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Abstract

The development of anoxic conditions in riparian wetland (RW) soils is widely known to release dissolved phosphorus (DP), but the respective roles of reductive dissolution of Fe-oxyhydroxide, pH changes and sediment inputs in this release remain debated. This study aimed to identify and quantify these respective roles via laboratory anaerobic/aerobic incubation of RW soils with and without the addition of sediment. The investigated soils came from two RWs with contrasting P status and organic matter (OM) content in their soils, while the added sediment came from an adjacent cultivated field. Results showed that the amount and speciation of the DP released during

anaerobic/aerobic incubations were controlled by soil P status and soil OM content. During anaerobic incubation, DP release in the soil with high extractable P and low OM contents was controlled by reductive dissolution of Fe-oxyhydroxides (83%), whereas that released in the soil with low extractable P and high OM contents was controlled by an increase in pH (88%). Anaerobic incubation of a mixture of eroded sediments and RW soils increased the release of DP, dissolved organic carbon and Fe(II) (by 16%, 4% and 18%, respectively) compared to the simple addition of the amounts released during their separate incubations. Management practices should decrease soil erosion from upland fields to avoid deposition of P-rich sediments on RW soils. Management efforts should focus preferentially on RWs whose Fe:P molar ratios in the soil solution during reduction are the lowest, since they indicate a high risk that the DP released will be transferred to watercourses.

Keywords: Anaerobic incubation, dissolved phosphorus, Fe-oxyhydroxides, pH changes, riparian wetland

1. Introduction

Riparian wetlands (RWs), i.e. uncultivated hydromorphic zones between agricultural fields and watercourses, have long been promoted to reduce diffuse losses of phosphorus (P) from agricultural sources. However, several studies have reported that they can also act as source zones of dissolved P (DP, operationally defined as the <

45 0.45 µm fraction) in agricultural watersheds after long-term function (Dorioz et al.,
46 2006; Dupas et al., 2015; Gu et al., 2017; Stutter et al., 2009). This could partly explain
47 the re-increase in dissolved reactive P concentrations in some large rivers since the mid-
48 1990s (Jarvie et al., 2017; Michalak et al., 2014), which has caused harmful algal
49 blooms in receiving water bodies (Smith et al., 2015). Two main mechanisms have been
50 hypothesized to cause this increased DP release, both related to the periodic water table
51 fluctuations that affect RW zones (Blackwell et al., 2009; Bünemann et al., 2013; Dupas
52 et al., 2015; Gu et al., 2017). The first is due to the rewetting of soils after a dry period,
53 which causes osmotic shock in soils and the subsequent release of P from microbial
54 cells (Turner and Haygarth, 2001). The second mechanism is due to the waterlogging
55 of RW zones during wet periods, which promotes development of anoxic conditions.
56 Studies investigating the dynamics of DP release in RW soils during water-saturated
57 periods both in the field and laboratory reported positive correlations between this
58 development and DP release in RW soils (Dupas et al., 2015; Gu et al., 2017; Knorr et
59 al., 2013; Surridge et al., 2007).

60 At least two hypotheses can explain the DP release in anoxic RW soils: i) reductive
61 dissolution of Fe-oxyhydroxides by soil bacteria, resulting in solubilization of
62 associated inorganic and organic P species, and ii) an increase in pH during Fe-
63 oxyhydroxide reduction reactions, resulting in desorption of inorganic and organic P
64 species from soil particles (Kirk et al., 2004). The “dissolution” hypothesis assumes
65 that the released DP consists of P originally incorporated into, or adsorbed onto, soil
66 Fe-oxyhydroxides. Because of their highly reactive and strongly protonated surfaces,

67 Fe-oxyhydroxides have a strong ability to adsorb oxyanions such as phosphate groups
68 or P-bearing, negatively charged dissolved organic molecules/colloids (Borch and
69 Fendorf, 2007; Wilson et al., 2004). When soils become water-saturated and flow
70 velocity decreases, O_2 depletion is often observed. In response, microorganisms change
71 their terminal electron acceptors from O_2 to other acceptors such as iron. This results in
72 reductive dissolution of Fe-oxyhydroxides (Stumm and Sulzberger, 1992; Zak et al.,
73 2004) and thus release of the associated substances, including the adsorbed phosphate
74 groups and/or P-bearing, dissolved organic molecules/colloids (Jeanneau et al., 2014;
75 Knorr et al., 2013; Surridge et al., 2012). In this case, the ultimate sources of the DP
76 species released in RWs under anoxic conditions are soil Fe-oxyhydroxides.

77 In contrast, the "desorption" hypothesis assumes that the DP release is associated
78 with the increase in pH caused by reduction reactions. Several studies have reported
79 increases in pH in soil solutions following the consumption of protons in reduction
80 reactions of NO_3^-, Fe or Mn oxides (McBride, 1994; Ponnamperuma, 1972; Quantin et
81 al., 2001; Stumm and Sulzberger, 1992). At pH less than 7, protonated hydroxyl groups
82 generate a positive charge on soil mineral surfaces, which induces adsorption of
83 negatively charged species such as phosphate groups or P-bearing organic
84 molecules/colloids on mineral surfaces via the formation of surface complexes (Buffle
85 et al., 1989; Zak et al., 2004). However, when the pH increases to neutral or slightly
86 basic during reduction reactions, soil particles become electronegative. Hence, mineral
87 surfaces and phosphate groups and/or negatively charged P-bearing organic
88 molecules/colloids repel each other, limiting the complexation of these P compounds

89 by soil mineral surfaces. Therefore, DP, including dissolved organic/inorganic P and
90 fine colloidal P species, is released into the soil solution (Liang et al., 2010; VandeVoort
91 et al., 2013). In this case, the ultimate sources of the DP species released in RWs under
92 anoxic conditions are not only soil Fe-oxyhydroxides, but all mineral surfaces in the
93 soil.

94 Another important aspect of P-release processes in RW soils is that these soils
95 often receive P-rich soil particles that are eroded from adjacent cultivated fields
96 (Ockenden et al., 2014). It is commonly observed that this soil particle input to RWs
97 occurs mainly through overland flow processes developed during high-magnitude
98 rainfall events (Haygarth and Jarvis, 1999). Stutter et al. (2009) assessed the influence
99 of sediment addition on DP release processes in vegetated buffer strips in riparian zones.
100 Using laboratory experiments, they showed that adding fine sediments to RW soils
101 stimulated release of inorganic DP, an effect they interpreted as being caused largely by
102 biological processes. However, their experiments were performed under aerobic
103 conditions, which preclude assessing whether adding P-rich sediments to RW soils also
104 stimulated DP release during anoxic conditions. This possibility is worth considering
105 since RW soils generally have greater microbial biomass and diversity than adjacent
106 cultivated soils and contain bacteria accustomed to reducing soil Fe-oxyhydroxides
107 (Dia et al., 2015; Krutz et al., 2006, Pédrot et al, 2011). The encounter between these
108 bacteria and soil particles rich in P-bearing Fe-oxyhydroxides, such as particles eroded
109 from adjacent cultivated fields, could increase DP release during the development of
110 anoxic conditions.

111 Assessing the relative influence of Fe-oxyhydroxide dissolution, increase in pH
112 and sediment input on DP release during anoxic conditions in RW soils is important
113 to better understand how RWs control DP release in agricultural landscapes. This
114 assessment is difficult, however, because these processes occur simultaneously during
115 the development of anoxic conditions in soils. In this study, we conducted laboratory
116 soil incubation experiments to study and quantify each of these processes separately,
117 using RW soils which have been shown to release DP under natural field conditions.
118 In order to assess the influence of soil P speciation on DP release during soil reduction,
119 two RW soils that differed in their organic matter (OM) content and their inorganic
120 P:organic P ratio were selected.

121 Thus, our objective in this study was to use laboratory incubation to: i) estimate
122 the relative influence of Fe-oxyhydroxide dissolution and an increase in pH on DP
123 release in RW soils under anoxic conditions, ii) assess the influence of soil P speciation
124 on the amount and speciation of the DP released, and iii) assess how inputs of P-rich
125 sediments from upland cultivated fields influence the overall DP release process in RW
126 soils under anoxic conditions.

127 # 2. Materials and Methods

128 ## *2.1 Sampling sites and soil preparation*

129 The soil samples came from two RWs (A and B) in the Kervidy-Naizin watershed,
130 a small-scale (5 km^2) agricultural headwater watershed located in Brittany, western
131 France (48.012° N, 2.835° W). Belonging to the Agrhys environmental research
132 observatory (http://www6.inra.fr/ore_agrhys_eng), this watershed has been intensively

investigated since 1993. Therefore, its hydrological, pedological and geochemical characteristics are well constrained (Aubert et al., 2014; Gascuel-Odoux et al., 2018; Lambert et al., 2013; Mérot et al., 1995). The substrate lithology of the watershed consists of impervious Brioverian schists capped with 2-30 m of unconsolidated weathered materials in which a shallow aquifer has developed. The upland domains are well-drained, and the valley bottoms are hydromorphic, resulting in the development of RWs at the interface between cultivated hillslopes and the stream network. Soils from wetlands A and B (soils A and B, respectively) are silt loam, classified as Luvisols.

