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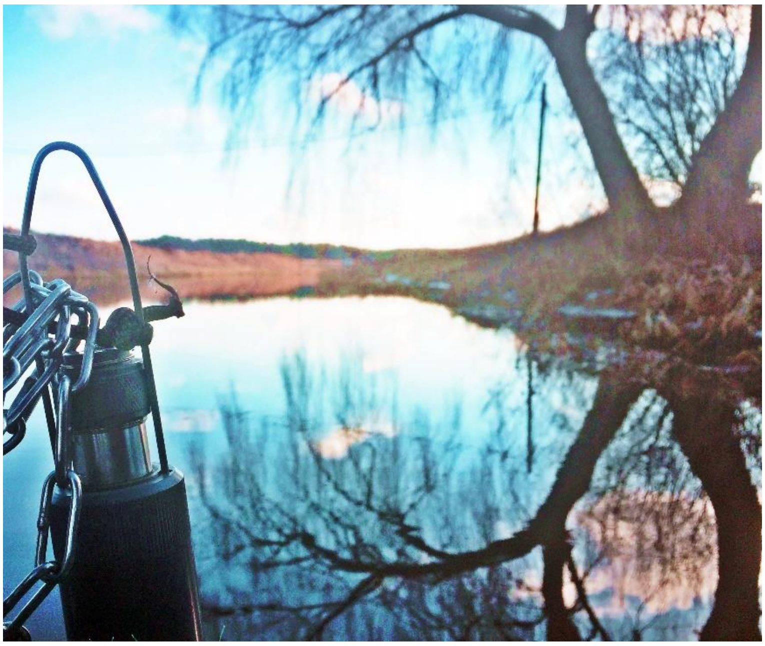

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Abstract

Transport of particles carrying nutrients and contaminants from land to sea is a challenge to monitor due to the high temporal variability in concentrations. Phosphorus is a particle associated nutrient, largely affecting the state of waters due to its effects on eutrophication. When using traditional monitoring methods, there is a prevailing risk of misjudging the state of water and transport of phosphorus due to lack of data. Therefore, this study aimed to evaluate the potential use of continuous high frequency turbidity as a proxy for total phosphorus concentration. An in situ sensor monitoring turbidity every 10th minute was deployed from 2012-2015 in Sävjaån, a river draining a mixed land use catchment in central Sweden. The sub-catchment is an agricultural area dominated by clay soil close to Uppsala in Sweden. The results from measuring high frequency turbidity with the sensor were compared to traditional monthly grab sampling. A significant information loss could be observed when performing grab sampling, the turbidity from the sensor varied more and showed higher maximum values (9-15 times). The correlation between the different parameters was evaluated by linear regression. The results show very high correlation between turbidity and total phosphorus (r^2= 0.79) and high correlation between turbidity and total suspended solids (r^2= 0.67). The relationships seemed to be affected by calibration of the sensor, spatial variation and the proportion of phosphate and total phosphorus in Sävjaån. The phosphorus load was calculated from the high frequency data and compared to linear interpolation and piecewise constant interpolation of grab samples. Loads calculated from high frequency data was during two years (2012 and 2015) 31% and 17% larger than when using linear interpolation. However, the timing and the instant flow at the time of grab sampling had large impact on the estimated load when using linear interpolation (2013 and 2014). It could be concluded that most P was transported when high discharge and high concentrations coincided. When comparing the calculations of ecological quality ratios from grab sampling and high frequency data the difference was modest.

Populärvetenskaplig sammanfattning

Kontinuerligt rapporteras det i svenska medier om algblomning och övergödning i ytvatten och i Östersjön. Ökat antal algplankton och bakterier skapar en grön och grynig vattenmassa. Det leder även till potentiell syrebrist i vattnet och störda ekosystem. Ur ett historiskt perspektiv har mängden näringsämnen som transporteras till Östersjön ökat. Idag är det främst jordbruk, vattenreningsverk, industrier, privata avlopp och dagvatten som bidrar till problemet. Fosfor är ett av näringsämnena som till stor del påverkar övergödningsproblematiken.

För att kunna hantera övergödningsproblematiken behöver vi veta hur det är ställt i svenska sjöar och vattendrag. Vanligtvis tas månatliga vattenprover som analyseras i ett laboratorium, tiden mellan vattenproverna estimeras med hjälp av olika metoder. Fosforhalten i vattnet varierar dock avsevärt i tid och rum. På grund av det är den årliga transporten fosfor från ett vattendrag svår att uppskatta på ett trovärdigt sätt.

I den här studien har en ny metod för att beskriva förhållandena i Sävjaån testats och utvärderats. En sensor som mäter grumlighet i vatten (turbiditet) var 10:e minut har monterats i Sävjaån i närheten av Uppsala under perioden 2012-2015. Fosfor transporteras ofta tillsammans med partiklar och dessa bidrar till grumlighet i vattnet. Därför har möjligheten att använda turbiditet som ett substitut för fosformätningar undersökts.

Det visade sig finnas ett väldigt starkt samband mellan turbiditet och fosfor i Sävjaån. Ett starkt samband kunde även observeras mellan turbiditet och mängd vattenburna partiklar (suspenderat material/slamhalt).

När förhållandena i vattnet övervakades med hjälp av sensorn var det tydligt att mycket information saknades när endast månatliga vattenprover togs. När de två metoderna jämfördes varierade grumligheten mer och 9-15 gånger högre maximala värden uppmättes. Den totala mängden transporterat fosfor per år visade sig vara 31% and 17% (2012 och 2015) större när den beräknades med hjälp av informationen från sensorn i jämförelse med den vanligen använda metoden. När höga vattenflöden inträffade samtidigt med höga fosforkoncentrationer transporterades störst mängd fosfor.

Även om det innebär en osäkerhet att använda grumlighet som ett mått för fosfor finns stora möjligheter till bättre uppskattningar av fosfortransport. Med en välskött sensor och noggrant kontrollerad data finns potential för mer representativa resultat som kan hjälpa samhället att hantera övergödningsproblematiken på ett bättre sätt.

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Abbreviations

Al	Aluminium
Ca	Calcium
DIP	Dissolved inorganic phosphorus
DOP	Dissolved organic phosphorus
EQR	Ecological Quality Ratio
Fe	Iron
FNU	Formazin Turbidity Unit
HELCOM	Convention of Helsinki
HF	High frequency
ISO	International Organization for Standardization
N	Nitrogen
NTU	Nephelometric turbidity units
P	Phosphorus
PIP	Particulate inorganic phosphorus
POP	Particulate organic phosphorus
PO_4-P	Orthophosphates
PP	Particle phosphorus
RMSE	Root mean square error
SE	Standard error
TP	Total phosphorus
WFD	Water Framework Directive
TSS	Total suspended solids

1 Introduction

The continuous movement of particles from land to sea is part of our constantly changing environment. Terrestrial erosion could be initiated by movement of water, wind or gravitational forces (Owens, 2007). The largest particle loads are transported during high discharge, possibly caused by snowmelt or heavy rain but also by landslides or anthropogenic activities such as machinery use or dredging. In Sweden soil erosion has historically not been considered as a severe problem compared to other parts of the world (Brandt, 1990). The situation is favoured by comparably low rain intensities, limited surface run-off, permeable soils and a dense vegetation cover. Yet, soil particles are major carriers of pollutants such as phosphorus (P), heavy metals, pesticides and organic contaminants (Brandt, 1990; Bilotta & Brazier, 2008; Gao *et al*., 2008). Despite the relatively moderate level of soil erosion in Sweden, the yearly amount total suspended solids (TSS) has a significant influence on the total load of nutrients and pollutants transported every year (Djodjic *et al*., 2012).

Freshwater systems and oceans are usually limited by nitrogen (N) or P availability (Elser *et al*., 2007). During the last century, surface waters flowing to the Baltic Sea have been exposed to accelerated nutrient loads caused by anthropogenic activities (Gustafsson *et al*., 2012a). Total phosphorus (TP) loads have increased by a factor of 3.1 and N loads by a factor of 2.4 throughout the last 100 years (Humborg *et al*., 2007). Nutrient over-enrichment results in high primary production and low oxygen levels due to decay of aquatic vegetation (Gustafsson *et al*., 2012a; Kiedrzyńska *et al*., 2014; Lundberg, 2005). Partial oxygen deficit and expanding hypoxia in deep waters certainly affects the biodiversity in water bodies (Lundberg, 2005).

Human-related pressures from primarily agriculture (Larsson & Granstedt, 2010) but also wastewater effluents, industrial pollution and storm water are influencing the export of nutrients (Kiedrzyńska *et al*., 2014). Eutrophication is today considered to be one of the most serious problems regarding the state and health of surface waters and the Baltic Sea (Kiedrzyńska *et al*., 2013; Ahlvik & Pavlova, 2013). In the 1980's, the Helsinki Convention (HELCOM) was established with the aim of reducing nutrient export to the Baltic Sea with 50% (Grimvall & Stålnacke, 2001). In the year of 2000, concerns about water and environmental sustainability led to approval of the Water Framework Directive (WFD) in EU (EU, 2000).

The WFD was accepted in EU with the objectives to improve, protect and prevent further deterioration of European water bodies (Allan *et al.,* 2006). Yet to handle water policy and make reliable decisions, the state of the environment needs to be known. To comply with the WFD, a lot of resources are annually spent on producing reliable data to monitor and assess surface waters (Allan *et al*., 2006). When remediation plans and strategies should be elaborated, reliable water quality monitoring is critical to make trustworthy decisions (Glasgow *et al*., 2004). Accurate load estimations are also of highest importance when working with input loads in the HELCOM agreement. In spite of this, in many cases the data obtained have insufficient temporal and spatial resolution to give a representative picture of the water body (Allan *et al*., 2006). Use of low-cost tools, for example passive samplers and sensors, needs to be established to successfully implement legislation, for example the WFD.

Highly temporal variable parameters, for example TP, are a challenge to monitor at good resolution (Skarbøvik & Roseth, 2015). Traditional monitoring methods such as monthly grab sampling and composite sampling come with different complications. When performing grab sampling, a lot of time is unmonitored and an unrealistically high sampling frequency is required to get a representative picture of the water body (Koskiaho *et al*., 2015; Jones *et al.,* 2011). This is especially valid during periods with flashy hydrology (Gippel, 1995; Jones *et al*., 2011). Therefore, infrequent grab sampling might result in inaccurate estimates of average and maximum concentrations (Skarbøvik & Roseth, 2015). When using composite sampling, several sample units are combined into a mixed sample. This leaves less time unmonitored and accordingly gives a representative general picture, yet minimum and maximum values cannot be obtained from the data (Skarbøvik & Roseth, 2015). Both grab sampling and composite sampling also need funding of lab costs.

It is important to estimate transport of particles (TSS) and P to assess output loads, sources of contamination, evaluate measures taken and estimate nutrient losses for international regulations (for example HELCOM) (Moatar & Meybeck, 2005).

When calculating load, a concentration of a certain parameter (for example P) and water flow are used (Grayson *et al.,* 1996). For example a monthly concentration is interpolated to daily values and multiplied with daily flow rates. The instantaneous concentration is usually only representative for the flow at the time of sampling, yet it is often used for the whole flow range in between the sample occasions. This results in a systematic bias and unrepresentative estimations of load. The bias is also connected to the fact that high flow events, which generally transport a lot of TSS and P, might not be monitored. Sampling frequency is also important when using water quality models, large datasets are desirable to get trustworthy estimates (Jones *et al*., 2011).

Accordingly, the sampling frequency needs to be increased when monitoring temporally varying parameters to comply with legislation and assess the state of the environment. In a study by Cassidy & Jordan (2011), it is even stated that only near-continuous monitoring is sufficient to perform comparative monitoring and evaluation of P. An available method for performing high frequency monitoring is deploying an in situ sensor in a stream to explore spatial differences and riverine fluxes (Koskiaho *et al*., 2015). Yet, not all parameters can be recorded by an in situ sensor collecting information continuously. A parameter that can be recorded in situ is turbidity. Skarbøvik & Roseth (2015) state that sensor recordings of turbidity have been proved better at recording high concentrations of turbidity than both fortnightly grab sampling and composite sampling. Earlier studies described the method to be especially useful during high flow events (Ruzycki *et al*., 2014; Kronvang *et al*., 1997). Grayson *et al*. (1996) accentuate that dependent on the quality of correlation, continuous measurement of one parameter (e.g. turbidity) can be used as a proxy for another parameter of interest (e.g. TP).

Earlier studies have analysed the potential of using high frequency monitoring of turbidity as a proxy for TSS and TP or particulate P (PP) concentrations (Grayson *et al.,* 1996; Jones, *et al.* 2011; Ruzycki *et al.* 2014; Skarbøvik & Roseth, 2015; Koskiaho *et al.,* 2015). Results show significant correlations between the parameters which indicate that the high frequency data could be useful when assessing eutrophication. With detailed data regarding P concentration over time, understanding of P transport in the catchment would increase. Well-functioning and maintained automatic systems can produce more accurate estimations of loads than manual grab water sampling since less time is unmonitored and interpolated (Koskiaho *et al*., 2015; Jones *et al.,* 2011). Data would also be more statistically robust and more reliable when making remediation plans and strategies in order to fulfil the requirements of the WFD.

Still, studies assessing the suitability in different types of water bodies are scarce (Skarbøvik & Roseth, 2015). The method also needs to be calibrated at each new site to obtain highest accuracy (Ruzycki *et al*., 2014). There is also a need for evaluation of different types of sensors, parameters and what they can substitute as well as advantages and disadvantages. Also Kronvang & Bruhn in 1996 stressed that studies identifying the most reliable load estimating method is of highest importance.

In this study the possibilities of using an in situ sensor measuring high frequency turbidity will be explored. The sensor has been operated from 2012-2015 and is located in a meso-scale catchment (733 km^2) in a stream called Sävjaån, central Sweden. In the area, excessive nutrients are a major problem, since nearly 50% of the lakes and streams are regarded as eutrophic (Vattenmyndigheten, 2016b).

1.1 Objectives

The aim of this study is to evaluate the use of continuous turbidity measurements as a proxy for TP concentrations in Sävjaån. The study will assess the suitability and the result of using the method. High frequency data will be used to generate an estimate of TP load from the catchment and the result will be compared with fluxes calculated with conventional methods.

The following research questions will be assessed:

- How well correlated are the turbidity detected by the sensor and turbidity from grab sampling and laboratory analysis? Is it possible to distinguish a difference between the two methods and what is the magnitude of the difference?
- Is turbidity a useful proxy for TSS and TP in Sävjaån? How well correlated are the turbidity detected by the sensor and TSS and TP, respectively? To what extent can we observe the assumption of turbidity and TP concentration following the same patterns in Sävjaån with current data?
- What are the consequences of using high frequency data? How are load estimations affected when using high frequency turbidity as a proxy for TP compared to other methods?
- What are the limitations and advantages with high frequency monitoring according to the observations in this study?

2 Theoretical framework

The relation between turbidity and TSS has been studied historically motivated by the challenge in monitoring highly variable parameters in running waters. Since particles create cloudiness in water, which is measured as turbidity, the two parameters are closely connected. In addition, TSS and TP are two connected parameters since P is often particle bound. Consequently, the idea of using turbidity as a proxy for TP originates from the connection between the two parameters through particles. This section will describe the parameters of interest and what could affect the relationship between them.

2.1 Turbidity

According to the ISO standard 7027:1999 (International Organization for Standardization) turbidity is defined as:

> "reduction of transparency of a liquid caused by the presence of undissolved matter"

Turbidity is an optical expression of cloudiness in water. It is estimated by emitting a light beam into the water and measuring light that is scattered off from particles present instead of going straight through it (YSI, 2012). Mineral or organic suspended particles and colloids including suspended sediments, algae, humus, clay or air bubbles, scatter or adsorb the light (Gippel *et al*., 1995; Naturvårdsverket, 1999; Ruzycki *et al*., 2014). Hence turbidity does not represent a mass of substance in water and cannot be directly used when calculating material fluxes (Koskiaho *et al.,* 2015). In streams, inorganic particles dominate the effect on turbidity, to a large part coming from soil erosion or sediment (Naturvårdsverket, 1999).

According to the definition in ISO 7027:1999 dissolved particles are not included in the term turbidity. Dissolved particles are commonly recognized as particles that will pass a 0.45 µm membrane filter (Horowitz, 1992). However, what will pass through a filter is not only dependent on particle size but also on the filter and the filtration method. Technical problems can create biased results when differentiating dissolved and particulate matter. Problems can, for example, be adsorption to the filter creating filtration artefacts (Horowitz, 2013), clogging of the filter (Ulén, 2004) and the aggregation and breakup mechanism of colloids (Zeidan *et al.,* 2007). This makes the physical definition of dissolved particles quite arbitrary. The sensor manufacturer (YSI) and prevailing literature include dissolved particles in the term 'turbidity'. Bilotta & Brazier (2008) describe turbidity as influenced by dissolved humic substances, dissolved minerals < 0.45 µm, algal cells > 0.1 µm, sediment particles between 0.45 - 63 µm and detrital organic matter of all sizes. In this study, both dissolved and undissolved matter will be included in the term 'turbidity'.

