Water Research 98 (2016) 326–333

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Phosphate binding by natural iron-rich colloids in streams

Stijn Baken [a, *, 1], Claudia Moens [a, 1], Bas van der Grift [b, c], Erik Smolders [a]

[a] KU Leuven, Department of Earth and Environmental Sciences, Kasteelpark Arenberg 20 bus 2459, 3001, Leuven, Belgium
[b] Copernicus Institute of Sustainable Development, Faculty of Geosciences, Utrecht University, P.O. Box 80115, 3508 TA, Utrecht, The Netherlands
[c] Deltares, Unit Soil and Groundwater Systems, P.O. Box 85467, 3508 AL, Utrecht, The Netherlands

ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
6 April 2016
Accepted 13 April 2016
Available online 23 April 2016

Keywords:
Natural water
Iron oxides
Colloids
Phosphate binding
Coprecipitation
Surface adsorption

ABSTRACT

Phosphorus (P) in natural waters may be bound to iron (Fe) bearing colloids. However, the natural variation in composition and P binding strength of these colloids remain unclear. We related the composition of “coarse colloids” (colloids in the 0.1–1.2 μm size range) in 47 Belgian streams to the chemical properties of the streamwater. On average, 29% of the P in filtered (<1.2 μm) samples of these streams is present in coarse colloids. The concentration of Fe-rich colloids in streams decreases with increasing water hardness and pH. The P bearing colloids in these streams mostly consist of Fe hydroxyphosphates and of Fe oxyhydroxides with surface adsorbed P, which is underpinned by geochemical speciation calculations. In waters with molar P:Fe ratios above 0.5, only a minor part of the P is bound to coarse colloids. In such waters, the colloids have molar P:Fe ratios between 0.2 and 1 and are, therefore, nearly saturated with P. Conversely, in streams with molar P:Fe ratios below 0.1, most of the P is bound to Fe-rich colloids. Equilibration of synthetic and natural Fe and P bearing colloids with a zero sink reveals that colloids with low molar P:Fe ratios contain mostly nonlabile P, whereas P-saturated colloids contain mostly labile P which can be released within 7 days. Equilibration at a fixed free orthophosphate activity shows that the Fe-rich colloids may bind only limited P through surface adsorption, in the range of 0.02–0.04 mol P $(\text{mol Fe})^{-1}$. The P:Fe ratios measured in naturally occurring Fe and P bearing colloids is clearly higher (between 0.05 and 1). These colloids are therefore likely formed by coprecipitation of P during oxidation of Fe(II), which leads to the formation of Fe hydroxyphosphate minerals.

1. Introduction

Phosphorus (P) is the limiting nutrient for primary production in many aquatic systems. Excessive emissions of phosphorus to the environment have caused cultural eutrophication of surface waters (Schindler, 2012). These emissions may originate from point sources (wastewater effluents) as well as from diffuse sources, such as P losses from agricultural land. Due to the large remediation costs, P in surface waters is in many regions one of the greatest concerns for environmental managers (Neal and Jarvie, 2005).

The filtered fraction of natural waters contains inorganic P compounds, organic P compounds, and P bound to small inorganic particles. Orthophosphate (PO_4), *i.e.* phosphate in its simplest, free ionic form, is the main inorganic form of P. Organic P compounds are highly diverse; examples of simple organic P compounds include phytic acid, adenosine triphosphate (ATP), and ribonucleic acid (RNA) (Turner et al., 2005). The fraction of P in organic forms in filtered surface water has been estimated at 12% (Ekholm, 1994) and 20% (Van Moorleghem et al., 2011). The term “colloidal P” refers to the P bound to particles between 1 nm and 1 μm in size. Colloidal P is a quantitatively important fraction of the P in filtered (<0.45 μm) streamwater (Haygarth et al., 1997); one study estimates the average contribution of colloidal P in Belgian streams at 52% (Van Moorleghem et al., 2011).

The fate and environmental effects of P in natural waters depend on its chemical speciation. The fraction of total P in water that is available to algae span the entire 0–100% range (Ekholm and Krogerus, 2003; Ekholm et al., 2003). In freshwater systems, free orthophosphate is presumably the only P species which is taken up by algae. Organic P compounds are not directly available, but may undergo enzymatic hydrolysis to release free orthophosphate (Cembella et al., 1984). This hydrolysis may be catalyzed by

---

[*] Corresponding author. Present address: European Copper Institute, Avenue de Tervueren 168 b-10, 1150, Brussels, Belgium.
E-mail address: stijn.baken@gmail.com (S. Baken).
[1] Claudia Moens and Stijn Baken contributed equally to this work.

http://dx.doi.org/10.1016/j.watres.2016.04.032

enzymes: algae produce extracellular phosphatase enzymes in order to increase the bioavailability of organic P. The colloidal P is not directly available to algae (Baken et al., 2014), but it may partly become available after release of P from the colloids (Ekholm, 1994; Uusitalo et al., 2003, 2000). The bioavailable P is often measured by colorimetric methods and reported as molybdate reactive phosphorus (MRP) or soluble reactive phosphorus (SRP), an approach followed in water quality monitoring programs worldwide (Jarvie et al., 2002). These colorimetric assays generally exclude most organic P compounds, but include the P bound to colloidal oxyhydroxides of Fe and Al (Sinaj et al., 1998; Van Moorleghem et al., 2011).

Phosphorus bearing colloids in natural waters are highly heterogeneous in nature and composition, but they mostly contain Fe (Gunnars et al., 2002; Lienemann et al., 1999; Mayer and Jarrell, 1995; Regelink et al., 2013; Stolpe et al., 2010). This Fe may be present as oxyhydroxides (Regelink et al., 2014; Sjöstedt et al., 2013) or as Fe (hydroxy)phosphate (Griffioen, 2006; van der Grift et al., 2014). In addition, these heterogeneous colloids may contain clay minerals, natural organic matter (NOM), Al, Ca, and Si. Along the same lines, the colloidal P in soils is mostly associated with associations of organic matter and Fe and Al oxyhydroxide phases (Henderson et al., 2012; Ilg et al., 2008; Liu et al., 2014). At chemical equilibrium, amorphous Fe hydroxyphosphate colloids govern the partitioning of P between free orthophosphate and colloidal P in many streams (Fox, 1989, 1993). It is not clear to what extent this generally applies to field conditions due to kinetic limitations.

