



Phosphate binding by natural iron-rich colloids in streams



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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 (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.

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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 (PO₄), 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

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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 Moorleggem 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 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 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 $\mu\text{g L}^{-1}$ for P and 1 $\mu\text{g L}^{-1}$ 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 $\text{Fe}(\text{OH})_3$. Since WHAM7.0 does not allow precipitation of other mineral phases than $\text{Fe}(\text{OH})_3$, 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 $\text{Fe}_{1.61}(\text{PO}_4)(\text{OH})_{1.83}$ (molar P:Fe ratio 0.62), or as a Fe oxyhydroxide with stoichiometry $\text{Fe}(\text{OH})_3$ (van der Grift et al., submitted). Surface complexation of Fe(II) and PO_4 to the precipitated $\text{Fe}(\text{OH})_3$ was considered using the

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