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

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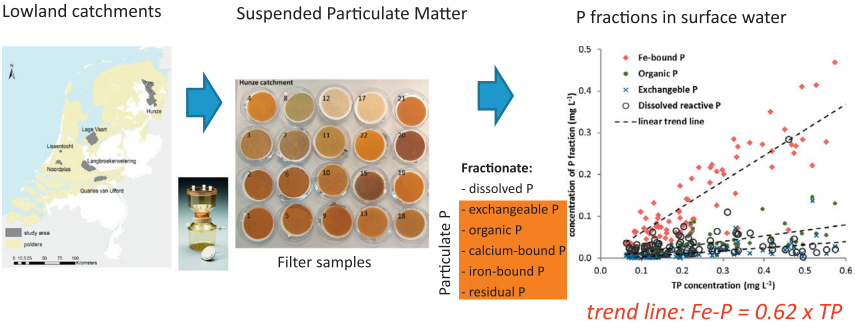
HIGHLIGHTS

- 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



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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

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Abbreviations: TP, Total Phosphorus; DRP, Dissolved Reactive Phosphorus; PP, Particulate Phosphorus; SPM, Suspended Particulate Matter; Fe-P, Ferric Iron-bound Phosphorus; exch-P, Exchangeable Phosphorus; Ca-P, Calcium-bound Phosphorus; res-P, residual P; org-P, Organic Phosphorus.

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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.

(2000) are relatively easy to handle but also have the drawback that the fine fraction does not settle out in the sampler. The routine method for determination of the SPM concentration in surface water itself is filtration (ISO, 2005). It is an easy method, requiring a small amount of water, but has limitations for chemical analyses of SMP. For example, only a small amount of SPM can be sampled and particles cannot be separated from the filters after filtration. Consequently, the filter itself has to be included in the chemical analysis. As these aspects may adversely affect the reliability of the chemical analysis of SPM, experiments on the effects of filtration and centrifugation on substances associated with SPM should be carried out on identical natural samples.

The PP fractionation in the water phase may be influenced by alternative sources of PP (e.g., erosion of soils, remobilisation of bed sediments, authigenic production) and in-stream transformation processes (e.g., biological uptake/release). We therefore hypothesise that the PP fractionation will be dynamic in space and time: firstly, a spatial difference in PP fractionation in lowland catchments from headwater ditches to catchment outlets; secondly, a seasonal difference between winter and summer in response to biological growth and decay; and thirdly, a rapid temporal change following variation in flow velocities. We expect that insight into the PP fractionation of SPM would help improve understanding of the properties of PP and thereby contribute to the improvement of water quality management in catchments.

The objective of this study was to characterise the chemical forms of PP as present in small surface waters in the geographical setting of agriculture-dominated lowland catchments in the Netherlands. The four specific objectives of this study were: (1) to determine if the widely recognised sequential chemical extraction procedure applied on SPM sampled with filters for the determination of the chemical forms of PP in small surface waters; (2) to determine the P content of SPM and the chemical forms of PP in different types of lowland catchments and explore if a spatial variation exists within catchments from headwater ditches to catchment outlets; (3) to assess whether a temporal variation exists in PP fractionation from winter to summer and (4) to explore whether a temporal variation exists in PP fractionation and TP concentrations during changes in flow velocities that are typical for a lowland water system.

2. Materials and methods

2.1. Study areas

To analyse the spatial and temporal variation in chemical forms of PP in surface water of agriculture-dominated lowland catchments in the Netherlands, samples were collected during field surveys in six areas: the Noordplas polder, the Lissertocht polder, the Quarles van Ufford polder, the Langbroekerwetering polder, the Lage Vaart polder and the Hunze catchment (Fig. 1). These areas differ with respect to type of lowland catchment (free drainage or polder catchment), sampling procedure and period, and flow velocities (Table 1). All study catchments are located in areas with anoxic Fe-bearing groundwater (Griffioen et al., 2013) and are dominated by agricultural land use. Catchments size ranged from 10 to 300 (km^2) (Table 1). Maps of the study areas with the sampling locations and a short description of the sampling locations, including the order of the watercourse are given in Fig. S1 and Table S1. The Hunze catchment is a free drainage catchment that consists of sandy soils, with peat in the riparian zones whereas the other areas are in polders (embanked catchments where water levels are managed by discharge via pumping stations and via the inlet of diverted river water during dry periods) that consists of fluvial or marine clay soils. Such polder catchments are found in many delta areas worldwide and are important urban and agricultural areas.

The objective of the PP fractionation analysis was different for the six areas: a spatial characterisation for the Hunze catchment and Lissentocht polder; a combined spatial and temporal characterisation for Quarles van Ufford and Langbroekerwetering; a temporal (seasonal) characterisation for the Lage Vaart and a temporal (flow induced) characterisation for the Noordplas polder. For the Lage Vaart samples were taken every two to four weeks from at the outlet pumping station from January to August 2015.

The sampling in Noordplas polder had a different focus than the other studies: at three locations, it focused specifically on the effect of changes in flow conditions on the SPM and TP concentrations and the distribution of the different PP fractions of the SPM. Therefore, time differentiated sampling was performed at three locations in during flow events: (1) in the main channel 375 m upstream from the pumping station (PLS), (2) in a secondary channel in a long (5 km) open flow connection with the pumping station (SLT) and (3) in a secondary channel, 25 m upstream from a weir that separates its polder from the influence of the pumping station (STW). The water level in this polder is 20 cm higher than that in the polder. Samples were taken during flow events created by the pumping station (PLS and SLT) or by removing a 20-cm high plank from the weir (STW).

Regional water authorities provided time series of DRP and TP concentrations from their routine monitoring programmes for the main watercourse of the study area at or near the outlet of the catchment. Samples were collected every 2 or 4 weeks from 2005 to 2014 and analysed by standard colorimetric methods (APHA-AWWA-WPCF, 1989).

2.2. Sampling and measurement techniques

2.2.1. General sample treatment and field measurements

The surface water samples were collected with peristaltic pumps from a depth of approximately 10 to 20 cm. Sub-samples were filtered in the field (0.45 μm cellulose nitrate filter). A sub-sample was collected in a 60 mL HDPE vial and acidified to a pH of 1, using suprapur nitric acid. This sample was analysed for metals by ICP-OES. Another sub-sample was collected in a 100 mL PE vial, analysed for Cl, NO_3 and SO_4 by ion chromatography and analysed for DRP by using the colorimetric molybdate blue method (Koroleff, 1983). The TP concentration was measured in an unfiltered sub-sample that was digested before analysis by using persulfate and sulphuric acid (Koroleff, 1983). Another set of sub-samples was collected for analysis of the SPM concentration and for sequential chemical extraction either by filtration (2 L glass bottles) or centrifugation (15–25 L plastic tanks), as explained in the following sections.

The flow velocities during the field experiments in the Noordplas polder were measured using electromagnetic flow velocity meters. The device used at locations PLS and STW is an automated continuous measurement system, which was set to log at a 5-second interval. The flow velocities were measured throughout the field experiments. The device used at location SLT had no data logging capabilities. Flow velocities were only measured at the sampling times.

The particle size distribution and volume concentration of the SPM in the surface water at location PLS in the Noordplas polder was measured in-situ at 10-minute intervals using a LISST-100 Particle Size Analyzer (Gartner et al., 2001) (Supplement 4).

2.2.2. Suspended particulate matter sampling

All samples for SPM extraction were transferred to a refrigerator (4 °C) within 6 h of collection and processed within 48 h. For extraction by centrifugation we used a single-speed continuous-flow centrifuge (20.000 RPM) in which the water sample is introduced from above through a funnel and directed to the centre of the column at a flow rate of 0.65 L min^{-1} using a peristaltic pump. Centrifugal forces then push the water out from the centre against the walls of the column. The column walls are covered with removable Teflon™ collection sheets which capture the particles on impact. The SPM samples obtained from the Teflon™ sheets were immediately transferred to a

Fig. 1. Location of the study areas.

freezer and freeze-dried at the earliest opportunity, mostly within 3 days. Sample weights and water volumes were tracked throughout the entire procedure.

Filtration of the water samples from the 2 L glass bottles was performed in the laboratory, using pre-dried, pre-weighed glass fibre filters that retain fine particles down to 0.7 μm (Whatman GF/F) and vacuum pumps. The filters with SPM were dried at 50 °C and reweighed, to measure the SPM concentration. The average and standard deviation of the SPM concentration at each location were calculated from three to six filters. The filters plus SPM were stored

Table 1
Suspended particulate matter characteristics of the six study areas.

