Arsenic immobilization in anaerobic soils by the application of by-product iron materials obtained from the casting industry

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37   **Abstract**

38   Reducing the arsenic (As) concentration in rice grains is of great interest from a human health

39   perspective. Iron (Fe) materials immobilize As in soils, thereby effectively reducing the As

40   concentration in rice grains. We investigated the effect of by-product Fe materials obtained from the

41   casting industry on the As mobility in two soils (soil A and soil B) by a long-term (approximately 100

42   days) flooded soil incubation experiment. The examined Fe materials were spent steel shot (SSS), fine

43   spent casting sand containing steel shot (SCS), and two kinds of residual Fe materials from steel shot

44   production (RIMs). Commercial Fe materials used to immobilize As (zero-valent Fe and ferrihydrite)

45   were tested for comparison. The dissolved As in soil solution of controls for soil A and soil B reached

46   approximately 100 and 800 μg L^{-1}, respectively. The effect on As immobilization of all the by-product

47   Fe materials increased with time and was comparable to or greater than that of commercial ferrihydrite,

48   except for SCS. The additions of SSS and RIMs decreased by more than 90% of the dissolved As in

49   soil A and decreased by more than 50% in soil B after 100 days incubation. Overall, the effect of the

50   by-product Fe materials on the solubility of silicon and phosphorus was much less than that of the

51   commercial Fe materials. Considering the cost advantage over commercial Fe materials, the Fe

52   materials obtained from the casting industry as by-products are promising amendments for the

53   immobilization of As in paddy soils.

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56   ***Key Words: Anaerobic soil, Arsenic immobilization, By-product iron, Phosphorus, Silicon***

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1. Introduction

Arsenic (As) species are hazardous chemicals that are ubiquitous in soils and plants. Since inorganic As species have greater toxicity than methylated species (Jain and Ali 2000), we need a strategy to decrease the concentration of inorganic As in foods. An important source of inorganic As for the Asian population is rice. For example, approximately 60% of the total intake of inorganic As by the average Japanese population was estimated to originate from rice (Oguri *et al*. 2014). In recent years, the Codex Alimentarius Commission adopted maximum permitted concentrations for inorganic As in polished and husked rice of 0.2 mg kg^{-1} and 0.35 mg kg^{-1}, respectively (Codex 2014; Codex 2016). Calculated from an investigation in Japan, approximately 2% of polished rice and 6% of brawn rice grains produced in 2012 contained inorganic As levels exceeding 0.20 mg kg^{-1} and 0.35 mg kg^{-1}, respectively (MAFF 2014). Therefore, agronomic management practices to attenuate the uptake of inorganic As in rice grains must be established.

Honma *et al*. (2016a) showed that the As concentration in rice grains was positively correlated with the dissolved As concentration in soils. Since rice plants absorb As from the soil solution, restricting As dissolution from soil to decrease As uptake by rice is an effective strategy. Rice cultivation under aerobic (i.e., oxidative, water-saving) conditions decreases the As load in rice grains (Xu *et al*. 2009) because the As dissolution from soils decreases under aerobic conditions. However, aerobic cultivation results in the undesired accumulation of another harmful element, cadmium (Cd), in rice grains (Arao *et al*.2009).

Another strategy for decreasing As dissolution from soils is the application of amendments to immobilize As in soils. Many studies reported that iron (Fe) materials such as Fe oxides (including hydroxides and oxyhydroxides) and zero-valent iron (ZVI) successfully immobilize As in soils (Kumpiene *et al*. 2008). Although most of the studies on As immobilization using amendments focused on polluted soils under aerobic conditions, some studies investigated the effect of Fe materials on As

85   mobility in non-polluted anaerobic soils, which are typical of Japanese paddy fields (Makino *et al.*

86   2016; Suda *et al.* 2016). Makino *et al.* (2016) showed that the combination of flooded cultivation and

87   the application of Fe materials was an effective measure to keep both As and Cd in rice grains at low

88   concentrations. Honma et al. (2016b) also demonstrated that commercially available converter furnace

89   slag and Fe hydroxide decreased As and Cd uptake, respectively, by rice plants grown on paddy fields.

90   However, the high cost of Fe materials would limit their agricultural use.

91   Less-expensive Fe materials can be supplied by the casting industry from the use and production

92   of steel shot. After the use of the steel shot, large amounts of spent steel shot (SSS) and fine spent

93   casting sand (SCS) collected with dust collectors are produced. Residual iron materials (RIMs), which

94   contain substantial amounts of Fe materials, are formed in the process of steel shot production. These

95   by-product Fe materials could be sold for agricultural use at low prices. Some reports showed that the

96   application of steel shot was effective at immobilizing As in contaminated soils under aerobic

97   conditions (Boisson *et al.* 1999; Mench *et al.* 2003).

98   Another concern regarding the agricultural use of Fe materials is the possible decrease in silicon

99   (Si) and phosphorus (P) availability because both ZVI and Fe oxides remove these elements from

100   solution (Jordan *et al.* 2007; Zhu *et al.* 2011; Su *et al.* 2001). These elements are useful or essential

101   for the growth of rice plants and affect As uptake by rice because rice plants take up arsenite via the

102   silicate transport pathway (Ma *et al.* 2008) and arsenate via phosphate-arsenate co-transporters

103   (Meharg 2004). Therefore, how the application of Fe materials affects dissolved Si and P in anaerobic

104   soils must be understood.

105   The objectives of the present study were to investigate (1) the effect of by-product Fe materials

106   from the casting industry on As mobility during long-term soil incubation under anaerobic conditions,

107   (2) the effect of Fe materials on solubility of P and Si in soils, and (3) to discuss the availability of these

108   materials as practical amendments to immobilize As in anaerobic paddy fields.

109

2. Materials and methods

2.1 Soil samples

Soil samples were collected from the surface layer of a paddy field in 2013 (Soil A) and from the surface layer of a fallow paddy field in 2010 (Soil B_1) and in 2008 (Soil B_2). These soil samples were air-dried and then screened through 2-mm mesh sieves. Selected soil properties, including soil pH, total carbon and nitrogen content, clay content, content of selectively extractable (with dithionite-citrate, oxalate and pyrophosphate) elements, and hydrochloric acid-extractable As content, were measured as described by Suda *et al*. (2015). The data on the selected soil properties are listed in Table 1.