Fresh soil cores (ca. 1.5 kg) from the surface layer (0-15 cm) of the two RWs were sampled with a 75-mm diameter auger in January 2014. Sampling sites lay within 1 m^2 of the lysimeters investigated by Dupas et al. (2015) and Gu et al. (2017) for in-situ monitoring of P concentrations in the soil solution (WetDown-A and WetDown-B sites, respectively, in their studies). Meanwhile, eroded sediments (sediment S, ca. 1.0 kg) re-deposited at the interface between wetland B and the upland cultivated field were collected manually with a PVC cup. Soils and sediments were transferred to the laboratory in plastic bags and air-dried (20 days, at 25 ± 2 °C). They were sieved to < 2 mm after removing visible non-soil materials and stored in a refrigerator at 4 °C before use.

2.2 Experimental design

Three experiments were conducted. In the first, soils A and B were incubated anaerobically under a nitrogen (N_2) stream, without a pH buffer, to simulate natural anoxic conditions observed in the two soils. In the second experiment, the two soils

were incubated aerobically, but an increase in pH, equivalent to that recorded during their anaerobic incubations, was applied. This second experiment was used to quantify the effect of an increase in pH (from 6.0 to 7.6) on the amount of DP released during anaerobic incubation (and by difference, the effect of reductive dissolution of Fe-oxyhydroxides alone). Finally, in the third experiment, sediment S was incubated anaerobically, firstly alone and secondly mixed in equal percentages (50% each of dry soil/sediment by mass) with soil B (referred to hereafter as "sample M"). This third experiment was used to assess whether the sediment released more DP during reduction when incorporated into RW soils, as would be expected by the increasing influence of wetland Fe-reducing bacteria on the reduction of soil Fe-oxyhydroxides.

The incubation system and protocol were similar to those developed by Grybos et al. (2009), who investigated similar research questions but focused on dissolved organic carbon (DOC) and ignored P. Suspensions were prepared at a 1:20 soil dry weight:solution ratio, with a solution consisting of 0.48, 0.85 and 0.1 mol l^{-1} of NO_3^-, Cl^-, and SO_4^{2-}, respectively, to mimic the anion composition of the shallow groundwater in RWs during the water-saturated period. The suspensions (50 g dried soil, sediment or their mixture in a 1 L solution) were placed in air-tight, 1-litre batch Prelude reactors (Guerin, Biolafite) in a water bath with temperature maintained at 20 ± 2 °C (**Fig. S1**). The suspension was continuously stirred at 150 rpm, and simultaneously supplied with a continuous stream of N_2 gas via an automatic gas-injection system at 0.5 l min^{-1} for the first 2 h and then at 0.15 l min^{-1}. For the aerobic incubations simulating the pH changes alone, the pH was adjusted manually by adding

177 1.0 M NaOH; the other incubation parameters were the same as those used during
178 anaerobic incubations (with no N_2 streaming and plugs opened to allow equilibrium of
179 the suspension with ambient air).

180 Aliquots (ca. 20 ml) of soil suspension were sampled with a sterile syringe into
181 flasks prefilled with argon gas (for anaerobic incubations only) twice a day during the
182 first 3 days of incubation, and then once a day during the remaining 10 days. pH and
183 Eh were immediately measured with combined electrodes (Malter Pt 4805 DXK-
184 S8/225 and Malter HA 405-DPA-SC-S8/225, respectively). Flasks were then
185 centrifuged for 10 min at 2000*g*. The supernatant was collected using a sterile syringe
186 equipped with a soft PVC tube at the mouth, allowing its transfer without contact with
187 the air. The supernatants were then filtrated using pre-washed cellulose acetate filters
188 of 0.45 µm pore size for P and 0.2 µm pore size for DOC, anions (NO_3^-, SO_4^{2-}), and
189 Fe(II) analyses, respectively. Aliquots for P, DOC, and Fe(II) analyses were
190 immediately acidified with diluted sulfuric acid, and samples for anions analysis were
191 directly placed in argon-filled analysis tubes. All analyses were performed within 24 h
192 after sampling. The rapid sampling (a few minutes), acidification of filtrated aliquots
193 and brief storage of subsamples under the argon atmosphere prevented potential
194 interference with redox-sensitive parameters (e.g. Fe(II)) and precipitation of Fe-
195 hydroxides prior to measurement.

196 ## *2.3 Analyses*

197 ### 2.3.1 Soil and sediment analyses

198 Portions of the sieved air-dried soil and sediment samples were analyzed for

199 particle size fractions (NF X 31-107), OM/nitrogen/carbon contents (NF ISO 13878,
200 NF ISO 10694), pH in water (1:5 v:v water extraction, NF ISO 10390), extractable P
201 (oxalate-P, NF X 31-161; Dyer-P, NF X 31-160; Olsen-P, NF ISO 11263), Si/Al/Fe
202 (ICP-AES after extraction with ammonium oxalate and oxalic acid, according to Tamm,
203 1922), and total P (ICP-AES after total solubilization with hydrofluoric and perchloric
204 acid, NF X 31-147).

205 **2.3.2 Solution analyses**

206 Molybdate-reactive dissolved P (MRDP) concentrations of filtrates were
207 determined using the standard colorimetric method of Murphy and Riley (1962). The
208 same method was used for total dissolved P (TDP), but after digestion of filtrates in
209 acidic potassium persulfate. The precision of MRDP and TDP measurements was ± 4
210 and ± 13 µg l^{-1}, respectively. The difference between TDP and MRDP was defined as
211 the molybdate-unreactive dissolved P (MUDP) fraction, which includes organic P as
212 well as both organic and inorganic P associated with colloidal particles (Haygarth and
213 Sharpley, 2000).

214 NO_3^- and SO_4^{2-} concentrations were analyzed by ionic chromatography (Dionex,
215 DX120), with a precision of ± 4%. DOC concentrations were analyzed with a total
216 organic analyzer (Shimadzu TOC-5050A), with a precision of ± 5% (using potassium
217 hydrogen phthalate as the standard solution). Specific Ultraviolet Absorbance (SUVA)
218 values (mg l^{-1} m^{-1}, ± 5% precision) were calculated by dividing ultraviolet (UV)
219 absorbance at 254 nm normalized by the DOC concentration. SUVA values were then
220 converted into the aromaticity percentage of the OM using the equation of Weishaar et

al. (2003) (aromaticity = 6.52 × SUVA + 3.63). UV absorbance measurements were performed on a Lambda 25 (PerkinElmer) spectrophotometer using deionized water as a blank. Fe(II) concentrations were determined using the 1.10 phenanthroline colorimetric method (AFNOR, NF T90-017, 1997), with a precision of ± 5%. Approximately 1 ml of sample was filtered directly into a 30 ml beaker containing 0.2 ml 1.10 phenanthroline solution (0.5%) and 0.2 ml acetate buffer (pH = 4). After dilution to 5 ml and coloration for 10 min, absorbance was measured at 510 nm. The same method was used for total Fe, but after reducing the samples by an ascorbic acid solution (10%, 0.1 ml per 1 ml filtrate).

3. Results

3.1 Soil/sediment composition

Soil A and sediment S had similar concentrations of clay, loam and silt (24%, 60% and 16% *vs.* 22%, 66% and 12%, respectively), whereas soil B had relatively higher clay (35%) and lower silt (4%) concentrations (**Table 1**). Soil B also differed from soil A and sediment S by having higher organic carbon, total nitrogen, and OM contents, as well as higher C:N ratios. pH values of the three soil/sediment samples were slightly acidic (5.9-6.5). Soil A and sediment S had similar total P contents, with contents (0.93-1.07 g kg^{-1} in dry weight) about two times as high as that in soil B (0.46 g kg^{-1} in dry weight). Extractable P concentrations, including oxalate-P, Dyer-P and Olsen-P, all decreased in the order of soil A > sediment S > soil B, as did their proportions relative to total P contents. All extractable P concentrations were one order of magnitude higher in soil A than in soil B. Oxalate-extractable Fe (oxalate-Fe) contents were in the order

243 of sediment S ≈ soil B > soil A, while oxalate-extractable Si and Al contents were in
244 the order of sediment S > soil B > soil A.

245 ### *3.2 Anaerobic incubations of RW soils*

246 During anaerobic incubation of soils A and B, pH increased rapidly in the first ca.
247 100 h (75 h for soil A) and then increased more slowly to equilibrium values ranging
248 from 7.5-7.6 at the end of incubation (**Figs. 1-2, a**). Eh values, in contrast, decreased
249 rapidly from ca. 300 to 0 mv during the first 70-80 h of incubation and then more slowly
250 to equilibrium values ranging from -150 to -200 mv at the end of incubation.

251 In both soils, NO_3^- concentrations decreased rapidly from initial concentrations of
252 ca. 30 mg l^{-1} to 0 after ca. 75 h of incubation (**Figs. 1-2, b**). SO_4^{2-} concentrations
253 remained constant throughout the two incubations (**Figs. 1-2, b**), unlike DOC
254 concentrations, which increased throughout the incubations. Soil B released more DOC
255 than soil A (149 *vs.* 78 mg l^{-1}, respectively). Aromaticity of the DOC released was low
256 at the beginning of incubation (< 28%), then increased (more slowly in soil A than in
257 soil B) to statistically equivalent ($p = 0.508$, ANOVA) equilibrium values of 31.8 ± 1.4%
258 and 35.1 ± 1.8% for soils A and B, respectively (**Fig. 3**).

