

1 **Iron oxidation kinetics and phosphate immobilization along the flow-path from**  
2 **groundwater into surface water.**

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13 **Abstract**

14 The retention of phosphorus in surface waters through co-precipitation of phosphate with Fe-  
15 oxyhydroxides during exfiltration of anaerobic Fe(II) rich groundwater is not well understood. We  
16 developed an experimental field set-up to study Fe(II) oxidation and P immobilization along the  
17 flow-path from groundwater into surface water in an agricultural experimental catchment of a  
18 small lowland river. We physically separated tube drain effluent from groundwater discharge  
19 before it entered a ditch in an agricultural field. Through continuous discharge measurements  
20 and weekly water quality sampling of groundwater, tube drain water, exfiltrated groundwater, and  
21 surface water, we investigated Fe(II) oxidation kinetics and P immobilization processes. The  
22 oxidation rate inferred from our field measurements closely agreed with the general rate law for  
23 abiotic oxidation of Fe(II) by O<sub>2</sub>. Seasonal changes in climatic conditions affected the Fe(II)  
24 oxidation process. Lower pH and lower temperatures in winter (compared to summer) resulted in  
25 low Fe oxidation rates. After exfiltration to the surface water, it took a couple of days to more than  
26 one week before complete oxidation of Fe(II) is reached. In summer time, Fe oxidation rates  
27 were much higher. The Fe concentrations in the exfiltrated groundwater were low, indicating that  
28 dissolved Fe(II) is completely oxidized prior to inflow into a ditch. While the Fe oxidation rates

1 reduce drastically from summer to winter, P concentrations remained high in the groundwater  
2 and an order of magnitude lower in the surface water throughout the year. This study shows very  
3 fast immobilisation of dissolved P during the initial stage of the Fe(II) oxidation proces which  
4 results in P-depleted water before Fe(II) is competyly depleted. This cannot be explained by  
5 surface complexation of phosphate to freshly formed Fe-oxyhydroxides but indicates the  
6 formation of Fe(III)-phosphate precipitates. The formation of Fe(III)-phosphates at redox  
7 gradients seems an important geochemical mechanism in the transformation of dissolved  
8 phosphate to structural phosphate and, therefore, a major control on the P retention in natural  
9 waters that drain anaerobic aquifers.

10

## 11 **Keywords**

12 Iron, phosphate, groundwater-surface water interface, retention, oxidation kinetics

13

## 14 **1 Introduction**

15 Eutrophication of freshwater ecosystems following high nutrient loads is a widely recognized  
16 water quality problem in agricultural catchments. Phosphorus (P) is often a limiting nutrient in  
17 wetlands or fresh aquatic ecosystems (Elser et al., 2007;Wassen et al., 2005) and therefore a  
18 key parameter in controlling eutrophication. P enters surface waters through point-sources such  
19 as waste water treatment plants and non-point sources via surface runoff and exfiltration of soil  
20 water and groundwater. Especially, the fate of P in surface waters originating from non-point  
21 sources is controlled strongly by biogeochemical nutrient cycling processes at the soil-water  
22 interface (Dahm et al., 1998;Reddy et al., 1999;Dunne et al., 2006).

23 To date, research and policy on P pollution from non-point sources have focused almost entirely  
24 on transfer of particulate phosphate from agricultural land to surface waters via overland flow or  
25 other fast flow paths during storm flow events (Withers and Haygarth, 2007;Sharpley et al.,  
26 2008;Jordan et al., 2012). However, several studies in fresh water systems suggested that  
27 substantial dissolved-phosphate loads in surface waters may originate from exfiltration of shallow  
28 or deep groundwater (Holman et al., 2008;Dahlke et al., 2012;Scanlon et al., 2005). This is

1 especially likely to occur in delta areas (Griffioen, 2006;Hayashi and Yanagi, 1-3 October 2009),  
2 where the soil water and shallow groundwater is typically pH-neutral to slightly acid, anoxic, and  
3 iron-rich. The anoxic conditions are very suitable to dissolve phosphate in groundwater, which  
4 may result in relative high concentrations of dissolved phosphate from natural origin (Griffioen et  
5 al., 2013) or from leached manure or fertilizers (Chardon et al., 2007). In contrast, the chemical  
6 composition of surface waters in delta areas is normally pH-neutral to slightly alkaline and oxic  
7 with low dissolved iron and phosphate concentrations. This difference in chemical composition  
8 between groundwater and surface water creates strong redox and pH gradients at the  
9 groundwater-surface water interface (Frei et al., 2012;Carlyle and Hill, 2001). At this interface,  
10 the oxidation of iron(II) followed by iron(III) hydrolysis and precipitation of iron oxyhydroxides is  
11 the dominant chemical reaction (Griffioen, 2006;Gunnars et al., 2002;Kaegi et al., 2010;von  
12 Gunten and Schneider, 1991;Baken et al., 2013), that determines the fate of many biochemically  
13 important solutes that co-precipitate with the iron oxyhydroxides such as  $\text{PO}_4$  (Châtellier et al.,  
14 2004;Deppe and Benndorf, 2002;Fox, 1989;Lienemann et al., 1999;Mayer and Jarrell,  
15 2000;Voegelin et al., 2013) and  $\text{AsO}_4$  (Meng et al., 2002;Roberts et al., 2004;Hug and Leupin,  
16 2003).

17 The majority of studies on redox processes and P dynamics at the groundwater-surface water  
18 interface focus on mobilization of phosphate by reductive dissolution of Fe oxyhydroxides in  
19 riparian zones or wetlands in response to rewetting (Macrae et al., 2011;Maassen and Balla,  
20 2010;Shenker et al., 2005). In contrast, relatively little is known about the oxidation of Fe(II) in the  
21 transition zone from groundwater into surface water in lowland delta areas with (periodic)  
22 exfiltration of anaerobic groundwater in relation to P retention in surface water. The rate of Fe(II)  
23 oxidation strongly depends on pH. At neutral pH, it is a fast reaction that is expected to occur  
24 within hours when molecular oxygen is not limited (Stumm and Lee, 1961). At pH values around  
25 6, it may take a couple of days before complete abiotic oxidation of Fe(II) occurs. The reaction  
26 rate also depends on oxygen concentration and temperature. Spiteri et al. (2006) investigated  
27 the effect of  $\text{O}_2$  and pH gradients on oxidative precipitation of Fe(II) and subsequent phosphate  
28 sorption along a flow-line in a subterranean estuary where groundwater discharges to the sea.  
29 Their results showed that the pH is a more controlling factor than the  $\text{O}_2$  concentration.

1 To our knowledge there are no field studies on the mechanisms and rates of iron oxidation with  
2 associated binding of phosphate in lowland catchments that drain anaerobic groundwater while  
3 these processes may have an important control on mobility of P in surface water (Baken et al.,  
4 2013;Griffioen, 2006;Fox, 1989). Moreover, as most of the work on Fe(II) oxidation and  
5 incorporation of phosphate into Fe(III) precipitates is performed on synthetic media, the kinetics  
6 of these processes in the natural environment are poorly known. A better understanding of these  
7 processes will improve our knowledge of P retention mechanisms in surface waters with  
8 exfiltration of anaerobic groundwater as driving force.

9 To study the dynamics in Fe(II) oxidation and P immobilization along the flow-path from  
10 groundwater into surface water, we developed an experimental field set-up in an agricultural  
11 catchment of a small lowland river (the Hupsel Brook). Previous studies in the Hupsel Brook  
12 catchment have demonstrated that the groundwater in the catchment is predominantly anoxic  
13 and contains relatively high dissolved P concentrations in a range of 0.3 to 1.0 mg/l (Rozemeijer  
14 et al., 2010a). At the catchment outlet particulate P is, however, the major contributor to the total  
15 P concentrations in the surface water (Rozemeijer et al., 2010b). This indicates that  
16 transformation from dissolved P in the groundwater to particulate P in the surface water must  
17 have occurred.

18 In this study we aim (1) to measure the dynamics of Fe(II) and phosphate concentrations along  
19 the flow-path from groundwater into surface water in a typical lowland catchment in the  
20 Netherlands (2) to infer reaction rates and mechanisms that influence the iron oxidation process  
21 by a combination of data analysis and chemical modelling and (3) to explore the phosphate  
22 immobilization process during the flow of anaerobic iron-rich groundwater towards surface water.