Study area	Type of area	Size (km^2)	Surface elevation (m vs MSL[a])	Soil type	Objective of PP speciation analysis	No. of sampling locations	Period of sampling	No. of samples	Type of SPM sampling
Hunze catchment (Hun)	Free drainage catchment	300	1–8	Sand	Spatial	22	March 2013	22	Filtration
Lissentocht polder (LT)	Polder	10	−6–−3.5	Marine clay	Spatial	9	April 2013	9	Filtration
Quarles van Ufford polder (QvU)	Polder	120	3–7	Fluvial clay	Spatial and temporal	8	February–June 2016	19	Filtration
Langbroekerwetering polder (LB)	Polder	180	0.5–10	Fluvial clay	Spatial and temporal	6	February–April 2016	10	Filtration
Lage Vaart (LV)	Polder	243	−5–−3	Marine clay	Temporal	1	January–August 2015	9	Filtration
Noordplas polder (NPP)	Polder	45	−5–−4	Marine clay	Flow-induced and spatial	3	February–March 2014	19	Centrifugation and filtration

[a] Mean sea level.

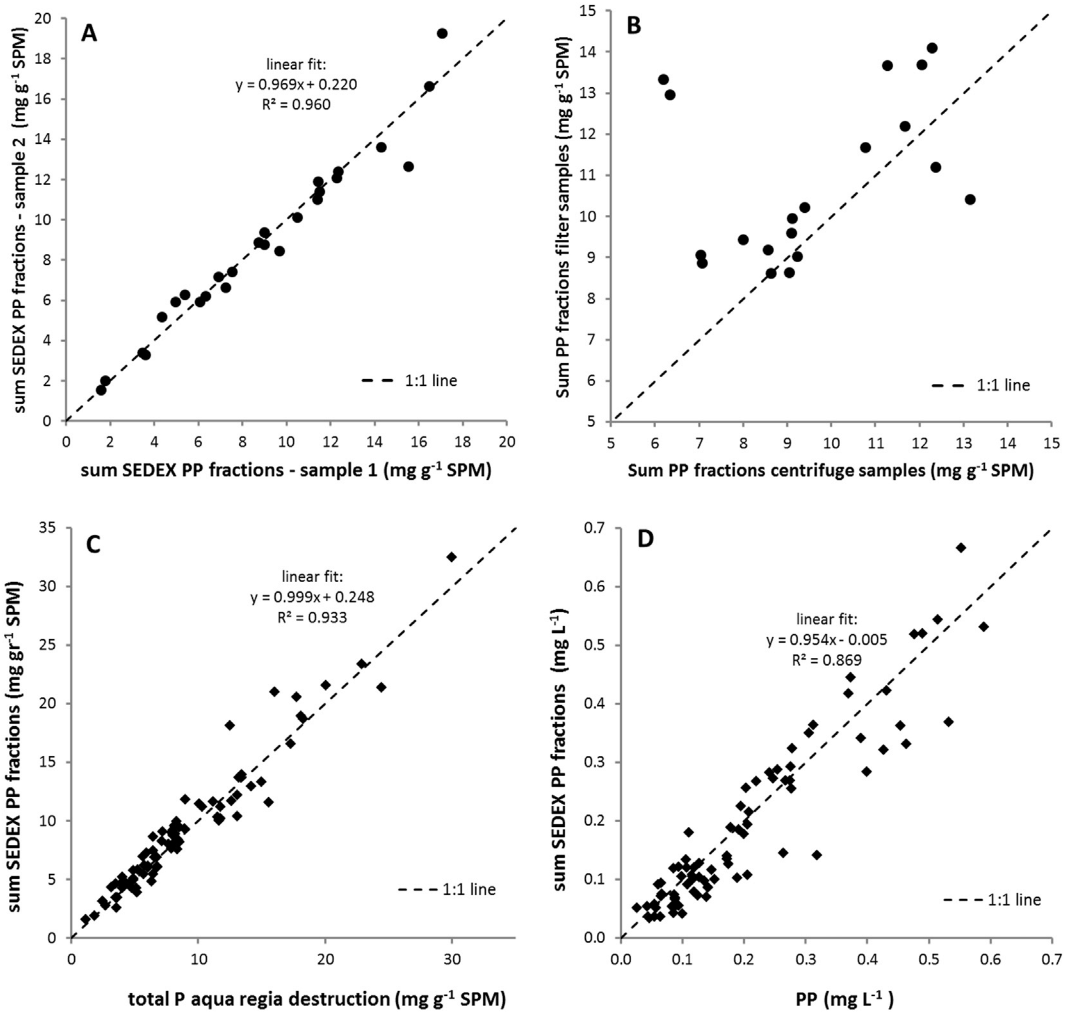

Fig. 2. Validity of sequential chemical extractions: (A) sum of the SEDEX PP fractions of duplicate samples, (B) sum of the SEDEX PP fractions from the centrifuge samples plotted against those of the filter samples, data from the Noordplas polder, (C) total P content of SPM samples from aqua regia destruction plotted against the sum of the SEDEX PP fractions and (D) particulate P concentration calculated as difference between TP and DRP concentrations versus sum of the SEDEX PP fractions converted to the aqueous concentrations (by multiplying the sum SEDEX PP fractions by the measured SPM concentration).

dry prior to sequential chemical extraction. A picture of the filters with SPM is shown in Figs. S2–S4.

2.2.3. Sequential phosphorus extraction

Phosphorus fractionation of the SPM was determined by using the SEDEX method as proposed by Ruttenberg (1992) and modified by Slomp and Epping (1996), but including the exchangeable P step. The dried filters were folded into 15 mL Greiner tubes, placed approximately in the middle of the tube and then submerged by adding the extraction solution. To determine the possibility of P leaching from the GF/F filters, the SEDEX method was applied to a series of four blank filters (only filtered with 500 mL UHQ). The extraction started with loosely bound, exchangeable P (exch-P) (1 M $MgCl_2$, pH = 8.0, 0.5 h, 20 °C). The filter was subsequently treated with citrate dithionite bicarbonate buffer (1 M CDB, pH = 7.5, 8 h, 20 °C) to extract P associated with iron oxyhydroxides (Fe-P), followed by a second and third rinse with 1 M $MgCl_2$ solution (0.5 h, 20 °C). The filters were then treated with a sodium acetate buffer (1 M, pH = 4, 6 h, 20 °C) and another $MgCl_2$ rinse (0.5 h, 20 °C) to extract calcium-bound P, i.e. authigenic carbonate fluorapatite + biogenic apatite + $CaCO_3$-associated P (Ruttenberg, 1992). The remaining inorganic P was subsequently extracted with 1 M HCl (24 h, 20 °C). This fraction was referred to as detrital apatite P of igneous or metamorphic origin in Ruttenberg (1992). Because detrital is also used to refer to organic remains of algae and plants, we prefer to call this fraction residual inorganic P (res-P). For determination of organic P, the sample was dried for 48 h at 50 °C. Next, the sample was ashed (2 h, 550 °C) and the filter was subjected to another HCl rinse (24 h, 20 °C).

In all solutions except for the CDB extracts and the first $MgCl_2$ rinse after the CDB step, P concentrations were determined using colorimetric analysis. A standard series was created from a stock solution. For the standard series and the samples, the stock solution was diluted in a combination of UHQ and the matrix of the extract for which the standard series was created. The amount of matrix equalled the volume of sample used. In this way, matrix effects that may obscure the signal were prevented. Phosphorus concentrations in the CDB extracts and the first $MgCl_2$ rinse after the CDB step were measured with ICP-OES, in order to prevent the citrate from interfering with the reduction of the molybdate complex.

A separate series of filter samples was treated with aqua regia for determining the total P and total Fe content of the SM. For this destruction, a filter was put in a Teflon™ vessel and concentrated HCl and concentrated HNO_3 were added in the ratio 3:1. The closed vessel was left overnight on a hot plate at 90 °C and then condensed at 160 °C. The extract was diluted with a 5% HNO_3 solution prior to analysis with ICP-OES.

Table 2
Average content and standard deviation of particulate P fractions in the SPM collected by filtration and centrifugation of identical samples from the Noordplas polder (in mg P g^{-1} SPM), N = number of samples.

	N	exch-P	Fe-P	Ca-P	res-P	Org-P	Sum of all fractions
Filter samples	19	0.51 ± 0.35	8.14 ± 1.42	0.35 ± 0.20	0.14 ± 0.03	1.47 ± 0.65	10.6 ± 1.93
Centrifuge samples	19	0.16 ± 0.05	8.22 ± 1.75	0.18 ± 0.09	0.07 ± 0.03	0.91 ± 0.46	9.54 ± 2.09

3. Results

3.1. Validity of sequential chemical extractions on filter samples

The PP fractionation of SPM samples determined by the SEDEX method was performed on 96 filter samples, 19 centrifuge samples and four blank filters as a control. The analysis was performed in duplicate For 26 of the 96 filter samples (Fig. 2A). The average difference between both samples for these 26 duplicates was 0.1 ± 4.5%.

Except for the org-P step, the P extraction of the blank filters was below the detection limit and did not differ from that of the blanks without filters. Between 0.9 and 1.8 μg P was extracted from the glass fibre filters in the org-P step. This was approximately one order of magnitude lower than the median value of P extracted during the org-P step in the 96 SPM samples (16 μg P). The org-P content of the SPM samples was corrected for the recovery of the blank filters.

