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1 Phosphorus losses from agricultural land to natural  
2 waters are reduced by immobilization in iron-rich  
3 sediments of drainage ditches

4  
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15  
16 **Abstract**

17 Redox reactions involving iron (Fe) strongly affect the mobility of phosphorus (P) and its  
18 migration from agricultural land to freshwater. We studied the transfer of P from groundwater  
19 to open drainage ditches in an area where, due to Fe(II) rich groundwater, the sediments of  
20 these ditches contain accumulated Fe oxyhydroxides. The average P concentrations in the  
21 groundwater feeding two out of three studied drainage ditches exceeded environmental limits

22 for freshwaters by factors 11 and 16, but after passing through the Fe-rich sediments, the P  
23 concentrations in the ditch water were below these limits. In order to identify the processes  
24 which govern Fe and P mobility in these systems, we used diffusive equilibration in thin films  
25 (DET) to measure the vertical concentration profiles of P and Fe in the sediment pore water  
26 and in the ditchwater. The Fe concentrations in the sediment pore water ranged between 10  
27 and 200 mg L<sup>-1</sup> and exceeded those in the inflowing groundwater by approximately one order  
28 of magnitude, due to reductive dissolution of Fe oxyhydroxides in the sediment. The  
29 dissolved P concentrations only marginally increased between groundwater and sediment pore  
30 water. In the poorly mixed ditchwater, the dissolved Fe concentrations decreased towards the  
31 water surface due to oxidative precipitation of fresh Fe oxyhydroxides, and the P  
32 concentrations decreased more sharply than those of Fe. These observations support the view  
33 that the dynamics of Fe and P are governed by reduction reactions in the sediment and by  
34 oxidation reactions in the ditchwater. In the sediment, reductive dissolution of P-containing  
35 Fe oxyhydroxides causes more efficient solubilization of Fe than of P, likely because P is  
36 buffered by adsorption on residual Fe oxyhydroxides. Conversely, in the ditchwater, oxidative  
37 precipitation causes more efficient immobilization of P than of Fe, due to ferric phosphate  
38 formation. The combination of these processes yields a natural and highly efficient sink for P.  
39 It is concluded that, in Fe-rich systems, the fate of P at the sediment-water interface is  
40 determined by reduction and oxidation of Fe.

41

#### 42 **Keywords**

43 phosphorus sorption, iron oxyhydroxides, iron oxidation, phosphorus binding, water quality,  
44 diffusive equilibrium in thin films

45

## 46 **1. Introduction**

47 Excessive fertilization of agricultural land has resulted in large losses of phosphorus (P) from  
48 soils to the aquatic environment. This has caused cultural eutrophication of lakes, streams,  
49 and estuaries in many developed countries worldwide (Correll, 1999; Schindler, 2012; Smith,  
50 2003). Losses of P from agricultural land may occur either by soil erosion and overland flow  
51 or by leaching, *i.e.* vertical transport through the soil profile. Globally, overland flow is the  
52 principal pathway in most catchments (Hansen et al., 2002). Such losses are related to erosion  
53 of particulate P during storm events, mostly in fine-textured soils (Sharpley et al., 2001). The  
54 transport and environmental effects of eroded P have been studied in great detail (Delgado  
55 and Scalenghe, 2008; Ekholm, 1994). Conversely, in well-drained soils with low P sorption  
56 capacity, P losses predominantly occur through leaching (Van der Zee, 1988). Such percolates  
57 may cause P-enrichment of shallow groundwater and may ultimately reach the aquatic  
58 environment via the groundwater flow. The lowland areas of Belgium and the Netherlands  
59 have acid sandy soils with a long history of excessive fertilizer application. These soils are P-  
60 saturated and exhibit large leaching losses to shallow groundwater (Lookman et al., 1995;  
61 Van der Zee et al., 1990). In such soils, it is difficult to balance agronomic needs (optimal  
62 crop production) and environmental concerns (limited P leaching) (del Campillo et al., 1999).

63 The transport of P from percolate or groundwater through drains to the aquatic environment is  
64 often assumed to be conservative, *i.e.* it is not much affected by chemical processes  
65 (Schoumans et al., 2013; van der Salm et al., 2011). However, as P-enriched groundwater  
66 surfaces, it seeps through micro-oxic and highly redox-active environments, such as the  
67 linings of drainage tubes or the sediments of streams and ditches. In such environments, P  
68 may undergo complex chemical interactions with several redox-active elements, most notably  
69 with Fe. As hydrous ferric oxides are submerged and become anoxic, they may undergo  
70 reductive dissolution, which is often microbially mediated (Lovley, 1997). Conversely, in

71 oxic or micro-oxic environments, the reduced and highly mobile Fe(II) may be re-oxidized  
72 either chemically (Davison and Seed, 1983) or biotically (Druschel et al., 2008). The oxidized  
73 Fe(III) readily precipitates as authigenic hydrous ferric oxides, such as ferrihydrite or  
74 lepidocrocite (Baken et al., 2013; Duckworth et al., 2009; Fortin et al., 1993).

75 Several studies have already addressed the interactions between Fe and P at the interface  
76 between anoxic and oxic environments. Reductive dissolution of hydrous ferric oxides  
77 generally releases associated P (Liu, 2010), and the release of P from reconstructed wetlands  
78 is of environmental concern (Zak and Gelbrecht, 2007; Zak et al., 2010). However, in some  
79 cases, the release of P from anoxic sediments is limited, possibly due to formation of vivianite  
80 (Heiberg et al., 2012, 2008). The subsequent oxidation of Fe(II) produces hydrous ferric  
81 oxides which combine a high specific surface area with a high affinity for oxyanions  
82 (Dzombak and Morel, 1990). They may bind P by adsorption or coprecipitation and are very  
83 efficient sinks for P. The formation of various ferric phosphate minerals with low molar Fe:P  
84 ratios, in some cases even down to unity, have been reported in synthetic solutions (Kaegi et  
85 al., 2010; Mayer and Jarrell, 2000; Voegelin et al., 2010), stream sediments (Hyacinthe and  
86 Van Cappellen, 2004), and lakes (Gunnars et al., 2002; Lienemann et al., 1999).

87 The coupling of reductive dissolution and oxidation of Fe may lead to intense Fe cycling,  
88 which has been observed in a variety of environments including sediments, groundwater  
89 seeps, and lakes (Blöthe and Roden, 2009; Davison, 1993; Gault et al., 2011; Kleeberg et al.,  
90 2013). Diffusive techniques, such as Diffusive Gradients in Thin films (DGT) or Diffusive  
91 Equilibration in Thin films (DET), are highly suited for probing the chemical composition of  
92 such environments. Some recent methodological studies have already simultaneously  
93 determined spatially resolved Fe and P concentrations using diffusive techniques (Cesbron et  
94 al., 2014), and a study by Xu et al. (2013) showed a strong relationship between Fe and P  
95 concentrations in the pore waters of an incubated sediment. However, few studies have

96 examined Fe-P interactions in systems with combined reduction and oxidation reactions.  
97 Based on column experiments, Kjaergaard et al. (2012) speculate that if P and Fe(II) are  
98 concomitantly released from submerged soils, the export of P may be attenuated by the  
99 downstream re-oxidation of Fe(II) and subsequent binding of P. Zak and Gelbrecht (2004)  
100 and Zak et al. (2010) showed that even if high P concentrations are measured in the pore  
101 waters of reconstructed wetlands, the risk of P export is limited if molar Fe:P ratios in soils  
102 and pore waters do not fall below critical values. Immobilization of P by such processes may  
103 be a key process limiting P export from selected environments, but the limited evidence  
104 warrants further studies.