23

## 24 **2 Methods**

### 25 **2.1 Study area**

26 An experimental set-up was installed in the Hupsel Brook agricultural lowland catchment, The  
27 Netherlands (Fig. 1) (52°03' N; 6°38' E). The size of this catchment is 6.64 km<sup>2</sup>, with altitudes  
28 ranging from 22 to 36 m +MSL (above mean sea level). A weather station of the Royal Dutch

1 Meteorological Institute (KNMI, De Bilt, The Netherlands) is located within the catchment. The  
2 Hupsel brook catchment has a moderate maritime climate with an average annual temperature of  
3 9.5°C and average annual precipitation of 770 mm. Our field-scale experiment location in the  
4 Hupsel catchment is a 9000 m<sup>2</sup> tube drained meadow dominated by the grass *Lolium perenne*;  
5 surface elevation ranges from 28 to 31 m +MSL and a ditch (average depth of 1.2 m below soil  
6 surface) borders the field at the eastern side. This ditch drains a sub-catchment of the Hupsel  
7 Brook as indicated in Fig. 1. The direction of the groundwater flow in the field is from northwest to  
8 southeast. The groundwater drains towards the eastern ditch or flows into the adjacent field  
9 south of the experimental field (Rozemeijer et al., 2010c). The drainage tubes are separated 14.5  
10 m from each other and discharge into the eastern ditch at 90 cm depth. To separate the water  
11 fluxes of different flow routes towards the eastern ditch, three adjacent sheet pile reservoirs were  
12 built in the ditch (Fig. S1 in the supplement). These in-stream reservoirs were constructed around  
13 single drainage outlets and stretched along 43.5 m of the field. The wooden sheet piles were  
14 driven into an impermeable 30m thick Miocene clay layer starting at a depth of 3 to 5 m to  
15 capture all groundwater flow from the field into the ditch. The in-stream reservoirs captured  
16 overland flow, interflow, direct precipitation, and groundwater flow from the thin, phreatic aquifer  
17 above the Miocene clay layer. The water levels in the reservoirs were measured continuously  
18 with pressure sensors from Nov. 2007 to Oct. 2008. The water levels inside the in-stream  
19 reservoirs were maintained at the ditch water level by pumps. Excess water was pumped from  
20 the in-stream reservoirs into the ditch, and the pumped volumes were recorded with digital flux  
21 meters (Van der Velde et al., 2010). The water flow from the individual tube drains was  
22 separated from the other flow routes by connecting each drain to a 500-L vessel. Water from  
23 these vessels was pumped into the ditch and volumes were measured with water flux meters  
24 (Van der Velde et al., 2010). The water temperature was measured continuously direct  
25 downstream the reservoirs.

26 Four groundwater wells were installed for sampling of groundwater in a transect across the  
27 experimental field parallel to the ditch at a distance of 20 m from the ditch. The filters of the wells  
28 were installed 2-3 meters below the surface. More detailed information about the Hupsel  
29 catchment and all installations and measurements is found in Van der Velde et al. (2010).

1

## 2 **2.2 Water quality measurements**

3 We collected water samples from the four groundwater wells, the three tube drains and the three  
4 in-stream reservoirs from May 2007 until December 2008. In addition surface water samples  
5 were taken from the sub-catchment outlet and the catchment outlet. All samples were taken  
6 weekly using a peristaltic pump. During the dry summer period (July to October), the tube drains  
7 and in-stream reservoirs occasionally ran dry and sampling was sometimes not possible. We  
8 reduced the sampling to a biweekly scheme during this period. The samples were filtered in situ  
9 (0.45  $\mu\text{m}$ ) and subsamples for ICP analysis were directly acidified with  $\text{HNO}_3$ . The electrical  
10 conductivity and pH were measured immediately in the field using a flow-through cell. The  
11 samples were analyzed for metals, nutrients and anions within 48h using Ion Chromatography  
12 ( $\text{NO}_3$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ), ICP-AES (Na, K, Ca, Fe, Mg, Si), ICP-MS (P, Al) and AA3 (Automated  
13 Segmented Flow Analyzer) ( $\text{NH}_4$ ). Alkalinity was measured by titration. We used a variable span  
14 smoother based on local linear fits (Friedman, 1984) to aggregate trends through the  
15 concentration measurements.

16

## 17 **2.3 Modeling reaction kinetics**

18 To test the validity of existing chemical models developed under laboratory condition for the  
19 oxidation of Fe and co-precipitation of  $\text{PO}_4$  for our field situation, we modelled the Fe and  $\text{PO}_4$   
20 concentrations in the reservoirs with PHREEQC (Parkhurst and Appelo, 1999) with the  
21 WATEQ4F database (Ball and Nordstrom, 1991) using the representative aqueous composition of  
22 the groundwater (Table S1 in the supplement). We compared the range and yearly average trend  
23 of measured Fe concentrations with increasing transit time of the water within the reservoirs with  
24 model scenarios. Therefore, we performed model scenarios representing a typical summer  
25 situation, a typical winter situation and a yearly average situation with their accompanying rate  
26 controlling parameters, as discussed later. First, the Fe oxidation kinetics in the reservoirs were  
27 described as a first-order reaction process following the general rate law for chemical oxidation of  
28 Fe(II) by  $\text{O}_2$ :

$$1 \quad -\frac{dFe(II)}{dt} = k[Fe(II)][OH^-]^2 P_{O_2} \quad (1)$$

2 with a value for the abiotic rate constant  $k$  at 20°C of  $7.9 (\pm 2.47) \cdot 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$  (Stumm  
3 and Lee, 1961). Now by assuming a continuous stirred tank reactor (CSTR) with perfect mixing  
4 and steady-state concentrations, we can describe Fe(II) concentrations in the reservoir as  
5 function of mean transit times of water through the reservoirs. (Perry et al., 1997):

$$6 \quad Fe_r = \frac{Fe_i}{1 + (k \cdot \bar{T})} \quad (2)$$

7 where  $Fe_r$  is the Fe(II) concentration of the water in the reservoir,  $Fe_i$  is the Fe(II) concentration  
8 of the groundwater that flows into the reservoir,  $k'$  is the reaction rate according Eq. (1) ( $k [OH^-]^2$   
9  $pO_2$ ) and  $\bar{T}$  is the mean transit time.

10 The mean transit time  $\bar{T}$ , of the water leaving the reservoirs at time  $t$  can be approximated  
11 through the assumption of fully mixed reservoirs with a variable flow ( $q(t)$ ) and volume ( $V(t)$ ),  
12 following (Botter et al., 2011):

$$13 \quad \bar{T}(t) = \int_0^\infty \frac{q(t-T)}{V(t-T)} e^{-\int_0^T \frac{q(t-T+\tau)}{V(t-T+\tau)} d\tau} \cdot T dT \quad (3)$$

14 where  $q(t-T)$  is the reservoir discharge and  $V(t-T)$  is the reservoir volume at time  $t$  that has been  
15 inside the reservoir (i.e. the transit time) for a period  $T$ .

16 In a second step, the uptake of phosphate to Fe precipitates was modelled with two models  
17 using different concepts. First, surface complexation to ferrihydrite was considered using the  
18 Dzombak and Morel (1990) model. Surface complexation of carbonate and silicate to ferrihydrite  
19 was included, using the stability constants of Van Geen et al. (1994) and Bonte (2013). Second,  
20 precipitation of an ideal solid-solution with two endmembers, amorphous Fe hydroxide ( $Fe(OH)_3$ )  
21 and strengite ( $FePO_4 \cdot 2H_2O$ ), was considered (Fox, 1989; Griffioen, 2006). The formation of the  
22 solid-solutions during the oxidation of Fe(II) was modelled using the solubility products of  
23 amorphous Fe hydroxide and strengite from the WATEQ4F database. Surface complexation was  
24 not included in the solid-solution model.

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## **3 Results**

### **3.1 Fe concentrations**

The groundwater samples (Fig. 2A) had Fe concentrations ranging between 0.2 and 45.5 mg/l with an average of 15.9 mg/l and a median value of 14.5 mg/l. The groundwater showed a temporal and spatial variation in Fe concentrations, but they were generally higher than in the other water types. The NO<sub>3</sub>-N concentrations of the groundwater were commonly low with an average of 0.20 mg/l and a median value of 0.045 mg/l. The redox status of the groundwater can, therefore, be assessed as anaerobic and the measured Fe concentration can be attributed to Fe(II). The measured groundwater concentrations are common values for anaerobic groundwater in the eastern part of the Netherlands (Griffioen et al., 2013). The measured Fe concentration at sampling locations other than the groundwater may partly be attributed to dissolved Fe(III) colloids or complexed Fe(II) that penetrates through the 0.45 µm filters and dissolve in the acidic media, this is discussed in the next section.

The tube drain water samples (Fig. 2B) had Fe concentrations ranging between 0.4 and 18.9 mg/l with an average of 4.5 mg/l and a median value of 1.9 mg/l. The Fe concentrations of tube drains 1 and 2 were for the majority of samples lower than 2 mg/l. This At some moments in the winter months of 2007-2008 tube drain 2 had Fe concentrations around 5 mg/l. Tube drain 3 showed a large change in Fe concentration: the Fe concentrations increased from values around 2 mg/l to values between 10 and 15 mg/l during the period Sept. 2007 – Nov. 2007 and exceeded 15 mg/l in Nov. and Dec. 2008. This water approached the Fe concentrations of the groundwater. A change in concentration of redox-sensitive components like NO<sub>3</sub>, NH<sub>4</sub>, Mn, As, HCO<sub>3</sub> was also observed in the drain 3 water (not shown).

