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Sources, composition and transport of fluvial suspended sediment and attached phosphorus in agricultural catchments

A cross-scale analysis

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Cover: An agricultural stream.
(Illustration by: Bengt Sandström)

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Källor, sammansättning och transport av fluvialt suspenderat sediment och bundet fosfor i små jordbruksområden

Sammanfattning

Erosion av markpartiklar och fosfor (P) bunden till dessa partiklar som transporteras från jordbruksområden bidrar till övergödning av söt- och saltvatten, som är ett stort miljöhot. Huvudsyftet med denna avhandling har varit att få en djupare förståelse av förhållandet mellan P och slamhalt (SS) i små jordbruksbäckar, att studera kvantitet och kvalitet av P på partiklarna samt vilken roll avrinningsområdets egenskaper har. Genom att använda långa mätserier miljöövervakningsdata från små jordbruksområden kunde det fastställas att SS fungerar som en vektor för P transport, samt att SS halter i vatten är bra korrelerade till åkermarkens lerhalt och andel jordbruksmark. Dessa samband skalades upp och kunde bekräftas även för större avrinningsområden, tillflöden till Mälaren, med mer blandad markanvändning. Här testades även trender, men få signifikanta nedåtgeående trender under de senaste 20 åren i näringsämneshalter kunde fastställas. Detta förklarades med en tröghet i systemet samt en låg nivå av genomförda åtgärder. Samma avrinningsområdes egenskaper användes i högupplöst distribuerad dynamisk modellering av SS transport från sex små områden med bra överensstämmelse mot uppmätta data, vilket möjliggör tillförlitlig kvantifiering av SS transporter även i övriga områden utan mätprogram. Fält och labb studier av tre små områden där fluvialt suspenderat sediment provtogs visade variation i järnbundet P, som anses vara biotillgänglig, med säsong, med ökande koncentrationer under sommaren och minskande under vintern och högflöden. De olika områdena hade olika dominerande P fraktioner, trots liknande totala P halter. Om vi vill återfå en god ekolgoisk status i bäckar och sjöar, med minskad övergödning och algblomning, måste vi fokusera resurserna där de har högst effekt.

Nyckelord: fosfor, suspenderat sediment, erosion, högupplöst distribuerad modellering, markanvändning, jordtyp, jordbruksbäckar, vattenkvalitetstrender

Sources, composition and transport of fluvial suspended sediment and attached phosphorus in agricultural catchments

Abstract

Soil loss from arable land is a major environmental issue, as well as freshwater and marine eutrophication. Both these issues are well connected, since particles often transport phosphorus (P) from agricultural areas to surface waters, causing eutrophication. The main objective of this thesis was to gain a deeper understanding of the relationship between P and suspended solids (SS) in agricultural streams, to study the quantity and quality of P on SS and the role of catchment properties. By using long-term monitoring data on small agricultural catchments it was established that SS is a vector for P transport, and that SS concentrations in small streams are well correlated to clay content and share agricultural land. These relations were also up-scaled and corroborated for the tributaries to Lake Mälaren in spite of their larger size and more heterogeneous land use. Testing stream nutrient concentration trends in these catchments over the last 20 years resulted in few significant decreasing trends, due to the low degree of implementation of mitigation measures and the historical legacy effects. Catchment properties such as elevation, land use and soil type were also used as input variables in high resolution distributed dynamic modelling of SS transport from six small catchments with good agreement to observed data, which makes possible reliable modelling of similar, unmonitored catchments. Field and laboratory studies of three small catchments sampling fluvial suspended sediment showed variation in iron-bound P with seasons, with increases during summer and decreases during winter, high flow periods. Each catchment had different dominating P fractions, in spite of similar total P concentrations. To achieve water quality goals we need to focus resources where they have the highest effect.

Keywords: phosphorus, suspended sediment, erosion, high resolution modelling, headwaters, agricultural streams, land use, soil distribution, water quality trends, GIS

Dedication

Till Valter.
Jag hoppas att jag alltid kan se världen så som du gör, alltid något nytt att upptäcka.

"Happiness can be found even in the darkest of times, if one only remembers to turn on the light"
Dumbledore, Harry Potter and the Prisoner of Azkaban

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. **Sandström S.**, Futter M. N., Kyllmar K., Bishop K., O'Connell D. W. & Djodjic F. (2020). Particulate phosphorus and suspended solids losses from small agricultural catchments: links to stream and catchment characteristics. *Science of the Total Environment,* 711 134616.

II. **Sandström S.,** Futter M. N., O'Connell D. W., Lannergård E. E., Rakovic J., Kyllmar K., Gill L. W. & Djodjic F. (2021). Variability in fluvial suspended and streambed sediment phosphorus fractions among small agricultural streams. *Journal of Environmental Quality*, 50:612-626.

III. **Sandström S.**, Markensten H., Futter M. N., Kyllmar K., O'Connell D. W., Bishop K. & Djodjic, F. Distributed dynamic modelling of suspended sediment mobilisation and transport from small agricultural catchments (manuscript).

IV. **Sandström S.**, Lannergård E. E., Futter M. N. & Djodjic F. Water quality in Lake Mälaren tributaries – trends and relations to catchment characteristics (manuscript).

Papers I-II are reproduced with the permission of the publishers.

The contribution of Sara Sandström to the papers included in this thesis was as follows:

I. Planned the study together with the co-authors. Had the main responsibility for statistical analysis and data handling, writing the original draft of the manuscript and revising, with input from the co-authors.

II. Designed and planned the field and laboratory studies together with the co-authors. Had the main responsibility for carrying out the field and laboratory work with assistance from co-authors EEL, JR and FD, and for writing the original manuscript draft and revision with input from the co-authors.

III. Planned the study together with the co-authors. Set up and implemented the model in Python with input from HM and FD. Together with HM and FD set up the calibration and validation of the model. Had the main responsibility for writing the original manuscript and revision with input from co-authors.

IV. Planned the study together with the co-authors. Had the main responsibility for data preparation and statistical analysis of relationships found previously. Together with EEL, had the main responsibility for time trend analysis, for writing the original manuscript and for revision with input from the co-authors.

Additional publications

Lannergård E.E., Agstam-Norlin O., Huser B.J., **Sandström S.,** Rakovic J., Futter M.N. (2020). New insights into legacy phosphorus from fractionation of streambed sediment. *Journal of Geophysical Research: Biogeosciences*, 125(9), e2020JG005763.

Abbreviations

Al	Aluminium
CSA	Critical Source Area
DEM	Digital Elevation Model
Fe	Iron
FSS	Fluvial suspended sediment
fw	Flow-weighted
GIS	Geographical Information System
N	Nitrogen
Org	Organic
P	Phosphorus
P-AL	Ammonium lactate-extracted phosphorus
PP	Particulate Phosphorus
RP	Phosphate phosphorus
RUSLE	Revised Universal Soil Loss Equation
SS	Suspended solids
TOC	Total Organic Carbon
TP	Total Phosphorus
USLE	Universal Soil Loss Equation
USPED	Unit Stream Power Deposition

1. Introduction

Streams, lakes and rivers are natural components of the landscape and their beneficial values are immeasurable. Surface waters are used as a drinking water resource and for recreational values such as fishing, swimming and much more. However, the ecological status of many streams and lakes is less than desirable. Different anthropogenic activities have led to degradation of water quality, including acidification of surface waters and pollution with environmental toxins and pesticides. Freshwater and marine eutrophication has been identified as a major threat to humanity (Carpenter & Bennett, 2011). Eutrophication occurs when there are excess inputs of nutrients into a surface water system resulting in an increase in primary production. In general, plant growth is limited by the nutrient for which the discrepancy between plant demand and supply is greatest. This is a general rule for most terrestrial plants, and also applies for primary production in aquatic ecosystems. Phosphorus (P) is often the limiting nutrient in freshwater systems, while nitrogen (N) is generally the limiting nutrient in saline and brackish waters (Schindler, 1974; Tunney et al., 1998). Anthropogenic eutrophication, i.e. eutrophication caused and intensified by different human activities, is a widespread problem mainly connected to surplus supply of the two key nutrients N and P. The most well-known problem connected to eutrophication is excessive growth of cyanobacteria (blue-green algae) which often results in toxic algal blooms. Cyanobacteria have the ability to fix N from the atmosphere which means they have an almost endless supply of N, and therefore P is the limiting nutrient for their growth. When inputs of P increase, algal growth also increases. The new conditions that develop as a consequence of this, favour further growth of certain types of algae and phytoplankton. Some species thrive under these conditions, but others are suppressed, leading to reductions in biodiversity.

Since anthropogenic eutrophication has long been established as a problem, there has been much research on how to reduce P and N losses to surface waters. This is an especially common research topic in the Nordic countries, surrounding the Baltic Sea, which suffers from eutrophication and severe associated consequences such as reoccurring toxic algal blooms, an anoxic bottom layer, and negative impacts on fish communities. To decrease excess inputs of P to surface waters, there is a need for clear identification of the sources of this P. External P sources can be divided into point sources and diffuse sources. Point sources includes e.g. wastewater treatment plants, septic tanks etc., whereas agriculture is an example of a diffuse source. During the 1970s, a P removal step was implemented in many wastewater treatment plants in northern Europe, leading to dramatic decreases in P emissions and in P concentrations in surface waters in many countries including Finland and Sweden (e.g. Räike et al., 2020; Persson, 2001) (Figure 1), an example of a successful mitigation measure. During the second half of the 20th century, a growing population, industrialisation and increasing demand for food production led to increasing use of chemical fertilisers and manure in agriculture. In Sweden this trend continued until the late 1970s, when a decline here began (Figure 1).

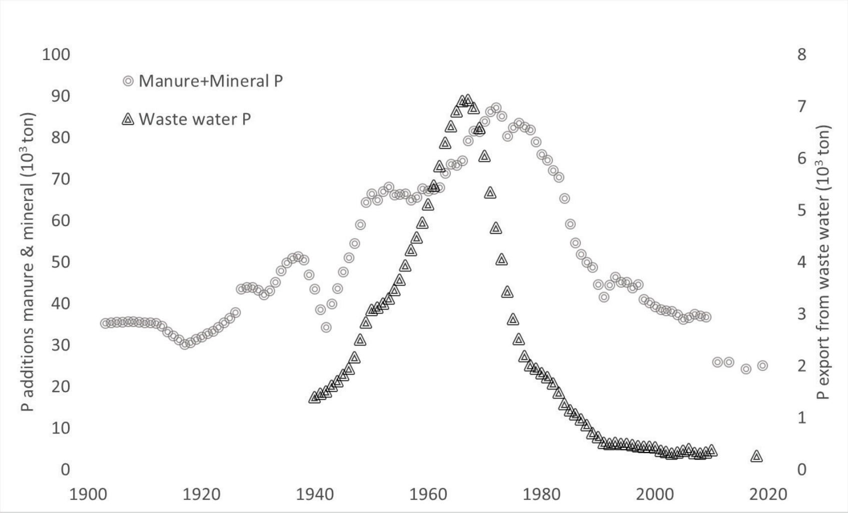

Figure 1. Historical changes (1900-2020) in exports of phosphorus (P) from waste water treatment plants in Sweden (triangles) and in addition of P in manure and mineral fertilisers to agricultural fields in Sweden (circles). Source: Antonson & Jansson (2011) (manure and fertilisation data) and Åkerblom et al. (2020) for P export from wastewater. Note differences in the y-axes.

While additions of P in the form of fertilisers have decreased, previous inputs and use have caused a build-up of P in soils and sediments, so rivers and streams not impacted by wastewater have still not seen a marked decline in P concentrations. For example, a comparison of two nearby rivers in Uppsala, Sweden, one with no large wastewater input (Sävjaån) and one receiving all wastewater from Uppsala City (Fyrisån), shows that a reduction in the main point source (wastewater) in the beginning of the 1970s made a major difference to the P levels in Fyrisån (Figure 2).

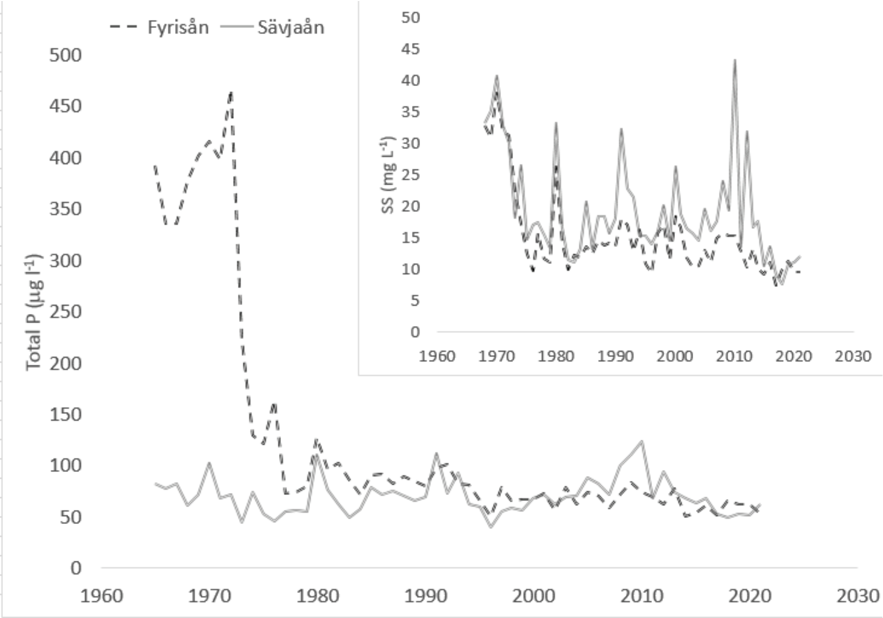

Figure 2. Historical changes in Total phosphorus (P) concentrations in two rivers (Fyrisån and Sävjaån) in Uppsala, Sweden, and (insert) historical changes in suspended solids (SS) concentration in the same two rivers. Source: MVM-Miljödata (2022).

However, the P levels in Fyrisån are still high. The variation in total P (TP) concentrations over time that occurred in Sävjaån, also became apparent in Fyrisån after the implementation of a P removal step in wastewater treatment in the 1970s (Figure 2). The pattern of variation seen in P concentrations, is matched by that in suspended solids (SS) concentrations in both Sävjaån and Fyrisån. A similar decrease in SS concentrations in Fyrisån as in TP concentrations was seen in the late 1970s, most likely connected to the same point source reduction (Figure 2, insert). Since P inputs from external point sources have more or less been cut off since then, most of the current inputs can be attributed to diffuse sources, such as agricultural activities (Räike et al., 2020, Bol et al., 2018), where P losses often can be connected to SS losses. Particle losses to surface waters can besides carrying nutrients and pesticides to streams (Kronvang et al., 2003), e.g. contribute to reduced light penetration and changes in temperature (Bilotta & Brazier, 2008). A deeper understanding of these patterns of variation and of the underlying processes is needed to decrease P and SS concentrations in surface waters. Therefore this thesis explored these patterns and their interconnections.

1.1 Sources of suspended solids and phosphorus – mobilisation and transport

Soil loss from agricultural land is a major issue world-wide, because of degradation of arable land needed for crop production, but also because of transport of different nutrients and pesticides from fields to receiving surface waters impairing water quality. Wind-induced erosion can be an important process in many countries, but in Europe, water induced erosion is the most important process (Panagos et al., 2015). Hydrology in the landscape and hydrological conductivity need to be considered when analysing the processes of water-induced erosion. Erosion can occur both as surface erosion and within the soil structure. Different soil types are more or less prone to erosion, e.g. finer soil types are more prone to erosion than coarser soils (Ulén & Jakobsson, 2005). Surface erosion can be divided into different types, including sheet, rill and gully erosion. Sheet erosion refers to the uniform loss of a thin layer of top soil (Villa Solis, 2014) which mainly mobilises and transports smaller particles with a large surface area, and can carry nutrients, especially P (Haygarth et al., 2006). In rill erosion, small channels are formed on the soil surface, while in gully erosion, these small channels are carved into deeper channels that cannot be mitigated by regular machinery (Villa Solis, 2014).

Due to soil tillage and a temporary low degree of crop cover, agricultural soils are especially vulnerable to erosion. In general, agriculture has been identified as an important, non-point source of both SS and P to degraded waters, with an episodic and spatially highly variable input pattern (Sharpley et al., 2009; Ulen et al., 2010; Sharpley et al., 2013, Kronvang et al., 2013, Withers & Jarvie, 2008). This high variability creates difficulties in predicting P losses from agriculture. In agricultural waters, legacy P, deriving from historical land and P management causing P build-up in soils and sediments over time, is an issue (Kleinman et al., 2011; Sharpley et al., 2013). This legacy P continues to pollute streams, rivers and lakes, even when external inputs are drastically reduced (Figure 1, Figure 2). Besides the built up soil P, legacy P includes P that was once transported from field to stream and settled in the streambed. This P can be remobilised and transported onwards to pollute waters further downstream, which makes it difficult to determine the original source of P, as discussed by Withers & Jarvie (2008). Phosphorus can be falsely considered to originate from diffuse agricultural sources, when the original source can in fact be a point source that delivers P to the stream and settles in the sediment, to be remobilised at a later point in time. This highlights the difficulties associated with determining the effects of remediation measures, when legacy P is disturbing the system. When a measure is implemented, the effects can be masked even if external inputs of P have decreased, since legacy P in stream sediment can continue to leak and keep the P concentrations in the water at high levels.

Mobilisation of P can be described as the initial separation of P molecules from their source (Haygarth et al., 2005). This occurs in two different ways, either by solubilisation or mechanical separation. Erosion is an example of a mechanical process that is often coupled to P transport from the field and that separates P-carrying particles from the soil. It is well established that certain parts of the agricultural landscape are responsible for the majority of all P losses, with roughly 80 % of total losses coming from around 20 % of the contributing land area (Sharpley et al., 2009). This is known as the 80:20 rule, and these high-risk areas for P loss are called Critical Source Areas (CSA) (Sharpley et al., 2009). CSAs are typically very prone to erosion and well hydrologically connected, creating paths for surface runoff in the landscape. The concept of CSAs has been described many times e.g. (Gburek & Sharpley, 1998, Pionke et al., 2000), and CSAs have also been referred to as “hot spots” that are activated at certain “hot moments” (McClain et al., 2003). Surface runoff is a main pathway for P (especially particulate P) transport to streams, while another main pathway is subsurface runoff. This can occur through soil water, groundwater, and as rapid transport through cracks and macropores in the soil. Almost half (47%) of Sweden’s agricultural fields are artificially drained (Statistics Sweden, 2017), which creates pathways for P to be rapidly transported through macropores to drainage pipes and thereafter directly to streams and rivers (Djodjic, 2001). Phosphorus attached to particles and dissolved P can both be carried through drainage pipes and macropores. Dissolved P losses from agricultural areas are usually connected to fertiliser and manure inputs (Edwards & Daniel, 1993, Tarkalson & Mikkelsen, 2004). They can also be the result of high P content in the soil (Heckrath et al., 1995), with surplus P leading to lower P soil buffering capacity and a higher P content in the soil solution. Soils are generally considered to act as sinks for P, adsorbing the added P that is not taken up by plants. However, if a continuous surplus of P is added to a soil, the P soil adsorption capacity of the soil will eventually be exceeded and the soil will become P-saturated (Kleinman et al., 2011). When saturation occurs, surplus P will be lost from the soil to surface waters, and the soil will turn from a sink to a source of P.

1.2 Distributed high resolution erosion modelling

As mentioned previously, there is high spatial variability in P losses from agricultural fields. Certain areas are hydrologically active, more prone to erosion and contribute the majority of P losses in general and PP losses in particular, to surface waters. To identify these CSAs in the agricultural landscape, high resolution digital elevation models (DEM) can be used as a basis, since topography exerts first-order control on spatial variations in hydrological conditions (Sörensen et al., 2006). For example, Djodjic and Villa (2015) used high-resolution modelling to identify CSAs for erosion and P losses in five small agricultural catchments in Sweden. They evaluated the potential of the modified Unit Stream Power Deposition (USPED) model in combination with high-resolution DEM to identify these areas, together with field surveys. The modified USPED model is based on the Universal Soil Loss Equation (USLE) (Wischmeier & Smith, 1978) and the Revised Universal Soil Loss Equation (RUSLE) (Renard et al., 1991), empirical equations used to calculate soil loss from agricultural fields. However, the modified USPED model considers the influence of flow convergence or divergence on erosion and deposition processes (Mitasova et al., 1996).This model can be used to predict the spatial distribution of erosion and deposition patterns through surface runoff. Surface runoff can occur either when the rain intensity exceeds the infiltration capacity of the soil (Hortonian surface runoff) or when the soil in lower parts of the landscape is saturated and thus no more water can flow into the soil (Grip & Rodhe, 2019). Hortonian surface runoff is rare in the Swedish landscape, as Swedish soils usually have high infiltration capacity and high-intensity rain events are uncommon. However, surface runoff on saturated soils is rather common especially during winter and spring (Boye et al., 2012). In the modified USPED model, accumulation of material follows the topography, which makes the model suitable for Swedish conditions.

In the study by Djodjic and Villa (2015) there was high agreement between modelled erosion risk areas and observed erosion areas. Since these CSAs are activated mainly during certain conditions, such as prolonged periods when the water supply exceeds soil water-holding capacity and causes high flows (especially during spring flow), they may not be active all year. However, a single event that activates these areas, causing high erosion and creating gullies can produce a high proportion of the total annual losses of SS and TP. This highlights the significance of identifying these areas for mitigation purposes. Further refinements to the modified USPED model have been made, e.g. Djodjic and Markensten (2019) calculated risk maps for erosion on agricultural land in the southern half of Sweden, for which they modelled a "worst case scenario" with high spring flow on bare soils. Comparison of the modelled "worst case" erosion against measured 90th percentile values for 11 Swedish fields and 19 small catchments, showed high agreement (R^2=0.81) for SS loads.

Improvements in GIS-based maps over the years, with higher resolution of DEMs and improved soil maps have allowed even further refinement of models for identification of CSAs, including the development of dynamic modelling. Dynamic modelling allow comparisons with time series of measured transports of both sediment and P, for identification of erosion-prone areas over the year, and determination of critical periods and climatic conditions in which CSAs are most active, enabling better targeting of mitigation measures.

1.3 Phosphorus bound in stream sediments

The different forms of P present in water and sediment are more or less available for uptake by plants and biota, and more or less easily lost from soils and sediments to surface waters. The total amount of P present can be divided into different fractions, for example phosphate P and particulate P, where phosphate P is directly available for uptake, and particulate P (PP) describes the amount of P bound to particles. Particulate P can also be referred to as unreactive P (UP) (Haygarth & Sharpley, 2000) and the concentration in water is usually determined by filtering with a filter pore size of 0.45 µm. However, in the majority of the work in this thesis, the PP concentration in water samples was determined as the filtrate fraction by filtering through 0.2 µm, which captured P bound to smaller particles. This is further described in Chapter 3.1.1 and 3. 3 (Methodology).

Retention of P in flowing water depends both on physical processes and on biogeochemical processes in the stream. The actual processes governing P retention and release in streams are highly variable, both in time and space (e.g. Bowes et al., 2003), and are dependent on environmental conditions and the form of P entering the stream. For simplicity, the mechanisms involved can be divided into physico-chemical controls and biological controls. Physico-chemical controls includes mineral precipitation and dissolution (Pierzynski et al., 2005), and sorption and desorption reactions, where P can adsorb (and desorb) to surfaces of iron (Fe) and aluminium (Al) hydroxides/oxides (Records et al., 2016), and to different minerals, like clay minerals. It is also possible for P to absorb into the solid phase of different minerals (Withers & Jarvie, 2008). Phosphorus can co-precipitate with e.g. calcium (Ca) as calcium phosphate and with Fe, to form Fe phosphates and hydroxides. Phosphorus advection and diffusion is another physico-chemical process that affects P cycling in streams, especially at the sediment-water interface. Iron bound P (Fe-P) is sensitive to changes in reduction-oxidation (redox) potential, e.g. P can be released as PO_4^{3-} under reducing anoxic conditions when Fe is reduced from ferric Fe (Fe^{3+}) to ferrous Fe (Fe^{2+}) (Records et al., 2016). The redox potential at the sediment surface can also be affected by different microorganisms (Pusch et al., 1998), affecting the potential for P release from sediment, a biological control on P cycling. Other biological controls includes macrophytes, periphyton and phytoplankton, where periphyton and phytoplankton can assimilate both inorganic and organic P forms (Dodds, 2003).

Phosphorus bound to organic material can potentially be bioavailable, after degradation of labile forms of organic material and following release of P (Rydin, 2000; Ahlgren et al., 2011). Iron-bound P is usually considered bioavailable, due to its sensitivity to redox changes. Aluminium-bound P (Al-P) is not sensitive to changes in redox potential, but it is sensitive instead to changes in pH and can be released either at high (pH>8) or low pH values (pH<4) (Agstam-Norlin, 2022). Since pH is usually neutral (approx. pH 7) in streams and rivers and seldom displays large falls or rises, Al-P is usually considered stable and not available for algal uptake.

1.4 From headwaters to larger streams and catchments

A review by Bol et al. (2018) examined the challenges that need to be resolved to reduce P related eutrophication in agricultural landscapes in north-west Europe. One of the main conclusions was that future research needs to focus on headwaters and headwater catchments. Several studies have reported high variability in P losses from agricultural headwater catchments, e.g. Legeay et al. (2015), reported an increase in the variability of P losses when moving upstream in the catchment to the headwaters. Similar observations have been made for P losses in small, agricultural headwater catchments in Sweden (Bol et al., 2018). Better knowledge of the main factors contributing to this high variability in losses would be valuable for overall management of losses. Further, targeting management efforts and measures at headwater catchments with the highest losses, where they will have greatest effect would be an ideal situation. In Sweden and several Nordic countries, there are existing monitoring programmes for nutrient losses from agriculture (Vagstad et al., 2004; Bechmann et al., 2008; Kyllmar et al., 2014). Using available long-term monitoring data is a good approach to study losses and their dynamics in relation to water quality parameters and catchment characteristics (Sharpley et al., 2015). Studying headwaters is also important because the findings can be used as a proxy for larger catchments since headwaters are more easily controlled and the inputs of P are influenced by fewer different factors. Using findings from headwater catchments on larger catchments would allow for design of more effective mitigation programmes for larger, more strongly affected catchments, e.g. great lakes and possibly also enclosed seas, e.g. the Baltic Sea. However, before this can be done, there is a need to confirm the applicability of findings from headwater catchments to larger catchments. Therefore this thesis will study P and SS concentrations in agricultural headwaters (Papers I-II) and scale up the results through modelling (Paper III) and through inclusion of more mixed land use and larger catchments (Paper IV). The results were scrutinised to see whether headwater P and SS dynamics and relationships can be applied on a larger scale.