105 This study was set up in order to identify the processes which govern the dynamics of Fe and  
106 P at the anoxic-oxic boundary. More specifically, we set out to determine how chemical Fe-P  
107 interactions in the sediment of drainage ditches can reduce the dissolved P concentrations  
108 from far above to well below environmental limits. The transport of dissolved P from Fe(II)-  
109 bearing groundwater to open drainage ditches was monitored in an agricultural area where P  
110 losses predominantly occur through leaching (Lookman et al., 1995; Van der Zee, 1988 and  
111 references therein). Vertical concentration profiles of dissolved P and Fe at the sediment-  
112 water interface of open drainage ditches were measured at 1 cm resolution using the DET  
113 (diffusive equilibrium in thin films) technique. Our approach relied on field measurements,  
114 since laboratory studies of redox-sensitive systems are inherently prone to artefacts (Brand-  
115 Klibanski et al., 2007). We hypothesize that P export from drainage ditches is reduced by  
116 binding on freshly produced hydrous ferric oxides, and that P is scavenged in the oxic zone as  
117 long as the Fe:P ratio in the source (groundwater or sediment) exceeds a threshold value.

## 118 2. Materials and methods

### 119 2.1. Study sites

120 The study sites are located in the Kleine Nete catchment (Northern Belgium) which is  
121 characterized by acid sandy soils with iron-rich groundwater. The geography, geology, and  
122 hydrology of this catchment have been described in detail elsewhere (Vanlierde, 2013;  
123 Vanlierde et al., 2007). The land use in the area is characterized by intensive agriculture and  
124 animal husbandry, which cause diffuse emissions of P to the environment. After decades of  
125 excessive manure application, the soils are P-saturated (Lookman et al., 1995). The P losses  
126 mainly occur through leaching to the groundwater: the P concentrations in phreatic  
127 groundwater in the area commonly range between 0.02 and 2 mg L<sup>-1</sup>. Greensands in the  
128 underground supply reduced Fe(II) to the groundwater, which yields groundwater Fe  
129 concentrations between 1 and 90 mg L<sup>-1</sup> (Vanlierde, 2013). Due to the flat topography, the  
130 streams are predominantly fed by phreatic groundwater: the groundwater contribution to the  
131 discharge of the Kleine Nete near the town of Grobbendonk is estimated at 87% (Vanlierde et  
132 al., 2007). The groundwater table is shallow and fluctuates seasonally. The groundwater may  
133 seep directly into the streams, or it may be exported from agricultural fields in the lowlands  
134 by drainage systems which are abundantly present in the area. Especially in winter and early  
135 spring, when the phreatic groundwater tables are at their highest level, export through  
136 drainage systems is likely the major pathway of P export from groundwater to streams.

137 Two lowland agricultural sites adjacent to streams of the Kleine Nete catchment were selected  
138 for this study (Figures S1 and S2). At both sites, agricultural fields are drained by open  
139 ditches. At the bottom of the ditches, a reddish brown precipitate occurs, suggesting  
140 enrichment of Fe. Since the groundwater table fluctuates seasonally, the ditches generally  
141 drain groundwater from October to April, whereas in summer, the groundwater table is

142 usually just below the bottom of the ditches. The top sediment layer is, therefore, oxic during  
143 the summer months but submerged and likely more reduced during the winter. Site 1, located  
144 in the municipality of Retie, has two similar open drainage ditches (labelled ditch 1 and ditch  
145 2) adjacent to the same agricultural field. They receive no inputs from tributary ditches or  
146 pipes until their outlet into the nearby stream. The ditches are approximately 1 m wide and  
147 200-300 m in length, and the sediment surface is around 70 cm below the soil surface. The  
148 field was used for growing fodder maize during the summer of 2013. Before that, the field  
149 had been permanent grassland for at least 5 years and received annual organic manure inputs  
150 corresponding to at most 35 kg P ha<sup>-1</sup>. According to the Belgian soil map, the soils consist of  
151 (very) wet and strongly gleyic sandy loam with a reduction horizon at 100—120 cm below the  
152 soil surface (Belgian soil classification: Sep3z). According to WRB, the soil is classified as a  
153 fluvic gleyic umbrisol (Dondeyne et al., 2014). The groundwater table at this site fluctuates  
154 seasonally between 5 and 70 cm below the soil surface. Site 2, located in the municipality of  
155 Vorselaar, consists of an area of fallow fields drained by a network of ditches. One ditch of  
156 this network was selected for this study and was labelled ditch 3. These ditches are smaller  
157 than at site 1: approximately 30 cm wide and 20 cm deep. According to the Belgian soil map,  
158 the soils consist of wet and strongly gleyic sandy loam with a reduction horizon between 100  
159 and 120 cm depth and with a thick humic accumulation in the topsoil (Belgian soil  
160 classification: s-Pep3). According to WRB, the soil is classified as a fluvic gleyic umbrisol  
161 (Dondeyne et al., 2014). The adjacent fields had been permanent grassland for at least two  
162 years, and they receive organic manure inputs similar to those at site 1. The groundwater table  
163 fluctuates seasonally between 10 and 40 cm below the soil surface.

## 164 *2.2. Sampling of sediment, ditchwater, and groundwater*

165 At two locations next to each drainage ditch, two groundwater monitoring wells (filtered  
166 between 1 and 2 m depth) were installed at close distance (< 5 m) to the ditch. Automatic



167 hydraulic head loggers (Mini-divers, Schlumberger Water Services) were installed which  
168 measured the height of the water table every 15 minutes. In August 2013, when the drainage  
169 ditches were dry, the sediment of each ditch and the underlying parent material was sampled  
170 down to 60-90 cm below the sediment surface with a gouge auger. The sediment cores were  
171 subdivided into 10 cm-sections, air-dried, and the concentrations of oxalate extractable  
172 elements ( $P_{ox}$ ,  $Fe_{ox}$ ,  $Al_{ox}$ ,  $Mn_{ox}$ ) were determined according to Schwertmann (1964). This  
173 procedure is generally used in order to quantify the poorly crystalline oxyhydroxides of Fe,  
174 Al, and Mn, and the associated P. The P sorption capacity (PSC) and the degree of P  
175 saturation (DPS) of each section were calculated as (Lookman et al., 1995; Van der Zee et al.,  
176 1990):

$$PSC = 0.5 \cdot (Fe_{ox} + Al_{ox})$$

$$DPS = \frac{P_{ox}}{PSC}$$

177 (Equation 1)

178 with  $Fe_{ox}$ ,  $Al_{ox}$  and  $P_{ox}$  in molar units.