The sum of the PP fractions from the centrifuge samples was on average 10% lower than the sum of the PP fractions from the filter samples (Fig. 2B, Table 2). Analysis of variance (ANOVA) revealed a statistically significant difference between the centrifuge and filter samples ($F = 2.66$, $p = 0.11$). With the exception of the Fe-P fraction, in all fractions the P contents for the centrifuge samples were lower than those for the filter samples (Table 2). The average Fe-P pool was almost identical. A statistically significant difference was found between the filter and centrifuge samples for all PP fractions except for Fe-P. This indicates that the difference in the sum of the PP fraction comes from fractions other than the Fe-P pool.

We evaluated the performance of the SEDEX method applied to filter samples by comparing the sum of the PP fractions of the SEDEX with the total P content measured after the aqua regia destruction (Fig. 2C). When plotted against each other, the samples followed the 1:1 line almost perfectly. Linear fitting revealed a slope of 0.998 and an R^2 of 0.93. The average residual content ($\sum$SEDEX PP fractions – PP aqua regia) was −0.38 mg g^{-1} SM, which resulted in an average error of 4% (for individual samples the residual concentration ranged up to a maximum of 5.8 mg g^{-1} SPM, resulting in an error up to 28%). In addition, we found a reasonably good match between the 'routinely' calculated PP concentrations in the water phase (TP – DRP concentration) and the sum of the SEDEX PP fractions converted to aqueous concentrations (Fig. 2D). Although there was more variation around the 1:1 line in comparison with the total P content from the aqua regia destruction, linear regression modelling revealed a slope of 0.954 and an R^2 of 0.87.

Given that the precision of spectrophotometrically quantified dissolved P concentration is generally 2–3% (Monaghan and Ruttenberg, 1999) and that the precision of SPM concentration measurements is about 9%, the results showed that the SEDEX method performed on filter samples is an appropriate method for reliable determination of the PP fractionation in SPM. The results obtained by this method are used for the next sections of this paper.

3.2. General characteristics of P and SPM in six areas

Total P concentrations in the individual samples from the six areas ranged between 0.06 and 0.61 mg L^{-1} except for two locations in the Lissertocht polder (LT4 and LT8), which had TP concentrations of 2.98 and 1.49 mg L^{-1} and DRP concentrations of 2.47 mg L^{-1} and 0.3 mg L^{-1} (Table S2). The ditch water at these locations is strongly influenced by boils, where deep nutrient-rich groundwater discharges directly into the ditch through preferential flow paths (Delsman et al., 2013). Groundwater sampled from a groundwater piezometer located 2 km outside the Lissertocht polder and part of the national groundwater quality monitoring network (no. 2211) has a P concentration of 3 mg L^{-1} and a Fe concentration around 20 mg L^{-1}. No concentrations of this magnitude were found at other locations in the Lissertocht polder, indicating a quick turnover from DRP to PP during aeration of exfiltrated groundwater.

The lowest average TP concentrations were found in the Hunze catchment, Quarles van Ufford and Langbroekerwetering, followed by the Lage Vaart, Lissertocht polder and Noordplas polder (Table 3). The latter three are all marine clay polders (Table 1). On average, the DRP concentration was 17% of the TP concentration, which implies strong dominance of PP (Table 3 and Fig. S1 for PP/TP ratios at individual locations). The dominance of PP is also clearly apparent in the monthly average values of DRP and TP at the outlets of the areas (Fig. 3). DRP concentrations were always low during winter. Substantial DRP concentrations were measured in only a limited number of samples from the Lissertocht polder, Langbroekerwetering and the Lage Vaart sampled during the summer and early autumn months.

Table 3
Characteristics of P fractionation in the six areas: total P, dissolved reactive P and SPM concentrations (in mg L^{-1}) and P content of the SPM calculated as sum of the SEDEX PP fractions (in mg g^{-1}). The number of samples and monitoring period are given in Table 1.

	Hunze	Lissertocht	Quarles van Ufford	Langbroeker-wetering	Lage Vaart	Noordplas
TP - average	0.14	0.78	0.17	0.18	0.23	0.39
TP - min	0.07	0.06	0.11	0.11	0.08	0.21
TP - max	0.49	2.98	0.27	0.28	0.46	0.61
DRP - average	0.03	0.33	0.02	0.03	0.07	0.03
DRP - min	0.01	0.01	0.01	0.01	0.01	0.01
DRP - max	0.08	2.47	0.04	0.06	0.28	0.06
SPM - average	15	71	34	11	22	34
SPM - min	3	8.3	4	2	13	19
SPM - max	71	222	76	33	37	60
P content SPM -average	7.2	9.2	8.9	14.2	6.1	10.6
P content SPM - min	2.6	4.2	1.6	3.4	3.4	8.2
P content SPM - max	21.4	28.5	23.4	32.5	9.2	14.1

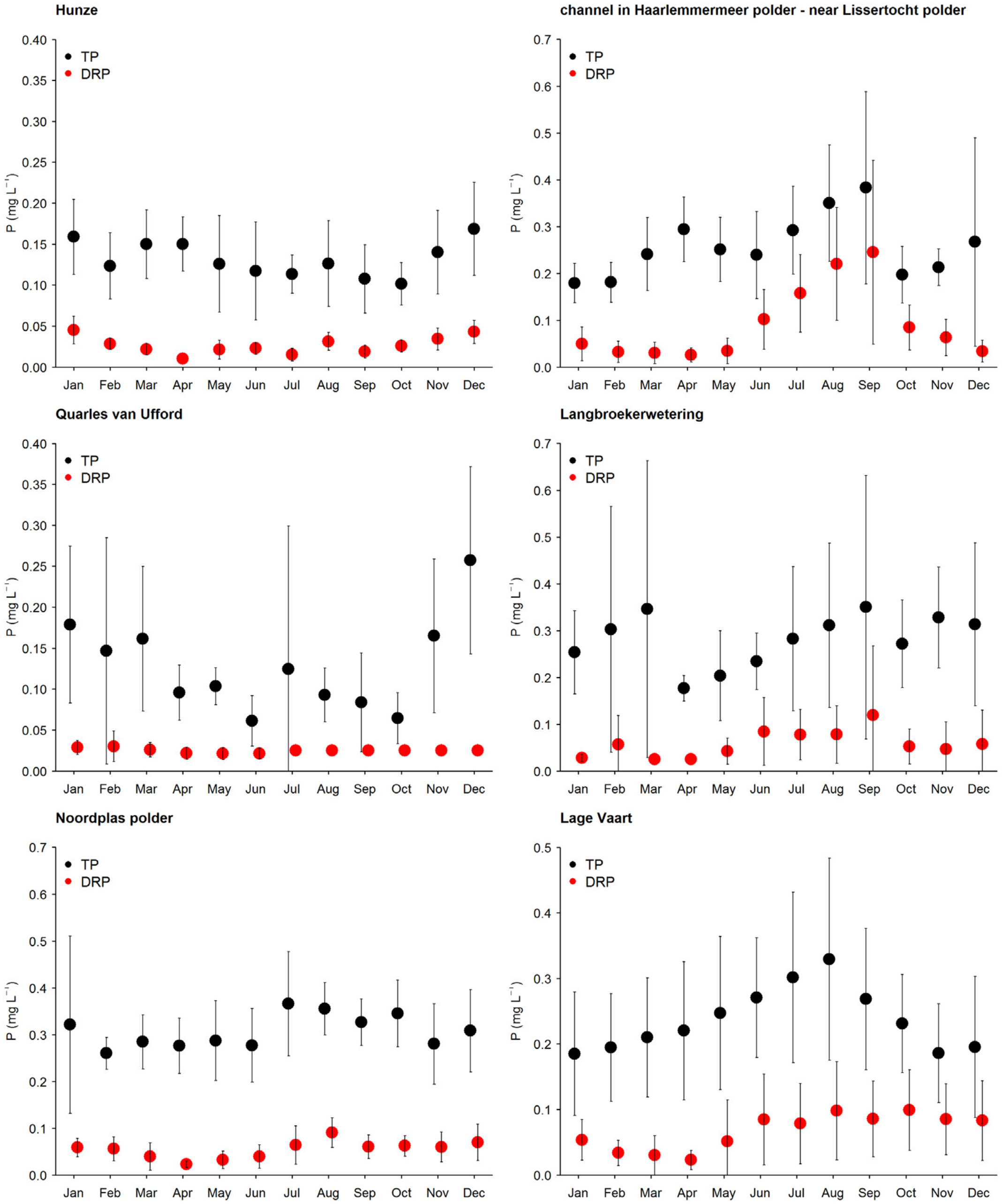

Fig. 3. Monthly average dissolved reactive phosphorus (DRP) and total phosphorus (TP) concentrations for the main watercourse in each of the six study areas at or near the catchment outlet, calculated from time series of concentrations measured from 2005 to 2014. The difference between the TP and DRP concentrations is particulate P (PP). Data from the regional water authorities: Hunze en Aa's, Rivierenland, de Stichtse Rijnlanden, Zuiderzeeland and Rijnland. The monitoring location in the Haarlemmermeer polder is located 1 km outside the Lissertocht polder.