259 Little Fe(II) was released before NO_3^- concentrations reached 0, as indicated by
260 the low Fe(II) concentrations recorded during the first 75 h (**Figs. 1-2, c**). Afterwards,
261 Fe(II) concentrations increased until the end of incubation without reaching equilibrium
262 concentrations. Soil B released more Fe(II) than soil A (9.7 *vs.* 2.6 mg l^{-1}, respectively)
263 (**Figs. 1-2, c**). In both incubations, nearly 100% of the Fe released in solution was in
264 the form of Fe(II).

Like Fe(II) concentrations, MRDP and TDP concentrations continuously increased during anaerobic incubation of soils A and B, without reaching equilibrium values (**Figs. 1-2, c**). Interestingly, the releases accelerated slightly after the first 75 h, when NO_3^- concentration reached 0 and Fe(II) concentration started to increase, indicating a close connection between P and Fe(II) release processes (**Figs. 1-2, b-c; S2**). This was further supported by strong positive correlations between the amounts of Fe(II), TDP and MRDP released in soils A and B ($r > 0.921$, **Fig. S3**), except for that between MRDP and Fe(II) in soil B because of its low MRDP concentrations ($r = 0.526$).

Unlike DOC and Fe(II) concentrations, MRDP and TDP concentrations were higher in soil A than in soil B. More importantly, speciation of the TDP released differed greatly between soils A and B, in which it was mainly MRDP (mean = 75%) and MUDP (mean = 71%), respectively (**Figs. 1-2, c**).

3.3 Aerobic incubations of RW soils

Eh values remained constant throughout the 200 h of aerobic incubation of RW soils A and B with increasing pH (from 6.0 to 7.5-7.6), suggesting that aerobic conditions were properly maintained throughout the entire incubations (**Figs. 4-5, a**). SO_4^{2-} concentrations also remained constant throughout these incubations (**Figs. 4-5, b**). Unlike in the corresponding anaerobic incubations, NO_3^- concentrations increased from the initial value of ca. 30 mg l^{-1} to 46 and 65 mg l^{-1} for soils A and B, respectively, from the beginning to the end of the incubation (**Figs. 4-5, b**). Like in the corresponding anaerobic incubations, DOC concentrations increased from ca. 20 mg l^{-1} to 32 and 61 mg l^{-1} in soils A and B, respectively, but their final concentrations were 60% lower than

287 those in the corresponding anaerobic incubations (**Figs. 1-2, 4-5, b**).

288 Fe(II) concentration remained low in the two aerobic incubations (less than 0.29
289 mg l^{-1}), but MRDP and TDP concentrations increased, in line with the increase in pH
290 (**Figs. 4-5, c**). TDP and MRDP increased less than in the corresponding anaerobic
291 incubations, particularly in soil A, whose final TDP concentration was 77% lower than
292 that in the anaerobic incubation (**Figs. 1c, 4c**). Like in the corresponding anaerobic
293 incubations, TDP speciation differed between soils A and B, in which it was mainly
294 MRDP (mean = 83%) and MUDP (mean = 75%), respectively (**Figs. 4-5, c**). DOC,
295 NO_3^-, MRDP and TDP concentrations did not reach equilibrium values after the 200 h
296 of aerobic incubation.

297 ### *3.4 Anaerobic incubation of sediment with and without RW soil*

298 Anaerobic incubation of sediment S alone and mixed with soil B (sample M)
299 yielded Eh, pH, NO_3^-, SO_4^{2-}, DOC and Fe(II) release dynamics (**Figs. 6-7**) similar to
300 those observed during anaerobic incubation of soils A and B (**Figs. 1-2**). Sample M
301 released more Fe(II) and DOC than sediment S alone (**Figs. 6-7, b-c**), which was not
302 unexpected given the high DOC and Fe(II) release potential of soil B under anaerobic
303 conditions (**Fig. 2a-b**). Like in the case of soils A and B, nearly 100% of the Fe released
304 in solution during anaerobic incubation of sediment S and sample M was in the form of
305 Fe(II). Regarding the aromaticity of the DOC released from sediment S and sample M,
306 it was low at the beginning of incubation (< 29%), then increased to similar equilibrium
307 values of 34.2 ± 1.2% and 35.7 ± 0.6%, respectively (**Fig. 3**).

308 Like the anaerobic incubation of soils A and B, anaerobic incubation of sediment

309 S and sample M resulted in progressive releases of TDP and MRDP (**Figs. 6-7, c**), which
310 were linearly correlated with the release of Fe(II) ($r > 0.955$, **Fig. S3**). Sediment S and
311 sample M yielded final TDP concentrations similar to that of soil B alone. Neither
312 incubations performed with sediment S yielded TDP or MRDP concentrations as high
313 as those of incubation of soil A. MRDP was the dominant fraction of TDP during
314 incubation of sediment S (mean = 63%) (**Fig. 6c**). During incubation of sample M,
315 MRDP represented, on average, 47% of the TDP released, a value between those
316 observed during anaerobic incubations for sediment S (63%) and soil B (29%) alone
317 (**Fig. 7c**).

318 # 4. Discussion

319 The experimental approach used in the present study demonstrates that DP can be
320 released under anoxic conditions in RW soils, which is consistent with several previous
321 studies (Dupas et al., 2015; Gu et al., 2017; Knorr et al., 2013; Ponnamperuma, 1972;
322 Reddy et al., 2005; Surridge et al., 2012). During anaerobic incubation, DP and Fe(II)
323 were released simultaneously in the soil solutions, which was also observed during in-
324 situ monitoring of the same soils under natural anoxic conditions (Dupas et al., 2015;
325 Gu et al., 2017). The DOC release and pH increase observed during reduction reactions
326 were also observed during previous incubations performed on the same soils in studies
327 of dissolved OM and trace metal release dynamics under anoxic conditions (Grybos et
328 al., 2007, 2009).

329 ## *4.1 Influence of soil properties on the concentration and speciation of*
330 ## *released DP*

331 The amount and speciation of DP released from RW soils under anoxic conditions
332 can vary among soils, influenced by differences in soil P content and speciation. The
333 release of more TDP, with higher proportion of MRDP, from soil A is consistent with
334 the higher total P and extractable inorganic P (oxalate-P, Dyer-P and Olsen-P) contents
335 in soil A than in soil B. The release of TDP with a higher percentage of MUDP from
336 soil B appears consistent with the higher OM and organic P contents in soil B than in
337 soil A. Previous studies suggested that the differences in P content and speciation
338 observed between soils A and B likely resulted from a combination of factors, including
339 differences in P inputs (annual rate and fertilizer type) before conversion into preserved
340 buffer zones, differences in current vegetation cover, and differences in soil OM
341 mineralization rates (Eriksson et al., 2016; Gu et al., 2017; Khatiwada et al., 2014). As
342 Gu et al. (2017) suggested, prolonged saturation of Kervidy-Naizin wetland B could
343 have decreased the mineralization rate of soil OM, thereby promoting the buildup of
344 organic P in the soil and explaining why soil B released mainly MUDP.
345 The two soils also differed in the Fe:P molar ratios recovered in the soil solutions.
346 The Fe:P molar ratio of reduced soil solutions is an important factor in assessing the
347 risk of whether the DP released can be transferred to watercourses because it determines
348 the capacity of Fe to immobilize DP once re-oxidized at the soil/stream water interface
349 (Baken et al., 2015; Van der Grift et al., 2014, 2016; Zak et al., 2004). Fe:P molar ratios
350 in soil A were low (< 0.5) during the entire anaerobic incubation, whereas those in soil
351 B were much higher, reaching 11.8 at the end of the incubation (**Fig. 8**). The higher
352 Fe:P molar ratios found in soil B could be due to the smaller amount of TDP released

during its anaerobic incubation, but also to the higher amount of reducible Fe found in soil B compared to soil A. Soil Fe-oxyhydroxides mobilized by the oxalate solutions are regarded to consist of amorphous and poorly crystalline Fe phases, which are more susceptible to bioreduction reactions under anoxic conditions (Ehrlich 1990; Lovley and Phillips, 1986), resulting in the release of associated P (i.e. oxalate-P). Thus, the differences in Fe:P molar ratios between soil A and B solutions could also be related to the higher oxalate-Fe content in soil B (**Table 1**).

However, the Fe:P ratio in soil A solution during anaerobic incubation (< 0.5) is much lower than the Fe:P molar ratio anticipated from its soil oxalate-Fe:oxalate-P ratio (16.6). One possibility to explain this discrepancy could be that part of the Fe(II) released precipitated as Fe(II)-bearing minerals such as green rust or Fe(II)-hydroxide minerals. Grybos et al. (2009) have tested this possibility in their previous study of Kervidy-Naizin RW soils which showed a comparable strong deficit in Fe(II) release during anaerobic incubations of these soils. Using the geochemical modeling code PHREEQC (version 2.12.5), they showed that the experimental solutions were under-saturated with respect to green rust and Fe(II)-hydroxide minerals. Thus, the Fe(II)-mineral precipitation hypothesis could not be retained as a possible explanation of the Fe(II) deficit. In fact, Grybos et al. (2009) pointed out that this deficit was more likely explained by the potential (re)adsorption of part of the released Fe(II) onto soil minerals, which is a well-known feature during soil reduction (e.g. Roden, 2003). It is also well-known that this sorption increases with increasing pH (Catrouillet et al., 2017). Given the final pH (≈ 7.5) of the anaerobic incubations in this study, this Fe(II) re-adsorption

hypothesis could explain why the Fe:P molar ratio in soil A solution is much lower than that of the corresponding solid soil.