2. Objectives and research questions

The overall aims of this thesis work were to gain a deeper understanding of the relationship between suspended material and P in agricultural streams, to determine the quantity and quality of P in suspended material and to identify the role played by the catchment and its properties. To achieve these overall aims more specific objectives were specified for the separate studies in Papers I-IV:

(I) Gain an improved understanding of the processes and variables controlling mobilisation and transfer of SS and P in agricultural headwaters.

(II) Quantify patterns in the distribution of P fractions in fluvial suspended sediment (FSS) and streambed sediments, investigate potential controlling factors and chart seasonal changes in the distribution of P fractions in FSS.

(III) Identify and quantify the temporal and spatial variability in SS losses through development of a high-resolution distributed erosion model, and calibration and validation of this model for a range of small agricultural catchments using a long time series of high-quality monitoring data.

(IV) Exploring the use of relationships derived from small agricultural headwater catchments for larger, mixed land use catchments by investigating water quality relations and trends in the tributaries to a great lake, including previously identified relationships between PP and SS and catchment characteristics and identification of potential trends in nutrient losses in the past 20 years.

3. Methodology

3.1 Catchment descriptions

The catchments used in this thesis are all part of the National Agricultural Catchment Monitoring programme studying nutrient losses from agriculture (Papers I-III) or are included in other monitoring programmes for rivers or streams (Paper IV). The catchments used in Papers I-III are all small, agricultural catchments (<35 km^2) with more than 50% agricultural land, spread out over southern Sweden (Figure 3). Thus they represent a broad range of different soil texture classes and climate (Table 1). For Paper I, 11 catchments representing a wide range of soil texture and SS and P losses were chosen, and six of these were also used in Paper III (Figure 3, Table 1). For Paper II, three of these catchments with a previous history of high P and SS losses were chosen (U8, C6 and E23).

In Paper IV, previous findings were scaled up to larger catchments using the tributaries to Lake Mälaren and its catchment Norrström (Figure 3).

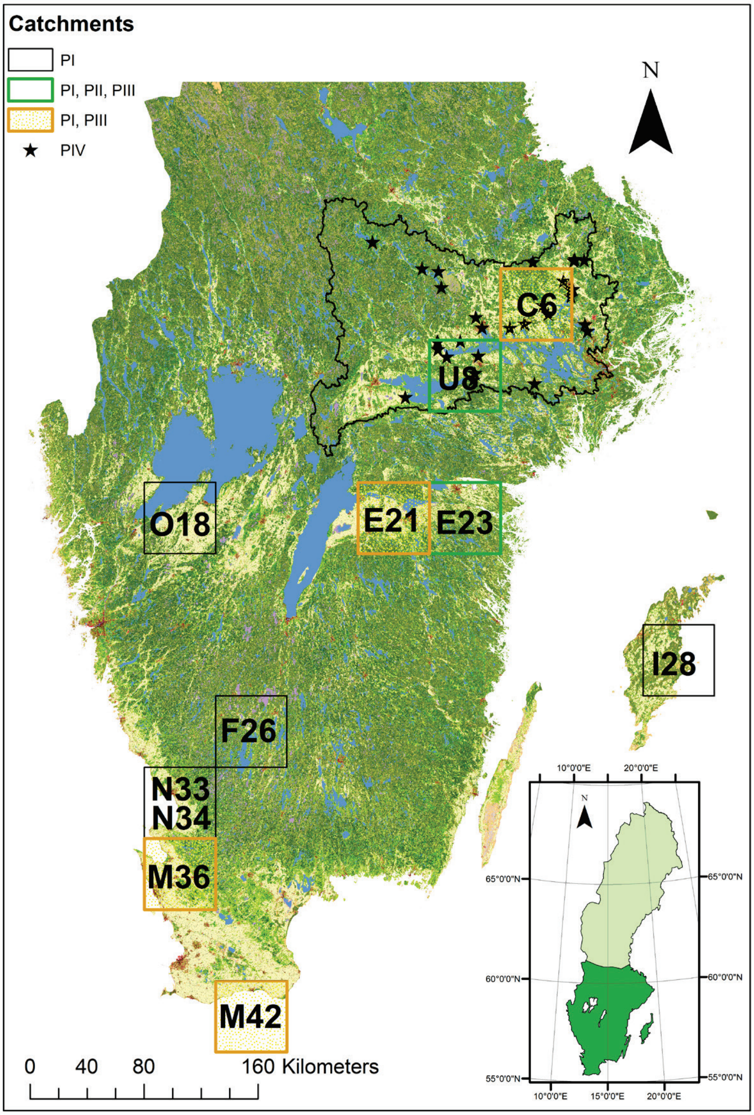

Figure 3. Approximate locations of all study catchments from the National Agricultural Catchment Monitoring programme used in Papers I-III. (PI-III, see colour key). The outline of the Norrström catchment (Paper IV) is marked with a solid black line, with stars representing sampling points.

Table 1. Catchment characteristics for monitoring catchments used in Papers I-III (Sources: Linefur et al., 2019, Kyllmar et al., 2014, Stjernman Forsberg et al., 2013). Water discharge is a mean value of the period 1995/1996-2016/2017, for station N33 for the period 1990/1991-2010/2011 Precipitation and temperature are normal values for 1961-1990 (SMHI, 2001)

ID	Area (km^2)	Arable land (%)	Dominant soil texture class (USDA)	Precipitation (mm)	Temp. (^oC)	Water discharge (mm)	Paper
C6	33.1	59	Clay loam	623	5.5	220	I, II, III
E21	16.3	89	Sandy loam	506	6.0	157	I, III
E23	7.4	54	Clay	594	6.3	176	I, II, III
F26	1.8	70	Loamy sand	1066	6.2	482	I
I28	4.7	84	Sandy loam	587	6.9	158	I
M36	7.9	86	Clay, sandy loam	719	7.6	272	I, III
M42	8.2	93	Sandy loam, loam	709	7.7	270	I, III
N33	6.6	87	Loam, sandy loam	823	7.1	288	I
N34	13.9	85	Sandy loam and silt loam	886	7.2	361	I
O18	7.7	92	Clay	655	6.1	325	I
U8	5.7	56	Clay	539	5.9	230	I, II, III

Norrström basin is the main catchment to Lake Mälaren. In Paper IV, 30 stations in the tributaries to Lake Mälaren were chosen, from the main tributaries to headwater stations (not including U8 and C6) (14-4111 km^2). These catchments have a wider range of land uses, from 0-64% arable land to 22-76% forest. There is also a wide range of soil texture, with a mean clay content on arable land ranging from 10 to 46%. More detailed information about the catchments can be found in Paper IV.

3.1.1 Agricultural Catchments Monitoring Programme (Papers I-III)

The national monitoring programme covers 19 small agricultural catchments (area <35 km^2), spread across southern Sweden and representing the majority of Sweden's agricultural landscape. The programme focuses on nutrient losses from agriculture under various climate and geohydrological conditions as well as in different agricultural production systems (Kyllmar et al., 2014). All catchments have been monitored since 1995 or longer. Daily water discharge is measured at the outlet of each catchment by continuous water level recordings at defined stream cross sections (Kyllmar et al., 2014). The programme is divided into two parts; one national monitoring programme and a regional monitoring programme, where the catchments in the national monitoring programme are more intensively monitored. These catchments have both grab sampling (until 2010) and automatic flow-proportional water sampling (from 2004). In flow-proportional sampling, used in this thesis, sub samples are collected using a peristaltic pump and then stored in a 10-L glass bottle kept in a fridge. Composite samples are taken from the bottle every two weeks, and then the bottle is emptied (Kyllmar et al., 2014). Within the regional programme water samples are taken as grab samples every two weeks, except in three catchments (E23, U8 and N33) where flow-proportional water samples are also taken as part of the project *Focus on Phosphorus* (Malgeryd et al., 2015). In flow-proportional water sampling more sub samples are taken during high-flow events. When a pre-defined amount of water (individual for each station) has passed the monitoring station, a sub sample is taken. During low-flow periods, sub samples are taken time-proportionally with two samples per day (Kyllmar et al., 2014). Water quality is analysed at the geochemistry laboratory at the Department of Aquatic Sciences and Assessment, SLU, which is certified by the Swedish Board for Accreditation and Conformity Assessment (SWEDAC) following Swedish Standard methods. The parameters analysed are total nitrogen (TN), nitrite and nitrate N (NO_2/NO_3-N), TP, phosphate-P (hereafter termed RP following Haygarth & Sharpley (2000)), SS, total organic carbon (TOC), alkalinity, conductivity and pH. Total P is analysed on unfiltered samples after digestion, and RP is analysed after filtration at 0.2 µm to avoid particle disturbance, in both cases using the molybdate blue method (Murphy & Riley, 1962). Particulate P (PP) is determined as the filtrate fraction of TP. The water quality parameters used in this thesis were SS, TP, PP and RP (Papers I-III). In Paper I, RP is referred to as DP.

3.1.2 Monitoring data – tributaries to Lake Mälaren (Paper IV)

In Paper IV, monitoring data from Miljödata MVM were used (Miljödata-MVM, 2022). This data base contains monitoring data from all over Sweden on e.g. different biological parameters and water chemistry in streams, rivers and lakes analysed on accredited laboratories. Data collected through different monitoring programmes are gathered and presented in this freely available database. The stations used in Paper IV are situated along the main tributaries to Lake Mälaren, which belong to different monitoring programmes. Some are a part of Recipient Monitoring programmes by e.g. private companies, municipalities etc. that deliver the data to SLU where a quality check of the data is performed and thereafter the data are made freely available. The main tributaries to Lake Mälaren were previously a part of a separate programme monitoring water chemistry during the period 1965-1995, initially at 14 stations, and later at 12 stations (Persson, 2001). However, the monitoring has been taken over by different counties and municipalities over the years. In Paper IV, headwater stations to the main tributaries which have not been a part of the main monitoring of Lake Mälaren's tributaries, were also used.

Besides the water quality parameters in listed in section 3.1.1., additional water quality parameters were included in the analysis in Paper IV. These were: TN, NO_2/NO_3-N, ammonium-N (NH_4-N) and TOC.

3.2 Sediment sampling and phosphorus fractionation (Paper II)

3.2.1 Fluvial suspended and streambed sediment sampling

To study P fractions in FSS over seasons and the connection between P fractions in FSS and in streambed sediment, a two-year sampling campaign was conducted in three catchments (U8, C6 and E23) (Figure 3). Two Phillips samplers (Phillips et al., 2000) were placed at the outlet of each catchment to collect FSS (Figure 4). Sampling started in C6 and U8 during autumn 2017, and E23 was added in autumn 2018.

Streambed sediment cores were taken in each catchment using a Willner gravity corer on a rod or by simply pushing the tube in manually, capturing the sediment with two plugs creating a vacuum. In U8 and C6, cores were collected in May 2018. The E23 core was collected in May 2019. Further details of sampling and sample handling are provided in Paper II.

Figure 4. Collection of fluvial suspended sediment from a Phillips sampler in catchment C6. Photo by Mikael Östlund.

3.2.2 Sequential phosphorus fractionation

For analysis of P concentration and different P fractions in the sediment samples (FSS and streambed sediment), a sequential P fractionation method was used. There are several sequential extraction methods available for determining different P fractions in sediment. For example, Psenner (1988), Psenner et al. (1984) and Psenner and Pucsko (1988) developed a method where they divided the different P fractions in sediment into loosely sorbed P, redox-sensitive P (Fe-/Mn- bound P), non-reducible P and P bound to Al-hydroxides, organically bound P, Ca-bound P and refractory P. This method has since been modified for different types of sediment by e.g. Jensen and Thamdrup (1993) for marine sediment, and by Hupfer et al. (2009) for better use on calcite rich sediment. Other methods for analysing P fractions in sediments or soils includes ^{31}P Nuclear Magnetic Resonance (NMR) spectroscopy (Newman & Tate, 1980), which is mainly used for analysis of organic P fractions and XANES (X-ray absorption near-edge structure) spectroscopy, which is a method for analysis of mainly inorganic P fractions. Both these methods are used for more precise definition of P fractions, but they are quite costly and requires access to certain instruments and infra-structures. Sequential P fractionation is a relatively cost-effective method, that has been proven to provide good estimates of operational P fractions (e.g. Jensen & Thamdrup, 1993). The version of the method used in this thesis and previously at the Swedish University of Agricultural Sciences (SLU) is based on the Psenner and Pucsko (1988) method with adaptations by Hupfer et al (1995, 2009), omitting the step of refractory P (Figure 5).

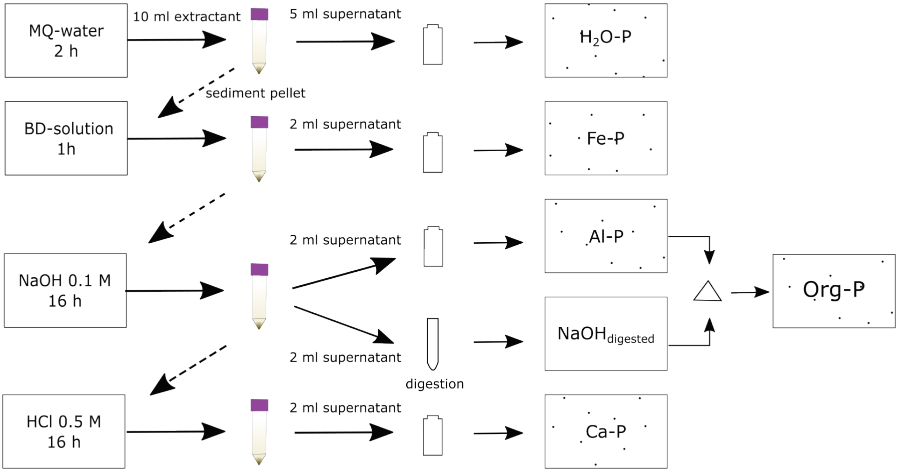

Figure 5. Flow chart of sequential phosphorus fractionation. White boxes (left) represents extractants used, while speckled boxes (right) represents operationally defined fractions.

All sediment samples were analysed as fresh sediment with triplicate subsamples following the analytical flow chart in Figure 5. At the end of the procedure all sample aliquots were analysed for RP (unfiltered) concentration on a spectrophotometer at 880 nm using the molybdate blue method (Murphy & Riley, 1962). All results from P fractionation are presented as mg g^{-1}, unless otherwise stated. All fractions are operationally defined based on the form of P to which they are assumed to be bound, and are referred to by their operational name (as described in Figure 5) in the remainder of this thesis. The sum of all P fractions is hereafter termed TP, since it has been found to be within ± 10% of total sediment P (Huser & Rydin, 2005) The sum of the first two steps in the sequential P fractionation method (H_2O-P and Fe-P) is commonly referred to as mobile P (Reitzel et al., 2005, Reitzel et al., 2006, Huser et al., 2016), as it is more mobile and easily exchanged with the water column. The H_2O-P and Fe-P fractions were used here to make comparisons with RP in the water column.

All samples were analysed for dry matter content by first freezing for at least 12 h at -20^{0}C and then freeze-drying for at least four days. Analyses for loss on ignition (LOI) to determine organic matter content in the samples were performed by igniting a freeze dried sample in a furnace for 2 h at 550^{0}C (Håkanson & Jansson, 1983).

3.3 Water quality load calculations and flow-weighted concentrations

In Papers I-III, data collected through the National Agricultural Catchments Monitoring Programme were used as described in section 3.1.1. These data included calculated loads of TP, PP, RP and SS. In Paper IV, RP was analysed on unfiltered samples, in contrast to the other papers. Hence, comparisons of RP and PP concentrations between Paper IV and the other papers should be made with caution.

Flow-weighted concentrations were calculated to minimise/normalise the impact of changes in flow on changes in concentration levels. Nutrient and SS loads were calculated based on flow-proportional samples, where each sample analysed was assumed to represent average daily concentrations back until the previous sample collection day. These daily concentrations were then multiplied by average daily discharge, to give daily loads, which were added together to give monthly loads. A similar procedure for calculating loads and flow-weighted (fw) concentrations was used in Paper II, but instead of monthly values, the periods when the Phillips samplers were placed in the streams were used. In Paper III, monthly calculated loads of SS and PP were used. In Paper IV fw concentrations and loads were also used, calculated following the same procedure as in Paper III, but here based on grab samples and modelled discharge data from the Swedish Meteorological and Hydrological Institute (SMHI) since not all stations had measured discharge data. In Papers I, II and IV, estimates of loads and fw concentrations were based on Linefur et al. (2019), where monthly fw concentrations (mg L^{-1}) were calculated by dividing monthly loads (kg km^{-2}) by monthly runoff (mm).

3.4 Dynamic modelling of suspended solids losses (Paper III)

To study temporal and spatial variations in SS losses the modified USPED model was further developed, set up and calibrated using the PCRaster (Karssenberg et al., 2010) and SPOTPY (Houska et al., 2015) packages within Python.

3.4.1 Model description

The influence of flow convergence or divergence on erosion and deposition processes is considered in the modified USPED model (Mitasova et al., 1996) while slope length (L) and steepness (S) factors are replaced with upslope contributing area (Moore & Burch, 1986). This model can be used to predict the spatial distribution of erosion and deposition patterns, using flow accumulation, upslope contributing area, slope angle, slope profile and tangential curvature. By considering the local geometry, each cell in an area is assigned either a negative net deposition value or a positive net erosion value (Djodjic & Villa, 2015). Based on this, each cell is given a value representing the amount of accumulated material that will flow out of that cell into its neighbouring downstream cell. The different equations used in the model, describing different processes such as erosion, are based on the local geometry, parameters describing surface cover (land use cover value (c)), and soil texture (permeability (p), erodibility (k)). The accumulated material is transported through simulated surface runoff in the model. Surface runoff on saturated soils is rather common especially during winter and spring in Sweden (Boye et al., 2012). In the modified USPED model, accumulation of material follows the topography, which makes the model suitable for Swedish conditions. The modelling outputs are a map showing where eroded material is mobilised and another map showing accumulated eroded material along flow paths, allowing for identification of areas with the highest risk of erosion.

3.4.2 Modelling setup

The modified USPED model calculates erosion and deposition patterns by the use of distributed high-resolution maps. Each cell within the catchment is assigned a net erosion/deposition (ED) value depending on the properties of that cell in the form of land use and soil texture as described above, and the erosion/deposition of upstream cells. The main equation describing ED patterns is then:

$$ED = R * LS * k * c * (1 - 1 * ProfCurv) * (1 - 1 * TanCurv) * 4 \quad \text{(eq.1)}$$

where R is monthly runoff (mm), LS is a land slope factor accounting for the slope angle and the upslope contributing area. *ProfCurv* describes the shape of the slope profile where a positive value indicates a concave shape and a negative value represents a convex shape, calculated using the tool *profcurv* (PCRaster, 2013), and *TanCurv* describes the tangential curvature, where a positive value represents diversion of flow and a negative value represents concentration of flow, calculated using the tool *plancurv* (PCRaster, 2013). Finally, 4 is a scaling factor representing the cell size of the maps (2 m x 2 m). A more detailed model description can be found in Paper III.

3.4.3 Calibration strategy

To calibrate the model, long-term monitoring data from each catchment were used, with available data-sets split into a calibration and validation period. The validation period was set to be the same length for all catchments (2013-2021). The Python optimisation/calibration package SPOTPY (Houska et al., 2015) was implemented, and three pseudo parameters, p_{par}, k_{par} and c_{par} that caused a percentage change in the initial p, k and c values during the calibration were calibrated. This method was chosen since p and k values differ depending on soil texture, while c values change depending on land use, resulting in multiple values for each parameter. Monte Carlo (MC) simulations were chosen as the calibration strategy, (see Houska (2021) for further description). Kling-Gupta efficiency (KGE) (Gupta et al., 2009) was used as an evaluation equation (-Inf – 1), where a value close to 1 represents a perfect model fit. KGE was chosen as an evaluation measure based on its ability to account for the high variability in hydrological data (and SS losses in this case). A total of 1000 MC simulations were run for each catchment for the calibration period, and the top 50 best parameter combinations were chosen and run for the validation period, since a certain degree of equifinality (equally good model fit for several parameter combinations) was found during the calibration. For further details, see Paper III.

3.5 Statistical analysis

3.5.1 Time trend analysis (Papers I & IV)

In Paper I, to investigate whether fw concentrations of PP, SS, RP, TP and PP/SS ratio changed over time in the 11 monitoring catchments, a two-sided Mann-Kendall test was used. Trend analyses were also performed on monthly discharge, and on monthly loads.

In Paper IV, a generalised additive model (GAM) as described in von Brömssen et al. (2021) was used to investigate changes in water quality parameters in Lake Mälaren's tributaries based on raw concentrations, monthly fw concentrations and monthly loads.

3.5.2 Linear regressions, relations and multivariate analysis (Papers I, II & IV)

To explore relationships between water quality parameters and catchment characteristics in Paper I, linear regressions of monthly flow-weighted concentrations of different in-stream parameters were performed using JMP® 13.0.0 (2019). Principal Components Analysis (PCA) for catchment characteristics, regression parameters from linear regressions and total average fw concentrations for all water quality parameters was carried out in Canoco 5. Catchment characteristics included in the PCA were e.g. mean clay content, percentage agricultural land, dominating crop type and plant available P, determined as P extracted by ammonium lactate/acetic acid (P-AL) at pH 3.75 (Egnér et al., 1960). The P-AL content was based on samples collected in different projects, resulting in a varying number of samples for each catchment in several years. An average value was used, and as the P-AL value was rather stable, the difference in sampling years was assumed to be insignificant (Djodjic & Spännar, 2012). Based on correlations identified in PCA, multiple linear regressions were calculated to explain the variance in PP and SS, using total average values and monthly fw concentrations. Factor of variation (FV) was calculated as the ratio between the highest and lowest value obtained for each parameter. A similar procedure as in Paper I was followed for statistical analysis in Paper IV, apart from PCA being the starting point for further multiple regressions. Linear regressions based on Paper I were performed to test relationships identified in Paper I.

In Paper II, two-sided Wilcoxon rank sum tests were performed to determine significant differences in P fractions between and within catchments. All P fractionation results presented are a mean value of three sub samples. Linear regressions were performed in Paper II to explore relationships between water quality parameters and P fractions.

A p-value<0.05 was set as the significance level in all papers. In Papers II-IV, R software was used for all statistical analyses (R 3.6.2 in Paper II, R 4.0.3 in Papers III & IV) (R Core Team, 2020).

4. Results and discussion

4.1 Processes and variables controlling mobilisation and transfer of suspended solids and phosphorus

The catchment and its properties, specifically soil texture and percentage of agricultural land, were found to play the main role in controlling the transfer of SS and P to streams (fulfilling research objective I). Suspended solids were found to work as a vector for P transport, and the findings from small agricultural headwater catchments scale up well to larger, mixed land use catchments (research objective IV). In addition, temporal and spatial patterns of SS losses were successfully identified by distributed dynamic high-resolution modelling (research objective III). This was achieved by accounting for catchment properties, i.e. land use through land use cover value (*c*), soil textural distribution through soil permeability (*p*) and soil erodibility (*k*) factors. Calibration and validation of six catchments produced results that can be used on other, similar unmonitored catchments. This section presents the results from Papers I, III and IV**.**

4.1.1 Relationships between water quality and catchment characteristics (Papers I, III & IV)

There was a positive correlation between P and SS concentrations and average clay content, according to the PCA results for the small agricultural monitoring catchments (Paper I). Similar results were found for the larger, more mixed land use catchments in Paper IV, but in that case upstream catchment area and percentage of surface water area in the catchment had a negative correlation with P and SS concentrations.

Monthly fw SS concentrations were a strong explanatory variable for monthly fw PP concentrations ($R^2=0.67$, N=1441, p-value<0.001), likewise for total average values of PP and SS ($R^2=0.98$, N=11, p<0.001). The relationship between total fw average values of PP and SS was monotonic, but did not seem to be linear (Figure 6). A power law equation described the relationship better, as there seemed to be a steeper increase in PP with increasing SS in the lower ranges (and also lower clay content and share agricultural land in the catchment), and then a more linear relationship for the catchments with higher losses and more clay soils and agricultural land (Figure 6). The higher R^2 value for the linear regression can be explained by one extreme catchment (O18) which seemed to drive the relationship towards linearity. However, excluding this catchment from the relationship still resulted in a high degree of explained variance.

The power law relationship was tested for the larger, mixed land use catchments in Paper IV. It is worth noting that these catchments are all in the lower range of PP and SS losses (falling within the dashed red box in Figure 6). Even though the losses of both PP and SS were much lower for these larger catchments, the relationship was still valid ($R^2=0.74$, N=30, p<0.001). There was a larger variability for these catchments, but catchments with a lower clay content and less agricultural land were still on the lower range of losses, and catchments with higher clay content and more agricultural land appeared to have higher losses (Figure 6, insert). The method used for analysing RP (and thereby also for determination of PP) in Paper IV differed from that in the other papers, which probably also contributed to a difference in the relationship.

