	22.04±4.22c	21.06±4.84c	22.24±4.50c	22.71±5.06c	552.56±83.11a	28.48±6.09b
[Cl$^-$]	15.41±2.88c	15.79±3.01bc	19.36±4.05b	16.49±3.47bc	22.01±4.49b	63.12±25.40a
Porewater properties (mg l^{-1})						
[NH$_4^+$]	1.19±0.29a	1.23±0.29a	0.74±0.23b	1.15±0.38a	1.26±0.29a	1.39±0.31a
[NO$_2^-$]	0.25±0.05a	0.20±0.05a	0.24±0.05a	0.16±0.04a	0.25±0.05a	0.21±0.04a
[NO$_3^-$]	0.42±0.09b	0.51±0.09ab	0.51±0.09ab	0.54±0.10ab	0.68±0.11a	0.74±0.15a
[TN]	2.49±0.26b	3.07±0.32a	2.69±0.26ab	3.21±0.45a	3.37±0.39a	3.86±0.35a
[TP]	0.40±0.19b	0.65±0.30ab	0.51±0.24ab	0.74±0.38ab	0.64±0.30ab	0.80±0.22a
[DOC]	16.48±1.86b	18.59±2.05ab	20.94±2.65a	16.86±1.94ab	17.42±2.16ab	17.92±1.14ab
[SO$_4^{2-}$]	22.55±3.93c	19.65±4.22c	25.01±5.05bc	24.52±5.70bc	747.53±84.71a	38.06±6.49b
[Cl$^-$]	17.75±2.34c	18.12±2.43bc	21.29±2.88b	18.21±2.41bc	22.74±3.09b	41.78±7.70a

Dissolved greenhouse gases (μmmol l⁻¹)						
$[CO_2]$	655.55±60.20ab	575.54±59.77b	807.36±66.53a	532.49±48.44b	438.99±45.12b	215.94±30.23c
$[CH_4]$	10.94±2.73a	7.66±3.19ab	6.19±1.22abc	5.08±1.19abc	0.79±0.20d	3.23±1.17c
$[N_2O]$	0.10±0.02a	0.14±0.04a	0.13±0.04a	0.08±0.03a	0.14±0.06a	0.04±0.01a

Different letters indicate significant differences among treatments ($P<0.05$) for each variable.

Table 2

Correlation coefficients between the porewater concentrations of nutrients and dissolved CO_2, CH_4 and N_2O gases and of dissolved ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), total nitrogen (TN), total phosphorus (TP), sulphate (SO_4^{2-}) and chloride (Cl^-).

Variable	Dissolved CH_4	Dissolved N_2O	NH_4^+	NO_2^-	NO_3^-	TN	TP	DOC	SO_4^{2-}	Cl^-
Dissolved CO_2	0.416**	0.143*	-0.416**	-0.167**	-0.259**	-0.516**	-0.168**	-0.019	-0.086	-0.387**
Dissolved CH_4	1	-0.047	-0.199**	-0.016	-0.074	-0.241**	-0..112*	-0.111*	-0.165**	-0.190**
Dissolved N_2O	-0.047	1	-0.112*	0.165**	0.109*	-0.047	-0.030	0.581**	0.187**	0.107
NH_4^+	-0.199**	-0.112*	1	-0.088	-0.195**	0.807**	0.660**	0.182**	0.103	0.580**
NO_2^-	-0.016	0.165**	-0.088	1	0.550**	0.091	0.010	-0.044	0.028	-0.024
NO_3^-	-0.074	0.109*	-0.195**	0.550**	1	0.152*	-0.122*	-0.043	0.070	-0.023
TN	-0.241**	-0.047	0.807**	0.091	0.152*	1	0.614**	0.166**	0.151*	0.605**
TP	-0.112*	-0.030	0.660**	0.010	-0.122*	0.614**	1	0.077	0.094	0.333**
DOC	-0.111*	0.581**	0.182**	-0.044	-0.043	0.166**	0.077	1	0.134*	0.448**
SO_4^{2-}	-0.165**	0.187**	0.103	0.028	0.070	0.151*	0.094	0.134*	1	0.143*

*, correlation is significant at the 0.05 level; **, correlation is significant at the 0.01 level.

1 **Table 3**

2 Correlation coefficients of the concentrations of dissolved CO_2, CH_4, and N_2O with the

3 production and emission of the corresponding gases.

Variable	Dissolved CO_2	Dissolved CH_4	Dissolved N_2O
Production	0.190**	0.217**	0.109*
Emission	0.188**	0.369**	0.096

4 *, correlation is significant at the 0.05 level; **, correlation is significant at the 0.01 level.

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7   **Figure legends**

8   **Fig. 1.** The location of the study area and sampling sites (▲) in Fujian province,

9   southeastern China.

10   **Fig. 2.** Biplot of the standardized canonical discriminate function coefficients for the

11   first two roots representing the soil variables as independent variables and the various

12   grouping dependent factors (means ± S.E. of canonical scores) corresponding to the soil

13   amendments.