Turbidity is a parameter commonly used to assess TSS, and would tell something about the amount of particles in the water as well as light conditions (Jalón-Rojas *et al*., 2016). The cloudiness in water could, for example, depend on soil erosion, turbulence, TOC concentrations and primary production. According to the Swedish Environmental Protection Agency (Naturvårdsverket, 1999) turbidity in streams can be evaluated according to Table 1 from May until October or annually (if a mean is taken from monthly values).

Table 1. *Interpretation of turbidity according to the Swedish EPA (Naturvårdsverket, 1999).*

Interpretation	Range (FNU)
Not turbid	< 0.5
Weakly turbid	0.5 - 1.0
Moderately turbid	1.0 - 2.5
Significantly turbid	2.5 - 7.0
Strongly turbid	> 7.0

2.2 Total suspended solids

According to the standard SS-EN 872:2005, the parameter suspended solids is defined as:

> "solids removed by filtration under specific conditions"

The standard states that the water should be filtered through a glass fibre filter using vacuum pressure, the filter is then dried (105°C) and the mass residue weighed. An arbitrarily defined boundary is that particles >0.45 µm are considered as sediment (Owens, 2007). Another definition is that the parameter TSS describes inorganic and organic fine particulate matter generally between 0.7-63 µm (Bilotta & Brazier, 2008). Colloidal particles are excluded in both of these definitions since they range between 0.001-1 µm (Owens, 2007). When describing the transport of suspended solids, the colloidal fraction is usually trivial (Bilotta & Brazier, 2008). Nevertheless it could contribute significantly to the transport of contaminants (Bilotta & Brazier, 2008) as for example micro colloids of clay make the largest contribution to surface area of TSS (Ulén, 2004). The source and size of particles included in the terms TSS and turbidity differs (figure 1).

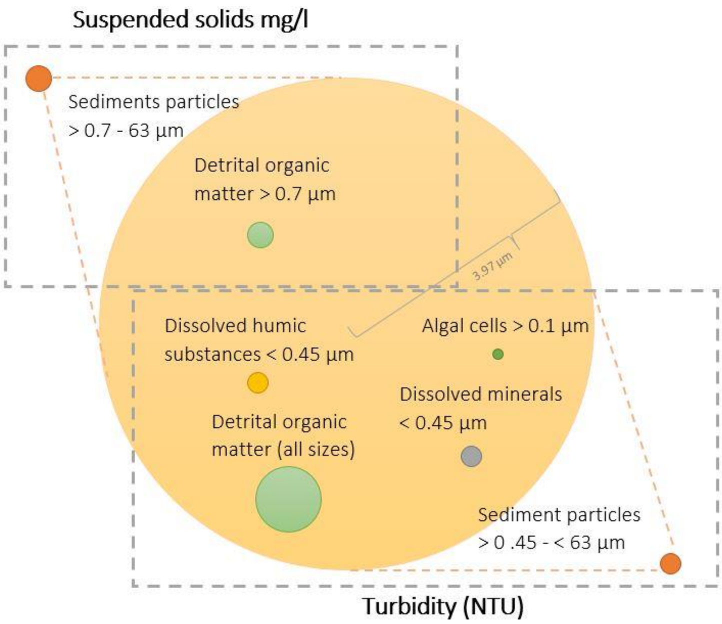

Figure 1. *Type and size of particles included in the terms TSS and turbidity. Data from Bilotta & Brazier (2008). Please observe that for the definition of Owens (2007) 0.7 µm, the category of suspended solids would be 0.45 µm.*

The difference in definition makes a direct translation between TSS and turbidity biased (for example during summer when primary production is high). Gippel *et al.* (1995) suggest that correlation between turbidity and TSS works best if particle size varies between 1.2-1.4 µm, but that adequate relationships could be expected in most situations. The relationship between turbidity and TSS is, however, dependent on particle composition, water colour and particle size distribution (clay to sand).

The particle composition could affect the relationship since organic particles give higher turbidity than mineral particles (2-3 times) (Gippel *et al.*, 1995). This is related to the shape and surface area, since organic particles have lower specific gravity and a fluffy surface texture. Pfannkuche & Smith (2003) conclude that inorganic sediment primarily scatters light in water but agree that living particles (algae and bacteria) also could affect the relation between turbidity and TSS. In a study by Viviano *et al*. (2014) it is argued that the relationships in urban catchments are more complex due to organic matter of anthropogenic origin. The composition of particles should vary in time and space, connected to the mechanisms controlling sediment transport (Gippel *et al*., 1995).

In a study by Gippel *et al.* (1995) it was shown that dissolved organic matter (water colour) could alter the turbidity by 10%. Today the manufacturer (YSI, 2016) argues that by choosing near infrared light at a certain wavelength this problem is minimized.

Also, other studies have identified particle size distribution as important for the relationships between turbidity and TSS and TP (Jones *et al*., 2011; Stubblefield *et al.,* 2007; Skarbøvik & Roseth, 2015; Ruzycki *et al*., 2014). Particle sizes could affect the relationship since different size ranges contribute unevenly to the turbidity (Yao *et al.,* 2014).

The characteristics of the catchment affect spatial variation of particle size distribution which could be a possible explanation to why the relationship between turbidity and TSS are site specific (Gippel *et al.,* 1995, Walling & Moorehead, 1987). Spatial variation in particle size distribution is considerable and important factors affecting the distribution include slope erosion which would generate finer particles, local soil properties, sediment delivery from other sites (Walling & Moorehead, 1987), stream morphology and bank vegetation (Schlosser & Karr, 1981).

Moreover, particle size distribution could vary dependent on season (Bogen, 1992) and specific storm events (Walling & Moorehead, 1987; Pfannkuche & Smith, 2003). In a literature review by Walling & Moorehead (1987), larger particles increased with flow in 8 of 11 scientific studies. Pfannkuche & Smith (2003) found that the relationship between turbidity and TSS generally had a good correspondence. However, during certain high flow events the relationship was inverted (TSS exceeded turbidity), the turbidity also varied more. This was later explained by the fact that particle size varies more at high flow since larger particles are suspended and that the size distribution is more homogeneous at low flow.

2.3 Phosphorus

In water P can be present in several operationally defined forms, dissolved or particle bound each of which contain inorganic and organic forms (Figure 2; Yoshimura *et al.*, 2007). TP accounts for P in all the different forms.

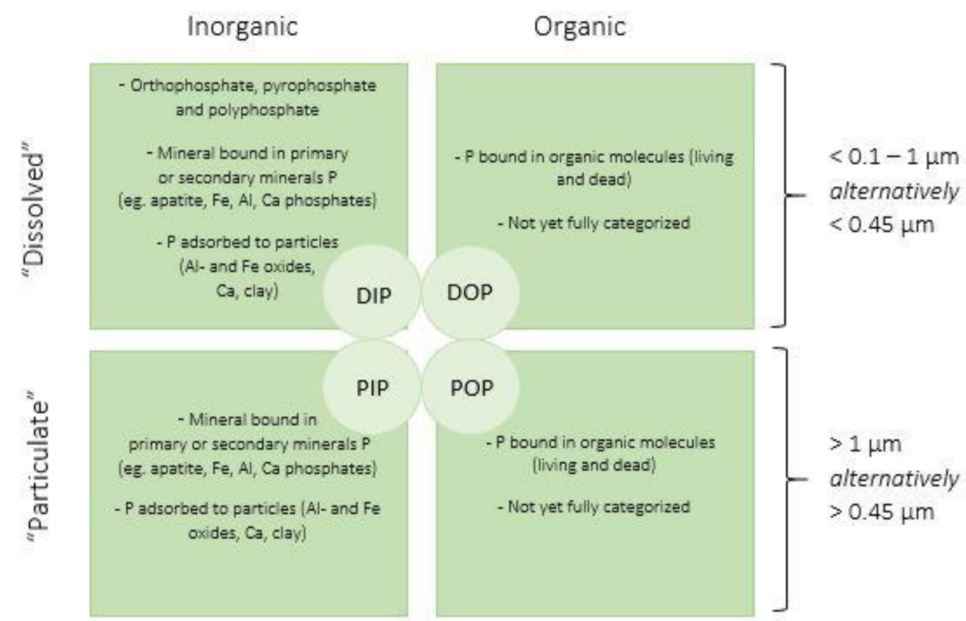

Figure 2. *Operational definitions of different forms of P. Data from Spivakov et al., 2009; Ruttenberg, 2014; Ulén, 2004; Yoshimura et al., 2007.*

Particulate inorganic P (PIP) consists of mineral bound P in the form of primary or secondary minerals, the most abundant primary mineral is apatite (Ruttenberg, 2014). Secondary minerals can be aluminium (Al), iron (Fe) and calcium (Ca) phosphates (Spivakov *et al.*, 2009). But more importantly, P can be adsorbed to particles, which is considered the most important process controlling P availability in the terrestrial environment (Ruttenberg, 2014). Both adsorption and precipitation to secondary minerals depend on the amount available cations (e.g. Al^{3+}, Fe^{3+} and Ca^{2+}), pH and time for reaction (Figure 3) (Morgan, 1997; Brady & Weil, 2008). At low pH, orthophosphates (PO_4-P) are commonly adsorbed to Al- and Fe oxides (Gustafsson *et al.,* 2012b). The oxides can be present as discrete particles or coatings on, for example, clay or other soil particles (Morgan, 1997; Brady & Weil, 2008). The adsorption increases with decreasing pH and thus the process is more important at low pH. P could also precipitate with Al^{3+} and Fe^{3+} but only at low pH and high PO_4-P availability (Gustafsson *et al.,* 2012b). Moreover, at higher pH PO_4-P precipitates with Ca, and Ca-phosphates would dominate the composition (around pH 8). P could also be adsorbed to hydroxyl-Al polymers in clays (for example Vermiculite and Smectite) (Karathanasis & Shumaker, 2009), in the diffuse layer of clay colloids (Pissarides *et al*., 1968) and to carbonate minerals (Gustafsson *et al*., 2012b). Hence PO_4-P is more soluble at intermediate pH values. Both absorption and precipitation processes connected to P are complex, hard to assess and often oversimplified (McBride, 1994).

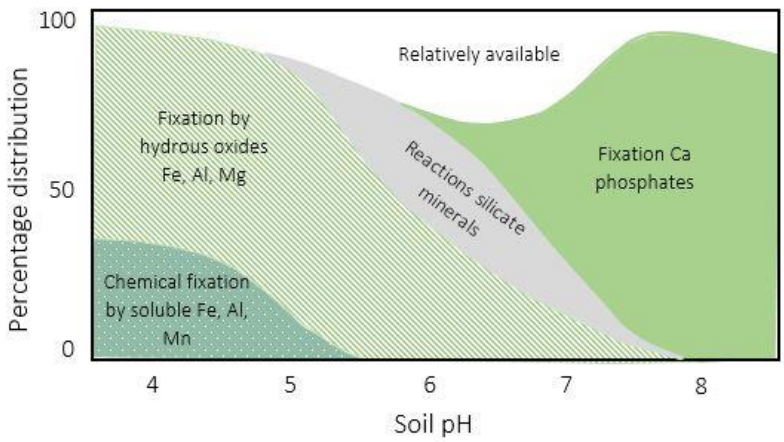

Figure 3. *Conceptual model of P precipitation, adsorption and availability at different pH-values. Please note that the pH ranges are approximate. Adapted from Brady & Weil, 2008.*

Dissolved P is defined as fractions that will pass through a filter of a certain size, for example 0.1-1.0 µm (Yoshimura, 2007) or 0.45 µm (Spivakov *et al.,* 2009). Dissolved inorganic P (DIP) includes orthophosphates (HPO_4^-, H_2PO_4), pyrophosphate ($P_2O_7^{4-}$) and polyphosphate (polymeric oxyanions) (Yoshimura, 2007). DIP could also include all the different forms of PIP if the particles are small enough to be defined as dissolved.

P is an essential nutrient for living organisms and is used in genetic material, for energy transfer and in membranes (phospholipids) (Ruttenberg, 2014). Therefore particulate organic P (POP) is found in both dead and living organisms (Yoshimura *et al*., 2007). Dissolved organic P (DOP) also consist of P incorporated in organic molecules smaller than the filter size, however the pool is not fully characterized.

Different pools of P have varying availability to primary producers which would affect the impact on eutrophication. Dissolved orthophosphates are directly available to biota (Ruttenberg, 2014; Spivakov *et al.,* 2009). The availability of adsorbed P would depend on sorption and adsorption processes, which could depend on, for example, redox state, pH and competition for adsorption sites by anions (Ruttenberg, 2014). This makes the adsorbed P not immediately bioavailable. P bound in recalcitrant minerals and complex organic molecules (humus) is least bioavailable. Nevertheless, in a study by Uusitalo *et al*., (2003) PP was shown to be an important source of bioavailable P in runoff and drainage water from a clay soil. The study showed that about 6-10% of the PP was immediately bioavailable.

Which form of P that is most common in running waters has been discussed in previous studies. In a study by Ulén & Jakobsson (2005), it was stated that the fraction of PO_4-P <0.45 µm is generally high in the running water of Sweden, for example 50% drainage water and 56% in small agricultural streams (when 50-90% agricultural land use in the catchment). High leachate of orthophosphates could depend on a highly P saturated soil, sandy soils with low sorption capacity or P fertilization without contact with the mineral fraction in the soil. On the contrary, Ruttenberg (2014) state that most P transported in rivers is associated with particulate matter since P is surface reactive. TP concentrations are highly variable over the year and strongly correlated with suspended sediments (Hatch *et al*. 2001). TP concentrations increase during run-off and erosion events (Ruzycki *et al.,* 2014; Kronvang *et al*., 1997, Jordan *et al*., 2007). In two studies, PP associated with inorganic material was the predominant form of P transported during the year (Hatch et al., 2001; Kronvang, 1992). Moreover, P associated with particles is of high importance when calculating P load (Kronvang, 1992). Clay soils in central plains of Sweden are prone to lose P in particulate form through erosion of tile drains (Ulén & Jakobsson, 2005).

In a study comparing 27 agricultural streams (located mostly in the middle and south of Sweden) the mean annual P concentration was highest in clay dominated areas, 0.3 mg/l (Kyllmar *et al.,* 2006). In addition the highest P load was observed in catchments with clay or clay loam and high water discharge levels. According to the WFD, all water bodies in Sweden should reach good ecological status before 2021 (Vattenmyndigheten, 2016b). A threat to good ecological status is undoubtedly eutrophication. Eutrophication in a stream could be assessed by monitoring for example diatoms but certainly also the total phosphorus concentration (Naturvårdsverket, 2007). The TP status should be interpreted according to Table 2. The guidelines from 2007 require a comparison between reference conditions and prevailing conditions (equation 1).

$$\log(\mathrm{ref}-\mathrm{P}) = 1.380 + 0.240 \times \log(\mathrm{AbsF}) - 0.0143\sqrt{height\ over\ the\ sea} \quad \text{(equation 1)}$$

Absorbance (AbsF) which is used when calculating the reference condition is a parameter describing water colour and light conditions (Naturvårdsverket, 2007). It is measured with a photometer in the laboratory on filtrated water (0.45 µm) and at a wavelength of 420 nm. Absorbance could be affected by humus, chemical and biological parameters.

Table 2. *Interpretation of TP in lakes and streams according to the Swedish EPA (Naturvårdsverket, 2007)*

Interpretation	*EQR*	*Concentration (µg/l)*
High	≥ 0.7	and <12.5
Good	≥ 0.5 to < 0.7	
Moderate	≥ 0.3 and < 0.5	
Poor	≥ 0.2 and < 0.3	
Bad	< 0.2	

In a study by Jordan *et al*. (2007) acute storm dependent episodes transported 90% of the total TP load during 39% of the time monitored. A lot of P was transported during high discharge but P dynamics were not only linearly correlated to flow. TP was positively correlated to flow but included hysteresis effects. The phenomenon called hysteresis gives a different concentration change on the rising limb than on the falling limb of the hydrograph. Also in Bieroza & Heathwaite (2015) continuous measurements of P in situ showed patterns of non-linear concentration-discharge relationships during storm events connected to hysteresis. However, P variation was not only dependent on flow but also connected to biogeochemical processes. These observations indicate that load calculations from monthly interpolated concentration and flow are rough calculations at best. Also diurnal patterns of TP variation connected to physical and biological interactions as well as anthropogenic activities have been observed (Jordan *et al.,* 2007).

In a study by Crossman *et al.* (2013) PO_4-P concentrations were again shown not to be linearly correlated to flow. Phosphate concentrations were highest at high and low flows both in measured and modelled data sets. Flow below 40 m^3/s was negatively correlated to PO_4-P and above 60 m^3/s positively correlated. An explanation for this pattern could be dilution of P concentration in the intermediate flow range and a wash out of P from diffuse sources at high flow. If the turbidity would not follow this pattern, it could affect the relationship of turbidity and TP.

Using turbidity as a proxy for TP could also be affected by the ratio of dissolved and particulate P (Jones *et al*., 2011). Jones *et al*. (2011) mean that particulate P could be better estimated than dissolved P.

3 Materials and methods

This section describes the study area, sampling routines and available data. The statistical methods used to evaluate correlation are presented as well as how the different load calculations were performed.