The reservoir water samples (Fig. 2C) had Fe concentrations ranging between 0.1 and 34.6 mg/l with an average of 3.9 mg/l and a median value of 2.0 mg/l. There was a winter peak in the Fe concentration of the in-stream reservoirs. During the winter (Nov. – Feb.), the Fe concentration reached the level of the Fe concentrations of the groundwater (5-35 mg/l), while in summer season (April – Sept.) a majority of samples had Fe concentrations lower than 5 mg/l with an



1 average of 1.76 mg/l. The range and average of the Fe concentrations differed between the three  
2 reservoirs during the winter period (Table 1). Reservoir 2 showed the highest concentrations  
3 followed by reservoir 3 and subsequently reservoir 1. Likely, this was the result of spatial  
4 variation of Fe concentrations in the groundwater, where reservoir 2 and 3 drained groundwater  
5 with higher Fe concentrations than reservoir 1. On average, groundwater wells 1 and 2 had the  
6 highest Fe concentrations (Fig. 2A). The groundwater flow in the field is approximately from  
7 northwest to southeast (Rozemeijer et al., 2010c). Therefore, it is conceivable that this Fe- rich  
8 groundwater flows into reservoir 2 and 3 (Fig. 1).

9 The surface water samples (Fig. 2D) had Fe concentrations ranging between 0.15 and 2.21 mg/l  
10 with an average of 0.68 mg/l and a median value of 0.60 mg/l. There was no seasonal variation  
11 and no difference between the sub-catchment outlet and catchment outlet.

12

### 13 **3.2 P concentrations**

14 The dissolved P concentrations of the groundwater were an order of magnitude higher than that  
15 of the tube drain water, reservoir water and surface water (Fig. 3). Where the median P  
16 concentration equaled 0.33 mg/l in the groundwater, it was around 0.02 mg/l for all other water  
17 types. Despite some short-scale temporal variation in the P concentration at individual  
18 groundwater wells, the data showed increased P concentrations during summer (Fig. 3A) (we did  
19 not investigate this further).

20 There was an increase in P concentration at tube drain 3 starting in Nov. 2007 (Fig. 3B). This  
21 was two months after the increase of Fe (Fig 3B). However, the P concentration at tube drain 3  
22 after the redox transition did not reach the level of the P concentration of anaerobic groundwater  
23 (Fig. S3 in the supplement).

24 There was no clear seasonal trend in P concentrations in the reservoirs and surface water (Fig.  
25 3C and 3D). Note that the Fe concentrations of the reservoir water in winter time almost matched  
26 that of the anaerobic groundwater but the P concentrations were an order of magnitude lower.

27

### 28 **3.3 Supporting variables**

1 Following Eq. (1) and Eq. (2), Fe concentrations can be explained from, pH, temperature, oxygen  
2 pressure of the water and the transit time of water inside the reservoirs. These variables have  
3 been measured directly or approximated. There was a seasonal variation in the pH of the water  
4 in the reservoirs (Fig.4). The pH varied between 6 and 6.5 with an average of 6.16 during the  
5 cold November to March. Although the sampling frequency was lower during the warmer April to  
6 October, the majority of samples had pH values above 6.5 with an average of 6.6. The  
7 temperature of the ditch water varied between 2.7°C and 21.5 °C (Fig. 5).

8 To explore Fe oxidation kinetics and P immobilization during exfiltration on anaerobic  
9 groundwater into surface water we calculated the mean transit time of the exfiltrated groundwater  
10 in the reservoirs from the reservoir discharge and the reservoir volume according Eq. (3). The  
11 reservoir discharge, and therefore, the groundwater inflow into the reservoirs showed an  
12 decrease from winter to summer (Van der Velde et al., 2010). The reservoir volumes decreased  
13 as well but to a lesser extent than the reservoir discharge (supplement S1). This resulted in an  
14 increase of the mean transit time of the water in the reservoirs. The mean transit time varied  
15 between 2 and 6 days during the period Nov. 2007 – March 2008 (Fig. 5) with longer mean  
16 transit times during relatively short, drier periods and mean transit times shorter than 2 days  
17 during the intensive discharge peaks. From April 2008 to Dec. 2008 the variation in mean transit  
18 time was larger compared to the period Nov. 2007 – March 2008. Mean transit times longer than  
19 8 days were common in the period from April 2008 to Dec. 2008. During dry periods the mean  
20 transit time increased gradually up to 20 days. Precipitation events following these dryer periods  
21 reduced the mean transit time immediately to a few days. During five events in the summer of  
22 2008 reservoir 1 went dry and, therefore, no transit time could be calculated.

23

## 24 **4 Discussion**

### 25 **4.1 Behavior of Fe**

26 The first objective of our study was to measure the dynamics of Fe concentrations along the flow  
27 path from groundwater into surface water. We measured a clear trend in dissolved Fe  
28 concentration with concentration in the groundwater and low concentrations in the surface water.

1 The Fe concentrations of the reservoir water and tube drain water were dynamic over the year.  
2 The higher Fe concentrations of the reservoir water during winter time suggest that only a part of  
3 the Fe(II) in the groundwater that was leached into the reservoirs was oxidized at the time of  
4 sampling. In summer time, the dissolved Fe concentrations of the water in the reservoirs are low.  
5 Not all the dissolved Fe in the tube drain water, reservoir water and surface water samples can  
6 be assumed as Fe(II). The presence of dissolved Fe after 0.45  $\mu\text{m}$  filtration in oxygenated water  
7 has been variously attributed to Fe(III) in colloidal phases (Lyvén et al., 2003) or complexed  
8 Fe(II) (Lofts et al., 2008). The particulate colloidal Fe(III) can exist as both organic complex and  
9 small hydroxide particle (Lyvén et al., 2003; Allard et al., 2004; Benedetti et al., 2003). Colloidal  
10 Fe(III) is stabilized against aggregation by binding of dissolved organic carbon (DOC) on its  
11 surface. Neal et al. (2008) found positive correlations between Fe and DOC concentrations of  
12 river water. However, dissolved Fe concentration in streams and rivers with near neutral pH  
13 values do only seldom exceed 0.5 mg/l (Salminen, 2005; Neal et al., 2008). The Fe concentration  
14 in our drain water and reservoir water samples are commonly much higher and can, therefore,  
15 largely be attributed to Fe(II).

16

#### 17 4.1.1 Reservoirs

18 The Fe concentrations of the reservoir water depend on the rate of the Fe oxidation process in  
19 combination with the flux of Fe-rich groundwater into the reservoirs and the transit time in the  
20 reservoirs. The pH, oxygen concentration and temperature are the major controls on the Fe(II)  
21 oxidation rate. The difference in maximum and minimum temperature of the ditch water is almost  
22 20°C (Fig. 5). A tenfold increase of the rate upon raising the temperature by 15°C is reported for  
23 abiotic oxidation of Fe(II) by oxygen (Sung and Morgan, 1980). This is mainly caused by the  
24 change in  $\text{OH}^-$  activity due to the temperature dependence of the ionization constant of water.

25 There was a seasonal variation in the pH of the water in the reservoirs (Fig 4), with lower values  
26 in winter and higher values in summer. According to the rate law for abiotic Fe(II) oxidation Eq.  
27 (3), a drop of half a pH unit for pH around 6-7 results theoretically in a nine-fold increase in the  
28 half-life time of Fe(II). Therefore, the seasonal variation in the pH is another control on the

1 dynamics in the Fe concentration of the reservoirs water. The smaller seasonal variation in the  
2 pH and Fe concentration in reservoir 1 compared to reservoir 2 and 3 supports this conclusion.