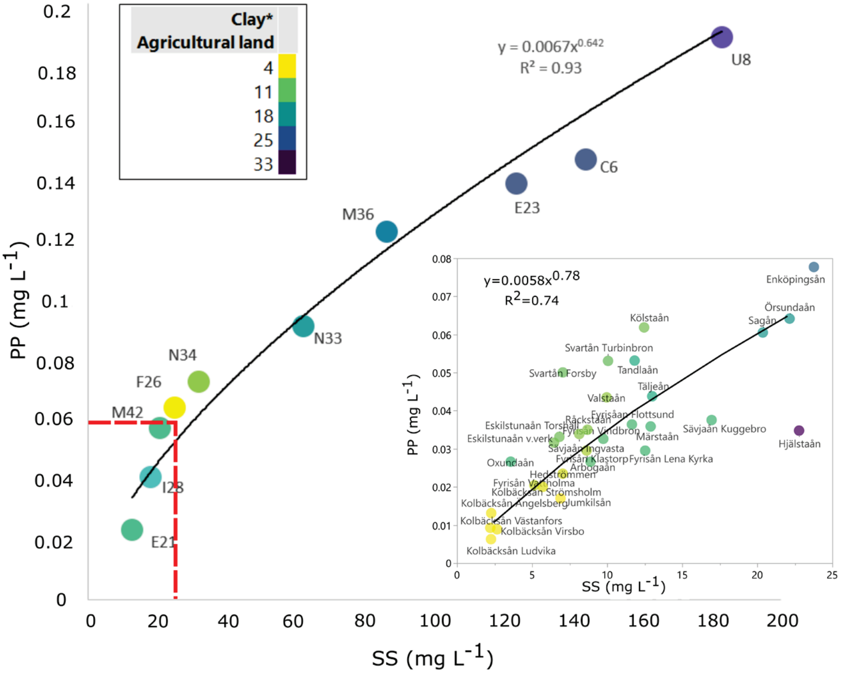

Figure 6. Main diagram: Flow-weighted total average concentrations of particulate phosphorus (PP) and suspended solids (SS) in the agricultural monitoring catchments studied in Paper I, excluding extreme catchment (O18). Insert: Corresponding graph for catchments to tributaries of Lake Mälaren studied in Paper IV. The solid black lines represents a power law relationship. The dashed red line in the main graph encloses the positions of all catchments studied in Paper IV. The colours of the dots represents clay content x share agricultural land within the catchment. Adapted from Papers I and IV.

Suspended solids concentrations was established as the main correlating factor with PP, while the product of clay content and share of agricultural land was the main correlating factor with log(SS) (R^2=0.75, N=11, p<0.001) in the small agricultural catchments in Paper I. In linear regression, silt content also merged as an important predictor variable for SS and log(SS). However, it did not add any more significance in comparison with clay content. In this regard too, the extreme catchment O18 seemed to influence the relationship significantly and that between SS and silt content towards linearity, and that between SS and clay content away from linearity. On removing catchment O18, clay content became a much stronger predictor variable (R^2=0.91 for clay vs. R^2=0.66 for silt) than it was when O18 was included (R^2=0.36 vs. 0.77).

In Paper III, the importance of catchment properties in the form of soil texture and land use was used to model transport of SS: The parameters *k* (soil erodibility) and *p* (soil permeability) can be described as proxies for the effect of soil texture (clay and silt content) on SS losses, while *c* (land use cover) is a proxy for land use, including proportion of agricultural land. The high KGE values obtained (Figure 8) and the proximity of simulated values to observed values again confirmed the importance of catchment properties for SS transport.

The relationship obtained for SS and catchment properties was also scaled up and tested for the larger catchments in Paper IV with good results (R^2=0.59, N=30, $p<0.001$). However, in multiple linear regression for SS, percentage of surface water area (lakes and watercourses) in the catchment, together with percentage of arable land and clay content were the most significant predictor variables (R^2=0.76, N=30, $p<0.001$). Since the small catchments in Paper I have no surface waters, it is reasonable that this variable influence the larger catchments containing surface waters. Lakes can retain SS and thus slow down the transport of SS to rivers and streams (Brandt, 1990).

The PCA results (Paper IV) indicated that larger upstream catchment area also resulted in lower fw concentrations of SS and P. Low-relief landscapes in larger catchments, such as the flat landscape where Norrström is located, tend to encourage sediment deposition and storage and result in lower SS transport and concentrations (Woodward & Foster, 1997). This negative relationship between catchment area and SS transport has also been identified elsewhere, e.g. by Milliman and Syvitski (1992) in a study of 280 rivers discharging into oceans across the world. The SS concentrations in the majority of the small catchments in Paper I were higher than in the catchments in Paper IV. Similar results were obtained by Brandt (1990) who concluded, based on Swedish monitoring data for 36 stations, that the SS concentrations in small catchments can be more than twice the mean value of those in nearby larger basins due to settlement of suspended material in lakes, reservoirs and floodplains.

Average clay content was negatively correlated with the ratio between PP and SS according to the PCA results for the small agricultural catchments in Paper I, as well as the regression slope of the PP-SS relationship. Exploring this further, a natural logarithmic decrease was found for the PP/SS ratio with increasing clay content, while the decrease was stagnant at a clay content of around 30%. The negative correlation between average clay content and the regression slope for the PP-SS relationship indicates that less P is transported per SS particle in catchments with higher SS concentrations and higher clay content. Soil erosion is selective with regards to soil particle size (Sharpley, 1980) resulting in greater transport and mobilisation of smaller clay particles. Clay particles have a higher specific surface area and thus higher P sorption potential compared with coarser soil particles (silt and sand). This results in enrichment ratios, i.e., a higher P content in eroded sediment particles compared with the P content of bulk soil. However, as Kleinman et al. (2011) state, ‘‘sediment P enrichment ratios tend to decline with increasing rates of erosion (and greater removal of larger soil particles and aggregates)”. This statement is in agreement with the finding in this thesis of decreased PP/SS ratio with increasing clay content, suggesting that catchments with soil textures more prone to erosion have lower PP/SS (Villa Solís, 2014). High clay content catchments were found to have higher SS transports, but less P transported per unit SS. Further, Villa Solís (2014) showed a strong decrease in P enrichment ratio in small agricultural catchments with increasing concentrations of SS. Catchments with a coarser soil texture seem to have higher enrichment of P on particles as they usually have lower SS concentrations.

No significant correlations were found between P concentrations in the stream and P content in the soil (P-AL) (Paper I). This could be the result of using an average value of P-AL for the entire catchment, since the variation in P-AL was quite great in some catchments (standard deviation: 1.73-12.75). Due to the episodic nature of P losses and the importance of CSAs as discussed previously and shown in Paper III, there is a possibility of a relationship between P-AL content in CSAs and P concentrations in stream water. Sampling in CSAs in close conjunction to expected flow events would be a possible way to confirm this. In addition, the strong correlation between SS and PP (Figure 6) (and thus also TP) might override potential correlations between P in the stream and P-AL. Among the small catchments studied in Paper I, fine textured soil catchments (O18, U8 , C6 and E23) had lower P-AL content (Figure A1) than coarser-textured soil catchments with higher P-AL content (E21, N34 and M42). These coarser-textured catchments were also found to be less erosion prone and had the lowest observed PP and TP losses. According to previous work by Withers et al. (2009), the P enrichment ratio of SS particles declines exponentially with increasing soil P content, with relatively small increases in PP on SS when soil P increased from average to high fertility status. In the small agricultural catchments studied in Paper I, the FV-value of P-AL content (between catchment variation, FV=3.4) was markedly lower than the variation in TP and PP concentrations (FV= 8.5, and 17 respectively). Goyette et al. (2018) defined a threshold for accumulated P in soils of 2.1 t km^{-2} with exceedance of this threshold expected to lead to linear increases in P losses to streams. Since all these small agricultural catchments studied in this thesis have more than 50% agricultural land, and since P accumulation on agricultural soils in Sweden are between 59-75 t km^{-2} (Andersson et al., 1998), they should all be above this threshold. This could partly explain the lack of connection to P-AL, since if this threshold is already passed there will be no connection to specific concentrations in the soil. As discussed, measured P load at the catchment outlet can derive from a remobilised secondary P source rather than from direct P delivery from catchment sources (Jarvie et al., 2013).

4.1.2 Water quality trends (Papers I & IV)

Studying water quality trends in the catchments in Paper I, mainly revealed trends in the ratio of PP/SS. An increasing trend in the PP/SS ratio was found in eight of the 11 catchments, even when no trends in either PP or SS could be detected. Five of the catchments (C6, E23, M36, U8 and O18) have medium to high clay content. There could have been small changes in PP or SS that were too small to be significant by themselves, but became significant when combined in a ratio. The observed increase in PP/SS ratio can also point towards a shift in the size of particles being transported from fields to the streams, with a higher amount of smaller, P rich clay particles being transported (Kleinman et al., 2011). The behavior seen in some catchments where there was either only a change in the ratio, or in one of the concentrations, strengthens this statement. Despite the increases observed in PP/SS ratio, and in some concentrations, no significant increases in the different loads were found, except for in catchment U8. In three of these eight catchments, a significant decrease in discharge was found. In U8, despite an increase in PP/SS ratio, there was a significant decrease in the loads of PP, SS and TP, probably due to a significant decreasing trend in water discharge. U8 is one of the catchments that participated in a Swedish project focusing on measures to decrease nutrient losses called *Focus on Phosphorus* (Malgeryd et al., 2015). One reason for the lack of decreasing trends in loads despite decreasing discharge may be the increase in PP/SS ratios and some concentrations. The results indicated a change in water quality, with approximately the same amount of P being exported from the catchments into the streams with less volume of water, leading to increasing concentrations of finer, more P rich particles being lost from the soil to the stream. Due to the difference in determination of RP (and thus PP) in Paper IV, the changes in PP/SS ratio in the larger catchments were not studied.

Few trends were discovered in the different water quality parameters studied in Paper IV, for raw concentrations, fw concentrations and loads. Barely any trends were detected for SS and thus detection of trends in TP was not expected, due to their strong correlation. Previous studies have detected decreasing TP trends in the study area (Persson, 2001; Sonesten et al., 2013), although their analyses included the time period in the late 1970s when a P removal step was implemented in wastewater treatment plants (Figure 1), contributing to these detected trends. Since that time, most of the P losses can be attributed to diffuse sources (Räike et al., 2020). Despite the lack of TP trends, a temporal decreasing trend was detected in raw RP concentrations in several catchments around the years 2010-2015 (Figure 7). Some of these trends can be attributed to a shift in laboratory methodology with background correction of RP concentrations starting 2014, which can cause what looks like a shift from higher to lower concentrations in the time series (von Brömssen et al., 2014). However, in all Kolbäcksån catchments the decrease in raw RP concentrations happened around 2010, and should not have been affected by background corrections. The few decreasing trends detected in TP were found in the forested catchments Kolbäcksån Strömsholm, Kolbäcksån Västanfors and Kolbäcksån Virsbo and the more agricultural catchments Sävjaån Kuggebro and Tandlaån (Figure 7). The forested catchments had low P concentrations throughout the study period. Ongoing oligotrophication has been identified in several forested-catchment Swedish lakes with minimal anthropogenic impact (Huser et al., 2018), which may be what was detected in this study as well. Huser et al. (2018) found increases in dissolved organic carbon (DOC) in many of these lakes and concluded that this DOC increase masked decreases in TP in several cases. Further, the TP concentrations in the forested catchments studied in this thesis were already at a low level, and if they keep decreasing to below the detection limit, future trends and potential oligotrophication will be difficult to identify. Sävjaån Kuggebro and Tandlaån have a considerable amount of arable land (>20%) and the temporal decreasing trend in RP, could possibly be attributed to the background corrections mentioned, while the decreasing trend for TP in Tandlaån might be attributable to a combination of lower amounts of P applied to the fields and higher yields (see Paper IV).

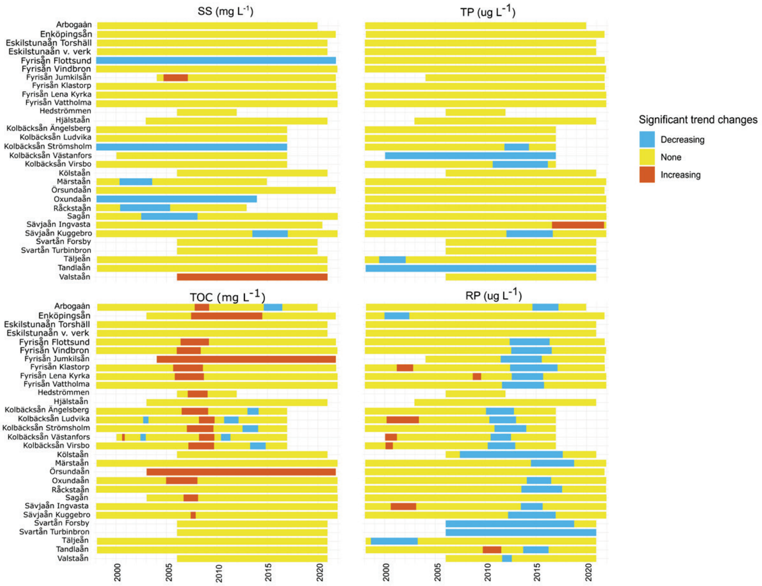

Figure 7. Water quality trends in terms of raw concentrations of suspended solids (SS), total phosphorus (TP), total organic carbon (TOC) and phosphate P (RP) in the catchments studied in Paper IV. Yellow indicates no significant changes, red a significant increasing trend and blue a significant decreasing trend. Adapted from Paper IV.

In addition to RP trends, temporal increases in TOC raw concentrations were detected in several catchments (Figure 7). A similar pattern was observed by Eklöf et al. (2021) studying changes in TOC in Swedish rivers, where previous increases in TOC had been reported. They detected a similar pattern as seen in Paper IV, i.e. a temporal increase that seemed to cease. This indicates that the brownification which has been happening in many places in Northern Europe may have ceased.

The rate of implementation of mitigation measures in the catchments in Paper IV was in general low (<5% of arable land). The most common measures were structure liming and spring tillage, where structure liming is intended to decrease particle and P losses and spring tillage is mainly intended to reduce N losses. There was also a low rate of implementation of mitigation measures targeting CSAs such as adjusted buffer zones, and constructed wetlands which must be designed with optimal placement for highest effect (Djodjic et al., 2020). However, some catchments had implemented a considerable amount of measures, e.g. Kölstaån (25% of arable land), Oxundaån (22%) and Enköpingsån (16%). Oxundaån with a high implementation rate of structure liming, displayed a decreasing trend in SS raw concentrations (Figure 7). Otherwise, no real connections between implemented measures and trends were seen. Beside the low implementation rate (percentage of catchment land affected) and poor targeting, there are several other possible explanations for this lack of detectable connections. These include changing environmental conditions in the area, such as increased precipitation and higher temperatures during winter (Sonesten et al., 2013), indications of a changing climate, which could counteract the effects of mitigation measures (Räike et al., 2020). It could also simply be the case that mitigation measures help to keep concentrations from increasing, so no trend will be detected. Finally, some of the mitigation measures were implemented rather recently. Catchments with a higher percentage of implemented measures (Kölstaån, Oxundaån, Råckstaån, Sagån) need to be carefully monitored in the coming years to assess the effects of implemented measures.

In Paper I, where three catchments (U8, E23 and N33) were part of a separate project focusing on mitigation measures, a detectable decreasing trend was only seen in U8. This highlights the need to continue monitoring efforts after implementation of mitigation measures, to identify potential effects. In addition, there is a lag time between implementation of a mitigation measure and when an effect can be seen, which could mean that changes in concentrations due to recently implemented mitigation measures will occur years into the future. Furthermore, the effect of mitigation measures could be counteracted by legacy P sources within stream sediments (Lannergård et al., 2020), which can keep P concentrations at a high level even when external sources are decreased or cut off.

4.1.3 Temporal and spatial erosion patterns (Paper III)

The model developed in Paper III generally simulated erosion and deposition patterns and transported SS amounts well over both the calibration and validation period, for all catchments studied (Figure 8). The KGE values for the best parameter combination in the calibration period were all >0.45 and those for the validation period were all >0.64. Catchment M42 had the lowest KGE value during calibration (0.45), but this greatly improved during the validation period to 0.77. The low calibration value was attributable to one large SS peak in the beginning of the calibration period that was not captured by the model at all (data not shown). For the other catchments, the KGE values during calibration and validation were more similar. Catchments with finer soil texture and higher SS transport (C6, U8, M36 and E23), were better simulated by the model than catchments with coarser textured soils and lower SS transport (M42 and E21). As previously mentioned, coarse-textured soils may have alternative dominating pathways for P transport. In similar catchments, other pathways and processes for P losses should thus be the focus, e.g. leaching through the soil profile and optimal nutrient content in the soil (Djodjic et al., 2018).

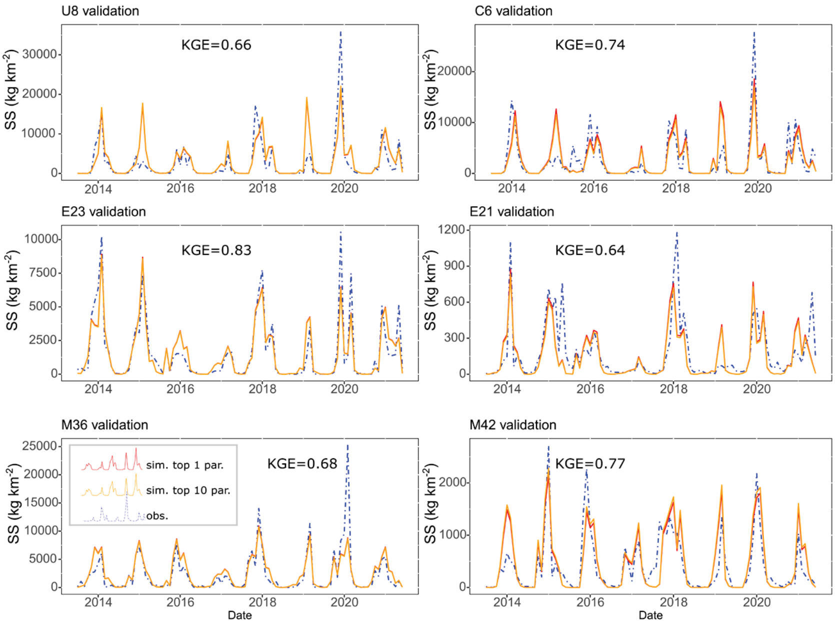

Figure 8. Simulated and observed suspended solids (SS) transport in the six study catchments in Paper III during the validation period. Dashed blue lines indicates observed values, red solid lines indicates values simulated by the best parameter combination, solid orange lines indicate values simulated by the 10th best parameter combination. Kling-Gupta efficiency (KGE) values are shown in the respective panels. Adapted from Paper III.

Annual transport of SS in the study catchments was low in comparison with erosion levels in other European and Nordic countries. Comparing Norway, Sweden and Denmark, Norway has considerably higher erosion levels than both Sweden and Denmark (Bechmann et al., 2008), potentially due to differences in topography. A study by Ulén et al. (2012) examining actual erosion rates in the Nordic countries used different risk erosion classes for standard autumn ploughing in Norway that ranged from low (<500 kg ha^{-1} year^{-1}), to medium (500-2000 kg ha^{-1} year^{-1}), high (2000-8000 kg ha^{-1} year^{-1}) and very high (>8000 kg ha^{-1} year^{-1}). Two studied Swedish sites included in the study were classed as medium and low risk while two sites in Norway and one in Finland were classed as high risk (Ulén et al., 2012). The catchments studied in this thesis would be in the low or medium risk class. Even though the total erosion losses were not high compared with those in other countries, critical events where a lot of material is lost at the same time can still can have major impacts on receiving waters. For example, in certain conditions extreme flow events can create gully erosion that leads to formation of channels, transporting large amounts of SS. Examples of this have been seen in an agricultural field in Krusenberg, Sweden (Villa Solís, 2014). The connection between mobilisation and losses of particles and P losses is well-known as established in Paper I and confirmed in Paper IV. These large amounts of SS losses and associated high P losses, have negative impacts on water quality.

The spatial erosion/deposition patterns followed the topography lines in the catchments more distinctly than CSAs previously modelled by a steady state approach as in Djodjic and Markensten (2019), which are marked with light blue lines in the map in Figure 9. Erosion/deposition patterns were also more visible around wetter areas in the fields. Monthly runoff was used in this thesis, while in Djodjic and Markensten (2019) runoff as a sum of three winter/spring months (February-April) was used. This will naturally lead to higher simulated surface runoff and transported SS, and hence more distinct CSAs. The accumulated erosion mainly followed the ditches and streams in the catchments, as expected (Figure 9).

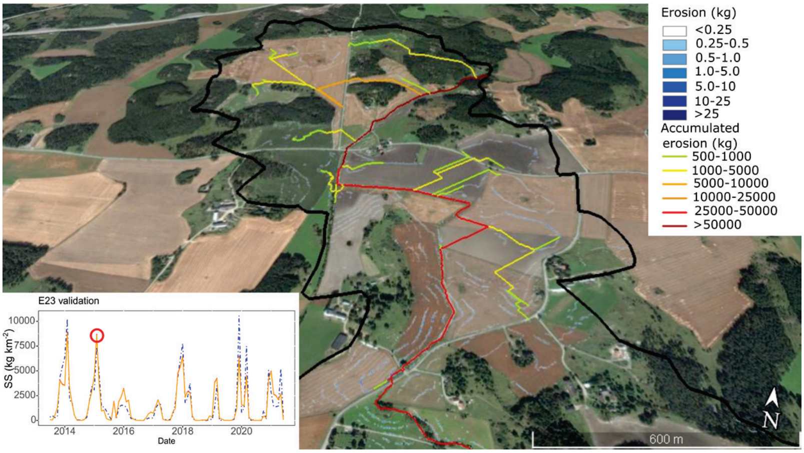

Figure 9. Simulated erosion deposition patterns in catchment E23 from February 2015. The accumulation lines change from green to red, CSAs are displayed in blue. The red circle in the insert graph indicates the simulated time point shown in the main image. Adapted from Paper III.

Upscaling and studying SS transport in the form of modelling was successful, confirming that a range of catchments can be successfully modelled. Calibration and validation of the model using high quality monitoring data resulted in a good model fit of all catchments. Once again, as found in Papers I and IV, accounting for the land use distribution in general and proportion of arable land in particular (parameter c in the model) as well as soil textural distribution (parameters k and p), gives us important understanding of the transport of SS, and consequently PP. By using our approach and mentioned nationally available input variables, modelling of SS transport on similar, but unmonitored catchments is possible. This can be especially useful for farmers and stakeholders to create and target mitigation measures where and when they are most effective.

4.2 Distribution of P fractions in sediment and seasonal changes (Paper II)

There was a significant difference in the dominant P fractions in all three catchments sampled in Paper II, even though they were found to have quite similar soil type and TP and SS losses. This difference in distribution of P fractions is likely due to differences in geology, soil clay content, flow conditions and external P sources (research objective II). A clear seasonal pattern in Fe-P in FSS was discovered in all three catchments. This section presents and discuss the findings in Paper II.

4.2.1 Dominant P fractions

Different P fractions dominated in FSS in the three catchments (C6, U8 and E23). Wilcoxon rank sum tests showed that Al-P was significantly greater than all other fractions in U8, but also greater than in the other catchments (Figure 10c). For C6, Fe-P was determined as dominating, while org-P dominated in E23 (Figure 10b, 10d). The dominance of Al-P in U8 can probably be attributed to the high clay content in the soil, with clay minerals containing Al. The bedrock mineralogy in C6 does not imply a high Fe content, although in the areas around the location of C6 there are iron-rich soils (Djodjic, 2015). The most probable explanation for the Fe-P dominance is Fe hydroxides/oxides present in the sediment and soil. The dominance of org-P in E23 can probably be explained by larger input of manure and a higher stocking density in the E23 area, as org-P was frequently high in FSS but not in streambed sediment, suggesting presence of org-P forms that does not settle in the streambed.

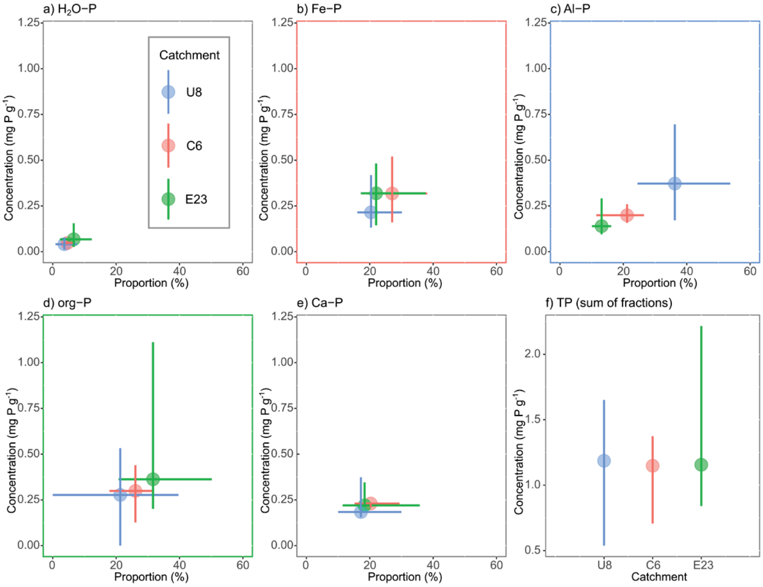

Figure 10. (a-f) Range of different phosphorus (P) fractions in fluvial suspended sediment (FSS). The y-axes show concentrations and the x-axes proportion of the fraction. Line length runs from minimum to maximum value, while dots represents the median value. The frames are colour-coded (except black, see key) by the catchment in which the fraction is dominant. Adapted from Paper II.

The proportion of H_2O-P in FSS was low in all catchments. Naturally, most of the loosely bound P will be used up by plants or microorganisms as soon as it enters the stream or will be further transported since FSS is in constant motion. It is also possible that during sampling, sample storage and extraction, some H_2O-P was determined as Fe-P. This is a reason for referring to both of these fractions as mobile P. The behaviour was likely similar for H_2O-P in the active streambed sediment, where H_2O-P concentrations were low in all catchments. Low H_2O-P concentrations in streambed sediment were also found by McDowell et al. (2020), with Fe-P as the general dominating fraction at their sampling sites. This seems to be quite consistent with previous reports of low H_2O-P concentrations (or corresponding fractions in other fractionation schemes) in both streambed sediment and lake sediment (Kaiserli et al., 2002, McDowell et al., 2020, Pettersson, 1998).

All three catchments had similar TP concentrations in FSS (Figure 10f), but there was still a large difference in the dominant fractions. There are marked differences in the bioavailability of the fractions, which highlights the importance of studying the different fractions, since important information may be missed by only analysing TP.