2.2 Fe materials

Fe materials from the casting industry were obtained from Sintokogio, Ltd. (Nagoya, Aichi, Japan). SSS is a mixture of spent steel shots collected from several foundries after use and then magnetically screened. SCS is composed of fine particles of spent casting sand with a small amount of steel shot. It is collected using dust collectors at foundries after sand removal in casting production. RIM-1 and RIM-2 are residual Fe materials of steel shot production. RIM-1 was obtained under wet conditions and was therefore dried at 30°C for several days. RIM-2 was collected using dust collectors at a steel shot production factory. Two types of commercial Fe materials, ZVI powder (cZVI) (Kobe Steel, Ltd., Tokyo, Japan) and ferrihydrite-based powder (cFH) (Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) were used for comparison. Both cZVI and cFH are commercially supplied as amendments to immobilize As and heavy metals in soils. All the Fe materials were screened using 1-mm mesh sieves before use.

These Fe materials were digested with aqua-regia on a heating block, and the residue was

133 dissolved with hydrofluoric acid in a tightly sealed polypropylene tube at room temperature. Saturated

134 boric acid was added to the tube to dissolve possible insoluble fluorides. The digested solution was

135 used to quantify Fe, Si, Mn and P in the Fe materials. The Fe materials were also digested with an acid

136 mixture (nitric acid:hydrochloric acid, 1:1) on a heating block to analyze the pseudo-total As in the Fe

137 materials. The concentrations of elements in the digested solution were determined by inductively

138 coupled plasma–optical emission spectrometry (ICP-OES; Vista-Pro, Agilent, California, USA) after

139 dilution with ultra-pure water.

140 X-ray diffraction (XRD) analysis was carried out to clarify the mineral composition of the Fe

141 materials. The Fe materials were passed through 212-μm mesh sieves after gentle grinding with an

142 aluminum mortar if necessary and possible. Since most of the SSS particles were >212 μm and too

143 hard to be crushed, both non-sieved (<1 mm) and sieved (<212 μm) fractions were analyzed by XRD.

144 We adopted such a relatively large particle size to minimize the transformations of Fe minerals [e.g.,

145 Fe(II) oxidation] during long-term grinding. The Fe in SCS was condensed using a magnet because of

146 the low Fe content of this material. XRD patterns were obtained under the following conditions: X-

147 ray diffractometer, Rint2200 (Rigaku, Tokyo, Japan); Cu Kα, Ni filter; 40 kV, 40 mA; slit system, 1°–

148 1°–0.15 mm. The scanned range was 20 to 85°2θ in 0.02° steps, with a scanning rate of 1° per min.

149 The particle-size distributions of the Fe materials were evaluated by sieving through mesh sizes

150 of 0.850, 0.710, 0.600, 0.500, 0.425, 0.355, 0.300, 0.250, 0.212, 0.180, 0.150, 0.125, 0.106, 0.075, and

151 0.045 mm.

152

153 *2.3. Anaerobic incubation of soil and quantification of elements in the soil solution*

154 Soils A and B$_1$ were incubated under anaerobic conditions to clarify the effects of the Fe materials on

155 the concentrations of As, Si and P in the soil solution. An air-dried soil sample (10 g, oven-dried basis)

156 and 100 mg of each Fe material were mixed with 30 mL of ultra-pure water in a glass vial. A similar

157 sample without any Fe material was also prepared as a control. After nitrogen gas (N_2) bubbling for 2

158 min, the vial was capped with a butyl rubber cap and then tightly sealed with an aluminum cap. The

159 capped vial was shaken by hand and then incubated at 30 °C for approximately 20, 60 and 100 days.

160 The precise incubation periods were 21, 60, and 102 days for soil A and 20, 60, and 99 days for soil

161 B_1, respectively. The vial was shaken by hand with at 1-2-day intervals. These incubation experiments

162 were performed in triplicate.

163 After incubation, the soil solution was collected by a syringe connected to a needle (NN-2360C,

164 Terumo Corporation, Tokyo, Japan) with a 0.2-μm filter (DG2M-330, Spectrum Laboratories, Inc.,

165 CA, USA). The sampling unit was purged with N_2 before use. Approximately 4.5 mL of filtrate was

166 immediately mixed with 0.5 mL of 1.6 mol L^{-1} nitric acid to prevent Fe-hydroxide precipitation. The

167 acidified filtrate was diluted, and the Fe, Si, P and As concentrations in the diluted solution were

168 measured using ICP-OES and inductively coupled plasma–mass spectrometry (ICP–MS; Elan DRC-

169 e, PerkinElmer, Waltham, MA, USA).

170 The efficacy of the Fe materials in immobilizing As, Si and P in soils at each sampling time was

171 evaluated as the percent decrease in the dissolved elements compared with those in the control soils,

172 as defined by the following equation:

173 $$\text{Percent decrease in dissolved element} = \frac{(CE_{cont} - CE_{Fe})}{CE_{cont}} \times 100 \ (\%) \quad (Eq.\,1)$$

174 where (CE_{Fe}) and (CE_{cont}) are the concentrations of the element in the soil solution incubated with and

175 without the Fe material, respectively.

176

177 ### 2.4. Speciation of As in the soil solid phase

178 Soil B_2 with or without cZVI was anaerobically incubated for 100 days in triplicate as described

179 in the former paragraph. The three incubated soil samples of each treatment were mixed under a N_2

180 atmosphere, and the mixture was then centrifuged to separate the soil solution from the solids. After

181   removing the soil solution, an aliquot of wet soil paste was packed into a polyethylene bag and kept

182   frozen until analysis.

183   As K-edge (11867 eV) X-ray absorption near-edge structure (XANES) spectra were obtained on

184   BL12C of the photon factory, KEK, and on BL5S1 of the Aichi Synchrotron Radiation Center.

185   Reference materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3), and arsenopyrite

186   (FeAsS, Francisco I. Madero Mine, Mexico, N's Mineral) were diluted by boron nitride, and the

187   XANES spectra were collected in the transmission mode. The XANES spectra of the incubated soil

188   pastes were collected in the fluorescence detection mode using a 19-element Ge semiconductor

189   detector. The relative proportion of As species in the soil solid phases were calculated by linear

190   combination fitting (LCF) of the XANES spectra with the reference materials. The fitting range was

191   11855 to 11885 eV. Athena in the Demeter 0.9.25 program package was used for XANES data analysis.