179 The groundwater and ditchwater were sampled on 6 occasions between September 2013 and  
180 February 2014 in each ditch. The groundwater was sampled with a peristaltic pump after first  
181 discarding at least three well volumes. The drainage water was sampled at two locations in  
182 each ditch with a syringe and was withdrawn either 1 or 10 cm below the water surface. The  
183 pH, water temperature and  $O_2$  concentration were measured in the field (CellOx 325 and  
184 SenTix 21 electrodes, WTW, Germany). Groundwater and ditchwater samples were  
185 membrane filtered in the field (Acrodisc syringe filters with Supor 0.45  $\mu m$  membrane), and  
186 subsamples were immediately acidified (HCl, final concentration 0.01 M). The dissolved  
187 organic carbon (DOC), Fe(II), and total element concentrations were determined in the

188 acidified subsamples. The DOC was measured as the non-purgeable organic carbon on an  
189 elemental analyzer (AnalytikJena, Multi N/C 2100), the Fe(II) was determined  
190 colorimetrically using the ferrozine method (Viollier et al., 2000), and total element  
191 concentrations were measured with ICP-MS (Agilent 7700x). The soluble reactive P (SRP)  
192 was determined in selected samples by the molybdenum blue method (Murphy and Riley,  
193 1962). The dissolved concentrations of anions (Cl, SO<sub>4</sub> and NO<sub>3</sub>) were determined in the non-  
194 acidified subsamples of selected samples with anion chromatography (Dionex ICS-2000 with  
195 AS18 column), and dissolved inorganic carbon (DIC) was determined with an elemental  
196 analyzer (AnalytikJena, Multi N/C 2100). All constituents were determined after membrane  
197 filtration (0.45 µm) and are hereinafter referred to as “dissolved”.

### 198 *2.3. Concentration profiles of Fe and P by diffusive equilibration*

199 The diffusive equilibration in thin films (DET) technique was used to collect vertically  
200 resolved profiles (resolution 1 cm) of the Fe and P concentrations in the sediment pore water  
201 and in the overlying layers of water in the drainage ditches (Davison et al., 1994, 1991). The  
202 diffusive gel is in contact with the sampled water through a 0.45 µm membrane filter, and  
203 after diffusive equilibration, the composition of the water in the DET gel is equal to that of the  
204 sediment pore water. Details of the DET procedure are described in the supporting  
205 information. Briefly, assembled and deoxygenated DET probes were inserted into the  
206 sediment for 24 hours. At the same moment, groundwater and ditchwater was sampled as  
207 described in section 2.2. Upon retrieval, the probes were immediately immersed in 0.01 M  
208 NaOH in order to immobilize Fe and P. Upon return to the lab, the probes were disassembled,  
209 the diffusive gels were sliced in sections of 10 mm, immersed in 1 M HCl, and the Fe and P  
210 concentrations were measured by ICP-MS. The detection limits in sediment pore waters  
211 sampled by this method were 0.1 mg L<sup>-1</sup> for P and 0.03 mg L<sup>-1</sup> for Fe.

212 We anticipated that the precipitation of Fe oxyhydroxides, caused by immersion in NaOH,  
213 also causes immobilization of P as long as sufficiently large amounts of Fe are present to bind  
214 the P. This was verified in synthetic solutions containing  $10 \text{ mg L}^{-1}$  Fe(II) (as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ )  
215 and varying concentrations of P (from a stock solution of  $1000 \text{ mg L}^{-1}$   $\text{PO}_4$  as  $\text{KH}_2\text{PO}_4$ , Merck  
216 Millipore) buffered at pH 4 by 0.01 M acetic acid. The low pH was adopted in order to avoid  
217 oxidation of Fe(II) to Fe(III) under ambient conditions. Four gel slices were inserted into each  
218 solution and were deployed for 24 hours. Immediately after retrieval from the solution, the Fe  
219 and P in the gel slices were immobilized by immersion in 0.01 M NaOH. Thereafter, the gels  
220 were re-eluted by immersing them in 1 M HCl for 24 hours. The concentrations of Fe and P in  
221 the synthetic solutions and in the gel eluates were measured with ICP-MS.

222

## 223 3. Results

### 224 3.1. Sediment cores

225 The cores of the ditch sediment and the underlying parent material exhibited markedly similar  
226 characteristics in all three studied ditches. The top 1 cm of the sediment layer consisted  
227 mostly of finely textured, reddish brown material. A reduction horizon was observed between  
228 30 and 50 cm below the surface of the ditch sediment (pictures in the Supplementary  
229 Material). Above the reduction horizon, black and reddish brown colours dominated, which  
230 are indicative of accumulations of organic matter and Fe oxyhydroxides. Below the reduction  
231 horizon, the soil was permanently reduced and consisted of pale, greenish grey sands. Oxalate  
232 extractions (Figure 1, Figure S3, and Table S1) showed that the top sediment layer was highly  
233 enriched in poorly crystalline Fe oxyhydroxides: the concentration of oxalate extractable Fe  
234 was up to 11% on a dry weight basis. The oxalate extractable concentrations of Fe and P in  
235 the top layers exceeded those in the deeper layers by one or two orders of magnitude. In  
236 contrast, the Fe:P ratio did not differ more than by a factor of 4, and the vertical distribution  
237 patterns of Fe and P were markedly similar. The concentrations of oxalate extractable Al and  
238 Mn did not follow the vertical distribution of Fe, and molar concentrations of Al and Mn were  
239 much lower than those of Fe in the top sediment layer. This shows that P was strongly  
240 associated with poorly crystalline Fe oxyhydroxides, but less so with oxyhydroxides of Al and  
241 Mn. The degree of P saturation in the top sediment layers of the studied ditches was between  
242 13 and 31%. Acid sandy soils are considered P-saturated and pose a risk for leaching of P if  
243 they have a degree of P saturation in excess of 25% (Van der Zee et al., 1990). Therefore, at  
244 first glance, it appears that the drainage ditches may have limited ability to retain inputs of  
245 groundwater-borne P.

246

247        3.2. *Composition of groundwater and ditchwater*

248        The average composition of groundwater and ditchwater is reported separately for each  
249        studied ditch (Table 1). The groundwater was slightly acidic to neutral (pH between 5.5 and  
250        7.0), moderately hard, and contained dissolved oxygen concentrations below 1 mg L<sup>-1</sup>. The  
251        groundwater contained, on average, 9 mg L<sup>-1</sup> Fe (near ditch 1) and 7 mg L<sup>-1</sup> Fe (near ditch 3),  
252        with little temporal variation, whereas the groundwater near ditch 2 contained much less Fe  
253        (0.2 mg L<sup>-1</sup>). The average P concentrations in the groundwater near ditches 1 and 3 also  
254        exceeded that near ditch 2 by approximately one order of magnitude. The molybdate reactive  
255        P (MRP) concentrations in selected groundwater samples were almost equal to the P  
256        concentrations measured by ICP-MS, suggesting that nearly all P in the groundwater is  
257        present as inorganic orthophosphate, and that organic P compounds play a minor role (Van  
258        Moorlehem et al., 2011). The P concentrations in two ditches appeared to decrease between  
259        the autumn and the winter season. The exact reason for this decrease is not clear, but it may  
260        be related to fertilization of the adjacent fields.