During the sampling campaign, the TP concentration in the samples from the Lage Vaart channel in the Flevo polder increased from 0.09 mg L^{-1} in January to 0.46 mg L^{-1} in August (Table S2). This increase can partly be attributed to the relatively high DRP concentrations in the samples from June (0.11 mg L^{-1}) and early August (0.28 mg L^{-1}). This observation is supported by the increase of monthly averaged DRP concentrations during the summer months (Fig. 3).

SPM concentrations ranged from 2 to 76 mg L^{-1}, except for the boil location LT4 in the Lissertocht area, which had an exceptionally high SPM concentration of 222 mg L^{-1}. The P content of the SPM samples (as sum of the SEDEX PP fractions) ranged between 1.6 and 32.5 mg g^{-1}. The SPM from the Langbroekerwetering had the highest P content and the Lage Vaart the lowest.

3.3. Spatial variation in PP fractionation

In all SPM samples the most important PP fraction was Fe-P (Tables S2 and S3). The Fe-P content of the SPM ranged from 0.6 to 27.1 mg g^{-1} (Fig. 4). As percentage of total PP, the Fe-P fraction ranged from 38 to 95%. The contents of the other PP fractions were much lower and showed less variation as well. Organic P was the second largest PP pool, with values ranging from 0.4 to 4.7 mg g^{-1} (2–38% as percentage of total PP). SPM with the highest org-P content was sampled at location H12, a channel in the Hunze catchment that received effluent discharge from a waste water treatment plant (WWTP) (Table S1). The exch-P content ranged from 0.01 to 2.0 mg g^{-1} (0.2–27% as percentage of total PP). Calcium-bound P ranged from 0.01 to 1.39 mg g^{-1} (0.1–11%

as percentage of total PP). Residual inorganic P was present only as a minor fraction (0–6% as percentage of total PP).

3.3.1. Differences between areas

The Fe-P content differed appreciably between the areas: median values range from 2.7 mg g^{-1} for the Lage Vaart to 9.2 mg g^{-1} for the Langbroekerwetering (Fig. 4). SPM from the Lage Vaart had the lowest Fe-P content (range 1.8–4.5 mg g^{-1}). SPM samples with a Fe-P content above 10 mg g^{-1} were collected from the Hunze catchment, and the Quarles van Ufford, Langbroekerwetering and Noordplas polders. The exch-P fraction was abundant in four study areas: Quarles van Ufford, Langbroekerwetering, Noordplas polder and the Lage Vaart. The Hunze catchment contained only a marginal exch-P fraction. The org-P fraction did not vary greatly between the areas: median values ranged from 0.95 mg g^{-1} for the Lissertocht polder to 1.7 mg g^{-1} for the Langbroekerwetering and Lage Vaart.

3.3.2. Differences within areas

The Hunze catchment and the Lissertocht polder had the highest spatial sampling densities. For these areas, we determined whether there was a difference in PP fractionation between drainage ditches, secondary channels and the main watercourse (Fig. 5). There was no structural difference in PP speciation between the different orders of watercourses in either the Hunze catchment or the Lissertocht polder: Fe-P was already the dominant PP fraction in the drainage ditches and this remained in the secondary channels and the main channel. A large variation in the Fe-P fraction was observed in the drainage ditches of Lissertocht polder (3.0–27 mg g^{-1}), with the highest Fe-P contents being for samples LT4 and LT8, i.e. the boil locations. It should be noted that the samples were not in equilibrium with atmospheric conditions at the time of sampling (which can be seen from by the high DRP concentrations) and also that they were not kept under anaerobic conditions between sampling and processing in the lab. Hence, oxidation of the recently exfiltrated groundwater continued after sampling and some of the SPM in samples LT4 and LT8 must have formed after sampling, due to aeration and degassing of the water (Griffioen, 2006). The high SPM concentration of sample LT4 (222 mg L^{-1}) cannot solely be explained by the formation of P-rich Fe hydroxides and indicates the incorporation of other solutes such as calcium, natural organic matter in the precipitate. In addition, these two samples contained the smallest org-P fraction (0.47 and 0.45 mg g^{-1}) and exch-P fraction (0.60 and 0.48 mg g^{-1}). Exchangeable P and org-P were, however, more significant PP pools in the other samples from the Lissertocht polder, with values between 0.72 and 1.3 mg g^{-1} for org-P and between 0.59 and 1.6 mg g^{-1} for exch-P.

Results from the other three study areas with sampling locations from smaller headwaters to polder outlets matched the results from the Hunze catchment and the Lissertocht polder. Although the total PP content of the SPM from Quarles van Ufford and Langbroekerwetering ranged between 1.5 and 32 mg g^{-1} there is strong dominance of Fe-P (Fig. S5). Hence, there is only a modest difference in the chemical forms of PP between sampling locations within catchments.

3.4. Temporal variation in PP fractionation

The P content of the SPM samples from the Lage Vaart (as sum of the SEDEX PP fractions) increased gradually, from 3.4 mg g^{-1} in January to approximately 7.5 mg g^{-1} in August, except for the sample from April, which had a P content of 9.2 mg g^{-1} (Fig. 6). Throughout the measuring period, Fe-P varied from 1.8 to 4.5 mg g^{-1}, with the lowest value on 20 February and the highest value on 8 April. Organic P, as being the second largest PP pool ranged between 0.68 and 2.4 mg g^{-1}. The sample from 8 April had the highest org-P content and the sample from 15 January the lowest. The exch-P fraction increased from 0.13 to 2.0 mg g^{-1} during January–August. The Ca–P fraction varied between 0.20 and 0.48 mg g^{-1}, with its highest value on 8 April.

The two other study areas with multiple sampling moments (Quarles van Ufford and Langbroekerwetering) showed no structural trend in the Fe-P fraction during the period from February to June (Fig. S5). The org-P content at all sampling locations in Langbroekerwetering and at three

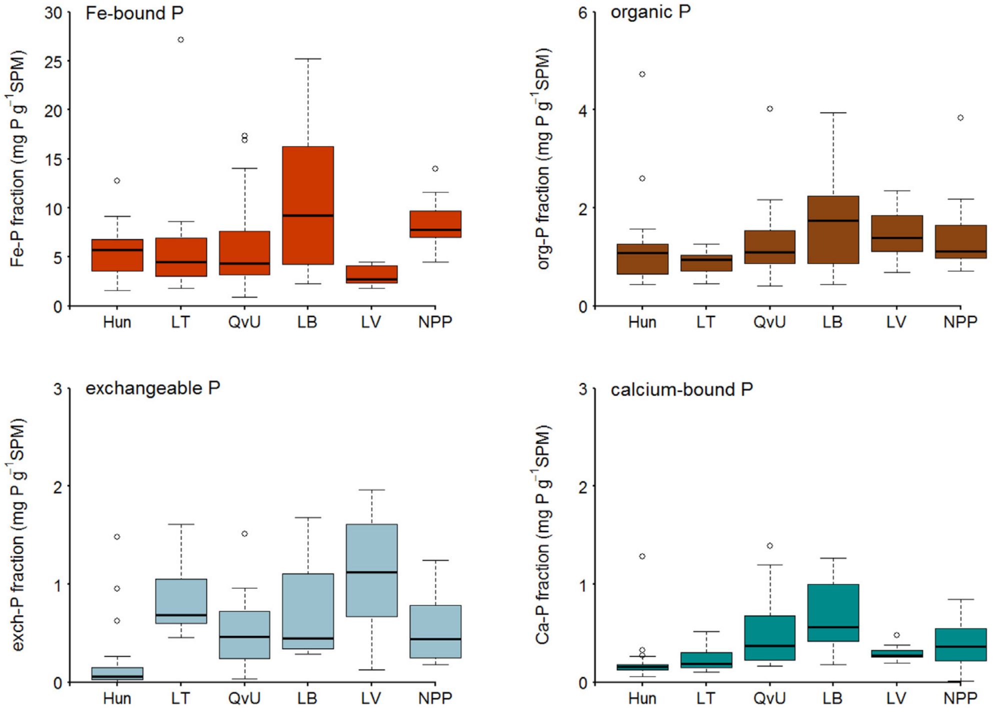

Fig. 4. Boxplots of chemical speciation of particulate P in SPM samples from the six study areas. Note the difference in scale of the y-axis. The bold solid line within each box plot is the median concentration. The bottom and top of the box represent the 0.25 and 0.75 quantiles, respectively. Whiskers extend to the maximum and minimum value unless the values exceed 1.5 times the box height. Open circles are extreme values. For abbreviations of the study area, see Table 1.