In their field study of German peatlands, Zak et al. (2004) proposed that a Fe:P molar ratio of 3.0 could be used as a threshold to assess the risk that the MRDP released in anaerobic pore water could be exported to stream and river water. According to their results, a Fe:P molar ratio greater than 3.0 would decrease MRDP concentrations to less than 1 $\mu mol\ l^{-1}$ when soil water enters aerobic conditions at the soil/stream water interface. Conversely, a Fe:P molar ratio less than 3.0 in the solution would result in the export of MRDP to adjacent stream waters because the Fe re-oxidation process could not precipitate enough Fe-oxyhydroxides to immobilize all the DP present in the anoxic soil water. Thus, Fe:P molar ratios in the present study suggest that soil A poses a greater threat than soil B of exporting DP from RW soils to adjacent surface waters under anoxic conditions. This corresponds with field observation of Kervidy-Naizin soil and stream waters which showed that most DP conveyed by the stream at the watershed outlet comes from wetland A, with little contribution from wetland B (Gu et al., 2017).

4.2 Assessing the respective roles of reductive dissolution of Fe-oxyhydroxides and an increase in pH

The DP release under anoxic conditions was concomitant with the reductive dissolution of Fe-oxyhydroxides and the distinct increase in soil solution pH. The increase in pH during reduction of these acidic soils is commonly interpreted as a by-product of the reduction of NO_3^- and Fe(III) by bacteria, since both reduction reactions consume protons (McBride, 1994; Quantin et al., 2001). The fact that reductive

dissolution of Fe-oxyhydroxides occurred only after soil bacteria had completely consumed the NO_3^- is consistent with the order of electron acceptors used by bacteria to oxidize OM in anaerobic soils (Christensen et al., 2000; Stumm and Sulzberger, 1992). The non-equilibrated Fe(II) concentrations could explain the continuous increase in pH and decrease in Eh during anaerobic incubation.

The relative percentages of DP released due to soil Fe-oxyhydroxide reduction and the increase in pH can be estimated by comparing results of the anaerobic (both processes combined) and aerobic (increase in pH alone) incubations of soils A and B. To do so, from the final TDP concentration of each anaerobic incubation, we subtracted the initial TDP concentration in the soil suspension immediately after its preparation, which is likely due to the P release upon rewetting of dry soil (Blackwell et al., 2010; Turner and Haygarth, 2001). TDP release from soils A and B thus reached 3.95 and 0.34 mg l^{-1}, respectively, in the anaerobic incubations, and 0.67 and 0.30 mg l^{-1}, respectively, in the aerobic incubations (**Table 2**). Consequently, the mass balance calculation indicates that the percentage of DP released due to the increase in pH was 17 and 88% during anaerobic incubation of soils A and B, respectively. This suggests that DP release in soil A was controlled mainly by reductive dissolution of Fe-oxyhydroxides, whereas that in soil B was controlled mainly by the increase in pH. This difference in the mechanisms controlling DP release in soils A and B during anaerobic incubation could be related to different capacities of their soil Fe-oxyhydroxides to host P. As indicated by their P and Fe(II) release dynamics, soil Fe-oxyhydroxides in soil A are a major host phase for P, while those in soil B host only a small amount of P. This hypothesis strongly

419 fits with the oxalate-Fe- and -P obtained for the two soils. While soil A has an oxalate-
420 Fe:oxalate-P ratio of ca. 30, soil B has a ratio of >1000, yielding the same conclusion
421 that Fe-oxyhydroxides in soil A contain more P than those in soil B.

422 The difference in mechanisms controlling DP release in soils A and B during
423 anaerobic incubation could also be related to the difference in the two soils' P speciation.
424 As shown in a recent study, soil P is predominantly inorganic (ca. 65%) in wetland A
425 surface soils but predominantly organic in wetland B surface soils (ca. 75%) (Gu et al.,
426 2017). OM generally carries a negative charge in soils, and its sorption on soil minerals
427 reacts highly to changes in pH (Allison, 1973). Thus, the predominance of organic P
428 and high OM content in soil B could explain the strong connection between DP release
429 and the increase in pH in this soil.

430 Interestingly, the same mass-balance calculation for DOC indicated that ca. 63%
431 of its release in both soils was due to reductive dissolution of Fe-oxyhydroxides. These
432 percentages differ from those reported by Grybos et al. (2009), who observed that the
433 increase in pH controlled most DOC release (> 60%) under anoxic conditions. The
434 difference in experimental temperatures (30°C in their study *vs.* 20°C in this study) and
435 pH control protocols of aerobic incubation (direct incubation at pH 7.4 in their study
436 *vs.* gradual increase in the pH from 6.0 to 7.6 in this study) could explain the difference.

437 Mineralization of soil organic P also could have contributed to DP release during
438 the aerobic incubations, a hypothesis that cannot be excluded in this study since the
439 soils were not sterilized prior to incubation. Thus, the DP release quantified due to the
440 increase in pH might be partially from the mineralization of soil organic P by microbes

441 during the incubation process. Further studies are needed to fully assess the potential
442 influence of this third mechanism.

443 ### *4.3 Influence of sediment deposition in RWs on DP release under anoxic*
444 ### *conditions*

445 The eroded soil sediment (sediment S) had higher TDP and extractable P
446 concentrations than soils in their adjacent RWs (soil B). The sediment's oxalate-
447 Fe:oxalate-P ratio (157) suggests that the Fe-oxyhydroxides in this sample are a major
448 P carrier. These findings emphasize the importance of assessing the fate of sediment-
449 borne P when mixed with RW soils. We used soil B as the RW soil end-member given
450 its high content of easily reducible Fe (and thus presumably high Fe-reducing bacterial
451 biomass) and low DP release during reduction. The results of anaerobic incubations of
452 soil B, sediment S and sample M were used to calculate the influence of mixing
453 sediment and soil on DP release under anoxic conditions (**Table 3, Fig. S4**). The
454 potential positive effect of mixing RW soil B and sediment S on DP release under
455 anoxic conditions was assessed by comparing the amount of DP released during
456 incubation of sample M (taking into account of the influence of soil B on sediment S's
457 DP release), with the amount of DP that should be theoretically released by simple
458 addition of the amounts released during their separate incubations (no influence of soil
459 B on sediment S's DP release). Results showed that the sediment-soil mixture released
460 16%, 4% and 18% more TDP, DOC and Fe(II), respectively, than expected from the
461 simple sum of the amounts released during separate incubation. Thus, soil erosion not
462 only can physically transfer P-rich sediments to RWs but also seems to potentially

463 stimulate release of DP from them. Based on the relatively higher increase in DP and
464 Fe(II) release (16 and 18%, respectively) than the increase in DOC release (4%), the
465 stimulation most likely occurs because Fe-reducing bacteria in RW soils increase the
466 reductive dissolution of Fe-oxyhydroxides in the sediments.

467 After their long-term function to limit sediment and nutrient fluxes from field to
468 watercourses, RWs have been reported to act as source zones of DP in agricultural
469 watersheds (Dorioz et al., 2006; Dupas et al., 2015; Gu et al., 2017; Stutter et al., 2009).
470 Several biogeochemical processes have been identified that cause DP release in RW
471 soil solutions, such as drying-rewetting of soils, reductive dissolution of P-rich Fe/Mn
472 oxides, etc. (Blackwell et al., 2009; Bünemann et al., 2013; Dupas et al., 2015; Gu et
473 al., 2017). The present study suggests that deposition of eroded soil sediments onto
474 RWs has a potential to increase DP release by stimulating the reductive dissolution of
475 Fe-oxyhydroxides carried by these sediments and should be accounted for in the
476 management of agricultural landscapes. However, it should be taken into account that
477 the increase in DP release observed here due to sediment addition is low and the results
478 presented here concern only a particular type of sediment incubated with a particular
479 type of RW soil. Other experiments, based on a diversity of sediments and RW soils
480 will be required to fully evaluate the general effect of sediment input on DP release in
481 RWs and identify the detailed mechanisms involved in this release.

482 # 5. Conclusions

483 The present study confirmed the release of DP in RW soils under anoxic conditions.
484 Soil chemical properties, especially OM content and P status, controlled the

concentration and speciation of the DP released. Soil properties, especially the oxalate-extractable Fe and P contents, also influence Fe:P molar ratios in soil solutions during anaerobic incubations, thus controlling the risk of transferring the released DP to watercourses. This study also confirmed the two mechanisms of DP release under anoxic conditions: i) reductive dissolution of Fe-oxyhydroxides and ii) increase in pH. More importantly, the present study provided an approach to identify the nature of the mechanisms involved in mobilizing DP under anoxic conditions in RW soils. The controlling processes of DP release differed between soils: i) by reductive dissolution of soil Fe-oxyhydroxides in soils with high extractable P but low OM contents and ii) by an increase in pH in soils with low extractable P but high OM contents. Under anoxic conditions, the input of eroded sediments into RW soils increased the release of DP, DOC and Fe(II) compared to when the components were incubated separately.