261        The ditchwater was stratified: 10 cm below the surface of the ditchwater, the O<sub>2</sub> concentration  
262        was around 1 mg L<sup>-1</sup>, *i.e.* not much different from that in the groundwater, whereas just below  
263        the water surface, the O<sub>2</sub> concentration generally increased to 2—5 mg L<sup>-1</sup>. Conversely, the Fe  
264        concentrations in the ditchwater at 10 cm below the surface exceeded those near the water  
265        surface by up to two orders of magnitude. In most samples, the dissolved Fe was almost  
266        exclusively present as reduced Fe(II). No clear temporal trend was observed in the Fe and P  
267        concentrations in ditchwater. The groundwater and ditchwater contained relatively high  
268        concentrations of SO<sub>4</sub>, and the SO<sub>4</sub> concentrations in the ditchwater are above those in the  
269        groundwater. This shows that the ditch was no sink for SO<sub>4</sub>, suggesting that no extensive SO<sub>4</sub>  
270        reduction occurred in the studied systems.

271        *3.3. Concentration profiles of Fe and P by diffusive equilibration*

272        The Fe and P in synthetic solutions are almost quantitatively recovered from diffusive gels  
273        after equilibration, immobilization in 0.01 M NaOH, and re-elution in 1 M HCl (> 87%, mean  
274        94% for both elements, Table 2). The P measured in the diffusive gels differed from that in  
275        solution in only one treatment, which was likely because the P concentration was near the  
276        detection limit ( $100 \mu\text{g L}^{-1}$ ) of this method. Surprisingly, the recovery of P remained  
277        unaffected when the molar Fe:P ratio in the synthetic solutions decreased to unity. The above  
278        results show that the P is effectively bound to the Fe after immersion in NaOH, likely as  
279        coprecipitate with hydrous ferric oxide or as ferric phosphate. The diffusive gels appear to  
280        underestimate the Fe and the P concentrations slightly but systematically by about 6%. This  
281        may be caused by minor errors in gel thickness or porosity. Alternatively, upon immersing the  
282        gel in NaOH, a small part of the Fe and P may diffuse out of the gel before it is precipitated  
283        and immobilized. Despite these minor issues, the experiment overall shows that Fe and P can  
284        be quantified at molar Fe:P ratios down to unity by means of diffusive gel equilibration,  
285        immobilization in NaOH, and re-elution in HCl.

286        Seventeen concentration profiles of Fe and P in the sediment pore water and in the overlying  
287        ditchwater were obtained with the DET method. The probes revealed Fe concentrations in the  
288        sediment pore water between 10 and  $200 \text{ mg L}^{-1}$ , which is up to two orders of magnitude  
289        above those in groundwater (Table 1 and Figure 2). In the sediment pore water, the profiles of  
290        the Fe concentrations were variable: they decreased, remained more or less constant, or  
291        increased with elevation (Figure 2; more details in the Supplementary Material). In the  
292        overlying ditchwater, some profiles showed a sharp decrease in Fe concentrations just above  
293        the sediment-water interface (e.g. profiles C and D in Figure 2), but in other profiles, the Fe  
294        concentrations remained more or less equal to those in the sediment pore water (e.g. profiles  
295        A and B in Figure 2). The spatial heterogeneity was large: probes installed 50 cm apart

296 yielded markedly different concentration profiles. We did not observe any clear temporal  
297 trends in sediment pore water concentrations of Fe and P, possibly because such trends are  
298 overshadowed by the large spatial heterogeneity. However, in spite of the large variability, the  
299 ditchwater samples taken with a syringe at 1 cm and 10 cm below the water surface invariably  
300 contained lower Fe concentrations than those measured with DET probes in the water layers  
301 close to the sediment-water interface. The average Fe concentrations decreased from 77 mg L<sup>-1</sup>  
302 in the sediment pore water to 5 mg L<sup>-1</sup> near the water surface. Hence, Fe concentrations in  
303 the ditchwater decreased with increasing elevation.

304 The P concentrations in the sediment pore water varied from below detection limit  
305 (< 100 µg L<sup>-1</sup>) to 6000 µg L<sup>-1</sup>. The P concentrations in the sediment pore water of ditch 1  
306 covered the range of the corresponding groundwater, whereas the P concentrations in the  
307 sediment pore water of ditches 2 and 3 exceeded those in the groundwater by a factor of 4.  
308 Four out of 17 concentration profiles contained sections in which the P concentrations were  
309 below the detection limit of the DET sampling method (100 µg L<sup>-1</sup>), e.g. profile C in Figure 2,  
310 and for plotting purposes these data points are shown at an arbitrary value of 50 µg L<sup>-1</sup>. In the  
311 sediment pore water, the P concentrations generally did not vary much with depth below the  
312 sediment-water interface. However, most P concentration profiles, including profiles B, C,  
313 and D in Figure 2, showed a sharp decrease in P concentrations near the sediment-water  
314 interface. The P concentrations measured in the ditchwater at 1 cm and 10 cm below the water  
315 surface were invariably lower than those in the sediment pore water. The average P  
316 concentrations decreased from 890 µg L<sup>-1</sup> in the sediment pore water to 26 µg L<sup>-1</sup> near the  
317 water surface. No clear temporal trends in P concentrations in the sediment pore water were  
318 observed. In summary, as groundwater flows into the drainage ditches, the P concentrations  
319 decrease sharply.

#### 320 **4. Discussion**

321       4.1. Reductive dissolution and oxidative precipitation of Fe

322       Similar mechanisms appear to govern the behaviour of Fe and its interaction with P in the  
323       three studied ditches. The concentrations of Fe and P in the groundwater, sediment pore  
324       water, and ditchwater of the three ditches are summarized in Figure 3. As groundwater flows  
325       into the sediment of the drainage ditch, the Fe concentrations strongly increase by up to two  
326       orders of magnitude (Figure 3). Reductive dissolution of hydrous ferric oxides in the sediment  
327       likely explains this increase. The oxalate extractions of the sediment cores showed that there  
328       is an abundant stock of readily reducible Fe oxyhydroxides available. There is also ample  
329       supply of electron donors, *i.e.* readily degradable organic C derived from decaying vegetation  
330       which grows lavishly in the ditch in the summer season. The abundant stock of readily  
331       reducible Fe oxyhydroxides in the sediment of the studied drainage ditches may be the result  
332       of a process similar to the formation of bog iron ore: an accumulation of groundwater-borne  
333       Fe over prolonged periods of time in hydromorphic soils. Due to the fluctuating groundwater  
334       table, the top sediment layer is oxic in summer, but it is likely gradually more reduced as it  
335       becomes submerged in autumn. Previous studies have shown similar or greater increases in  
336       dissolved Fe concentrations upon waterlogging of soils (Hofacker et al., 2013; Van Laer et al.,  
337       2010), and the reduction of Fe oxyhydroxides may occur at rates well above those needed to  
338       explain the observed increase in dissolved Fe concentrations from the groundwater to the  
339       sediment pore water (Blöthe and Roden, 2009; Kleeberg et al., 2013). Possibly, oxidation and  
340       reduction reactions occur simultaneously and at approximately the same location in the  
341       sediment, which result in strong Fe redox cycling. We were unable to measure the O<sub>2</sub>  
342       concentrations in the sediment, and therefore the extent of Fe redox cycling in the sediment of  
343       the studied systems remains unknown. Possibly, the ditch sediments exhibit transitions in  
344       redox regime as they are submerged for increasingly longer times during the winter. Our data  
345       did not show any clear temporal trends in Fe concentrations in the sediment pore water or in



346 the overlying ditchwater, but such temporal trends may be overshadowed by the large  
347 variability due to spatial heterogeneity. In addition, we studied the ditches only from  
348 September to February, but they are usually submerged until April or May. Any shifts in  
349 redox regime during these final months of waterlogging are not reflected in this study.

