Forms of phosphorus in suspended particulate matter in agriculture-dominated lowland catchments: Iron as phosphorus carrier

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HIGHLIGHTS

- The chemical speciation of particulate P was determined by sequential chemical extraction.
- Iron-bound P is the most important total P fraction in surface water during various conditions.
- P fraction distribution in surface water does not change considerably within catchments.
- Internationally high P contents of the SPM were found.
- Fe(III) precipitates contribute considerably to the total SPM concentration.

GRAPHICAL ABSTRACT
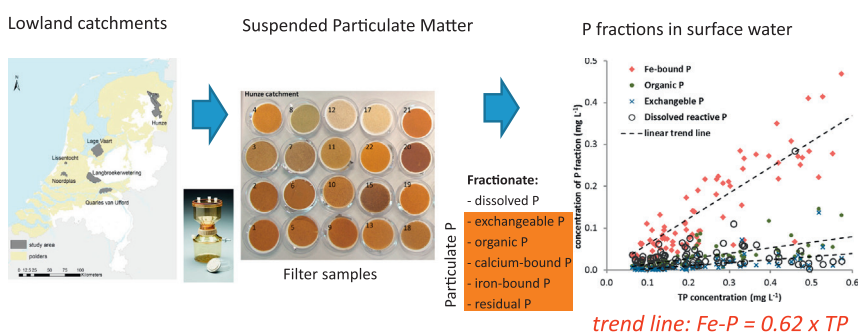
trend line: Fe-P = 0.62 x TP

ARTICLE INFO

ABSTRACT

The fate and environmental effects of phosphorus (P) in natural waters depend on its chemical forms. The particulate P (PP) concentration is dominant over the dissolved P concentration in agriculture-dominated headwaters in the Netherlands. Routine water quality monitoring programmes do not include the chemical fractionation of PP. To quantify the chemical forms of PP under various conditions in six agriculture-dominated lowland catchments in the Netherlands, a sequential chemical extraction method was applied to suspended particulate matter (SPM) samples collected by centrifugation or filtration. Centrifuge samples had lower values for the sum of the PP fractions compared with the filtration samples due to lower contents from PP fractions other than the Fe-P pool. With an average value of 8.8 mg g^{-1}, internationally high P contents of the SPM were found. Ferric iron-bound P was the most important PP fraction in SPM samples (38–95%; median 74%), followed by organic P (2–38%; median 15%). Exchangeable P ranged from 0.2 to 27%, with a median of 4.4%, Ca-P ranged from 0.1 to 11% with a median of 3.9% and detrital P was present in only a small fraction (0–6%; median 1.1%). Ferric iron-bound P was the dominant PP pool throughout the entire range of watercourses (from headwater ditches to catchment outlets) and in samples taken during winter months as well as those taken during summer months. Furthermore, the PP fraction distribution did not change markedly when flow conditions were altered from low to high discharge. The dominance of the Fe-P pool denotes the presence of Fe(III) precipitates in SPM that originate from exfiltration of anoxic Fe-bearing groundwater. These Fe(III) precipitates are a major fraction of the total SPM concentration (4 to 67% as Fe(OH)$_3$; median 18%). Although not measured directly, our results suggest

that formation of authigenic Fe(III) precipitates causes a rapid transformation of dissolved P in groundwater to PP in surface water. We advise including sequential chemical extraction of SPM monitoring programmes because the composition of particles is critical for P bioavailability, which is a key driving factor for eutrophication.

1. Introduction

Phosphorus (P) is an important driver of the primary production in surface waters and it needs to be managed to avoid or reduce eutrophication. Phosphorus occurs in numerous chemical forms that are distributed throughout the aqueous and solid media. Consequently, the fate and environmental effects of P supply (concentration and flux) in flowing water cannot be established unless the biogeochemical reactivity of P associated with different chemical compounds is understood (Pacini and Gächter, 1999). In aquatic systems, P species are found in 'dissolved', 'colloidal' and 'particulate' fractions (Robards et al., 1994; Worsfold et al., 2005). Particulate P (PP) may be bound to Fe, Mn, Al and Ca, either sorbed onto the surfaces of particles or precipitated as a mineral. Organic P compounds are also associated with PP. Hence, PP is present in a range of compounds with highly diverse stabilities, bondings and exchangeabilities (Poulenard et al., 2008), which influences its bioavailability, i.e. the overall ability of PP to release phosphate in response to an uptake demand by plants or algae (Worsfold et al., 2005).

The composition of PP plays thus a critical role in eutrophication (Poulenard et al., 2008). However, routine surface water quality monitoring programmes worldwide, including in the Netherlands, only analyse dissolved reactive phosphorus (DRP) and total phosphorus (TP) (CIW, 2001; Jarvie et al., 2002). Separation of 'dissolved' and 'particulate' P phases is based mainly on filtration using 0.45 μm or 0.7 μm membrane filters. The PP concentration is calculated from the difference between total phosphorus (TP) and dissolved reactive phosphorus (DRP) (Jarvie et al., 2002). Not measuring the chemical forms of PP in water quality monitoring programmes may be a serious source of uncertainty in addressing eutrophication problems.