Thus, an important measure to reduce transfer of DP from RWs to watercourses is to decrease soil erosion from upland fields to avoid deposition of P-rich sediments onto RW soils. Management practices to decrease P transfer from agricultural watersheds to rivers should focus not only on installing buffer zones to decrease delivery of P to water, but also on decreasing soil erosion in cultivated fields to avoid these buffer zones become enriched in P. Management practices should also be based on basic soil properties, especially Fe:P molar ratios in anaerobic soil solutions (e.g. soil A), which could be used to estimate the potential risk of transferring DP to watercourses and thus of the potential eutrophication of surface waters. Management efforts should focus preferentially on RW soils whose Fe:P molar ratios upon release during reduction are

the lowest, because they have the highest risk of transferring DP to watercourses.

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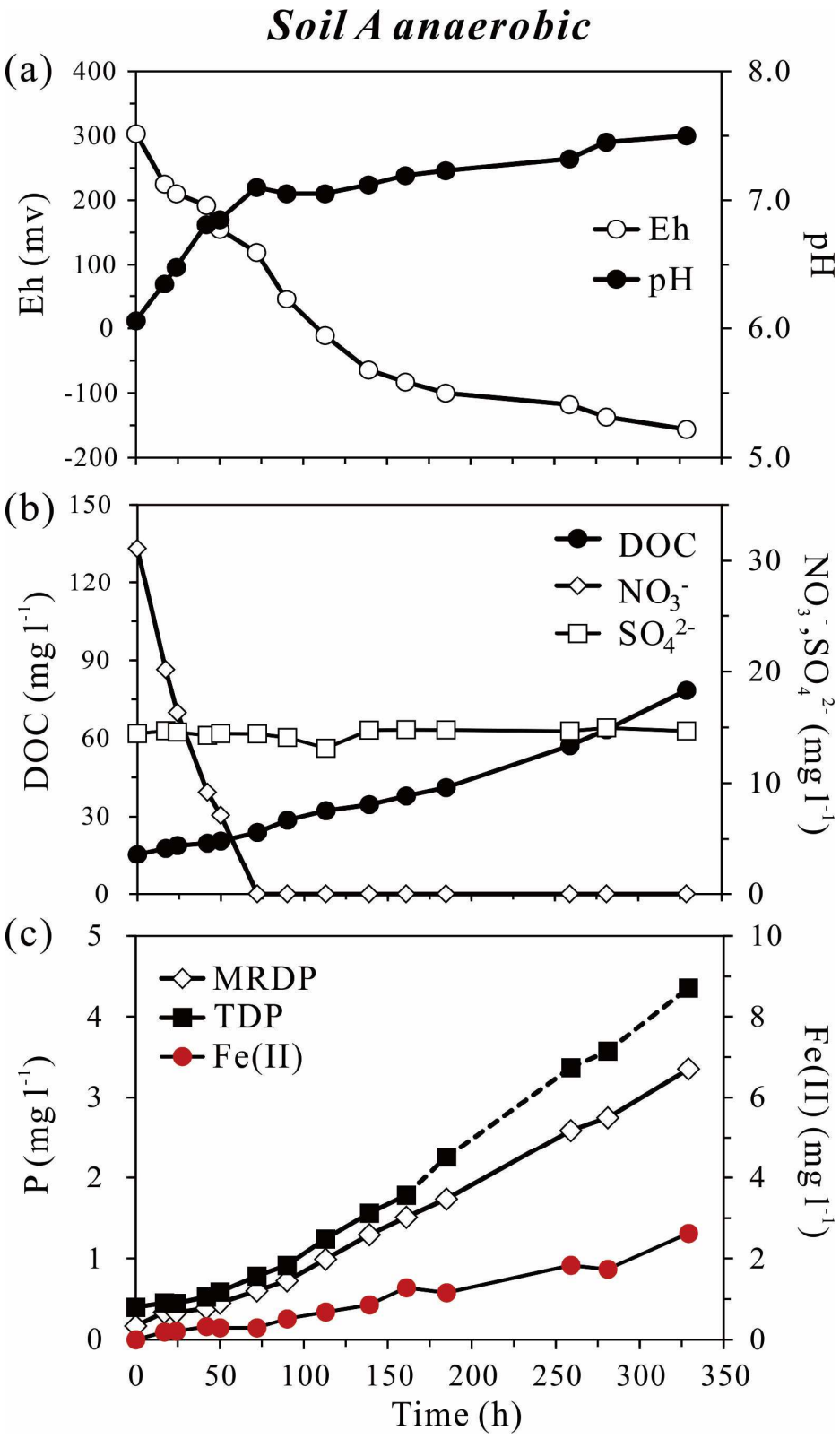


Figure 1. Dynamics of parameters during anaerobic incubation of soil A. (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations. Note that TDP concentrations of samples after 200h were not measured, but rather calculated using a constant TDP:MRDP ratio of 1.3.

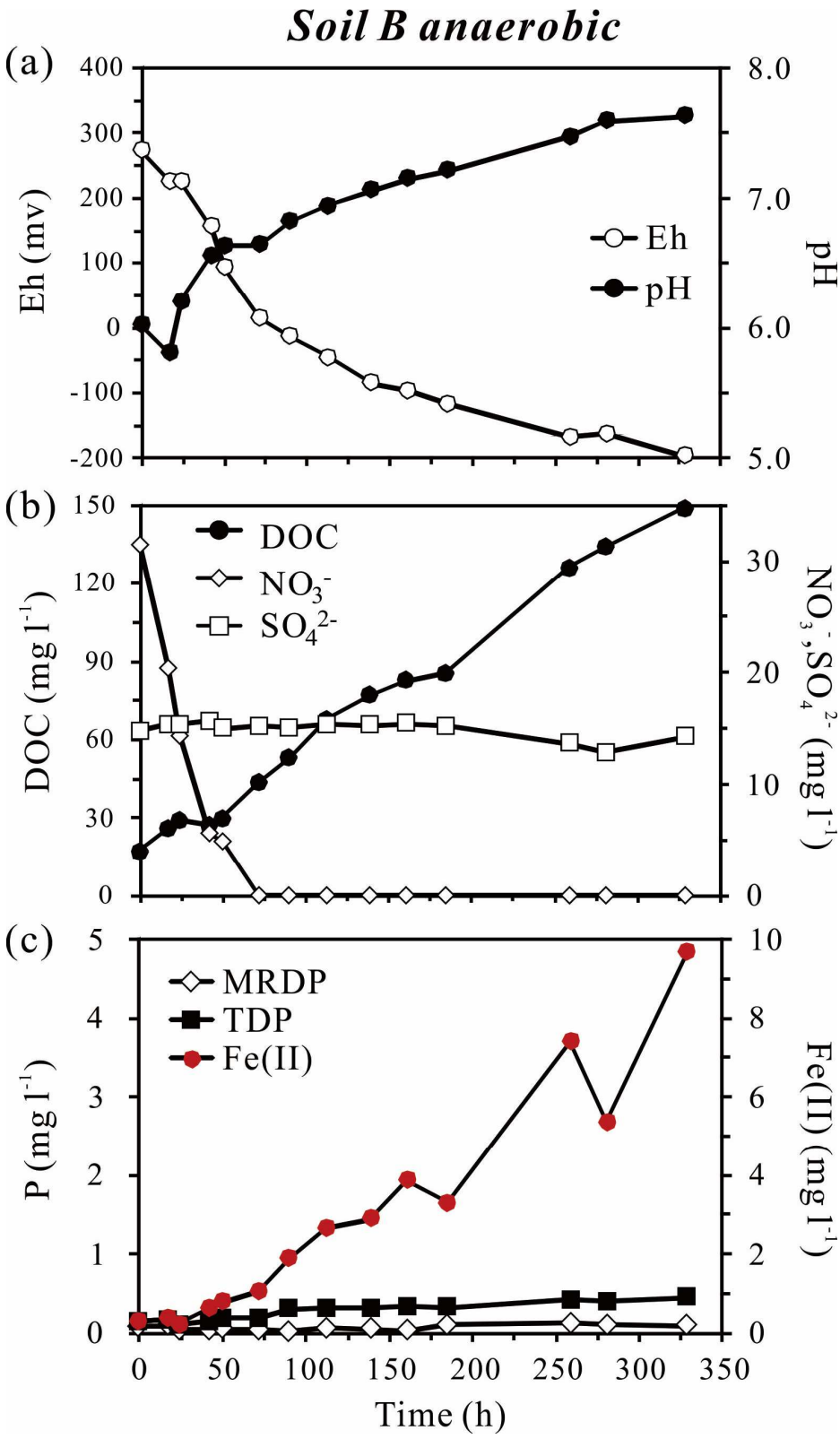


Figure 2. Dynamics of parameters during anaerobic incubation of soil B. (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations.