350 Based on the results of oxalate extractions and on previous studies (Voegelin et al., 2010), we  
351 assume that poorly crystalline oxyhydroxides and perhaps amorphous ferric phosphates are  
352 the most important reactive Fe phases present in the sediment. We did not study e.g. the  
353 conversion of poorly crystalline Fe oxyhydroxides to more crystalline phases. Goethite may  
354 occur in systems similar to the ones in this study (Mansfeldt et al., 2012). However, goethite  
355 would not be dissolved in oxalate extractions, and its presence would therefore not affect our  
356 results (Schwertmann, 1973). Furthermore, other reactive Fe phases, such as vivianite or Fe  
357 sulphides, may be present, even though  $\text{SO}_4$  measurements suggest that no extensive sulphate  
358 reduction occurred in the studied systems.

359 In the ditch, *i.e.* above the sediment-water interface, the Fe concentrations decrease with  
360 increasing elevation above the interface (Figure 3). Oxidation of Fe(II) and subsequent  
361 precipitation of Fe oxyhydroxides is the key mechanism by which removal of Fe from the  
362 dissolved phase occurs. Assuming pH values between 5.5 and 7.0, dissolved  $\text{O}_2$   
363 concentrations of 2—6  $\text{mg L}^{-1}$ , and temperatures between 5 and 15°C, the rate of chemical  
364 Fe(II) oxidation in the studied systems is predicted to result in half-lives of Fe(II) between 2  
365 hours and 3 years (Davison and Seed, 1983). However, groundwater seeps are typical  
366 environments where Fe oxidizing (and reducing) bacteria thrive (Blöthe and Roden, 2009),  
367 and therefore it is likely that microbially mediated Fe oxidation outpaces the chemical  
368 oxidation reaction. The vertical concentration profiles of Fe in the ditchwater were highly  
369 variable, which may mostly be due to physical processes such as the local flow velocity,  
370 turbulence, and mixing. Nevertheless, the average Fe concentration near the water surface was

371 only 7% of that in the sediment pore water, showing that most of the Fe produced in the  
372 sediment is re-oxidized and precipitated in the ditch before it is drained into the receiving  
373 streams. The kinetics of Fe oxidation in drainage systems have recently been studied in  
374 greater detail by Van der Grift et al. (2014). In summary, as drainage water flows upward into  
375 the ditch, the Fe concentrations decrease due to oxidation of Fe(II).

#### 376 *4.2. Release and binding of P*

377 The average P concentrations in the sediment pore water were similar to those in  
378 groundwater, or they exceeded those in the groundwater by at most a factor of four (Figure 3  
379 and Table 1). Surprisingly, this increase (in relative terms) is much less pronounced than that  
380 of Fe. Since Fe and P are strongly associated with each other in the sediment, it is expected  
381 that reductive dissolution releases Fe and P at a molar ratio equal to that in the sediment. Most  
382 likely, the released P is bound again by the residual pool of Fe oxyhydroxides in the sediment.  
383 The oxalate extractions showed that Fe is present in excess in the sediments  
384 (Fe:P > 5 mol:mol in the top sediment layer). Previous work on Fe-rich submerged soils has  
385 also shown that the release of P is less than expected based on the release of Fe and the molar  
386 Fe:P ratio in the solid (Rakotoson et al., 2014). Alternatively, the P-containing Fe  
387 oxyhydroxides may be less available for microbial reductive dissolution than P-free Fe  
388 oxyhydroxides, as previously shown by O'Loughlin (2013). Based on our data, we can neither  
389 confirm nor rule out that the P concentrations in the sediment pore water vary temporally due  
390 to shifts in redox regime as the ditch sediment is inundated for increasingly longer times: we  
391 did not observe such temporal trends, but they may be overshadowed by the high spatial  
392 variability. Based on the oxalate extractions, it is expected that poorly crystalline Fe  
393 oxyhydroxides are primarily responsible for binding and release of P in the sediments.  
394 Perhaps also ferric phosphates play a role (Hyacinthe and Van Cappellen, 2004). Other  
395 minerals, such as vivianite (Walpersdorf et al., 2013), may also contribute to binding and

396 release of P, but vivianite formation could not explain the rapid removal of P as the  
397 groundwater surfaces and reaches (micro-)oxic environments. In summary, the above shows  
398 that reductive dissolution solubilizes P in the sediments of drainage ditches, but due to the  
399 abundantly present Fe oxyhydroxides, much of this P is again bound by the residual pool of  
400 Fe oxyhydroxides.

401 The sharp change in P concentrations near the sediment-water interface (Figure 2 and Figure  
402 3) is most likely caused by oxidation of Fe(II) and binding of P. Despite the variable sediment  
403 pore water P concentrations, those in the top ditchwater layer were invariably low ( $<100 \mu\text{g L}^{-1}$ ),  
404 showing that P removal was efficient during the studied period (September—February).  
405 The rapid removal of P from oxidizing Fe-containing groundwater samples has previously  
406 been noted. Studies in synthetic solutions have shown that, as Fe(II) is oxidized in the  
407 presence of phosphate, amorphous ferric phosphate with a molar Fe:P ratio of 1.8 is formed  
408 until P is nearly depleted from solution. Thereafter, during continued oxidation of Fe(II), the  
409 ferric phosphate is converted to a P-containing hydrous ferric oxide (Voegelin et al., 2013,  
410 2010). Results from a recent field study strongly suggest that these mechanisms also occur in  
411 the environment as Fe-containing groundwater is oxidized (van der Grift et al., 2014).

412 Taken together, reductive dissolution of P-containing Fe oxyhydroxides in the sediment  
413 preferentially solubilizes Fe, because the released P is bound again by residual Fe  
414 oxyhydroxides. Conversely, oxidative precipitation in the overlying water preferentially  
415 immobilizes P: since the water contains molar Fe:P ratios far above unity, ferric phosphate  
416 formation causes more efficient immobilization of P than of Fe. The combination of these  
417 processes results in a natural and highly efficient sink for P: the average P concentrations in  
418 the groundwater feeding two out of three studied drainage ditches exceeded environmental  
419 limits for freshwaters ( $70 \mu\text{g L}^{-1}$ , commonly measured as MRP in unfiltered samples (Flemish  
420 Government, 1995)) by factors 11 and 16, but after passing through the Fe-rich sediments, the

421 dissolved P concentrations in the drainage water were below these limits. Therefore, our  
422 results combined with previous studies appear to confirm that oxidizing Fe in groundwater or  
423 drainage water is a highly efficient natural mechanism for immobilization of dissolved P.

#### 424 *4.3. Implications for P-removal technology and watershed management*

425 Interactions between Fe and P have already been utilized in technological applications. For  
426 example, Fe-coated sand as a liner in drainage systems reduce the P export (Chardon et al.,  
427 2005; Groenenberg et al., 2013). We showed that a similar result is obtained by reaction of P  
428 with naturally present Fe. One difference is that, in the present study, the P was removed  
429 while oxidation of Fe was ongoing. Previous studies in synthetic solutions have shown that,  
430 under such conditions, ferric phosphates are formed (Voegelin et al., 2013). Ferric phosphates  
431 may contain up to one mole of P per mole of Fe, which is stoichiometrically the highest  
432 possible efficiency for P binding. We speculate that technology for the removal of P from  
433 diffuse sources, such as agricultural drainage systems, may be based on the oxidation of  
434 reduced Fe. However, key challenges include the mode of Fe addition to the system, and the  
435 retention of the formed Fe oxyhydroxide particles at the outlet.