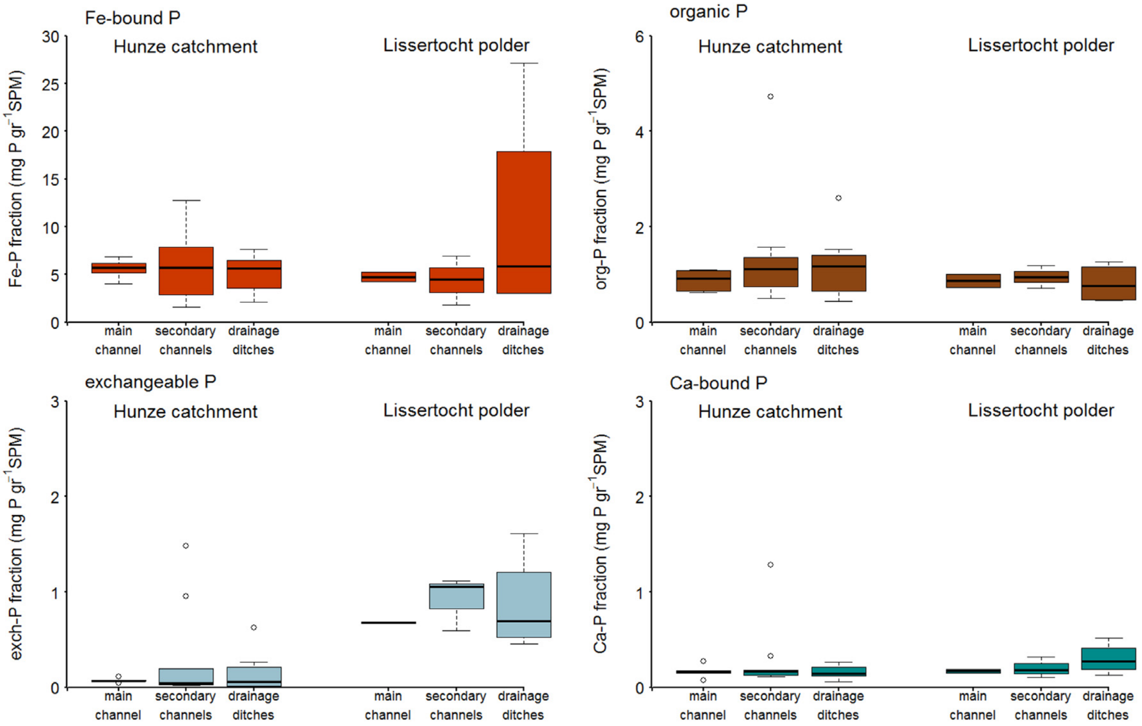

Fig. 5. Boxplots of chemical speciation of particulate P in different orders of watercourses in the Hunze catchment and the Lissertocht polder. Note the difference in scale of the y-axis. Remarks as for Fig. 4.

locations in Quarles van Ufford was higher in February/March than in June. The exch-P contents showed no structural increase or decrease from February/March to June.

3.5. Flow-induced changes in PP fractionation

Before and during the experiment with changes in flow conditions in the Noordplas polder, the TP concentration of the surface water at the three locations was dominated by PP (83–97%). This dominance is also apparent in the multi-year time series of DRP and TP concentrations at the outlet of the Noordplas polder (location PLS) (Fig. 3).

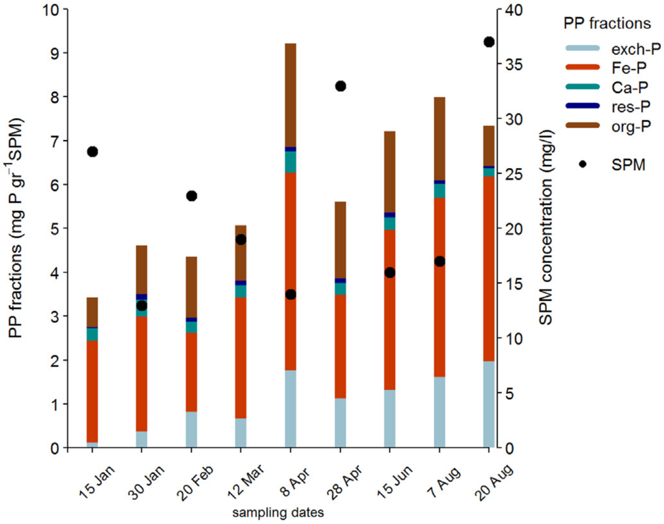

Fig. 6. Chemical speciation of particulate P and SPM concentrations in samples from the Lage Vaart channel at the Blocq van Kuffeler pumping station of the Flevo polder.

3.5.1. Main channel near pumping station (PLS)

Activation of the pumping station resulted in a quick change in flow velocities at the sampling location. The flow velocity with one pump in operation was around 0.1 m s^{-1} and with two pumps in operation it was 0.3 m s^{-1} (Fig. 7 top). The flow velocity induced by two pumps had a strong influence on SPM and TP concentrations as well as on the particle size distribution. The highest SPM concentration during pumping was almost double the pre-pumping concentration (Fig. 7 top). Both particle size distribution and particle volume concentration (as measured with the LISST-100) changed markedly upon pumping. The particle volume concentration increased from 100 to 300 μL L^{-1} and the mean particle size from 90 to 150 μm (Fig. S6). The TP concentration of a sample taken at minute 88 showed a response to pumping but the SPM did not. The large difference between the TP and the SPM concentrations of this sample suggests that the SPM concentration measurement is erroneous. Similar to the SPM concentration, the PP concentrations doubled during operation of the pumping station. Dissolved species showed little variation during the experiment, indicating that there was no major change origin of the water that could have influenced the SMP and TP concentration (Table S3). The DRP concentrations remained close to the detection limit.

The PP content of the SPM varied between 8.8 and 9.4 mg g^{-1} and did not show a significant change during operation of the pumping station. The contribution of the different PP fractions remained fairly constant during the experiment and was largely unaffected by changes in flow velocity and the SPM concentration: Fe-P 6.9–7.7 mg g^{-1}, org-P 1.0–1.1 mg g^{-1}, exch-P 0.18–0.25 mg g^{-1} and Ca-P 0.28–0.58 mg g^{-1} (Fig. 7 top). Hence, the SPM did not change markedly in composition.

SPM remobilised by the pumping station showed a decrease in concentration to approximately 75% of its peak value in less than 30 min after the pumps were stopped. This indicates relatively high fall velocities of the SPM eroded by the increase of flow velocity. The particle size distribution as measured with the LISST-100 device (Supplement 4) and the TP concentration (Fig. 7 top) follow a similar

