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

4 W. Wang^{a,b*}, C. Zeng^{a,b}, J. Sardans^{c,d}, C. Wang^{a,b}, D. Zeng^a, J. Peñuelas^{c,d}

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6 ^a*Institute of Geography, Fujian Normal University, Fuzhou 350007, China*

7 ^b*Key Laboratory of Humid Subtropical Eco-geographical Process, Ministry of Education,*
8 *Fujian Normal University, Fuzhou 350007, China*

9 ^c*CSIC, Global Ecology Unit CREAM-CEAB-CSIC-UAB. 08913 Cerdanyola del Vallès.*
10 *Catalonia. Spain*

11 ^d*CREAF. 08913 Cerdanyola del Vallès. Catalonia. Spain*

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14

15 **Author to whom correspondence should be addressed; E-Mail: wangweiqi15@163.com Tel.: +86-*
16 *591-83465214; Fax: +86-591-83465397.*

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19 **Type:** *Article*

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

22

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 CO₂ concentration was 68% lower in the plots amended with silicate and calcium slag
38 than the control plots. Mean dissolved CH₄ concentrations were 92 and 70% lower in
39 the plots amended with gypsum slag and silicate and calcium slag, respectively. Mean
40 dissolved N₂O concentrations did not differ significantly among all plots. The
41 concentrations of dissolved CO₂ and CH₄ were correlated with their production and
42 emission. The concentration of dissolved CO₂ was negatively correlated with porewater
43 concentrations of NH₄⁺, NO₂⁻, NO₃⁻, TN, TP and Cl⁻. The concentration of dissolved
44 CH₄ was negatively correlated with porewater concentrations of NH₄⁺, 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.

51

52 *Keywords: Porewater nutrients; dissolved CH_4 ; dissolved N_2O ; dissolved CO_2 ;*

53 *Industrial and agricultural wastes*

54

55 **1. Introduction**

56 Rice (*Oryza sativa*) is the most important cereal crop globally, currently feeding over
57 50% of the population (Haque et al., 2015). Rice production, however, needs to increase
58 by 40% by the end of 2030 to cope with the increasing demand by a growing population
59 worldwide (FAO, 2009). The leaching of nutrients from agricultural activities, though,
60 contributes to the eutrophication of aquatic ecosystems and approximately 20% of the
61 total emissions of atmospheric greenhouse gases (GHGs) (Hütsch, 2001).

62 Eutrophication is a major environmental concern (Sunda and Cai, 2012; Sardans
63 et al., 2012; Peñuelas et al., 2012, 2013), with large impacts on water quality and human
64 health (Svirčev et al., 2014). The causes of the sharp increase in water eutrophication
65 driven by increases in nitrogen (N) and phosphorus (P) pollution (Lewis et al., 2011;
66 Sardans et al., 2012) include both point-source (Kiedrzyńska et al., 2014) and nonpoint-
67 source (Vilches et al., 2014) pollution. Agricultural nonpoint-source pollution is the
68 direct cause of 60-70% of the global pollution of rivers and lakes (Zhu, 2006). Methods
69 to minimize these environmental impacts of agricultural activities must be continuously
70 improved. The rates of fertilizer application continue to rise, so the potential risk of
71 nutrient loss from paddy fields and the consequent eutrophication are also increasing
72 (Savci, 2012). Strategies of agricultural management, e.g. water management (Díaz et
73 al., 2012) or the application of straw (Wang et al., 2014a), biogas slurry (Guo et al.,
74 2014) or biochar (Liu et al., 2015), are being investigated and developed to both reduce
75 environmental risks and achieve sustainable rice production. Different studies,
76 however, have come to different conclusions, so further research is clearly warranted.

77 GHGs are produced by microorganisms and stored in porewater. Knowing the
78 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 CO₂, CH₄ and N₂O. 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 CO_2 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-P₂O₅-K₂O=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 P₂O₅ ha⁻¹ and 40 kg K₂O 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 P₂O₅ ha⁻¹ and 20 kg K₂O 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 P₂O₅ ha⁻¹
156 and 10 kg K₂O ha⁻¹.