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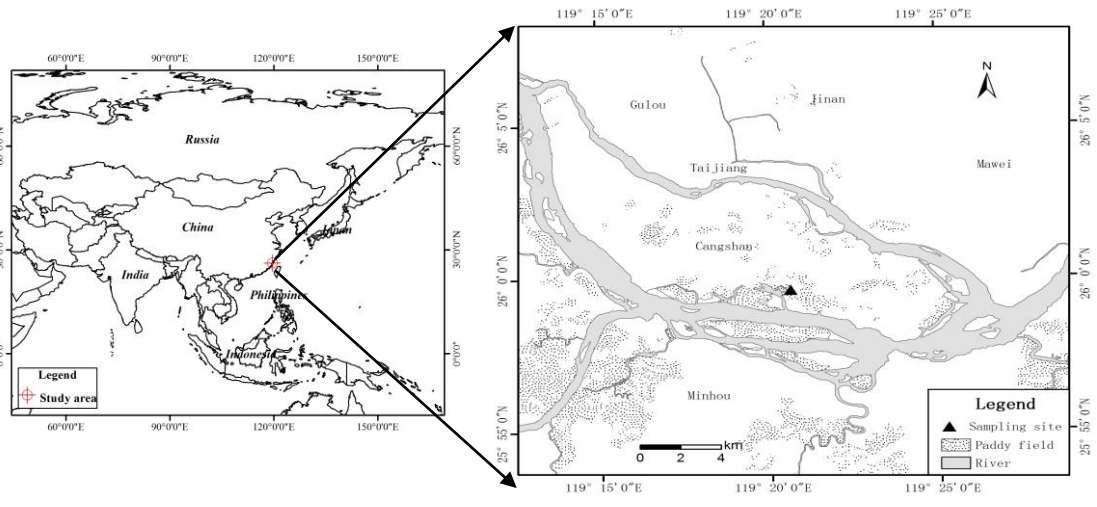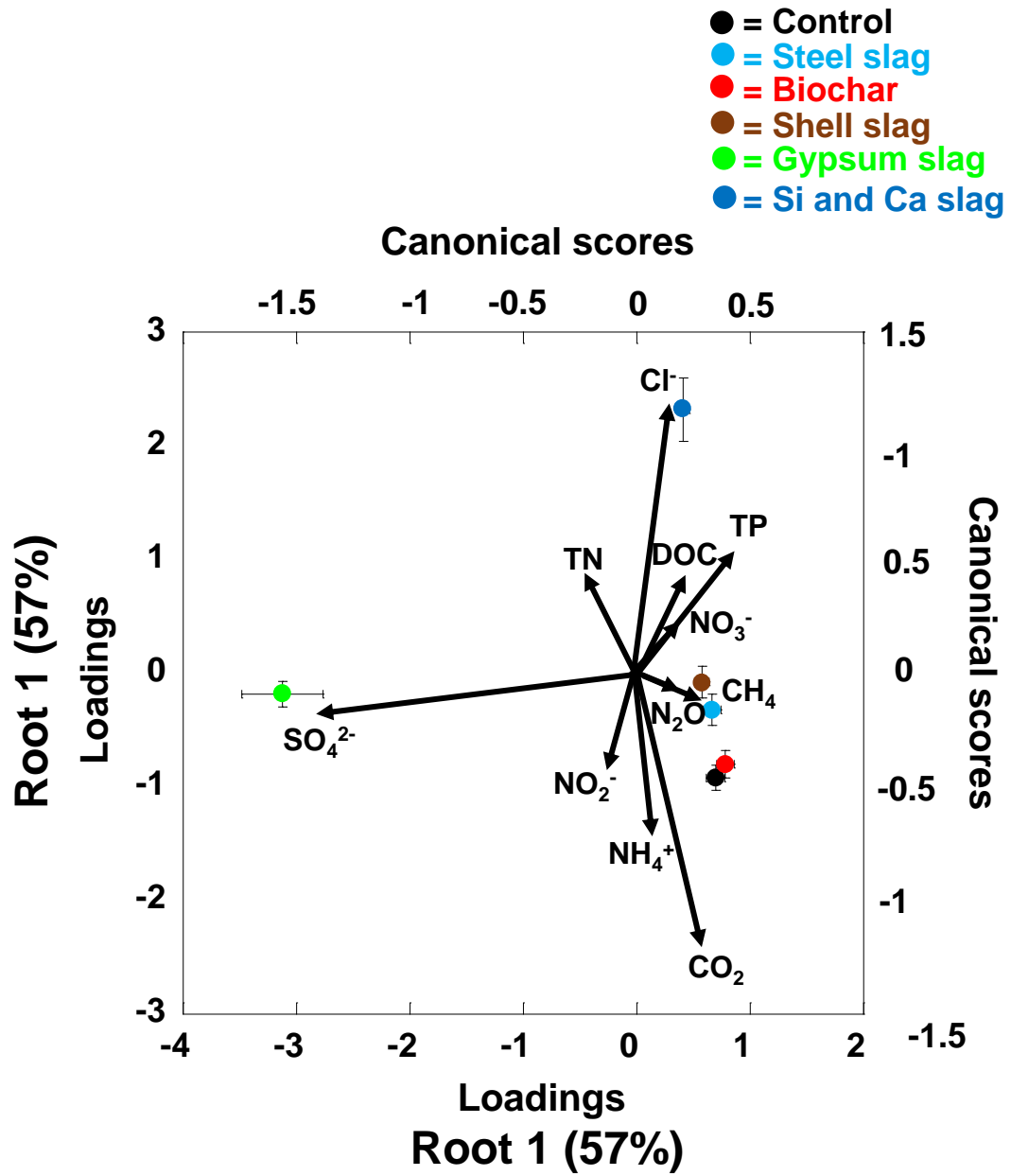54
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Fig. 2