It is well established in soil science that surface adsorbed P in soil colloids is gradually fixed, i.e. it becomes less available over time. This is attributed to slow solid-state diffusion of the P into soil particles (Barrow, 1983). The P release from soils is typically characterized by a relatively fast initial release, followed by a slower release of phosphate which may continue for over two months (Koopmans et al., 2004; Lookman et al., 1995). Two key mechanisms are commonly distinguished by which phosphate may bind to iron-rich mineral phases. First, the P may bind to the surface of existing mineral phases, i.e. surface adsorption. Alternatively, the P may be bound during the formation of Fe-rich mineral phases. Such coprecipitation may e.g. occur during oxidation of Fe(II) in the presence of P (Sahai et al., 2007) and typically leads to the formation of poorly crystalline Fe hydroxyphosphate minerals (van der Grift et al., 2014; Voegelin et al., 2010, 2013). It is unsure by which mechanism the Fe and P bearing colloids in soils and natural waters are mostly formed. Upon aeration of anoxic groundwater, coprecipitation and Fe hydroxyphosphate formation may be expected to dominate (Baken et al., 2015a, b; Wolthoorn et al., 2004). One study showed that adding P to soil solutions did not result in increased binding of P by colloids, whereas adding Fe (as $FeCl_3.6H_2O$) resulted in increased colloidal P concentrations due to coprecipitation of P and Fe (Hens and Merckx, 2001). The binding mechanism of P to Fe-rich colloids affects the reactivity of the colloidal P. Coprecipitated P is less labile, and becomes available to biota more slowly, than surface adsorbed P (Baken et al., 2014). However, as far as we are aware, the lability of the colloidal P in natural waters has not yet been addressed.

The goal of this study was to characterize the colloidal P in streams in terms of its composition and reactivity, i.e. the binding and release of P from colloids. The composition of "coarse colloids" (0.1–1.2 μm) in a wide range of streams was determined by membrane filtration with different pore sizes. The reactivity of colloidal P was determined in batch equilibration experiments. The main hypotheses were 1) that Fe-rich colloids are the key vectors of colloidal P in streams; 2) that the composition of streamwater (the total concentrations of P and Fe) governs the composition of the P-bearing colloids it carries, and 3) that the binding and release of colloidal P depends on the composition of the colloids.

2. Materials and methods

2.1. Field survey

The study area for this work is approximately 7000 km^2 in Northeast Belgium and covers a wide range of topographical, geomorphological, and hydrogeological properties (details: SM, Section 1). The 47 sampling locations were selected in order to reflect this wide variability and to represent a wide range of catchment sizes. Each stream was sampled once in August or September 2014. Sampling occurred during contrasting hydrological regimes: August 2014 was a very wet month and sampling occurred during and shortly after rainfall events, whereas September 2014 was relatively dry.

The pH, water temperature, dissolved oxygen (DO) concentration, and electrical conductivity (EC) were measured in the field. Samples were filtered in the field using membrane filters with nominal pore sizes of 1.2 μm (Chromafil Xtra PET 120/25) and 0.1 μm (Pall Acrodisc Supor). The membrane filter was replaced after filtering 6 mL of streamwater, and the first mL was always discarded. Preliminary tests showed that the contamination picked up during filtration of ultrapure water over these membranes was below 2 $\mu g\ L^{-1}$ for P and 1 $\mu g\ L^{-1}$ for Fe. The concentrations of major and trace elements in both filtrates were determined by ICP-MS. The concentrations of Fe(II), Fe(III), organic carbon, inorganic carbon, and major anions were determined in the 1.2 μm filtrates (details: SM, Section 2). Element concentrations in the 0.1–1.2 μm size fraction, hereinafter referred to as "coarse colloids", were calculated as the difference in element concentrations between both filtrates. Pearson correlation coefficients between the concentrations of different elements were calculated with JMP Pro 11. Since the distribution of all variables (except pH) were better approximated by a lognormal distribution rather than by a normal one, correlation coefficients were calculated based on log-transformed data.

2.2. Geochemical modelling

The speciation of Fe in filtered (<1.2 μm) streamwater samples was calculated by geochemical modelling. The input consisted of pH, temperature, and the measured concentrations of Na, Mg, Al, K, Ca, Cr (entered as Cr(III)), Mn, Fe(II), Fe(III), Co, Ni, Cu, Zn, Cd, Pb, Cl, NO_3, SO_4, DIC (entered as CO_3), and P (entered as PO_4). The fulvic acid concentration was calculated assuming that 65% of the DOC is present in fulvic acids and that 1 g of DOC equals 2 g of DOM (Bryan et al., 2002). The oxyanions of V, Cr, As, Se, and Mo were not included in the speciation modelling, but the average concentrations of these elements were more than two orders of magnitude below those of P (Table S2). It is therefore unlikely that they affected the partitioning of P between colloids and free orthophosphate.

WHAM7.0 with the Humic Ion-Binding Model VII (Tipping et al., 2011) was used to estimate complexation of Fe(II) and Fe(III) by natural organic matter. Fe(III) was allowed to precipitate as oxyhydroxides with a stoichiometry of $Fe(OH)_3$. Since WHAM7.0 does not allow precipitation of other mineral phases than $Fe(OH)_3$, PHREEQC (Parkhurst and Appelo, 1999) with the WATEQ4F database (Ball and Nordstrom, 1991) was used to calculate precipitation of colloidal mineral Fe phases. Fe(III) was allowed to precipitate as a Fe hydroxyphosphate with stoichiometry $Fe_{1.61}(PO_4)(OH)_{1.83}$ (molar P:Fe ratio 0.62), or as a Fe oxyhydroxide with stoichiometry $Fe(OH)_3$ (van der Grift et al., submitted). Surface complexation of Fe(II) and PO_4 to the precipitated $Fe(OH)_3$ was considered using the

Dzombak and Morel (1990) model. The log value of the solubility constant for the Fe hydroxyphosphate was calculated using PHREEQC from the solubility constant of a Fe hydroxyphosphate with a P:Fe ratio of 0.4 as published by Luedecke et al. (1989):

$$\begin{aligned} Log\ K_{Fe_{2.5}PO_4(OH)_{4.5}} &= 2.5\log\left(Fe^{3+}\right) + \log\left(PO_4^{3-}\right) \\ &\quad + 4.5\log\left(OH^-\right) \\ &= -96.7 \end{aligned} \tag{1}$$

We assumed that the solubility of the Fe hydroxyphosphates with a P:Fe ratio of 0.62 is the same as that with a P:Fe ratio of 0.4. We replaced the stoichiometric coefficients in Eq. (1) with the corresponding values, and we calculated the Ion Activity Product (IAP) for the Fe hydroxyphosphate $Fe_{1.61}(PO_4)(OH)_{1.83}$ in a $Fe_{2.5}(PO_4)(OH)_{4.5}$ saturated solution (saturation index = 0). When assuming equilibrium for the $Fe_{1.61}PO_4(OH)_{1.83}$ phase in this system as well, the IAP of $Fe_{1.61}PO_4(OH)_{1.83}$ must equal its solubility product.

2.3. P binding and release from colloids: method development

Synthetic and natural Fe-rich colloids were equilibrated with a strongly P-binding resin (Adsorbsia AS600, Dow) in order to determine the binding and release of P by these colloids. The Adsorbsia resin consists of fine-grained Ti oxide and hydroxide on a vinyl alcohol polymer support. The release of P from colloids was addressed by equilibration with P-free Adsorbsia resin, which served as a zero sink for P (experiment A). The P-free resin removes the reversibly bound (labile) P from colloids, whereas irreversibly bound P (nonlabile P) is unaffected. This method is conceptually similar to previous work which used Fe oxyhydroxide suspensions as a zero sink to measure reversibly bound P in soils (Freese et al., 1995). The binding (adsorption) of P by colloids was quantified by equilibration with P-loaded Adsorbsia resin, which buffers the activity of free orthophosphate ions in solution at a fixed value (experiment B). Under such conditions, Fe-rich colloids may bind P by surface adsorption, but not by coprecipitation. The use of a loaded resin to impose a fixed free ion activity is conceptually similar to previous experiments on trace metal binding by natural organic matter (Amery et al., 2007; Baken et al., 2011).