The concentration ranges of the P fractions in streambed sediment were similar to those in FSS (TP 0.32-2.32 mg g^{-1} and 0.53-2.21 mg g^{-1}, respectively). There was some resemblance in the distribution of fractions in FSS and streambed sediment, mainly in catchments U8 and C6 (Figure 11), with similar dominating fractions. This implies that P found in FSS and streambed sediment has the same origin, i.e. surrounding fields, and that FSS is partially remobilised from the streambed sediment. In E23, there was no resemblance between FSS and streambed sediment and the streambed was also different from that in U8 and C6, being much coarser and providing less potential for remobilisation from the streambed to FSS. This could again be due to the dominance of org-P in FSS and very low org-P concentrations in the streambed sediment, shifting the distribution in favour of other fractions. Apart from containing coarser material, the streambed in E23 also included stones and twigs, while the streambeds in U8 and C6 consisted mainly of clay, overlain by a layer of organic material. This could have affected exchange of P between the streambed and FSS. To obtain a clearer picture of the exchange processes between FSS and streambed sediment, it would be necessary to perform more frequent streambed sediment sampling in conjunction with FSS sampling.

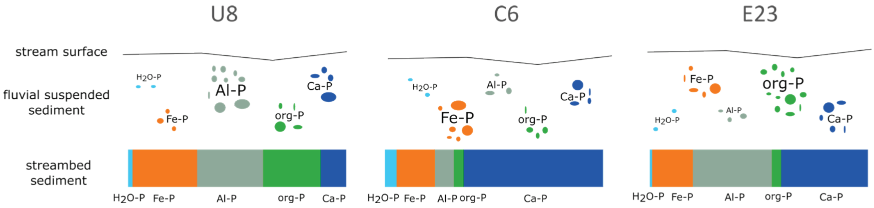

Figure 11. Illustration of phosphorus (P) fractionation results from Paper III, where the colours represents the different fractions. The lower bars show the proportions in the streambed sediment, while icon font size and particle sizes indicate the proportions in the fluvial suspended sediment.

4.2.2 Seasonal changes in phosphorus fraction in fluvial suspended sediment

All P fractions in FSS changed over the study period, however, the most prominent change was observed in the mobile P fractions and particularly in Fe-P (Figure 12b). Iron-bound-P is usually the largest pool of bioavailable P, as was also the case here with very low H_2O-P concentrations throughout. This is, due to the high sensitivity to changes in redox potential, causing a high potential for release of Fe-P from sediments under changing conditions (Li et al., 2016). The pattern of change was similar in all catchments, with an increasing concentration during the summer and a decreasing concentration during the winter periods. This coincided with periods of low flow during the summer and high flow during the winter, displaying an almost reverse pattern to Fe-P (Figure 12a). Changes in fw RP concentrations in the water column displayed a similar pattern to flow (Figure 12a, 12c), however no significant relationship was found between mobile P concentrations in the FSS and RP in the water column. High Fe-P concentrations in FSS during summer can be promoted by reducing conditions at the streambed sediment surface, due to high microbial and biological activity in combination with low flow (Sallade & Sims, 1997) or due to intrusion of anoxic groundwater (Krause et al., 2011). These conditions in combination with higher temperatures during the summer, can cause dissolution and release of ferric Fe and phosphate from the streambed into the water column (Records et al., 2016, Smolders et al., 2017, Sallade & Sims, 1997). In a water column with potentially more aerobic conditions, Fe oxidation may occur converting Fe^{2+} to ferric Fe^{3+}, which can react with water column RP. This Fe oxidation and sorption of P can occur on fluvial sediment particles, resulting in higher Fe-P concentrations in FSS, and lower RP concentrations in the water column. In the two smaller streams (U8 and E23), a potential relationship between RP and Fe-P was evident (Figure 12). These two streams have almost stagnant flow during the summer, favouring reducing conditions near the streambed sediment surface. The stream in C6 is much larger, remains in constant motion and rarely stagnates, and did not display the same pattern between Fe-P and RP as seen in the other two streams (Figure 12).

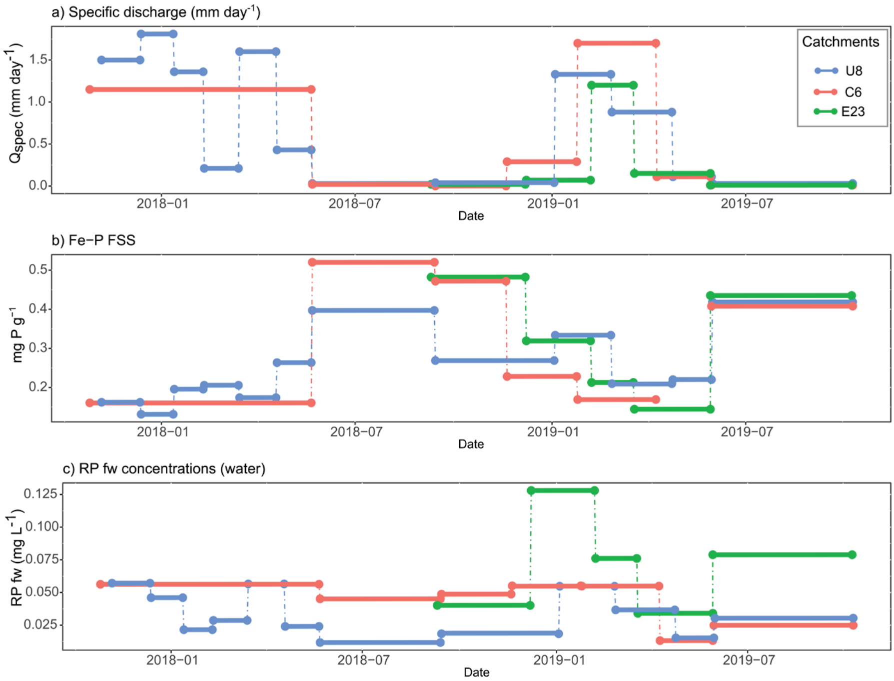

Figure 12. a) Specific stream discharge (mm day-1) from the three catchments over the sampling period, b) changes in iron-bound phosphorus (Fe-P) concentrations (mg g-1) in fluvial suspended sediment (FSS) over the sampling period and c) changes in flow-weighted (fw) concentrations of phosphate P (RP) in the water column. The solid bars indicate periods when the Phillips samplers were placed in the stream and colours represent the different catchments. Adapted from Paper II.

There are ongoing discussions on the bioavailability of different P fractions. Actual bioavailability depends on environmental conditions such as redox conditions (Records et al., 2016, Sharpley, 1993), pH (Lukkari et al., 2007) and turbulence (Withers & Jarvie, 2008). The most bioavailable fraction is H_2O-P, with PO_4^{3-} being directly available for uptake by aquatic organisms (Zhou et al., 2001). Apart from H_2O-P and Fe-P, org-P is also considered potentially bioavailable (Kaiserli et al., 2002), since it can be mineralised to RP (Reitzel et al., 2005, Schütz et al., 2017). Aluminium is sensitive to low and high pH, Al-P is considered stable in the pH range of surface waters (Stumm & Morgan, 1995). Calcium-bound P is usually considered unavailable, or even inert since it is generally bound in mineral lattices (Lukkari et al., 2007). More studies are needed on the potential bioavailability of the different P fractions, and especially effects of environmental conditions on P fractions in FSS and streambed sediment, since these can differ between headwater streams, larger rivers and lakes (Lannergård et al., 2020).

5. Phosphorus and particle losses from arable land – the way forward

5.1 Catchment properties

This thesis showed that the surrounding catchment and its properties play a major role in losses of SS and P to streams. In general, higher losses of P occur from catchments with a high clay content than from catchments with sandy soils. This is due to several factors, e.g. the higher P sorption capacity of clay particles and finer-textured soils being more erosion-prone and thus more vulnerable to SS losses. In addition, clay soils are naturally P-rich, especially the young clay soils found in Sweden. These clay soils have been used for agriculture for a long time due to their nutrient-rich nature and high water-holding capacity, which has led to continuous build-up of P. This thesis also showed that large SS losses leads to large P losses. All these factors combined lead to higher P losses from clay soils than from sandy soils. Even when inputs of P to clay soils in the form of fertilizers or manure are in balance with (or lower than) outputs in the form of harvested crops, there can still be P losses from the system. A study by Goyette et al. (2018) examining historical P accumulation in 23 catchments in Canada, found a critical threshold of 2.1 t P km^{-2} with exceedance of this threshold leading to linear increases in P losses to nearby streams. Many of the catchments in Paper IV already exceeds this threshold of P accumulation (see Paper IV), helping to maintain high P concentrations in the streams. As the small headwater catchments studied in Papers I-III are dominated by arable land, these catchments almost certainly exceed the proposed threshold too. A certain level of P losses from agricultural fields is inevitable with a growing population and increased demand for food production. The aim should be to restrict losses to an acceptable level that will not impact water quality. Apart from P accumulation in soils, legacy P in stream and lake sediment will also contribute to elevated P concentrations in streams. The critical threshold of 2.1 t P km^{-2} could be used as a target, i.e. with P accumulation in soils kept below the threshold value, minimising the risk of further losses.

5.2 Importance for stakeholders and farmers – mitigation measures and their implementation

Correct field placement, timing and type of mitigation measures are key to decreasing losses from fields to streams, and farmers know their fields best. Therefore, clear communication between scientists, stakeholders and farmers is essential when designing measures and fertilisation strategies to minimise P losses. Considering field properties in the form of soil texture (clay and silt content) will help in identifying which fields to prioritise. Use of modelling and resulting maps as a communication tool has great potential to make modelling results comprehensible and concrete. Focusing resources where they have most effect will benefit both stakeholders and farmers, e.g. constructed wetlands can be modelled in advance to find the optimal placement and size of this mitigation measure within catchments for highest possible retention of P (Djodjic et al., 2020). Using modelled maps of CSAs for placement of adjusted buffer zones is another example of how to increase the efficiency of mitigation measures. Further, to monitor, evaluate and report effects of mitigation measures is essential to give both farmers and stakeholders the right guidance. In addition, the current variation in both SS and P losses will probably increase with a changing climate and more extreme precipitation and flow events, emphasising the need for targeted mitigation measures, in both time and space.

6. Conclusions and future outlook

The main aims with this thesis were to gain a deeper understanding of the relationship between suspended material and P in agricultural streams, to study the quantity and quality of P on suspended material and to identify the role of the catchment and its properties. Quantitative evidence obtained in Papers I-IV demonstrated that SS, governed by catchment soil texture distribution and land use, works as a vector for P transport to streams. I have been able to deepen, expand and refine previous knowledge (Papers I, III and IV), and add new knowledge on sequential P fractionation on FSS (Paper II). The main conclusions were as follows:

- Catchment characteristics in the form of soil texture (specifically clay content) and land use (amount agricultural land) determines SS losses, and thus also P losses.
- The P content in FSS is within in the same range as the P content in streambed sediment, and the P fraction that dominates depends on catchment properties, such as soil texture, geology and flow conditions.
- Seasonal changes in P fractions (specifically for Fe-P) in FSS occur in all catchments, which is important for potential algal uptake during the growing seasons.
- High-quality monitoring data can be used for modelling SS transport, both spatially and temporally. The modelling approach developed in this thesis can be used with available input data on topography, land use and soil distribution to model other similar, unmonitored catchments.
- Water quality relationships identified for P and SS in headwater catchments can be scaled up and used for larger, mixed land use

catchments. This is promising for future work as headwater catchment findings can be applied to larger, more complex systems. Few water quality trends were detected in the catchments discharging into Lake Mälaren, which indicates stability of the water quality relationships over time, but also a need to improve water quality in these catchments.

6.1 Areas for future work

The work in this thesis has added to the knowledge about P and SS transfer from agriculture to surface waters, in particular how the catchment and its properties contributes and determines the amount of losses. It also improved understanding of the role of FSS in P transport and of how the P fractions in FSS differs between catchments and seasons. Future studies should examine the bioavailability of the different P fractions. In general, H_2O-P, Fe-P and parts of org-P are considered bioavailable, but there is a possibility that other fractions can become bioavailable under certain circumstances. Using detailed techniques such as ^{31}P NMR and XANES in combination with sequential P fractionation could be a promising approach. In addition, most of previous research has been done on lake sediment or streambed sediment, while our study is among the few studies to date to study P fractions in FSS. The environmental conditions in a lake and a stream are different, and will thus affect the fractions differently.

The potential for scaling up findings from studies on headwaters to larger catchments is great, and we have just scratched the surface of this topic here. Using available monitoring data is a great way to test found relations on larger catchments, which is why it is crucial to keep current monitoring. Future studies could try applying findings from great lakes (such as Lake Mälaren) to seas, which could aid in the work to combat eutrophication on larger scales.

There is definitely a need for mitigation measures implemented in a catchment to be followed up. Better planning before implementing measures, to enable correct placement and timing, is essential. The modelling results obtained in this thesis can be used in future studies on other, similar unmonitored catchments for temporal and spatial quantification of SS losses, to determine the optimal timing and placement of mitigation measures. The work in Paper IV shows that a higher implementation rate of mitigation measures is possible and necessary to improve water quality. Again, keeping current monitoring in place is critical, in order to evaluate the effect of mitigation measures and detect future trends and changes in water quality.

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Populärvetenskaplig sammanfattning

I ett land med tusentals sjöar och desto fler åar och bäckar, kan det ibland vara lätt att ta vatten för givet. Vattnet i landskapet har otaliga användningsområden som exempelvis till dricksvatten, bevattning av grödor eller trädgårdar, för att simma, bada och fiska. Eller bara för att det är vackert och härligt att ta en promenad längs med en porlande bäck, å kanske läsa en bok vid strandkanten till en sjö. För att kunna fortsätta använda vårt vatten till alla dessa saker behöver ekosystemen och vattnet ha en god status.

Alla som har spenderat tid vid någon av alla Sveriges sjöar under sommaren, eller varit på Gotland eller Öland, har förmodligen stött på algblomning. Oftast i form av en grön, inte så trevlig, sörja som gör att det inte går att bada, simma eller använda vattnet. Algblomningen beror på att sjön, ån eller havet har fått ett överskott av näring, som gör att vissa typer av alger gynnas, växer och och tar över. Detta innebär att sjön eller bäcken innehåller för mycket näring, vilket kallas för övergödning.

Övergödning är ett stort problem, inte bara i svenska sjöar och Östersjön, utan i stora delar av världen, och beror framförallt på överskott av de två näringsformerna fosfor (P) och kväve (N). Överskottet av P viktigast för övergödningen av sötvatten och av N för övergödningen av marina vatten. Fokuset i den här avhandlingen har legat på sötvatten och P. Överflödet av P som når bäckar, åar och sjöar kan komma från diffusa källor, såsom jordbruk, men också från exempelvis enskilda avlopp, eller avloppsreningsverk (såkallade punktkällor). Utsläppen från jordbruk är svårare att kontrollera och förutse än punktkällor, då de varierar över både tid och rum. En majoritet av förlusterna av P från jordbruk kommer från specifika områden i jordbrukslandskapet (kritiska källområden), och transporteras bundet till partiklar. För att kunna återfå god ekologisk status i sjöar, bäckar och åar och minska P förluster till vattnet så behöver vi förstå hur P transporteras, samt vilken roll omrkingliggande området har.

Huvudsyftet med min avhandling har varit att studera förluster av P och markpartiklar från avrinningsområden till små jordbruksbäckar; hur P transporteras bundet till partiklarna samt hur områdets egenskaper påverkar transporten.

Ett avrinningsområde är det landområde som bäcken eller sjön får allt sitt vatten ifrån. Avrinningsområdets egenskaper innefattar exempelvis jordtyp och markanvändning. Jag har även tittat på hur vi kan koppla fosforkoncentrationer samt slamhalt (koncentration av partiklar) i bäcken till varandra och till ovan nämnda egenskaper, samt hur dessa samband kan skalas upp till större områden, som förutom jordbruk även innehåller andra markanvändningar. Dessutom har jag beräknat transport av partiklar (suspenderat sediment) över tid och var partiklarna mobiliseras (kommer ifrån) i området.

Genom att använda data från *Miljöövervakningsprogrammet av små jordbruksområden* som går tillbaka flera år (från ca 2004 för majoriteten av områden i den här avhandlingen), har vi analyserat samband mellan fosforkoncentrationen i vattnet, slamhalt, markanvändning, jordtyp samt andra parametrar såsom fosforinnehåll i jorden, grödtyp och djurtäthet i elva områden (Artikel I). Dessa analyser visade att slamhalt och fosfor har en stark korrelation (ett bra samband): mängden partiklar i vattnet och mängden fosfor bunden till partiklar hänger ihop.

Jag har även visat att slamhalt är korrelerat med andel jordbruksmark i avrinningsområdet samt lerhalt i jordbruksmarken. Jordtyper med hög lerhalt och finare struktur är mer erosionbenägna (lättare att förlora partiklar från jorden), vilket leder till högre förluster av partiklar och därmed även fosfor. För att hitta var i områdena dessa förluster kommer ifrån, samt kunna modellera dessa förluster över tid så, utvecklade jag och kollegor en modell för sex utav områdena, baserat på högupplösta höjdkartor (Artikel 3). Som indata till modellen användes även kartor över markanvändning och jordtyp. Modellresultat jämfördes med miljöövervakningsdata, för att se hur pass bra modellerade data stämmer överens med uppmätta data. Tidigare modeller har endast kunnat modellera dessa områden spatialt, men inte över tid. Här har vi vidareutvecklat en modell som även kan modellera dessa förluster över tid, med bra överensstämmelse med uppmätta data. Detta möjliggör för användning av modellen på liknande områden som saknar mätdata, vilket kan vara ett bra verktyg för lantbrukare, för möjligheten att se var och när i deras områden som förluster av partiklar och därmed också P kan ske.

Vi tillämpade samma samband vi hittade i de små jordbruksområdena till ett antal större områden i huvudavrinningsområdet till sjön Mälaren (Artikel 4). Resultaten visade att sambanden mellan fosfor och slamhalt och även slamhalt, lerhalt och andel jordbruksmark i området gäller även för dessa större, mer mixade områden. Här undersökte vi också förändringar i vattenkvalitén i tillrinningsåarna över en ungefärlig 20 års period, hur och om koncentrationer av fosfor, kväve, totalt organiskt kol (TOC) och slamhalt har förändrats. Resultaten visade få trender. Vi jämförde andelen implementerade åtgärder mot näringsförluster men hittade inga generella kopplingar till trender. Generellt var det en låg implementeringsgrad (<5% av andel jordbruksmark) i de flesta områdena, medan några områden hade en ansenlig mängd (>20% av andel jordbruksmark). Orsakerna till avsaknaden av koppling och brist på minskande trender är förmodligen flera. Dels är flertalet åtgärder nyligen implementerade, vilket gör att effekten troligtvis inte är märkbar förrän flera år framöver och dels kan placeringen av åtgärden vara ineffektiv. Det kan även vara så att trots att tillförseln av P till åarna har minskat, så kan det finnas P lagrad i bottensedimentet, som frigörs och bidrar till att hålla en hög koncentration i ån.

För att gå mer på djupet av hur P binds till partiklarna så gjordes en fältstudie där suspenderat sediment (partiklar i vattnet) provtogs i tre jordbruksbäckar (Artikel II) över en period på två år. Dessa prover analyserades sedan för att bestämma i vilka former P binds till partiklarna, samt hur detta förändras över säsong. Resultaten visade att järnbundet P förändrades mest med säsong, med höga koncentrationer under sommaren och lågflöden, samt låga koncentrationer under vintern och högflöden. Denna fraktion kan släppa P till växter och organismer under vissa förhållanden (den anses biotillgänglig), och speciellt under sommaren med höga temperaturer och låga flöden, vilket då gynnar tillväxt och algblomning extra mycket. Resultaten visade även på en skillnad i hur P binds mellan de olika avrinningsområdena beroende på geologi, lerhalt och flödesnivåer, trots att alla tre områden hade ganska liknande halter av total P.

Sammanfattningsvis, i denna avhandling har vi kunnat konstatera att området kring bäckar och åar och dess egenskaper i form av jordtyp och markanvändning har stor betydelse för mängden fosfor och partiklar som hamnar i bäcken. Hur fosfor binds till partiklar varierar mellan områden, och kan ha betydelse för tillgänglighet för växter och alger. Vi ser även att samband för små jordbruksbäckar är applicerbara på större områden och åar. Att kunna modellera partikeltransport över tid och rum med bra överensstämmelse mot uppmätta data är ett lovande verktyg för lantbrukare och andra att använda på områden utan uppmätta data. Vi kunde inte hitta några nämnvärda trender i vattenkvaliteten i Mälarens tillrinningsområden, och kan konstatera att högre implementeringsgrad av åtgärder är möjlig och nödvändig för att uppnå god ekologisk status i flertalet åar, och även i Mälaren. För att minska transporten av P och partiklar från jordbruk behövs fler åtgärder, med bättre placering och anpassning till avrinningsområdets egenskaper samt kritiska källområden. En inriktning på områden med höga förluster krävs, samt anpassning till typ av fosfor för bäst effekt. Det är viktigt med fortsatt miljöövervakning för att kunna utvärdera effekten av åtgärder samt åar, bäckar och sjöars fortsatta status. Jag kan slutligen konstatera att vi behöver fokusera resurserna där de har högst effekt om vi vill återfå en god ekologisk status i Östersjön och andra sjöar runtom i Sverige, och i världen.

Popular science summary

In a land of thousands of lakes and even more rivers and streams, water is easily taken for granted. The water in the landscape has endless beneficial values and is used for e.g. drinking, irrigation of crops or gardens, swimming and fishing, or just as an attractive background scene when taking a walk along a swirling stream, or reading a book on the shore of a lake. In order to continue using waters for all these things, aquatic ecosystems and the water itself needs to have a good ecological status.

Anyone who has spent some time by many of Sweden's lakes during the summer has probably encountered algal blooms, most commonly in the form of a green sludge on the surface and in the water, making it unattractive for use. Algal blooms happen when a lake, river, stream or sea receives excessive inputs of nutrients, which encourage certain types of algae to grow and take over. A lake or stream that contains too much nutrients is said to suffer from eutrophication.

Eutrophication is a major problem, not only in Swedish lakes and the Baltic Sea, but all over the world. The main reasons for eutrophication are excess inputs of the two nutrients phosphorus (P) and nitrogen (N). In general, excess P is most important for eutrophication of fresh-waters and excess N is most important for eutrophication of marine waters. The focus of this thesis was on fresh-water eutrophication and excess P. The supply of excess P reaching streams, rivers and lakes can come from different sources, such as private local on-site wastewater treatments or municipal/industrial waste water treatment plants (so called point sources) or from diffuse sources, such as agriculture. Since losses from agriculture are variable over time and space, they are more difficult to control and predict than losses from point sources. The majority of P losses from agriculture derive from specific areas within the agricultural landscape, so called critical source areas

(CSAs), from where P is transported often bound to particles. To achieve good ecological status in lakes, streams and rivers and decrease P losses to surface waters, it is necessary to understand how P is transported and what role the surrounding area (catchment) has in P transport. A catchment describes the land area from which all water in a stream or a lake come from.

This thesis examined losses of soil particles and P from agricultural catchments to small agricultural streams, how P is transported bound to particles and how catchment characteristics such as distribution of soil type and land use affect P transport. It also examined how P concentrations and suspended solids concentrations (SS, the concentration of soil particles) relate to each other and to catchment characteristics. Additionally, these relations were up-scaled to larger catchments that encompass other land uses. A model was developed to simulate transport of SS both over time and identify areas where the particles are mobilised (their source) within the catchment.

Using data from the *National Agricultural Catchments Monitoring Programme*, going back several decades (from around 2004 for the majority of the catchments studied in this thesis), connections between P concentrations in stream water, SS, land use, soil type and other parameters (such as P content in the soil, crop type and animal density) in 11 catchments within Sweden (Paper I). The results showed that SS and P have a strong correlation (relationship), with the amount of suspended soil particles in water and the amount of P bound to particles being closely connected.

To examine how P is bound to particles, we conducted a field study where suspended sediment (particles in the water) was sampled in three small agricultural streams (Paper II). These samples were analysed in laboratory to determine in the forms in which P is bound to SS particles, and how this changes over the seasons. Iron-bound P was found to change most prominently with season, with high concentrations during summer and low flows, and low concentrations during winter and high flows. The iron-bound fraction can release P to plants and organisms under certain environmental conditions, especially high temperatures and low flows in summer, favouring growth and algal blooms. The results also showed differences in how P is bound in different catchments, depending on geology, clay content and flow levels, despite similar concentration levels of total P.

Suspended solids concentrations in stream water were also connected to percentage of agricultural land in the surrounding catchment and clay content in arable soil. Soil types with a high clay content and finer structure are more erosion-prone (lose particles more easily) than coarser soil (e.g. sand), which leads to higher losses of particles and P from finer-textured soils. To identify where in the catchment these losses occur, and to model the losses over time, we set up a model for six of the 11 selected catchments, based on high-resolution elevation maps (Paper III). Detailed maps over elevation, land use and soil type were used as input data to the model. The model results were compared with monitoring data, to see how well simulated values matched observed values. Previous version of the same model have only modelled these areas spatially, but not over time. Here, I further developed a model to simulate these losses over time with good agreement to observed data. This means that the model can be applied on similar catchments that lack observation data. It can thus be a good tool for farmers, giving them the possibility to see where and when losses of soil particles and P can happen in their fields.

The relationships found for small agricultural catchments were scaled up to a number of lager catchments, i.e. the main catchment for the great Lake Mälaren, one of Sweden's largest lakes, and the streams and rivers that run into Lake Mälaren (Paper IV). The results showed that the relationships identified between P and suspended particle concentrations, and between particle concentrations, clay content and proportion of agricultural land were valid for these larger, more mixed catchments. Changes in water quality in these rivers and streams were studied over an approximate 20-year period, to examine whether and how concentrations of P, N, total organic carbon (TOC) and SS have changed over time. Very few trends were detected. Comparison with the number and extent of measures implemented in the catchments to control nutrient losses revealed no general connection to trends. In general, the implementation rate of mitigation measures was low (<5% of arable land) in the majority of the areas although some areas had a higher percentage (>20% of arable land). The reasons for the lack of connection and lack of decreasing trends are probably multiple. For example, many mitigation measures have been implemented only recently, and the effects will probably not be noticeable immediately as a consequence of inertia in the system due to decades of nutrient build up in the systems. On the other hand, the placement of the mitigation measure might not be optimal and therefore inefficient. In addition, even if P inputs to the systems have decreased, stored P in streambed sediment could still be released over time and keep concentrations in stream water at a high level.