3.1 Study area

The sensor was placed close to the outlet of Sävjaån, a stream in Sävjaån watershed (733 km^2) in central Sweden during 2012-2015 (Figure 4) (SMHI Vattenwebb, 2016). Sävjaån is connected to Fyrisån which is a tributary to Lake Mälaren and part of Norrström basin (22 656 km^2) (VISS Vattenkartan, 2016). Fyrisån holds significant importance in the local area as a drinking water source, communication route and recreational area (Vattenmyndigheten, 2016a). Nevertheless, it is also a recipient of discharge from industries, municipal waste water treatment and run-off from agriculture.

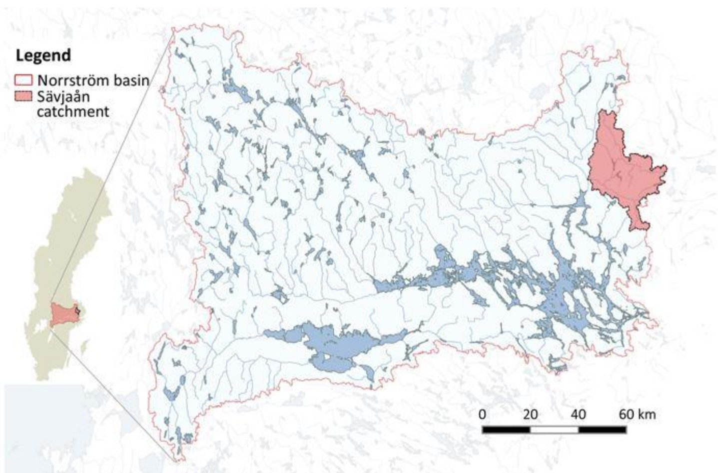

Figure 4. Norrström basin located in Sweden and Sävjaån watershed. Map created from shapefiles "Huvud- och delavrinningsområden, vattendelare (SVAR2010)" and "Vattenförekomster, vattendrag/vattenytor" distributed by © SMHI.

Water from north (Funbosjön and Lejstaån), south (Vidboån, Storån) and east come together in Sävjaån (Figure 5). Sävjaån transports water to Fyrisån, which drains into Mälaren-Ekoln. Sävjaån is the main tributary to Fyrisån and not so heavily affected by anthropogenic activity compared to other catchments in the area (Vattenmyndigheten, 2016a). Furthermore, a part of the stream is classified as a Natura 2000 area due to high limnologic values and presence of the species otter (*Lutra lutra)*, asp (*Aspius aspius)*, spined loach (*Cobitis taenia)* and bullhead (*Cottus gobio)* (Länsstyrelsen i Uppsala län, 2016).

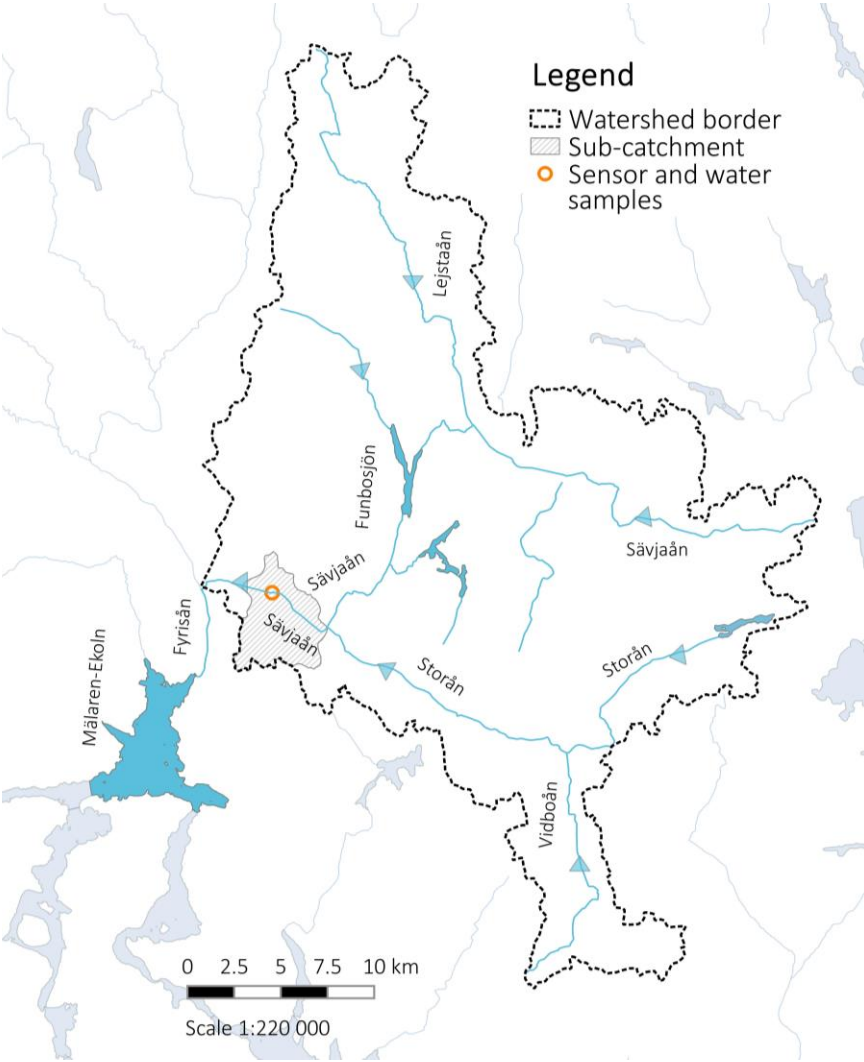

Figure 5. Map showing lakes and streams in the watershed, location of the sensor and water samples taken in Sävjaån sub-catchment. Map created from shapefiles "Huvud- och delavrinningsområden, vattendelare (SVAR2010)" and "Vattenförekomster, vattendrag/vattenytor" distributed by © SMHI.

Land use in the watershed consists of mostly forestry (70%) with some agriculture (28%) and urban area (1%) (SMHI Vattenwebb, 2016). The agricultural areas are primarily located in the south and west parts of the watershed. The soil in Sävjaån watershed mainly consists of moraine (43%), clay (30%), and bare rock (16%). The sub-catchment closest to the high frequency sensor is mostly used for agriculture (45%) and 43% of the sub catchment consist of clay soils. In the region close to Uppsala there are between 105-135 mmol exchangeable Ca (kg/TS) in the top soil (MarkInfo, 2016) which is quite high compared to other parts of Sweden.

The part of Sävjaån closest to the high frequency sensor (SE663553-160798) is regarded as having moderate ecological status according to the WFD. The status is mainly based on increased growth of diatoms and high nutrient concentrations (VISS Vattenkartan, 2016). In the watershed, P is considered to originate from agriculture and private sewage facilities (SMHI Vattenwebb, 2016). The stream is also hydromorphologically altered since it is channelized and hold obstacles for migrating fish (VISS Vattenkartan, 2016). The chemical status is regarded as bad due to high levels of mercury compared to reference values. At present, all surface waters in Sweden have a bad chemical status due to mercury contamination.

The mean annual precipitation during the years 2012 to 2015 was 600 mm. No seasonality of spring or autumn rains could be distinguished for the years 2012-2015 (Figure 6). The mean daily discharge in Sävjaån is 5.0 m^3/s (min 0.10 m^3/s and max 46 m^3/s from 2012-2015). The flow is generally flashier during spring and low during summer.

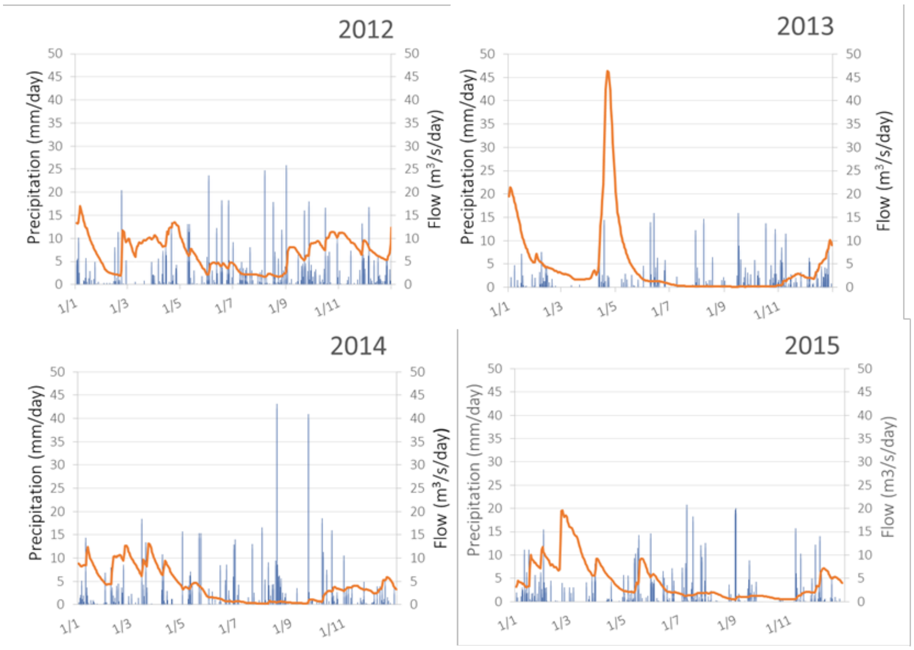

Figure 6. Precipitation and flow 2012 - 2015. Blue staples precipitation in mm/day, orange line water discharge in m^3/day. The annual rain amounts and discharges were (2012) 739mm; 2519 m^3/yr, (2013) 440mm; 1665 m^3/yr, (2014) 649 mm; 1477 m^3/yr and (2015) 573 mm; 1589 m^3/yr. Data from SMHI Vattenwebb (2016).

3.2 Sensor and water quality monitoring

A sensor of the brand YSI 600OMS VS was used. It works by emitting a near infrared light beam into the water which is scattered by suspended particles in the water and measured by a photodiode of high sensitivity (Figure 7) (YSI, 2016). The wavelength used is between 830-890 nm and the angle between emitted and detected light is 90° which conforms to ISO recommendations when determining turbidity (860 nm) (ISO 7027:1999). If using a wavelength greater than 800 nm disturbance from, for example, substances that affect water colour and absorb light is minimized. The more particles in the water, the higher the turbidity (YSI, 2016). The sensor range is between 0-1000 nephelometric turbidity units (NTU) with a resolution of 0.1 NTU. The data is processed with the software *EcoWatch Lite* and reported in NTU. Turbidity can be measured in NTU but also in FNU (Formazin Turbidity Unit). Both units are used when emitted and detected light is measured in 90°, but FNU is the reported unit for instruments using the ISO 7027 method. No conversions are needed in between the units (U.S Geological Survey, 2016).

Errors might occur due to sensor fouling from biological and chemical debris but also from outgassing air bubbles (YSI, 2012). The probe used has a mechanical wiper that cleans the sensor with certain time intervals (10 min) to enhance quality of data. According to YSI (2012), the nature of particles (TSS) could affect turbidity readings with 0.5-1.0 NTU and in long term studies up to 10 NTU. Ruzycki *et al*. (2014) also suggest the results of the readings could change with discharge, colour, particle size, sediment concentrations, mineral composition and organic matter. The sensor was calibrated in April 2014 according to the instructions from YSI manual (YSI, 2012) by field personnel.

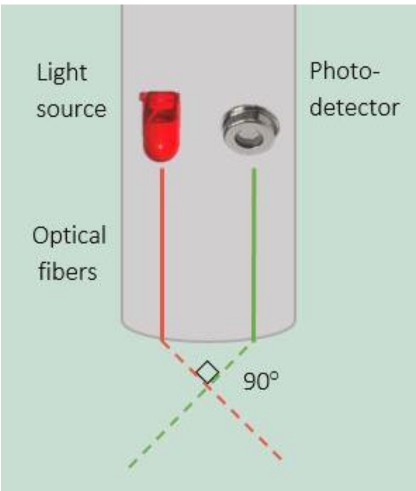

Figure 7. *Components of the sensor showing angle from the near infrared light source and the light observed by the photodetector. Information from YSI, 2016.*

Monitoring carried out during temperatures below zero is hard to manage, which makes it hard to record turbidity over the whole year (Skarbøvik & Roseth, 2015; Koskiaho *et al*., 2015). Several studies have tried to manage winter measurements in different ways, for example by applying a heating cable to the sensor (Skarbøvik & Roseth, 2015). The sensor used in this study was operated during ice-free periods, according to Table 3. It was manually cleaned, batteries changed and data collected every 2^{nd}-4^{th} week during operating times. There are several data gaps in the time series, one in 2012 (lasted 17 days), 10 in 2013 (lasted 50 min to 7 days), 5 in 2014 (lasted 1 h 10 min to 46 days), one in 2015 (18 days). The data gap in 2015 was explained by battery failure due to water temperature. The data will be labelled HF turbidity (high frequency turbidity) in the subsequent analysis.

Table 3. *Sensor operating periods from 2012 - 2015.*

Year	Period	Period covered per year (%)
2012	21 Sep – 12 Oct	19
2013	7 Mar – 26 Sep	53
2014	25 Apr – 17 Dec	53
2015	17 Mar – 31 Dec	79

Water samples were collected by manual monthly grab sampling during 2012-2015 by SLU field personell. The water samples were taken at the opposite side of Sävjaån (Kuggebro) compared to where the sensor is located (Figure 8). The samples were funded by Fyrisåns vattenförbund as a joint initiative by the municipality, County Administrative Board, industries in the area and landowners with water works or dams. The data will be labelled SRK in the analysis (Samordnad recipientkontroll). A full chemistry analysis was performed by an accredited laboratory with standardized methods (e.g. Turbidity - SS-EN ISO 7027:1999, Suspended solids - SS-EN 872:2005 mod., TP- SS-EN ISO 6878:2005, PO_4-P - ISO 15923-1:2013).

Figure 8. *Location of water sampling (SRK) and HF sensor in Sävjaån. Map created from "Ortofoto raster ESPG 3006, colour" © Lantmäteriet*

During 2015, grab sampling was also carried out just before managing the sensor (every 2nd-4th week) as near to it as possible. The samples were later analysed for turbidity in the same accredited laboratory. These samples where funded by the

Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Science and will be labelled SLU (Sveriges lantbruksuniversitet) in the analysis.

When analysing turbidity in laboratory a turbidimeter with the wavelength 860 nm is used, the angle should be 90° (ISO 7027:1999). A formazin suspension is used as reference for calibration. A measurement is done in a well-mixed sample and the results reported in FNU.

3.3 Data treatment

At the time of maintenance, the observations from the sensor were not valid. When one or more parameters had invalid readings connected to management, observations were excluded from the data set. Data treatment was done in *Microsoft Excel*.

3.4 Statistics and data evaluation

3.4.1 General statistics

Descriptive statistics as mean, median, standard deviation, variance and normal distribution were performed in the software *JMP Pro 12*. A Student t-test was used to compare the turbidity data sets (grab samples and sensor) evaluating if there was a difference between the means of the two groups, the data set was log transformed. Only data from the period when the sensor was active and grab samples taken were used. The data was log transformed since it was not normally distributed, a t-test was chosen to detect a potential difference and size of it (Wahlin, 2011).

3.4.2 Linear regression

The correlation between two parameters can be quantified through a linear regression model (Wahlin, 2011). The method describes to what extent one variable can be explained by another. The observations are plotted and a regression curve is applied where the squared distances to the observations are the shortest. The equation of the regression curve ($y = a + bx$) can help forecast one parameter with help of another. When evaluating the fit of the curve, the degree of explanation (r^2) is used (Table 4).

Table 4. *Interpretation of degree of explanation (Wahlin, 2011).*

Degree of explanation	r^2
Very high	> 0.7
High	0.5-0.7
Moderate	0.3-0.5
Low	< 0.3

When using linear regression, it is important to evaluate the suitability of the model (curve) and data (Wahlin, 2011). The residuals between the points of observation and curve should be of constant variance, normally distributed and independent. To ensure the constant variance of residuals data can be log transformed (Montgomery *et al.,* 2012). The transformation will have little effect on a narrow range of values and a large effect on a wide range of values. When data is log transformed, the risk that some point influences the model disproportionately decreases. Hypothesis testing was done and the significance of the slope differing from 0 was evaluated. The significance level (p) is usually set to 0.05.

Three data sets were evaluated with linear regression (Table 5) to assess if turbidity were correlated to TSS and TP respectively. In the analyses only water samples taken when the sensor was deployed (Table 3) could be used. Correlation between grab samples analysed in the laboratory and the hourly mean values from the high frequency data were used. The hourly mean was calculated from the observations closest to the time of grab sampling. Moreover correlation analyses were made between the grab samples and the one high frequency observation closest in time of sampling (snapshot). This was done in order to investigate the impact of time on the correlation. A differentiation has been made between the samples taken at the time of managing the sensor (SLU) and the monthly samples taken by field crew (SRK).

