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

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ABSTRACT

Redox reactions involving iron (Fe) strongly affect the mobility of phosphorus (P) and its migration from agricultural land to freshwater. We studied the transfer of P from groundwater to open drainage ditches in an area where, due to Fe(II) rich groundwater, the sediments of these ditches contain accumulated Fe oxyhydroxides. The average P concentrations in the groundwater feeding two out of three studied drainage ditches exceeded environmental limits for freshwaters by factors 11 and 16, but after passing through the Fe-rich sediments, the P concentrations in the ditch water were below these limits. In order to identify the processes which govern Fe and P mobility in these systems, we used diffusive equilibration in thin films (DET) to measure the vertical concentration profiles of P and Fe in the sediment pore water and in the ditchwater. The Fe concentrations in the sediment pore water ranged between 10 and 200 mg L^{-1} and exceeded those in the inflowing groundwater by approximately one order of magnitude, due to reductive dissolution of Fe oxyhydroxides in the sediment. The dissolved P concentrations only marginally increased between groundwater and sediment pore water. In the poorly mixed ditchwater, the dissolved Fe concentrations decreased towards the water surface due to oxidative precipitation of fresh Fe oxyhydroxides, and the P concentrations decreased more sharply than those of Fe. These observations support the view that the dynamics of Fe and P are governed by reduction reactions in the sediment and by oxidation reactions in the ditchwater. In the sediment, reductive dissolution of P-containing Fe oxyhydroxides causes more efficient solubilization of Fe than of P, likely because P is buffered by adsorption on residual Fe oxyhydroxides. Conversely, in the ditchwater, oxidative precipitation causes more efficient immobilization of P than of Fe, due to ferric phosphate formation. The combination of these processes yields a natural and highly efficient sink for P. It is concluded that, in Fe-rich systems, the fate of P at the sediment–water interface is determined by reduction and oxidation of Fe.

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1. Introduction

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

The transport of P from percolate or groundwater through drains to the aquatic environment is often assumed to be conservative, *i.e.* it is not much affected by chemical processes (Schoumans et al., 2013; van der Salm et al., 2011). However, as P-enriched groundwater surfaces, it seeps through micro-oxic and highly redox-active environments, such as the linings of drainage tubes or the sediments of streams and ditches. In such environments, P may undergo complex chemical interactions with several redox-active elements, most notably with Fe. As hydrous ferric oxides are submerged and become anoxic, they may undergo reductive dissolution, which is often microbially mediated (Lovley, 1997). Conversely, in oxic or micro-oxic environments, the reduced and highly mobile Fe(II) may be re-oxidized either chemically (Davison and Seed, 1983) or biotically (Druschel et al., 2008). The oxidized Fe(III) readily precipitates as authigenic hydrous ferric oxides, such as ferrihydrite or lepidocrocite (Baken et al., 2013; Duckworth et al., 2009; Fortin et al., 1993).

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

The coupling of reductive dissolution and oxidation of Fe may lead to intense Fe cycling, which has been observed in a variety of environments including sediments, groundwater seeps, and lakes (Blöthe and Roden, 2009; Davison, 1993; Gault et al., 2011; Kleeberg et al., 2013). Diffusive techniques, such as Diffusive Gradients in Thin films (DGT) or Diffusive Equilibration in Thin films (DET), are highly suited for probing the chemical composition of such environments. Some recent methodological studies have already simultaneously determined spatially resolved Fe and P concentrations using diffusive techniques (Cesbron et al., 2014), and a study by Xu et al. (2013) showed a strong relationship between Fe and P concentrations in the pore waters of an incubated sediment. However, few studies have examined Fe–P interactions in systems with combined reduction and oxidation reactions. Based on column experiments, Kjaergaard et al. (2012) speculate that if P and Fe(II) are concomitantly released from submerged soils, the export of P may be attenuated by the downstream re-oxidation of Fe(II) and subsequent binding of P. Zak and Gelbrecht (2004) and Zak et al. (2010) showed that even if high P concentrations are measured in the pore waters of reconstructed wetlands, the risk of P export is limited if molar Fe:P ratios in soils and pore waters do not fall below critical values. Immobilization of P by such processes may be a key process limiting P export from selected environments, but the limited evidence warrants further studies.