192

193   *2.5. Statistical analysis*

194   The dissolved element concentrations were subjected to two-way analysis of variance (ANOVA).

195   Based on the output from ANOVA, multiple comparisons were made using Tukey's test at a 0.05

196   probability level. All statistical analyses were performed using Microsoft Excel and R software

197   (version 3.1.1).

198

199   **3. Results**

200   *3.1. Properties of Fe materials*

201   Table 2 shows the concentrations of major elements and kinds of XRD-detectable minerals in the

202   Fe materials. The concentrations of Fe and Si followed orders of cZVI > SSS >> RIM-2 > RIM-1 >

203   cFH >>> SCS and SCS >>> RIM-1 = RIM-2 = SSS > cZVI = cFH, respectively. The As and P

204   concentrations ranged from 3.27 to 76.8 mg kg^{-1} and from 102 to 639 mg kg^{-1}, respectively. The major

205 Fe minerals in each Fe material were Fe(0) for SSS, SCS and cZVI; wüstite and magnetite/maghemite

206 for RIM-1 and RIM-2; and ferrihydrite for cFH (Table 2, Fig. S1). Since steel shot-like spherical

207 particles were observed in the <212 mm fraction that accounted for approximately 12% of total weight,

208 the Fe(0) in RIM-2 (Fig. S1, f) should be derived from fine steel particles. All Fe materials were mainly

209 composed of Fe minerals except for SCS, which was dominated by quartz. Quartz in SSS and SCS

210 should originate from casting sand.

211   The particle distributions of the Fe materials are shown in Figure S2. RIM-1, cFH and cZVI

212 contained substantial amounts of particles in their finest fractions (less than 0.045 mm). The coarsest

213 Fe material was SSS. More than 30 wt% of the SSS particles did not pass through a 0.5 mm mesh

214 sieve.

215

216 *3.2. Effect of Fe materials on As dissolution*

217   After soil incubation without Fe materials, the As concentrations in solution were 21.9 (day 20),

218 108 (day 60) and 98.2 (day 100) μg L^{-1} for soil A and 367, 649 and 817 μg L^{-1} for soil B$_1$, respectively

219 (Table 3). Two-way ANOVA demonstrated the significant effects ($P < 0.001$) of the Fe material, the

220 incubation time, and the interaction between the Fe material and incubation time on the dissolved As

221 concentration. Except for day 20 in soil A, the percent decrease in dissolved As in both soils decreased

222 in the following order at all incubation times: cZVI > SSS > RIM-2 = RIM-1 > SCS (Fig. 1). The

223 effect of these Fe materials on As immobilization increased over time, while that of cFH remained at

224 a similar level or gradually decreased.

225

226 *3.3 As speciation in the soil solid phase with the addition of ZVI*

227   Figure 2 shows the As K-edge XANES spectra of soil B$_2$ incubated with and without cZVI under

228 anaerobic conditions. Without cZVI, the major As species in the soil solid phase was As(III), and the

229   percentages of As_2S_3-like species, As(III) and As(V) were 10, 72 and 18%, respectively. The XANES

230   spectra of soil incubated with cZVI had a distinct shoulder at approximately 11870 eV, which was not

231   apparent in the spectrum of the soil incubated without cZVI. This shoulder peak indicated the presence

232   of As associated with S. The percentages of FeAsS-like species, As_2S_3-like species, As(III) and As(V)

233   in the soil incubated with cZVI were 28, 15, 20 and 37%, respectively. Thus, the addition of cZVI

234   decreased the percentage of As(III) while increasing the percentages of As(V) and As associated with

235   S in the soil solid phase. Since we used synthesized or natural minerals as reference materials for As

236   associated with S in the LCF, the mineral crystallinity and exact elemental composition may be

237   different from those of As associated with S in the incubated soil. In addition, the LCF results represent

238   the presence of As species which have similar local coordinations with As_2S_3 and FeAsS, and not

239   necessary represent the presence of As_2S_3 and FeAsS exactly. Nonetheless, an increased contribution

240   of As species associated with S from the addition of cZVI was clearly observed in the XANES spectra.

241

242   ***3.4. Effect of Fe materials on the dissolved Si, P and Fe concentrations***

243   The concentration of Si dissolved from soils increased over time regardless of the addition of Fe

244   materials (Table 3). The Si concentrations were 8.02 (day 20), 11.3 (day 60) and 12.5 mg L^{-1} (day

245   100) in soil A and 11.1, 12.0, and 13.2 mg L^{-1} in soil B_1, respectively, without any Fe materials. Two-

246   way ANOVA revealed the significant effects of the Fe material, the incubation time, and the interaction

247   between the Fe material and incubation time on the dissolved Si ($P < 0.001$) (Table 3). The impact of

248   Fe materials on the dissolved Si concentration in soil A was slightly larger than that in soil B. For soil

249   A, the additions of SSS, SCS, and especially RIM-1 and RIM-2 caused significant increases in

250   dissolved Si (except for SSS at day 100). On the other hand, the applications of cFH and cZVI caused

251   statistically significant decreases in dissolved Si (Tukey test, $P = 0.05$) in all cases.

252   The dissolved P in soils increased with the incubation time (Table 3). The P dissolved from soils

253 without Fe materials was 1.15 (day 20), 2.01 (day 60) and 2.24 mg L^{-1} (day 100) in soil A and 0.480,

254 0.597, and 0.667 mg L^{-1} in soil B$_1$, respectively. Significant effects of the Fe material, the incubation

255 time, and their interaction on the dissolved P concentration were demonstrated by two-way ANOVA

256 ($P < 0.001$). The dissolved P significantly decreased due to the applications of cFH and cZVI, except

257 in soil A with cZVI at day 20. The additions of by-product Fe materials tended to decrease the

258 dissolved P in soil B$_1$, although the change was small and not statistically significant (Tukey test, $P =$

259 0.05) in most cases.