Table 5. *Scenarios used in the analysis.*

Name	Description	Number of observation pairs
EQ1	Data from 2012-2015	25
EQ2	Data from 2014-2015, after calibration of the sensor	16
EQ3	Data from 2012-2015, without the dates 2012-12-11, 2013-04-17 and 2013-05-16	22

3.4.3 Multiple linear regression

If it is suspected that two or more parameters (regressors) can explain another parameter, a multiple regression model could be used (Montgomery *et al.,* 2012). The multiple regression model describes a relationship where y simultaneously depend on two (or more) regressors x. In equation 2, y denotes for example TP, a an unknown term describing the expected change in response per unit, x_1 represents for example turbidity, x_2 flow and b denotes the intercept. The idea behind adding x_2 is to explain the relation to y not yet explained by x_1 (Montgomery *et al.,* 2012).

$$y = b + (a_1 \times x_1) + (a_2 \times x_2) + (a_3 \times x_1 \times x_2) \text{ (equation 2)}$$

A hypothesis test is done to evaluate if one of the regressors contributes significantly to the model (Montgomery *et al.,* 2012).

3.5 Estimations of load

When estimating the P load from the high frequency data, the equations from the linear regression were applied (EQ1, EQ2 and EQ3). The average daily turbidity was used to estimate the daily average TP concentration.

Estimations of load can be done in many different ways. In this study, two interpolation methods were chosen, linear interpolation (I1) and piecewise constant interpolation (nearest neighbour interpolation) (I2). When using linear interpolation, concentrations between two known observations are interpolated day by day (c_i in µg/l equation 3) (Moatar & Meybeck, 2004). The daily TP concentration (interpolated or observed) is then multiplied with daily runoff (Q_i in m^3/day). The daily loads (kg/day) are then summarized to an annual load (L, kg/year). K denotes the factor of conversion to account for difference in measurement units.

$$L = K \times \sum_{i=1}^{365} c_i \times Q_i \qquad (equation\ 3)$$

When using piecewise constant interpolation, a constant concentration around the sample is assumed (Moatar & Meybeck, 2004). The load is calculated by using the same concentration (c_j in µg/l) for half the period between the samples but using the mean of daily flow observations (m^3/day) for the period summarized (equation 4). The annual load (L, kg/year) is calculated by summarizing the daily loads (kg/day). K denotes the factor of conversion to account for difference in measurement units.

$$L = K \times \sum_{j=1}^{365} c_j \times \overline{Q_{j,ji-1}} \qquad (equation\ 4)$$

When calculating loads, it is hard to avoid under- or overestimations (Kronvang & Bruhn, 1996). Sampling frequency has a large impact on estimation accuracy. In a study comparing different load calculation methods, simple linear interpolation was considered the best for estimating annual P load (Kronvang & Bruhn, 1996). Moatar & Meybeck (2004) also recommend linear interpolation if monthly values are available. Because of this, linear interpolation was chosen to represent a conventional method when calculating load. However with this method there is an serious risk of losing diurnal patterns and flushing episodes (Jordan *et al*., 2007). Moosmann *et al.* (2005) state that 30-50 data pairs describing flow and concentration per year are needed to avoid large errors. Piecewise constant interpolation was chosen for comparison to linear interpolation.

4 Results

In this section, the results from the data analysis will be presented. The data from grab sampling and HF sensor will be compared, the conditions in Sävjaån described and the correlation between turbidity-TSS and TP presented. This section will also describe the results of using high frequency measurements when calculating load and nutrient status (EQR).

4.1 Monitoring methods and surface water quality

To evaluate the difference between the methods and understand the current situation in Sävjaån, the water chemistry data was examined. As a basis for further analysis, the different data sets were compared.

According to the interpretation from the Swedish EPA (1999, Table 1), water in Sävjaån is strongly turbid (>7 FNU). When comparing turbidity observations from grab sampling (SLU and SRK) and the sensor, the sensor records both lower and higher concentrations (Table 6, Figure 9). The average from the sensor recorded data (28.9 NTU) is higher than the average SRK turbidity (22.3 FNU). The reason behind this is that maximum values are 9 (SRK) and 15 (SLU) times higher from continuous monitoring than from grab sampling. The sensor turbidity data covers periods of high turbidity which is shown by the large standard deviation and in Figure 9.

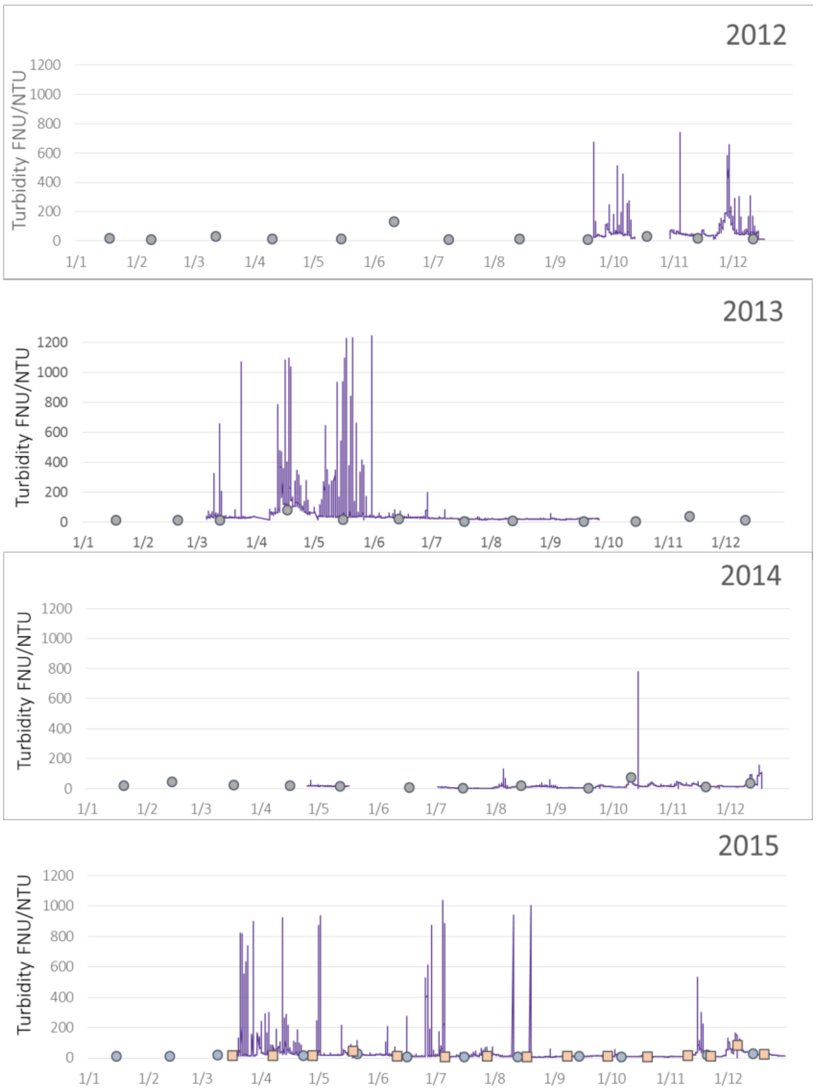

Figure 9. Turbidity from the sensor and grab samples. Turbidity measured from sensor (purple line) and grab samples (SRK grey circles, SLU yellow squares).

Additionally, when comparing the mean of the two methods statistically, a significant difference can be confirmed (Student t-test, p-value = 0.007). The mean difference was 72% and the sensor based values were higher (Figure 10). In Figure 10 the observations below 0 (y-axis) indicates that the HF turbidity was higher than SKR turbidity. This was the case in the majority of the compared observations.

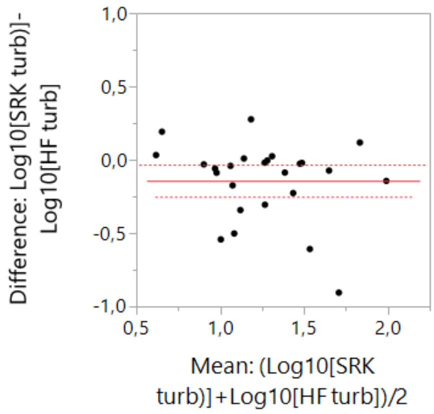

Figure 10. *Comparison between two groups (HF turbidity and SRK turbidity). The x-axis represents the mean of the two groups and the y axis the difference between the two groups. The horizontal line represents the mean difference and the dotted lines the 95% confidence interval. Note the log-scale.*

The grab samples show an average TP of 74.7 µg/l (Table 6), varying between 25.6 and 282 µg/l. Since the sensor was not in the water for some periods of the year, only 25 observations could be used in the linear regression (compared to 49 existing observations). The variance was slightly lower in the subset used. TSS was on average 18.7 mg/l, varying between 4.4 and 242 mg/l. For the 25 samples used the average was slightly lower but the maximum concentration was considerably lower.

Table 6. *Water chemistry compared between the different data sets.*

Parameter	Mean, ±SD	Median	Range of results	*n* samples
Sensor				
Turbidity (NTU)	28.9, 44.8	18.6	1.0 – 1245	105 116
Turbidity mean used LR (NTU)	31.8, 34.0	19.6	3.6 – 145	25
SRK, grab samples				
Turbidity (FNU)	22.3, 22.8	15.0	4.3 – 135	49
Turbidity used LR (FNU)	20.9, 20.0	17.0	4.3 – 83	25
TP (µg/l)	74.7, 45.8	64.0	25.6 – 282	49
TP used in LR (µg/l)	72.6, 41.4	63.2	25.6 – 239	25
PO_4-P (µg/l)	41.5, 28.3	37.5	3.0 – 174	48
TSS (mg/l)	18.7, 34.3	11.4	4.4 – 242	49
TSS used in LR (mg/l)	15.2, 13.9	10.8	4.5 – 62.9	25
SLU, grab samples				
Turbidity (FNU)	19.7, 19.7	13.0	7.5 – 82	15

The concentration of orthophosphates (PO_4-P) was also analysed in the SRK samples. The result shows that concentrations of PO_4-P are slightly lower than TP especially when TP is high (Figure 11).

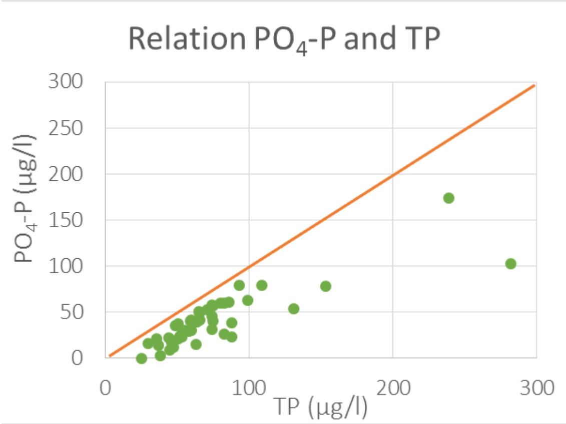

Figure 11. Relationship between PO_4-P and TP (green markers), red line represents the 1:1 ratio.

When looking at the ratio between PO_4-P and TP, the proportion varied between 8-78%, on average 47%. In Figure 12, the variation over the years can be seen. It is hard to distinguish any patterns between the variation of PO_4-P and TP. The lowest ratio 8% was observed in June 2014 and the highest 78% in March 2013. The water in Sävjaån has an average pH-value of 7.4, but varies between 7.1 and 7.8.

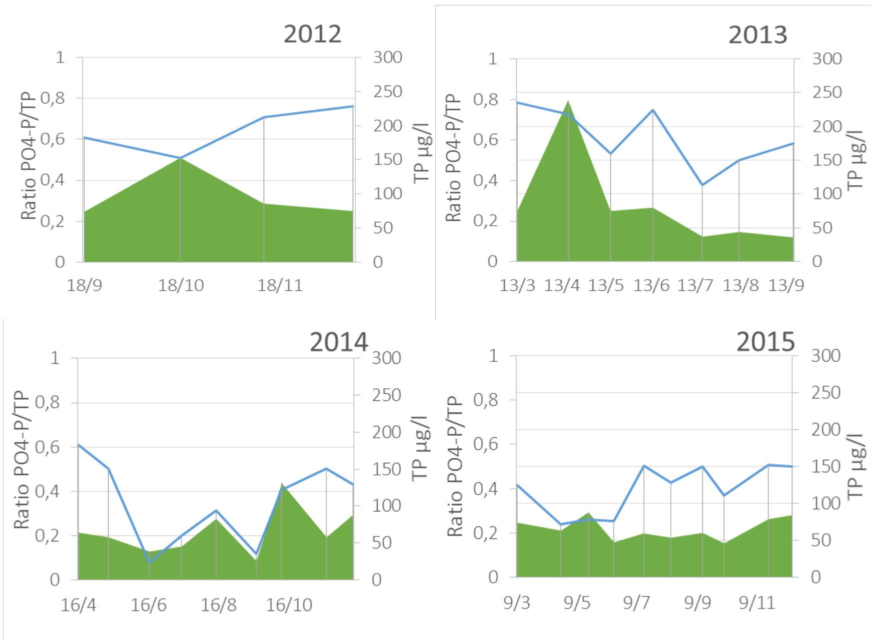

Figure 12. *Ratio of PO_4-P compared to TP. The line describes the ratio of PO4-P/TP (left y-axis) and filled surface represents TP concentration (right y-axis).*

The parameters of interest were plotted versus flow to observe the behaviours at different flow rates (Figure 13). Turbidity, TP and TSS are positively correlated to flow which means that with higher flow the concentrations increase. At some occasions, turbidity, TP and TSS all are high during high flow. The turbidity seems to vary more during high flows than the other parameters. However, the largest number of observations are quite low during high flow (especially for turbidity and TSS). The flow could only moderately explain turbidity (0.40) and TP (0.36). The strength of the relationship between flow and TSS was low (0.20). All relationships were significant (p-value <0.001).

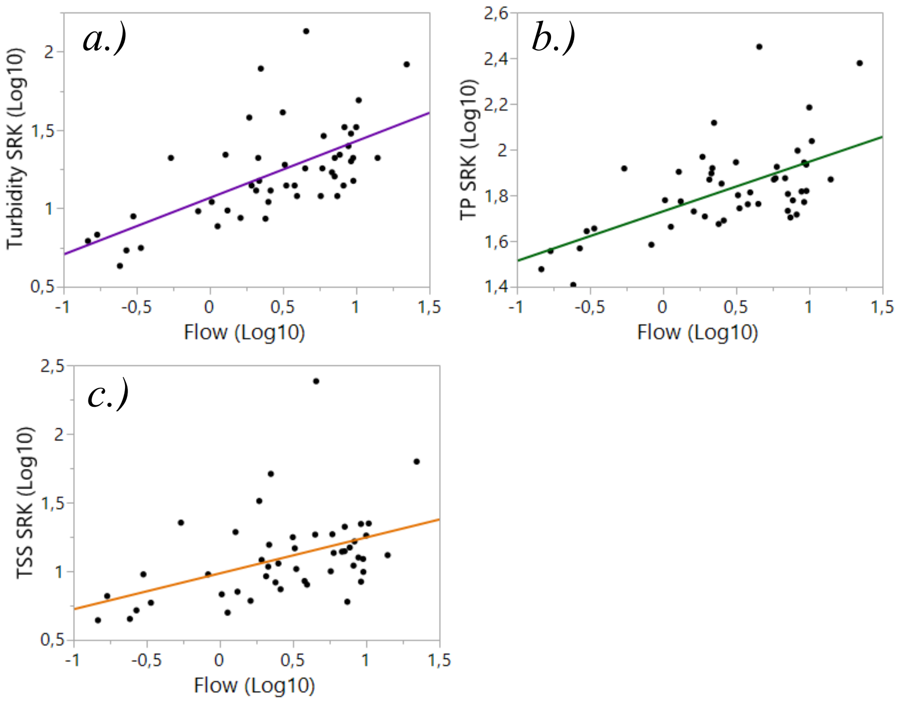

Figure 13. *Plots of flow vs turbidity (a), TP (b) and TSS (c).* Data from grab sampling (SRK).

4.2 Turbidity as a proxy

It is crucial to validate that the sensor has been functioning correctly when evaluating the applicability of using turbidity as a proxy. However, when comparing the different data sets (SLU and SRK samples) not only the methods are compared. Since the sensor and SRK samples were taken at different locations (Figure 8) the role of spatial heterogeneity was also examined. Moreover, the relationships between turbidity - TSS and TP are presented.

4.2.1 Comparison between methods

The grab samples taken at the time of managing the sensor (SLU) and the HF turbidity data have the highest r^2 (0.99) which indicates a very high degree of explanation by the model (Table 7, Figure 14a). This correlation represents data from 2015 when the sensor was calibrated, just cleaned and at the location of the sensor. The grab samples taken 60 m downstream the sensor (SRK) and HF turbidity had an r^2 of 0.34 (Table 7, Figure 14b). This analysis includes data from 2012-2015. The degree of explanation is thus moderate. The SLU turbidity and HF turbidity have lower standard error (SE) and root mean square error (RMSE) than the SRK and HF turbidity.

When making an analysis with only one value (snapshot), the correlation coefficient was slightly lowered and had a higher RMSE, which indicates that the method becomes more robust when using a mean value which reduces the impact of small scale variation, Table 7. All tests had a p-value <0.05 which indicate that the slopes were significantly different from 0.