157

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 CO₂, CH₄ and N₂O*

170 The sample vials were thawed at room temperature and then vigorously shaken for 5
171 min to equilibrate the CH₄ concentrations between the water and the headspace. Gas
172 samples were collected from the headspace of the vials and analyzed for CO₂, CH₄ and
173 N₂O concentrations by gas chromatography (Shimadzu GC-2010 and Shimadzu GC-
174 2014, Kyoto, Japan).

175 The concentrations (*C*) of CO₂, CH₄ and N₂O dissolved in the water were
176 calculated by (Ding et al., 2003):

$$177 \quad C = \frac{Gh \cdot Vh}{22.4 \cdot Vp}$$

178 where *Gh* is the CO₂, CH₄ and N₂O concentration (μl 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 NH₄⁺, NO₂⁻, NO₃⁻, 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 SO₄²⁻ 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 CO₂, CH₄ and N₂O 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 CO₂, CH₄ and N₂O
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. CO₂, CH₄ and N₂O 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 N₂ for 3 min to replace
209 the headspace oxygen (O₂) 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. CO₂,
211 CH₄ and N₂O 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).

214

215 *2.7. Statistical analysis*

216 The difference in the nutrient concentrations of the surface water and porewater and in
217 the dissolved CO₂, CH₄ and N₂O concentrations among the treatments and controls
218 were tested for statistical significance by repeated-measures analyses of variance (RM-
219 ANOVAs). The relationships between dissolved GHG emissions and porewater
220 properties were determined by Pearson correlation analysis. These statistical analyses
221 were performed using SPSS Statistics 18.0 (SPSS Inc., Chicago, USA).

222 We also performed multivariate statistical analyses. We determined the overall
223 differences in the changes of the porewater N fractions (dissolved NH₄⁺, NO₃⁻ and NO₂⁻),
224 organic carbon (SOC) and CO₂, CH₄ and N₂O concentrations among the control and
225 treated soils using general discriminant analysis (GDA), including the component of
226 the variance due to the different sampling dates as an independent categorical variable.
227 Discriminant analyses consist of a supervised statistical algorithm that derives an
228 optimal separation between groups established a priori by maximizing between-group
229 variance while minimizing within-group variance (Raamsdonk et al., 2001). GDA is
230 thus an adequate tool for identifying the variables most responsible for the differences
231 among groups while controlling the component of the variance due to other categorical
232 variables. The GDA was performed using Statistica 6.0 (StatSoft, Inc., Tulsa, USA).

233

234

235

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 , $6.16 \pm$
284 0.03 and 6.81 ± 0.03 , respectively).

285

286 *3.3. Porewater dissolved CO₂, CH₄ and N₂O concentrations*

287 Porewater dissolved CO₂, CH₄ and N₂O concentrations varied significantly among the
288 treatments and sampling dates ($P<0.01$, Tables 1 and S5). The temporal variations of
289 mean CO₂, CH₄ and N₂O concentrations in the control and treatment plots are shown in
290 Table S6. Mean values of all sampling days of CO₂ 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 CH₄ 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 N₂O
295 concentrations did not differ significantly among the amended and control plots (Table
296 1).

297

298 *3.4. Relationships of the porewater dissolved CO₂, CH₄ and N₂O concentrations with* 299 *the nutrient concentrations*

300 The dissolved CO₂ concentration was significantly and negatively correlated with
301 porewater NH₄⁺, NO₂⁻, NO₃⁻, TN, TP and Cl⁻ concentrations (Table 2). The dissolved

302 CH₄ concentration was negatively correlated with porewater NH₄⁺, TN, TP, DOC, SO₄²⁻
303 and Cl⁻ concentrations. The dissolved N₂O concentration was correlated positively with
304 porewater NO₂⁻, NO₃⁻, DOC and SO₄²⁻ concentrations and negatively with porewater
305 NH₄⁺ concentration.