3 Seasonal increases in pH may be induced by CO<sub>2</sub> degassing of surface water or by  
4 photosynthesis in the surface water column (House and Denison, 1997; Neal et al., 2002). The  
5 average  $P_{\text{CO}_2}$  of all groundwater samples is 0.056 atm., which is a common value for  
6 groundwater in the Netherlands (Griffioen et al., 2013). For the reservoir water during the  
7 summer months and winter months this is 0.024 and 0.048 atm. respectively. Degassing of CO<sub>2</sub>  
8 is kinetically controlled and, therefore, it may take a couple of days before equilibrium with air is  
9 reached. Obviously, photosynthesis occurs mainly during summer months. So, we assume that  
10 longer transit times and higher temperatures of the water in the reservoirs during summer  
11 months compared to the winter months resulted in more extensive CO<sub>2</sub> degassing. This resulted  
12 into higher pH values during summer. In contrast to CO<sub>2</sub> degassing, hydrolysis following  
13 oxidation of Fe(II) to Fe(III) generates acidity. This reduces the alkalinity of water and tempers  
14 the pH increase following CO<sub>2</sub> degassing. Modelling calculations with PHREEQC indicated that  
15 oxygenation and degassing of groundwater with a pH of 6.16, Fe(II) concentration of 15.9 mg/l,  
16 and  $P_{\text{CO}_2}$  of 0.056 atm. to the summer-average  $P_{\text{CO}_2}$  of the reservoir water of 0.024 atm. results  
17 in pH values of 6.54 and 6.39 without and with oxidative hydrolysis, respectively. These pH  
18 values are somewhat lower than a majority of pH measurements of the reservoir water during the  
19 summer months (Fig. 4). So degassing of the surface water is not the only process that induces  
20 the seasonal pH increase.

21 The transit time of the water in the reservoirs also explains the low Fe concentrations in the  
22 summer months. Fig. 6A shows that the measured concentrations decrease with an increase of  
23 the mean transit time, although a large variation of the Fe concentrations around the variable  
24 span smoother exists. Iron concentrations higher than 5 mg/l were only found when the  
25 residence time was less than 5 days. Samples from Nov. to Feb. have predominantly residence  
26 times shorter than 5 days and Fe concentrations above the smoother line. The Fe concentrations  
27 of samples from March to Oct. were predominantly lower than the smoother line.

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#### 29 4.1.2 Tube drains

1 The increase in Fe concentration of tube drain 3 indicates a change in the redox status of the  
2 drained water. The flow data of the tube drains showed a decrease of the discharge rate of drain  
3 3 starting in Dec. 2007 (Fig. S4 in supplement). This indicates that the redox change was caused  
4 by clogging of the tube drain due to precipitation of Fe oxyhydroxides in combination with the  
5 growth of microbial biomass in the tube drain. Clogging results in an increase of the water  
6 saturation of the tube drain and therefore in a decrease of atmospheric oxygen penetration in the  
7 tube drain itself and the surrounding soil. The Fe oxidation, therefore, no longer occurs in the  
8 tube drain or the surrounding soil but after groundwater is discharged to the ditch. Clogging of  
9 filter material at redox boundaries is a common phenomenon for example in drilled wells for  
10 groundwater abstraction and also tube drains (Houot and Berthelin, 1992; Van Beek et al.,  
11 2009; Wolthoorn et al., 2004).

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#### 13 *4.1.3 Surface water*

14 Unlike the water in the reservoirs, the Fe concentrations of the surface water samples from the  
15 sub-catchment outlet and the catchment outlet ranges year-round around 1 mg/l. This value  
16 range that is commonly found in (oxygenated) surface water in the Netherlands. For example, Fe  
17 concentration in filtered stream and ditch water samples in the FOREGS database for the  
18 Netherlands ranges between 0.014 and 0.787 mg/l (Salminen, 2005). This indicates that the  
19 Fe(II) from the groundwater is completely oxidized at these sampling locations. The absence of  
20 water with Fe concentrations in the range of the reservoir water is explained by the longer  
21 residence time of the surface water at the sub-catchment and catchment outlet and by  
22 contributions of the dominantly aerobic Fe-depleted tube drain water to the surface water  
23 discharge. Tube drain water was physically separated from the groundwater at our experimental  
24 field and, therefore, did not contribute to the inflow to the reservoirs. Van der Velde et al. (2010)  
25 concluded that during normal flow conditions, the tile drain contribution to surface water  
26 discharge is more important than the groundwater contribution.

27 Although ranging around 1 mg/l, the Fe concentrations of the surface water samples were higher  
28 than concentrations predicted by assuming equilibrium of Fe(III) with a Fe oxyhydroxide phase.

1

## 2 4.2 Fe oxidation kinetics

3 The second objective of our study was to infer reaction rates and mechanisms that influence the  
4 Fe oxidation process. The kinetic oxidation of dissolved Fe(II) was modeled according the  
5 general rate law as reported by Stumm and Lee (1961). The Fe oxidation rates inferred from our  
6 field measurements closely agree with the general rate law for abiotic oxidation of Fe(II) by O<sub>2</sub> ( $k$   
7 =  $7.9 \times 10^{13} \text{ M}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$ ) (Fig. 6A). Seasonal changes in pH and temperature of the reservoir  
8 water had a major effect on the Fe(II) oxidation rate as explained below.

9 The grey lines in Fig. 6A represents the steady-state Fe(II) concentration as function of the mean  
10 transit times as calculated with the CSTR-model. The model simulates the Fe(II) oxidation in the  
11 reservoirs for the yearly average conditions, a typical summer situation, and a typical winter  
12 situation. Table 2 gives the input parameters for the CSTR model. The Fe concentration of the  
13 groundwater (Fig. 2A) was used as inflow concentration ( $\text{Fe}_i$  in equation 2) to the reservoir. This  
14 is variable in space and time between 0.2 and 40 mg/l. Because we don't know the values of  $\text{Fe}_i$   
15 at sampling moments exactly, it was not possible to derive field-based oxidation rates for the  
16 individual measured Fe concentrations. The Fe concentration of the groundwater that flows into  
17 the reservoirs ( $\text{Fe}_i$ ) was set to 14.5 mg/l representing the median concentration of Fe in the  
18 groundwater. The median concentration was preferred above the average concentration due to  
19 the skewness of the Fe concentration distribution to high values. The thin lines in Fig. 6A  
20 represent a typical summer and winter situation. The  $\text{Fe}_i$  for the summer and winter situations  
21 were set to the 25-percentile and 75-percentile of Fe concentration in the groundwater (10.6 and  
22 21.3 mg/l, respectively). The input values for the rate controlling parameters were assigned as  
23 follows: 1) the pH values are calculated from the yearly averaged and seasonally averaged [H<sup>+</sup>]  
24 measurements from the reservoirs (6.31, 6.17 and 6.53, respectively); 2) Biological, chemical and  
25 physical processes control the dissolved oxygen concentration of drainage ditches (Kersting and  
26 Kouwenhoven, 1989). Therefore the oxygen concentration of our reservoirs will be variable over  
27 the year and even over the day. However, low oxygen saturation levels or even hypoxia are not  
28 likely for the reservoir water. Hypoxia is not an uncommon phenomenon in ditches with free-  
29 floating plant mats (Verdonschot and Verdonschot, 2014; Kersting and Kouwenhoven, 1989) but

1 this was not the situation for our reservoirs. Moreover, because of a high degree of atmosphere–  
2 water contact (the reservoirs have typically a small wetted volume as opposed to its wetted  
3 perimeter) equilibrium with atmospheric oxygen might be possible. In the winter situation we  
4 assume that the equilibrium time to reach complete saturation is less than the half-life time of  
5 Fe(II). Therefore, we used complete oxygen saturation ( $P_{O_2} = 0.21$  atm.) for the winter situation.  
6 The Fe(II) oxidation rate is clearly higher in the summer situation. The Fe(II) is presumably  
7 completely oxidized before the reservoir water is in equilibrium with atmospheric oxygen. For this  
8 reason we modelled the reaction for the summer situation with a  $P_{O_2}$  of 0.1 atm.; 3) the  
9 temperature for the yearly average model was set to the yearly averaged temperature of the  
10 ditch water (9.3 °C) and to 17°C and 5°C for the summer and winter situation respectively (Fig.  
11 5).

12 Fig. 6A shows that the variable span smoother through the observations matches with the model  
13 for the yearly average conditions. Although our modelled reaction rate might probably slightly be  
14 overestimated due to the presence of colloidal Fe(III) in the reservoir water samples we may  
15 safely conclude that the decrease of the Fe concentration with increasing mean transit time of  
16 the water in the reservoirs closely agreed with the reported rate law of abiotic Fe(II) oxidation in  
17 laboratory systems with a rate constant of  $7.9 \cdot 10^{13} \text{ M}^{-2} \cdot \text{atm}^{-1} \cdot \text{min}^{-1}$  (Stumm and Lee, 1961). Most  
18 measured Fe concentrations fall between the summer-type and winter-type lines. The winter-type  
19 model seems to underestimate the Fe(II) oxidation rate slightly. This is likely due to microbial  
20 Fe(II) oxidation that become increasingly important when abiotic rates are retarded by low  
21 temperatures (de Vet et al., 2011), like in our winter situation. Although microbial Fe(II) oxidation  
22 at low oxygen concentration and autocatalytic Fe(II) oxidation due to adsorption of Fe(II) onto  
23 surfaces of previously formed Fe(III) oxyhydroxides may happen in the reservoirs, enhanced  
24 reaction rates caused by these processes were not considered in our model. The effect of  
25 autocatalytic Fe(II) oxidation on the reaction rate is currently under debate. Sung and Morgan  
26 (1980) concluded that autocatalytic Fe(II) oxidation is only observed in experiments with a pH of  
27 7 and higher. However, Pedersen et al. (2005) showed that Fe(II) can interact with Fe(III)  
28 oxyhydroxides surfaces and can be oxidized at pH 6.5. Schaefer et al. (2010) showed that the  
29 electron transfer between dissolved Fe(II) and structural Fe(III) can occur at the surface of

1 Fe(III)-bearing clay minerals such as smectite. Moreover, Vollrath et al. (2012) argue that the rate  
2 law originally proposed by Stumm and Lee (1961) was already influenced by surface catalysis  
3 and, therefore, not strictly represents homogeneous Fe(II) oxidation.