Table 7. *Results of linear regression analyses of SRK/SLU turbidity and HF turbidity.*

Relation	Equation	r^2	RMSE	p-value	SE slope
SLU turb – HF turb mean (1h)	SLU turb = -0.482+1.04* HF Turb	0.99	1.87	<0.0001	0.026
SLU turb – HF turb snapshot	SLU turb = -0.715+1.04* HF Turb	0.98	2.68	<0.0001	0.038
SRK turb – HF turb mean (1h)	SRK turb = 10.0 + 0.342* HF Turb	0.34	16.6	0.0023	0.10
SRK turb – HF turbidity snapshot	SRK turb = 10.1 + 0.323* HF Turb	0.32	16.9	0.0035	0.10

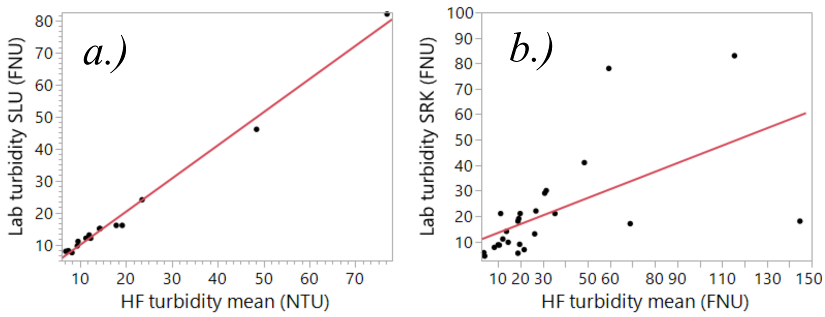

Figure 14. Plots showing *linear regression analyses with turbidity from grab samples and HF turbidity mean (1h). Graph a: grab samples analysed in the lab taken at the time of managing the sensor (SLU), graph b: grab samples (SRK) compared to HF turbidity.*

A further investigation of the correlation between the montly grab sampling (SRK) and hourly mean of HF turbidity was made (Figure 15). When performing a linear regression analysis using data from 2014-2015, the correlation coefficient was 0.90 (very high correlation). Hence it is possible to distinguish a closer connection between the sampling methods after the calibration of the sensor in April 2014. At some occasions there are large differences between the observed values, for example 2012-12-11 (difference 52 FNU), 2013-04-17 (33 FNU) and 2013-05-16 (127 FNU) (figure 15).

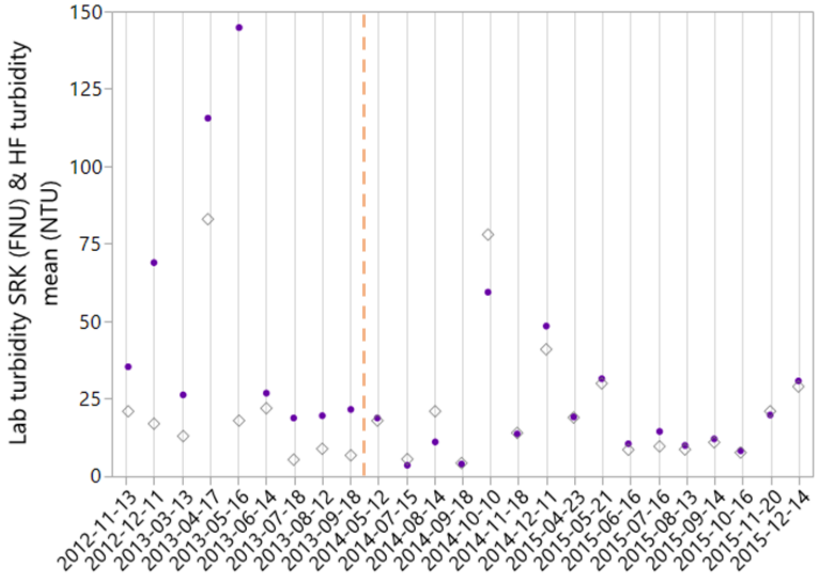

Figure 15. *Comparison of SRK turbidity and HF turbidity by sampling date. Grey squares represent lab turbidity SRK and purple dots are HF turbidity mean, vertical line represents time of calibration.*

The daily variation during 2012-12-11 and 2012-05-16 is large (Figure 16). On the 11^{th} of December 5.2 mm rain came after 17.30 and the flow was 6.8 m^3/s (mean daily discharge 5.0 m^3/s). On the 16^{th} of May it was not raining, the flow was 5.9 m^3/s. Thus, the weather and flow does not explain the large fluctuations.

No reason could be found to disregard the large variation during some days of operating the sensor. Because of this, the data set was divided into three scenarios for further analysis (EQ1, EQ2, EQ3) where EQ1 represents the whole data set (2012-2015), EQ2 the data after calibration (2014-2015) and EQ3 the data set (2012-2015) without the three days with the largest discrepancies between SRK turbidity and HF turbidity.

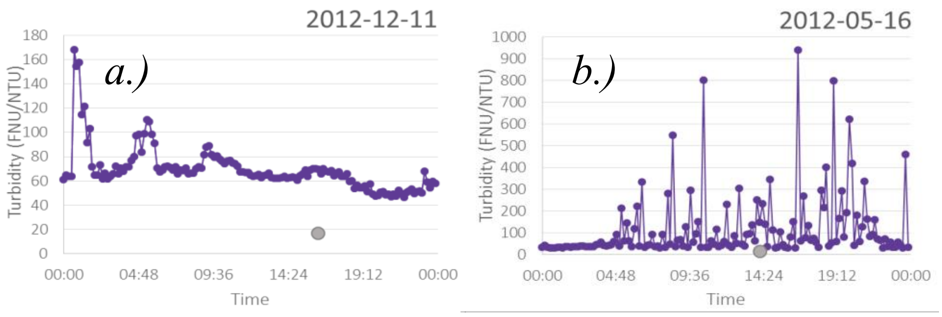

Figure 16. *Daily observations of HF turbidity (purple line) and the result from the grab sample SRK (grey dot).*

4.2.2 TSS and TP

To further investigate if high frequency turbidity can be used as a proxy for TP, linear regression was used to examine the relationships in between the parameters. TSS was investigated since particles play a large role carrying TP and therefore can give understanding about the prevailing conditions in Sävjaån.

When observing the correlations in the water collected by grab sampling and analysed in the lab (SRK), the correlation between TSS and turbidity was very high (0.92). Also, the correlation between TP and turbidity was very high (0.84).

The analyses have been done according to the three scenarios (Table 8, Figure 17). The coefficient of correlation shows a moderate degree of explanation (0.39) between TSS and turbidity for the whole time period EQ1, but a high correlation (0.67) for the time scenario EQ2 and EQ3 (0.57). The RMSE is low for EQ2 and EQ3 which indicates a high accuracy.

Table 8. *Results of linear regression analyses of turbidity and TSS.*

Parameter	Equation	r^2	RMSE	p-value	SE slope
EQ1 TSS – HF turbidity	TSS= 7.10 + 0.256*HF turb	0.39	11.0	0.0008	0.066
EQ2 TSS – HF turbidity	TSS = 1.99 + 0.606*HF turb	0.67	6.95	<0.0001	0.11
EQ3 TSS – HF turbidity	TSS = 1.11 + 0.562*5 HF turb	0.57	6.91	<0.0001	0.11

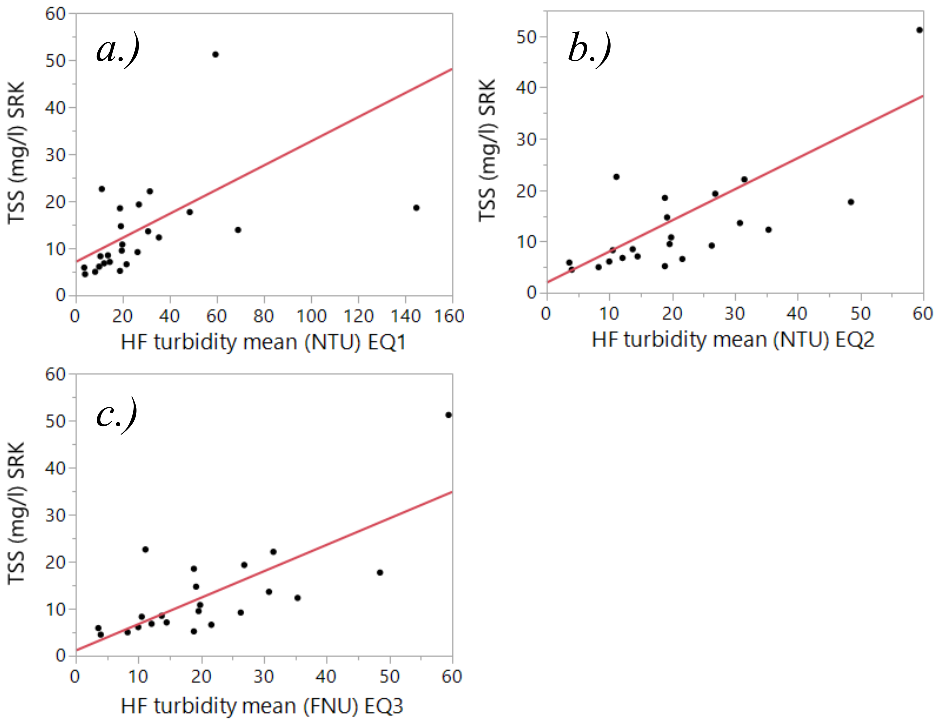

Figure 17. Plots of linear regression analysis of TSS vs HF turbidity EQ1, EQ2, EQ3.

The correlation between turbidity and TP was examined. The relationship between TP and HF turbidity was described moderately well by the model in EQ1 (0.42) (Table 9, Figure 18). In scenario EQ2 (after calibration) the correlation was very high (0.79) and also in EQ3 correlation was high (0.66). Moreover, when analysing the relation between PO_4-P and turbidity with data from 2014-2015 (EQ2) the correlation was high (r^2= 0.57, p-value = 0.001).

Table 9. *Results of linear regression analysis of turbidity and TP.*

Parameter	Equation	r^2	RMSE	p-value	SE slope
EQ1 TP – HF turbidity 2012-2015	TP = 47.6+0.787* HF turb	0.42	32.2	0.0005	0.193
EQ2 TP – HF turbidity 2014-2015	TP = 39.1+1.40* HF turb	0.79	11.6	<0.0001	0.191
EQ3 TP – HF turbidity 2012-2015 except 3 obs.	TP = 34.9+1.42*HF turb	0.66	14.2	<0.0001	0.22

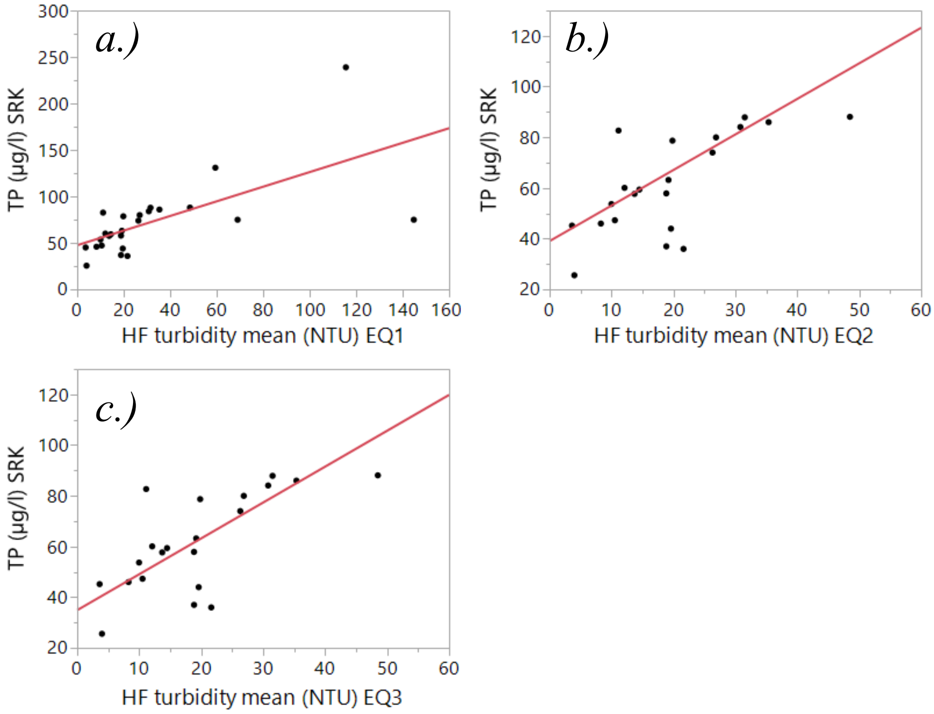

Figure 18. Plots of *linear regression analysis of TP and HF turbidity EQ1, EQ2, EQ3.*

The average TP concentration was lower when calculating it from the high frequency data from scenario EQ1 than when performing grab sampling (Table 10). When using scenario EQ2 and EQ3 the calculated TP concentrations were higher. If especially observing the average from EQ2 and grab sampling used in LR, the average was 10% higher for the high frequency data. Generally the high frequency data does not generate a large difference in average and median values. In contrast when comparing the variation it shows that the minimum and maximum values for all the scenarios were higher than from grab sampling. In scenario EQ2 and EQ3 the maximum value was more than twice as high. Regarding the minimum value it should be considered that when using linear regression, the concentration of TP never gets below the intercept.

Table 10. *Descriptive statistics of TP concentrations (µg/l) from grab sampling and from using the sensor.*

Method	Mean ±SD	Median	Range	*n* samples
Grab sampling	74.7, 45.8	64.0	25.6 – 282	49
Grab sampling used LR	72.6, 41.4	63.2	25.6 – 239	25
Sensor EQ1	70.5, 26.8	62.5	48.8 – 358	746
Sensor EQ2	79.9, 47.7	65.7	41.2 – 592	746
Sensor EQ3	76.1, 48.2	61.7	37.1 – 593	746

To investigate the relation between HF turbidity and TP further the data set were divided into seasons. Visually, there seemed to be less correlation between turbidity and TP during summer months (June, July and August). Yet, when doing a multiple regression analysis it was clear that seasons did not significantly affect the relationship between turbidity and TP (p-value = 0.80). The data set was also divided into two groups representing high and low flows. Low flow was decided to represent discharge below 2 m^3/s since the median discharge for the observed data were 1.95 m^3/s. Visually it seemed there was a weaker correlation between turbidity and TP during low flow periods. However when doing a multiple regression analysis, the flow could not be significantly proved to have an impact on the relationship between HF turbidity and TP with prevailing information (p-value= 0.19).

4.3 Application high frequency data

4.3.1 Load estimations

Load estimations of TP in Sävjaån were performed to further understand the advantages and limitations of using high frequency data. The load estimations were then compared to loads from linear interpolation and piecewise constant interpolation representing conventional methods. TP loads were estimated for the periods when the sensor was in the water.

From Table 11, load estimations can be seen from the three scenarios (EQ1, EQ2, EQ3) and the two interpolation methods (I1, I2) used. The results from the two conventional interpolation methods show a larger load when performing piecewise constant interpolation (I2) for 2013, 2014 and 2015. When comparing the different scenarios the linear regression models are evaluated since flow and turbidity are equivalent for all scenarios. The load estimations were low when using the equation of scenario EQ1 (r^2= 0.42). Equation EQ2 (r^2= 0.79) and EQ3 (r^2= 0.63) gave quite similar results. EQ2 with the closest relation between SRK TP and HF turbidity gave the largest loads if comparing the three scenarios. The variation of the results from the different equations and interpolation methods seems to be smaller when the flow is low (2014).

Table 11. *Summary of load estimations from 3 scenarios and 2 interpolation methods by year. The period when the sensor was in the water is presented (%) and the discharge of that period*.

Year	Period covered per year (%)	Period discharge (m^3/s/period)	Load EQ1 (kg)	Load EQ2 (kg)	Load EQ3 (kg)	Load linear interpolation I1 (kg)	Load piecewise constant interpolation I2 (kg)
2012	19	602	4980	6496	6320	4977	4811
2013	53	881	9267	13 032	12 808	12 858	13 905
2014	53	374	2110	2284	2158	2456	2463
2015	79	852	5308	6065	5784	5162	5241

If comparing the loads from EQ1, EQ2 and EQ3 to the linear interpolation (I1), the variance differs between years (Table 12, Figure 19). In 2012 and 2015 the loads estimated from high frequency data were larger than the load from linear interpolation. In 2013 the load from EQ1 was lower than from I1 while the loads from EQ2, EQ3 and I1 were almost equivalent. In 2014 when the discharge in Sävjaån was low, the loads from EQ1, EQ2 and EQ3 were lower than the load from I1.

Table 12. *Comparison of loads given from the scenarios EQ1, EQ2, EQ3 and (best) linear interpolation (I1).*

Year	Period discharge (m^3/s/period)	Difference EQ1 and I1 (%)	Difference EQ2 and I1 (%)	Difference EQ3 and I1 (%)
2012	602	+ 0.060	+ 31	+ 27
2013	881	- 28	+ 1.4	- 0.39
2014	374	- 14	- 7.0	- 12
2015	852	+ 2.8	+ 17	+ 12

In Figure 19, the standard deviation from the linear regression curve has been included (bars). The SE of the slopes does not vary largely between the scenarios (0.191-0.22). This can be observed since the difference between the uncertainties (bars) does not vary largely between the scenarios.