260   The concentration of Fe dissolved from soils without Fe materials increased over time, although

261 the change was not remarkable compared to the change in As (Table S1). The dissolved Fe content

262 was 49.8 (day 20), 97.6 (day 60) and 109 mg L^{-1} (day 100) in soil A and 85.0, 97.5, and 104 mg L^{-1}

263 in soil B$_1$, respectively (Table S1). The additions of Fe materials did not increase the dissolved Fe in

264 most cases. SSS and cZVI increased the dissolved Fe at day 20 in soil A, whereas cZVI (soil A and

265 B$_1$) and cFH (soil B$_1$) substantially decreased the dissolved Fe.

266

267 **4. Discussion**

268 *4.1. As immobilization*

269 *4.1.1. SSS, SCS and cZVI*

270 SSS and cZVI, which are composed mainly of ZVI, effectively decreased the As dissolution from soils

271 under the anaerobic conditions (Table 3, Fig. 1). The larger effect of cZVI on As immobilization

272 compared to that of SSS was probably attributable to the smaller particle size of cZVI (Fig. S2). SCS

273 decreased As dissolution less than SSS and cZVI did, reflecting the low content of Fe in SCS (Table

274 2). The percent decrease in dissolved As with the addition of these materials increased as time

275 proceeded (Fig. 1a and b). These results indicated that the Fe materials can immobilize As over a long

276 period even under anaerobic conditions.

277   Corrosion products of ZVI, mainly Fe oxides, are known to sorb As under aerobic conditions.

278   However, development of a corrosion layer of ZVI and the subsequent removal of As from solution is

279   limited under anaerobic conditions compared with aerobic conditions (Klas and Kirk 2013). Therefore,

280   the sorption of As onto the corrosion products of ZVI might not be a major mechanism restricting As

281   dissolution from soils under anaerobic conditions as in the present study.

282   The XANES spectra indicated that cZVI addition substantially increased the formation of As

283   species associated with S under anaerobic conditions (Fig. 2). Arsenopyrite was not observed in the

284   control soil but accounted for 28% of the total As in the soil incubated with cZVI. Therefore, As

285   precipitation as sulfides, especially as FeAsS-like species, might contribute to the As immobilization

286   caused by the application of cZVI, SSS and SCS. Hydrogen gas generation accompanying water

287   reduction by ZVI promotes microbial sulfate reduction (Gu *et al.* 1999) and possibly induces the

288   subsequent formation of insoluble sulfides of As and Fe.

289   The percentage of As(V) in the soil incubated with cZVI was substantially higher than that in the

290   control soil. Since the affinity of As(V) for soil solid phase is greater than that of As(III) (Takahashi *et*

291   *al*. 2003), As(III) oxidation is expected to decrease the As mobility in soils. Considering the strictly

292   anaerobic conditions of the incubation experiment, As(III) oxidation by dissolved oxygen and Fenton's

293   reaction unlikely occurred substantially. Instead, As(III) oxidation at the Fe oxide shell on ZVI surface

294   (Yan et al. 2010) might be an explanation. Yan et al. (2012) inferred that the As(III) oxidation by ZVI

295   caused via an Fe oxide-Fe(II)-As(III) ternary complex, which was an As(III) oxidation mechanism in

296   anaerobic Fe oxide-Fe(II) systems previously suggested by Amstaetter *et al.* (2010). Although we have

297   no evidence, the reaction should not be ruled out as a candidate mechanism for the As immobilization

298   in soils anaerobically incubated with cZVI, SSS and SCS.

299

300   *4.1.2. RIM-1 and RIM-2*

301   The additions of RIM-1 and RIM-2 immobilized As in soils, although this immobilization was

302   less effective than that by SSS and cZVI. Since these RIMs contained magnetite/maghemite and a

303   small amount of hematite (only RIM-1), the sorption of As on these Fe oxides (Giménez *et al*. 2007)

304   would contribute to As immobilization. However, As removal by wüstite, which is a major Fe mineral

305   in these Fe materials, is limited under low-dissolved-oxygen conditions (Mishra and Farrell 2005).

306   Interestingly, the percent decrease in dissolved As increased with time in both soils (Fig. 1). Although

307   RIM-2 contained Fe(0), As immobilization by Fe(0) would be limited due to the small amount of Fe(0).

308   Arsenic(III) was oxidized to As(V) at the surface of Fe oxides, including magnetite and hematite, even

309   under anaerobic conditions (Yan *et al*. 2010). Since the oxidation is considered to occur via reactive

310   Fe(III)-Fe(II) species and/or secondary Fe(II)/Fe(III) mineral phases (Amstaetter *et al*. 2010), it might

311   be facilitated by increase of Fe(II) dissolution and secondary Fe precipitation as time proceeded.

312   However, there is no experimental evidence to support this hypothesis. Further studies are needed to

313   investigate Fe and As speciation in order to propose mechanisms for As immobilization under

314   anaerobic soil conditions amended with Fe materials containing Fe(II) and Fe(II)/Fe(III) minerals.

315   ***4.1.3. cFH***

316   The major component of cFH, ferrihydrite, has a large specific surface area (100-700 m^2 g^{-1};

317   Cornel and Schwertmann 2003) and therefore adsorbs large amounts of oxyanions such as arsenate

318   and phosphate. The high specific surface area expected based on the small particle size (Fig. S2) might

319   explain high efficiency of cFH in As immobilization. Unlike other Fe materials, the percent decrease

320   in dissolved As remained at a similar level (Soil A) or gradually decreased (Soil B) over time. A similar

321   trend was observed in a previous study (Suda *et al*. 2015) showing that As immobilization by synthetic

322   ferrihydrite decreased with time under similar incubation conditions. Although the reductive

323   transformation of ferrihydrite to magnetite temporary increases As retention (Kocar *et al*. 2006),

324   prolonged anaerobic conditions cause As release that results from diminishing binding sites on the

325   surface of Fe oxides (Tufano and Fendorf 2008). Furthermore, As sorption onto Fe oxides would be

326   inhibited by co-existing substances, such as silicate, phosphate, carbonate species, and dissolved

327   organic matter (Jain and Loeppert 2000; Swedlund and Webster 1999; Brechbühl *et al*. 2012; Grafe *et*

328   *al*. 2002). In the present study, the concentrations of carbonate and dissolved organic carbon were not

329   measured, but Table S1 shows a decreasing trend in the dissolved Si/As and P/As ratios in the control

330   soils as time proceeded. Therefore, the competition for adsorption sites on the cFH surface with co-

331   existing dissolved silicate and phosphate would not be a major cause of the decrease in As

332   immobilization efficiency with the addition of cFH.