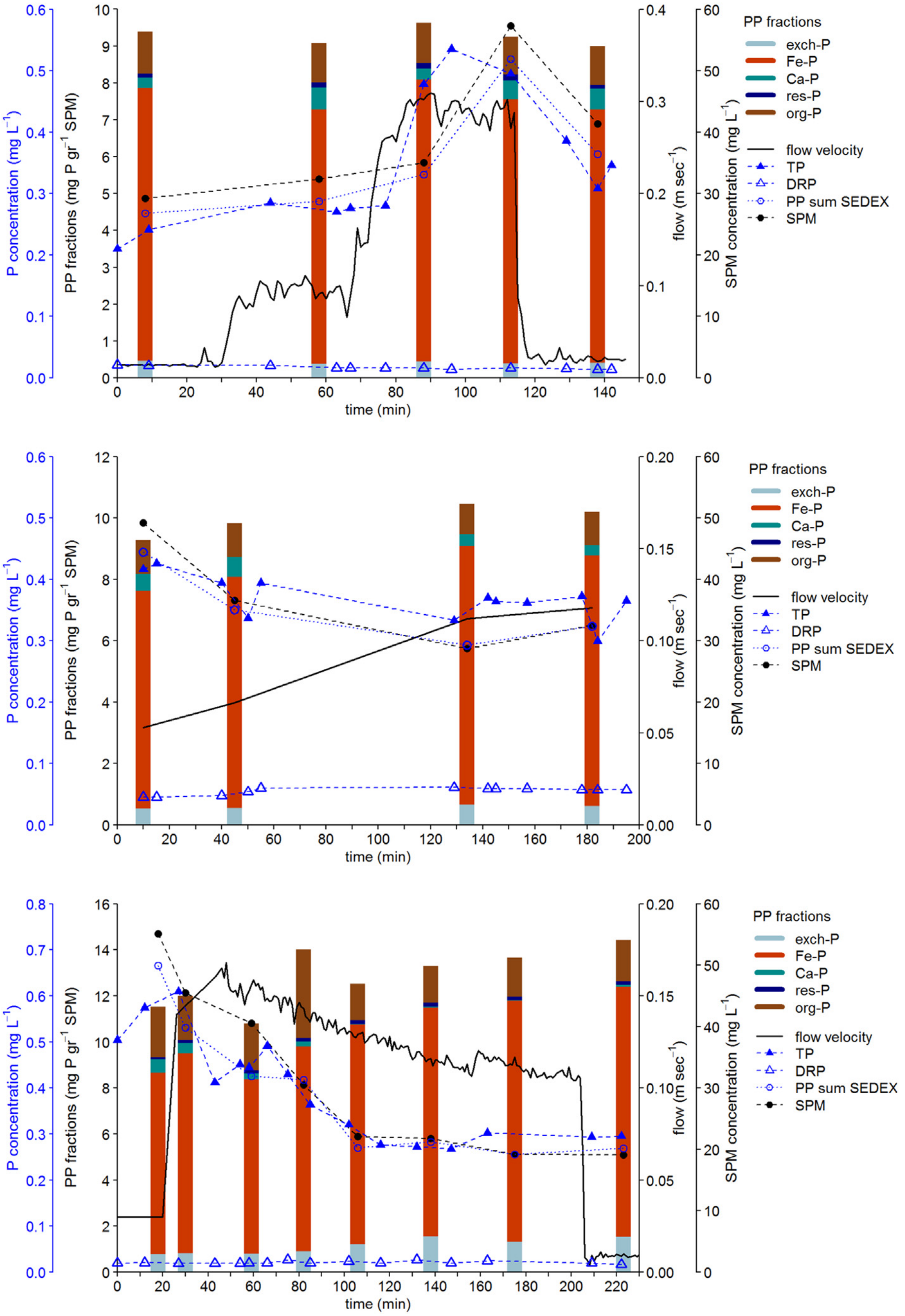

Fig. 7. Particulate P speciation distribution, flow velocities, TP concentrations, DRP concentrations and SPM concentrations during the field experiments in the Noordplas polder: (top) in the main channel near Palenstein pumping station during pumping event (PLS), (middle) in a secondary channel during pumping event (SLT) and (bottom) in a secondary channel during a discharge event generated by lowering of a weir (STW).

pattern, but 30 min after stopping the pumps the values were even closer to pre-pumping levels.

3.5.2. Secondary channel in open connection with pumping station (SLT)

The headwater secondary channel (location SLT) was sampled simultaneously with the main channel near the pumping station. The pull effect of the pumping station was also observed at this location, although flow velocities were lower and lagged behind in time (Fig. 7 middle). The maximum velocity was 0.12 m s^{-1}, which is less than half the maximum velocity at PLS. The SPM concentration initially showed a decrease over time. The TP concentration also slightly decreased during the initial period of the field experiment. Hence, changes in flow velocity did not result in resuspension of particles from the channel bed. The DRP concentration varied little during the experiment (0.04–0.06 mg L^{-1}).

The results of sequential chemical extraction indicate that the relative contribution of PP fractions and the P content of the SPM did not vary during the experiment (Fig. 7 middle). Likewise to other locations: the largest PP fraction was Fe-P (7.1–8.4 mg g^{-1}), followed by org-P (0.85–1.0 mg g^{-1}).

3.5.3. Secondary channel with weir (STW)

Lowering the weir by 20 cm in another secondary channel at minute 25 caused flow velocity in this channel to increase suddenly from 0.03 m s^{-1} to approximately 0.16 m s^{-1}, thereafter diminishing gradually over the next 3 h to approximately 0.11 m s^{-1} (Fig. 7 bottom). The highest SPM concentrations were observed before the opening of the weir and declined steadily after the weir was lowered. This showed that the increased flow did not result in resuspension of particles from the channel bed. The concentrations of dissolved species changed during the experiment (Table S3): the water became less saline, while the SO_4 concentration increased from 290 to 380 mg L^{-1}. This indicates a gradual change in source of the water during the experiment.

The Fe-P fraction showed an increase from the first stage (60 min) to the last stage of the experiment (from 7.6 to 10.9 mg g^{-1}). This increase was accompanied by an increase in the exch-P fraction (from 0.46 to 1.24 mg g^{-1}) and a decrease in the Ca-P fraction (from 0.57 to 0.01 mg g^{-1}). The org-P fraction was also lower during the second stage of the experiment (after 100 min) than in the first stage (0–100 min). The change in PP fractions during the experiment resulted in the P content of the SPM increasing from 11 mg P g^{-1} during the initial stage to 14 mg P g^{-1} SPM during the final stage.

4. Discussion

4.1. Validity of sequential chemical extractions on filter samples

Our results show that SPM collected by centrifugation had lower values for the sum of the PP fractions compared with SPM collected by filtration. This was due to lower contents from all PP fractions other than the Fe-P pool (Table 3). From literature is it known that the recovery efficiency of centrifugation samples is generally lower than that of filtration samples (Duinker et al., 1979; Horowitz et al., 1989; Van Eck, 1982), largely because the finer and less dense particles may not be included in particulate matter obtained by centrifugation (Duinker et al., 1979). Van Eck (1982) reported the recovery efficiency of a continuous-flow centrifugation was 85–95% of 0.45 μm filtration. The recovery efficiency becomes even more important when dealing with low SPM concentrations (<30 mg L^{-1}) (Horowitz et al., 1989), which are typically the case for streams and ditches in lowland catchments and which also applies to a large majority of the samples in our study (Tables S2 and S3). Moreover, Duinker et al. (1979) showed that compared with centrifugation as procedure to collect SPM, filtration results in higher contents of metals (Cu, Cd, Pb and Zn) that are associated with the smaller and less dense particles. The largest relative difference between the centrifugation and filtration samples was found in the average of the exch-P fraction (Table 2). This is in line with results from Poulenard et al. (2008) and Pacini and Gächter (1999), who reported that the exch-P fraction is most abundant in the finest particles. These fine particles are presumably not captured by the centrifuge while all fine particle particles down to 0.7 μm are retained by filtration. Collection SPM by filtration has also the advantage that the PP fraction matches with the determination of PP concentrations in routine water quality monitoring programmes where it is calculated from the difference between TP and DRP.

Sequential chemical extraction is known to have some limitations. Besides the risk of particulate matter loss during the sequential chemical extraction procedure (Ruttenberg et al., 2009), two other limitations may impact the results of SEDEX extractions and thus should be considered. Firstly, some forms of PP could be missed by the SEDEX analysis (Jordan et al., 2008). Any organic P dissolved by extractions for exch-P, auth Ca-P and detr-P would not be measured by the subsequent colorimetric analysis of PO_4. The agreement between the sums of the SEDEX PP fractions with the total P content measured after aqua regia destruction (Fig. 2C) showed that that this potential shortcoming did not adversely affect our results. Secondly, the CDB extraction could represent P species that are bound to reduced Fe minerals (at least vivianite) as well (Dijkstra et al., 2014). However, such reduced Fe minerals are not expected in SPM sampled from oxygenated surface water. Hence, sequential chemical extraction of SPM sampled by filtration is amenable to large-scale sampling and analysis programmes of the PP fractionation in freshwater systems.

4.2. Chemical fractionation of PP in lowland catchments

4.2.1. Phosphorus content of SPM

There is consensus about the correlation between SPM and PP concentration in surface waters (e.g. Beusen et al., 2005; Kronvang et al., 1997). This correlation was also apparent in the present study and this implies that variation in P content of the SPM is limited (Fig. 8A). The average P content of all SPM samples in our study was 8.8 mg g^{-1} but ranged from 1.5 to 32.5 mg g^{-1}. This average P content is higher than the annual average value of 5.7 mg g^{-1} reported for an estuary in the southwest of the Netherlands receiving water from the river Rhine during the pollution peak of the early 1980s (Van Eck, 1982). Also, it is double the value reported by Kronvang et al. (1997) for a Danish arable catchment (4.2 mg g^{-1}). Other studies reported even lower values. Evans et al. (2004) found an average value of 1.7 mg g^{-1} for two lowland streams in England. Owens and Walling (2002) compiled a table of P content in SPM based on a substantial number of studies. They reported values ranging between 0.1 and 4.4 mg g^{-1}, except for one study in France that had values up to 13.5 mg g^{-1}. The latter is still a factor 2.5 lower than the highest values we found. Huisman et al. (2013) found values between 1.7 and 2.7 mg g^{-1} in an agricultural watershed in the US. Martínez-Carreras et al. (2012) observed P contents of SPM between 0.7 and 2.1 mg g^{-1} in several catchments in Luxembourg. Finally, Ballantine et al. (2008) reported average P contents of SPM samples between 0.1 and 2.5 mg g^{-1} for three groundwater-dominated lowland catchments in the UK. The contents we observed are thus internationally high. This observation, in combination with low observed DRP concentrations, can be explained by a strong tendency for biogeochemical transformation of dissolved P tot PP during exfiltration of groundwater in lowland catchments in the Netherlands (Griffioen, 2006; Van der Grift et al., 2014). This will be elaborated on in the following sections.

Phosphorus contents above 15 mg g^{-1} were mostly found in samples with low SPM concentrations (<15 mg L^{-1}) (Fig. 8B). Finer particles have lower fall velocities and remain longer in the water column. Therefore, it can be assumed that SPM collected from surface water with low SPM concentration consists of finer particles than SPM collected from surface water with higher concentrations. This indicates that finer particles are relatively more enriched with P, which is in line with the results from Evans et al. (2004).