The resin was prepared by washing with ultrapure water, and by adjusting its pH to 6.85 with MOPS (3-(*N*-morpholino)propanesulfonic acid) buffer. Preliminary experiments showed that P binding by the resin is pH-dependent, and therefore a constant pH of 6.85 was selected for all equilibrations. For experiment B, the resin was amended with 5.5 g P (kg dry resin)$^{-1}$ (added from a mixed stock of KH_2PO_4 and K_2HPO_4 at pH 6.85), which results in buffered P concentrations in solution of approximately 100 μg L^{-1} (Supplementary Material, Section 3.1). Finally, 40 mL of test solution (which either or not contained synthetic or natural Fe-rich colloids) were equilibrated with resin suspension (1 g dry resin suspended in ultrapure water) by gentle end-over-end shaking (1 rpm) at 4 °C for 7 days. The low temperature was selected to limit microbial activity in the natural samples. A dialysis membrane (Spectrumlabs, Spectra/Por 4 regenerated cellulose, 10–12 kDa) separated the colloid containing solution from the resin. This membrane readily allows passage of ions but prevents direct contact between colloids and resin particles, and thereby it avoids adsorption of the colloids to the resin particles. After 7 days, the concentrations of P and Fe (ICP-MS) and those of MRP (Murphy and Riley, 1962) were measured.

The method for measuring P binding and release from colloids was tested by equilibrating a set of synthetic test solutions (containing various concentrations of P, Fe-rich colloids, and inorganic anions) with aliquots of P-free and P-loaded resin, and by monitoring the concentrations of P, Fe, and MRP in solution for 7 days (details in the SM, Section 3.2). The physical separation of the colloids from the resin particles using the dialysis membrane was successful: all Fe-rich colloids remained in solution, no resin particles were detected in the colloid containing solution, and the transfer of free phosphate anions through the dialysis membrane was fast (equilibrium was reached within 1 d). Overall, it was shown that this method can quantify P binding and release from synthetic Fe-rich colloids (details in the SM, Section 3.2). It was noted that the activity of free orthophosphate ions imposed by the P-loaded resin (experiment B) depends on the ionic composition of the test solution, e.g. on alkalinity. Therefore, the P concentrations after equilibration in the colloid-containing test solutions are always compared to those in colloid-free reference treatments with identical ionic composition. This difference then corresponds to the P additionally bound by colloids (experiment B, equilibration with P-loaded resin).

2.4. P binding and release from colloids: application to synthetic and natural colloids

The above method was applied to determine binding and release of P from synthetic Fe oxyhydroxide colloids. All test solutions contained 10 mg L^{-1} natural organic matter (Suwannee River natural organic matter, SRNOM, purchased from the International Humic Substances Society) and 20 mM MOPS at pH 6.85. The test solutions for experiment A (measuring P release from colloids) additionally contained aliquots of KH_2PO_4 (86–232 μg P L^{-1}), whereas the test solutions for experiment B (measuring P binding by colloids through surface adsorption) did not contain any added P. Aliquots of Fe(II) were added to the test solutions (as $FeSO_4{\cdot}7H_2O$; 0.32–5.2 mg Fe L^{-1}) and were subsequently allowed to oxidize for 48 h at 20 °C in darkness. This procedure yields <0.45 μm Fe oxyhydroxide colloids, which are stabilized by the NOM (Baken et al., 2014). After oxidation of the Fe(II), each test solution was equilibrated with P-free or P-loaded resin in triplicate as described above, and the concentrations of P, Fe, and MRP were measured after 7 days. The P:Fe ratios of the equilibrated colloids were calculated from the difference in MRP and Fe concentrations between each treatment and the reference treatment. It was thereby assumed that most of the Fe was present in colloidal minerals: WHAM7.0 predicts that only 30 μg Fe L^{-1} is complexed by NOM, the remainder being present as colloidal precipitates. The P:Fe ratio of the colloids before equilibration could not be quantified, since the initial partitioning of P between colloids and free orthophosphate is unknown. However, it may be assumed that most of the P in these test solutions was colloidal: P is coprecipitated with oxidizing Fe(II) up to molar P:Fe ratios of 0.5 (Gunnars et al., 2002; Senn et al., 2015; Voegelin et al., 2013). Therefore, the initial P:Fe ratio of the test solution was likely close to that of the colloids, perhaps with the exception of the treatment with the highest P:Fe ratio (treatment A in Table 3) of which the P:Fe ratio in the colloids is somewhat uncertain.

The method was subsequently applied to three streamwater samples which were taken at locations also included in the field survey. The water samples were prepared by removing larger particles (<0.45 μm borosilicate membrane filter, Atlas Filtri AC-BX) and by reducing water hardness (Dowex HCR-S/S softening resin, sodium form, Dow Liquid Separations) in order to avoid aggregation of colloids during equilibration. They were subsequently subjected to cross-flow filtration (CFF, Vivaflow 200 with 30 kDa HydroSart membrane, Sartorius). The permeate (free of >30 kDa colloids) was collected whereas the retentate was continuously recirculated to the inlet vessel. This process was continued until the volumes of permeate and retentate were equal. This resulted in separation of the natural waters into two fractions with identical ionic (<30 kDa) composition: 1) the permeate, which is free of >30 kDa colloids and served as reference treatment in the equilibration experiments, and 2) the retentate, which has identical ionic composition but approximately 2-fold higher concentration of colloids (30 kDa–0.45 µm) than the original water sample (Supplementary Material, Section 4). The retentate and permeate were amended with 20 mM MOPS buffer (pH 6.85) and were subsequently equilibrated with P-loaded and P-free resin aliquots in triplicate as described above. The equilibrations were started no more than 2 days after sampling of the natural waters.

3. Results and discussion

3.1. Composition of natural Fe and P bearing colloids (field survey)

The composition and chemical properties of the streams sampled in the field survey range widely (Table 1 and Table S1), reflecting the contrasting geochemical conditions present in the study area. Nearly all streams were oxic (mean O_2 concentration 7.6 mg L^{-1}). The pH ranges between 6.4 and 8.0, and the hardness between 0.5 and 4.5 mM. The average P concentration in filtered (<1.2 µm) streamwater samples (358 µg P L^{-1}) greatly exceeds the environmental limit in Flanders (140 µg P L^{-1}, measured in unfiltered samples). On average, 29% of this P is present in coarse colloids (range 7–91%, Table 2). This highlights that P is of environmental concern in these streams, and that colloidal P is a quantitatively important P fraction. The relatively large colloidal P fraction is in line with previous studies (Mayer and Jarrell, 1995; Van Moorleghem et al., 2011). In the field survey, we could not discriminate between inorganic and organic P forms. A previous study on Belgian streams showed that on average only 20% of the P is in organic forms (Van Moorleghem et al., 2011). It is assumed here that the majority of the P is present as orthophosphate (either or not bound to colloids). Nevertheless, the presence of organic P forms may have affected the results to some extent, e.g. because it is poorly known what factors govern the partitioning of organic P forms between solution and colloids.