333

334   *4.2. Si and P dissolution*

335   The impact of Fe materials on the dissolved Si concentration in soil A was greater than that on soil B.

336   In soil A, the additions of RIM-1 and RIM-2 increased the dissolved Si most significantly, although

337   the Si content in SCS was approximately six times greater than those in RIM-1 and RIM-2. This result

338   reflects the difference in Si minerals among these Fe materials. RIM-1 and RIM-2 contain amorphous

339   (i.e., not XRD-detectable) Si, whereas SCS contains quartz, which is hardly soluble in soil solution

340   (Table 4). Since As(III) is transported by the same pathways as Si (Ma *et al*. 2008), dissolved Si inhibits

341   the uptake of As by rice plants (Li *et al*. 2009). Therefore, RIM-1 and RIM-2 potentially decrease As

342   uptake in rice plants by supplying dissolved Si. On the other hand, cFH resulted in the largest percent

343   decrease in dissolved Si among all the Fe materials, which reached 24% in soil A and 18% in soil B_1,

344   because of the Si sorption onto ferrihydrite (Swedlund and Webster 1999).

345   Figure 3 shows the relationships between the percent decrease in dissolved As and that in

346   dissolved P in soil B_1 incubated with Fe materials. The regression line for the by-product Fe materials

347   indicates that the percent decrease in dissolved P was positively correlated with that in dissolved As

348   ($r = -0.723$, $P < 0.001$). This result indicated that As immobilization was accompanied by a decrease

349 in P solubility. However, the percent decrease in dissolved As was much greater than the percent

350 decrease in dissolved P, except in the case of cFH. The considerable difference in the ratio of the

351 percent decrease in dissolved As to that in dissolved P between cFH and the other Fe materials might

352 reflect the presence of different mechanisms of As immobilization between these materials, i.e., the

353 adsorption of As onto the surface hydroxyl groups of Fe oxides was not main mechanism of As

354 immobilization by the Fe materials, other than cFH. The same analysis was not carried out for soil A

355 because the percent decrease in dissolved As at day 60 and day 100 reached nearly 100% in most cases.

356 Overall, the by-product Fe materials did not substantially decrease dissolved P in soil A as the

357 commercial Fe materials did, except for SSS at day 100 (Table 3).

358

359 *4.3. Potential of the by-product Fe materials to immobilize As in paddy soils*

360   Due to their complex compositions, determining the precise mechanisms of As immobilization

361 by the application of by-product Fe materials is difficult. However, the present study clearly showed

362 the high ability of by-product Fe materials, namely SSS, RIM-1 and RIM-2, to immobilize As in

363 flooded anaerobic soils. Although cZVI more effectively restricted As dissolution from soils, the

364 application of by-product Fe materials is more cost-effective than the application of cZVI. Furthermore,

365 the application of by-product Fe materials did not cause significant decreases in Si and P dissolution

366 compared with cFH. (Table 3, Fig. 2). This is desirable for both plant growth and the inhibition of As

367 uptake by these elements. Therefore, we concluded that these by-product Fe materials are promising

368 amendments for As immobilization in paddy soils, at least on a single-use basis.

369   In most cases, the dissolved Fe in soils incubated with the Fe materials did not substantially

370 increase (Table S1). This result indicated that the Fe materials were relatively stable under anaerobic

371 conditions. However, we cannot rule out the possibility that excess the Fe(II) derived from Fe materials

372 adsorbed onto the soil solid phase and/or precipitated as secondary Fe minerals such as siderite

373   (Yamaguchi *et al.* 2011). In either case, the applied Fe materials eventually dissolve as Fe(II), followed

374   by reoxidization to Fe(III) by dissolved oxygen. Therefore, regardless of their mineral composition,

375   the applied Fe materials will ultimately dissolve, but their effect will persist to some extent due to the

376   increase in Fe oxides in the applied soils. The Fe materials applied to paddy soil are most likely altered

377   after repeated cycles of anaerobic and aerobic conditions, but their resistance against dissolution in

378   soil under paddy field conditions remains unclear. Long-term and field-scale experiments should be

379   carried out to assess the time course of As mobility in soils with Fe materials before agricultural use.

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397 **References**

398 Amstaetter K, Borch T, Larese-Casanova P, Kappler A 2010: Redox transformation of arsenic by

399   Fe(II)-activated goethite (α-FeOOH). Environ. Sci. Technol., 44, 102–108.

400 Arao T, Kawasaki A, Baba K, Mori S, Matsumoto S 2009: Effects of water management on cadmium

401   and arsenic accumulation and dimethylarsinic acid concentrations in Japanese rice. Environ. Sci.

402   Technol., 43, 9361–9367.

403 Boisson J, Mench M, Vangronsveld J, Ruttens A, Kopponen P, De Koe T 1999: Immobilization of

404   trace metals and arsenic by different soil additives: Evaluation by means of chemical extractions.

405   Commun. Soil Sci. Plant Anal., 30, 365–387.

406 Brechbühl Y, Christl I, Elzinga EJ, Kretzschmar R 2012: Competitive sorption of carbonate and arsenic

407   to hematite: combined ATR-FTIR and batch experiments. J. Colloid Interface Sci., 377, 313–321.

408 Codex Alimentarius Commission. 2014: Thirty-Seventh Session CICG, Geneva; 2014 Jul 14–18.

409   http://www.fao.org/fao-who-codexalimentarius/sh-

410   proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252

411   FMeetings%252FCX-701-37%252FREP14_CACe.pdf (April, 2017)

412 Codex Alimentarius Commission. 2016: Thirty-Ninth Session CICG, Rome; 2016 27 June - 1 July.

413   http://www.fao.org/fao-who-codexalimentarius/sh-

414   proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252

415   FMeetings%252FCX-701-39%252FREPORT%252FREP16_CACe.pdf (April, 2017)

416 Cornell RM, Schwertmann U 2003: Surface area and Porosity. In: The Iron Oxides: Structure,

417   Properties, Reactions, Occurrences and Uses, pp. 87–102. Wiley-VCH: Weinheim.

418 Giménez J, Martínez M, de Pablo J, Rovira M, Duro L 2007: Arsenic sorption onto natural hematite,

419   magnetite, and goethite. J. Hazard. Mater., 141, 575–80.

420 Grafe M, Eick MJ, Grossl PR, Saunders AM 2002: Adsorption of arsenate and arsenite on ferrihydrite

421   in the presence and absence of dissolved organic carbon. J. Environ. Qual., 31, 1115–1123.