In conclusion, this thesis showed in multiple studies that the catchment around rivers and streams and their characteristics in the form of soil type and land use have a large effect on the amount of P and particles that end up in streams. How P is bound to particles varies between areas, and the binding form can be important for P availability for plants and algae. Connections between factors established for small agricultural streams were applicable to larger areas and rivers. Reliable modelling of particle transport over time and space is a promising tool for farmers and other stakeholders in areas without monitoring measurements. There were few trends in the water quality in Lake Mälarens catchment, and we can conclude that a higher implementation rate of mitigation measures is possible and necessary to reach a good ecological status in several of the streams and the lake itself. In particular, mitigation measures with better placement and adaptation to CSAs are needed to decrease the transport of P and particles from agriculture. A focus on high-loss areas and an adaptation to P forms is needed for best effect. Continuous monitoring is important in order to evaluate the effect of mitigation measures in the long-term and the continuous ecological status of rivers, streams and lakes. Finally, there is a need to focus our resources were they have the greatest effect to regain a good ecological status in the Baltic Sea and other lakes and surface waters around Sweden, and worldwide.

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Appendix

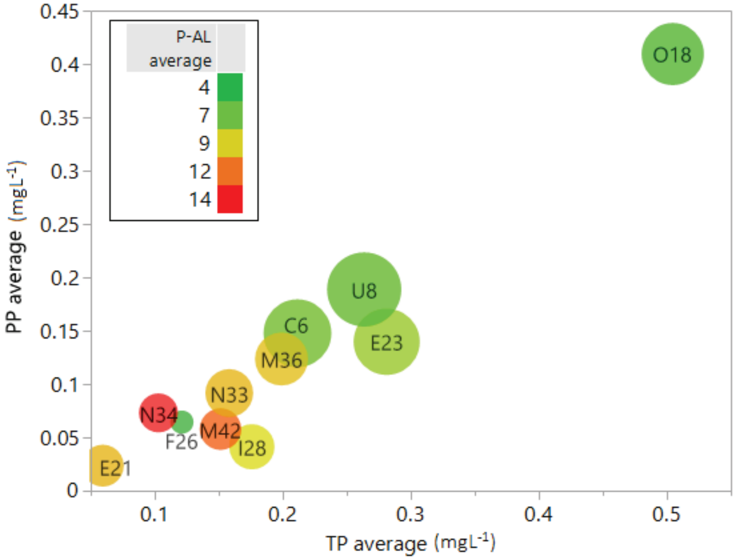

Figure A1. Total flow-weighted mean values of particulate phosphorus (PP) (y-axis) and total phosphorus (TP) (x-axis) of the small agricultural catchments. Coloured by average phosphorus acetate lactate (P-AL) content in the soil (see colour key). Size of the bubbles represents average clay content, larger bubbles indicates more clay. Adapted from Paper I.

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Particulate phosphorus and suspended solids losses from small agricultural catchments: Links to stream and catchment characteristics

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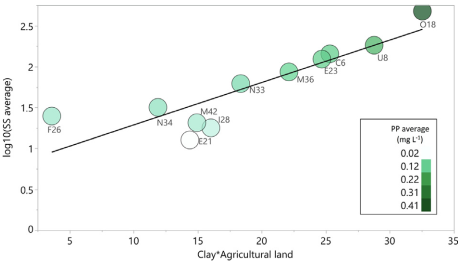
HIGHLIGHTS

- Identification of catchment and in-stream factors correlating to phosphorus losses.
- Long-term time series of flow and water quality from 11 headwater catchments.
- Principal components analysis, linear regression and trend analysis were performed.
- Soil texture (primarily clay content) strongly linked to losses of suspended solids.
- Suspended solids form a clear, monotonic relationship with particulate phosphorus.

GRAPHICAL ABSTRACT



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ABSTRACT

Excessive phosphorus (P) inputs from agriculture are well established as a contributor to freshwater eutrophication. Decreasing these inputs is an important step in improving the ecological state of impaired waters. Particulate P (PP) is a significant contributor to diffuse P inputs in agricultural catchments. Identifying the main correlates for PP losses is an important step in reducing these inputs. However, there are few studies of long term temporal and spatial dynamics of PP in agricultural streams. Here, we investigate the relative importance of hydrology, catchment characteristics and geochemistry on PP concentrations and fluxes in agricultural headwaters. We evaluate long-term monitoring data from eleven small (<35 km^2) Swedish catchments with at least seven years of measured flow and flow proportional water quality sampling. Using parametric and non-parametric regression together with principal components analysis (PCA), we identify in-stream and catchment variables relevant for predicting PP concentrations, e.g., suspended solids concentrations (SS), soil texture and average catchment soil P content, measured as ammonium lactate/acetic acid extractable P (P-AL). We show that PP is primarily correlated to SS concentrations, which in turn are correlated to average clay content and land use. However, the SS:PP relationships differ between catchments. No correlation between PP concentrations in the stream and soil P content was found. An increasing clay content decreases the slope of the relationship between SS and PP, i.e., in catchments with higher clay content, less PP is transported per unit SS. The

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PP/SS ratio increased significantly ($p < 0.05$) over time in four catchments, despite limited changes in SS or PP concentrations. Our study highlights the importance of long time series since the enrichment of P on SS in the streams is only detected when using long term monitoring data.

1. Introduction

Excessive phosphorus (P) inputs are well established as a contributor to freshwater eutrophication (Sharpley et al., 2015). Decreasing these inputs is an important step towards improving the ecological state of impaired waters, and thereby reaching goals set by, e.g., the European Water Framework Directive (WFD) (European Commission, 2000). To decrease P loading to surface waters, the headwater sources and instream processes influencing P need to be identified. Agriculture has been identified as an important non-point source of P to degraded waters in many countries, with an episodic and spatially highly variable input pattern (Sharpley et al., 2009, Ulen et al., 2010, Sharpley et al., 2013, Kronvang et al., 2005, Withers and Jarvie, 2008). This variability in P inputs to streams and lakes is one of the main issues when designing measures against P losses from agricultural land (Sharpley et al., 2011, Thomas et al., 2016, Djodjic and Markensten, 2018). In northern Europe, there is a significant focus on P control measures to mitigate Baltic Sea eutrophication. To successfully address eutrophication of the Baltic, coordinated regional efforts are needed across the Nordic and Baltic states, but many of the actual actions must take place on the smaller scale of individual farms.

Globally, a significant proportion of the P applied to crops accumulates in soils. Some of this P is subsequently transported by surface water runoff and drains into nearby lakes, rivers and streams, largely in different particulate mineral and/or organic forms (Walling et al., 1997; Bowes et al., 2003; Baulch et al., 2013; Cooper et al., 2015). This accumulated 'legacy phosphorus' gradually leaches into the water in a more biologically available soluble form, i.e., PO_4^{2-}, thereby impacting surface water quality for decades. This time lag of P release to aquatic ecosystems means that the effects of nutrient abatement measures for the reduction in P loads may be significantly delayed (Sharpley et al., 1994, 1999; Brogan et al., 2002).

An earlier compilation of water quality monitoring data from Swedish streams (71–4187 km^2) showed the high temporal variability and importance of particulate P (PP) as a vector for P transport (Persson, 2001). The importance of suspended solids (SS) for P transport was also highlighted, and it was established that land management (% arable land in the catchment) was linearly related to PP ($R^2 = 0.85$) and SS concentrations ($R^2 = 0.76$). A significant amount of TP transported in rivers, is in particulate form in the UK, Sweden and other regions (Ballantine et al., 2008, Persson, 2001, Sharpley et al., 2013) which again highlights the importance of understanding mechanisms of PP loss.

Other studies have addressed PP export from agricultural headwater catchments (Walling et al., 1997; Ballantine et al., 2008). Here, we focus on the relationships and correlations between TP-, PP loss and catchment characteristics (i.e., clay content and soil texture). Kyllmar et al. (2014) studied long-term patterns in nutrient losses (TP and total N (TN)) in small Swedish agricultural streams and established a linear relationship between TP and catchment clay content ($R^2 = 0.68$). These losses often occur via erosion and surface runoff, but also via preferential macropore flow where PP is mobilized and transported during storm events (Djodjic et al., 1999). Almost half (47%) of Sweden's agricultural fields are artificially drained (Statistics Sweden, 2017a), where P is rapidly transported through macropores to drainage pipes and thereafter transported directly to the stream. An earlier study of temporal trends in nutrient loads in Swedish agricultural streams (Kyllmar et al., 2006), based on manual fortnightly sampling, has shown significant downward trends for phosphate P (in 8 out of 24 catchments) and PP (in 2 out of 24 catchments), but also a significant upward trend for PP in two catchments. Similar studies of nutrient losses in agricultural catchments have been made elsewhere. Bechmann et al. (2008) studied losses of TN, TP and SS from eight agricultural catchments in Norway, focusing on long term trends and the effects of agricultural management practices. They found a linear relationship between SS and TP for three catchments, ($R^2 = 0.84–0.97$), with a different slope for the relationship in each catchment (Bechmann et al., 2008). Baulch et al. (2013) reported on spatio-temporal patterns of P loss from a mixed land use catchment in Canada with similar climate and soil properties as are found in Sweden. Crossman et al. (2019) evaluated the connection between catchment measures and improvements in downstream water quality. Wilcock et al. (2013) studied both TP and N in New Zealand agricultural streams and their change over time after introducing measures to reduce nutrient losses from dairy farms, highlighting the importance of long-term monitoring data for water quality assessment as well as for determining trends.

Larger rivers in Sweden are well monitored (Fölster et al., 2014). However, smaller, poorly monitored headwaters comprise around half of the stream network length (Bishop et al., 2008). Bishop et al. (2008) called these streams "aqua incognita, the unknown headwaters", where the water begins its journey towards larger streams and lakes. Bol et al. (2018) highlight the need to focus on agricultural headwater catchments, since variability in both dissolved and particulate P fluxes is higher in headwater catchments and the processes controlling P in headwaters have a large influence on the larger catchment.

The environmental monitoring program in Sweden conducts long-term monitoring on nutrient losses and water quality in several, small, contrasting agricultural catchments in southern Sweden (Kyllmar et al., 2014). Similar monitoring programs exists in other Nordic and Baltic countries (Vagstad et al., 2004; Bechmann et al., 2008; Granlund et al., 2005). Previous Nordic and Baltic studies have focused primarily on losses of TN and TP, while measurements of different P-species and their connection to catchment characteristics are rare outside the Swedish and Norwegian monitoring programs. The Swedish monitoring program has been collecting water quality data with fortnightly sampling in 21 agricultural catchments for a time period of at least seven years, and in some catchments for over 25 years.

Since only a few headwater catchments are intensively monitored, there is a need to scale up results from existing monitoring programs. Therefore identification of factors influencing levels and forms of P losses in agricultural headwaters are needed. Specifically, we hypothesize that additional factors beyond clay content, e.g., SS and percentage of agricultural land, are needed for adequate prediction of stream PP concentrations and fluxes in agricultural headwaters. Here, we investigate (i) how TP and PP concentrations, based on biweekly flow proportional water quality measurements, are affected by other in-stream and catchment factors, (ii) to identify correlates of PP concentrations in agricultural streams and to deepen the understanding of these connections.

This study aims to gain improved understanding of the processes and variables controlling P mobilization and transfer in the unknown agricultural headwaters.

2. Material & methods

2.1. Monitoring catchments

The environmental monitoring program includes 21 small agricultural catchments (area < 35 km^2), where some catchments have been monitored since the 1990 s, with focus on nutrient losses (Kyllmar et al., 2014). The main purpose of the monitoring program is to evaluate agricultural policy measures (subsidies, rules and agricultural advisory campaigns), follow the effects of these policies on farmer's practices on their fields and in turn how that affects the water quality in draining streams as well as increasing the knowledge of these connections and how they evolve over time. For this project, 11 out of the 21 catchments in the monitoring program were chosen (Fig. 1). The 11 catchments all had at least seven years of biweekly flow proportional water quality measurements and measured streamflow (Table 1).

The data used in the analysis are mainly from the same time period (Table 1). Flow-proportional sampling for three catchments started in 2007 and monitoring of N33 was discontinued in 2014. Data for crops grown in the catchments generally covers the same time period as the water quality data, except for E23, N33 and U8 where crop data was available for shorter time periods (2006–2013, 2007–2013 and 2007–2013, respectively).

2.2. Water quality sampling and laboratory analysis

The water quality data used in this project was based on automatic flow proportional water sampling (Kyllmar et al., 2014). Samples are collected and stored in a 10 L glass bottle from which

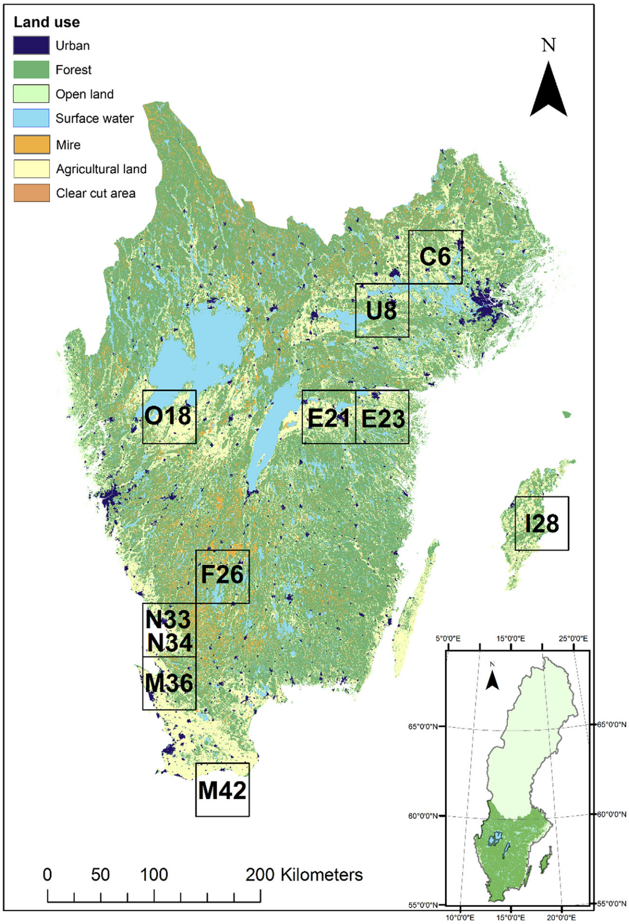

Fig. 1. Approximate location of all catchments used in the analysis, zoomed in to southern Sweden, with a land use map as a background. Latitude and longitude lines are shown in the inset figure, displaying the whole of Sweden.

Table 1
Catchment characteristics for all study catchments (Linefur et al., 2017; Kyllmar et al., 2014). Average annual runoff is given for each catchment's respectively monitoring period. Precipitation and temperature are normal values from SMHI 1961–1990 (SMHI, 2001).

Catchment ID	Area (km^2)	Arable land (%)	Stocking density (AU ha^{-1})	Scattered households (pers. km^{-2})	Monitoring period for water quality data	Dominant soil texture class (USDA)	Precipitation (mm)	Temp. (°C)	Runoff (mm)
C6	33.1	59	0.05	10	2004–2017	Clay loam	623	5.5	220
E21	16.3	89	0.05	9	2004–2017	Sandy loam	506	6.0	157
E23	7.4	54	0.6	7	2007–2017	Clay	594	6.3	181
F26	1.8	70	1.2	33	2005–2017	Loamy sand	1066	6.2	482
I28	4.7	84	0.5	11	2005–2017	Sandy loam	587	6.9	156
M36	7.9	86	0.3	37	2004–2017	Clay, sandy loam	719	7.6	277
M42	8.2	93	0.1	10	2006–2017	Sandy loam, loam	709	7.7	282
N33	6.6	87	0.1	7	2007–2014	Loam, sandy loam	823	7.1	251
N34	13.9	85	0.4	19	2004–2017	Sandy loam and silt loam	823	7.2	372
O18	7.7	92	0.05	8	2004–2017	Clay	655	6.1	332
U8	5.7	56	0.05	11	2007–2017	Clay	539	5.9	206

composite samples are taken every two weeks, followed by emptying the glass bottle (Kyllmar et al., 2014). The intensity of sub sampling is dependent on flow, with more sub samples collected during high flow periods, and time proportional sampling is used during low flow periods, with two sub samples per day. The sampler is calibrated to cover high flow periods for each specific station. A full description of the sampling protocol is presented in Kyllmar et al. (2014).

Samples are analyzed at a water laboratory certified by the Swedish Board for Accreditation and Conformity Assessment (SWEDAC), following Swedish Standard Methods (Kyllmar et al., 2014). Several different parameters are analyzed, the ones used in this study are TP, phosphate phosphorus (DP), SS and the concentration of PP which is the filtrate fraction of TP.

Sediment and P loads are calculated based on daily average values of water flow and estimated daily nutrient concentrations extrapolated backwards from the fortnightly composite samples, using the same concentration for the entire two week period between sampling occasions. Measured daily flows are multiplied by estimated daily concentrations to obtain daily loads, which are summarized to monthly and annual loads. Area specific loads (kg km^{-2}) are calculated by dividing the load by the catchment area. The flow weighted concentrations (mg L^{-1}) used in the data analysis are obtained by dividing the calculated load (kg km^{-2}) by the runoff (mm) for the relevant time period (Table 2). In some catchments, the stream is periodically dry and hence some months lack data. Average annual runoff was calculated as the average of the annual runoffs from the evaluated time period.

To explore the influence of land use and crop distribution on P losses, three crop type groups were created: 1) Ley 2) Cereals & Rape and 3) Other Crops. The three groups reflect different management intensities and P loss potential. The average percentage of each crop type over the time period was used to get a value for each group. The "Ley" group includes both ley and fallow. Ley is the most common individual crop in Sweden and has considerably lower P losses compared to cereals (Johnsson et al., 2016). The "Cereals & Rape" group covers the largest area in all studied catchments and includes crops with similar management systems and P losses. Finally, crops with higher P inputs and higher risk for P losses, e.g., potato and sugar beets, were assigned to the category

Table 2
Additional catchment data used in the PCA. PP = particulate phosphorus, SS = suspended solids, TP = total phosphorus, DP = PO4-phosphorus, P-AL = Phosphorus extracted by ammonium lactate/acetic acid, representing soil P content. The crop types Ley, Cereals & Rape and Other crops are given as a percentage of arable land. All concentrations are given as total average values with the standard deviation in parentheses. FV = Factor of variation, describes the relationship between the highest and the lowest value among the catchments.

ID	TP (mg L^{-1})	PP (mg L^{-1})	DP (mg L^{-1})	SS (mg L^{-1})	PP/SS	PP/TP	P-AL (mg/100 g)
C6	0.21 (0.06)	0.15 (0.06)	0.05 (0.01)	143.6 (65.3)	1.0E−03 (1.8 E−04)	0.61 (0.17)	6.34 (1.73)
E21	0.059 (0.02)	0.02 (0.01)	0.03 (0.02)	12.7 (5.0)	1.9 E−03 (7.8 E−04)	0.49 (0.28)	10.30 (5.08)
E23	0.28 (0.02)	0.14 (0.03)	0.12 (0.02)	123.6 (39.2)	1.1 E−03 (2.0 E−04)	0.46 (0.16)	7.41 (12.75)
F26	0.12 (0.05)	0.06 (0.03)	0.03 (0.01)	24.9 (18.0)	2.6 E−03 (1.5 E−03)	0.54 (0.14)	4.17 (5.95)
I28	0.18 (0.06)	0.04 (0.02)	0.12 (0.05)	17.8 (5.9)	2.3 E−03 (1.0 E−03)	0.26 (0.14)	9.01 (7.96)
M36	0.20 (0.04)	0.12 (0.04)	0.06 (0.009)	86.2 (21.3)	1.4 E−03 (4.2 E−04)	0.55 (0.14)	9.97 (3.26)
M42	0.15 (0.03)	0.06 (0.02)	0.08 (0.03)	20.6 (10.7)	2.8 E−03 (9.7 E−04)	0.37 (0.15)	12.60 (5.16)
N33	0.16 (0.02)	0.09 (0.02)	0.05 (0.01)	62.0 (17.4)	1.5 E−03 (2.5 E−04)	0.57 (0.18)	10.27 (5.55)
N34	0.10 (0.03)	0.07 (0.03)	0.02 (0.004)	31.8 (10.2)	2.3 E−03 (5.8 E−04)	0.70 (0.15)	14.24 (7.38)
O18	0.50 (0.16)	0.41 (0.15)	0.07 (0.02)	476.9 (220.8)	8.6 E−04 (2.7 E−04)	0.65 (0.20)	5.28 (3.12)
U8	0.26 (0.07)	0.19 (0.06)	0.06 (0.02)	182.9 (71.7)	1.0 E−03 (2.2 E−04)	0.69 (0.15)	5.90 (6.85)
FV:	8.5	17	6.3	38	3.3	2.7	3.4
ID	Regression slope PP-SS	Agricultural land (%)	Ley (%)	Cereals & rape (%)	Other crops (%)	Clay average (%)	Silt average (%)
C6	8.3 E−04	61	22	76	2	41.8	42.0
E21	1.5 E−03	90	10	78	11	16.1	32.5
E23	6.3 E−04	62	38	55	7	39.8	40.2
F26	1.6 E−03	73	72	26	2	4.9	29.9
I28	2.2 E−03	86	23	64	13	18.6	33.4
M36	8.8 E−04	87	34	54	11	25.6	28.5
M42	1.5 E−03	95	7	76	17	15.8	32.0
N33	1.2 E−03	88	24	67	9	20.9	36.8
N34	1.9 E−03	86	16	61	23	13.9	28.5
O18	6.8 E−04	93	5	88	7	35.2	51.0
U8	7.4 E−04	58	24	75	1	50.0	40.8
FV:	3.4	1.6	14	3.4	30	10	1.8

"Other crops". Crop types are reported as a percentage of arable land (Table 2). Percentage of agricultural land in the catchment is given as the sum of arable and pasture land. The majority of the catchments have a small percentage of pasture, i.e., <3%, except for E23 with 8% pasture.

Catchment arable soil characteristics include clay and silt content. Average, median and maximum values of percentages of both clay and silt in the catchment were calculated using the GIS software ArcMap (ESRI, 2015) and the tool *Zonal Statistics as Table* based on catchment digital soil maps (Söderström & Piikki, 2016).

The P content in arable soil was estimated based on P extracted by ammonium lactate/acetic acid (P-AL) at pH 3.75, the standard method to measure plant available soil P content in Sweden (Egnér et al., 1960). Average soil P-AL values (mg/100 g; Table 2) are based on top soil samples collected at one sampling occasion, but at different years for each catchment, with sample points spread out over the catchment. In a majority of catchments, the number of sampling points range from 4 to 14 samples km^{-2}, except for E23, where 63 samples km^{-2} were taken. Data are collected from several different projects, hence the spread in number of sampling points and differences in sampling years. P-AL content is assumed to be stable over time, and the difference in sampling years is not assumed to be important (Djodjic & Spännar, 2012; Mattsson, 2002).

2.3. Data analysis – Multivariate analysis

Data were evaluated in several steps. First, individual correlations between in-stream variables were explored using linear regressions of monthly flow weighted concentrations for each catchment. Regressions were performed in JMP® 13.0.0 (2019). Second, regression parameters for the relationships between PP and SS were compiled together with in-stream and in-catchment variables to be used for Principal Components Analysis (PCA) (Table 2), performed using Canoco 5. The PCA was used as a base for further analysis, to find correlations between catchment properties and in-stream properties, and their connection to P, especially PP. All variables were put in the PCA at first. However after examination of the results, several variables describing the same property were removed, and the variables having the highest impact, i.e., the highest loadings, on the principal components were kept. Variables having low/no impact, i.e., loadings close to zero, were also removed, e.g., average flow and a number of regression parameters. Multiple linear regression was performed to explore how different combinations of variables could explain the variance in PP, as well as the variance in the slope of the regression between PP and SS. This analysis was made using monthly flow weighted concentrations, as well as using total average values for the whole monitoring period in each catchment (Table 2). A factor of variation (FV) was calculated as the ratio between the highest and the lowest obtained value for each parameter (Table 2), to illustrate the variation in catchment factors and water quality parameters between catchments.

Finally, to investigate whether flow-weighted concentrations of PP, SS, DP and TP and the PP/SS ratio changed over time, a two-sided Mann-Kendall test was used. Trend analyses were also performed on monthly discharge, as well as on monthly loads.

3. Results

3.1. Variation between catchments – Concentrations, catchment characteristics and land use

There is a high variability in the catchments and their in-stream and soil characteristics (Fig. 2, Table 2). Catchments with a high average clay content generally have a lower P-AL content, while catchments with coarser textured soils (mainly sandy loam) have a higher P-AL content. However, F26 with the coarsest soil texture deviates from this pattern as it has the lowest P-AL content of all catchments (Fig. 2, Table 2). For many catchments the particulate P fraction is the main part of the TP (seven catchments having PP > 50%), especially for catchments with a high clay content (O18, U8, E23 and C6) (Fig. 2, Table 2). Concentrations of SS and PP also showed high variation between catchments (FV = 38 and 17, respectively, Table 2). The variation of DP was considerably lower, with a FV of 6.3. Clay content (FV = 10) showed much higher variation than both P-AL (FV = 3.4), silt content (FV = 1.8) and fraction of arable land (FV = 1.6).