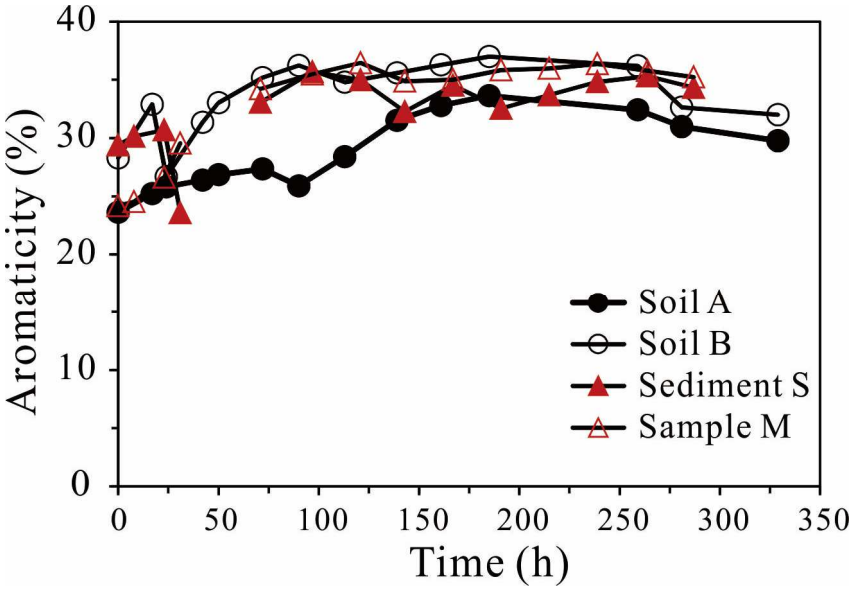


Figure 3. Dynamics of aromaticity of dissolved organic matter released during anaerobic incubation of the soil and sediment samples studied. Sample M is 50% soil B and 50% sediment S by mass.

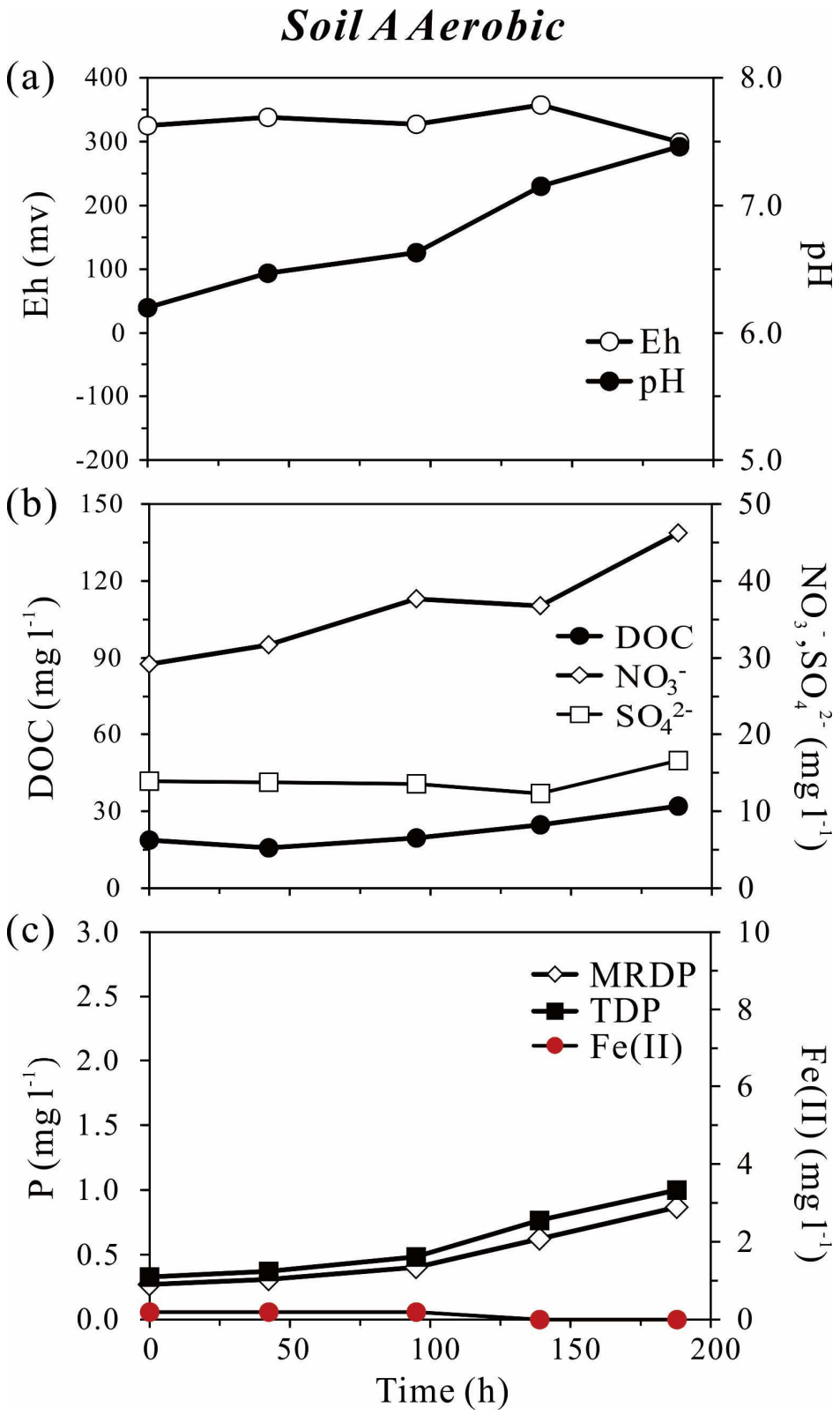


Figure 4. Dynamics of parameters during aerobic incubation of soil A. (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations.

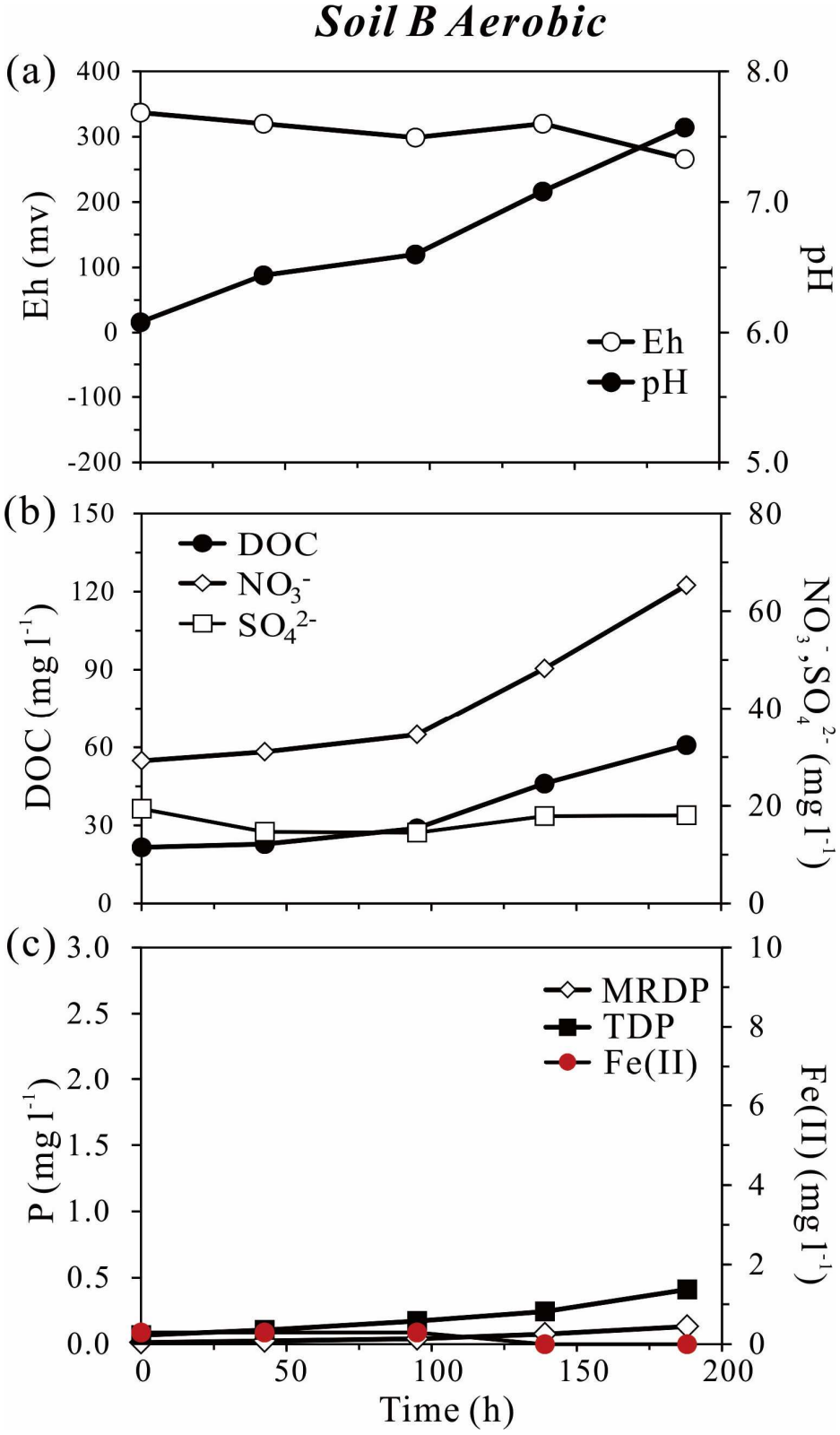


Figure 5. Dynamics of parameters during aerobic incubation of soil B. (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations.