Iron was identified as a key constituent of the coarse colloids (0.1–1.2 µm; Table 2 and Table S2). On average, 70% of the Fe in filtered (<1.2 µm) samples is present in this size range. Geochemical modelling (WHAM7.0) shows that, on average, only 2% of the Fe occurs as complexes with humic substances. This agrees with previous work showing that Fe(III) in freshwaters at circumneutral pH is mostly present as colloidal Fe minerals, such as oxyhydroxides, whereas Fe(III)-DOC complexes are quantitatively less important (Lofts et al., 2008). The concentrations of colloidal Fe are higher in the softer and more acidic waters, as evidenced by the negative correlations between the colloidal Fe concentrations and pH ($r = -0.53$, $p < 0.001$), and between the colloidal Fe concentrations and water hardness ($r = -0.60$, $p < 0.001$; Table S3). Natural Fe-rich colloids commonly contain organic C as a key constituent (Mikutta et al., 2014; Perret et al., 2000), and DOC-rich waters typically also contain more Fe (Kritzberg and Ekström, 2012). Surprisingly, we observed no correlation between the concentrations of Fe (or colloidal Fe) and those of DOC. We were unable to quantify the concentrations of colloidal organic C: the uncertainty of the colloidal organic C measurement, which is based on a difference in DOC concentration after filtration, exceeds the expected concentrations of colloidal C. Other potential constituents of coarse colloids in streams include clay minerals, Al oxyhydroxides, and Ca phosphates (Regelink et al., 2013; Turner et al., 2004), but these do not appear to play a major role in the studied streams: the average concentration of Al in coarse colloids is one order of magnitude below that of Fe, and those of Ca and K are below the LOQ (Table 2). A drawback of this work is that membrane filtration is prone to serious artifacts (Morrison and Benoit, 2004), and the reported size range is therefore only an indication of the true size of these colloids. Nevertheless, membrane filtration has yielded valuable insights into natural colloids (Mayer and Jarrell, 1995; Sinaj et al., 1998; Turner et al., 2004). We selected this simple and cheap technique in order to apply it to a large sample set and to confirm previous findings obtained by field-flow fractionation on a very limited number of samples (Baken et al., 2016).

The positive correlation between the concentrations of P and Fe in coarse colloids (0.1–1.2 µm) suggests that Fe-rich colloids are the dominant vectors of colloidal P ($r = 0.66$ on log-transformed data; $p < 0.001$; Fig. 1A), as previously observed by Mayer and Jarrell (1995). The composition of these Fe and P bearing colloids is related to the composition of the streamwater. At low P:Fe in the 1.2 µm-filtered streamwater, most of the P is bound by colloids (Fig. 1B). The P:Fe ratio of the colloids is therefore close to that of the water, as evidenced by the proximity of the data points to the 1:1 line (Fig. 1C). Conversely, at high P:Fe ratio in the water, the molar P:Fe ratio in the colloids levels off to values between 0.2 and 1 (Fig. 1C), indicating that the colloids are saturated with P. Under such conditions, only a minor fraction of the P is bound to coarse colloids (Fig. 1B), and most of the P is present as truly dissolved species, e.g. free orthophosphate and organic P compounds, or as P bound to <0.1 µm colloids.

The wide range of P:Fe ratios measured in colloids suggests that they may consist of a mixture of Fe oxyhydroxide and Fe hydroxyphosphate minerals. This is corroborated by speciation calculations with PHREEQC. Precipitation of Fe hydroxyphosphate is predicted in all samples, with additional precipitation of Fe oxyhydroxide in 24 out of 48 samples. In streams with P:Fe ratios above 0.62, the model predicts precipitation of Fe hydroxyphosphate but not of Fe oxyhydroxides, which results in prediction of a constant molar P:Fe ratio of 0.62 in colloids (Fig. 1C and D). On average, the geochemical model estimates that 70% of the Fe in the precipitates is present as Fe hydroxyphosphate, and 30% is present as Fe oxyhydroxides. The model predicts virtually no surface adsorption of P on Fe oxyhydroxides.

Plots of the measured and modelled P:Fe ratio in colloids exhibit

Table 1
Composition of filtered (<1.2 µm) streamwater samples.

	pH	Hardness mM	Na mg L^{-1}	Mg mg L^{-1}	K mg L^{-1}	Ca mg L^{-1}	Fe µg L^{-1}	Fe(II) µg L^{-1}	Al µg L^{-1}	P µg L^{-1}	DOC mg L^{-1}	DIC mg L^{-1}	Cl mM	SO_4 mM
Mean	7.2	2.1	27	9	10.6	68	1070	203	85	358	8	32	1.08	0.54
Min	6.4	0.5	8	2	2.6	13	147	<5	5	11	3	5	0.01	0.01
P_{10}	6.5	0.7	13	4	4.4	20	175	<5	12	47	3	10	0.51	0.21
Median	7.3	1.7	22	9	7.9	56	879	48	40	178	6	24	0.96	0.57
P_{90}	7.7	3.7	49	15	20.7	128	2824	667	275	708	18	62	1.99	0.80
Max	8.0	4.5	104	18	46.7	158	4068	1406	439	3151	38	84	3.07	1.31

DOC: dissolved organic carbon, DIC: dissolved inorganic carbon, P_{10} and P_{90}: 10th and 90th percentile.

Table 2
Composition of coarse colloids (0.1–1.2 μm) in streamwater samples, as determined by the difference in composition between 1.2 μm filtrates and 0.1 μm filtrates.

	Na mg L^{-1}	Mg mg L^{-1}	K mg L^{-1}	Ca mg L^{-1}	Fe μg L^{-1}	Al μg L^{-1}	P μg L^{-1}	P:Fe mol mol^{-1}	P:(Fe +Al) mol mol^{-1}
Mean	<LOQ	<LOQ	<LOQ	<LOQ	747	61	105	0.28	0.23
Min					134	<0.7	4	0.02	0.02
P_{10}					166	6.4	16	0.08	0.06
Median					444	24	59	0.22	0.14
P_{90}					1884	217	252	0.58	0.53
Max					3744	309	762	0.96	0.88
LOQ	0.09	0.003	0.07	0.02	0.6	0.7	3	n.a.	n.a.

P_{10} and P_{90}: 10th and 90th percentile; LOQ: limit of quantification; n.a.: not applicable.