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

2. Materials and methods

2.1. Study sites

The study sites are located in the Kleine Nete catchment (Northern Belgium) which is characterized by acid sandy soils with iron-rich groundwater. The geography, geology, and hydrology of this catchment have been described in detail elsewhere (Vanlierde, 2013; Vanlierde et al., 2007). The land use in

the area is characterized by intensive agriculture and animal husbandry, which cause diffuse emissions of P to the environment. After decades of excessive manure application, the soils are P-saturated (Lookman et al., 1995). The P losses mainly occur through leaching to the groundwater: the P concentrations in phreatic groundwater in the area commonly range between 0.02 and 2 mg L^{-1}. Greensands in the underground supply reduced Fe(II) to the groundwater, which yields groundwater Fe concentrations between 1 and 90 mg L^{-1} (Vanlierde, 2013). Due to the flat topography, the streams are predominantly fed by phreatic groundwater: the groundwater contribution to the discharge of the Kleine Nete near the town of Grobbendonk is estimated at 87% (Vanlierde et al., 2007). The groundwater table is shallow and fluctuates seasonally. The groundwater may seep directly into the streams, or it may be exported from agricultural fields in the lowlands by drainage systems which are abundantly present in the area. Especially in winter and early spring, when the phreatic groundwater tables are at their highest level, export through drainage systems is likely the major pathway of P export from groundwater to streams.

Two lowland agricultural sites adjacent to streams of the Kleine Nete catchment were selected for this study (Figs. S1 and S2). At both sites, agricultural fields are drained by open ditches. At the bottom of the ditches, a reddish brown precipitate occurs, suggesting enrichment of Fe. Since the groundwater table fluctuates seasonally, the ditches generally drain groundwater from October to April, whereas in summer, the groundwater table is usually just below the bottom of the ditches. The top sediment layer is, therefore, oxic during the summer months but submerged and likely more reduced during the winter. Site 1, located in the municipality of Retie, has two similar open drainage ditches (labelled ditch 1 and ditch 2) adjacent to the same agricultural field. They receive no inputs from tributary ditches or pipes until their outlet into the nearby stream. The ditches are approximately 1 m wide and 200–300 m in length, and the sediment surface is around 70 cm below the soil surface. The field was used for growing fodder maize during the summer of 2013. Before that, the field had been permanent grassland for at least 5 years and received annual organic manure inputs corresponding to at most 35 kg P ha^{-1}. According to the Belgian soil map, the soils consist of (very) wet and strongly gleyic sandy loam with a reduction horizon at 100–120 cm below the soil surface (Belgian soil classification: Sep3z). According to WRB, the soil is classified as a fluvic gleyic umbrisol (Dondeyne et al., 2014). The groundwater table at this site fluctuates seasonally between 5 and 70 cm below the soil surface. Site 2, located in the municipality of Vorselaar, consists of an area of fallow fields drained by a network of ditches. One ditch of this network was selected for this study and was labelled ditch 3. These ditches are smaller than at site 1: approximately 30 cm wide and 20 cm deep. According to the Belgian soil map, the soils consist of wet and strongly gleyic sandy loam with a reduction horizon between 100 and 120 cm depth and with a thick humic accumulation in the topsoil (Belgian soil classification: s-Pep3). According to WRB, the soil is classified as a fluvic gleyic umbrisol (Dondeyne et al., 2014). The adjacent fields had been permanent grassland for at least two years, and they receive organic manure inputs similar to those at site 1. The groundwater table fluctuates seasonally between 10 and 40 cm below the soil surface.

2.2. Sampling of sediment, ditchwater, and groundwater

At two locations next to each drainage ditch, two groundwater monitoring wells (filtered between 1 and 2 m depth) were installed at close distance (<5 m) to the ditch. Automatic hydraulic head loggers (Mini-divers, Schlumberger Water Services) were installed which measured the height of the water table every 15 min. In August 2013, when the drainage ditches were dry, the sediment of each ditch and the underlying parent material was sampled down to 60–90 cm below the sediment surface with a gouge auger. The sediment cores were subdivided into 10 cm-sections, air-dried, and the concentrations of oxalate extractable elements (P_{ox}, Fe_{ox}, Al_{ox}, Mn_{ox}) were determined according to Schwertmann (1964). This procedure is generally used in order to quantify the poorly crystalline oxyhydroxides of Fe, Al, and Mn, and the