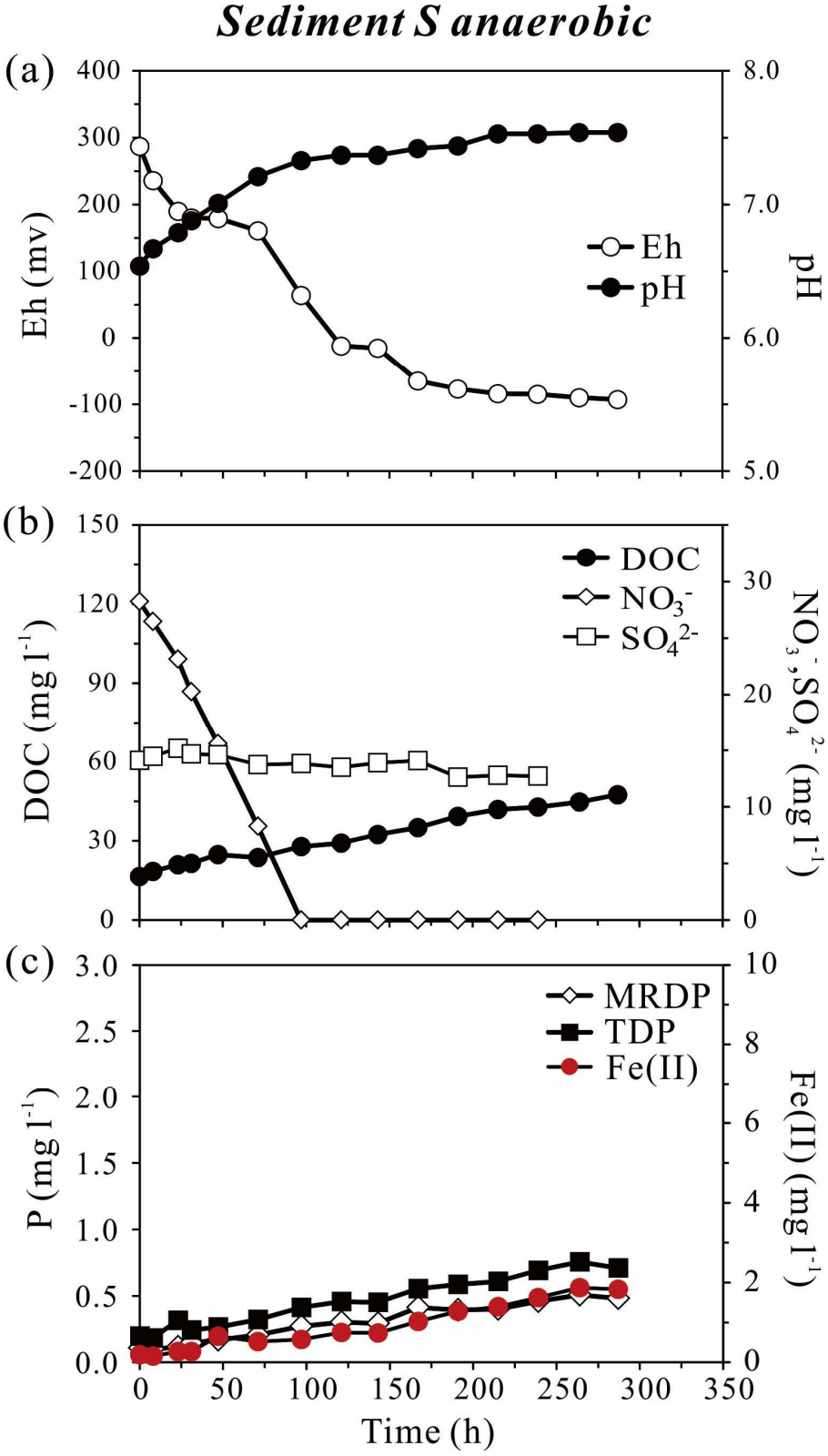


Figure 6. Dynamics of parameters during anaerobic incubation of sediment S. (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations.

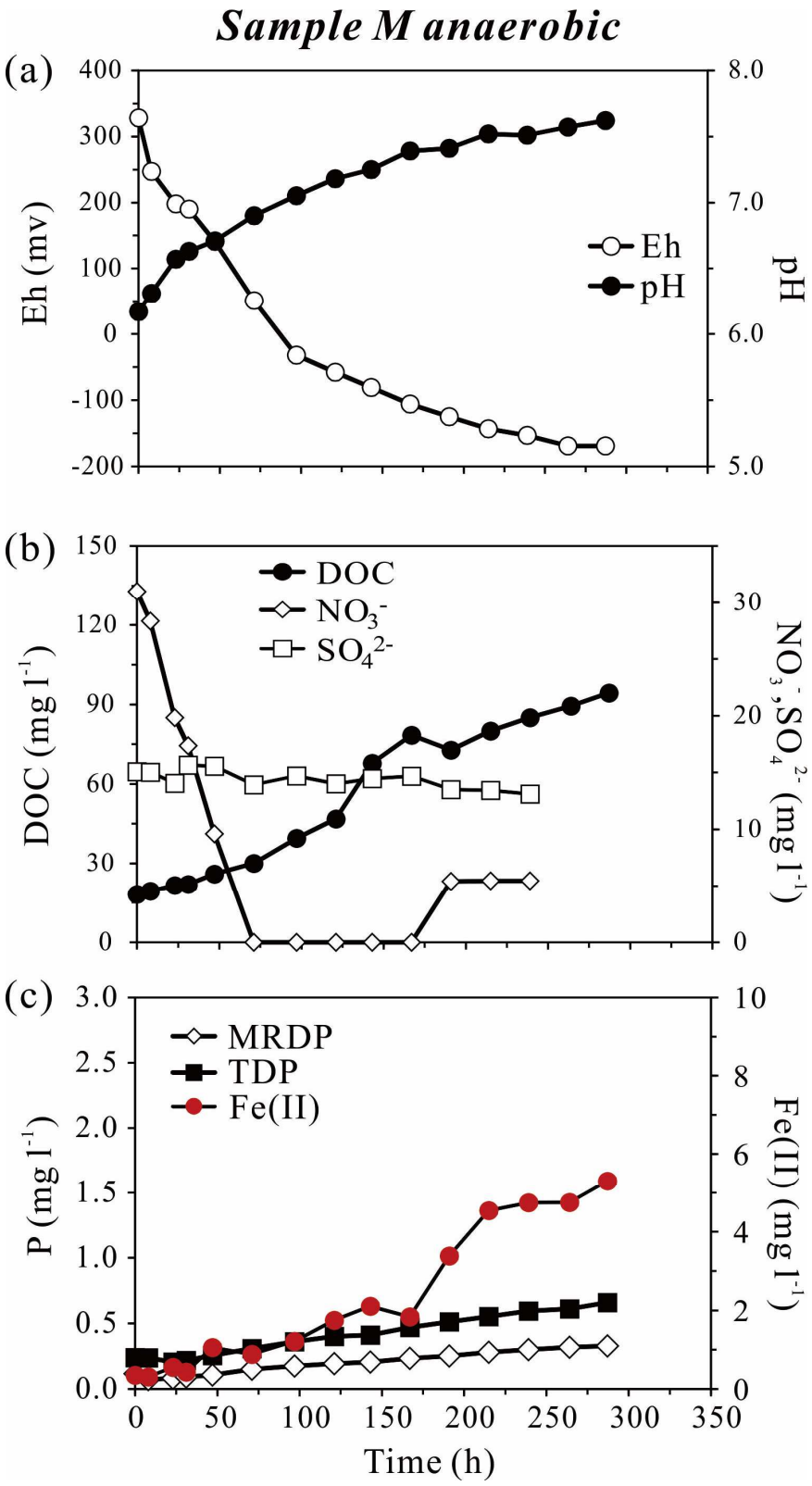


Figure 7. Dynamics of parameters during anaerobic incubation of sample M (50% soil B and 50% sediment S by mass). (a): Eh and pH; (b): dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} concentrations; (c): molybdate-reactive dissolved P (MRDP), total dissolved P (TDP) and Fe(II) concentrations.