4 The large difference between the summer-type and winter-type model illustrates the effect of the  
5 temperature and pH on the abiotic Fe(II) oxidation rate. Fig. 6A makes clear that the oxidation of  
6 Fe in anaerobic groundwater after being discharged into surface water is not instantaneous. It  
7 will take a couple of days to more than one week before complete oxidation of Fe(II) is reached,  
8 especially under winter conditions.

9

### 10 **4.3 Behavior of P**

11 The third objective was to measure the dynamics in P concentrations and to explore the  
12 phosphate immobilization process during flow of anaerobic iron-rich groundwater towards  
13 surface water. Our field data show that dissolved P preferentially precipitates from solution during  
14 the initial stage of the Fe(II) oxidation process. When high Fe concentrations happened in the  
15 reservoir water and the water from tube drain 3, substantially lower P concentrations were found  
16 in these waters compared to the groundwater. The average molar P/Fe ratios of the reservoir  
17 water and tube drain 3 varied between 0.004 and 0.014 during winter time (Table 1); this is  
18 distinctly lower than the P/Fe ratio in the groundwater that varied between 0.016 and 0.079. A  
19 single Fe-oxide flocs sample from a drain had a molar P/Fe ratio of 0.033. This is in the range of  
20 the groundwater P/Fe ratio. Moreover, there is no relation between the P concentration of the  
21 reservoir water and the mean transit time (Fig. 6B) and no clear seasonal dynamics in P  
22 concentrations in the waters other than groundwater exist (Fig. 3). For tube drain 3, two  
23 mechanisms might cause these observations: (1) the average P concentration of the anaerobic  
24 groundwater that flowed into the tube drain was lower than the groundwater sampled from the  
25 four wells or (2) there was continuous immobilization of dissolved P in tube drain 3 despite the  
26 observation that complete oxidation of Fe no longer occurred in this drain. For the reservoirs, it is  
27 not likely that the inflow of groundwater with low P concentrations determined the P  
28 concentration of this water. After all, the groundwater was sampled from four wells parallel to the



1 reservoirs covering almost the entire stretch of the reservoirs. So the observations point to a  
2 rapid transformation of dissolved P to structural P during the initial stage of Fe(II) oxidation along  
3 the flow-path of groundwater into surface water. This resulted in nearly complete P depletion in  
4 the water before Fe(II) was depleted.

5 The blue and gray lines in Fig. 6B are the steady-state P concentration according to the two  
6 CSTR-models for phosphate immobilisation as function of the mean transit time. The models  
7 simulates the binding of phosphate by surface complexation to Fe oxyhydroxide precipitates that  
8 formed during Fe(II) oxidation and precipitation of a solid-solution between amorphous Fe  
9 hydroxide ( $\text{Fe}(\text{OH})_3$ ) and strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ). The P concentrations of the inflow water were  
10 set to 0.33, 0.52 and 0.19 mg/l representing the median, 75-percentile and 25-percentile of P  
11 concentration in the groundwater (Table 2). Figure 6B indicates clearly that the measured P  
12 concentrations are distinctly lower than the concentrations according to the surface complexation  
13 model for the whole range of mean transit times. The immobilisation of P during aeration of  
14 groundwater could not solely be attributed to surface complexation to a Fe-oxide type of phase.  
15 The concentrations according to the model that simulate the precipitation of a solid-solution  
16 between amorphous Fe hydroxide and strengite are in the range of the measured  
17 concentrations. The variable span smoother through the observations matches with the model for  
18 the year average conditions. The fast immobilisation of P during the short mean transit times,  
19 where Fe(II) was still present in high concentration, could satisfactory be described by the model.  
20 This indicates the formation of Fe(III)-phosphate precipitates during the initial stage of Fe(II)  
21 oxidation until phosphate is depleted from solution. The model overestimates the lowest  
22 measured P concentration. This could be attributed to additional adsorption of phosphate to the  
23 Fe-oxides that were as well formed in the solid-solution or by uncertainty in the logK value of  
24 strengite.

25 Recently, Voegelin et al. (2013) studied the effect of phosphate on the formation of Fe  
26 precipitates upon oxidation of Fe(II) at near-neutral pH. Their data verifies that Fe(II) oxidation  
27 initially results in the precipitation of a phosphate-rich Fe-precipitate whose P/Fe ratio reaches  
28 ~0.52 at the time of near-complete phosphate depletion from solution. This is supported by a

1 limited number studies (Deng, 1997;Gunnars et al., 2002) which indicated that during Fe(II)  
2 oxidation in solutions with initial dissolved P/Fe ratio less than ~0.5, a phosphate-rich precipitate  
3 with molar P/Fe ratio of ~0.5-0.6 forms first. Rather than a simple formation of Fe(III)-hydroxide  
4 coupled with competitive ion adsorption, Voegelin et al. (2013) concluded that several types of  
5 Fe(III)-precipitates may form and transform over the course of Fe(II) oxidation in the presence of  
6 phosphate. Fe(III)-phosphate, phosphate-saturated hydrous ferric oxide, goethite and  
7 lepidocrocite were successively formed in their study depending on the dissolved molar P/Fe  
8 ratios. The observations from our experimental field site are thus supported by laboratory  
9 experiments on synthetic samples.

10

## 11 **4.4 Implications**

### 12 *4.4.1 Dynamics in the redox gradient*

13 The higher Fe concentration of the reservoir water during winter compared to summer are  
14 explained by a reduction of the Fe(II) oxidation rate combined with an increased inflow of  
15 groundwater into the reservoirs during winter. Based on our data, we argue that the oxidation  
16 rate of Fe(II) in combination with groundwater inflow to the ditch is such that the Fe(II) oxidation  
17 occurs at the sediment-water interface or deeper in the soil domain during summer, resulting in  
18 low Fe(II) concentrations of the reservoir water (Fig. 2c). Fe(II) oxidation shifts to the surface  
19 water in winter evidenced by high Fe(II) concentrations. This argument is supported by visual  
20 observations of the ditch water during the field experiment. The easily resuspendable Fe-oxide  
21 flocs which have sedimented on ditch bottoms were predominantly found in winter time (Fig. 7).  
22 So, the position of the redox gradient in the groundwater-surface water interface of our  
23 experimental field is dynamic in time as a result of dynamics in hydrological and biogeochemical  
24 conditions. Krause et al. (2009) measured highly complex temporal changes in redox status and  
25 pore water nitrate concentrations at the groundwater-surface water interface of a small river.  
26 Maassen and Balla (2010) measured the effect of these redox dynamics on phosphorus  
27 mobilization from the sediment to the surface water. We show that dynamics in redox processes  
28 as well may impact the Fe(II) oxidation process and phosphorus immobilization during flow from  
29 groundwater into surface water.

1 Due to deeper groundwater tables in summer oxygen-saturated surface water may start to  
2 infiltrate and atmospheric oxygen may penetrate the soil surrounding the tube drains. Through  
3 higher groundwater tables and more discharge this oxygen-saturated water is flushed out again  
4 in winter time. Moreover, the abundant growth of grasses and reeds inside the ditches is likely to  
5 actively transfer oxygen through the groundwater-surface water interface during summer time. In  
6 a previous experiment at the same field site an iron-rich zone was observed directly around the  
7 drain tube, causing an orange-colored 'ring' in the soil around the tube drain (Van den Eertwegh,  
8 2002). The P content of the solid material in this ring was three times higher than for soil samples  
9 taken just outside this iron-rich zone. Although the Fe content of the soil samples and the P  
10 concentrations of the groundwater were not measured this indicates at least a partial retardation  
11 of dissolved P in this soil domain.