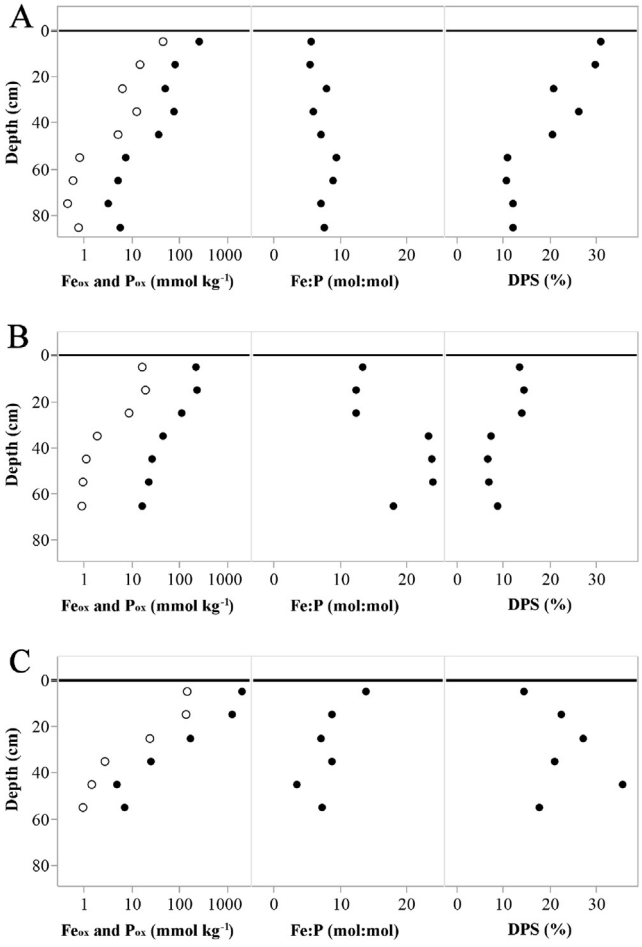

Fig. 1 – Oxalate extractable concentrations of Fe and P (Fe_{ox}: closed symbols; P_{ox}: open symbols), their molar ratios, and the degree of P saturation (DPS) in the ditch sediment and the underlying parent material of the three studied ditches (A: ditch 1; B: ditch 2; C: ditch 3). The depth was measured from the surface of the ditch sediment.

associated P. The P sorption capacity (PSC) and the degree of P saturation (DPS) of each section were calculated as (Lookman et al., 1995; Van der Zee et al., 1990):

$$PSC = 0.5 \cdot (Fe_{ox} + Al_{ox})$$
$$DPS = \frac{P_{ox}}{PSC}, \quad (1)$$

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

The groundwater and ditchwater were sampled on 6 occasions between September 2013 and February 2014 in each ditch. The groundwater was sampled with a peristaltic pump after first discarding at least three well volumes. The drainage water was sampled at two locations in each ditch with a syringe and was withdrawn either 1 or 10 cm below the water surface. The pH, water temperature and O_2 concentration were measured in the field (CellOx 325 and SenTix 21 electrodes, WTW, Germany). Groundwater and ditchwater samples were membrane filtered in the field (Acrodisc syringe filters with Supor 0.45 μm membrane), and subsamples were immediately acidified (HCl, final concentration 0.01 M). The dissolved organic carbon (DOC), Fe(II), and total element concentrations were determined in the acidified subsamples. The DOC was measured as the non-purgeable organic carbon on an elemental analyzer (AnalytikJena, Multi N/C 2100), the Fe(II) was determined colorimetrically using the ferrozine method (Viollier et al., 2000), and total element concentrations were measured with ICP-MS (Agilent 7700x). The soluble reactive P (SRP) was determined in selected samples by the molybdenum blue method (Murphy and Riley, 1962). The dissolved concentrations of anions (Cl, SO_4 and NO_3) were determined in the non-acidified subsamples of selected samples with anion chromatography (Dionex ICS-2000 with AS18 column), and dissolved inorganic carbon (DIC) was determined with an elemental analyzer (AnalytikJena, Multi N/C 2100). All constituents were determined after membrane filtration (0.45 μm) and are hereinafter referred to as "dissolved".