Environmental measures to reduce P point sources have contributed to a decrease of dissolved P concentrations in major rivers and coastal seas (Burson et al., 2016; EEA, 2015; Grizzetti et al., 2012). As a result, the relative contribution from agricultural sources has risen in recent years in northwest Europe, and commercial fertilisers and animal manure are typically the primary sources of nutrient enrichment in freshwater systems (EEA, 2015). The general assumption worldwide is that soil erosion is a large contributor of PP transfer because a large share of phosphorus in agricultural catchments consists of PP (e.g. Van der Salm et al., 2012; Withers et al., 2009). However, in lowland areas like the Netherlands P loads commonly leach to surface water via subsurface flow, i.e. through interflow, tube drain discharge or, in well-drained lowlands with shallow groundwater tables, through groundwater (Schoumans and Groenendijk, 2000). These P loads have a more dissolved or colloidal nature (King et al., 2015; Regelink et al., 2013) but, as will be explained below, they are expected to be converted to PP during discharge to the surface water system or immediately thereafter.

A typical characteristic of the water bodies that drain agricultural areas in the Netherlands is that they are fed by groundwater from a subsurface with high contents of organic matter and reactive minerals like sulphides and carbonates (Griffioen et al., 2016). Sediments with such reactive properties typically results in anoxic, Fe-bearing, calcite-saturated groundwater with CO_2 partial pressures that are generally high, with high-end values above $10^{-1.5}$ atm partial pressure (Griffioen et al., 2013). Influxes of poorly oxygenated, CO_2-rich groundwater containing high concentrations of dissolved Fe(II) and Ca provide a continuous supply of Fe(II) and Ca to the surface water. During oxygenation and degassing of this exfiltrated groundwater, solid Fe(III)

and Ca phases will precipitate (Griffioen, 2006; Van der Grift et al., 2016a). As a result, fine solid aggregates are formed at the sediment/water interface or in the water column (Baken et al., 2013; Van der Grift et al., 2014). Dissolved P present during the oxidation process is removed from the water column into Fe(III) or Ca phases (Senn et al., 2015; Van der Grift et al., 2016a; Voegelin et al., 2013). Therefore, we hypothesise that the chemical forms of P in surface water in lowland catchments is critically dependent on such biogeochemical processes occurring at the groundwater/surface water interface. Recently, the P behaviour in water systems where ferric iron precipitates may be formed in the surface water as a result of aeration and degassing of exfiltrated groundwater has been subject of study (Baken et al., 2016; Baken et al., 2015a; Baken et al., 2015b; River and Richardson, 2018; Van der Grift et al., 2016a; Van der Grift et al., 2014). However, we still lack knowledge about the chemical fractionation of PP in lowland catchments that drain anoxic Fe-bearing groundwater.

Despite recent developments in the application of advanced spectroscopic techniques such as X-ray Absorption Near Edge Structure spectroscopy (XANES) and Nuclear Magnetic Resonance (NMR) spectroscopy (Liu et al., 2013), the generally accepted and widely used method to determine the chemical forms of P in sediments is sequential chemical extraction (Li et al., 2015). This P fractionation by means of sequential chemical extraction is an analytical method to split the overall P content of a solid phase sample into groups of compounds with similar chemical release patterns (e.g. Ruttenberg, 1992). It can be used to evaluate the various PP fractions, including labile fractions (loosely bonded or easily exchangeable) and the fractions associated with Al, Fe and Mn oxides and hydroxides, Ca, organic material and residual matter (Pardo et al., 2003). Sequential chemical extraction is widely applied to marine sediments (e.g. Dijkstra et al., 2014; Ruttenberg, 1992; Slomp et al., 1996) and lacustrine sediments (e.g. Golterman, 1996; Gu et al., 2016; Hieltjes and Lijklema, 1980) and a relative small number of studies have used sequential chemical extraction to identify chemical forms of PP in suspended particulate matter (SPM) from estuaries and rivers (Berner and Rao, 1994; Jordan et al., 2008; Subramanian, 2000; Van Eck, 1982). These studies have in common that they characterise riverine P loads into coastal seas. Studies that use sequential chemical extraction on SPM in small surface water in catchments are rare. To our knowledge, those by Pacini and Gächter (1999) and Poulenard et al. (2008) are the only ones that used this method to determine different inorganic PP fractions in SPM from freshwater catchments. The streams in these studies were located on the northern rims of the Alps in Switzerland and France – a very different geographical setting compared with lowland catchments.

Observations on SPM and associated substances are critically dependent on sampling and processing procedures (Duinker et al., 1979). Samples for chemical analysis of SPM are usually obtained by continuous-flow centrifugation (e.g. Horowitz, 2008; Van Eck, 1982). Large water samples are dewatered by centrifugation, either on site or by returning large bulk samples to the laboratory for processing (Walling, 2013). In the Netherlands, continuous-flow centrifugation is used to sample SPM for routine chemical analysis (CIW, 2001). The disadvantage of centrifugation is, however, that it requires a large volume of water and is time consuming. Additionally, the recovery efficiency of centrifugation samples is generally lower than that of filtration samples, largely because the finer and less dense particles may not be included in particulate matter obtained by centrifugation (Duinker et al., 1979). Time-integrated SPM samplers like the one designed by Phillips et al.