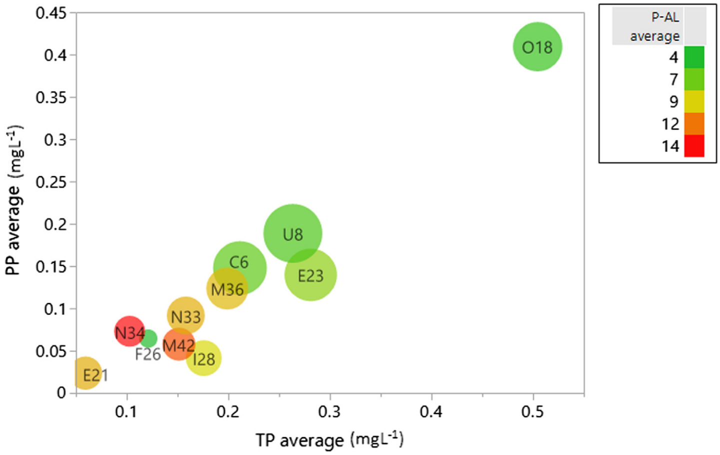

Fig. 2. Overall average values of flow-weighted concentrations of particulate phosphorus (PP) *vs.* total phosphorus (TP) for the study catchments. Symbol size is proportional to average clay content in the catchment, the bigger size, the more clay. The colors describe average phosphorus acetate lactate (P-AL, mg 100 g^{-1} of soil) content in the soil.

The average flow weighted SS concentrations ranged between 13 and 477 mg L^{-1}, and the average flow weighted TP concentrations ranged between 0.06 and 0.5 mg L^{-1}. The average flow weighted PP concentrations had approximately the same range as TP, i.e., between 0.02 and 0.4 mg L^{-1}, while DP concentrations were lower and ranged between 0.02 and 0.1 mg L^{-1} (Table 2). The sandy loam catchment E21 had the lowest SS, TP and PP concentrations while the clay catchment O18 represented the other end of the spectrum, with the highest SS, TP and PP concentrations. The R^2-value for the linear relationship between PP and SS for monthly flow-weighted concentrations for individual catchments varied between 0.26 and 0.83, with the highest value obtained for the clay catchment U8 and the smallest value for the clay/sandy loam catchment M36. In general, a higher R^2-value was obtained for the catchments with medium-high clay content. The slope of the linear relationship between PP and SS varied between 6E-04 and 2E-03, with the steepest slope for the small, sandy loam catchment I28, and the lowest slope for the clay catchment E23 (Table 2). The slopes for the catchments with a coarser soil texture are in general steeper, while the slopes for the catchments with a finer soil texture are lower.

3.2. Observed correlations between studied variables

In the PCA, PP positively correlated with SS and average clay content (Fig. 3). These three variables also have a positive correlation with average silt content, since they all line up next to each other (Fig. 3). No significant correlation between PP and P-AL was found. Different crop types do not seem to influence PP, whereas there seem to be a weak negative correlation between DP and Ley, as well as between PP/TP and P-AL (Fig. 3). The different catchments tends to group in the biplot according to their distinct characteristics. For instance, catchments with a higher clay content are grouped together (U8, C6, O18 and E23). Catchment F26, with a coarse soil texture and a large number of animals (Table 1) is instead highly correlated to Ley. Average clay content in the soil has a negative correlation with the slope of the linear relationship between PP and SS (Fig. 3).

The monthly flow weighted SS concentrations were a strong explanatory variable for the variance in monthly flow weighted PP concentrations (R^2 = 0.67, N = 1441, p-value < 0.01). Average clay content did not add any further statistical significance to this relationship in a multiple regression (R^2 = 0.67, N = 1441, p-value < 0.01). The same holds for a linear regression using total average values for PP and SS (R^2 = 0.98, N = 11, p-value < 0.001), where adding clay content gave the same results with no added significance to the regression. However, clay content did explain 62% of the variance in the slope of the relationship between PP and SS in a simple linear regression (R^2 = 0.62, N = 11, p-value < 0.05), where silt content explained 44% of the variance in the slope (R^2 = 0.44, N = 11, p-value < 0.05).

The relationships between PP, SS and average clay content identified in the PCA (Fig. 3) and the multiple linear regression, were further investigated together with average silt content (Fig. 4 and appendix Fig. A1). Average clay content is correlated with SS concentrations (R^2 = 0.36, N = 11, p-value < 0.05), with the clay catchment O18 deviating from the linear pattern (appendix Fig. A1). Average silt content of catchment soils also displays a linear relationship with SS (R^2 = 0.77, N = 11, p-value < 0.05), with O18 acting as an extreme value, but in this case, still lining up with the linear pattern (appendix Fig. A1). When fraction of agricultural land is taken into account together with the average clay content (Fig. 4), a linear relationship is found (R^2 = 0.75, N = 11, p-value < 0.01), where the product of average clay content and fraction of agricultural land is an explanatory variable for the logarithm of SS. Using the product of average silt content and fraction of agricultural land as a joint, explanatory variable for either SS or log(SS) does not result in a significant relationship (data not shown).

Multiple linear regression with SS as response variable and average clay content, average silt content and fraction of agricultural land as explanatory variables results in a significant linear relationship (R^2 = 0.81), with average silt content being the main explanatory variable (p-value < 0.05). A regression with just average silt content as the explanatory variable gives an R^2-value of 0.77, just slightly less then when adding both clay and fraction of agricultural land. Having clay content and fraction of agricultural

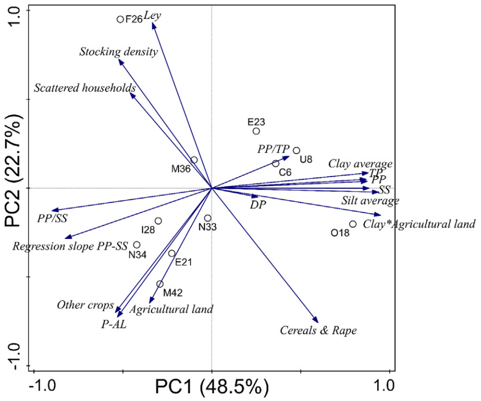

Fig. 3. Biplot from principal components analysis (PCA). Arrows represent variables, while circles represent catchments. All catchments are labelled by their abbreviation and all arrows are labelled by the variable they represent. PP = particulate phosphorus, TP = total phosphorus, SS = suspended solids and P-AL = plant available soil phosphorus content. The percentage on each axis describes the amount of variance explained by each principal component.

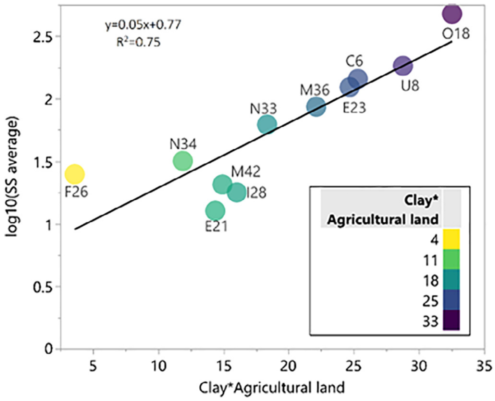

Fig. 4. The average in-stream suspended solids concentration (SS; logged values on the y-axis), *vs.* the product of average clay content and fraction of agricultural land in the catchment (x-axis; Clay*Agricultural land). The solid line represents a linear regression, with the R^2-value and regression equation shown in the figure. Symbol color represents the product of average clay content and fraction of agricultural land in the catchment.

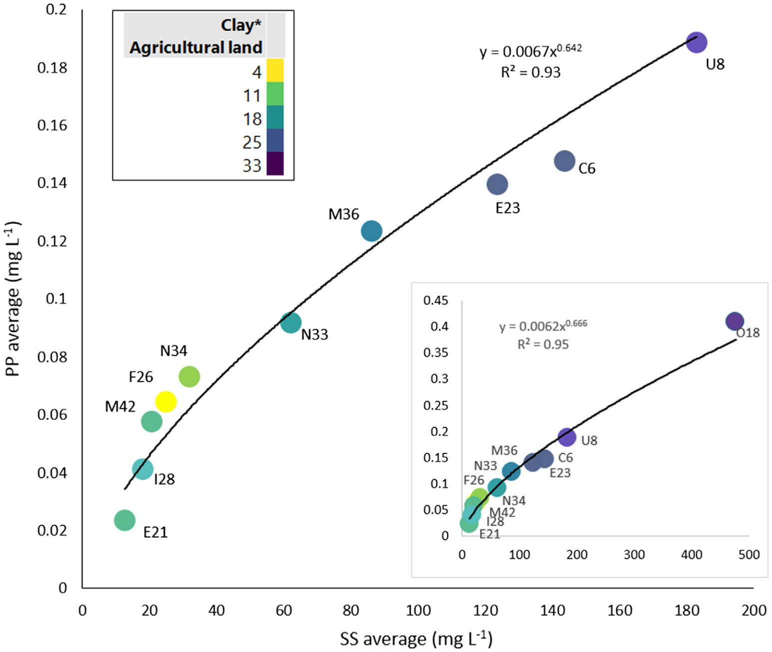

Fig. 5. Overall average flow weighted particulate phosphorus (PP) concentrations (y-axis) against overall average flow weighted suspended solids (SS) concentrations (x-axis). Symbol color represents the product of average clay content and fraction of agricultural land in the catchment. Catchment O18 is not included in the main figure. The inset figure shows a zoomed-out version of the main figure with the one extreme catchment (O18) included. The solid black lines in the main and inset figures represent fitted power law functions with the obtained equation and R^2-value shown.

land as separate explanatory variables for either SS or log(SS) in a regression, does not add the same significance as treating them as a joint variable, using the product of average clay content and fraction of agricultural land (Fig. 4).

Average clay and silt content in catchment soils correlates linearly with SS, while SS correlates with PP (Fig. 5). There is a strong, monotonic relationship between PP and SS, in both monthly flow weighted concentrations (R^2 = 0.67, N = 1441, p-value < 0.01), and total average values (Fig. 5). O18, the catchment with the highest values of TP, PP and SS, as well as a high clay content, acts as an extreme here as well (Fig. 5). There seem to be an exponential increase in the relationship between PP and SS in the lower concentrations ranges and for the catchments with a coarser soil texture, while the relationship increases more linearly for the higher concentration ranges and for catchments with a finer soil texture. The relationship can be described using a power law function (Fig. 5), where the exclusion of the more extreme catchment O18 results in only a slight decrease of the explained variance (R^2 = 0.93, Fig. 5).

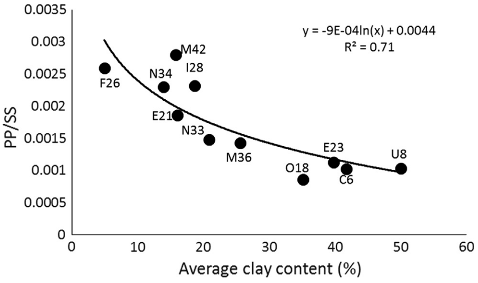

Fig. 6. The ratio between flow weighted average particulate phosphorus (PP) concentrations and flow weighted average suspended solids (SS) concentrations against average clay content. The circles describes each catchment, the solid black line describes a fitted logarithmic function. The equation and obtained R^2-value are shown.

Based on the left side of the biplot (Fig. 3), the relationship between the ratio PP/SS and average clay content was further investigated (Fig. 6). There is a decrease in the PP/SS ratio with an increase of average clay content, until around 30% average clay content, where it flattens out. The same pattern can be observed for PP/SS *vs.* average silt content, where the decrease of the ratio is observed at a silt content of approximately 42% (data not shown).

The relationships between DP, Ley, stocking density and scattered households observed in the PCA (Fig. 3) were further investigated with linear regression, but did not result in any significant relationships. The same was true for the correlation between P-AL and PP/TP.

3.3. Trend analysis of water quality parameters and discharge

A significant increase in the PP/SS ratio can be seen in 8 out of 11 catchments (Table 3). Four of the catchments, all having a medium to high clay content (E23, M36, O18 and U8), show no significant change in either PP or SS concentrations, while the PP/SS ratio is increasing. The sandy loam catchment E21 with the

Table 3
Results from the Mann-Kendall trend test of the ratio between PP/SS, discharge and flow-weighted concentrations of SS, PP, DP and TP over the whole monitoring period. The first column represents each catchment and the used time period in parenthesis. Each column represents the rate of change in the investigated variables where relevant and change in mgL^{-1}yr^{-1} for flow-weighted concentrations and Ls^{-1}yr^{-1} for discharge. Significant change with $p < 0.05$ is represented by * and $p < 0.01$ is represented by **. Empty cells means no significant change.

ID	PP/SS	PP (mgL^{-1}yr^{-1})	SS (mgL^{-1}yr^{-1})	DP (mgL^{-1}yr^{-1})	TP (mgL^{-1}yr^{-1})	Discharge (Ls^{-1}yr^{-1})
C6 (2004–2017)	2.3 E−06**	5.0 E−04**		1.5 E−04**	5.7 E−04**	
E21 (2004–2017)	5.3 E−06*	2.1 E−04**	7.1 E−02**			
E23 (2007–2017)	4.3 E−06*				−1.5 E−03**	
F26 (2005–2017)	2.3 E−05**		−0.14**	7.0 E−05*		
I28 (2005–2017)		3.1 E−04**	4.5 E−02*	1.1 E−03**	1.4 E−03*	
M36 (2004–2017)	3.4 E−06*			1.7 E−04**	2.5 E−04*	
M42 (2006–2017)				7.0 E−04**	5.9 E−04*	
N33 (2007–2014)						
N34 (2004–2017)	7.7 E−06**	2.1 E−04*				−6.70**
O18 (2004–2017)	2.4 E−06*					−4.30**
U8 (2007–2017)	7.9 E−06**					−2.44**

lowest SS, TP and PP concentrations has a significant increase in the ratio and the two concentrations as well, however, the rate of change differs. The clay catchment C6 and the more sandy loam catchment N34 both show an increase in the ratio and the PP concentrations, but no change in SS. The loamy sand catchment with the smallest area, F26, is the only catchment showing a decrease in any of the investigated concentrations, in this case SS (Table 3). Catchment I28 has an increase in both PP and SS concentrations, but no change in the ratio.

No significant changes in loads of PP, TP, SS and DP can be seen in the majority of the catchments, except for the clay catchment U8 where there is a significant decrease in the load of PP, SS and TP. In general, there is a decreasing trend in water discharge in all catchments, however, the decrease is statistically significant in only three of the catchments: N34, O18 and U8 (Table 3).

4. Discussion

4.1. Catchment characteristics, water quality and their variability between catchments

There is a high between-catchment variability, both in catchment properties, but also in the different water quality parameters (Table 2, Fig. 2). Average flow-weighted TP, PP and SS concentrations have a high variability among the catchments, confirming the conclusions of Bol et al. (2018). However, our findings suggest that catchments with similar soil texture and land use behave similarly. The large variation in P fluxes between catchments supports the necessity of targeted measures against P losses. Additionally, different types of measures and even the appropriate placement of measures in the catchment might vary depending on catchment properties.

All catchments are clearly grouped in the biplot (Fig. 3) according to their character. Catchment F26 is strongly driven by its high and increasing stocking density and a high production of ley, and it also has one of the coarsest soil textures. This catchment deviates from the general relationship between log(SS) and the product between average clay content and fraction of agricultural land with somewhat higher SS concentrations (Fig. 4, Table 2). The concentrations of Total Organic Carbon are also highest for this catchment (Linefur et al., 2017), which may imply that some of the SS is of organic origin. Catchments N34, N33, M42, I28 and E21 all have around 90% agricultural land, with high P-AL content in the soil and quite similar sandy soil texture (Table 2). Consequently, they all are placed in the bottom left quarter of the biplot (Fig. 3). Catchments C6, U8, E23 and O18 have the highest TP, PP and SS losses and also high clay content and they all plot on the right half of the biplot (Fig. 3).

Iron (Fe), aluminum (Al) and calcium (Ca) geochemistry may explain some of the differences in results between catchments. Specifically, mineral bearing PP phases are formed by the reaction of soluble reactive P (SRP) with Fe, Al-Bierooxyhydroxide, Ca carbonate and organic matter (OM) associated with the composition of the particular catchment soils and aquatic sediments (O'Connell et al., 2015; Cooper et al., 2015). The P retention capability of fluvial sediments has been associated with various correlations of P/Al/Fe ratios (Rydin and Welch, 1999; Norton et al., 2008). Particularly, it has been demonstrated that Fe–P ratios can be useful indicators of the P buffering capacity of aquatic sediments (Jensen and Thamdrup, 1993), with greater Fe–P ratios suggesting enhanced SRP adsorption capacity onto the surfaces of Fe containing clay and sediment particles. In contrast, Al-P ratios also indicate SRP adsorption capacity to Al-oxyhydroxides, however, these are more stable under fluctuating redox potentials than ferric-(hydr)oxides (Mortimer, 1941, 1971; Reitzel et al., 2013). The lack of data regarding more detailed P speciation for here studied catchments is a limiting factor for further studies. The logical, and currently undergoing, next step is therefore collecting samples of fluvial sediment in some of the catchments for analyses of various P fractions and P pools.

4.2. Correlations between variables – SS concentrations as a main correlate for PP concentrations

Average clay and silt content in the catchments have a strong influence on SS concentrations in the streams, where a higher clay and silt content result in higher transport of soil material. These catchments are also typically known for having high SS and TP losses (Linefur et al., 2017). The main part of TP in these catchments (mainly U8, O18 and C6) consists of PP (Fig. 2, Table 2), and as we have shown, SS acts as the main in-stream correlate for PP, while the product of clay content and fraction of agricultural land acts as the main correlate for SS. These three catchments are typical examples of how PP losses are influenced by soil characteristics. A better regression is found between SS and silt content (R^2 = 0.77) than SS and clay content (R^2 = 0.36) (Section 3.2), in contrast to what we expected and what other studies have found, since clay content is the soil type that is historically mostly connected to SS and P losses e.g., (Kyllmar et al., 2014). However, both the afore mentioned relationships are strongly influenced by one catchment, i.e., O18. Excluding this catchment from the analysis decrease the correlation between silt content and SS (R^2 = 0.66) but considerably increase the correlation between clay content and SS (R^2 = 0.91). Clay soils are also typically more prone to erosion, and will therefore lose more P rich material (Ulén and Jakobsson, 2005), supporting a stronger relationship between SS and clay content instead of silt content. At the same time, the factor of variation is much lower for silt (FV = 1.8) compared to the corresponding value for clay content (FV = 10). Consequently, the slope of the relationship between silt content and SS concentrations is much higher, leading to rapid increases in predicted SS concentrations even with small increases in silt content, which might lead to large errors. Therefore, if predictions of expected SS concentrations are to be made for ungauged small catchments, choosing clay content, with possible consideration to fraction of agricultural land (Fig. 5), would be a more forgiving method. Additionally, in the regression with clay, O18 deviates the relationship from the linear pattern, while for silt, it drives the relationship towards linearity. This is a plausible explanation to why silt stands out as a more significant explanatory variable for SS in the multiple regression using both clay and silt. O18 has extreme SS and P losses, with the highest TP losses of all studied catchments (Linefur et al., 2017) and the highest average flow weighted concentrations (Table 2). However, it still represents an example of how losses in similar catchments can look, and mainly follows the same patterns as the other clay catchments, except with more extreme values.

Kyllmar et al. (2014) found a linear relationship between soil clay content and TP at the stream outlet. We argue here that transport of SS is an important step between soil clay content and, in this case, PP, instead of a direct relationship between PP and clay content since P found at the stream outlet is mainly in particulate form. Modeling studies using erosion and SS as a proxy for P losses from agricultural land have shown good agreement both on field and catchment scale (Djodjic and Markensten, 2018), in line with our results. The correlations between SS and PP that we can establish in this study also agrees with findings for larger catchments (Persson, 2001), that also stresses the importance of SS for P transport, as well as the importance of land use, i.e., fraction of arable land for SS losses. Persson (2001) uses percentage of arable land, and in this study the product of clay content and fraction of agricultural land is used, showing that these factors have a big influence on P losses in agricultural headwater catchments.

No significant relationships between DP concentrations and other variables in the dataset were found (Fig. 3). This is probably due to the fact that PP comprises the majority of the TP in these catchments (Table 2) and thus, DP does not influence the variation in the dataset as much as PP, which is often the case in small, agricultural catchments (e.g., Withers and Jarvie, 2008). Additionally, the variation in DP concentrations (FV = 6.3) between the studied catchments is much lower compared to PP (FV = 17). Previous studies have found other processes controlling the transport of DP compared to PP, with DP mainly being transported via subsurface flow (Rodríguez-Blanco et al., 2013; Dupas et al., 2015). Based on results of a lysimeter leaching study, Andersson et al. (2015) concludes that the subsoil can act as a source or a sink for P leaching depending on P content, degree of P saturation and P sorption capacity. Unfortunately there is very scarce data on subsoil properties in different catchments studied here.

The negative correlation found between average clay content and the regression slope for the PP-SS relationship indicates that less P is transported per SS particle in catchments with a higher clay content and consequently higher SS concentrations. Soil erosion is a selective process with respect to soil particle size (Sharpley, 1980) resulting in larger mobilisation and transport of smaller clay particles. Clay particles have, due to their higher specific surface area, higher P sorption potential compared to coarser soil particles (silt and sand). This results in enrichment ratios, i.e., a higher P content of eroded sediment compared to the P content of bulk soil. However, as Kleinman et al. (2011) show, "sediment P enrichment ratios tend to decline with increasing rates of erosion (and greater removal of larger soil particles and aggregates)". This statement agrees with our results (Fig. 6), where the PP/SS ratio decreases with an increasing clay content, suggesting that catchments with soil textures more prone to erosion have lower PP/SS (Villa Solís, 2014). In catchments with a high clay content, more SS is transported, but less PP is transported per unit SS. Villa Solís (2014) showed a strong decrease of P enrichment ratio (calculated as the content P in SS to that in soil), with increasing concentrations of SS. There seem to be a higher enrichment of P on the particles in catchments with a coarser soil texture as they usually have lower SS concentrations. However, we see an increase in the ratio PP/SS over time (Table 3) in several catchments, especially those with a high clay content, which that more PP per unit SS is being transported in these clay catchments over time.

4.3. The lack of correlation between soil P content and stream P concentrations

In this study we could not find evidence of a significant correlation between P in the stream and the plant available P (P-AL) content in the soil (Fig. 3). This may be a result of using an average value of P-AL in the entire catchment, and for some catchments the variation in P-AL is quite big (Table 2). Since P losses are episodic, and usually come from only a small area of the catchment, typically referred to as critical source areas (CSAs) (Pionke et al., 2000), it is possible that there is a correlation between P-AL in CSA soils and PP. Furthermore, we have shown (Fig. 5) that the impact of SS losses on PP losses and thereby TP losses is strong and therefore overrides the possible influence of other factors, including soil P content. Catchments with finer soil texture in our data set (Fig. 2, catchments O18, U8, C6, E23) prone to higher erosion losses have low P-AL content (Table 2) whereas the lowest TP and PP losses were observed from catchments with high P-AL content (Fig. 2, catchments E21, N34, M42). Withers et al. (2009) showed that the P enrichment ratio of SS declined exponentially as soil P increased. They found relatively small increases (10%) in the PP content of SS when soil P content increased from average to high fertility status. In our data set, between-catchment variation in average P-AL content (FV = 3.4, Table 2) is much lower than the variation in TP and PP concentrations (FV = 8.5 and 17, respectively, Table 2). Phosphorus load at the catchment outlet is mainly a remobilized secondary P source rather than a result of direct P delivery from the catchment sources (Jarvie et al., 2013). For example, Haygarth et al. (2012) could not establish a relationship between soil-P content estimated using Olsen-P and P export in two headwater catchments, which is in line with our results. To conclude, when considering highly variable SS concentrations and rather low variation in soil P content, it is difficult to expect a clear detectable effect of the soil P content on P losses.

4.4. Increasing trends in PP/SS ratio

There is an increase in the PP/SS ratio in eight of the eleven catchments, where five of the catchments have medium to high clay content (Table 3). Four of these catchments show no significant changes in either PP or SS concentrations. The increase of the ratio may point towards a shift in the size of particles being transported from the fields to the streams, with a higher percentage of smaller clay particles being transported, leading to transport of a higher amount of P (Kleinman et al., 2011). There could also be a small change in concentrations of both PP and SS over time, which are not significant, but when looked at together in a ratio, the change becomes significant.

The small, loamy sand catchment F26 with the highest rate of change in the PP/SS ratio is the only catchment showing a decrease in SS concentrations (Table 3). In this catchment there is a clear enrichment of P on the SS particles, where more P is being transported with a lower amount of particles. There has been an increase in number of animals in F26 over the monitoring period, as well as an increase in applied nutrients, especially from manure (Linefur et al., 2018), leading to more P being transported to the stream. Fertilizer and manure application rates are generally quite low for all catchments and in line with current recommendations from Swedish Board of Agriculture (2015) and are in agreement with average values for the surrounding production area (Statistics Sweden, 2017b). Three catchments (C6, I28 and O18) have a slightly higher application rate of fertilizers than their surrounding area (Kyllmar et al., 2014), however, the application rates of both fertilizers and manure are more or less constant with minor changes for all catchments, except F26, during the study period. Therefore it is unlikely that catchments displaying increasing trends of PP/SS, PP, DP, TP or SS are affected by fertilizer and manure application. Crop distributions in the catchments did not change significantly over the studied time period. Three catchments have an increase in percentage of catch crops, while four have a decrease and the rest are more or less the same (Linefur et al., 2017). Catch crops are used in Sweden primarily to reduce N losses and may lead to increased P losses from biomass after freezing-thawing cycles (Liu et al., 2014). However, no obvious patterns could be found between the observed trends in several catchments (Table 3) and the changes in percentage of catch crops. Structural liming has been applied in six catchments at least once during the study period. Structural liming is used as a measure to reduce P losses through improvement of soil structure and the stability of soil aggregates, especially on clay soils. However, as mentioned earlier, no decreasing trends in SS were recorded for these clay catchments (Table 3).

The increasing ratio between PP/SS in general, and especially in the catchments where no increase in the individual parameters is visible, is an indication that it is not enough to only study losses of P or SS by themselves, but to also study the ratio to detect changes and evaluate abatement efforts. The material being transported in some catchments is richer in P than before and the behavior that can be seen in some catchments where either there is only a change in the ratio, or in one of the concentrations, strengthens this statement. Catchment N33 is the only catchment that has no significant change in any of the variables. It is also the catchment with the lowest number of data points and the shortest monitored time period, which could be a reason why no change is detected.