2.3. Concentration profiles of Fe and P by diffusive equilibration

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

Table 1 – The composition (mean ± standard deviation; $n = 1–7$ for anion and C measurements and 5–12 for other measurements) of drained groundwater at different stages along its trajectory from the subsurface to the surface. The groundwater was sampled using monitoring wells, the sediment pore water was sampled with DET probes at 1–10 cm below the sediment–water interface, and the ditchwater was sampled with a 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 on up to 6 occasions between September 2013 and February 2014.

		pH	O_2	Fe	P	Fe/P	Al	Mn	K	Ca	Na	Mg	Cl	SO_4	NO_3	DOC	DIC
			mg L^{-1}	mg L^{-1}	μg L^{-1}	mol:mol	μg L^{-1}	μg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
DITCH 1	Ditchwater, 1 cm deep	5.9 ± 0.3	4.5 ± 2.5	3.2 ± 3.6	20 ± 21	136 ± 108	15 ± 9	335 ± 57	13 ± 4	29 ± 2	22 ± 1	10 ± 2	50*	93*	11.0*	7*	5*
	Ditchwater, 10 cm deep	5.7 ± 0.3	0.7 ± 0.8	25.5 ± 27.9	71 ± 117	335 ± 117	12 ± 6	337 ± 61	10 ± 3	26 ± 7	21 ± 1	9 ± 1	nm	nm	nm	10 ± 4	5*
	Sediment pore water			77.5 ± 21.8	653 ± 430	233 ± 105											
	Groundwater	6.0 ± 0.4	0.5 ± 0.1	8.5 ± 3.6	1085 ± 1228	12 ± 9	18 ± 13	289 ± 156	24 ± 16	49 ± 21	23 ± 3	12 ± 5	44 ± 10	60 ± 31	1.2 ± 1.9	22 ± 15	36 ± 4
DITCH 2	Ditchwater, 1 cm deep	5.9 ± 0.7	3.9 ± 1.5	11.0 ± 9.0	18 ± 10	393 ± 323	10 ± 7	551 ± 289	7 ± 2	48 ± 5	22 ± 2	7 ± 1	44 ± 9	146 ± 66	0.5 ± 0.4	7 ± 0.4	11 ± 7
	Ditchwater, 10 cm deep	5.9 ± 0.3	0.7 ± 0.5	33.8 ± 23.2	19 ± 9	1010 ± 785	12 ± 6	630 ± 240	7 ± 2	54 ± 7	22 ± 2	7 ± 1	51 ± 3	195 ± 14	0.2 ± 0.04	10 ± 3	9 ± 6
	Sediment pore water			101.2 ± 57.9	219 ± 157	1006 ± 576											
	Groundwater	6.1 ± 0.2	0.6 ± 0.2	0.2 ± 0.3	49 ± 19	2 ± 3	11 ± 7	230 ± 254	24 ± 9	72 ± 17	30 ± 8	17 ± 4	59 ± 6	69 ± 6	84.3 ± 80.5	27 ± 5	53 ± 9
DITCH 3	Ditchwater, 1 cm deep	6.7 ± 0.3	3.1 ± 1.7	1.5 ± 2.2	37 ± 32	16 ± 12	5 ± 2	111 ± 87	3 ± 0.4	72 ± 8	9 ± 1	6 ± 1	20*	66*	0.1*	11 ± 2	49 ± 5
	Ditchwater, 10 cm deep	6.8 ± 0.2	1.1 ± 0.4	6.2 ± 10.5	100 ± 154	27 ± 21	5 ± 1	227 ± 211	3 ± 1	77 ± 8	10 ± 1	7 ± 0.4	16 ± 6	45 ± 28	0.2*	14 ± 3	50 ± 6
	Sediment pore water			47.7 ± 33.7	2743 ± 1903	30 ± 7											
	Groundwater	6.4 ± 0.4	0.5 ± 0.2	7.1 ± 1.2	744 ± 525	8 ± 4	4 ± 2	70 ± 47	4 ± 2	44 ± 8	7 ± 2	3 ± 1	10 ± 3	13 ± 6	1.9 ± 2.0	8 ± 1	30 ± 1

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

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

In synthetic solution			In diffusive gels				
Fe mg L^{-1}	P mg L^{-1}	Fe:P mol:mol	Fe mg L^{-1}	Recovery %	P mg L^{-1}	Recovery %	Fe:P mol:mol
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