4.2.2. Fe-bound P

The Fe-P content strongly dominates the total P content of the SPM in all six study areas, evidenced by a linear trend line between both parameters with a slope of 0.79 (Fig. 8C). The slope of the trend lines of the second and third largest PP pools, org-P and exch-P were with 0.10 and 0.038 much lower. Because the DRP concentrations are commonly low in the water systems studied, this all implies that TP concentrations in surface water in agriculture-dominated lowland catchments are strongly determined by the concentration of particulate Fe-bound P (Fig. 8D). The dominance of Fe-P is independent of the study area, the sampling location within the study area (from headwater ditch to outlet of the catchment), the time of sampling (winter or summer) and the increase in flow conditions typical for channels and ditches in polder catchments. Only during the summer months in the Lage Vaart did DRP become the most important TP fraction instead of Fe-P. Multi-year time series of DRP and TP concentrations in the Lage Vaart channel and in the Haarlemmermeer tocht (near Lissertocht polder) revealed comparable results: an increase of DRP concentration during the late summer and early autumns (Fig. 3). This is likely due to release of DRP from bed sediments or mineralisation of organic P from algae or plant debris (Van der Grift et al., 2016b) (see also Section 4.3).

The dominance of the Fe-P pool indicates the presence of Fe(III) precipitates in the SPM, which is also visible from the colours in the yellow/orange/red/brown range in the photos of the SPM (Figs. S1–S3). Groundwater exfiltration is the most likely source for the Fe(III)

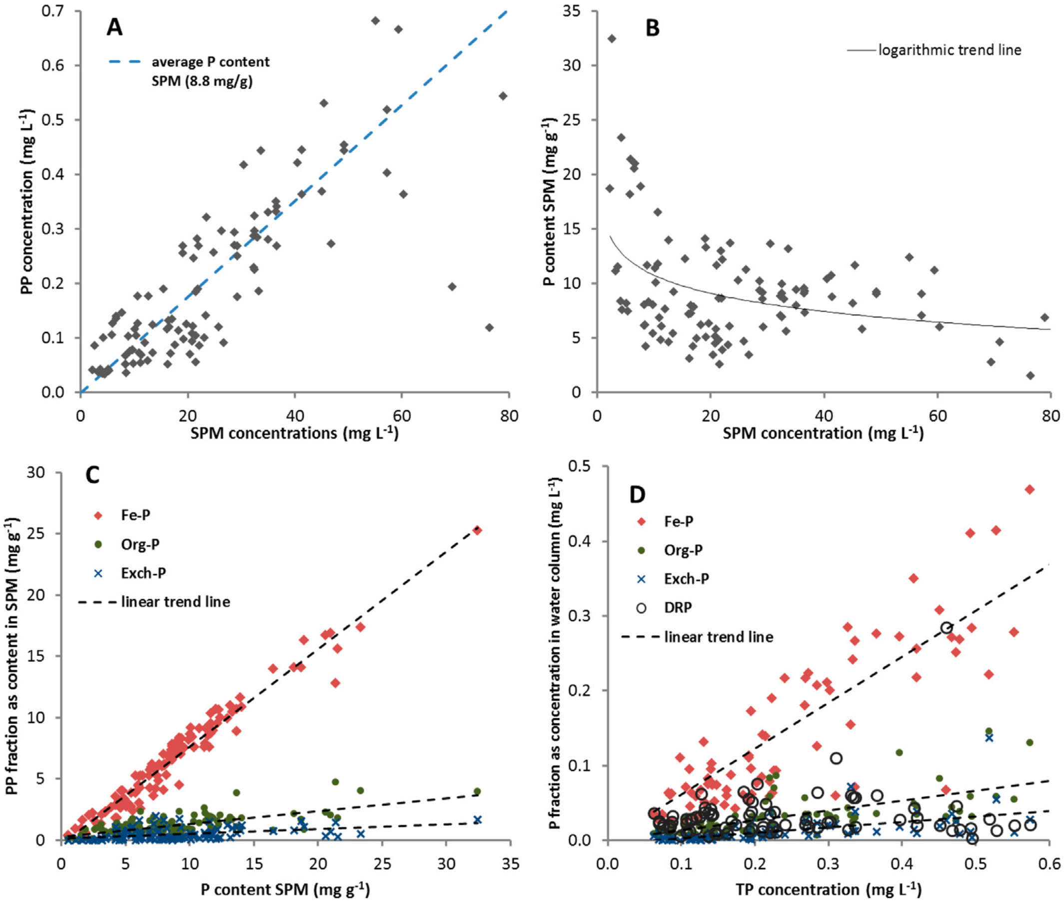

Fig. 8. Particulate P speciation and SPM concentration in agriculture-dominated catchments in the Netherlands: (A) particulate P concentration in the water column (sum of the SEDEX PP fractions) versus SPM concentration, (B) particulate P content of SPM (sum of the SEDEX PP fractions) versus SPM concentration, (C) extracted PP fractions versus total P content of the SPM (sum of the SEDEX PP fractions) and (D) P fractions as concentration in the water column versus TP concentration in water column.

precipitates. After exfiltration of anaerobic Fe-bearing groundwater to surface water, oxidation of Fe(II) to Fe(III) by atmospheric oxygen will lead to the formation of authigenic particles, i.e. particles formed when compounds in solution precipitate due to changing environmental conditions (Baken et al., 2013; Vanlierde et al., 2007). Dissolved phosphate that is present during oxidation of Fe(II) will immediately be immobilised, due to precipitation as Fe(III) hydroxyphosphates (Van der Grift et al., 2016a; Voegelin et al., 2013). Iron-bound P is already the dominant chemical PP fraction in the headwater ditches we sampled. This suggests a fast turnover of dissolved P to particle-bound P during exfiltration and subsequent oxygenation of anoxic groundwater which match results from Griffioen (2006) and Van der Grift et al. (2014). Exfiltration of anoxic Fe-bearing groundwater is thus a major control on P fractionation in surface waters of lowland catchments.

4.2.3. Organic P

The organic P fraction, the second largest PP pool, did not differ noticeably between the areas. In the three areas where samples were taken during different seasons, the highest org-P fraction was present in samples from the end of the winter or early spring. Although we have no hard evidence, we suspect this could be due to recent manure application. One of the measures in the Netherlands to reduce the risk of nutrient leaching to groundwater and surface water is to restrict manure application: on arable land it is permitted from 1 February to 1 August and on grassland from 15 February to 31 August (LNV, 2009). Two SPM samples from tube drains in Quarles van Ufford collected in February 2016 had high org-P fractions (40 and 47% for DQ2 and DQ3, Table S2). In addition, Van der Grift et al. (2016b) showed that manure application during the end of February and early March resulted in losses of NO_3 to the surface water. Although we did not detect an effect on the TP concentrations, recent manure application might have affected the chemical fractionation of PP by increasing the org-P pool in drainage ditches.

4.2.4. Exchangeable P

The most remarkable difference in PP fractionation among the study areas and in the temporal trends during the season is apparent in the exch-P fraction. This fraction is negligible in most samples from the Hunze catchment but is significantly higher in the polder catchments (range 2%–26%) (Fig. 4). This is likely the result of differences in soil types between these areas. Whereas the Hunze catchment consists mostly of sandy soils, the polder catchments are dominated by marine clay soils (Lissertocht polder and Noordplas polder) or fluvial clay soils (Quarles van Ufford and Langbroekerwetering). Particulate P associated with clay particles is expected to be loosely sorbed (Froelich, 1988) and thus extracted by the exch-P step. These particles are vulnerable to being lost from soil as a result of water discharge through trenches or drainage tubes (Regelink et al., 2013; Van der Salm et al., 2012).

The increase from 4 to 27% in the exch-P fraction in the Lage Vaart samples from winter to summer may be associated with mineralisation of organic P from algae or plant debris or dissolved P release from bed sediment which then is available for sorption on suspended particles. Baken et al. (2016) argued that the sequence of dissolved P and Fe(II) loads to the surface water may influence the P immobilisation process. If P is present during oxidation of Fe(II) to Fe(III) it will precipitate as an Fe hydroxyphosphate (Van der Grift et al., 2016a), which results in formation of Fe-P. In contrast, if Fe(III) particles are formed before mixing with P, e.g. P released from mineralisation, this may then be adsorbed to the surface of existing particles, which leads to formation of exch-P. We therefore hypothesise that this may explain the increase in exch-P during spring and summer.