436 Since Fe-P interactions can critically affect P fluxes, such processes should be taken into  
437 account when assessing the eutrophication risk associated with P losses from agricultural  
438 land. A key challenge is to determine the circumstances under which P is retained by Fe in  
439 drainage systems. Based on this study, it appears that the P concentrations in drainage water  
440 are mostly determined by the composition and reactivity of the sediment of the drainage ditch,  
441 and not much by the initial composition of the groundwater. We therefore suggest that the  
442 molar Fe:P ratio in oxalate extractions of drainage ditch sediments is a feasible candidate for  
443 predicting P losses from open drainage ditches with Fe-rich sediments. The molar Fe:P ratio  
444 has previously been proposed as a useful tool for estimating the mobility of P in sediments.

445 For example, in rewetted fens, molar Fe:P ratios of 10 in bicarbonate-dithionite extractions of  
446 sediment material have been suggested as a limit above which no critical P export is expected  
447 (Zak et al., 2010). However, for systems similar to those studied here, no Fe:P threshold  
448 below which there is a eutrophication risk in the receiving streams has been determined so far.  
449 In the present study, we measured molar Fe:P ratios in oxalate extracts of drainage ditch  
450 sediments between 6 and 14. Despite being close to or below the threshold for P-saturated  
451 soils (Van der Zee et al., 1990), the P concentrations in drainage water flowing through these  
452 sediments did not exceed environmental limits. Clearly, more work is needed in order to  
453 identify the relationship between the composition of the sediment and the resulting P  
454 concentrations in the drainage effluent.

455 We have based our study on measurements of concentrations in the operationally defined  
456 “dissolved” ( $< 0.45 \mu\text{m}$ ) fraction, and have so far ignored the transport of particulate P. It  
457 must be acknowledged that during periods of very high flow, particulate P may be mobilized  
458 from drainage ditches and exported to the receiving streams. The P associated with Fe  
459 oxyhydroxides is less available to biota than dissolved orthophosphate (Baken et al., 2014),  
460 but it may become available e.g. after undergoing reductive dissolution in the streambed  
461 sediment further downstream. Therefore, even though dissolved P losses are low in the  
462 studied areas, sediment losses from drainage systems may still impair water quality in the  
463 receiving streams.

## 464 **5. Conclusions**

465

466 - In the redox active zone between groundwater and surface water, P and Fe strongly interact.

467 - Immobilization of P may occur in periodically inundated drainage ditches with Fe-rich  
468 sediments. This is the result of two chemical processes: reductive dissolution in the sediment  
469 and oxidative precipitation in the ditchwater.

470 - This natural sequestration of P leads to a decreased P flux from groundwater to surface  
471 water. This must be taken into account in watershed management plans and in assessments of  
472 the environmental risk associated with P losses from agricultural land.

473 - Technologies for P removal from drainage water may be based on Fe-P interactions in the  
474 redox active zone.

475

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#### 480 **Supplementary Material**

481 Supplementary data associated with this article can be found, in the online version, at <insert  
482 link here>.

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656 Table 1: The composition (mean  $\pm$  standard deviation;  $n = 1-7$  for anion and C measurements and 5-12 for other measurements) of drained  
657 groundwater at different stages along its trajectory from the subsurface to the surface. The groundwater was sampled using monitoring wells, the  
658 sediment pore water was sampled with DET probes at 1-10 cm below the sediment-water interface, and the ditchwater was sampled with a  
659 syringe either 1 cm or 10 cm below the water surface. The reported values are derived from measurements at two locations along each ditch and  
660 on up to 6 occasions between September 2013 and February 2014.

		pH	O <sub>2</sub> mg L <sup>-1</sup>	Fe mg L <sup>-1</sup>	P μg L <sup>-1</sup>	Fe/P mol:mol	Al μg L <sup>-1</sup>	Mn μg L <sup>-1</sup>	K mg L <sup>-1</sup>	Ca mg L <sup>-1</sup>	Na mg L <sup>-1</sup>	Mg mg L <sup>-1</sup>	Cl mg L <sup>-1</sup>	SO <sub>4</sub> mg L <sup>-1</sup>	NO <sub>3</sub> mg L <sup>-1</sup>	DOC mg L <sup>-1</sup>	DIC mg L <sup>-1</sup>	
DITCH 1	ditchwater, 1 cm deep	5.9 $\pm$ 0.3	4.5 $\pm$ 2.5	3.2 $\pm$ 3.6	20 $\pm$ 21	136 $\pm$ 108	15 $\pm$ 9	335 $\pm$ 57	13 $\pm$ 4	29 $\pm$ 2	22 $\pm$ 1	10 $\pm$ 2	50 *	93 *	11.0 *	7 *	5 *	
	ditchwater, 10 cm deep	5.7 $\pm$ 0.3	0.7 $\pm$ 0.8	25.5 $\pm$ 27.9	71 $\pm$ 117	335 $\pm$ 117	12 $\pm$ 6	337 $\pm$ 61	10 $\pm$ 3	26 $\pm$ 7	21 $\pm$ 1	9 $\pm$ 1	nm	nm	nm	10 $\pm$ 4	5 *	
	sediment pore water			77.5 $\pm$ 21.8	653 $\pm$ 430	233 $\pm$ 105												
	groundwater	6.0 $\pm$ 0.4	0.5 $\pm$ 0.1	8.5 $\pm$ 3.6	1085 $\pm$ 1228	12 $\pm$ 9	18 $\pm$ 13	289 $\pm$ 156	24 $\pm$ 16	49 $\pm$ 21	23 $\pm$ 3	12 $\pm$ 5	44 $\pm$ 10	60 $\pm$ 31	1.2 $\pm$ 1.9	22 $\pm$ 15	36 $\pm$ 4	
DITCH 2	ditchwater, 1 cm deep	5.9 $\pm$ 0.7	3.9 $\pm$ 1.5	11.0 $\pm$ 9.0	18 $\pm$ 10	393 $\pm$ 323	10 $\pm$ 7	551 $\pm$ 289	7 $\pm$ 2	48 $\pm$ 5	22 $\pm$ 2	7 $\pm$ 1	44 $\pm$ 9	146 $\pm$ 66	0.5 $\pm$ 0.4	7 $\pm$ 0.4	11 $\pm$ 7	
	ditchwater, 10 cm deep	5.9 $\pm$ 0.3	0.7 $\pm$ 0.5	33.8 $\pm$ 23.2	19 $\pm$ 9	1010 $\pm$ 785	12 $\pm$ 6	630 $\pm$ 240	7 $\pm$ 2	54 $\pm$ 7	22 $\pm$ 2	7 $\pm$ 1	51 $\pm$ 3	195 $\pm$ 14	0.2 $\pm$ 0.04	10 $\pm$ 3	9 $\pm$ 6	
	sediment pore water			101.2 $\pm$ 57.9	219 $\pm$ 157	1006 $\pm$ 576												
	groundwater	6.1 $\pm$ 0.2	0.6 $\pm$ 0.2	0.2 $\pm$ 0.3	49 $\pm$ 19	2 $\pm$ 3	11 $\pm$ 7	230 $\pm$ 254	24 $\pm$ 9	72 $\pm$ 17	30 $\pm$ 8	17 $\pm$ 4	59 $\pm$ 6	69 $\pm$ 6	84.3 $\pm$ 80.5	27 $\pm$ 5	53 $\pm$ 9	
DITCH 3	ditchwater, 1 cm deep	6.7 $\pm$ 0.3	3.1 $\pm$ 1.7	1.5 $\pm$ 2.2	37 $\pm$ 32	16 $\pm$ 12	5 $\pm$ 2	111 $\pm$ 87	3 $\pm$ 0.4	72 $\pm$ 8	9 $\pm$ 1	6 $\pm$ 1	20 *	66 *	0.1 *	11 $\pm$ 2	49 $\pm$ 5	
	ditchwater, 10 cm deep	6.8 $\pm$ 0.2	1.1 $\pm$ 0.4	6.2 $\pm$ 10.5	100 $\pm$ 154	27 $\pm$ 21	5 $\pm$ 1	227 $\pm$ 211	3 $\pm$ 1	77 $\pm$ 8	10 $\pm$ 1	7 $\pm$ 0.4	16 $\pm$ 6	45 $\pm$ 28	0.2 *	14 $\pm$ 3	50 $\pm$ 6	
	sediment pore water			47.7 $\pm$ 33.7	2743 $\pm$ 1903	30 $\pm$ 7												
	groundwater	6.4 $\pm$ 0.4	0.5 $\pm$ 0.2	7.1 $\pm$ 1.2	744 $\pm$ 525	8 $\pm$ 4	4 $\pm$ 2	70 $\pm$ 47	4 $\pm$ 2	44 $\pm$ 8	7 $\pm$ 2	3 $\pm$ 1	10 $\pm$ 3	13 $\pm$ 6	1.9 $\pm$ 2.0	8 $\pm$ 1	30 $\pm$ 1	