306

307 *3.5. Relationship among porewater dissolved CO₂, CH₄ and N₂O and GHG production* 308 *and emission*

309 The dissolved CO₂ concentration was positively correlated with dissolved CH₄ and N₂O
310 concentrations (Table 2), but the dissolved CH₄ and N₂O concentrations were not
311 significantly correlated. The dissolved CO₂ concentration was positively correlated
312 with CO₂ production and emission (Table 3). The dissolved CH₄ concentration was
313 positively correlated with CH₄ production and emission (Table 3). The dissolved N₂O
314 concentration was positively correlated with N₂O production but was not significantly
315 correlated with N₂O emission (Table 3).

316

317 *3.6. GDA analysis*

318 Soil porewater CO₂, SO₄²⁻, Cl⁻, TN and NH₄⁺ concentrations significantly separated
319 the soil samples in the GDA (Table S7). The high SO₄²⁻ 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.

324 **4. Discussion**

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 CO₂ concentration varied during the growing season, increasing with
394 rice growth and temperature. Temperature plays an important role in controlling
395 dissolved CO₂ concentrations, due to its control of biological activity (Inglett et al.,
396 2012). The increase in dissolved CO₂ 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 Ca²⁺ can decrease dissolved CO₂ concentrations. These amendments would
400 increase the pH, facilitating the absorption of CO₂ by the carbonate-bicarbonate
401 buffer system (Gilfillan et al., 2009; Liu et al., 2011; Ma et al., 2013). Ca²⁺ can also
402 combine with CO₂ to form CaCO₃, which is deposited in the soil and decreases the
403 amount of dissolved CO₂ and thus CO₂ emission (Phillips et al., 2013).

404 The dissolved CH₄ 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 CH₄
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 CH₄ production by competing with CO₂ as an
411 electron acceptor, thus reducing the dissolved CH₄ 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

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459 **Conflicts of Interest**

460 The authors declare no conflicts of interest.

461

462 **References**

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Tables

Table 1. The annual means (\pm 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 \pm 0.34ab	1.30 \pm 0.35ac	1.45 \pm 0.33a	1.34 \pm 0.27ac	1.87 \pm 0.58a	1.15 \pm 0.17ac
[NO ₂ ⁻]	0.15 \pm 0.03a	0.08 \pm 0.02b	0.11 \pm 0.02b	0.10 \pm 0.03b	0.09 \pm 0.02b	0.09 \pm 0.01b
[NO ₃ ⁻]	1.06 \pm 0.43a	0.35 \pm 0.13b	0.47 \pm 0.17ab	0.26 \pm 0.07b	0.32 \pm 0.10b	0.26 \pm 0.09b
[TN]	4.69 \pm 0.93a	3.31 \pm 0.62b	3.64 \pm 0.57ab	3.18 \pm 0.48b	3.76 \pm 0.74ab	3.77 \pm 0.63ab
[TP]	0.19 \pm 0.06ab	0.08 \pm 0.02b	0.09 \pm 0.02b	0.06 \pm 0.01bc	0.11 \pm 0.05b	0.26 \pm 0.04a
[DOC]	38.04 \pm 7.69a	23.75 \pm 4.09b	22.46 \pm 3.29b	23.46 \pm 3.40b	22.19 \pm 2.72b	27.40 \pm 3.72ab
[SO ₄ ²⁻]	22.04 \pm 4.22c	21.06 \pm 4.84c	22.24 \pm 4.50c	22.71 \pm 5.06c	552.56 \pm 83.11a	28.48 \pm 6.09b
[Cl ⁻]	15.41 \pm 2.88c	15.79 \pm 3.01bc	19.36 \pm 4.05b	16.49 \pm 3.47bc	22.01 \pm 4.49b	63.12 \pm 25.40a
Porewater properties (mg l⁻¹)						
[NH ₄ ⁺]	1.19 \pm 0.29a	1.23 \pm 0.29a	0.74 \pm 0.23b	1.15 \pm 0.38a	1.26 \pm 0.29a	1.39 \pm 0.31a
[NO ₂ ⁻]	0.25 \pm 0.05a	0.20 \pm 0.05a	0.24 \pm 0.05a	0.16 \pm 0.04a	0.25 \pm 0.05a	0.21 \pm 0.04a
[NO ₃ ⁻]	0.42 \pm 0.09b	0.51 \pm 0.09ab	0.51 \pm 0.09ab	0.54 \pm 0.10ab	0.68 \pm 0.11a	0.74 \pm 0.15a
[TN]	2.49 \pm 0.26b	3.07 \pm 0.32a	2.69 \pm 0.26ab	3.21 \pm 0.45a	3.37 \pm 0.39a	3.86 \pm 0.35a
[TP]	0.40 \pm 0.19b	0.65 \pm 0.30ab	0.51 \pm 0.24ab	0.74 \pm 0.38ab	0.64 \pm 0.30ab	0.80 \pm 0.22a
[DOC]	16.48 \pm 1.86b	18.59 \pm 2.05ab	20.94 \pm 2.65a	16.86 \pm 1.94ab	17.42 \pm 2.16ab	17.92 \pm 1.14ab
[SO ₄ ²⁻]	22.55 \pm 3.93c	19.65 \pm 4.22c	25.01 \pm 5.05bc	24.52 \pm 5.70bc	747.53 \pm 84.71a	38.06 \pm 6.49b
[Cl ⁻]	17.75 \pm 2.34c	18.12 \pm 2.43bc	21.29 \pm 2.88b	18.21 \pm 2.41bc	22.74 \pm 3.09b	41.78 \pm 7.70a

