



# Iron-rich colloids as carriers of phosphorus in streams: A field-flow fractionation study



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## ABSTRACT

Colloidal phosphorus (P) may represent an important fraction of the P in natural waters, but these colloids remain poorly characterized. In this work, we demonstrate the applicability of asymmetric flow field-flow fractionation (AF4) coupled to high resolution ICP-MS for the characterization of low concentrations of P-bearing colloids. Colloids from five streams draining catchments with contrasting properties were characterized by AF4-ICP-MS and by membrane filtration. All streams contain free humic substances (2–3 nm) and Fe-bearing colloids (3–1200 nm). Two soft water streams contain primary Fe oxyhydroxide-humic nanoparticles (3–6 nm) and aggregates thereof (up to 150 nm). In contrast, three harder water streams contain larger aggregates (40–1200 nm) which consist of diverse associations between Fe oxyhydroxides, humic substances, clay minerals, and possibly ferric phosphate minerals. Despite the diversity of colloids encountered in these contrasting streams, P is in most of the samples predominantly associated with Fe-bearing colloids (mostly Fe oxyhydroxides) at molar P:Fe ratios between 0.02 and 1.5. The molar P:Fe ratio of the waters explains the partitioning of P between colloids and truly dissolved species. Waters with a high P:Fe ratio predominantly contain truly dissolved species because the Fe-rich colloids are saturated with P, whereas waters with a low P:Fe ratio mostly contain colloidal P species. Overall, AF4-ICP-MS is a suitable technique to characterize the diverse P-binding colloids in natural waters. Such colloids may increase the mobility or decrease the bioavailability of P, and they therefore need to be considered when addressing the transport and environmental effects of P in catchments.

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## 1. Introduction

The environmental impact of phosphorus (P) is mostly related to excessive emissions to natural waters, which contribute to cultural eutrophication of water bodies throughout the world (Schindler, 2012). Eutrophication may trigger summer algal blooms, which cause deep-water anoxia, odor problems, fish kills, toxin production, reduced biodiversity, and reduced recreational and amenity values of water bodies (Smith, 2003). The fate of P and its effects on aquatic ecosystems depend on its chemical speciation. In natural waters, P may occur as free ionic orthophosphate, polyphosphates,

organic P compounds, and P associated with inorganic particles (Van Moorlehem et al., 2011). Small particles, *i.e.* colloids (1–1000 nm) or nanoparticles (1–100 nm), are of interest due to their mobility and high specific surface area (Buffle and Leppard, 1995a). The colloidal P may constitute a large part of the “dissolved” (<0.45 μm) P load of streams (Filella et al., 2006; Haygarth et al., 1997) and contributes to P transport in the soil-water continuum (Jarvie et al., 2012; Turner et al., 2004; van der Salm et al., 2012). The environmental effects of colloidal P differ from those of free orthophosphate: for example, colloidal P is less available to algae, and the eutrophication risk associated with colloidal P is therefore lower than that of free orthophosphate (Baken et al., 2014). Clearly, the role of colloidal P needs to be appreciated in order to understand the transport and effects of P in natural waters.

Colloidal P in natural waters is associated with a variety of particles. Many studies highlight the presence of Fe in such

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particles, but P-bearing colloids may additionally contain various other constituents, including organic C, Al, Ca, and Si (Gunnars et al., 2002; Jones et al., 1993; Mayer and Jarrell, 1995; Shaw et al., 2000). Analysis of the speciation of Fe has shown that the Fe in these colloids can be present as Fe oxyhydroxides (Lofts et al., 2008; Sjöstedt et al., 2013), as structural Fe in clay minerals (Regelink et al., 2013a), or as ferric phosphates (Lienemann et al., 1999). The Fe-bearing colloids may bind P very effectively: molar P:Fe ratios in ferric phosphate colloids of up to 0.5 have been reported (Gunnars et al., 2002; Lienemann et al., 1999), and one study tentatively identified Ca–Fe–P colloids with a molar P:Fe ratio close to unity (Vega and Weng, 2013).

Characterization of colloids by asymmetric flow field-flow fractionation (AF4) coupled to UV-DAD and ICP-MS detection, allows for continuous size separation and online detection of element concentrations. Such studies on natural water samples have mostly emphasized the existence of two main types of colloids: humic-rich colloids (0.5–5 nm) and Fe-rich colloids (3–40 nm) which are usually assumed to consist of Fe oxyhydroxides (Andersson et al., 2006; Baalousha et al., 2006; Benedetti et al., 2003; Gottselig et al., 2014; Lyvén et al., 2003; Stolpe et al., 2013, 2010). These colloids can carry a wide range of other elements, which may be bound e.g. by surface complexation or coprecipitation. The association of P with such nanosized particles is poorly documented, likely due to the difficult detection of low P concentrations by ICP-MS. The available AF4 studies have yielded contrasting insights: one study identified clay particles as the key vectors of colloidal P in drainage waters (Regelink et al., 2013a), whereas others showed that colloidal P is associated with Fe and Al rich nanoparticles (Gottselig et al., 2014; Stolpe et al., 2010). It is unclear which processes determine colloidal P speciation in streams. Such information would enable a more accurate evaluation of the impact of P on surface water quality and of the eutrophication risk.