We anticipated that the precipitation of Fe oxyhydroxides, caused by immersion in NaOH, also causes immobilization of P as long as sufficiently large amounts of Fe are present to bind the P. This was verified in synthetic solutions containing 10 mg L^{-1} Fe(II) (as $FeSO_4 \cdot 7H_2O$) and varying concentrations of P (from a stock solution of 1000 mg L^{-1} PO_4 as KH_2PO_4, Merck Millipore) buffered at pH 4 by 0.01 M acetic acid. The low pH was adopted in order to avoid oxidation of Fe(II) to Fe(III) under ambient conditions. Four gel slices were inserted into each solution and were deployed for 24 h. Immediately after retrieval from the solution, the Fe and P in the gel slices were immobilized by immersion in 0.01 M NaOH. Thereafter, the gels were re-eluted by immersing them in 1 M HCl for 24 h. The concentrations of Fe and P in the synthetic solutions and in the gel eluates were measured with ICP-MS.

3. Results

3.1. Sediment cores

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

3.2. Composition of groundwater and ditchwater

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

The ditchwater was stratified: 10 cm below the surface of the ditchwater, the O_2 concentration was around 1 mg L^{-1}, *i.e.* not much different from that in the groundwater, whereas just below the water surface, the O_2 concentration generally increased to 2–5 mg L^{-1}. Conversely, the Fe concentrations in the ditchwater at 10 cm below the surface exceeded those near the water surface by up to two orders of magnitude. In most samples, the dissolved Fe was almost exclusively present as reduced Fe(II). No clear temporal trend was observed in the Fe and P concentrations in ditchwater. The groundwater and ditchwater contained relatively high concentrations of SO_4, and the SO_4 concentrations in the ditchwater are above those in the groundwater. This shows that the ditch was no sink for SO_4, suggesting that no extensive SO_4 reduction occurred in the studied systems.

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

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

Seventeen concentration profiles of Fe and P in the sediment pore water and in the overlying ditchwater were obtained with the DET method. The probes revealed Fe concentrations in the sediment pore water between 10 and 200 mg L^{-1}, which is up to two orders of magnitude above those in groundwater (Table 1 and Fig. 2). In the sediment pore water, the profiles of the Fe concentrations were variable: they decreased, remained more or less constant, or increased with elevation (Fig. 2; more details in the Supplementary Material). In the overlying ditchwater, some profiles showed a sharp decrease in Fe concentrations just above the sediment–water interface (e.g. profiles C and D in Fig. 2), but in other profiles, the Fe concentrations remained more or less equal to those in the sediment pore water (e.g. profiles A and B in Fig. 2). The spatial heterogeneity was large: probes installed 50 cm apart yielded markedly different concentration profiles. We did not observe any clear temporal trends in sediment pore water concentrations of Fe and P, possibly because such trends are overshadowed by the large spatial heterogeneity. However, in spite of the large variability, the ditchwater samples taken with a syringe at 1 cm and 10 cm below the water surface invariably contained lower Fe concentrations than those measured with DET probes in the water layers close to the sediment–water interface. The average Fe concentrations decreased from 77 mg L^{-1} in the sediment pore water to 5 mg L^{-1} near the water surface. Hence, Fe concentrations in the ditchwater decreased with increasing elevation.

The P concentrations in the sediment pore water varied from below detection limit (<100 μg L^{-1}) to 6000 μg L^{-1}. The P concentrations in the sediment pore water of ditch 1 covered