Despite these increases that we see in the ratio between PP/SS, and in some concentrations, no significant increases in the different loads are found. One catchment (U8), in spite of having an increase in the PP/SS ratio, shows a significant decrease in the loads of PP, SS and TP (Section 3.3), probably due to a significant decreasing trend in water discharge. This is also one of the catchments participating in a project focusing on measures to decrease nutrient losses as mentioned earlier. Generally, catchment discharges are decreasing (although with a statistically significant decrease in only three catchments, including the mentioned U8) (Table 3). One reason for the lack of decreasing trends in loads despite decreasing discharge may be the increase in PP/SS ratios and some concentrations. Our results suggests a change in water quality, with approximately the same amount of P being exported from the catchments into the streams with less volume of water, leading to increasing concentrations of finer, more P rich particles being lost from the soil to the stream.

With this paper we want to highlight the importance of long-term monitoring data from headwater catchments to look at more general trends and correlates for stream P concentrations. Monitoring over long time periods with continuous sampling is needed to detect small changes in concentrations, especially as we have shown that in the majority of the catchments, there are significant changes in either the ratio PP/SS, or in one of the concentrations. The only catchment showing no change at all has the shortest time period in the analysis, which also highlights the need for having longer time periods to be able to detect trends.

5. Conclusions

Studying long-term monitoring data from these eleven small, agricultural catchments has lead us to the following conclusions:

- Clay content and fraction of agricultural land in the catchment are the main correlates for in-stream suspended solids concentrations
- The concentration of suspended solids is the main correlate for particulate phosphorus concentrations in the stream, acting as the middle step between soil texture, land use and phosphorus concentrations
- If these results are to be used for predictions of suspended solids losses, we suggest using clay content and amount agricultural land in the catchment as these variables forms a more robust relationship
- There is an increasing trend in the PP/SS ratio in several catchments, pointing towards a change in water quality in the streams

Due to the high spatial variability and wide range in soil texture in the studied catchments together with the long, consistent measurements performed in the catchments, we believe that these results are applicable to other regions with similar soil types, climate, agricultural practices and hydrological conditions.

Declaration of Competing Interest

No conflicts of interest are relevant for this study.

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Appendix

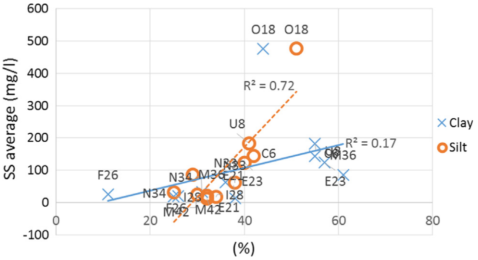

Fig. A1. The total average value of suspended solids (SS) against average clay content and average silt content for all catchments. The crosses describes clay content in each catchment, while the circles describes silt content in each catchment. Each catchment is labeled in the figure. The solid line is the regression line for the SS vs. clay relationship, and the dotted line is the regression line for the SS vs. silt relationship. Both regression's R^2-values are visible in the figure.

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TECHNICAL REPORTS

Surface Water Quality

Variability in fluvial suspended and streambed sediment phosphorus fractions among small agricultural streams

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Abstract

Agriculture is a major source of sediment and particulate phosphorus (P) inputs to freshwaters. Distinguishing between P fractions in sediment can aid in understanding its eutrophication risk. Although streams and rivers are important parts of the P cycle in agricultural catchments, streambed sediment and especially fluvial suspended sediment (FSS) and its P fractions are less studied. To address this knowledge gap, seasonal variations in FSS P fractions and their relation to water quality and streambed sediment were examined in three Swedish agricultural headwater catchments over 2 yr. Sequential fractionation was used to characterize P fractions in both streambed sediment and FSS. All catchments had similar annual P losses (0.4–0.8 kg ha^{-1}), suspended solids (124–183 mg L^{-1}), and FSS total P concentrations (1.15–1.19 mg g^{-1}). However, distribution of P fractions and the dominant P fractions in FSS differed among catchments ($p < .05$), which was most likely dependent on differences in catchment geology, clay content, external P sources, and flow conditions. The most prominent seasonal pattern in all catchments was found for iron-bound P, with high concentrations during low summer flows and low concentrations during winter high flows. Streambed sediment P fractions were in the same concentration ranges as in FSS, and the distribution of the fractions differed between catchments. This study highlights the need to quantify P fractions, not just total P in FSS, to obtain a more complete understanding of the eutrophication risk posed by agricultural sediment losses.

1 | INTRODUCTION

Phosphorus (P) is a primary limiting nutrient in freshwater ecosystems (Correll, 1998; Schindler, 1974). Agricultural activities generate spatially variable and episodic P inputs to surface waters (Sharpley et al., 2009). Such nonstationary dynamics can lead to challenges for understanding the primary processes governing P mobility in different catchments as well as difficulties in predicting and implementing appropriate mitigation policies and countermeasures. These issues are common in agricultural headwater catchments, which can have a considerable influence on downstream rivers and lakes (Bol et al., 2018).

Abbreviations: Al-P, aluminum-bound phosphorus; Ca-P, calcium-bound phosphorus; Fe-P, iron-bound phosphorus; FFS, fluvial suspended sediment; H_2O-P, loosely bound phosphorus; OM, organic matter; org-P, organically bound phosphorus; PP, particulate phosphorus; RP, reactive phosphorus; SS, suspended solids; TP, total phosphorus.

Historical land management practices have caused accumulation of legacy P in soils and freshwater sediments (Kleinman et al., 2011; Sharpley et al., 2013) where biogeochemical processes can transform recalcitrant P fractions to more bioavailable forms (Lannergård et al., 2020). Although streambed sediments are important sources and sinks for P cycling (Ezzati et al., 2020; Jarvie et al., 2005; Owens & Walling, 2002; Weigelhofer et al., 2018), the role of fluvial suspended sediment (FSS) in P cycling is rarely investigated despite its potential significance. Different P fractions (e.g., phosphate-P, organic P, and metal-bound P) differ in mobility and bioavailability, which governs impacts on water quality and aquatic ecosystem functioning (Kaiserli et al., 2002; Ye et al., 2017). New insights into the relative and absolute amounts of different P fractions in both streambed and FSS will support more comprehensive assessments of potential effects of agriculture on aquatic ecosystems and generate more focused and effective catchment-specific eutrophication mitigation strategies.

Several chemical sequential extraction schemes exist to quantify different P fractions in sediment (Goedkoop & Pettersson, 2000; Hupfer et al., 2009; Psenner, 1988; Ruttenberg et al., 2009; Williams et al., 1976). Most schemes define operational P fractions, including loosely sorbed P, metal-associated P (e.g., iron [Fe] and aluminum [Al]), and calcium (Ca)-bound P (Condron & Newman, 2011). Numerous studies exist on P fractions in lake sediment (Agstam-Norlin et al., 2020; Kaiserli et al., 2002; O'Connell et al., 2020; Pettersson, 1998), and there are a few studies of P fractions in streambed sediment (Audette et al., 2018; Lannergård et al., 2020; San-Clements et al., 2009). However, studies of FSS are rare (Ballantine et al., 2008; Nguyen & Sukias, 2002), and knowledge about seasonal variations is needed.

The study aims were to quantify patterns in the distribution of P fractions in FSS and streambed sediment in three headwater agricultural catchments and investigate potential controlling factors (Aim 1), to investigate seasonal changes in distribution of FSS P fractions (Aim 2), and to explore relationships between water column phosphate P and the labile FSS P fraction as well as between water column and FSS total P (TP) (Aim 3). To address the study aims, FSS and streambed sediment from three well-monitored agricultural headwater catchments in southern Sweden were sampled over 2 yr and analyzed for different P fractions.

Core Ideas

- Similar total phosphorus losses were seen in three agricultural headwater streams.
- P fractions in suspended and bed sediment varied significantly among catchments.
- Large seasonal variations in suspended sediment P fractions were seen.
- Dominant P fractions are dependent on clay content, geology, and flow.
- Suspended and bed sediment P fractions should be included in routine monitoring.

2 | MATERIALS AND METHODS

2.1 | Catchment descriptions

Three small southern Swedish agricultural catchments (C6, U8, and E23) in the Swedish Environmental Monitoring program (Kyllmar et al., 2014) with a history of high P load and suspended solids (SS) transport were selected (Figure 1; Tables 1 and 2) (Sandström et al., 2020). All three catchments are dominated by agricultural land (>50%) and clay-rich soils. The smallest catchment, U8, has the heaviest soil texture (Table 1). Streams in U8 and E23 are small and can experience extremely low flows, especially in summer. The most southern catchment, E23, has a markedly higher stocking density and higher rates of manure applications (Table 1), whereas C6 has the lowest rate (Linefur et al., 2019). The U8 outlet is surrounded by agricultural fields, and the stream channel can become overgrown with vegetation during summer. The C6 stream outlet is also surrounded by agricultural fields, and alongside the outlet there is a wetland-like terrace that is inundated during high flows. Streambed sediments at the outlet of both U8 and C6 consist mainly of clay, overlain by organic material (2–5 cm). In E23, the catchment outlet runs through a forested area, with stones and twigs in the stream. Streambed sediment in E23 is harder than in U8 and C6 and contains substantially more gravel and sand.

2.2 | Fluvial suspended sediment and streambed sediment: Sampling strategy and sample preparation

Two Phillips samplers (Supplemental Figure S1) (Phillips et al., 2000) were placed at the outlet of each catchment to collect FSS. The samplers were positioned mid-stream at approximately mean depth above the streambed, with the inlet facing upstream (Phillips et al., 2000). During the first year, samplers were emptied approximately every fourth week into 10-L buckets (to collect FSS for further analyses) and then put back into the stream (Figure 1). Sampling started in C6 and U8 during autumn 2017, and E23 was added in autumn 2018. During 2018/2019, samplers were emptied every 8–10 wk to ensure enough FSS was collected for later analyses. From October 2017 to May 2018, the C6 stream was flooded, and samplers were not retrievable during this period; hence,

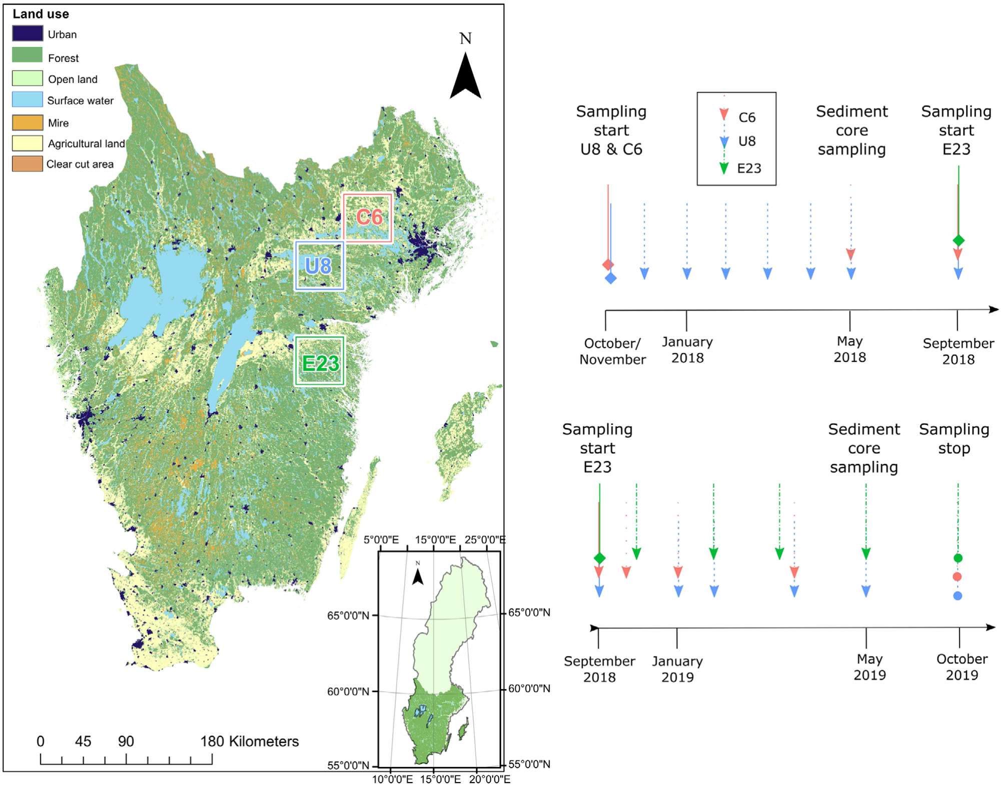

FIGURE 1 (Left) Locations of the three study catchments in southern Sweden including land use as the background map. Exact locations cannot be provided due to agreement with the farmers. The inset map displays Sweden with marked latitude and longitude lines. (Right) Illustration of sampling scheme of fluvial sediment and streambed sediment. The different colors represent the different catchments. Rhombi indicate sampling start for each individual catchment, filled circles represent the time at which sampling stopped, and colored arrows indicate sampling dates

one sample represents this entire 6-mo period. From April to May 2019 there was not enough material in the C6 samplers for analysis. All samples were brought back to the laboratory and wet sieved through a 0.063-mm nylon mesh to collect the smallest fractions and remove plant material. Samples were stored in 2-L buckets at 4 ˚C for at least 24 h to allow particles to settle. After sedimentation, as much supernatant as possible was removed through decanting and pipetting. The remaining material was transferred to a 50-cl centrifuge tube and centrifuged for 5 min at 3,500 rpm, and the supernatant was removed by decanting. Samples were stored in airtight boxes at 4 ˚C until analysis.

Streambed sediment cores were taken in each catchment at a mid-channel location as close as possible upstream from the Phillips samplers to get a representative sample from the stream rather than the streambanks. Each core was collected using a Willner gravity corer on a rod or by simply pushing the tube in manually, with two plugs creating a vacuum. In U8 and C6, cores were collected in May 2018. The E23 core was collected in May 2019. Cores were collected after the spring flood and before too much vegetation had grown to avoid plant disturbance. Due to the coarse and hard E23 streambed, this core was markedly shorter (4 cm) than cores from the other catchments (8–9 cm). All cores were sliced into 1 cm (where possible) slices in the field. Slices were stored in airtight cans at 4 ˚C until analysis (slices were held for a maximum of 6 wk).

2.3 | Water quality sampling and analysis

In each catchment, daily discharge was measured at the stream outlet by continuous water level recording at well-defined sections (i.e., a v-notch or broad-crested weir) (Kyllmar et al., 2014). Automatic flow-proportional and grab water samples were collected at the catchments' outlets within the frames of the Swedish Environmental Monitoring Program (Kyllmar et al., 2014). All samples were analyzed following Swedish Standard Methods (Kyllmar et al., 2014). Parameters reported here include total P (TP), phosphate-P (reactive P [RP], following Haygarth & Sharpley [2000]), and SS. Total P was analyzed on unfiltered water samples after digestion, whereas RP was analyzed after filtration at 0.2 µm, both using the molybdate blue method (Murphy & Riley, 1962). Particulate P (PP) was estimated as the difference between TP and RP. Estimates of flow-weighted concentrations and loads were based on Linefur et al. (2019) (see Methods in Supplemental Material).

2.4 | Sequential P fractionation

To analyze samples (suspended and streambed sediment) for P concentration and different P fractions, a sequential P fractionation method based on Psenner and Pucsko (1988), Psenner et al. (1984), and Hupfer et al. (1995), Hupfer, Zak et al. (2009) was used. The P fractions include loosely sorbed P, redox-sensitive P (iron/manganese [Fe/Mn] bound P), nonreducible and Al-hydroxide–bound P, organically bound P (org-P), Ca bound P (Ca-P), and refractory P. The main difference between the method used here and the aforementioned studies is omission of the refractory P step. All sediment samples were analyzed fresh and in triplicate. All fractions are operationally defined and will be referred to by their operational name as follows in parenthesis: extraction with Milli-Q water (H_2O-P), buffered dithionate solution (Fe-P), and NaOH (Al-P), organically bound P (org-P, defined as the difference between Al-P and extraction with NaOH following digestion), and extraction with HCl (Ca-P). All samples were analyzed at the end for RP (unfiltered) following Murphy and Riley (1962). All fractionation results are presented as mg g^{-1} in the context of FSS and streambed sediment comparisons or as mg L^{-1} for comparison to water column concentrations. The sum of all P fractions is hereafter termed "TP" because it has been found to be within ±10% of total sediment P (Huser & Rydin, 2005; Psenner, 1988). The first two steps in the sequential P fractionation method (H_2O-P and Fe-P) are commonly referred to as labile P (Huser et al., 2016; Reitzel et al., 2005, 2006) and were used for comparisons with RP in water columns.

All sediment samples were analyzed for dry matter content by freezing for at least 12 h at −20 °C and then freeze drying for at least 4 d. Loss on ignition to determine organic matter (OM) content of the sample was performed by igniting a freeze-dried sample for 2 h at 550 °C (Håkanson & Jansson, 1983).

TABLE 1 Catchment characteristics

Catchment ID	Sampling period	Area	Arable land	Stocking density[a]	Scattered households	Applied manure P (mean 2007–2010)	Three dominant soil texture classes[b]	Dominating bedrock (>50%) (main mineralogy)[c]	Precipitation[d]
		km^2	%	AU ha^{-1}	persons km^{-2}	kg ha^{-1}			mm
C6	Oct. 2017–Oct. 2019	33.1	59	<0.1	10	0.35	silty clay (77%), clay loam (14%), clay (4%)	quartz arenite (feldspar-mica-granite)	521
E23	Sept. 2018–Oct. 2019	7.4	54	0.6	7	17	clay loam (41%), silty clay (31 %), clay (19%)	granite (feldspar-mica-granite)	591
U8	Oct. 2017–Oct. 2019	5.7	56	<0.1	11	8	silty clay (85%), clay (14%), clay loam (1%)	granodiorite-granite (feldspar-mica-granite)	539

[a] Stocking density for all catchments, amount of P applied to E23, U8 (Kyllmar et al., 2014), and C6 (Linefur et al., 2017); 1 AU refers to one cow, three pigs, 10 sheep, or 100 hens.

[b] USDA data from Söderström and Piikki (2016).

[c] Bedrock information is from Geological Survey of Sweden (SGU, 2016).

[d] Precipitation and temperature are normal values (i.e., a long-term mean value, from SMHI 1961–1990; Alexandersson et al., 2001).

TABLE 2 Catchment data

Catchment ID	Temp.	pH (H_2O)[a]	TP conc.[b]	RP conc.[b]	PP conc.[b]	SS conc.[b]	TP load[c]	Discharge[d]
	°C		mg L^{-1}				kg ha^{-1}	mm
C6	5.5	7.5	0.21	0.05	0.15	144	0.4	226
E23	6.3	7.6	0.28	0.12	0.14	124	0.4	176
U8	5.9	7.3	0.26	0.06	0.19	183	0.8	230

[a] The pH value represents a mean value for the study period.

[b] Long-term mean concentrations of total P (TP), phosphate P (RP), particulate P (PP), and suspended solids (SS) (U8 and E23: 2007–2017; C6: 2004–2017) (Sandström et al., 2020).

[c] Long-term average load of TP (U8 and E23: 1995/1996–2014/2015; C6: 2005/2006–2014/2015) (Linefur et al., 2017).

[d] Long-term (1995/1996–2016/2017) average discharge (Linefur et al., 2019).

2.5 | Statistical analysis

Two-sided Wilcoxon rank sum tests were performed, where a p value <.05 was defined as significant. The same significance threshold was used for linear regressions and correlations. All sequential P fractionation results are presented as a mean of three subsamples. Standard deviations for each result are reported (Supplemental Tables S1 and S2).

To compare streambed sediment P fractions to concentrations in FSS, fluvial samples collected immediately prior to sediment core collections were used. Concentrations of P fractions in the top 4 cm of sediment were used because this depth is generally considered to be active (Reynolds & Davies, 2001). All statistical analyses were performed using R 3.6.2 (R Core Team, 2019).

3 | RESULTS

3.1 | Seasonal and between-catchment variations in FSS P fractions

Small temporal variations were observed for H_2O-P in U8 and E23 (Figure 2a). Proportions of H_2O-P were low and similar for all catchments (3.6–6.6% of TP; Figure 3a). The most prominent temporal change in concentration was recorded for the Fe-P fraction (Figure 2b), with a similar pattern in all catchments. The highest Fe-P concentrations (0.40–0.52 mg g^{-1}) were observed during summer; the lowest concentrations (0.13–0.23 mg g^{-1}) were observed during winter and spring (Figure 2b; Supplemental Table S1). Variation in Fe-P concentration was highest in C6 (CV, 56%; Supplemental Table S1), where it was the dominant fraction (Figure 3b).

In U8, Al-P was the dominant fraction (36%) and was significantly ($p < .005$) higher than in the other catchments (Figures 2c and 3c). For C6, the Al-P fraction was relatively stable over the study period (Figure 2c), with low total variation (0.16–0.26 mg g^{-1}; 11–27%) (Figure 3c). In E23 there seemed to be a monotonic decrease of Al-P with low total variation (0.09–0.30 mg g^{-1}; 10–16%) (Figure 3c).

Patterns for org-P were similar for all catchments, except for one peak in E23 in autumn 2018 (Figure 2d). In U8 and E23, the org-P fraction had the highest concentration variation among the different fractions (CV, 68 and 76%, respectively) (Figure 3d; Supplemental Table S2). In E23, org-P was the dominant fraction (32%) (Figures 2d and 3d). Organically bound P and Fe-P in FSS correlated positively ($R^2 = .37$, $n = 23$, $p < .05$). No other significant correlations between FSS P fractions were observed.

There was a significant difference between U8 and both C6 and E23 for the Ca-P fraction. However, the difference for Ca-P was not as clear as for Al-P (Figure 3e). Calcium-bound P was otherwise fairly stable for all catchments and had low total variation in concentrations (U8: CV, 30%; C6: CV, 6%, E23: CV, 23%) (Figures 2e and 3e; Supplemental Table S1), except for one peak in E23 and U8. Variation in TP concentrations was similar between catchments and had a clear seasonal pattern, with higher concentrations during summer and early autumn and a decrease during late autumn and winter (Figure 2f).

For U8, fractional H_2O-P concentrations were significantly lower ($p < .001$) than all other fractions, and Fe-P was significantly lower than the Al-P fraction, which was significantly higher than both the org-P and Ca-P fractions. At C6, the H_2O-P fraction was significantly lower ($p < .005$) than all other fractions. At E23, the H_2O-P fraction was significantly lower than all other fractions except for Al-P, which was significantly lower than the org-P fraction.

3.2 | Relations between water quality data, discharge, and FSS P fractions

Flow-weighted TP and SS concentrations correlated well when all catchments were used in the same linear regression ($R^2 = .71$, $n = 24$, $p < .001$). When tested separately, TP and SS correlated in U8 ($R^2 = .83$, $n = 12$, $p < .001$) and C6 ($R^2 = .90$, $n = 7$, $p < .01$) but not in E23 ($R^2 = .11$, $n = 5$, $p > .5$). The correlation between PP

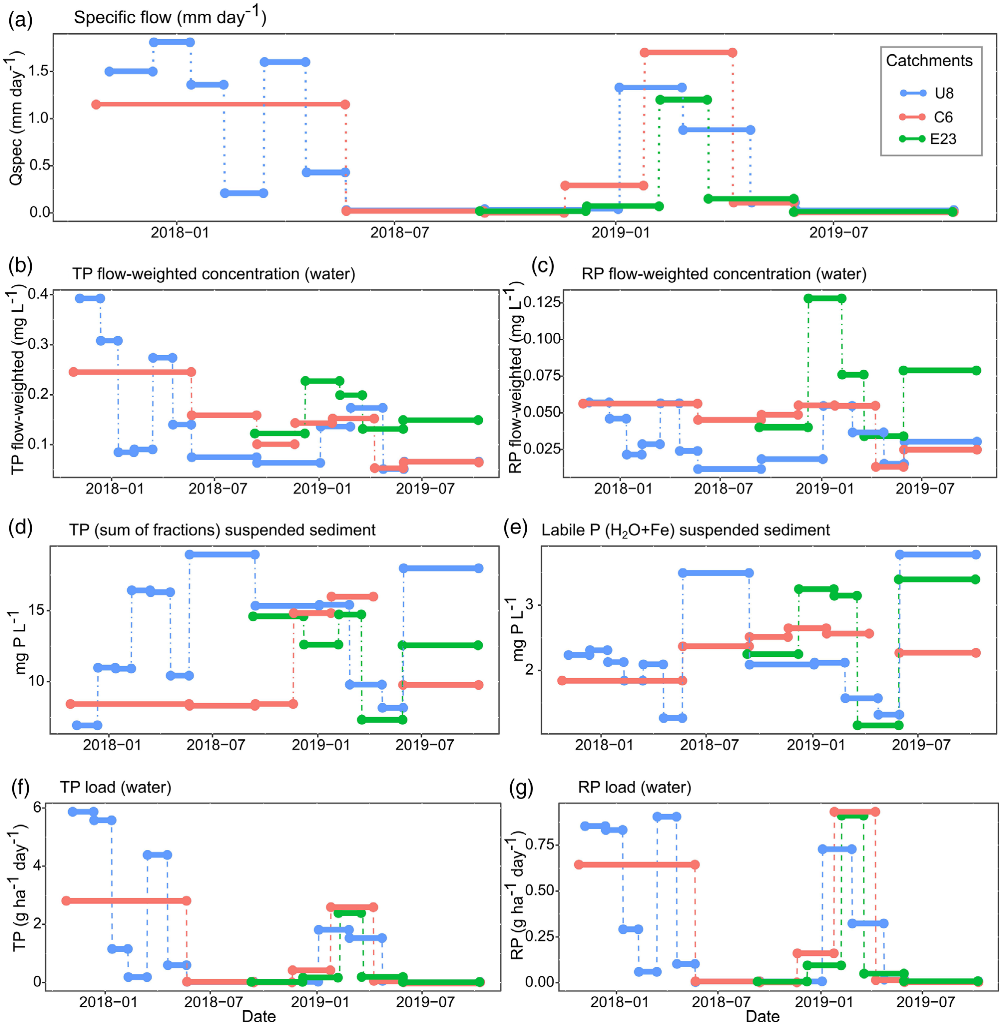

FIGURE 2 (a–e, g) Seasonal variations of the different phosphorus (P) fractions (Al-P, aluminum-bound P; Ca-P, calcium-bound P; Fe-P, iron bound P; H_2O-P, loosely bound P; org-P, organically bound P; TP, total P) over the sampling period in the three study catchments. Each bar in the graphs represents the concentration of the composite sample from the period the sampler was in the stream; different colors represent different catchments. The dotted lines are inserted to make it easier to differentiate the sampling periods. Sampling in E23 started approximately 1 yr after the other catchments, in September 2018 (green bars and dotted lines). Between April and May 2019 in catchment C6, not enough material was collected to perform the analysis, hence the tilted dotted red line. (f) Sum of the different fractions. Note that the y-axes are differently scaled for each fraction to enhance visibility of the individual changes of each fraction

and SS flow-weighted concentrations when all catchments were used in the same linear regression analysis was even higher ($R^2 = .80$, $n = 24$, $p < .001$) (Supplemental Figure S2). The only significant linear correlation between flow-weighted RP and SS concentrations was at U8 ($R^2 = .43$, $n = 12$, $p < .05$).