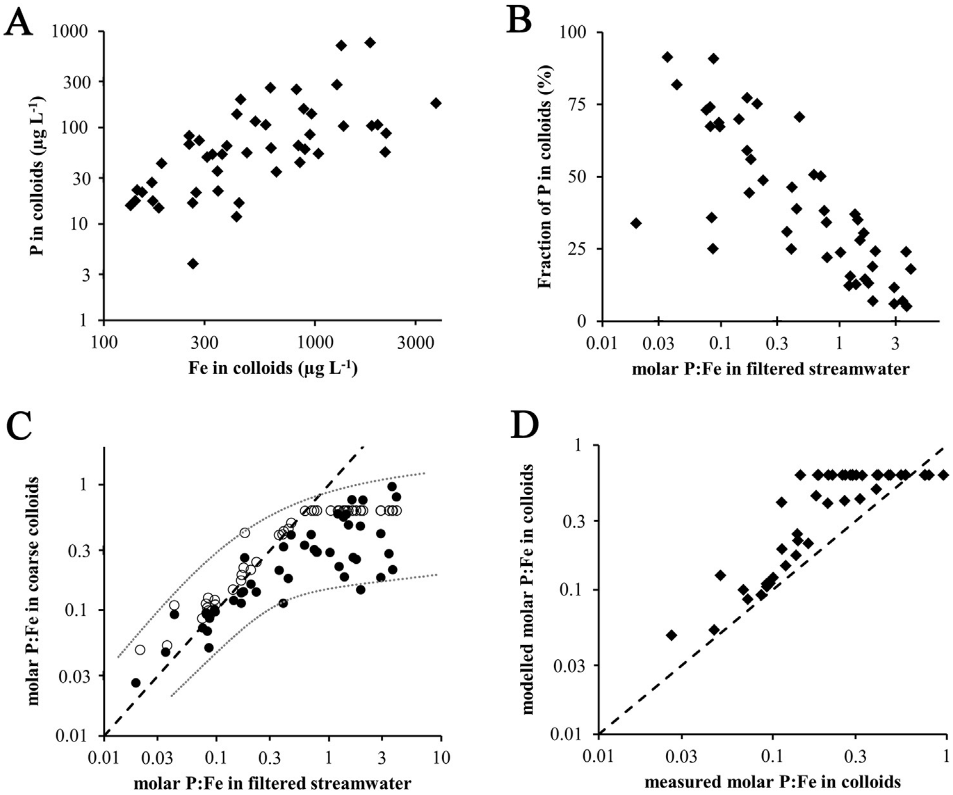

Fig. 1. **A**: The concentration of P in coarse colloids (0.1–1.2 μm) in streams, plotted against those of Fe ($r = 0.66$; $p < 0.001$). **B**: The fraction of P in filtered (<1.2 μm) streamwater that is present in coarse colloids, plotted against the molar P:Fe ratio in filtered (<1.2 μm) streamwater ($r = -0.78$; $p < 0.001$). **C**: The molar P:Fe ratio in coarse colloids (measurements: closed circles; predictions by geochemical speciation modelling: open circles), plotted against the molar P:Fe ratio in filtered (<1.2 μm) streamwater. The dashed line is the 1:1 line; the dotted grey lines are drawn to guide the eye. **D**: Modelled versus measured P:Fe ratios in colloids. The dashed line is the 1:1 line.

similar trends (Fig. 1C), but the modelled P:Fe ratio of the colloids is, on average, 1.8 times above the measured values (Fig. 1D). This may be due to formation of Fe hydroxyphosphate with lower molar P:Fe ratios than the assumed value of 0.62. It may also be due to the sequence of Fe and P loading of the stream. If PO_4 is present during the oxidation of Fe(II) to Fe(III), Fe hydroxyphosphate may be formed (Gunnars et al., 2002; van der Grift et al., 2014). In contrast, if Fe oxyhydroxide colloids are formed before mixing with P, e.g. if the P originates from a downstream point source, P is bound to Fe oxyhydroxides by surface complexation (Ding et al., 2012; Wang et al., 2013). Under such conditions, the P binding capacity is lower than if the P is present during oxidation of Fe(II), and lower P:Fe ratios in colloids are expected (Mayer and Jarrell, 2000). The difference between both binding mechanisms could not be simulated by the model. The predicted free phosphate concentration in waters with P:Fe below 0.62 (i.e. waters with excess Fe) is very low due to the low assumed solubility of the Fe hydroxyphosphate. The model therefore predicts virtually no surface adsorption of P on Fe oxyhydroxides. However, we speculate that in reality, surface complexation likely occurs at least to some extent. An additional explanation may be that, after their formation, amorphous Fe hydroxyphosphate minerals may undergo transformations over time to form minerals with lower P:Fe ratios (Mayer and Jarrell, 2000; Voegelin et al., 2013). In summary, the Fe and P bearing colloids in the streams of the study area consist of Fe hydroxyphosphates and of Fe oxyhydroxides which likely contain surface adsorbed P.

3.2. *Release of P from Fe-rich colloids (experiment A)*

After equilibration of synthetic P–Fe colloids with a zero P sink, a variable fraction of the P is released within 7 days (Table 3). The

Table 3
The concentrations of MRP and Fe in solutions with synthetic and natural Fe-rich colloids, before and after equilibration (7 days) with a zero P sink (experiment A) and with a P-loaded resin imposing a fixed free PO_4 activity (experiment B). The synthetic solutions subjected to experiment A initially contained varying P:Fe ratios, whereas those subjected to experiment B initially did not contain any added P. The three natural streamwater samples were separated by cross-flow filtration into a permeate (reference treatment, no colloids >30 kDa) and a retentate (which contains colloids) with identical ionic composition. Error estimates are standard errors ($n = 3$).

		Before equilibration				Experiment A Equilibrated with zero sink			Experiment B Equilibrated with P-loaded resin		
		MRP $\mu g\ L^{-1}$	Fe $\mu g\ L^{-1}$	P:Fe mol:mol	P:Fe of colloids mol:mol	MRP $\mu g\ L^{-1}$	Fe $\mu g\ L^{-1}$	P:Fe of colloids mol:mol	MRP $\mu g\ L^{-1}$	Fe $\mu g\ L^{-1}$	P:Fe of colloids mol:mol
SYNTHETIC COLLOIDS											
ref (no colloids)		86	30			6 ± 1	21 ± 1				
A		101	318	0.57	nm	15 ± 1	222 ± 2	0.081			
B		104	616	0.30	nm	34 ± 1	486 ± 5	0.108			
C		89	1001	0.160	nm	51 ± 1	834 ± 7	0.100			
D		232	5213	0.079	nm	185 ± 2	4857 ± 100	0.067			
E		89	2829	0.057	nm	70 ± 1	2542 ± 31	0.046			
ref (no colloids)		8	25						117 ± 1	14 ± 2	
F		5	1172	0.008[a]	nm				132 ± 2	1040 ± 4	0.026
G		6	3413	0.003[a]	nm				157 ± 3	3203 ± 43	0.022
H		4	5196	0.001[a]	nm				192 ± 6	5174 ± 132	0.026
NATURAL COLLOIDS											
Herseltseloop	ref (no colloids)	11	202			11 ± 1	144 ± 3		186 ± 1	131 ± 2	
	with colloids	207	8293	0.045	0.044	170 ± 3	7323 ± 132	0.040	529 ± 11	7383 ± 65	0.085
Kleine Nete	ref (no colloids)	10	25			8 ± 1	9 ± 1		165 ± 1	9 ± 1	
	with colloids	77	2868	0.048	0.043	49 ± 1	2112 ± 43	0.035	265 ± 2	2288 ± 44	0.079
Mark	ref (no colloids)	4	104			5 ± 1	22 ± 5		57 ± 3	18 ± 4	
	with colloids	200	3206	0.112	0.114	132 ± 7	2335 ± 207	0.099	240 ± 3	2386 ± 235	0.139

nm: not measured; ref: reference treatment.