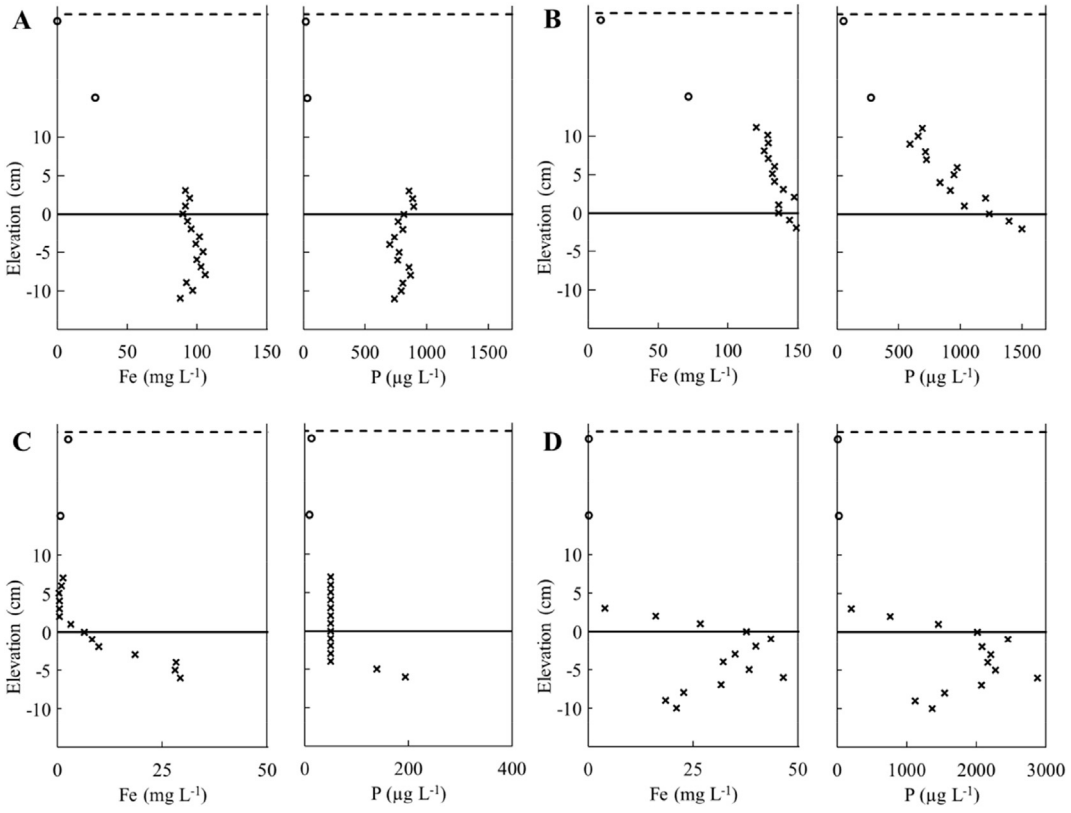

Fig. 2 – Examples of concentration profiles of Fe and P versus the elevation above the sediment–water interface of open drainage ditches. Open circles refer to water samples taken with a syringe either 1 or 10 cm below the water surface; crosses refer to concentration profiles determined by diffusive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

the range of the corresponding groundwater, whereas the P concentrations in the sediment pore water of ditches 2 and 3 exceeded those in the groundwater by a factor of 4. Four out of 17 concentration profiles contained sections in which the P concentrations were below the detection limit of the DET sampling method (100 μg L^{-1}), e.g. profile C in Fig. 2, and for plotting purposes these data points are shown at an arbitrary value of 50 μg L^{-1}. In the sediment pore water, the P concentrations generally did not vary much with depth below the sediment–water interface. However, most P concentration profiles, including profiles B, C, and D in Fig. 2, showed a sharp decrease in P concentrations near the sediment–water interface. The P concentrations measured in the ditchwater at 1 cm and 10 cm below the water surface were invariably lower than those in the sediment pore water. The average P concentrations decreased from 890 μg L^{-1} in the sediment pore water to 26 μg L^{-1} near the water surface. No clear temporal trends in P concentrations in the sediment pore water were observed. In summary, as groundwater flows into the drainage ditches, the P concentrations decrease sharply.