Annual specific discharge was well below average in all catchments in the second study year (Table 2; Supplemental Table S2; Supplemental Figure S3a). In all catchments, TP and RP loads followed the same pattern as the specific discharge (Supplemental Figure S3a,f,g). All catchments have similar flow-weighted TP concentrations, especially during

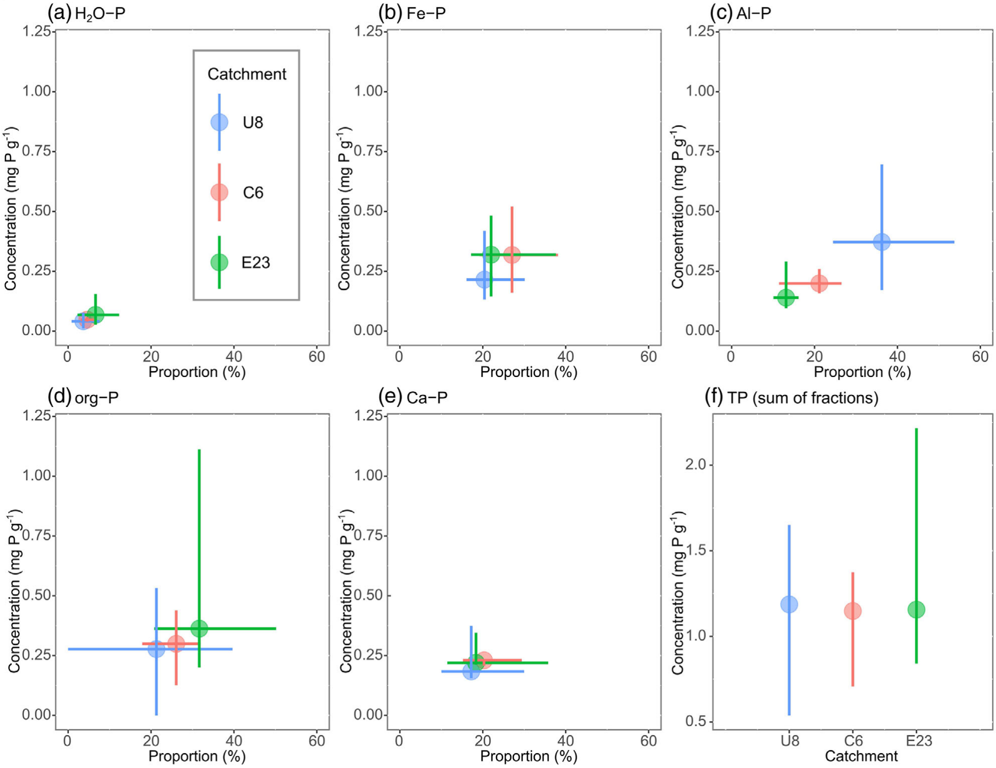

FIGURE 3 (a–e) Total variation of each phosphorus (P) fraction (Al-P, aluminum-bound P; Ca-P, calcium-bound P; Fe-P, iron bound P; H_2O-P, loosely bound P; org-P, organically bound P; TP, total P) in the fluvial suspended sediment and the sum of all fractions (f), colored by catchment. Dots represent the median value of each fraction, and the ends of the lines represent the minimum and the maximum values, respectively. The x-axis represents percentage of fraction, and the y-axis shows concentration of the fraction. In (f), only the variation in concentration of the sum of the fractions is displayed

the last study year (Supplemental Figure S3b). Flow-weighted water column and FSS TP concentrations showed no significant correlation (data not shown).

Flow-weighted water column RP concentrations seemed to follow a similar temporal pattern as FSS labile P (H_2O-P + Fe-P) (Supplemental Figure S3c,e). In C6 and E23, especially, a significant but weak correlation existed between the two variables ($R^2 = .16$, $n = 24$, $p < .05$) (Supplemental Figure S4). The RP/TP ratio was generally low for all catchments over the entire study period (Supplemental Table S2).

3.3 | Comparison of P fractions in FSS and the streambed active sediment layer

In all catchments, concentrations of different FSS P fractions immediately prior to sediment core collections generally followed concentrations in active streambed sediments (Figure 4) and were in the same concentration ranges. However, there were some clear differences.

In C6, Ca-P was higher in streambed sediment (64%) than in FSS (29%), where Ca-P was also the largest fraction (Figure 4a; Supplemental Figure S5). There were similar proportions (18 and 23%, respectively; Supplemental Figure S5) of the Fe-P fraction in the top streambed sediment and FSS. In streambed sediment, org-P was the smallest fraction, whereas H_2O-P was the smallest fraction in FSS (Figure 4a; Supplemental Figure S5).

In U8 streambed sediment, org-P, Al-P, and Fe-P concentrations and fractions were similar at 27, 30, and 30%, respectively (Figure 4b; Supplemental Figure S5). Relative fractions in FSS and streambed sediment were similar, except that org-P was the dominant fraction in FSS (40%) (Supplemental Figure S5).

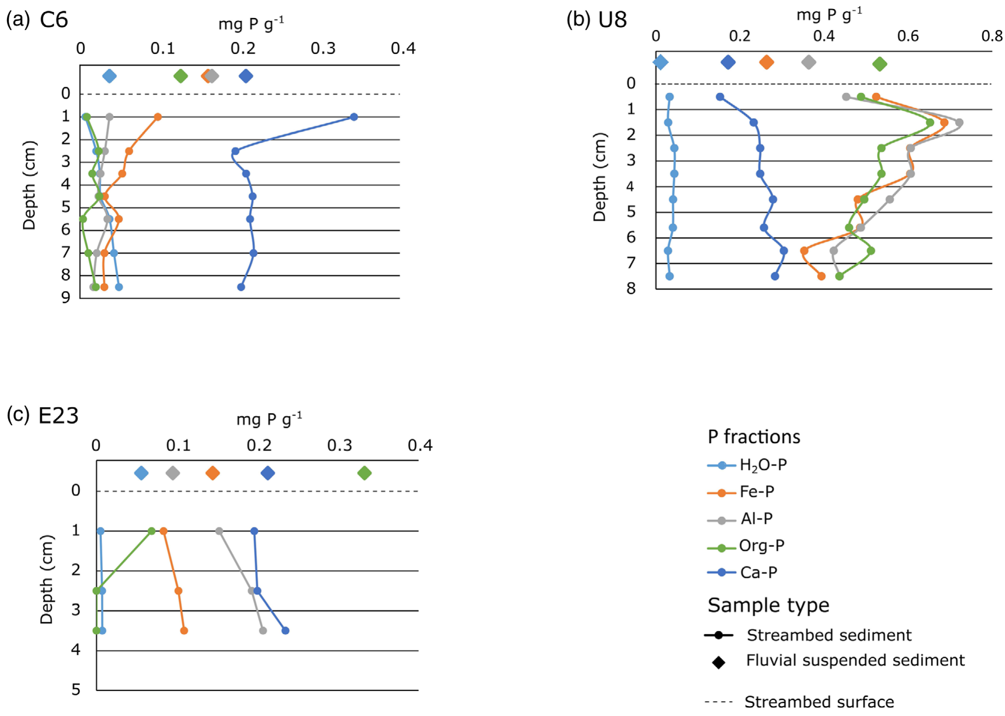

FIGURE 4 Concentrations of phosphorus (P) fractions (Al-P, aluminum-bound P; Ca-P, calcium-bound P; Fe-P, iron bound P; H_2O-P, loosely bound P; org-P, organically bound P; TP, total P) in sediment cores from the three catchments (dots and lines) and in fluvial suspended sediment (rhombi) from the period preceding sediment core collection. The different colors represent the different fractions, and a–c represent the different catchments. Each value is a mean value of triplicate samples from the same sediment sample

In E23, concentrations and fractions of org-P in FSS were clearly higher than in streambed sediment (Figure 4c), where Ca-P was dominant (Figure 4c). Calcium-bound P also contributed to a high proportion in the FSS (Supplemental Figure S5a). Concentrations and proportions of the Fe-P fraction were similar in the streambed and in FSS (Figure 4c; Supplemental Figure S5).

Organic matter content was markedly higher throughout the U8 streambed sediment profiles (20–30%) than in C6 and E23 (3 and 4%) (Supplemental Table S3). Streambed sediment profiles from U8 also had markedly higher water content (82–93%) than either C6 (40–64%) or E23 (31–35%) (Supplemental Table S3). No significant correlations between labile P in the active streambed sediment and corresponding RP flow-weighted concentrations were observed (data not shown).

4 | DISCUSSION

4.1 | Seasonal and between-catchment variations in P fractions in FSS and active streambed sediment

Although all catchments are dominated by clay soils and had similar FSS TP concentrations, the dominant P fraction in FSS differed between catchments. The identified differences between catchments are described below, and their probable explanations fullfil Aim 1 of the study. There was also a clear temporal variation in all catchments, especially for Fe-P, answering Aim 2.

4.1.1 | Labile P in FSS and streambed sediment

Bioavailability of different P fractions in sediments depends on environmental conditions, such as pH (Lukkari et al., 2007), redox conditions (Records et al., 2016; Sharpley, 1993), and turbulence (Withers & Jarvie, 2008). The labile P fraction (H_2O-P and Fe-P) together with org-P has been termed as "potentially bioavailable P" (Kaiserli et al., 2002). For H_2O-P, the most bioavailable fraction is PO_4^{3-}, which is directly available for uptake by aquatic organisms (Zhou et al., 2001). However, H_2O-P is likely to be of minor importance in these catchments due to its low concentrations. The Fe-P fraction is usually the largest pool of bioavailable P due to its high release potential from sediment undergoing changes in redox status (Li et al., 2016). Reducing conditions can occur in streambed sediment due to intrusion of anoxic groundwater (Krause et al., 2011) but also due to high microbial and biological activity in shallow, stagnant ditches during summer low flow (Sallade & Sims, 1997). Organically bound P can become bioavailable because it can be mineralized to RP (Reitzel et al., 2005; Schütz et al., 2017). Aluminum-bound P is considered stable in the pH range of surface waters (Stumm & Morgan, 1995). Calcium-bound P is usually contained in mineral lattices and hence is usually nonavailable or even considered inert (Lukkari et al., 2007). There is a need for further studies on the effect of environmental conditions on potential P bioavailability in FSS and streambed sediment in headwater streams because the environmental conditions affecting P release in headwater streams can differ from larger rivers as well as lakes (Lannergård et al., 2020).

In all catchments, the increases in FSS Fe-P during summer and early autumn corresponded to periods of lower specific discharge (Figure 2b; Supplemental Figure S3a). This decrease in discharge, along with higher temperatures and increased biological activity, could change the redox potential in streambed sediments, resulting in a reducing environment conducive to dissolution and in the release of ferric Fe and phosphate into the water column (Records et al., 2016; Sallade & Sims, 1997; Smolders et al., 2017). When sediment is mobilized from the streambed into the potentially more aerobic water column environment, Fe oxidation may occur converting Fe^{2+} to ferric Fe^{3+}, which can react with water column RP. Such Fe oxidation and RP sorption may occur on fluvial sediment particles, resulting in higher FSS concentrations and lower water column concentrations. The increase in FSS Fe-P is prominent in both summers, with a noticeable decrease during winter and spring months, when the specific discharge is higher (Figure 2b). Flow-weighted water column RP concentrations are also lower during summer, especially at the two smaller streams (U8 and E23), supporting this theory (Supplemental Figure S3c). Because the C6 stream is much larger than the other two streams, the flow rarely stagnates, staying in constant motion, with potentially less frequent anoxic conditions close to the streambed sediment surface. High amounts of FSS Fe-P during low flow periods, at times where anoxic conditions are more common, does suggest an increase in bioavailable P during the growing season. However, it is unknown whether these FSS particles would remain in suspension to settle in the streambed or be transported further downstream to receiving waters, potentially contributing to an increased P pool in receiving sediments.

The Fe-P fraction was dominant in FSS in C6 (Figure 3b), where soils around the catchment outlet are mainly silty clay loam. Catchment bedrock mineralogy (Table 1) does not imply a high Fe content, and there are no available measurements of Fe content in catchment soils or sediment. However, a probable explanation for the dominance of Fe-P in C6 is the presence of Fe hydroxides/oxides in the soil and sediment. Streambed sediment in C6 is similar to the FSS in that sense, with the Fe-P fraction being the second largest fraction, although decreasing with depth throughout the sediment profile. Earlier studies have found strong correlations between Fe and P in streambed sediment (Palmer-Felgate et al., 2009) and suspended sediment (Cooper et al., 2015), suggesting that when Fe is present in a higher amount under appropriate redox conditions, a majority of P will be bound to iron hydroxides/oxides. The national soil survey data show that Fe-P content in topsoils in this region, measured after extraction with ammonium lactate, was above the national average and the second highest among 20 studied regions of Sweden (Djodjic, 2015). Cooper et al. (2015) found strong correlations between Fe and P in suspended particulate matter in streams during base flow but not during storm flow. This supports our results with higher FSS Fe-P during low flow periods and lower Fe-P concentrations during high flow periods. Furthermore, McDowell et al. (2020) reported a decrease in streambed Fe-P with sediment depth, which was also observed in our study. Phosphorus release due to Fe hydroxides/oxides dissolution with progressively more reducing sedimentary conditions at depth may explain this pattern (Parsons et al., 2017).

The low concentrations and low variation in FSS H_2O-P in all catchments could be related to the low solubility of P because the pattern is similar in the streambed sediment. The FSS is in constant motion; thus, it is likely that any H_2O-P will either be taken up directly by biota or further transported. Similar behavior is likely to occur for H_2O-P in the active streambed sediment. Simpson et al. (2019) also found low concentrations of loosely sorbed P when studying the effects of different pretreatments on streambed sediment. McDowell et al. (2020) found low concentrations of H_2O-P in streambed sediment, with Fe-P as the general dominating fraction at their sampling sites. These low H_2O-P concentrations (or corresponding fractions in other fractionation schemes) seem to be quite consistent for streambed sediment and lake sediment (Kaiserli et al., 2002; McDowell et al., 2020; Pettersson, 1998).

4.1.2 | More stable P (Al-P and Ca-P) and geological conditions

In the smallest catchment (U8), Al-P is the dominant FSS P fraction, and the Al-P concentrations were markedly higher than in C6 and E23 (Figure 3c). In contrast, U8 had lower Ca-P concentrations than C6 and E23. Bedrock in U8 consists mainly of granodiorite-granite (Table 1) that contains plagioclase feldspar, generated from Al-containing minerals. Similarly, the Al-P fraction is high in U8 streambed sediment, which supports a geological weathering contribution to the Al-rich environment. The presence of particles such as Al-silicates (clay minerals) (House et al., 1998) and especially Fe and Al hydroxides and oxides (Zhang & Huang, 2007) will make RP react and bind to mineral or particle surfaces (Withers & Jarvie, 2008). The average clay content in U8 is approximately 10% higher than in C6 and E23 (Sandström et al., 2020), with Al as a primary element in most clay minerals. This also suggests more Al-P because clay minerals in soils having Al sheets in their structure have high P sorption capacity, depending on pH conditions (Gérard, 2016), where U8 has the lowest pH (Table 2). High P sorption to Al-containing clay minerals has also been found in lake sediments (Tonello et al., 2020). The C6 bedrock is instead mainly quartz arenite, and in E23, it is mainly granite. However, all catchments have similar mineralogy consisting of quartz, feldspar, and mica (Table 1). This implies that the bedrock might have less influence on P fractions in C6 and E23 because the mineralogy does not seem to be reflected in the P fractions as prominently as in U8.

The FSS Ca-P fraction was similar across all catchments, proving that parent soil material is quite comparable. However, there was one Ca-P peak in U8 at the end of the study period. This could be related to the practice of structural liming in the catchment. The practice, which is a popular mitigation measure to reduce P losses from clay soils in Sweden, is usually performed around that time of the year (Geranmayeh, 2017). Although no recorded data are available for structural liming during the study period in U8, structural liming was used in the catchment prior to 2013 when a product containing approximately 15% $Ca(OH)_2$ was applied at a rate of 4 t ha^{-1} (Malgeryd et al., 2015). In U8 streambed sediment profiles, Ca-P seemed to increase with sediment depth (Figure 4b), whereas in C6, the active streambed sediment had markedly higher Ca-P concentrations that then decreased and stayed more constant down through the core (Figure 4a). Calcium-bound P represents the most tightly bound P and is thus more stable deeper in the streambed sediment, where less, if any, exchange with the overlaying water column occurs.

4.1.3 | Organically bound P

The U8 catchment had a markedly higher OM content in streambed sediment (Supplemental Table S3) than C6 and E23. This was not reflected in the FSS, where OM content was more similar among the catchments (Supplemental Table S1). The low OM content in the streambed sediments compared with FSS in E23 and C6 was also reflected in the org-P fractions, with lower concentrations and proportions of org-P in streambed sediment but still moderately high concentrations of FSS (Figure 4b,c; Supplemental Figure S5). In U8, with a closer match in org-P content between the streambed and FSS, there was a lot of vegetation in the stream compared with C6 and E23. This catchment is also the smallest one (Table 1) and has periods of very low flow where the stream almost dries out. This contributes to slowing down the movement of water and FSS. In the larger C6 catchment, the stream flow was almost constant, and the FSS will likely not settle in the streambed for a longer time period. The vegetation itself in U8 is probably a contributor to the higher OM content in streambed sediment but could also contribute to trapping more OM by slowing flows, allowing it to settle in the streambed sediment (Cotton et al., 2006; Verschoren et al., 2017). In contrast, vegetation cover is much poorer in the coarser E23 streambed.

In E23, org-P was the dominant fraction in FSS, where it displayed a high variation in concentration but not as much variation in distribution (Figure 3d). The high concentration variation might be attributed to the peak in org-P at the start of the study period, although concentrations remained relatively high throughout, making the variation in distribution smaller. In comparison to the other catchments, FSS in E23 have generally higher org-P concentrations. The difference between the streambed and FSS in both org-P concentrations and OM content also suggests an external source of org-P. Differing from C6 and U8, E23 had a higher stocking density, higher manure inputs, and a horse paddock with a steep slope down to the stream located just upstream the sampling point (Ulén et al., 2011). The near-stream zone by the outlet of E23 is forested, unlike the other catchments that have mainly agricultural fields surrounding the outlet. The comparatively high FSS org-P concentration in E23 could reflect timing of manure application to the fields or direct inputs from the horse paddock, which are potential hotspots for P leaching (Parvage et al., 2015). This could have led to an increase in particulate P transport to the stream and thus to a peak in FSS org-P, which was not reflected in the streambed sediment. The weak but significant correlation between org-P and Fe-P might indicate that the org-P interacts with and contributes to the pool of bioavailable P.

4.1.4 | TP and general patterns between streambed and FSS

As stated in Section 3.3, P fractions and concentrations in FSS sampled immediately prior to streambed sediment sampling are in the same concentrations ranges as in the active streambed sediment having similar proportions of dominating fractions, especially in U8 and C6 (Figure 4). In contrast, mean values of FSS P fractions and concentrations over the whole study period did not reflect the active streambed sediment as well. Due to the marked variations in FSS P fractions and concentrations over time, a comparison with the time-aggregated mean value would not be representative. Unfortunately, due to high flow conditions, the C6 FSS sample was collected over a longer time period than in U8 and E23 and thus may not be as representative. Our study supports Palmer-Felgate et al. (2009), who found a significant correlation between TP in streambed sediment and P concentration in suspended sediment in catchments having different agricultural land use intensity, but the relationships with stream water P concentrations were not as clear.

All catchments had approximately the same median FSS TP concentrations (Figure 3f) and had similar seasonal variation. Selection of catchments was based on long-term monitoring indicative of high transport of P and SS. Interestingly, the two smallest catchments had the greatest total variation in FSS TP concentrations, even though the concentrations varied in all catchments. Notably, this study has important implications for understanding the P cycle in headwater catchments. It supports the argument of Bol et al. (2018) for a greater focus on headwaters due to their high variability in P losses (Haygarth et al., 2012). Moreover, it demonstrates that focusing solely on TP dynamics will provide an incomplete indication of P mobility and reactivity among headwaters because it neglects variation in FSS P fractions and bioavailability. The variation in FSS P fractions has been shown by increases in Fe-P during the growing season.

4.2 | Water quality and P in FSS

The observed correlations between flow-weighted PP and SS concentrations (Section 3.2; Supplemental Figure S2) support earlier work in these catchments (Sandström et al., 2020). The lack of significant relationships between SS and RP (except for in U8) and the low loads and concentrations of RP reflect the dominance of PP in these catchments.

Comparisons of water column P fractions with corresponding FSS P fractions to address Aim 3 of our study showed a weak correlation between FSS labile P and water column RP (Supplemental Figure S4). This illustrates the complexity of P circulation in small headwater catchments, where no clear relationship to flow was visible for all catchments. The U8 catchment had two outlying sampling occasions with low discharge (high FSS labile P and low water column RP concentrations; Supplemental Figure S4) and was the only catchment with a significant relationship between RP and SS. This suggests that during high discharge, some water column RP might consist of small clay particles or colloids that will pass through a filter and be identified as RP instead of PP. Indeed, Ulén (2003) showed that the colloidal P fraction was important in surface runoff, tile-drainage water, and stream water in a clay-dominated catchment in central Sweden. The significant but weak correlation between labile P and water column RP could also indicate the importance of external sources, such as manure.

In U8, where redox-independent Al-P was the dominant P fraction, FSS TP concentrations seemed to display an opposite pattern to water column TP concentrations (Supplemental Figures S3b and S5d). Here also FSS TP concentrations seemed to be highest during low flow periods, whereas water column TP was also low. This could be explained by low SS losses during low flow periods, resulting in P enrichment on SS particles (Sandström et al., 2020). It also points toward an exchange between FSS and the water column, where P could theoretically be sorbed to suspended sediment particles, increasing the concentration on the particles during periods with low concentrations of water column TP.

During the second study year there was a drought in Sweden (SMHI, 2018), resulting in low flows in all catchments (Supplemental Figure S3a), especially E23 (Supplemental Table S1). The drought affected TP loads and concentrations, with lower levels than usual in all catchments. Although the effect of the drought on FSS P fractions is difficult to establish from the 2-yr study period, effects of flow on redox conditions and temporal variability in the Fe-P fraction are visible.

5 | CONCLUSIONS

Based on time-integrated sampling of FSS in the three headwater catchments covering different seasons in combination with water quality monitoring data and streambed sediment sampling, the following conclusions can be drawn:

- There is a significant difference in the distribution of FSS P fractions in the three catchments. The differences are likely related to differences in geology, soil clay content, external P sources and flow conditions.
- There are seasonal variations, especially for Fe-P, in FSS P fractions and concentrations in all catchments that may

be due to seasonal changes in flow, temperature and redox conditions.

- Water column TP concentrations are not clearly related to FSS TP, with an almost opposite temporal pattern. There is a weak but significant positive correlation between water column RP and FSS labile P.
- The P fractions found in FSS are in the same concentration ranges as P fractions in the streambed sediment; however, the distribution of different P fractions differs. Although the dominant P fractions were the same in FSS and streambed sediment for C6 (Ca-P) and U8 (org-P, Al-P, and Fe-P), the fractional distribution in streambed sediment and FSS show no resemblance in E23.

This seasonality of FSS P fractions shows the importance of measuring different P fractions and not only TP during ecologically sensitive periods. Because the FSS may act as the interface between the streambed sediment and the water column, measuring and reporting P fractions in FSS will lead to a better understanding of the biogeochemical processes controlling P dynamics in agricultural headwaters.

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AUTHOR CONTRIBUTIONS

Sara Sandström, Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing-original draft, Writing-review & editing; Martyn N. Futter, Conceptualization, Data curation, Methodology, Supervision, Writing-review & editing; David W. O'Connell, Conceptualization, Funding acquisition, Methodology, Writing-review & editing; Emma E. Lannergård, Formal analysis, Investigation, Writing-review & editing; Jelena Rakovic, Formal analysis, Writing-review & editing; Katarina Kyllmar, Conceptualization, Methodology, Supervision, Writing-review & editing; Laurence W. Gill, Funding acquisition, Writing-review & editing; Faruk Djodjic, Conceptualization, Data curation, Investigation, Methodology, Project administration, Supervision, Writing-review & editing.

CONFLICT OF INTEREST

No conflicts of interest are relevant for this study.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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Environmental monitoring data, field and laboratory studies and computer modelling were used to study transport of suspended solids (SS) from headwater catchments, seasonal variations of phosphorus (P) fractions and connections between SS, P and catchment characteristics, to increase understanding of these processes to combat eutrophication. Clay content and share of arable land in the catchment control SS and P losses. Findings from headwater catchments scale up well to larger catchments. Phosphorus fractions on SS vary between catchments and over season.

Sara Sandström received her graduate education at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences. She received her M.Sc. degree in Aquatic and Environmental Engineering from Uppsala University.

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