422   Gu B, Phelps TJ, Liang L, Dickey MJ, Roh Y, Kinsall BL, Palumbo AV, Jacobs GK 1999:

423   Biogeochemical dynamics in zero-valent iron columns: implication for permeable reactive barriers.

424   Environ. Sci. Technol., 33, 2170–2177.

425   Honma T, Ohba H, Kaneko A, Nakamura K, Makino T, Katou H 2016b: Effects of soil amendments

426   on arsenic and cadmium uptake by rice plants (Oryza sativa L. cv. Koshihikari) under different

427   water management practices. Soil Sci. Plant Nutr., 62, 349–356.

428   Honma T, Ohba H, Kaneko-Kadokura A, Makino T, Nakamura K, Katou H 2016a: Optimal Soil Eh,

429   pH, and Water Management for Simultaneously Minimizing Arsenic and Cadmium Concentrations

430   in Rice Grains. Environ. Sci. Technol., 50, 4178–4185.

431   Jain A, Loeppert R 2000: Effect of competing anions on the adsorption of arsenate and arsenite by

432   ferrihydrite. J. Environ. Qual., 29, 1422–1430.

433   Jain CK, Ali I 2000: Arsenic: Occurrence, toxicity and speciation techniques. Water Res., 34, 4304–

434   4312.

435   Jordan N, Marmier N, Lomenech C, Giffaut E, Ehrhardt JJ 2007: Sorption of silicates on goethite,

436   hematite, and magnetite: Experiments and modelling. J. Colloid Interface Sci., 312, 224–229.

437   Klas S, Kirk DW 2013: Advantages of low pH and limited oxygenation in arsenite removal from water

438   by zero-valent iron. J. Hazard. Mater., 252–253, 77–82.

439   Kocar BD, Herbel MJ, Tufano KJ, Fendorf S 2006: Contrasting effects of dissimilatory iron (III) and

440   arsenic (V) reduction on arsenic retention and transport. Environ. Sci. Technol., 40, 6715–6721.

441   Kumpiene J, Lagerkvist A, Maurice C 2008: Stabilization of As, Cr, Cu, Pb and Zn in soil using

442   amendments-a review. Waste Manag., 28, 215–225.

443   Li RY, Stroud JL, Ma JF, McGrath SP, Zhao FJ 2009: Mitigation of arsenic accumulation in rice with

444   water management and silicon fertilization. Environ. Sci. Technol., 43, 3778–3783.

445   Ma JF, Yamaji N, Mitani N, Xu X-Y, Su Y-H, McGrath SP, Zhao F-J 2008: Transporters of arsenite in

446   rice and their role in arsenic accumulation in rice grain. Proc. Natl. Acad. Sci. U. S. A., 105, 9931–

447   9935.

448   MAFF 2014: Survey of arsenic levels in brown rice and polished rice produced in Japan.

449   http://www.maff.go.jp/j/press/syouan/nouan/pdf/140221-01.pdf (in Japanese, October, 2015)

450   Makino T, Nakamura K, Katou H, *et al*. 2016: Simultaneous decrease of arsenic and cadmium in rice

451   (Oryza sativa L.) plants cultivated under submerged field conditions by the application of iron-

452   bearing materials. Soil Sci. Plant Nutr., 62, 340–348.

453   Meharg AA 2004: Arsenic in rice-understanding a new disaster for South-East Asia. Trends Plant Sci.,

454   9, 415–417.

455   Mench M, Bussière S, Boisson J, Castaing E, Vangronsveld J, Ruttens A, DeKoe T, Bleeker P,

456   Assunção A, Manceau A 2003: Progress in remediation and revegetation of the barren Jales gold

457   mine spoil after in situ treatments. Plant Soil, 249, 187–202.

458   Mishra D, Farrell J 2005: Evaluation of mixed valent iron oxides as reactive adsorbents for arsenic

459   removal. Environ. Sci. Technol., 39, 9689–9694.

460   Oguri T, Yoshinaga J, Tao H, Nakazato T 2014: Inorganic arsenic in the Japanese diet: Daily intake

461   and source. Arch. Environ. Contam. Toxicol., 66, 100–112.

462   Su C, Puls RW 2001: Arsenate and arsenite removal by zerovalent iron: Effects of phosphate, silicate,

463   carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. Environ. Sci.

464   Technol., 35, 4562–4568.

465   Suda A, Baba K, Akahane I, Makino T 2016: Use of water-treatment residue containing polysilicate-

466   iron to stabilize arsenic in flooded soils and attenuate arsenic uptake by rice (Oryza sativa L.) plants.

467   Soil Sci. Plant Nutr., 62, 111–116.

468   Suda A, Baba K, Yamaguchi N, Akahane I, Makino T 2015: The effects of soil amendments on arsenic

469   concentrations in soil solutions after long-term flooded incubation. Soil Sci. Plant Nutr., 61, 592–

470   602.

471   Swedlund PJ, Webster JG 1999: Adsorption and polymerization of silicic acid on ferrihydrite, and its

472   effect on arsenic adsorption. Water Res., 33, 3413–3422.

473   Takahashi Y, Ohtaku N, Mitsunobu S, Yuita K, Nomura M 2003: Determination of the As(III)/As(V)

474   ratio in soil by X-ray absorption near-edge structure (XANES) and its application to the arsenic

475   distribution between soil and water. Anal. Sci., 19, 891–896.

476   Tufano KJ, Fendorf S 2008: Confounding impacts of iron reduction on arsenic retention. Environ. Sci.

477   Technol., 42, 4777–4783.

478   Xu XY, Mcgrath SP, Mehaarg AA, Zhao FJ 2009: Growing rice aerobically markedly decreases arsenic

479   accumulation. Environ. Sci. Technol., 43, 5574–5579.

480   Yamaguchi N, Nakamura T, Dong D, Takahashi Y, Amachi S, Makino T 2011: Arsenic release from

481   flooded paddy soils is influenced by speciation, Eh, pH, and iron dissolution. Chemosphere, 83,

482   925–932.

483   Yan W, Ramos MA V, Koel BE, Zhang WX 2010: Multi-tiered distribution of arsenic in iron

484   nanoparticles: Observation of dual redox functionality enabled by a core shell structure. Chem.

485   Commun., 46, 6995–6997.

486   Yan W, Ramos MA V, Koel BE, Zhang WX 2012: As(III) sequestration by iron nanoparticles: Study

487   of solid-phase redox transformations with X-ray photoelectron spectroscopy. J. Phys. Chem. C, 116,

488   5303–5311.