[a] These synthetic colloids initially did not contain any added P, the detected P is due to impurities in the NOM which was added to the test solutions.

reference treatment without Fe-rich colloids (which contained only ionic P) shows that nearly all ionic P is removed from the test solutions. The Fe in this treatment is due to impurities in the NOM which was added to the test solutions. The P release from synthetic colloids decreases with decreasing initial P:Fe ratio (Table 3). After 7 days of equilibration with a zero P sink, most of the P was released from treatments with high initial P:Fe ratio. In the three treatments with the highest initial P:Fe ratio (A—C), the molar P:Fe ratio of the colloids after equilibration is similar (around 0.1). The P:Fe ratio of treatment A is uncertain: the P concentration after equilibration of the reference solution (no colloids) is 40% of that in treatment A. In contrast, only a minor fraction of the P was released from treatments D and E (which had lower initial P:Fe ratios), and the P:Fe ratio of these colloids after equilibration was still close to the initial P:Fe ratio. In summary, the coprecipitated synthetic P—Fe colloids may release part of the P, and the fraction of reversibly bound P increases with increasing P:Fe ratios of the colloids.

In the treatments with synthetic colloids, most of the initially present Fe remained in solution after equilibration (recovery 70—93%). This recovery is encouraging, since colloids are prone to aggregation and attachment to recipient walls in many experimental set-ups (Buffle and Leppard, 1995). The concentrations of P (measured by ICP-MS) and MRP were similar in all treatments, and therefore only the MRP concentrations are reported.

The natural colloid samples isolated by cross-flow filtration (30 kDa—0.45 μm) mostly consist of Fe oxyhydroxides. Fe and organic C are the main constituents, whereas molar colloidal Al concentrations (which may indicate clay minerals or Al oxyhydroxides) are at least fourfold lower than those of Fe (Table S6). The pH of these waters is close to 7, their hardness approximately 1 mM, and their P:Fe ratio is between 0.05 and 0.13 mol P (mol Fe)$^{-1}$. The P speciation in these waters is dominated by colloidal P with only minor contributions of free orthophosphate, as evidenced by the low P concentrations in the <30 kDa size range. The contribution of organic P in these waters, as estimated by the difference between ICP and MRP measurements, was at most 25%. However, this organic P may to some extent have affected the results of the equilibration experiments, because it is e.g. unknown how it interacts with the resin.

Equilibration of these natural colloids with a zero P sink yields results in line with those obtained from synthetic samples. The P concentrations in the permeates, which did not contain any colloids and serve as reference treatments, remain low throughout the equilibration. The P concentrations in the retentates, which contain the 30 kDa—0.45 μm colloids, only marginally decrease after 7 days. The P:Fe ratios of the colloids decrease by less than 17%, implying that >83% of the colloidal P in these samples is nonlabile. Two natural colloid samples with higher P:Fe ratios had been included (data not shown), but the recovery of Fe after equilibration was unacceptably low (<30%). Therefore, the trends observed for synthetic colloids (*i.e.* colloids with high P:Fe ratio have mostly labile P) could not be verified for natural samples. Nevertheless, our combined data still support the view that Fe-rich colloids with high P:Fe ratios contain mostly labile P, whereas colloids with low P:Fe ratios contain mostly nonlabile P.

3.3. Surface adsorption of P by Fe-rich colloids (experiment B)

The synthetic and natural Fe oxyhydroxide colloids bind P through surface adsorption under the conditions of this experiment. The reference treatments show that the synthetic colloids were equilibrated at a free orthophosphate concentration of 117 μg P L^{-1}, whereas the natural colloids were equilibrated at concentrations between 57 and 186 μg P L^{-1} (Table 3). These values are of environmental relevance, since the regional environmental limit is 140 μg P L^{-1}. The presence of synthetic or natural Fe oxyhydroxide colloids cause an increased P concentration after equilibration compared to the colloid-free reference treatment. This is due to P adsorption on colloid surfaces and subsequent release of P from the resin which buffers the free orthophosphate concentration. For the synthetic colloids, the P concentration in solution increases with increasing Fe concentration (treatments F—H in Table 3), but the molar P:Fe ratio after equilibration is more or less constant. The natural colloids initially already contained some P, which was mostly nonlabile as indicated by experiment A. After equilibration, the molar P:Fe ratios of these colloids were between 0.025 and 0.041 mol P (mol Fe)$^{-1}$ larger than the initial values. This experiment shows that, under a set of environmentally relevant conditions, existing Fe oxyhydroxide colloids may bind additional P through surface adsorption.

The amount of P bound by colloids in this experiment, 0.02–0.04 mol P (mol Fe)$^{-1}$, is one order of magnitude below the average P:Fe ratio in coarse colloids measured in the field survey. Despite the limited number of samples and the limited range of environmental conditions (pH, free orthophosphate concentrations) tested here, it seems unlikely that the colloids with high P:Fe ratios are formed by adsorption of P onto the surface of existing Fe oxyhydroxide colloids. Our results therefore tentatively suggest that the Fe and P bearing colloids in the streams of the study area are mostly formed by coprecipitation of Fe and P after oxidation of Fe(II), which results in the formation of Fe hydroxyphosphate colloids. The relationship between the P:Fe ratio of colloids and that of the streamwater (Fig. 1C) is in agreement with what would be expected if such a mechanism prevails (Voegelin et al., 2010). In addition, this formation mechanism has been observed in many previous studies (Baken et al., 2015a, b; Gunnars et al., 2002; Lienemann et al., 1999; van der Grift et al., 2014). However, more work is needed to verify whether this formation also dominates in other areas with different geochemical characteristics than that studied here.

4. Conclusions and implications

Taken together, this work highlights that a large fraction of the P in streams may be associated with Fe-rich colloids. The P binding colloids consist of Fe hydroxyphosphates and of Fe oxyhydroxides with surface adsorbed P. The P binding by these colloids depends on the P:Fe ratio of the water: at low P:Fe ratios, most of the P is bound by Fe-rich colloids. Conversely, at high P:Fe ratios, most of the P is present as truly dissolved species (e.g. free orthophosphate) since the Fe-rich colloids are saturated with P.

The P-saturated colloids likely mostly contain labile P which can be released within 7 days, although this could not be verified for natural samples. In contrast, colloids with low molar P:Fe ratios contain mostly nonlabile P. Existing colloids may bind additional P by surface adsorption in the range of 0.02–0.04 mol P (mol Fe)$^{-1}$. This is much lower than the P content of the colloids isolated in this study (0.03–1 mol P (mol Fe)$^{-1}$). Therefore, surface adsorption of P onto existing colloids in surface water is likely limited, and the Fe and P bearing colloids in streams are mostly formed by coprecipitation of P during oxidation of Fe(II), resulting in Fe hydroxyphosphate containing colloids.