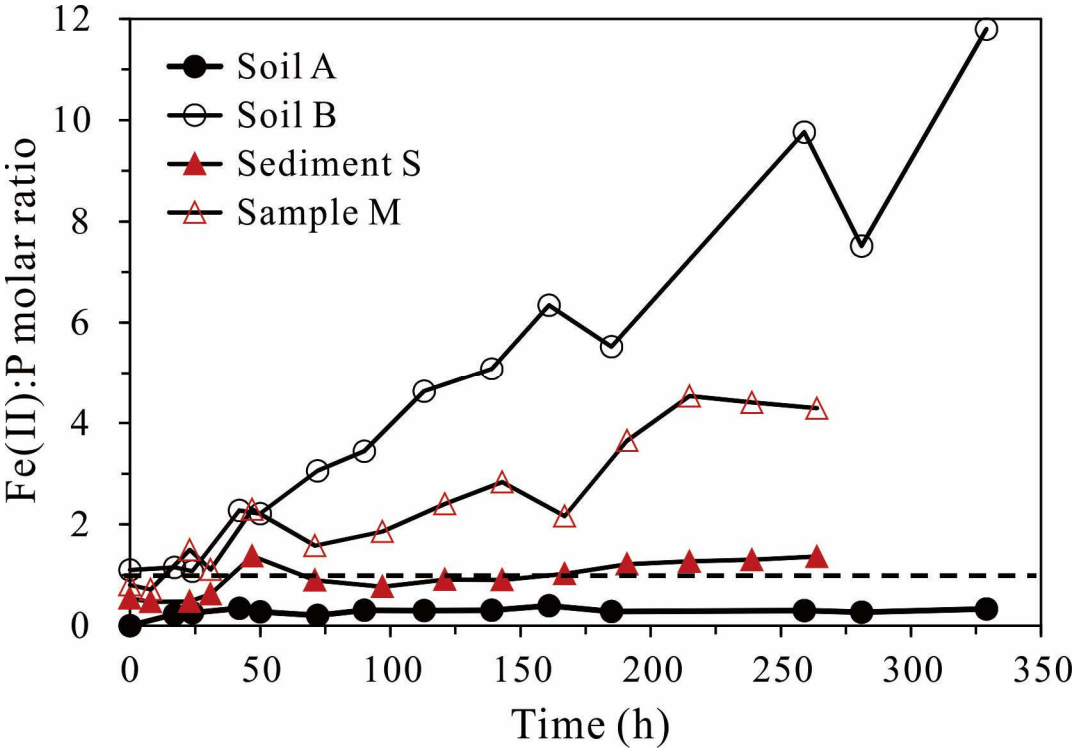


Figure 8. Dynamics of Fe:P molar ratios in anaerobic incubation of soil and sediment samples. "P" in the Fe(II):P ratio is the total dissolved P in the solution. The dashed line indicates the Fe:P ratio of 1.0. Sample M is 50% soil B and 50% sediment S by mass.

Table 1. Main properties of the soil and sediment samples studied.

Soil property (in dry weight)	**Soil A**	**Soil B**	**Sediment S**
Clay (<2 µm) (g kg^{-1})	242	354	222
Fine loam (2-50 µm) (g kg^{-1})	430	456	408
Coarse loam (20-50 µm) (g kg^{-1})	166	147	249
Fine silt (50-200 µm) (g kg^{-1})	87	29	72
Coarse silt (200-2000 µm) (g kg^{-1})	75	14	49
Organic carbon (g C kg^{-1})	37.6	89.1	34.0
Total nitrogen (g N kg^{-1})	3.38	6.35	2.98
C:N ratio	11.1	14.0	11.4
Organic matter (g kg^{-1})	65.0	154.0	58.8
pH	6.08	5.92	6.53
Oxalate-P (g P kg^{-1})	0.20	0.01	0.06
Dyer-P (g P kg^{-1})	0.72	0.03	0.25
Olsen-P (g P kg^{-1})	0.32	0.01	0.11
Oxalate-Si (g Si kg^{-1})	0.25	0.28	0.33
Oxalate-Al (g Al kg^{-1})	1.16	1.56	1.89
Oxalate-Fe (g Fe kg^{-1})	6.01	10.20	9.46
Total P (g P kg^{-1})	1.07	0.46	0.93
P_{Oxal}/P_{tot} (%)	19.1	2.6	6.0
P_{Dyer}/P_{tot} (%)	29.5	2.7	11.5
P_{Olsen}/P_{tot} (%)	5.8	1.5	3.4

Table 2. Calculated amounts of Fe(II), total dissolved P (TDP) and dissolved organic carbon (DOC) released in anaerobic and aerobic incubations of soils A and B.

Soils	Incubation	Concentration (mg l^{-1})			Released	Released	Released
		Fe(II)	Initial TDP	Final TDP	TDP (mg l^{-1})	TDP (%)[a]	DOC (%)[a]
A	Anaerobic	2.62	0.40	4.35	3.95	100.0	100.0
	Aerobic	0	0.33	1.00	0.67	17.0	36.6
B	Anaerobic	9.66	0.11	0.45	0.34	100.0	100.0
	Aerobic	0	0.11	0.41	0.30	88.2	37.8

[a] Calculated as a percentage of the release during anaerobic incubation (anaerobic incubation = 100%).

Table 3. Comparison of total dissolved P (TDP), dissolved organic carbon (DOC) and Fe(II) concentrations measured during anaerobic incubation of sample M (50% soil B and 50% sediment S by mass), and expected concentrations from separate anaerobic incubations of soil B and sediment S.

Parameters	Unit	[a]Soil B (329h)	[b]Soil B (normalized) (287h)	[a]Soil S (287h)	[c]Sample M (calculated) (287h)	[d]Sample M (measured) (287h)	[e]Increased release (%)
TDP	mg l^{-1}	0.45	0.43	0.71	**0.57**	**0.66**	15.7
DOC	mg l^{-1}	148.82	134.12	47.40	**90.76**	**94.26**	3.9
Fe(II)	mg l^{-1}	9.66	7.13	1.83	**4.48**	**5.30**	18.3

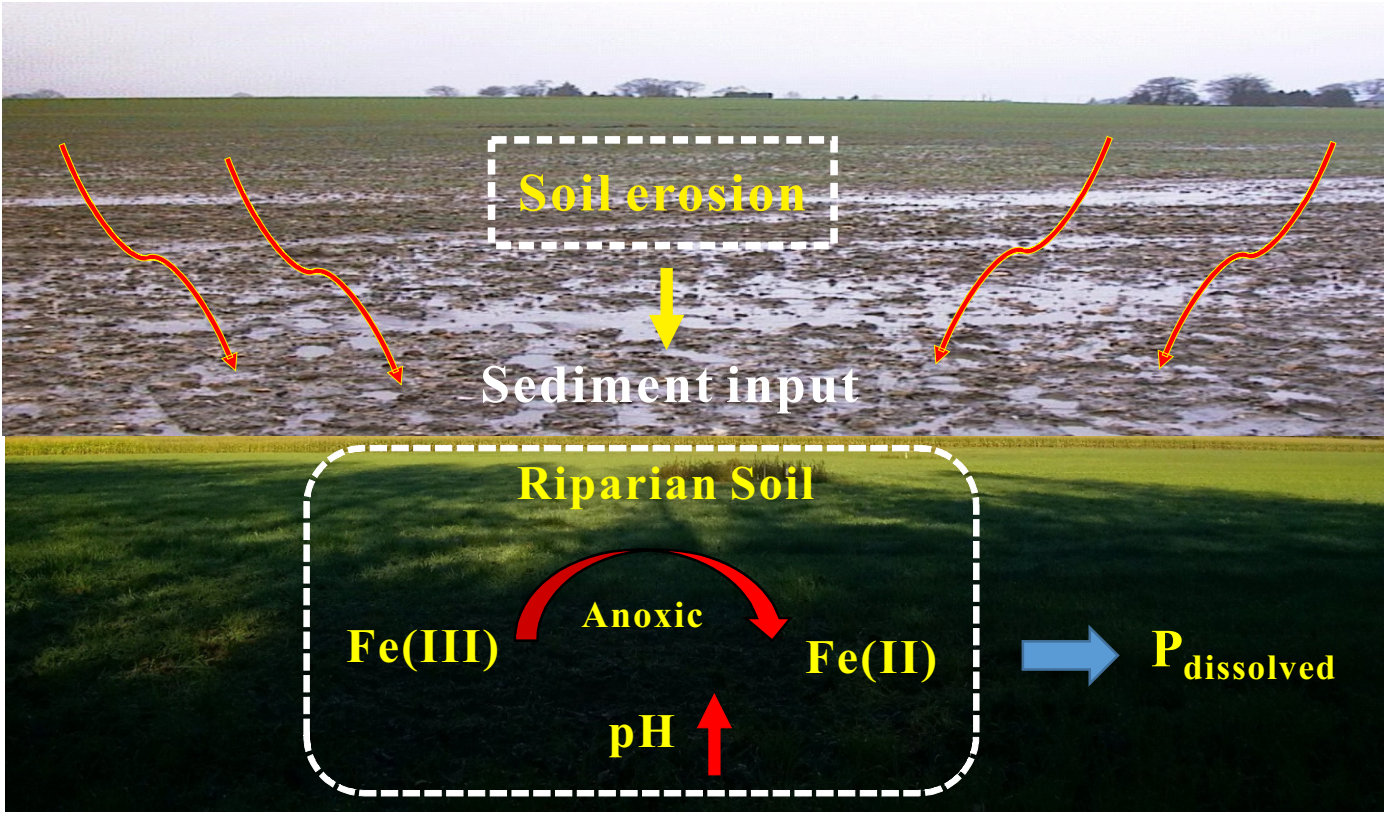
[a]Concentrations measured at the given time during separate anaerobic incubations of sediment S and soil B.

[b]Concentrations calculated using the concentration-time linear regression equations shown in **Figure S3.**

[c]Concentrations calculated from Soil B (normalized) (287 h) and Soil S (287 h) using mass balance equations, assuming that mixing had no effect on the release of TDP, DOC and Fe(II).

[d]Concentrations measured during anaerobic incubation of sample M.

[e]Calculated as the percentage increase in measured concentrations of Sample M compared to those calculated.


Soil erosion
Sediment input
Riparian Soil
Fe(III)
Anoxic
Fe(II)
pH
P dissolved