12

#### 13 4.4.2 *Suspended sediment*

14 The formation of Fe-oxide flocs in the surface water will contribute to the suspended sediment  
15 concentration of this surface water. The origin of suspended sediments and particulate-bound P  
16 in agricultural catchments is widely studied (Ballantine et al., 2008; Walling et al., 2008).  
17 Traditionally, two source types of suspended sediment are being distinguished: surface erosion  
18 and resuspension of streambed sediment. Rainstorm events and high discharge peaks are  
19 commonly considered as the trigger for mobilization of these source materials (Horowitz, 2008).  
20 Little attention has been paid to the formation of authigenic sediment in the surface water  
21 systems formed by exfiltration and oxygenation of anaerobic groundwater. However, we argue  
22 that it may be an important suspended sediment source in areas draining anaerobic  
23 groundwater. The only studies, known to us, on authigenic sediments in freshwater systems  
24 formed by oxidation of iron-rich groundwater are from Baken et al. (2013) and Vanlierde et al.  
25 (2007). They reported an average annual authigenic mineral contribution to the total suspended  
26 sediment flux between 31% and 75% for a catchment in Belgium. Based on the Hupsel field  
27 experiment data, we argue that the formation of authigenic suspended sediments in the surface  
28 water domain predominantly occurs in winter time and that this attributes to an increase in the

1 turbidity of surface water combined with a change in colour of the surface water compared to the  
2 summer situation.

3

#### 4 *4.4.3 Remobilization of phosphate*

5 Finally, the question arises what the effect of the preferential P precipitation during oxidation of  
6 Fe(II) will be on phosphate retention. The formation of Fe(III)-phosphate precipitates during  
7 oxygenation of groundwater in the soil surrounding the ditch or tube drain may result in  
8 permanent retention of phosphate at the transition zone from groundwater into surface water.  
9 However, the structural P stored in this zone may be discharged to the surface water by erosion  
10 during high flow conditions or remobilized to dissolved P by reductive dissolution or aging of  
11 Fe(III) precipitates. Thus, the transformation of the Fe precipitates may result in the release of  
12 dissolved phosphate. A limited number of time-resolved experiments addressed the effect  
13 transformation processes. All measured an increase in dissolved phosphate after (Mayer and  
14 Jarrell, 2000;Gerke, 1993;Voegelin et al., 2013). Voegelin et al. (2013) attributed this phosphate  
15 release to ongoing Fe(III) polymerization into (crystalline) Fe(III)-(hydr)oxides combined with no  
16 further Fe(III) supply to the solid phase that could have retained phosphate. The question  
17 remains if this phosphate release process due to aging of minerals occurs in the natural  
18 environment as well at these reported levels. After all, there is an ongoing Fe(II) supply in the  
19 natural environment resulting in the formation of new Fe(III) precipitates. Moreover, solutes such  
20 as silicate or humic acid interfere with Fe(III) polymerization and may markedly slow down Fe(III)  
21 polymerization, phase transformation and associated phosphate release (Gerke, 1993;Mayer  
22 and Jarrell, 2000).

23

## 24 **5 Conclusions**

25 This field study demonstrates that: 1) the Fe concentrations of water in in-stream reservoirs  
26 capturing exfiltrating anaerobic groundwater and the tube drain water were dynamic over the  
27 year. The Fe concentrations of the water in the reservoirs were high and reached the levels of  
28 the groundwater in winter time and were low in summer time. This indicates seasonal changes in

1 the Fe(II) oxidation rate. The dissolved P concentration of the reservoir water and tube drain  
2 water were an order of magnitude lower than observed in the groundwater throughout the year.  
3 Seasonal changes in the Fe(II) oxidation rate had no impact on the P immobilization; 2) the Fe(II)  
4 oxidation rate at our field site closely agrees with reported rate laws for abiotic oxidation of Fe(II)  
5 by O<sub>2</sub>. Due to lower a pH and temperature the Fe(II) oxidation rates are lower in winter time  
6 compared to summer time. Combined with higher groundwater fluxes during winter this likely  
7 resulted in a shift from Fe(II) oxidation occurring in the soil or ditch sediment in summer time to  
8 the surface water in winter time; 3) Phosphorus immobilization at our field site is much faster  
9 than the surface complexation model proposed by Dzombak and Morel (1990). This results in  
10 nearly depletion of phosphate water before Fe(II) is depleted. The fast P immobilization could  
11 satisfactory be described with the precipitation of an solid-solution between amorphous Fe  
12 hydroxide and strengite (Fe(III)-phosphate). The formation of Fe(III)-phosphates at redox  
13 gradients seems to be an important biogeochemical mechanism in the transformation of  
14 dissolved phosphate to structural phosphate and, therefore, a major control on the phosphate  
15 retention in streams and ditches that drain anaerobic groundwater.

16

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1 **Tables**

2

3 Table 1: Averaged P and Fe concentrations and molar P/Fe ratios of the groundwater, the  
4 reservoir water during winter time and the drain 3 effluent

	avg P μmol/l	avg Fe μmol/l	avg P/Fe ratio
groundwater 1	22.1	422	0.053
groundwater 2	5.6	353	0.016
groundwater 3	12.0	182	0.066
groundwater 4	14.6	184	0.079
drain 3 after Sept. 2007	2.6	235	0.011
Reservoir 1 Nov.-Feb.	0.5	56	0.009
Reservoir 2 Nov.-Feb.	1.0	229	0.004
Reservoir 3 Nov.-Feb.	1.6	119	0.014

5

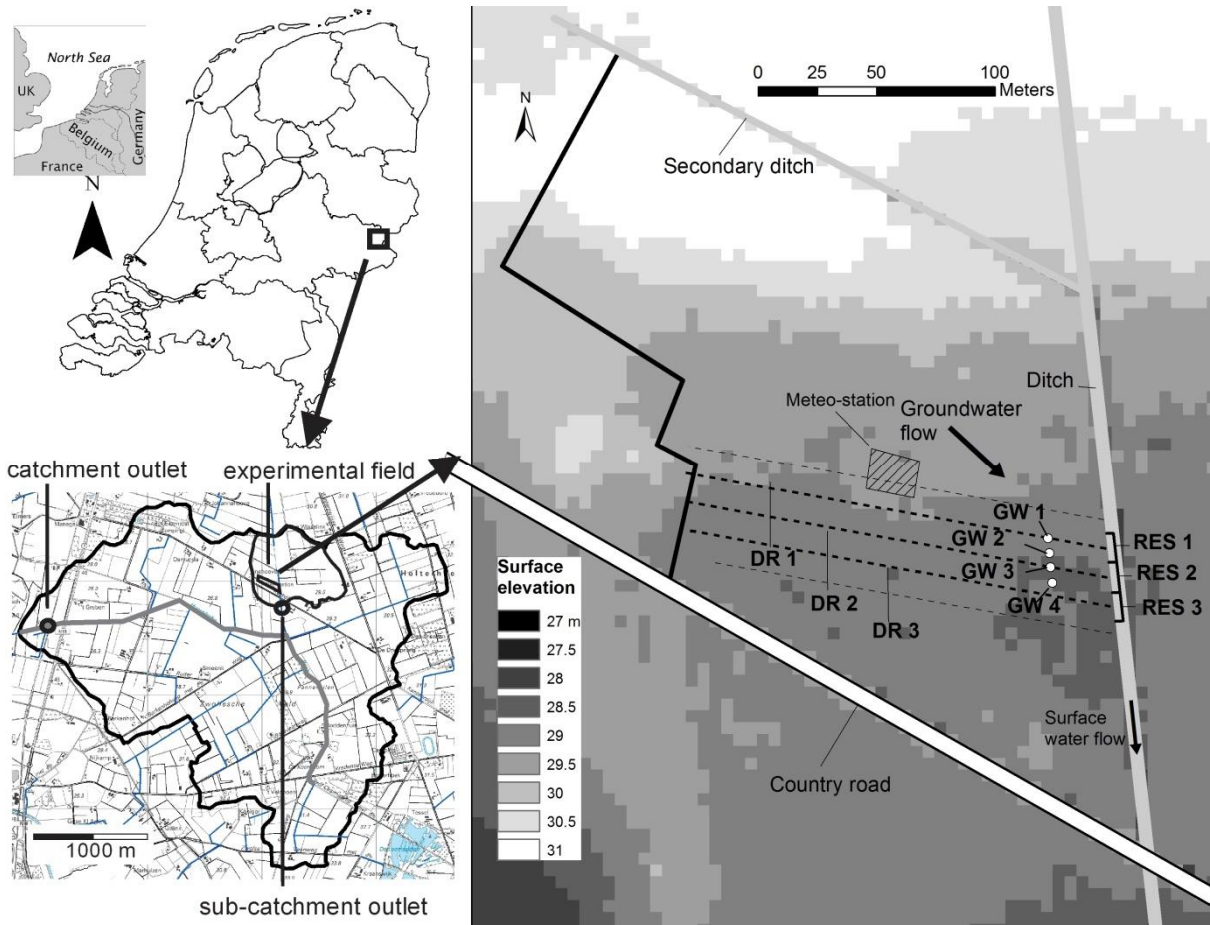
6 Table 2: Input parameters for the CSTR model