The eutrophication risk of colloidal P is less than that of free orthophosphate. The P in natural Fe and P bearing colloids is not immediately available to biota, and its availability on the longer term appears to be variable (Baken et al., 2014; Paerl and Downes, 1978; White and Payne, 1980). Therefore, the role of Fe-rich colloids needs to be considered when addressing the risk of P in natural waters. Environmental managers commonly monitor concentrations of "orthophosphate", which is typically assumed to equal the immediately bioavailable P concentration. However, despite the large nonlabile fraction of colloidal P, most of the colloidal P is included in these analyses. In addition, filtration procedures are typically poorly standardized. We therefore argue that environmental managers may need to pay more particular attention to the role of colloidal P by establishing a clear measure of immediately bioavailable P. One way forward may be to correct the measured P concentration for the presence of Fe, e.g. by using an empirically derived relationship between Fe and bioavailable P. Another option may be adopting more stringent and clearly defined filtration procedures in order to exclude most of the colloidal P. A pragmatic way for environmental managers to routinely measure the immediately bioavailable P may be to measure the MRP in 0.1 μm-filtered water samples. This narrow pore size excludes most of the colloidal P, whereas the MRP measurement excludes most of the organic P. However, both approaches need further experimental validation before they can be adopted for environmental monitoring purposes.

Acknowledgements

Thanks to Kristin Coorevits and Karlien Cassaert for assistance. S.B. thanks Onderzoeksfonds KU Leuven for a postdoctoral fellowship.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.04.032.

References

Amery, F., Degryse, F., Degeling, W., Smolders, E., Merckx, R., 2007. The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. Environ. Sci. Technol. 41, 2277–2281.

Baken, S., Degryse, F., Verheyen, L., Merckx, R., Smolders, E., 2011. Metal complexation properties of freshwater dissolved organic matter are explained by its aromaticity and by anthropogenic ligands. Environ. Sci. Technol. 45, 2584–2590.

Baken, S., Nawara, S., Van Moorleghem, C., Smolders, E., 2014. Iron colloids reduce the bioavailability of phosphorus to the green alga *Raphidocelis subcapitata*. Water Res. 59, 198–206.

Baken, S., Regelink, I.C., Comans, R.N., Smolders, E., Koopmans, G.F., 2016. Iron-rich colloids as carriers of phosphorus in streams: a field-flow fractionation study. Water Res. submitted.

Baken, S., Salaets, P., Desmet, N., Seuntjens, P., Vanlierde, E., Smolders, E., 2015a. Oxidation of iron causes removal of phosphorus and arsenic from streamwater in groundwater-fed lowland catchments. Environ. Sci. Technol. 49, 2886–2894.

Baken, S., Verbeeck, M., Verheyen, D., Diels, J., Smolders, E., 2015b. Phosphorus losses from agricultural land to natural waters are reduced by immobilization in iron-rich sediments of drainage ditches. Water Res. 71, 160–170.

Ball, J., Nordstrom, D., 1991. User's Manual for WATEQ4F, with Revised Thermodynamic Database and Text Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters. US Geological Survey, Menlo Park, California, USA.

Barrow, N.J., 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. 34, 733–750.

Bryan, S.E., Tipping, E., Hamilton-Taylor, J., 2002. Comparison of measured and modelled copper binding by natural organic matter in freshwaters. Comp. Biochem. Physiol. Part C Toxicol. Pharmacol. 133, 37–49.

Buffle, J., Leppard, G.G., 1995. Characterization of aquatic colloids and macromolecules. 2. Key role of physical structures on analytical results. Environ. Sci. Technol. 29, 2176–2184.

Cembella, A.D., Antia, N.J., Harrison, P.J., 1984. The utilization of inorganic and organic phosphorus compounds as nutrients by eukaryotic microalgae: a multidisciplinary perspective. Part 1. Crit. Rev. Microbiol. 10, 317–391.

Ding, X., Song, X., Boily, J.F., 2012. Identification of fluoride and phosphate binding sites at FeOOH surfaces. J. Phys. Chem. C 116, 21939–21947.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. Wiley-Interscience, New York.

Ekholm, P., 1994. Bioavailability of phosphorus in agriculturally loaded rivers in southern Finland. Hydrobiologia 287, 179–194.

Ekholm, P., Krogerus, K., 2003. Determining algal-available phosphorus of differing origin: routine phosphorus analyses versus algal assays. Hydrobiologia 492, 29–42.

Ekholm, P., Rita, H., Pitkänen, H., Rantanen, P., Pekkarinen, J., Münster, U., 2003. Algal-available phosphorus entering the Gulf of Finland as estimated by algal assays and chemical analyses. J. Environ. Qual. 38, 2322–2333.

Fox, L.E., 1989. A model for inorganic control of phosphate concentrations in river waters. Geochim. Cosmochim. Acta 53, 417–428.

Fox, L.E., 1993. The chemistry of aquatic phosphate: inorganic processes in rivers. Hydrobiologia 253, 1–16.

Freese, D., Lookman, R., Merckx, R., van Riemsdijk, W.H., 1995. New method for assessment of long-term phosphate desorption from soils. Soil Sci. Soc. Am. J. 59, 1295–1300.

Griffioen, J., 2006. Extent of immobilisation of phosphate during aeration of nutrient-rich, anoxic groundwater. J. Hydrol. 320, 359–369.

Gunnars, A., Blomqvist, S., Johansson, P., Andersson, C., 2002. Formation of Fe(III) oxyhydroxide colloids in freshwater and brackish seawater, with incorporation of phosphate and calcium. Geochim. Cosmochim. Acta 66, 745–758.

Haygarth, P.M., Warwick, M.S., House, W.A., 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. Water Res. 31, 439–448.

Henderson, R., Kabengi, N., Mantripragada, N., Cabrera, M., Hassan, S., Thompson, A., 2012. Anoxia-induced release of colloid- and nanoparticle-bound phosphorus in grassland soils. Environ. Sci. Technol. 46, 11727–11734.

Hens, M., Merckx, R., 2001. Functional characterization of colloidal phosphorus species in the soil solution of sandy soils. Environ. Sci. Technol. 35, 493–500.

Ilg, K., Dominik, P., Kaupenjohann, M., Siemens, J., 2008. Phosphorus-induced mobilization of colloids: model systems and soils. Eur. J. Soil Sci. 59, 233–246.

Jarvie, H., Withers, P., Neal, C., 2002. Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity. Hydrol. Earth Syst. Sci. 6, 113–131.

Koopmans, G.F., Chardon, W.J., Ehlert, P.A.I., Dolfing, J., Suurs, R.A.A., Oenema, O., van Riemsdijk, W.H., 2004. Phosphorus availability for plant uptake in a phosphorus-enriched noncalcareous sandy soil. J. Environ. Qual. 33, 965–975.

Kritzberg, E.S., Ekström, S.M., 2012. Increasing iron concentrations in surface waters – a factor behind brownification? Biogeosciences 9, 1465–1478.

Lienemann, C.-P., Monnerat, M., Dominik, J., Perret, D., 1999. Identification of stoichiometric iron-phosphorus colloids produced in a eutrophic lake. Aquat. Sci. 61, 133–149.

Liu, J., Yang, J., Liang, X., Zhao, Y., Cade-Menun, B.J., Hu, Y., 2014. Molecular speciation of phosphorus present in readily dispersible colloids from agricultural soils. Soil Sci. Soc. Am. J. 78, 47–53.