4. Discussion

4.1. *Reductive dissolution and oxidative precipitation of Fe*

Similar mechanisms appear to govern the behaviour of Fe and its interaction with P in the three studied ditches. The concentrations of Fe and P in the groundwater, sediment pore water, and ditchwater of the three ditches are summarized in Fig. 3. As groundwater flows into the sediment of the drainage ditch, the Fe concentrations strongly increase by up to two orders of magnitude (Fig. 3). Reductive dissolution of hydrous ferric oxides in the sediment likely explains this increase. The oxalate extractions of the sediment cores showed that there is an abundant stock of readily reducible Fe oxyhydroxides available. There is also ample supply of electron donors, *i.e.* readily degradable organic C derived from decaying vegetation which grows lavishly in the ditch in the summer season. The abundant stock of readily reducible Fe oxyhydroxides in the sediment of the studied drainage ditches may be the result of a process similar to the formation of bog iron ore: an accumulation of groundwater-borne Fe over prolonged periods of time in hydromorphic soils. Due to the fluctuating groundwater table, the top sediment layer is oxic in summer, but it is likely gradually more reduced as it becomes submerged in autumn. Previous studies have shown similar or greater increases in dissolved Fe concentrations upon waterlogging of soils (Hofacker et al., 2013; Van Laer et al., 2010), and the reduction of Fe oxyhydroxides may occur at rates well above those needed to explain the observed increase in dissolved Fe concentrations from the groundwater to the sediment pore water (Blöthe and Roden, 2009; Kleeberg et al., 2013). Possibly, oxidation and reduction reactions occur simultaneously and at approximately the same location in the sediment, which result in strong Fe redox cycling. We were unable to measure the O_2 concentrations in the sediment, and therefore the extent of Fe redox cycling in the sediment of the studied systems remains unknown. Possibly, the ditch sediments exhibit transitions in redox regime as they are submerged for increasingly longer times during the winter. Our data did not show any clear temporal trends in Fe concentrations in the sediment pore water or in the overlying ditchwater, but such temporal trends may be overshadowed by the large variability due to spatial heterogeneity. In addition, we studied the ditches only from September to February, but they are usually submerged until April or May. Any shifts in redox regime during these final months of waterlogging are not reflected in this study.

Based on the results of oxalate extractions and on previous studies (Voegelin et al., 2010), we assume that poorly crystalline oxyhydroxides and perhaps amorphous ferric phosphates are the most important reactive Fe phases present in the sediment. We did not study e.g. the conversion of poorly crystalline Fe oxyhydroxides to more crystalline phases. Goethite may occur in systems similar to the ones in this study (Mansfeldt et al., 2012). However, goethite would not be dissolved in oxalate extractions, and its presence would therefore not affect our results (Schwertmann, 1973). Furthermore, other reactive Fe phases, such as vivianite or Fe

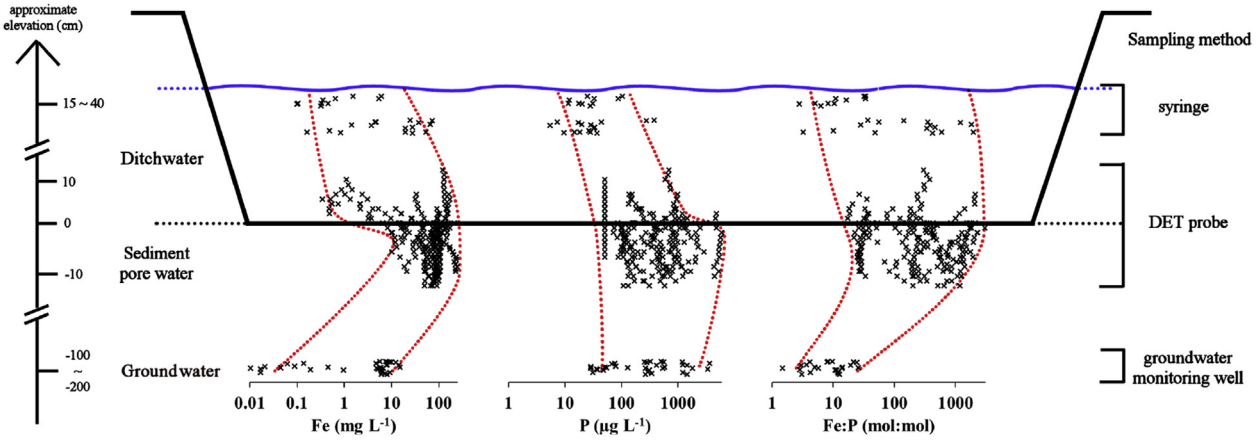

Fig. 3 – Schematic overview of the evolution of dissolved Fe and P concentrations (log scale) as groundwater flows through Fe-rich sediments into open drainage ditches. All available data from all three studied ditches are combined. Dotted lines are drawn to guide the eye.

sulphides, may be present, even though SO_4 measurements suggest that no extensive sulphate reduction occurred in the studied systems.