	Fe inflow (mg/l)	PO <sub>4</sub> inflow (mg/l)	pH	P <sub>O<sub>2</sub></sub> (atm.)	T (°C)
Year average	14.5	0.33	6.32	0.21	9.3
Summer situation	10.6	0.19	6.56	0.1	17
Winter situation	21.3	0.52	6.17	0.21	5

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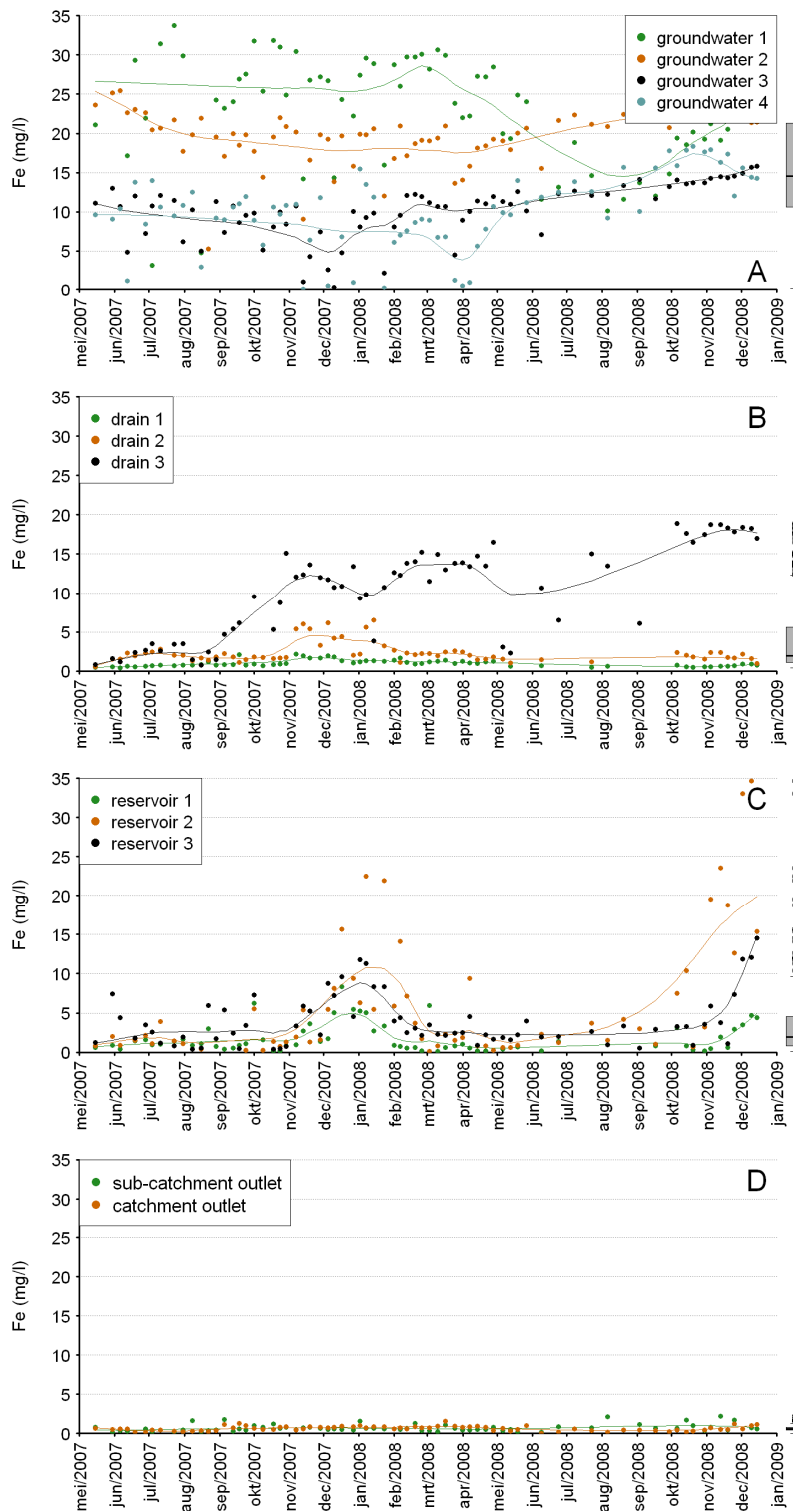
1 **Figures**



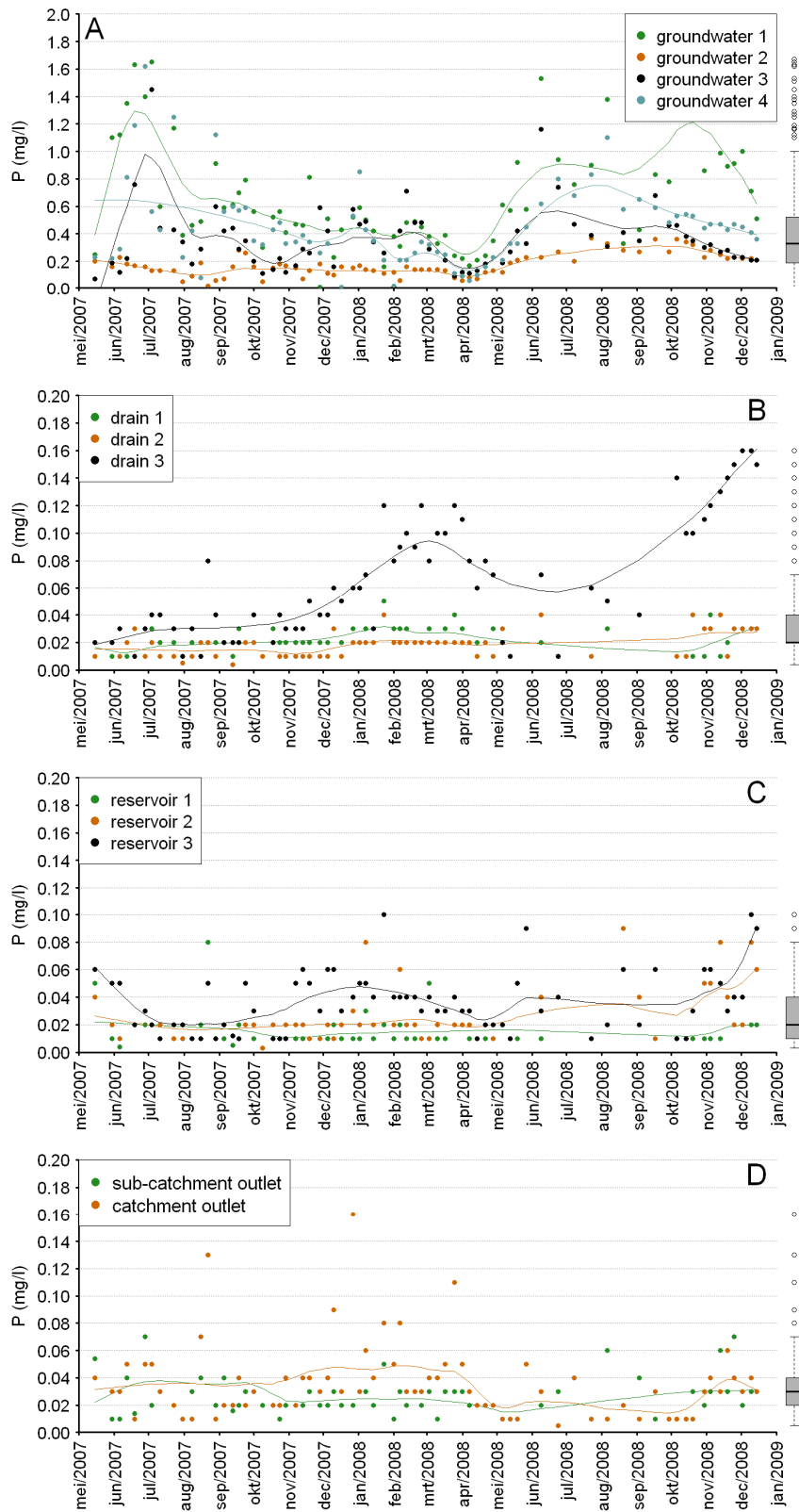
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3 Figure 1. Location of the Hupsel catchment and the experimental field. The catchment map  
4 shows the sub-catchment outlet and catchment outlet. The field map shows the three measured  
5 tube drains (DR), the four groundwater wells (GW) and the location of the in-stream reservoirs  
6 (RES). The direction of the groundwater flow is taken from Rozemeijer et al. (2010c).

7



1  
2 Figure 2. Time series and boxplots of Fe concentration of groundwater (A), tube drain water (B),  
3 in-stream reservoir water (C) and surface water (D). The smoothing line through the measured  
4 data points is calculated with the method of Friedman (1984). The bold solid line within each box  
5 plot is the median concentration. The lower and upper side of the box represents the 0.25 and  
6 the 0.75 quantile. Whiskers extend to the maximum and minimum value unless the values are  
7 larger than 1.5 times the box length. Open circles are extreme values.