489   Zhu J, Pigna M, Cozzolino V, Caporale AG, Violante A 2011: Sorption of arsenite and arsenate on

490   ferrihydrite: Effect of organic and inorganic ligands. J. Hazard. Mater., 189, 564–571.

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492

493   **Table and Figure Legends**

494

495   Fig. 1 Time course changes in the percent decrease in dissolved arsenic (As) in soil A (a) and soil B1

496   (b) incubated with each Fe material. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent

497   casting sand, residual iron material of steel shot production, commercial ferrihydrite and commercial

498   zero-valent iron, respectively. The percent decrease in dissolved As was calculated using Eq. 1.

499

500   Fig. 2 Arsenic K-edge XANES spectra of solid phases of (a) the control for soil B2 and (b) soil B2

501   incubated with commercial zero-valent iron. Broken lines indicate the spectra of the reference

502   materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3) and arsenopyrite (FeAsS). Linear

503   combination fittings from the spectra of the reference materials for the soils are shown as solid lines.

504

505   Fig. 3 Relationship of the percent decrease in dissolved arsenic (As) and phosphorus (P) in soil B_1

506   incubated with the Fe materials. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent

507   casting sand, residual iron materials of steel shot production, commercial ferrihydrite and commercial

508   zero-valent iron, respectively. The regression line is for the by-product Fe materials (SSS, SCS, RIM-

509   1 and RIM-2), and *** indicates significance at $P < 0.001$. The percent decrease in dissolved As and

510   P was calculated using Eq. 1.

511

512   Table 1 Selected physico-chemical properties of the soil samples

513

514   Table 2 Elemental and mineralogical composition of the iron materials

515

516   Table 3 Time course of the concentrations of arsenic (As), silica (Si) and phosphorus (P) in soil solution

Table 1 Selected physico-chemical properties of the soil samples

Soil sample	pH (H$_2$O)	TC (g kg^{-1})	TN (g kg^{-1})	Clay (g kg^{-1})	Selective extraction (g kg^{-1})				HCl-As (mg kg^{-1})
					Fe$_d$	Al$_o$	Fe$_o$	Si$_o$	
Soil A	5.18	14.3	1.22	170	9.13	2.77	5.47	0.36	2.80
Soil B$_1$	6.54	16.3	1.58	349	19.1	1.60	10.5	0.70	5.83
Soil B$_2$[†]	5.99	17.7	1.74	359	17.8	1.59	10.1	0.52	8.36

TC, Total carbon; TN, Total nitrogen; HCl-As, arsenic extractable in 1 mol L^{-1} hydrochloric acid

Subscripts "o" and "d" denote oxalate- and dithionite-citrate-extractable elements, respectively.

[†] Data from Suda et al. (2015)

Table 2 Elemental and mineralogical composition of the iron materials

Fe material	Elemental concentration					Mineral	
	Fe (g kg^{-1})	Si (g kg^{-1})	Mn (g kg^{-1})	As (mg kg^{-1})	P (mg kg^{-1})	Major	Minor
SSS	864±43	50.2±15.2	6.22±0.09	37.5±4.1	592±4	Z	Q
SCS	56.4±13.0	355±1	1.48±0.11	3.27±0.47	102±1	Q	Z
RIM-1	590±13	59.8±1.6	50.5±0.9	3.77±0.86	380±14	W, M	H
RIM-2	642±18	57.4±2.2	49.3±1.9	19.5±4.4	406±16	W, M	Z
cFH	532±3	10.8±4.2	2.10±0.04	3.41±0.90	239±4	F	
cZVI	982±4	15.9±0.4	48.4±0.3	76.8±0.7	639±21	Z	

SSS, spent steel shot; SCS, fine spent casting sand; RIM, residual Fe materials of steel shot production;

cFH, commercial ferrihydrite; cZVI, commercial zero-valent iron

Fe, iron; Si, silicon; Mn, manganese; As, arsenic; P, phosphorus

Z, zero-valent iron; Q, quartz; W, wüstite; M, magnetite and/or maghemite; H, hematite; F, ferrihydrite

Table 3 Time course of the concentrations of arsenic (As), silica (Si) and phosphorus (P) in soil solution and two-way analysis of variance (ANOVA)

Sample	Approximate incubation time (days)					
	Soil A			*Soil B₁*		
	20	60	100	20	60	100
Dissolved As (µg L⁻¹)						
Control	21.9±2.1 a	108±2 a	98.2±13.3 a	367±11 a	649±32 a	817±7 a
SSS	22.2±0.7 a	6.65±0.20 b	4.38±0.24 b	232±1 b	214±16 b	102±12 b
SCS	22.0±2.6 a	75.8±3.1 c	54.7±2.9 c	344±8 c	598±4 a	660±24 c
RIM-1	13.4±0.2 b	9.21±0.51 b	6.54±0.44 b	323±5 c	454±27 c	397±18 d
RIM-2	24.4±1.0 a	14.8±1.4 d	6.77±0.27 b	323±14 c	443±19 c	353±12 e
cFH	9.32±0.16 c	23.1±0.4 e	41.6±3.9 d	112±4 d	321±3 d	505±15 f
cZVI	2.67±0.36 d	1.57±0.02 f	2.53±0.35 b	72.9±5.7 e	11.1±0.9 e	5.36±0.17 g
Two-way ANOVA						
Fe material (*F*)	*P* < 0.001			*P* < 0.001		
Incubation time (*T*)	*P* < 0.001			*P* < 0.001		
F × *T*	*P* < 0.001			*P* < 0.001		
Dissolved Si (mg L⁻¹)						
Control	8.02±0.10 a	11.3±0.1 a	12.5±0.1 a	11.1±0.2 a	12.0±0.1 ab	13.2±0.1 a
SSS	8.82±0.09 b	12.0±0.2 b	12.5±0.2 a	10.6±0.2 b	11.7±0.1 b	12.5±0.2 b
SCS	8.49±0.02 c	11.8±0.2 b	13.1±0.0 b	11.1±0.1 ab	12.1±0.0 a	13.4±0.1 a
RIM-1	10.8±0.1 d	13.3±0.1 c	14.1±0.1 c	11.2±0.2 a	12.1±0.3 a	13.4±0.1 a
RIM-2	10.1±0.1 e	13.0±0.0 c	13.7±0.0 d	10.9±0.0 ab	12.0±0.1 ab	13.3±0.2 a
cFH	6.07±0.07 f	9.06±0.10 d	11.8±0.3 e	9.11±0.02 c	10.6±0.2 c	12.0±0.1 c
cZVI	8.38±0.10 c	10.1±0.1 e	11.3±0.1 f	10.1±0.2 d	10.6±0.0 c	11.0±0.1 d
Two-way ANOVA						
Fe material (*F*)	*P* < 0.001			*P* < 0.001		
Incubation time (*T*)	*P* < 0.001			*P* < 0.001		
F × *T*	*P* < 0.001			*P* < 0.001		
Dissolved P (mg L⁻¹)						
Control	1.15±0.03 a	2.01±0.01 ab	2.24±0.03 a	0.480±0.013 a	0.597±0.005 a	0.667±0.013 a
SSS	1.44±0.01 b	1.96±0.04 b	1.18±0.02 b	0.448±0.027 ab	0.579±0.034 a	0.561±0.016 b
SCS	1.17±0.02 a	2.02±0.02 ab	2.27±0.02 a	0.482±0.006 a	0.601±0.011 a	0.654±0.019 a
RIM-1	1.15±0.01 a	2.05±0.03 a	2.26±0.01 a	0.474±0.013 a	0.576±0.002 a	0.629±0.010 ac
RIM-2	1.20±0.02 c	1.99±0.02 ab	1.98±0.10 c	0.466±0.030 a	0.570±0.012 ab	0.604±0.017 c
cFH	0.435±0.01 d	1.03±0.02 c	1.27±0.14 b	0.259±0.000 c	0.359±0.012 c	0.459±0.012 d
cZVI	1.60±0.02 e	0.413±0.020 d	0.313±0.024 d	0.402±0.010 b	0.475±0.004 d	0.416±0.010 e
Two-way ANOVA						
Fe material (*F*)	*P* < 0.001			*P* < 0.001		
Incubation time (*T*)	*P* < 0.001			*P* < 0.001		
F × *T*	*P* < 0.001			*P* < 0.001		