661 DOC: dissolved organic carbon; DIC: dissolved inorganic carbon; nm: not measured; \*: single observation, no standard deviation available

662

663

664 Table 2: Fe and P concentrations, their standard errors ( $n = 4$ ), and their recovery measured in  
 665 diffusive gels after equilibration with synthetic solutions, fixation with NaOH, and re-elution  
 666 with HCl.

IN SYNTHETIC SOLUTION			IN DIFFUSIVE GELS				
Fe	P	Fe:P	Fe	recovery	P	recovery	Fe:P
$mg L^{-1}$	$mg L^{-1}$	<i>mol:mol</i>	$mg L^{-1}$	%	$mg L^{-1}$	%	<i>mol:mol</i>
10.4	0.14	41	9.3 ± 0.2	90	0.20 ± 0.01	141	26
10.2	0.29	19	9.3 ± 0.1	92	0.31 ± 0.02	105	17
10.0	0.57	10	9.7 ± 0.1	97	0.55 ± 0.04	96	10
10.2	1.18	4.8	9.5 ± 0.04	93	1.04 ± 0.03	88	5.1
10.1	1.50	3.8	9.8 ± 0.1	96	1.31 ± 0.07	87	4.2
10.1	1.95	2.9	10.0 ± 0.2	98	1.91 ± 0.06	98	2.9
10.2	2.94	1.9	9.5 ± 0.1	93	2.70 ± 0.09	92	2.0
10.2	5.93	1.0	9.3 ± 0.2	91	5.60 ± 0.13	94	0.9

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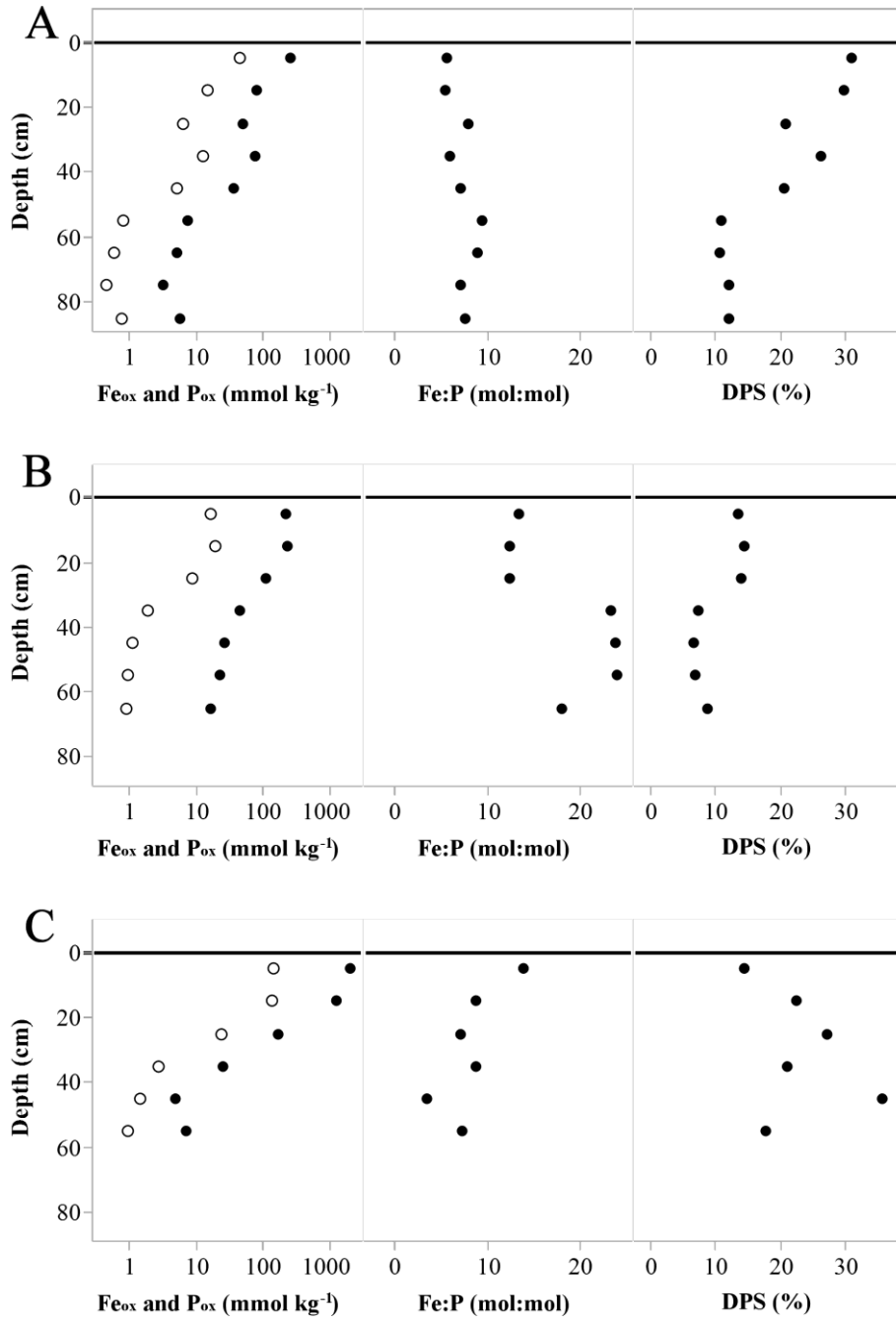
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671 **Figures**