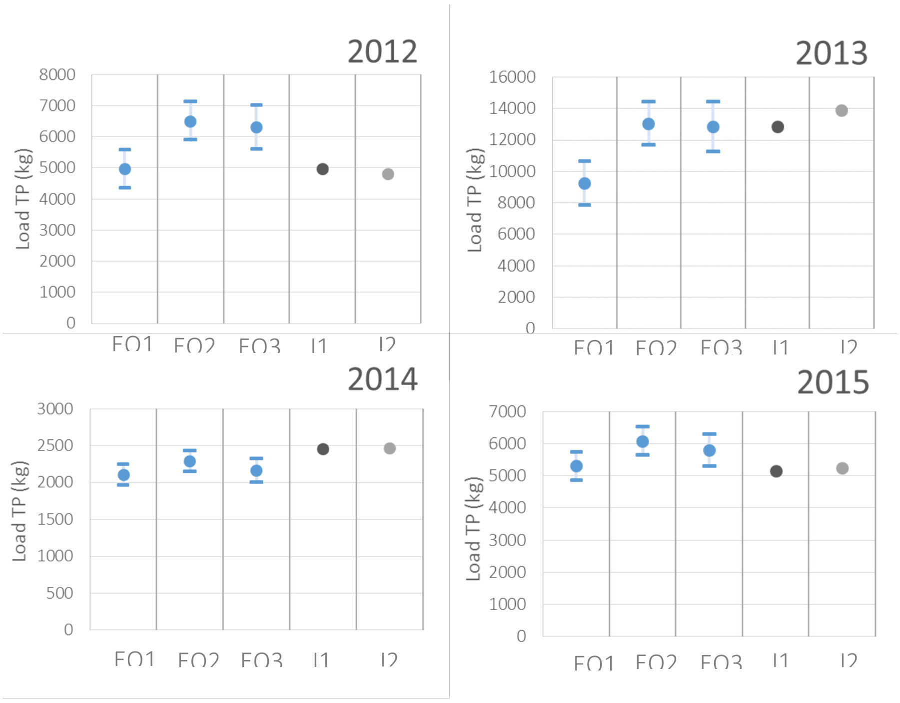

Figure 19. Plots of *loads from the different methods and SE of the slope. EQ1 SE=0.193, EQ2 0.191, EQ3 SE=0.22,; I1 grey dot; I2 grey dot).*

The results from using turbidity as a proxy for TP show that when the sensor caught peaks in concentrations which coincided with high discharge the load became larger than with linear interpolation (Figure 20). In the graphs where TP concentration is plotted against time (20a and 20b) it can be seen that the high frequency estimations of TP gave more variation and caught more peaks. However, when observing the graphs that compare the difference between EQ2 and I1 (kg/day) plotted against time (20c and 20d) it was clear that high concentrations without high discharges have a modest effect (July 2015) on load estimations. But in addition when discharge was high and concentration low not much TP was transported either (April 2015). On the contrary, when concentrations and discharges were high a large part of the TP was transported (November 2012). This results in 31% more transported TP in 2012 and 17% more TP for the observed period in 2015 (Table 12).

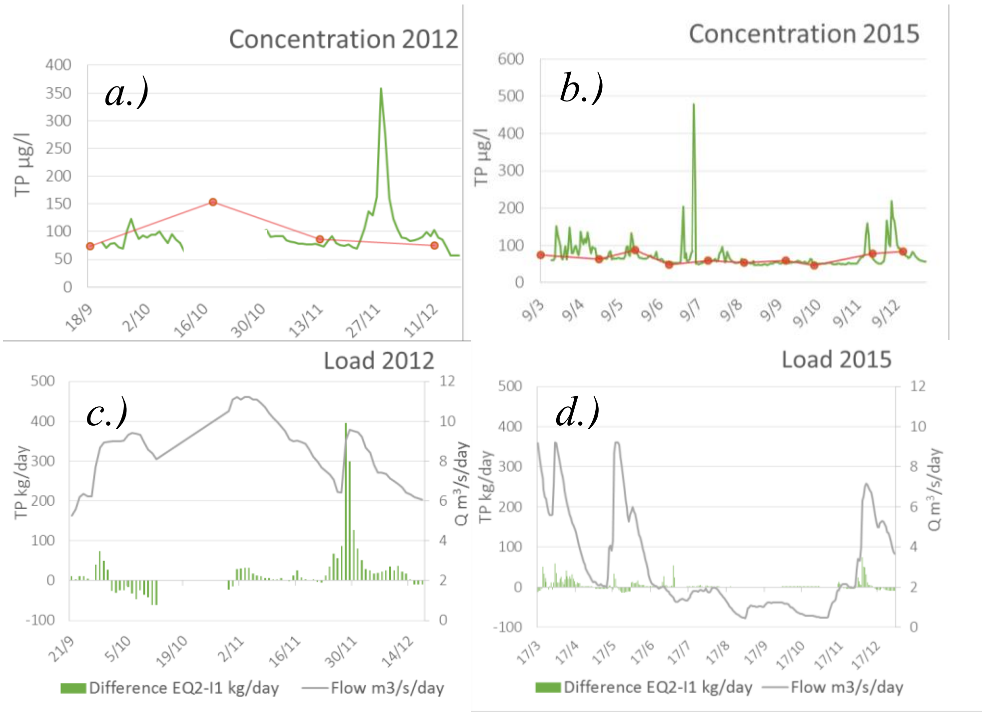

Figure 20. *Plots showing a comparison between two load estimation methods (EQ2 and I1) 2012 and 2015. Graph a and b describe concentration TP over the period when the sensor was in the water, red line and dots symbolize grab samples and linear interpolation while the green line represent high frequency TP. The graphs c and d are describing the difference between the load from EQ2 and I1 on the left y-axis (green staples), the right y-axis (grey line) is describing flow.*

During 2013, the load was in total 1.4% larger when calculated with scenario EQ2 than with I1. Figure 21 shows that the grab sample from 17 April 2013 has a high TP concentration that affects all concentrations in April and May, and moreover coincides with high flow. The same occurrence can be seen in 2014 when the load estimated by scenario EQ2 was 7% lower than when calculated with I1. Also during 2014, grab samples were taken at certain days that had high concentrations which affected the closest months and furthermore the comparison between loads.

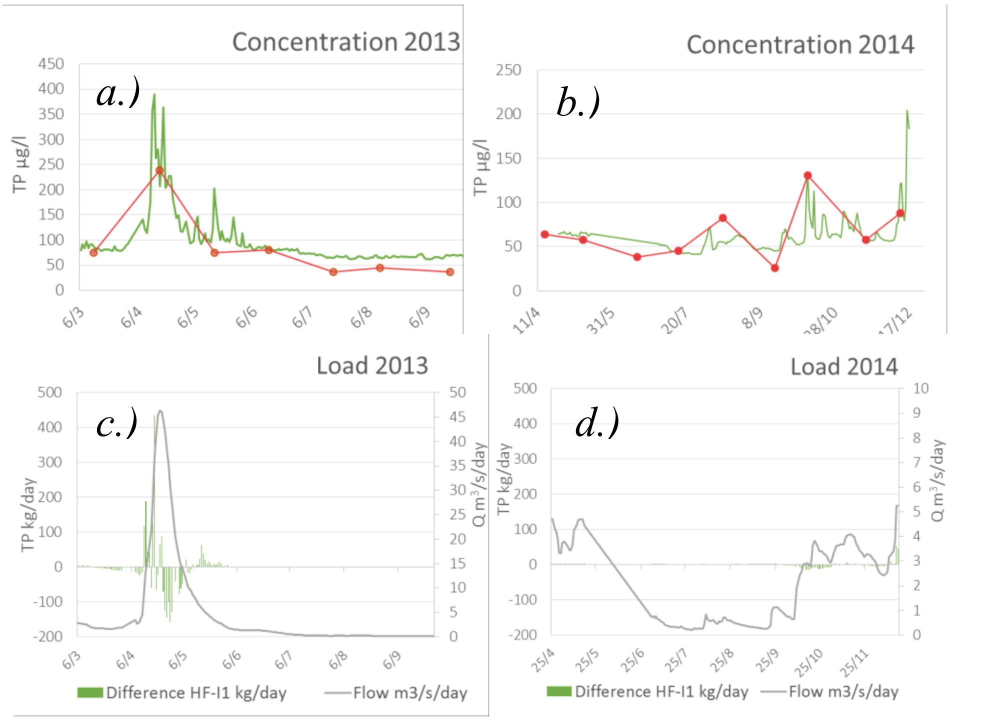

Figure 21. *Plots showing comparison between two load estimation methods (EQ2 and I1) 2013 and 2014. Graphs a and b are describing concentration TP over the period when the sensor was in the water, red line and dots symbolize grab samples and linear interpolation while the green line represent high frequency TP. Graphs c and d are describing the difference between the load calculated with scenario EQ2 and the load from the linear interpolation (I1) on the left y-axis (green staples) the right y-axis (grey line) are describing flow (Q). Please note that the scale of flow differs between 2013 and 2014.*

4.3.2 Water Framework Directive

TP is an essential parameter when evaluating status according to the WFD even though biology parameters have become more important when evaluating eutrophication (Cassidy & Jordan, 2011). Using high frequency estimates of TP based on turbidity to calculate the EQR for Sävjaån gave a different result than when calculating EQR from grab samples (SRK) (Figure 22).

When estimating reference conditions, the parameter absorbance is used (equation 1). Since absorbance could not be measured on a high frequency basis values from the grab sampling were used. The median, 25th percentile and 75th percentile absorbance from 49 samples from 2012-2015 contributed to the calculations of reference condition. When using TP measured by grab sampling and a mean EQR of all years the status in Sävjaån was poor, Figure 22a. When using high frequency TP from EQ2 the status was poor when using the 75th percentile and median absorbance. When using the 25th percentile absorbance the status was on the border between poor and bad. Almost no difference in between the three reference conditions (absorbance values) can be observed since the reference condition was very low (13.8-15.5 µg/l) compared to for example the average from EQ2 TP (79.9 µg/l).

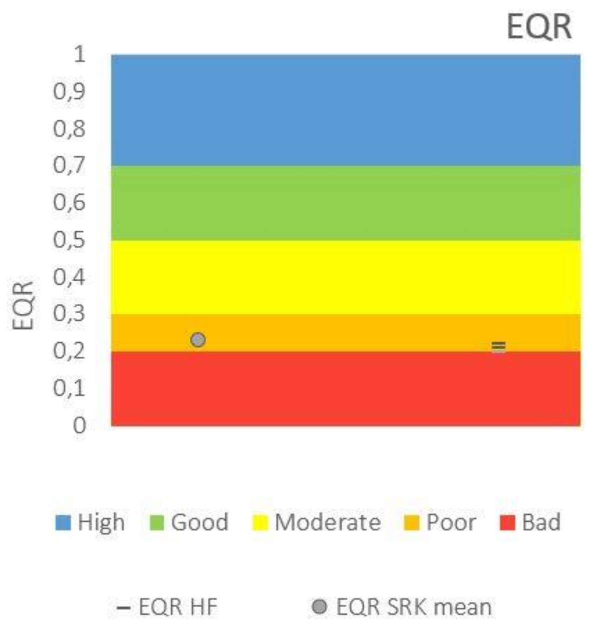

Figure 22. *Plot showing mean ecological quality ratio for 2012-2015 varying dependent on data source.*

5 Discussion

This section will connect the results to previous studies and theories. The research questions will be addressed and discussed.

5.1 Correlation between parameters

The first research question addressed how well the turbidity measured by the sensor correlated with grab samples analysed in the lab. When analysing the SRK and HF turbidity, a discrepancy between the two methods was identified. The unsynchronized samples gave low correlation (r^2=0.34). The occasions (3 days) with largest variation were further examined and showed a highly variable turbidity pattern despite no rain and normal discharge. Still no explanation for this variation has been found. According to the manufacturer (YSI, 2012), errors might occur due to sensor fouling from biological and chemical debris but also from outgassing air bubbles. Biofouling would be indicated by a steadily increasing turbidity from growth of aquatic vegetation on the equipment. No signs of biofouling could be seen in the data set. In Koskiaho *et al*. (2015), it is noted that well-functioning and maintained automatic systems can produce more accurate estimations of loads than manual grab water sampling. When examining data after calibration in April 2014, it appeared to be more closely correlated (r^2=0.90). This indicates that the calibration could be important for the accuracy of estimations. Therefore, the further analysis was based on three scenarios.

Another research question concerned turbidity as a useful proxy for TSS and TP in Sävjaån. The degree of correlation was to be described and the assumption of turbidity and TP following the same patterns explored. Firstly regarding the approach of the investigation, the high frequency data (every 10th minute) needed to be transformed to one value for use in the linear regression. Both an instant value (snapshot) and an hourly mean was applied in the linear regression. The result showed that using an hourly mean gave a more robust result and a slightly higher correlation.

In a study by Fölster & Rönnback (2015), the relationship between TP and turbidity from manual grab samples in 124 streams in Sweden was compared. The degree of explanation (r^2) varied significantly between sites, connected to the processes controlling TP concentrations. In the study, streams with high TP concentrations were divided into two groups. A theory was that the ones with fairly low correlations between the parameters could be affected by point sources. Sites with high correlation would rather be affected by agricultural areas with a lot of P transport connected to particles. To evaluate the use of continuous turbidity measurements as a proxy for TP in Sävjaån and get a deeper understanding of the situation, a comparison was made between the results and previous literature (Table 13).

Similar studies using turbidity as a proxy for TSS and TP in various catchments have been made. Regarding the correlation between turbidity and TSS the degrees of explanation were compared, most of the studies observed a closer relation between the parameters (in this study r^2= 0.39, 0.67). In other studies r^2 ranged between 0.46-0.98. Likewise in this study, when using the data from after calibration (scenario EQ2), the relation between turbidity and TSS in Sävjaån is in the lower 25th percentile compared to the other studies. The literature also evaluated the correlation of turbidity and TP. When using scenario EQ1 the correlation in Sävjaån was low compared to other published results (0.42), when using data from scenario EQ2 the relationship is comparable to the other studies (0.79). In other studies r^2 ranged between 0.49-0.90.

Table 13. *Previous studies investigating turbidity as a proxy of TSS and TP. In the study of Ruzycki et al. 2014 the data was log transformed, in the other studies not. *0.05, **<0.01, *** 0.001*

Study	Type of stream	Degree of explanation (r^2) TSS	Degree of explanation (r^2) TP
Stubblefield *et al*. 2007	Subalpine watershed	0.95**/ 0.91**	0.62**/0.83**
Jones *et al*., 2011	Forest, range land, agricultural land, urban area, fine to coarser grained soil	0.90***/ 0.71***	0.90***/ 0.49***
Ruzycki *et al*. 2014	Forest, shrub, urban area, temperate climate, clay	0.46***/0.75***	0.76***/0.74***
Koskiaho *et al*., 2015	Forest, agriculture, urban area, clay silt, glacial till.	0.95, 0.74, 0.85, 0.95, 0.98	0.86, 0.82, 0.59, 0.78, 0.87
Skarbøvik & Roseth, 2015	Arable land (60%), forest (8%) small catchment, silty clay	0.82	0.78

	loam		
Villa & Fölster, 2016 (unpublished manuscript)	Arable land (56%), small catchment (6 km^2), clay	0.87***	0.89***

When evaluating which parameter is more connected to turbidity (TSS or TP) 75% of previous studies (described in Table 13) report a better correlation with TSS, although not in this study. When measuring TSS, larger particle sizes are targeted, according to the definition from Bilotta & Brazier (2008) 0.7-63 µm but also commonly >0.45 µm (Owens, 2007). If it can be assumed that the definitions of TSS and turbidity are valid, and that smaller particles carry more P due to larger surface area (Figure 23) it would mean that suspended material in water in Sävjaån consists of more small particles (<0.45 µm / <0.7 µm) which carry P. The soil in Sävjaån catchment mostly consist of clay which would indicate finer grained particles and colloids in the water. Since clay colloids could range between 0.001-1 µm (Owens, 2007) that would support the argument.

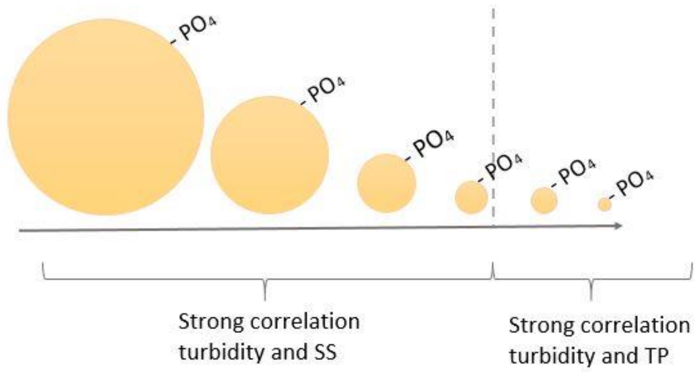

Figure 23. *Potential correlation of turbidity –TSS and TP connected to particle size. Smaller particles with a larger relative surface area are capable of transporting more P from left to right.*

According to the definitions from Yoshimura (2007), DIP is in the size range of 0.1-1 µm or by Spivakov *et al*. (2009) 0.45 µm. These definitions would then indicate that part of the P in Sävjaån is in the form of DIP. Interestingly, when analysing the correlation of parameters in the grab samples (SRK) turbidity and TSS had a stronger relationship (0.92) compared to turbidity and TP (0.84). That indicates that which parameter is more correlated is a product of model fit connected to the data set rather than being connected to physical or chemical properties of the stream.