SSS, spent steel shot; SCS, fine spent casting sand; RIM, residual iron material of steel shot production; cFH, commercial ferrihydrite; cZVI, commercial zero-valent iron. Values followed by the same letter within a column are not significant (*P* = 0.05, Tukey's test).

Fig. 1 Time course changes in the percent decrease in dissolved arsenic (As) in soil A (a) and soil B1 (b) incubated with each Fe material. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent casting sand, residual iron material of steel shot production, commercial ferrihydrite and commercial zero-valent iron, respectively. The percent decrease in dissolved As was calculated using Eq. 1.
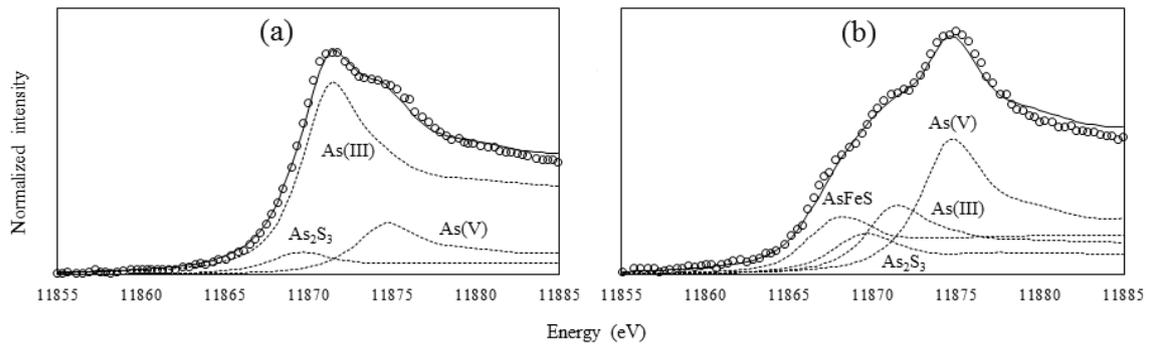
Fig. 2 Arsenic K-edge XANES spectra of solid phases of (a) the control for soil B2 and (b) soil B2 incubated with commercial zero-valent iron. Broken lines indicate the spectra of the reference materials, Na_2AsO_3 [As(III)], $NaHAsO_4$ [As(V)], orpiment (As_2S_3) and arsenopyrite (FeAsS). Linear combination fittings from the spectra of the reference materials for the soils are shown as solid lines.
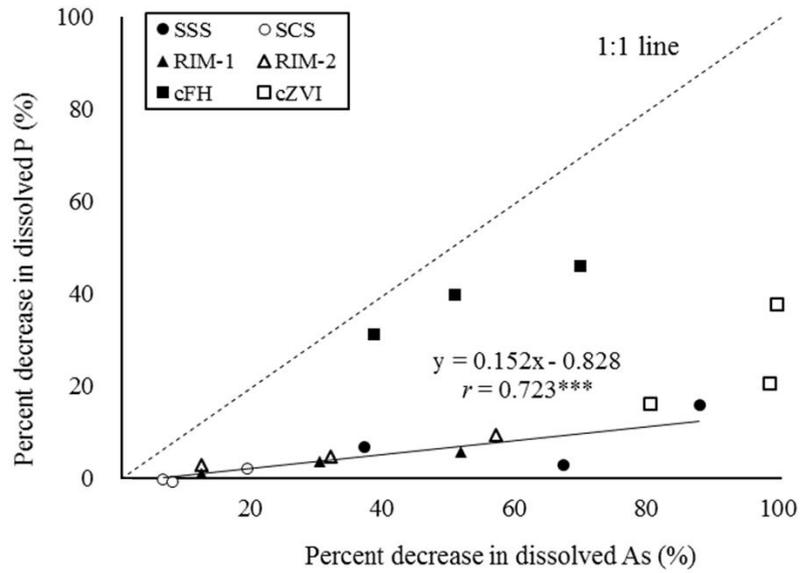
Fig. 3 Relationship of the percent decrease in dissolved arsenic (As) and phosphorus (P) in soil B_1 incubated with the Fe materials. SSS, SCS, RIM, cFH and cZVI denote spent steel shot, fine spent casting sand, residual iron materials of steel shot production, commercial ferrihydrite and commercial zero-valent iron, respectively. The regression line is for the by-product Fe materials (SSS, SCS, RIM-1 and RIM-2), and *** indicates significance at P < 0.001. The percent decrease in dissolved As and P was calculated using Eq. 1.