Lofts, S., Tipping, E., Hamilton-Taylor, J., 2008. The chemical speciation of Fe(III) in freshwaters. Aquat. Geochem 14, 337–358.

Lookman, R., Freese, D., Merckx, R., Vlassak, K., van Riemsdijk, W.H., 1995. Long-term kinetics of phosphate release from soil. Environ. Sci. Technol. 29, 1569–1575.

Luedecke, C., Hermanowicz, S.W., Jenkins, D., 1989. Precipitation of ferric phosphate in activated sludge: a chemical model and its verification. Water Sci. Technol. 21, 325–337.

Mayer, T.D., Jarrell, W.M., 1995. Assessing colloidal forms of phosphorus and iron in the Tualatin River basin. J. Environ. Qual. 24, 1117–1124.

Mayer, T.D., Jarrell, W.M., 2000. Phosphorus sorption during iron(II) oxidation in the presence of dissolved silica. Water Res. 34, 3949–3956.

Mikutta, R., Lorenz, D., Guggenberger, G., Haumaier, L., Freund, A., 2014. Properties and reactivity of Fe-organic matter associations formed by coprecipitation versus adsorption: clues from arsenate batch adsorption. Geochim. Cosmochim. Acta 144, 258–276.

Morrison, M.A., Benoit, G., 2004. Investigation of conventional membrane and tangential flow ultrafiltration artifacts and their application to the characterization of freshwater colloids. Environ. Sci. Technol. 38, 6817–6823.

Murphy, J., Riley, J., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36.

Neal, C., Jarvie, H.P., 2005. Agriculture, community, river eutrophication and the water framework directive. Hydrol. Process 19, 1895–1901.

Paerl, H.W., Downes, M.T., 1978. Biological availability of low versus high molecular weight reactive phosphorus. J. Fish. Res. Board Can. 35, 1639–1643.

Parkhurst, D., Appelo, C., 1999. User's Guide to PHREEQC (Version 2): a Computer Program for Speciation, Batch-reaction, Onedimensional Transport, and Inverse Geochemical Calculations. US Geological Survey, Denver, Colorado, USA.

Perret, D., Gaillard, J.-F., Dominik, J., Atteia, O., 2000. The diversity of natural hydrous iron oxides. Environ. Sci. Technol. 34, 3540–3546.

Regelink, I.C., Koopmans, G.F., van der Salm, C., Weng, L., van Riemsdijk, W.H., 2013. Characterization of colloidal phosphorus species in drainage waters from a clay soil using asymmetric flow field-flow fractionation. J. Environ. Qual. 42, 464–473.

Regelink, I.C., Voegelin, A., Weng, L., Koopmans, G.F., Comans, R.N.J., 2014. Characterization of colloidal Fe from soils using field-flow fractionation and Fe K-edge X-ray absorption spectroscopy. Environ. Sci. Technol. 48, 4307–4316.

Sahai, N., Lee, Y.J., Xu, H., Ciardelli, M., Gaillard, J.F., 2007. Role of Fe(II) and phosphate in arsenic uptake by coprecipitation. Geochim. Cosmochim. Acta 71, 3193–3210.

Schindler, D.W., 2012. The dilemma of controlling cultural eutrophication of lakes. Proc. Biol. Sci. 279, 4322–4333.

Senn, A.-C., Kaegi, R., Hug, S.J., Hering, J.G., Mangold, S., Voegelin, A., 2015. Composition and structure of Fe(III)-precipitates formed by Fe(II) oxidation in water at near-neutral pH: interdependent effects of phosphate, silicate and Ca. Geochim. Cosmochim. Acta 162, 220–246.

Sinaj, S., Mächler, F., Frossard, E., Faïsse, C., Oberson, A., Morel, C., 1998. Interference of colloidal particles in the determination of orthophosphate concentrations in soil water extracts. Commun. Soil Sci. Plant Anal. 29, 1091–1105.

Sjöstedt, C., Persson, I., Hesterberg, D., Kleja, D.B., Borg, H., Gustafsson, J.P., 2013. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling. Geochim. Cosmochim. Acta 105, 172–186.

Stolpe, B., Guo, L., Shiller, A.M., Hassellöv, M., 2010. Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation. Mar. Chem. 118, 119–128.

Tipping, E., Lofts, S., Sonke, J.E., 2011. Humic ion-binding model VII: a revised parameterisation of cation-binding by humic substances. Environ. Chem. 8, 225–235.

Turner, B.L., Frossard, E., Baldwin, D.S., 2005. Organic Phosphorus in the Environment. CABI Publishing, Wallingford, U.K.

Turner, B.L., Kay, M.A., Westermann, D.T., 2004. Phosphorus in surface runoff from calcareous arable soils of the semiarid Western United States. J. Environ. Qual. 33, 1464–1472.

Uusitalo, R., Turtola, E., Puustinen, M., Paasonen-Kivekäs, M., Uusi-Kämppä, J., 2003. Contribution of particulate phosphorus to runoff phosphorus bioavailability. J. Environ. Qual. 32, 2007–2016.

Uusitalo, R., Yli-Halla, M., Turtola, E., 2000. Suspended soil as a source of potentially bioavailable phosphorus in surface runoff waters from clay soils. Water Res. 34, 2477–2482.

van der Grift, B., Rozemeijer, J.C., Griffioen, J., van der Velde, Y., 2014. Iron oxidation kinetics and phosphate immobilization along the flow-path from groundwater into surface water. Hydrol. Earth Syst. Sci. Discuss. 18, 4687–4702.

Van Moorleghem, C., Six, L., Degryse, F., Smolders, E., Merckx, R., 2011. Effect of organic P forms and P present in inorganic colloids on the determination of dissolved P in environmental samples by the diffusive gradient in thin films technique, ion chromatography, and colorimetry. Anal. Chem. 83, 5317–5323.

Voegelin, A., Kaegi, R., Frommer, J., Vantelon, D., Hug, S.J., 2010. Effect of phosphate, silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied by X-ray absorption spectroscopy. Geochim. Cosmochim. Acta 74, 164–186.

Voegelin, A., Senn, A.-C., Kaegi, R., Hug, S.J., Mangold, S., 2013. Dynamic Fe-precipitate formation induced by Fe(II) oxidation in aerated phosphate-containing water. Geochim. Cosmochim. Acta 117, 216–231.

Wang, X., Li, W., Harrington, R., Liu, F., Parise, J.B., Feng, X., Sparks, D.L., 2013. Effect of ferrihydrite crystallite size on phosphate adsorption reactivity. Environ. Sci. Technol. 47, 10322–10331.

White, E., Payne, G., 1980. Distribution and biological availability of reactive high molecular weight phosphorus in natural waters in New Zealand. Can. J. Fish. Aquat. Sci. 37, 664–669.

Wolthoorn, A., Temminghoff, E.J.M., Weng, L., van Riemsdijk, W.H., 2004. Colloid formation in groundwater: effect of phosphate, manganese, silicate and dissolved organic matter on the dynamic heterogeneous oxidation of ferrous iron. Appl. Geochem 19, 611–622.