However, it is important to note that the size ranges of turbidity, TSS and DIP/DOP are based on operational judgements; for example a filter size of 0.45

µm. The arbitrarily defined categories put a name on what is measured, for example TSS or turbidity. Note, for example, that according to the ISO standard 7027:1999 turbidity does not include dissolved particles. Yet, when performing a study like this, exclusion of dissolved particles might have a large influence partly because they potentially influence turbidity but also because of the surface area of the small particles carrying P. Hence, it is important to evaluate and understand the relative significance of the definition to the processes controlling the relationships.

When evaluating the relationships between turbidity and TSS/TP in Sävjaån compared to the literature, there are several cases with better correlation between the parameters. This raises questions about what can affect the relationships between turbidity and TSS/TP and the prevailing conditions in Sävjaån.

Particle size distribution has been considered an important factor when describing the relation between turbidity and TSS and TP (Jones *et al*., 2011; Stubblefield *et al*., 2007; Skarbøvik & Roseth, 2015; Ruzycki *et al*., 2014). In this study, no information about particle size distribution has been considered. However, particle size distribution varies spatially in a stream dependent on, for example, stream vegetation and morphology but also with flow and seasons. According to the manufacturer, the readings can be altered 0.5-1 NTU due to particles sizes. Despite this, a significant change between SRK and HF turbidity was observed (Figure 14) when comparing samples taken at the location of the sensor (SLU, r^2=0.99) and 60 m further downstream (2014-2015 r^2=0.90). If spatial variation affects the relations of SRK turbidity and HF turbidity it could consequently also affect the relation between turbidity and TSS/TP. Therefore, it would be interesting to explore the spatial variation in Sävjaån further to connect the effect with the potential of using turbidity as a proxy for TP.

Since we have a temperate climate in Sweden, also seasons could affect the relation between turbidity and TP in other ways than regarding particle size distribution. Organic matter increases during summer which, according to Gippel *et al.* (1995), could give 2-3 times higher turbidity readings when using continuous measurements which would then also over-estimate TP during summer. In Figure 10 it could be seen that the continuous turbidity readings vary considerably more than the results from grab sampling, yet this variation is not restricted only to months with a lot of organic matter. To investigate if the relationships between turbidity and TSS/TP were affected by flow or seasons respectively, multiple regression analyses were performed. Nevertheless neither flow nor seasons seemed to affect the relationships enough to be significant.

In Viviano *et al.* (2014) urban areas was showed to affect the relationship between turbidity and TP, due to particle composition (urban area r^2=0.14, natural catchment r^2=0.85). Domestic waste water contamination was regarded as the explanation for this difference in correlation. Since the catchment in Sävjaån only consists of 1% urban area, this should not be an explanatory factor in this study. Moreover, the land use in the sub-catchment of Sävjaån consists mostly of agricultural areas which according to the study of Fölster & Rönnback (2015) should favour a good correlation between TP and turbidity.

TP has also been reported to increase at high discharge (Ruzycki *et al*., 2014; Kronvang *et al.,* 1997). In Sävjaån, TP from the grab sampling was positively correlated to flow but could just moderately be explained by it. This indicates that P in Sävjaån is possibly not only associated with particles. For example in the study by Villa & Fölster (2016), TP and discharge had a very high correlation (r^2=0.90). However, the correlation with flow might also be affected by the size of the stream. Moreover Figure 13b showed that in Sävjaån, TP does not seem to have the relation described in Crossman *et al*. (2013) with high P at high and low flow. Hence this is not considered a factor affecting the relation between turbidity and TP. Possibly also hysteresis effects could affect the transport TP in Sävjaån. Two studies (Jordan *et al*., 2007; Bieroza & Heathwaite, 2015) showed non-linear concentration-discharge relationships during storm events connected to hysteresis. The question is then if the turbidity follows the same pattern or if this is a phenomenon causing a weaker relationship between TP and turbidity. To explore this further in Sävjaån more detailed flow data need to be obtained to examine high frequency turbidity and possibly high frequency TP concentrations during a storm event.

When using turbidity as a proxy, Jones *et al*. (2011) report that particulate P could be better estimated than dissolved P. In that case, quite high levels of PO_4-P in Sävjaån could affect the relation between TP and turbidity in a negative way. Despite this, the correlation between turbidity and PO_4-P was high (r^2= 0.57). The ratio between PO_4-P and TP was on average 47% in Sävjaån during the periods when the sensor was in the water (though varying between 8-78%). According to Ulén & Johansson (2005), there could be around 50% PO_4-P transported in small streams in agricultural areas. This could be comparable to the data from Sävjaån. High orthophosphate concentrations could for example be connected to P saturated soils or leachate from fertilizers (Ulén & Johansson, 2005). Presently the 45% of the land in the sub-catchment is used for agriculture, nevertheless the high PO_4-P ratios are to some extent surprising since the sub-catchment to a large part consists of clay soils (43%). Clay soils in the central plains of Sweden are prone to lose P in particulate form (Ulén & Johansson, 2005). Since the pH-value in Sävjaån varies between 7.1 and 7.8 that indicates that most of the P is bound to Ca or adsorbed to Fe and Al, but also that some of it could be present in an available form. That could be part of an explanation to the relatively high levels of PO_4-P (Figure 3). Another explanation could be that loosely absorbed P is desorbed in the process of analysing PO_4-P in the lab and therefore gives higher apparent concentrations. It would be interesting to investigate the source of PO_4-P and connect potential agricultural activities in the area with high ratios of PO_4-P.

Finally, it is hard to answer the question if turbidity and TP are following the same patterns in Sävjaån. The assumption is to a large part based on the connection of turbidity and TP through particles. The fact that TP can only moderately be explained by flow and that the ratio of PO_4-P/TP is periodically very high indicates that TP in Sävjaån is not solely associated with particles. However, technical problems and spatial variation make the question harder to answer. When analysing grab samples (SRK), the correlation between turbidity and TP was 0.84 and for the HF turbidity and TP, the correlation was 0.79 (EQ2). This quite small difference indicates that the sensor is working sufficiently well despite technical problems and spatial variation. In the end it might be the technique of using one parameter as a proxy for another that is the challenge if precise estimations of the state of water are required.

5.2 Implications of using high frequency turbidity data

5.2.1 Differences between the methods

To describe the result from using continuous measurements, the possible differences between the methods firstly needed to be assessed. In this study it could be concluded that the high frequency turbidity varied more and that the maximum values were higher (9-15 times) when measuring it continuously which would agree with previous literature. Skarbøvik & Roseth (2015) state that grab sampling might lead to inaccurate estimates of average and maximum TP concentrations since most of the time is not monitored. By using turbidity as a proxy, TP concentrations also varied more than when performing grab sampling. The average TP concentration based on turbidity measurements was slightly higher (79.9 µg/l compared to 74.7 µg/l) and the maximum value twice as high (592 µg/l compared to 282 µg/l). The question is then if this is closer to the "true" concentration even though turbidity has been used as a proxy.

In a study by Kyllmar *et al.* (2006) the mean annual P concentration was highest in clay dominated areas with high discharge (300 µg/l). In Sävjaån the mean annual P concentration was far from 300 µg/l, the maximum measured value was 282 µg/l. The TP values calculated from turbidity (EQ2) were slightly higher, but the annual average was also not close to 300 µg/l (maximum 592 µg/l). Consequently the TP levels in Sävjaån are not extremely high. However, the ecological status is regarded as moderate by the Swedish Water Authority (VISS Vattenkartan, 2016). The status was poor when calculating it from both grab sampling and high frequency data. When comparing the EQR: s from grab sampling and HF data (Figure 22) the difference was modest.

5.2.2 Load

This study was going to examine how load estimations were affected when using high frequency turbidity as a proxy for TP compared to other methods. Jones *et al.* (2011) investigated the influence on sampling frequency when calculating annual loads. Dependent on when the monthly value was taken over- or underestimation of load was common. When samples were taken weekly or monthly, resolution was lost and peaks in concentration overlooked. In the study by Jones *et al*. (2011) the TP load when using monthly values was underestimated by 8-25% at one sampling site and showed no prominent difference at the other sampling site. At the sampling site where the load was underestimated, the variance of turbidity and discharge was higher which would indicate larger effects due to information gaps. Moreover in the study by Villa & Fölster (2016), load calculations based on different input data were compared and the differences between the methods varied with discharge. At low discharge the difference between the methods were not as big as when the discharge was high.

Kronvang *et al*. (1997) reported that fortnightly grab sampling could underestimate annual TP load by 8.6-151%. The impact of sampling estimation methods on loads were evaluated and the study stated that the highest increase in accuracy was found with increased sampling frequency. Nearly all investigated estimation methods underestimated TP and PP. In a study by Cassidy & Jordan (2011) the loads were normally underestimated by ~60% in three small agricultural catchments using standard interpolation methods. When instead trying to catch high discharge and storm events the load was overestimated by ~70%. In the study by Villa & Fölster (2016) loads calculated with data from manual grab sampling and high frequency turbidity (used as a proxy for TP) were compared, the loads were 34-70% larger with high frequency monitoring.

In this study, it could be confirmed that peaks in concentration were overlooked when using grab sampling and applying linear interpolation. Interestingly, it could also be observed that the timing and the instant flow when the grab sample was taken had large impact on the estimated load when using linear interpolation (during 2013 and 2014). However, loads calculated from high frequency data (for example EQ2) was during two years (2012 and 2015) 31 and 17% larger than when using linear interpolation which is in agreement with the study by Jones *et al*. (2011).

The large variation between SRK and HF turbidity during some sampling days led to the three scenarios (EQ1, EQ2 and EQ3). For EQ1 and EQ3, the linear regressions showed moderate to high correlations (r^2) with both TSS (EQ1 0.39; EQ3 0.57) and TP (EQ1 0.42; EQ3 0.66). When calculating load scenarios, EQ1 always estimated lower transport than the other scenarios. For two years the estimated loads from EQ1 were also lower than the conventional interpolation methods. In contrast, the loads from EQ3 were very similar to EQ2 (which had the highest degree of explanation). Interestingly, when comparing EQ2 and EQ3 to I1, the loads from the scenarios only differed by 0.5-5% from each other (Table 12).

When data is log transformed, the variation between observations points are given less influence since the curve is not pulled towards these observations (Montgomery *et al.,* 2012). The precondition of normal variance between residuals is also better fulfilled. When investigating the residuals of linear regression models, only EQ1 would probably have been favoured by log transformation. Since this scenario was influenced by other uncertainties and consistent treatment of the data was preferred the data was not presented as log transformed. This decision though implies that the reported loads from EQ1, EQ2 and EQ3 could be slightly larger because of "extreme" values pulling the curve and hence the slope in the equations.

5.3 Advantages and limitations with the method

The last research question addressed what advantages and limitations high frequency monitoring could have (in the perspective of this study). One issue motivating a study like this is the need for reliable data to make trustworthy decisions in remediation plans and strategies (Allan *et al*., 2006). TP is an important parameter but hard to asses because of the high variability over the year (Ruzycki *et al*., 2014; Kronvang *et al.,* 1997). In previous sections, it has been shown that turbidity and TP had a high correlation and thus, it can be used as a proxy for TP in Sävjaån. The results showed that large loads are transported when high concentration and high flow coincides which is significant for the yearly load. With the high frequency data TP varies more and is less influenced by chance (when the grab sample is taken). This ought to be a great advantage and generate a better estimation of the load.

It is known that grab sampling bring great uncertainties (Moosmann *et al*., 2005). When using turbidity as a proxy uncertainty is transferred to other parts of the process related to the accuracy of the sensor, unexplained diurnal large variations, forms of P and spatial variation. The linear correlation is also based on the grab samples which is often a one replicate sample taken arbitrarily once a month which in turn brings uncertainty. The question is then how different sources of uncertainty are evaluated with respect to each other. It might be a good idea to combine the methods with the purpose to minimize the effect of information gaps of grab sampling. A strategy could be to deploy sensors collecting data during high discharge to capture the variability and get a more accurate estimation. However this strategy would have similarities to automatic storm sampling which has the problem of over-estimating the load (Jordan *et al.*, 2007).

At the moment, the in situ sensors come with a significant investment. Yet from an economic perspective, costs connected to the laboratory should be lower than when performing composite sampling or grab sampling with high frequency. Though the turbidity data from the sensor needs to be calibrated with TP samples and consequently water samples will need to be analysed in the laboratory. The sensor also needs frequent maintenance to ensure sufficient data quality and complete data sets which imply a cost connected to personnel.

Before investing in an in situ sensor it would be desirable to be able to predict the efficiency of using turbidity as a proxy for TP. From the experiences and literature studies connected to this study a good idea might be to investigate to what extent P is particle bound in the stream before deploying a sensor. One indication of particle associated P could be determined from P behaviour with flow, especially during storm events or by analysing the ratio PO_4-P/TP, undoubtedly also other factors could be added. To further optimize the relationship between TP and turbidity the sensor and grab samples used for calibration should be located at the same spot to avoid influence from spatial variation.

Interestingly, spatial variation indicated to affect the relationship between TP and turbidity in this study. A consequence of this is that even if the in situ sensor gives a trustworthy prediction of load in the stream the representability can be questioned. Further investigations of variability caught by the sensor in depth and distance needs to be assessed in future studies.

In water management, the aim of environmental monitoring needs to be clarified before choosing the sampling method. If the aim is to roughly assess surface water in all Sweden, in situ sensors in all streams might not be a feasible solution with current investment costs and knowledge level. However, in streams where it is extra important to make a reliable estimation, there can be great benefits of using an in situ sensor. Examples of sites where sensors might be most useful include locations which could be at significant contributors of TP in a catchment or in areas where a lot of measures are performed to reduce nutrient load. A sensor campaign could also be done during a limited period (for example a year) to see how well the prevailing ecological status is described. With an in situ high frequency sensor it is possible to access the measurements instantly. In the end high frequency monitoring gives knowledge and an insight of the daily state of the waters that never can be accessed with conventional monitoring methods.

6 Conclusions

The results from this study have shown that data from the turbidity sensor varies more than the turbidity from grab sampling, the maximum readings were 9 respectively 15 times higher than the results from grab sampling. A significant information loss can be observed when only using grab sampling in comparison to high frequency data.

When comparing the different methods several discrepancies were shown between the grab samples (SRK) and high frequency turbidity data during 2012-2013. These discrepancies were connected to extensive diurnal variation. After the sensor was calibrated in April 2014 the methods were more synchronized.

Linear correlations of high frequency turbidity and TP were obtained which were in close agreement to the literature. For the years 2014-2015 TP and high frequency turbidity had a very high correlation, moreover TSS and high frequency turbidity had a high correlation. The relationships seemed to be affected by particle size distribution and spatial variation. Yet more importantly, the relations could be affected by the fraction of P associated with particles. In this study the proportion particle bound P was assessed though investigating the TP vs flow relationship and ratio between PO_4-P and TP. It was difficult to answer if the turbidity and TP in Sävjaån follows the same patterns since a lot of other factors are influencing the relationship between the parameters. However, since P is not merely associated with particles in Sävjaån that might indicate that the parameters are not entirely synchronized.

The load estimations were larger during 2012 (+31%), 2013 (+1%) and 2015 (+17%) when using turbidity as a proxy (EQ2) compared to linear interpolation (I1). These results conform to the literature. It can also be concluded that the two conventional methods gave similar results. However, it was clear that timing and the instant flow when the grab sample was taken had large impact on the estimated load when using linear interpolation. This was the reason to the estimations being approximately equal in 2013 (+1%) and lower in 2014 (-7%). This affected the result of the comparison between high frequency measurements and conventional methods.

From the results it could be concluded that the largest TP transport occurred when high P concentration coincided with high discharge. High concentration without high discharge did not give as significant results to the load calculation. When comparing the EQR: s from grab sampling and HF data the difference was modest.

When the aim of the environmental monitoring is to describe nutrient loads or status in a stream with high accuracy, the study showed that using turbidity as a proxy for TP is justified. Peaks are caught and combined with high discharge it gives significant effects in the load estimation. When using turbidity as a proxy uncertainty is transferred from lack of data (in conventional methods) to other parts of the process. The study also showed that the relationship between turbidity and TP could be affected by sensor maintenance and spatial variation. Also, large diurnal variations, particle size distribution and ratio between PO_4-P and TP could affect the relationship. Yet, when doing sensor maintenance and securing data quality the result gives a better more reliable estimate of load and concentrations than when using grab sampling and conventional interpolation methods.

References

Ahlvik, L. & Pavlova, Y. (2013). A Strategic Analysis of Eutrophication Abatement in the Baltic Sea. *Environmental and Resource Economics*, 56(3), pp 353–378.

Allan, I., Vrana, B., Greenwood, R., Mills, G., Roig, B. & Gonzalez, C. (2006). A “toolbox” for biological and chemical monitoring requirements for the European Union’s Water Framework Directive. *Talanta*, 69(2), pp 302–322.

Bieroza, M. Z. & Heathwaite, A. L. (2015). Seasonal variation in phosphorus concentration–discharge hysteresis inferred from high-frequency in situ monitoring. *Journal of Hydrology*, 524, pp 333–347.