1  
 2 Figure 3. Time series and boxplots of dissolved total P concentrations of groundwater (A), tube  
 3 drain water (B), in-stream reservoir water (C) and surface water (D). B, C and D share the same  
 4 y-axis. Remarks as for Figure 2.

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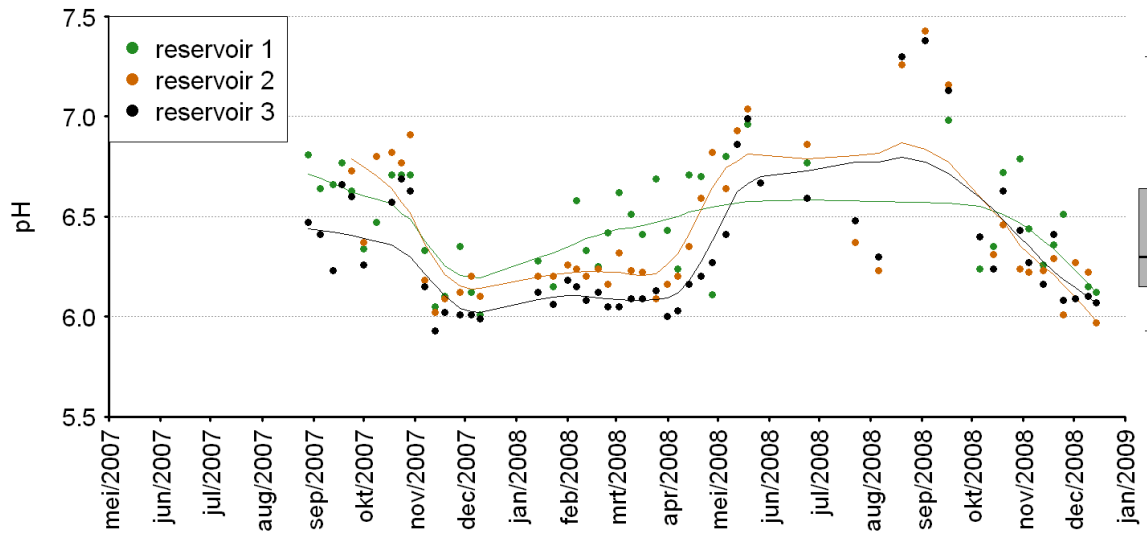
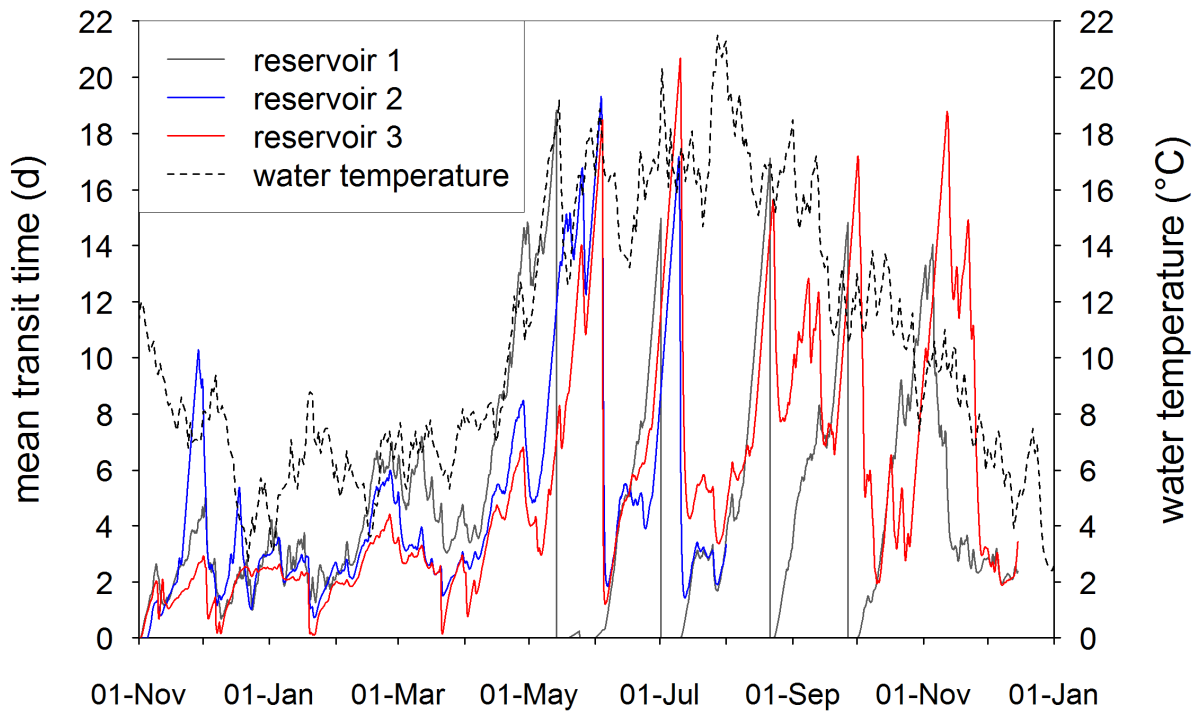


Figure 4. Time series of pH of reservoir water. Remarks as for Figure 2.

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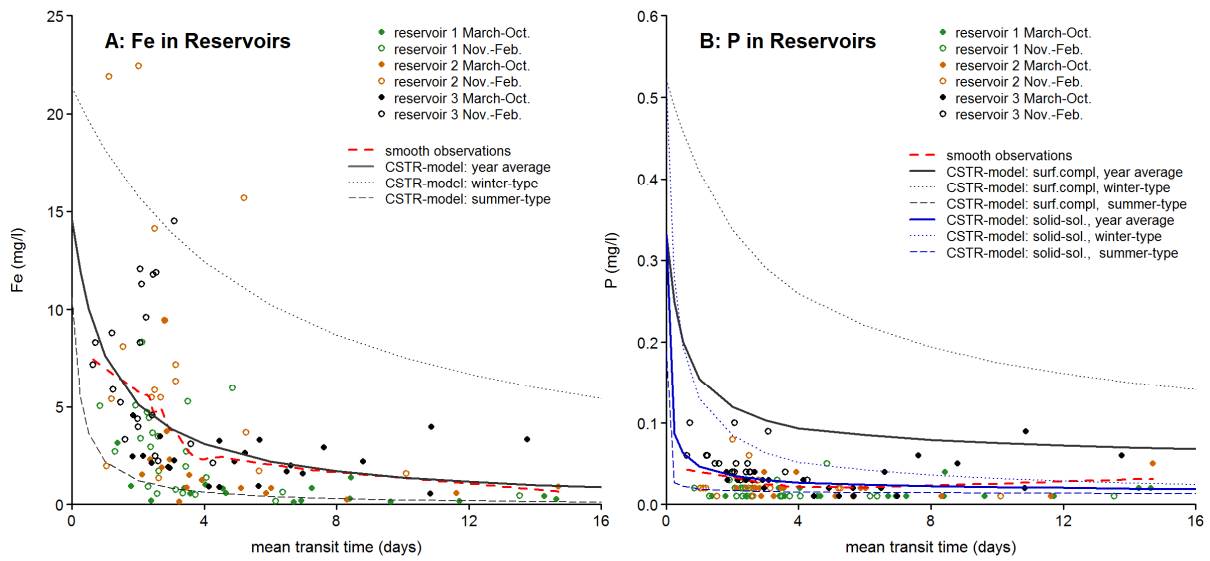


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3 Figure 5. Mean transit time of the water inside the in-stream reservoirs and the temperature of  
4 the ditch water direct downstream the reservoirs.

5

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3 Figure 6. Measured Fe and P concentrations vs. the mean transit time of the water in the  
4 reservoirs. The blue and gray lines show the steady-state Fe and P concentrations according to  
5 the CSTR-models as function of the mean transit time for the yearly average situation ( $T =$   
6  $9.3^{\circ}\text{C}$ ;  $\text{pH} = 6.32$ ;  $P_{\text{O}_2} = 0.21$ ), the winter-type conditions ( $T = 5^{\circ}\text{C}$ ;  $\text{pH} = 6.17$ ;  $P_{\text{O}_2} = 0.21$  atm.)  
7 and summer-type conditions ( $T = 17^{\circ}\text{C}$ ;  $\text{pH} = 6.53$ ;  $P_{\text{O}_2} = 0.1$  atm.).

8

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2

3 Figure 7. Pictures of the field ditch in the late summer (left) and winter (right). The red sediment  
4 indicates the presence of iron-hydroxides in the winter situation. These were absent in summer

5