In the ditch, *i.e.* above the sediment–water interface, the Fe concentrations decrease with increasing elevation above the interface (Fig. 3). Oxidation of Fe(II) and subsequent precipitation of Fe oxyhydroxides is the key mechanism by which removal of Fe from the dissolved phase occurs. Assuming pH values between 5.5 and 7.0, dissolved O_2 concentrations of 2–6 mg L^{-1}, and temperatures between 5 and 15 °C, the rate of chemical Fe(II) oxidation in the studied systems is predicted to result in half-lives of Fe(II) between 2 h and 3 years (Davison and Seed, 1983). However, groundwater seeps are typical environments where Fe oxidizing (and reducing) bacteria thrive (Blöthe and Roden, 2009), and therefore it is likely that microbially mediated Fe oxidation outpaces the chemical oxidation reaction. The vertical concentration profiles of Fe in the ditchwater were highly variable, which may mostly be due to physical processes such as the local flow velocity, turbulence, and mixing. Nevertheless, the average Fe concentration near the water surface was only 7% of that in the sediment pore water, showing that most of the Fe produced in the sediment is re-oxidized and precipitated in the ditch before it is drained into the receiving streams. The kinetics of Fe oxidation in drainage systems have recently been studied in greater detail by Van der Grift et al. (2014). In summary, as drainage water flows upward into the ditch, the Fe concentrations decrease due to oxidation of Fe(II).

4.2. *Release and binding of P*

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

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

Taken together, reductive dissolution of P-containing Fe oxyhydroxides in the sediment preferentially solubilizes Fe, because the released P is bound again by residual Fe oxyhydroxides. Conversely, oxidative precipitation in the overlying water preferentially immobilizes P: since the water contains molar Fe:P ratios far above unity, ferric phosphate formation causes more efficient immobilization of P than of Fe. The combination of these processes results in a natural and highly efficient sink for P: the average P concentrations in the groundwater feeding two out of three studied drainage ditches exceeded environmental limits for freshwaters (70 μg L^{-1}, commonly measured as MRP in unfiltered samples (Flemish Government, 1995)) by factors 11 and 16, but after passing through the Fe-rich sediments, the dissolved P concentrations in the drainage water were below these limits. Therefore, our results combined with previous studies appear to confirm that oxidizing Fe in groundwater or drainage water is a highly efficient natural mechanism for immobilization of dissolved P.

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

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

challenges include the mode of Fe addition to the system, and the retention of the formed Fe oxyhydroxide particles at the outlet.

Since Fe–P interactions can critically affect P fluxes, such processes should be taken into account when assessing the eutrophication risk associated with P losses from agricultural land. A key challenge is to determine the circumstances under which P is retained by Fe in drainage systems. Based on this study, it appears that the P concentrations in drainage water are mostly determined by the composition and reactivity of the sediment of the drainage ditch, and not much by the initial composition of the groundwater. We therefore suggest that the molar Fe:P ratio in oxalate extractions of drainage ditch sediments is a feasible candidate for predicting P losses from open drainage ditches with Fe-rich sediments. The molar Fe:P ratio has previously been proposed as a useful tool for estimating the mobility of P in sediments. For example, in rewetted fens, molar Fe:P ratios of 10 in bicarbonate-dithionite extractions of sediment material have been suggested as a limit above which no critical P export is expected (Zak et al., 2010). However, for systems similar to those studied here, no Fe:P threshold below which there is a eutrophication risk in the receiving streams has been determined so far. In the present study, we measured molar Fe:P ratios in oxalate extracts of drainage ditch sediments between 6 and 14. Despite being close to or below the threshold for P-saturated soils (Van der Zee et al., 1990), the P concentrations in drainage water flowing through these sediments did not exceed environmental limits. Clearly, more work is needed in order to identify the relationship between the composition of the sediment and the resulting P concentrations in the drainage effluent.

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

5. Conclusions

- In the redox active zone between groundwater and surface water, P and Fe strongly interact.
- Immobilization of P may occur in periodically inundated drainage ditches with Fe-rich sediments. This is the result of two chemical processes: reductive dissolution in the sediment and oxidative precipitation in the ditchwater.
- This natural sequestration of P leads to a decreased P flux from groundwater to surface water. This must be taken into account in watershed management plans and in assessments of the environmental risk associated with P losses from agricultural land.
- Technologies for P removal from drainage water may be based on Fe–P interactions in the redox active zone.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.01.008.

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