Bilotta, G. S. & Brazier, R. E. (2008). Understanding the influence of suspended solids on water quality and aquatic biota. *Water Research*, 42(12), pp 2849–2861.

Bogen, J. (1992). Monitoring grain size of suspended sediments in rivers. E*rosion and Sediment Transport Monitoring Programmes in River Basins* (Proceedings of the Oslo Symposium, August 1992). IAHS Publ. no. 210, 1992. pp 183-190.

Brady, N.C., Weil, R.R. (2008). *The Nature and Properties of Soils*. 14th edition. New York: McMillan Publisher Company

Brandt, M. (1990). Generation, Transport and Deposition of Suspended and Dissolved Material - Examples from Swedish Rivers. *Geografiska Annaler. Series A, Physical Geography*, 72(3/4), pp 273–283.

Cassidy, R. & Jordan, P. (2011). Limitations of instantaneous water quality sampling in surface-water catchments: Comparison with near-continuous phosphorus time-series data. *Journal of Hydrology*, 405(1–2), pp 182–193.

Crossman, J., Whitehead, P. G., Futter, M. N., Jin, L., Shahgedanova, M., Castellazzi, M. & Wade, A. J. (2013). The interactive responses of water quality and hydrology to changes in multiple stressors, and implications for the long-term effective management of phosphorus. *Science of The Total Environment*, 454–455, pp 230–244.

Djodjic, F., Hellgren, S., Futter, M. & Brandt, M. (2012). Suspenderat material–transporter och betydelsen för andra vattenkvalitetsparametrar. [online]. Available from: http://www.diva-portal.org/smash/record.jsf?pid=diva2:742978. [Accessed 2016-05-29].

Elser, J. J., Bracken, M. E. S., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., Ngai, J. T., Seabloom, E. W., Shurin, J. B. & Smith, J. E. (2007). Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecology Letters*, 10(12), pp 1135–1142.

EU (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *EUR-Lex* -

32000L0060 - EN - EUR-Lex. [online]. Available from: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32000L0060. [Accessed 2016-06-04]

Fölster J. & Rönnback, P. (2015). Turbiditet som mått på suspenderat material och totalfosfor. Institutionen för vatten och miljö, SLU Rapport 2015:2.

Gippel, C. J. (1995). Potential of turbidity monitoring for measuring the transport of suspended solids in streams. *Hydrological processes*, 9(1), pp 83–97.

Glasgow, H. B., Burkholder, J. M., Reed, R. E., Lewitus, A. J. & Kleinman, J. E. (2004). Real-time remote monitoring of water quality: a review of current applications, and advancements in sensor, telemetry, and computing technologies. *Journal of Experimental Marine Biology and Ecology*, 300(1–2), pp 409–448 (VOLUME 300 Special Issue).

Grayson, R. B., Finlayson, B. L., Gippel, C. J. & Hart, B. T. (1996). The potential of field turbidity measurements for the computation of total phosphorus and suspended solids loads. *Journal of Environmental Management*, 47(3), pp 257–267.

Grimvall, A. & Stålnacke, P. (2001). Riverine Inputs of Nutrients to the Baltic Sea. In: Wulff, P. D. F. V., Rahm, P. D. L. A., & Larsson, P. D. P. (Eds) *A Systems Analysis of the Baltic Sea*. pp 113–131. Springer Berlin Heidelberg. (148). ISBN 978-3-642-08727-1.

Gustafsson, B. G., Schenk, F., Blenckner, T., Eilola, K., Meier, H. E. M., Müller-Karulis, B., Neumann, T., Ruoho-Airola, T., Savchuk, O. P. & Zorita, E. (2012a). Reconstructing the Development of Baltic Sea Eutrophication 1850–2006. *AMBIO*, 41(6), pp 534–548.

Gustafsson, J. P., Mwamila, L. B. & Kergoat, K. (2012b). The pH dependence of phosphate sorption and desorption in Swedish agricultural soils. *Geoderma*, 189–190, pp 304–311.

Hatch, L. K., Reuter, J. E. & Goldman, C. R. (2001). Stream phosphorus transport in the Lake Tahoe basin, 1989–1996. *Environmental Monitoring and Assessment*, 69(1), pp 63–83.

Hering, D., Borja, A., Carstensen, J., Carvalho, L., Elliott, M., Feld, C. K., Heiskanen, A.-S., Johnson, R. K., Moe, J. & Pont, D. (2010). The European Water Framework Directive at the age of 10: A critical review of the achievements with recommendations for the future. *Science of the Total Environment*, 408(19), pp 4007–4019.

Horowitz, A. J., Elrick, K. A. & Colberg, M. R. (1992). The effect of membrane filtration artifacts on dissolved trace element concentrations. *Water Research*, 26(6), p 11.

Humborg, C., Mörth, C.-M., Sundbom, M. & Wulff, F. (2007). Riverine transport of biogenic elements to the Baltic Sea? Past and possible future perspectives. *Hydrology and Earth System Sciences Discussions*, 11(5), pp 1593–1607.

Jalón-Rojas, I., Schmidt, S., Sottolichio, A. & Bertier, C. (2016). Tracking the turbidity maximum zone in the Loire Estuary (France) based on a long-term, high-resolution and high-frequency monitoring network. *Continental Shelf Research*, 117, pp 1–11.

Jones, A. S., Stevens, D. K., Horsburgh, J. S. & Mesner, N. O. (2011). Surrogate measures for providing high frequency estimates of total suspended solids and total phosphorus concentrations. *JAWRA Journal of American Water Resources Association*, 47(2), pp 239-253.

Jordan, P., Arnscheidt, A., Mcgrogan, H. & Mccormick, S. (2007). Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser. *Hydrology and Earth System Sciences Discussions*, 11(1), pp 372–381.

Karathanasis, A. D. & Shumaker, P. D. (2009). Organic and inorganic phosphate interactions with soil hydroxy-interlayered minerals. *Journal of Soils and Sediments*, 9(5), pp 501–510.

Kiedrzyńska, E., Kiedrzyński, M., Urbaniak, M., Magnuszewski, A., Skłodowski, M., Wyrwicka, A. & Zalewski, M. (2014). Point sources of nutrient pollution in the lowland river catchment in the context of the Baltic Sea eutrophication. *Ecological Engineering*, 70, pp 337–348.

Koskiaho, J., Tattari, S. & Röman, E. (2015). Suspended solids and total phosphorus loads and their spatial differences in a lake-rich river basin as determined by automatic monitoring network.

Environmental Monitoring and Assessment [online], 187(4). Available from: http://link.springer.com/10.1007/s10661-015-4397-6. [Accessed 2016-03-09].

Kronvang, B. (1992). The export of particulate matter, particulate phosphorus and dissolved phosphorus from two agricultural river basins: Implications on estimating the non-point phosphorus load. *Water Research*, 26(10), pp 1347–1358.

Kronvang, B. & Bruhn, A. J. (1996). Choice of Sampling Strategy and Estimation Method for Calculating Nitrogen and Phosphorus Transport in Small Lowland Streams. *Hydrological Processes*, 10(11), pp 1483–1501.

Kronvang, B., Laubel, A. & Grant, R. (1997).Supended sediment andparticulate phosphorus transport and delivery pathways in an arable catchment, Gelbaek Stream, Denmark. Hydrological processes, 11, pp 627–642.

Kyllmar, K., Carlsson, C., Gustafson, A., Ulén, B. & Johnsson, H. (2006). Nutrient discharge from small agricultural catchments in Sweden. *Agriculture, Ecosystems & Environment*, 115(1–4), pp 15–26.

Larsson, M. & Granstedt, A. (2010). Sustainable governance of the agriculture and the Baltic Sea — Agricultural reforms, food production and curbed eutrophication. *Ecological Economics*, 69(10), pp 1943–1951.

Lundberg, C. (2005). Conceptualizing the Baltic Sea Ecosystem: An Interdisciplinary Tool for Environmental Decision Making. *AMBIO: A Journal of the Human Environment*, 34(6), pp 433–439.

Länsstyrelsen i Uppsala län (2016-05-30). *Sävjaån-Funbosjön*. [online]. Available from: http://www.lansstyrelsen.se/uppsala/Sv/djur-och-natur/skyddad-natur/Natura-2000/lanets-natura-2000-omraden/uppsala/Pages/savjaan-funbosjon.aspx. [Accessed 2016-03-09].

Markinfo (2016-05-30). Utbytbart kalcium i O-horisonten -MarkInfo. [online]. Available from: http://www-markinfo.slu.se/sve/kem/baskat/cao.html. [Accessed 2016-05-30].

McBride, M. B. (1994). *Environmental Chemistry of Soils*. New York: Oxford University Press

Moatar, F. & Meybeck, M. (2005). Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic River Loire. *Hydrological Processes*, 19(2), pp 429–444.

Montgomery, D. C., Peck, E. A. & Vining, G. G. (2012). *Introduction to Linear Regression Analysis*. 5th edition. Hoboken: John Wiley & Sons.

Morgan, M. A. (1997). The behaviour of soil and fertilizer phosphorus, 1997. pp 137–149. Wallingford: CAB INTERNATIONAL.

Moosmann, L., Müller, B., Gächter, R., Wüest, A., Butscher, E. & Herzog, P. (2005). Trend-oriented sampling strategy and estimation of soluble reactive phosphorus loads in streams. *Water Resources Research*, 41(1), p W01020.

Naturvårdsverket. (1999). *Bedömningsgrunder för miljökvalitet. Sjöar och vattendrag* (1999a). Stockholm: Naturvårdsverket. (Rapport 4913).

Naturvårdsverket (2016-05-30). *Bedömningsgrunder för sjöar och vattendrag Bilaga A*. [online] Available from: https://www.naturvardsverket.se/Documents/publikationer/620-0148-3.pdf. [Accessed 2016-05-29].

Owens, P. (2007). *Sediment Management at the River Basin Scale*. 1st edition. Amesterdam: Elsevier. Available: E-brary. [2016-04-27]

Gao, P. (2008). Understanding watershed suspended sediment transport. *Progress in Physical Geography*, 32(3), pp 243–263.

Pfannkuche, J. & Schmidt, A. (2003). Determination of suspended particulate matter concentration from turbidity measurements: particle size effects and calibration procedures. *Hydrological Processes*, 17(10), pp 1951–1963.

Pissarides, A., Stewart, J. W. B. & Rennie, D. A. (1968). Influence of Cation Saturation on Phosphorus Adsorption by Selected Clay Minerals. *Canadian Journal of Soil Science*, 48(2), pp 151–157.

Ruttenberg, K. C. (2014). 10.13 - The Global Phosphorus Cycle A2 - Holland, Heinrich D. In: Turekian, K. K. (Ed) *Treatise on Geochemistry.* (2nd edition). pp 499–558. Oxford: Elsevier.

Ruzycki, E. M., Axler, R. P., Host, G. E., Henneck, J. R. & Will, N. R. (2014). Estimating Sediment and Nutrient Loads in Four Western Lake Superior Streams. *JAWRA Journal of the American Water Resources Association*, 50(5), pp 1138–1154.

Schlosser, I. J. & Karr, J. R. (1981). Riparian vegetation and channel morphology impact on spatial patterns of water quality in agricultural watersheds. *Environmental Management*, 5(3), pp 233–243.

SGUs kartvisare Jordarter 1:1 miljon (2016-05-30). [cartographic material]: online map service. Available from: http://apps.sgu.se/kartvisare/kartvisare-jordarter-1-miljon-sv.html. [Accessed 2016-03-09].

SMHI Vattenwebb (2016-05-30). *Modelldata per område*. [online]. Available from: http://vattenwebb.smhi.se/modelarea/. [Accessed 2016-03-09].

SMHI Öppna data. [online]. Available from: http://opendata-catalog.smhi.se/explore/. [Accessed 2016-06-01].

Skarbøvik, E. & Roseth, R. (2015). Use of sensor data for turbidity, pH and conductivity as an alternative to conventional water quality monitoring in four Norwegian case studies. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science*, 65(1), pp 63–73.

Spivakov, B. Y., Maryutina, T. A. & Muntau, H. (2009). Phosphorus Speciation in Water and Sediments. *Pure and Applied Chemistry*, 71(11), pp 2161–2176.

Stubblefield, A. P., Reuter, J. E., Dahlgren, R. A. & Goldman, C. R. (2007). Use of turbidometry to characterize suspended sediment and phosphorus fluxes in the Lake Tahoe basin, California, USA. *Hydrological Processes*, 21(3), pp 281–291.

Swedish Standards Institute (2016-05-30). *ISO 7027:1999 - Water quality -- Determination of turbidity*. [online]. Available from: http://www.sis.se/milj%C3%B6-och-h%C3%A4lsoskydd-s%C3%A4kerhet/vattenkvalitet/unders%C3%B6kning-av-vattens-fysikaliska-egenskaper/iso-70271999. [Accessed 2016-03-09].

Swedish Standards Institute (2016-05-30). *Standard - Vattenundersökningar - Bestämning av suspenderade ämnen - Metod baserad på filtrering genom glasfiberfilter - SS-EN 872:2005.* [online]. Available from: http://www.sis.se/Templates/SIS/Pages/ProductStandardView.aspx?id=29&epslanguage=sv&pid=STD-40282&icslvl1=SIS_COMMON_13&icslvl2=SIS_COMMON_13.060&icslvl3=SIS_COMMON_13.060.20. [Accessed 2016-05-29].

Ulén, B. (2004). Size and Settling Velocities of Phosphorus-Containing Particles in Water from Agricultural Drains. *Water, Air, and Soil Pollution*, 157(1–4), pp 331–343.

Ulén, B. & Jakobsson, C. (2005). Critical evaluation of measures to mitigate phosphorus losses from agricultural land to surface waters in Sweden. *Science of The Total Environment*, 344(1–3), pp 37–50 (Linking Landscape Sources of Phosphorus and Sediment to Ecological Impacts in Surface WatersHaygarth S.I.).

U.S Geological Survey (2016-05-30). *Turbidity -- Units of Measurement*. [online]. Available from: http://or.water.usgs.gov/grapher/fnu.html. [Accessed 2016-05-29].

Uusitalo, R., Turtola, E., Puustinen, M. & Paasonen-kivekäs, M. (2003) *Contribution of Particulate Phosphorus to Runoff Phosphorus Bioavailability*. Journal of Environmental Quality, 32(6), pp 2007-2016.

Vattenmyndigheten Norra Östersjön (2016-05-30a). *Fyrisåns avrinningsområde*. [online]. Available from: http://www.vattenmyndigheterna.se/Sv/norra-ostersjon/distriktets-organisation/delomraden/norrstrom/Pages/fyrisan.aspx. [Accessed 2016a-03-21].

Vattenmyndigheten Norra Östersjön (2016-05-30b). *Förslag på förvaltningsplan för Norra Östersjöns vattendistrikt 2015-2021*. [online]. Available from: http://www.vattenmyndigheterna.se/Sv/publikationer/norra-ostersjon/samradsdokument/Pages/forslag-pa-forvaltningsplan-for-norra-ostersjons-vattendistrikt-2015-2021.aspx. [Accessed 2016-03-09].

Villa, A. & Fölster, J. (2016) Use of turbidity to determine suspended solids and total phosphorus concentrations and loads. Comparison of high frequency sampling with conventional monitoring methods. Unpublished manuscript

VISS Vattenkartan (2016-05-30). *Sävjaån - Vattendrag - VISS - VattenInformationsSystem för Sverige*. [cartographic material]: online map service. Available from: http://www.viss.lansstyrelsen.se/Waters.aspx?waterEUID=SE663553-160798. [Accessed 2016-03-09].

Viviano, G., Salerno, F., Manfredi, E. C., Polesello, S., Valsecchi, S. & Tartari, G. (2014). Surrogate measures for providing high frequency estimates of total phosphorus concentrations in urban watersheds. *Water Research*, 64, pp 265–277.

Wahlin, K. (2011). *Tillämpad statistik : en grundkurs*. Stockholm: Bonnier utbildning.

Walling, D. E. & Moorehead, P. W. (1987). Spatial and Temporal Variation of the Particle-Size Characteristics of Fluvial Suspended Sediment. *Geografiska Annaler. Series A, Physical Geography*, 69(1), pp 47–59.

Yao, M., Nan, J. & Chen, T. (2014). Effect of particle size distribution on turbidity under various water quality levels during flocculation processes. *Desalination*, 354, pp 116–124.

Yoshimura, T., Nishioka, J., Saito, H., Takeda, S., Tsuda, A. & Wells, M. L. (2007). Distributions of particulate and dissolved organic and inorganic phosphorus in North Pacific surface waters. *Marine Chemistry*, 103(1–2), pp 112–121.

YSI. (2012). *User Manual: 6-Series Multiparameter Water Quality Sondes.* Item #069300. Yellow Springs

YSI (2016-05-30). *600OMS V2 Optical Monitoring Sonde | ysi.com*. [online]. Available from: https://www.ysi.com/600OMS-V2?600OMS-V2-5. [Accessed 2016-03-09].

Zeidan, M., Xu, B. H., Jia, X. & Williams, R. A. (2007). Simulation of Aggregate Deformation and Breakup in Simple Shear Flows using a Combined Continuum and Discrete Model. *Chemical Engineering Research and Design*, 85(A12), pp 1645–165

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