672 Figure 1, Figure 2, Figure 3: see below.

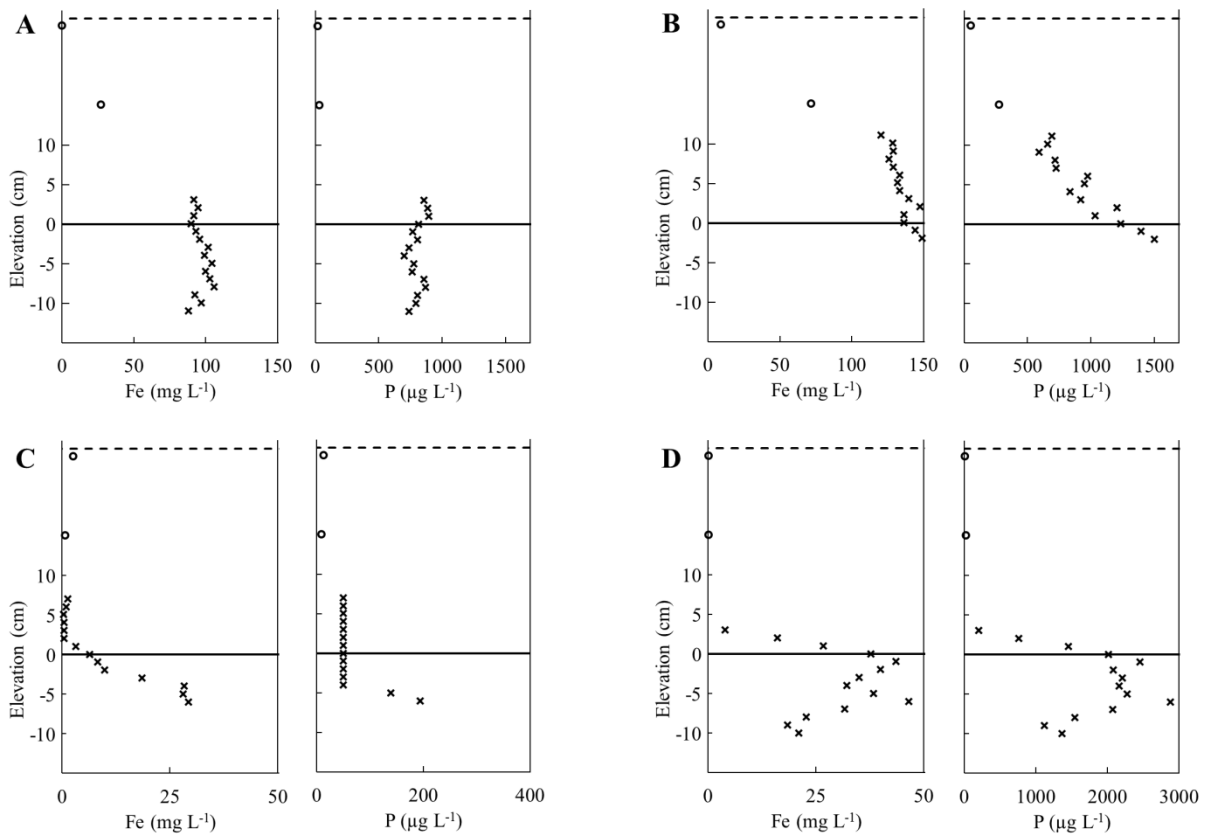
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674

675 Figure 1: Oxalate extractable concentrations of Fe and P (Fe<sub>ox</sub>: closed symbols; P<sub>ox</sub>: open  
676 symbols), their molar ratios, and the degree of P saturation (DPS) in the ditch sediment and  
677 the underlying parent material of the three studied ditches (A: ditch 1; B: ditch 2; C: ditch 3).

678 The depth was measured from the surface of the ditch sediment.

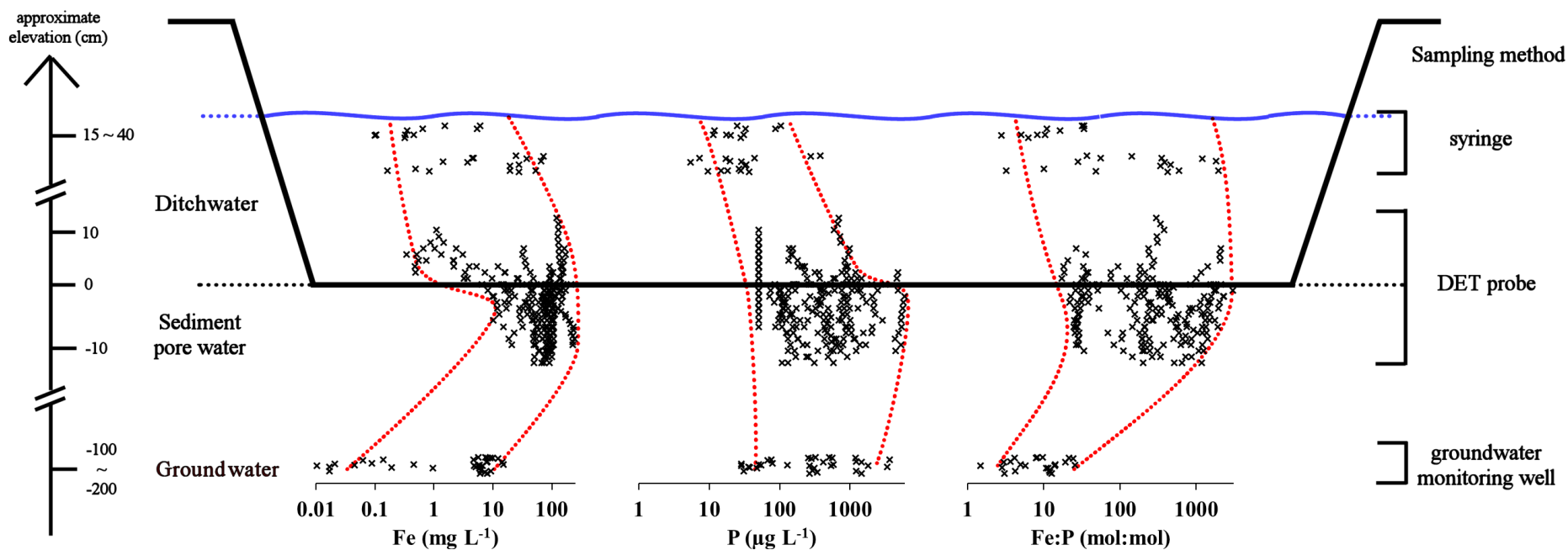


680

681 Figure 2: Examples of concentration profiles of Fe and P versus the elevation above the  
 682 sediment-water interface of open drainage ditches. Open circles refer to water samples taken  
 683 with a syringe either 1 or 10 cm below the water surface; crosses refer to concentration  
 684 profiles determined by diffusive equilibration (DET). The full line is the water-sediment  
 685 interface, the dashed line is the water surface.

686

687



688

689 Figure 3: Schematic overview of the evolution of dissolved Fe and P concentrations (log scale) as groundwater flows through Fe-rich sediments  
690 into open drainage ditches. All available data from all three studied ditches are combined. Dotted lines are drawn to guide the eye.

691