4.2.5. Ca-bound P

A small but detectable fraction was present in most SPM samples. Griffioen (2006) found uptake of phosphate by Ca phosphates and/or Ca carbonates that form upon degassing of exfiltrated groundwater and we expected that this would also play a role in groundwater-fed catchments like ours. After degassing, this water becomes supersaturated in calcium phosphates and these phases may, therefore, precipitate. The amount of Ca-P in the polder catchments was, however, less than expected, given the calcareous nature of the areas. Recently, Senn et al. (2015) showed that immobilisation of phosphate during oxidation of Fe(II) in the presence of Ca can be attributed to (Ca-)Fe(III) phosphate precipitation. It is possible that minerals of this type are extracted during the earlier Fe-P step.

The measured decrease of the Ca-P fraction during flow in the two secondary channels studied in the Noordplas polder (SLT and STW) may be explained by the residence time of the ditch water. The secondary channels act like a reservoir, with limited inflow from the headwater ditches and outflow over the weir. Hence, 'older' almost stagnant water was sampled before the increase in flow conditions. Both degassing of groundwater and precipitation of calcium phosphates and/or calcium carbonates are kinetically controlled processes, which means that the age of the surface water is a factor that influences the occurrence of Ca-P. The water in the headwater ditches that discharge to the secondary channels during the field experiment is likely younger in apparent age and thus would have had less time to undergo kinetically controlled processes. A pool of org-P may also be built up in this virtually stagnant water, due to early spring algal growth. This water was flushed out during the field experiment, which might explain the decrease of the SPM concentration and the org-P fraction during the experiment.

4.3. Bioavailability of particulate P

The PP fractions distinguished by sequential chemical extraction differ in bioavailability. While the $MgCl_2$ step represents a fully exchangeable and therefore bioavailable fraction, the bioavailability of other phases will depend on geochemical transformations and time allowed for diagenesis (Pacini and Gächter, 1999). The consensus is that Fe-P can only be considered largely bioavailable under anoxic conditions, due to the reductive dissolution of Fe oxyhydroxides (Golterman, 2001; Pacini and Gächter, 1999). In addition, limited bioavailability of colloidal Fe-P was shown by Baken et al. (2014). The greatest risk of mass release of P is during the end of the summer season, when anoxic conditions occur most frequently, due to the decomposition of the primary production during summer. Except for water systems with a full cover of duckweed or a floating mat of algae, which create light limitation, the water column in streams, channels and ditches of lowland catchments is unlikely to become anoxic during summer. This means that before it can become bioavailable, Fe-bound P must settle out in the bed sediment that typically has anoxic conditions. Iron-bound P in SPM that is too fine-grained to settle by gravity will not become bioavailable. Once settled by gravity on the sediment layer it does not mean that the PP becomes readily bioavailable. The experiment in the Noordplas polder showed that the PP fractionation of material that becomes eroded during an increase in flow velocity does not deviate from that of the SPM present originally. Therefore, we hypothesise that the potential bioavailability of PP in the systems studied mainly depends on the sedimentation behaviour of the SPM and burial of this matter in the sediment layer.

Once it has been buried in the sediment layer, it is not likely that the entire Fe-bound P pool become bioavailable. Phosphorus-rich Fe(III) phases have been detected in anoxic sediments that are resistant to reductive dissolution (Canavan et al., 2006; Hyacinthe and Van Cappellen, 2004). Moreover, 'P trap' layers rich in Fe oxyhydroxides have been reported to develop at the surface of bed sediments, which are capable of sorbing DRP from upward diffusion from sediment porewater (Baken et al., 2015b; Jarvie et al., 2008). However, the increase of DRP concentrations during the end of summer and early autumn we observed in time series from the Lage Vaart channel and the Haarlemmermeer tocht (Lissertocht polder) (Fig. 4) indicates that release of P from the sediment layer is a possibility in lowland areas.

4.4. Authigenic suspended particulate matter

Assuming the Fe that is extracted by the aqua regia destruction (Tables S2 and S3) is mostly present as Fe hydroxide ($Fe(OH)_3$), we can stoichiometrically calculate the contribution of Fe particles to the total SPM concentration. The area with the highest average contribution of Fe hydroxides in the SPM was the Hunze catchment (32%; range 5–57%), followed by the Quarles van Ufford polder (average 27% and range 11–67%) and the Langbroekerwetering polder (average 25%; range 18–51%) (Fig. 9). The individual study areas showed a larger Fe-P pool at higher $Fe(OH)_3$ contents. All SPM samples with $Fe(OH)_3$ contents below 10% had Fe-P fractions below 60% (Fig. 9). Hence, PP fractions other than Fe-P may become the dominant fraction in SPM with low $Fe(OH)_3$ contents. During the field experiment in the Noorplas polder, the $Fe(OH)_3$ content at location STW increased from 11% to 21%. This indicates that prior to the experiment, SPM consisting of material other than Fe hydroxides increased in the stagnant water. As described in Section 4.2 this material could be carbonates or organic matter (algae).

The Fe content of the SPM is much higher that typically found in soils. Soils with a Fe content around 2.5% are considered being iron-rich and relatively rare in the Netherlands (De Vries, 1999). Hence, the SPM in our study area does not originate form soil erosion and this indicates that a significant amount of the SPM is authigenic formed. At international level, little is known about the contribution of authigenic matter to the total sediment load. The only studies we know on authigenic SPM formed by oxidation of Fe-rich groundwater in fresh water are Baken et al. (2013) and Vanlierde et al. (2007). They reported an average authigenic matter contribution to the total SPM flux of between 31% and 75% for a catchment in Belgium. The limited focus on authigenic production of SPM and related impact on PP in freshwater catchments is probably because the hilly or mountainous regions

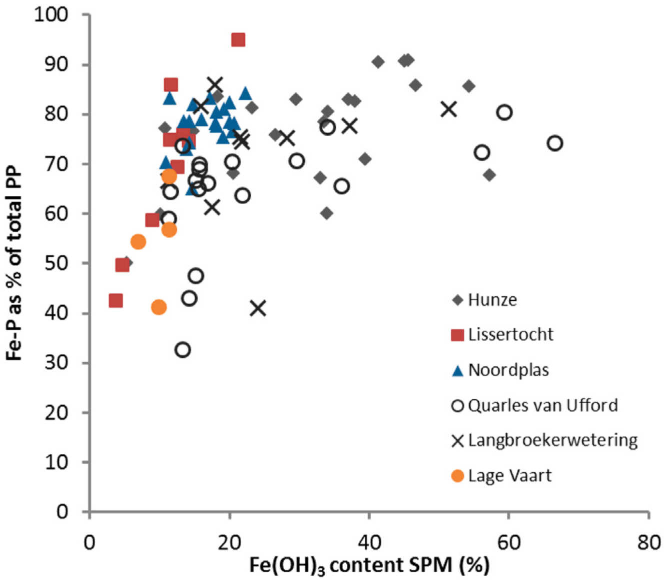

Fig. 9. Fe hydroxide content of SPM as extracted by the aqua regia destruction versus Fe-P fraction as percentage of total particulate P.

studied are often characterised by soil erosion, which will decrease the contribution of authigenic sediments to the total sediment load transported by a river. Moreover, in these regions, geological conditions are unlikely to favour the production of authigenic sediment, i.e. discharge of groundwater rich in anoxic Fe may be lacking (Vanlierde et al., 2007). However, when studying P dynamics and transport in lowland catchments that drain anoxic groundwater it is important to consider the origin and behaviour of authigenic versus detrital particles.

5. Conclusions

This study characterised the chemical fractionation of particulate P in six groundwater-fed lowland catchments in the Netherlands. To do so, suspended particulate matter (SPM) collected by either filtering or centrifuging surface water samples was analysed by means of sequential chemical extractions.

The main conclusions from this study are:

- Sequential chemical extraction of SPM collected by filtration is an appropriate method for determination of the chemical fractionation of particulate P in large-scale sampling and analysis programmes.
- The P content of SPM in these samples from agriculture-dominated lowland catchments in the Netherland ranged from 1.5 to 32.5 mg g^{-1}. The values in observed in this study are high compared with groundwater-fed lowland catchments elsewhere in Europe and North America.
- Ferric iron-bound P was the most important particulate P fraction in SPM sampled from surface water during various conditions in agriculture-dominated lowland catchments. Total P concentration (and therefore the transport of P) in surface water is strongly determined by the concentration of Fe-bound P, except for locations where DRP increases during the summer (especially late summer). Fe(III) precipitates are thus a major carrier of P in lowland catchment.
- The PP fraction distribution in surface water did not change considerably from headwater ditches to the catchment outlet; this indicates a fast turnover of dissolved P to Fe-bound P during the exfiltration and subsequent oxygenation of anoxic groundwater.
- The dominance of the Fe-P pool denotes the presence of Fe(III) precipitates in the SPM. These Fe(III) precipitates are most likely authigenically formed and contribute considerably to the total SPM concentration. For P studies of lowland catchments it is important to consider the origin and behaviour of authigenic versus detrital particles.

Based on these conclusions, it is advisable to include sequential chemical extraction of SPM collected by filtration in large-scale monitoring programmes, because particle composition is critical for P bioavailability, which is a key steering factor for eutrophication.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.02.266.

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