The first objective of this work was to demonstrate the potential of AF4-ICP-MS to characterize P-bearing colloids in natural waters. The main challenge was to quantify low P concentrations, since colloidal P in natural waters typically occurs at low concentrations in the  $\mu\text{g L}^{-1}$  range. The second objective was to elucidate how catchment geochemistry determines the nature, size, and properties of these colloids. Phosphorus containing nanoparticles (1 kDa–150 nm) in streamwater samples from five contrasting catchments were characterized using AF4 coupled to UV and high resolution ICP-MS detection. This was complemented by isolation and analysis of “coarse colloids” (100–1200 nm) by membrane filtration from the same samples.

## 2. Materials and methods

### 2.1. Sampling

Five Belgian streams draining catchments of contrasting size, geology, and hydrology were selected. The Schwarzbach and Roer streams drain the Hautes Fagnes, an upland peat area in eastern Belgium with no agricultural land use (Wastiaux et al., 2000). The Kleine Nete catchment is a lowland catchment predominantly fed by iron-rich groundwater (Baken et al., 2015). The upper part of the Meuse catchment is dominated by calcareous sedimentary rocks, whereas the Belgian part of the Meuse drains the Ardennes massif which mostly consists of slate rocks (de Mars et al., 2000). The Dijle catchment drains the undulating plateau of the Belgian loam belt, which is dominated by luvisols developed on calcareous loess (Notebaert et al., 2009). All three latter catchments have agricultural land, and surface runoff likely contributes significantly to the total discharge in the latter two. More details on the sampling locations and the catchments are available in Table S1 in the

Supplementary Material.

Sampling was done on January 14, 2014. The pH, water temperature, dissolved oxygen (DO) concentration, and electrical conductivity (EC) were measured *in situ* (Table 1). The streamwater samples were filtered in the field using membrane filters with nominal pore sizes of 1.2, 0.45, and 0.1  $\mu\text{m}$  (details in Section 2 of the Supplementary Material). The concentrations of major and trace elements (ICP-MS), Fe(II) (by colorimetry (Viollier et al., 2000)), Fe(III) (as the difference between total Fe and Fe(II)), organic and inorganic carbon (elemental analyzer), and major anions (anion chromatography) were determined in the filtrates as described in Section 2 of the Supplementary Material. The UV-absorbance at 254 nm of the filtrates was determined spectrophotometrically as an indicator of humic substances (Weishaar et al., 2003). The term ‘coarse colloids’ is used in this study to indicate the size fraction isolated by membrane filtration, *i.e.* between 100 and 1200 nm. The composition of the coarse colloids was calculated as the difference between the element concentrations in these filtrates. This size range should only be taken as an indication of the true size of these colloids, since the nominal filter pore sizes were not verified and since membrane filtration is prone to artifacts (Gimbert et al., 2005; Horowitz et al., 1996).

### 2.2. Asymmetric flow field-flow fractionation

The nanoparticles in filtered streamwater samples (0.45  $\mu\text{m}$ ; Atlas Filtri AC-BX filter cartridge) were characterized by AF4 (AF2000, Postnova Analytics) on January 29–31, 2014. The streamwater samples were stored for 2 weeks at 4 °C pending AF4 characterization; we were unable to reduce this storage time due to the extensive preparations involved in setting up and testing the coupled AF4-ICP-MS system. An in-depth discussion of the concepts and theory of AF4 can be found elsewhere (Giddings, 1984; Von der Kammer et al., 2011). The AF4 protocol was similar to that of a previous study (Regelink et al., 2013b). The polyethersulfone AF4 membrane had a nominal pore size of 1 kDa. A 3 mM  $\text{NaHCO}_3$  solution at pH 8.3 was used as carrier. The injected sample volume was 2 or 10 mL, depending on the expected concentrations of P in the nanoparticles. The elution protocol lasted for 2400 s. The cross flow rate was relatively high (3  $\text{mL min}^{-1}$ ) during the first 900 s in order to separate the smallest particles with a high resolution. The cross flow rate then decreased linearly within 120 s to 0.2  $\text{mL min}^{-1}$  and remained at that value during the final 1380 s in order to separate the large nanoparticles at a lower resolution. Size calibration showed that four proteins with hydrodynamic diameters between 3.3 and 17 nm were well separated within the first part of the elution protocol, whereas polystyrene spheres of 20, 46, and 102 nm were separated in the second part. For both parts of the elution protocol, the relationship between retention time and hydrodynamic diameter was linear. According to this size calibration, colloids with a size up to approximately 150 nm could be detected using this protocol, although this upper limit is uncertain because it is an extrapolation: calibration was performed with particles of at most 102 nm. Colloids >150 nm did not elute within the specified time and were, therefore, not detected. The elution protocol, the size calibration, and the rinsing procedure of the AF4 channel between different runs are described in Section 3 of the Supplementary Material. In this study, particles detected by AF4 (1 kDa–150 nm) are referred to as “nanoparticles”. An overview of the terminology used for different operationally defined size fractions used in this study is shown in Table S4. The actual size of natural nanoparticles may differ somewhat from the value obtained by using the above calibration, e.g. due to nonspherical particles or nonideal behavior of the particles (Baalousha and Lead, 2012). In addition, some artifacts may be introduced due to the

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