Dissolved greenhouse gases ($\mu\text{mmol l}^{-1}$)						
[CO ₂]	655.55±60.20a b	575.54±59.77b	807.36±66.5 3a	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 ₂ O]	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 CO₂, CH₄ and N₂O gases and of dissolved ammonium (NH₄⁺), nitrite (NO₂⁻), nitrate (NO₃⁻), total nitrogen (TN), total phosphorus (TP), sulphate (SO₄²⁻) and chloride (Cl⁻).

Variable	Dissolved CH ₄	Dissolved N ₂ O	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 ₂ O	-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 CO₂, CH₄, and N₂O with the
3 production and emission of the corresponding gases.

Variable	Dissolved CO ₂	Dissolved CH ₄	Dissolved N ₂ O
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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6

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 \pm S.E. of canonical scores) corresponding to the soil
13 amendments.

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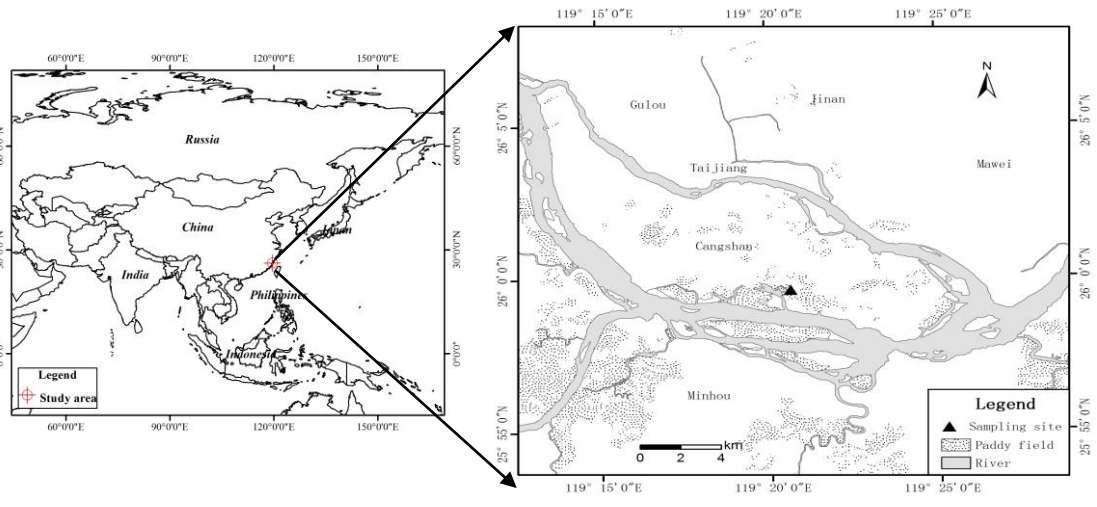
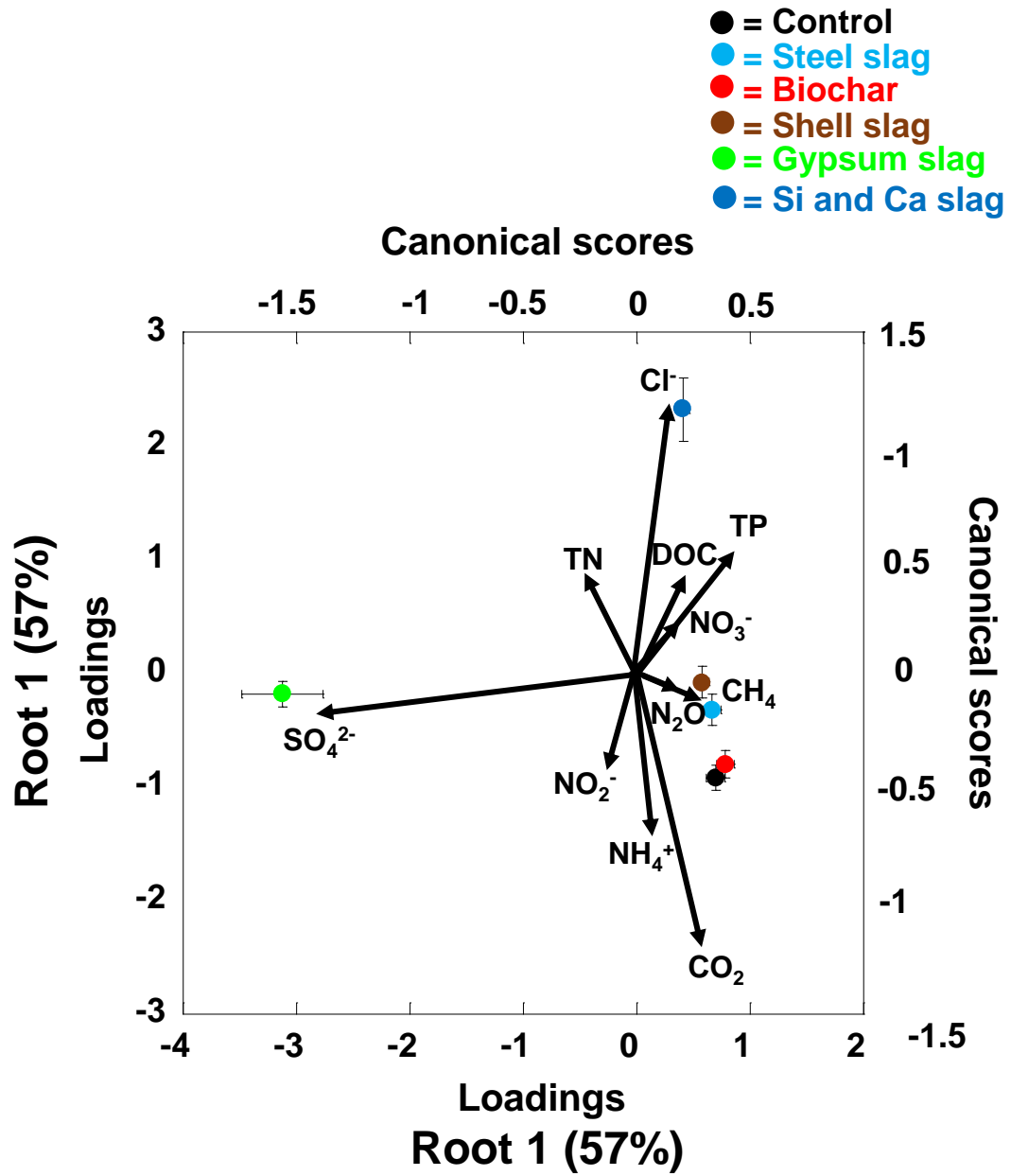


Fig. 1.



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80 Fig. 2