Sveriges lantbruksuniversitet
Swedish University of Agricultural Sciences

Department of Soil and Environment

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Abstract

Optical sensors are advanced technology capable of monitoring water quality continuously at high temporal resolution. Optical sensors are prone to errors when deployed in streams with high sediment content. Agricultural streams, with high and variable suspended sediment loads, can affect the performance of these instruments. This work aims to evaluate the capability of optical sensor measurements in highly turbid streams. The study was performed in an agricultural catchment with clay soils and high concentrations of phosphorus and sediments in stream, located in Långtora, Sweden. Sensor calibration and correction for temperature quenching effects were performed. Water samples were collected with an autosampler to be analyzed in a laboratory and the results were compared with the sensor measurements. Tryptophan-like fluorescence (TLF), chromophoric dissolved organic matter (CDOM), and turbidity were measured by the sensor. The results showed a strong similarity between laboratory and sensor results for TLF and turbidity. CDOM concentrations were similar apart from a linear trend present in the laboratory measurements but not sensor measurements. Additional data regarding sediment composition is presented to better understand dynamics of suspended and organic material in the stream.

Keywords: optical sensors, phosphorus and sediment losses, turbidity, organic matter, agricultural catchments

Populärvetenskaplig sammanfattning

Optiska sensorer är en avancerad teknik som kan mäta parametrar relaterade till vattenkvalitet under korta tidsintervaller. Vattendrag som passerar genom jordbruksområden och uppvisar höga koncentrationer av fosfor och sediment kan påverka optiska sensorers prestanda. Syftet med detta arbete är att utvärdera prestandan hos optiska sensorer i grumliga öppna diken. Studien genomfördes i ett dike med höga koncentrationer av fosfor och sediment belägen i ett jordbruksområde i Långtora, Sverige. Vattenprover samlades in med en automatisk uppsamlare, samtidigt som en optisk sensor registrerade data i diket. Vattenproverna analyserades sedan i ett laboratorium och jämfördes mot resultaten från sensorn. Mätvärden för bäckens grumlighet och koncentration av tryptofan visade stora likheter i de båda fallen. Resultaten av upplösta humusämnen visade också likhet i förhållande till koncentrationsförändringarna under experimentens gång, men laboratorieresultaten visade en linjär tillväxt som inte observerades av sensorn. Ytterligare information om sedimentets beståndsdelar presenteras för att bättre förstå förändringarna i humusämnen som finns i det öppna diket.

Nyckelord: optiska sensorer, fosfor- och sedimentförluster, turbiditet, humusämne, jordbruksavrinningsområden

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Abbreviations

C6	Catchment located in Långtora, Sweden
CDOM	Chromophoric Dissolved Organic Matter
DI	Distillated
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
E23	Catchment located in Norrköping, Sweden
EDTA	Ethylenediaminetetraacetic acid
NTU	Nephelometric Turbidity Unit
OM	Organic Matter
P	Phosphorus
QS	Quinine Sulfate
QSD	Quinine Sulfate Dihydrate
SDD	Secci Disk Depth
SS	Suspended Solids
TLF	Tryptophan-Like Fluorescence
TOC	Total Organic Carbon
TP	Total Phosphorus
TRY	Tryptophan
TSS	Total Suspended Solids

Study aim

The aim of this work was to evaluate the ability of optical sensors to measure water quality in highly turbid (0-1000 NTU) agricultural streams with high losses of phosphorus and sediments and thus an elevated risk of eutrophication. For this, data obtained with an optical sensor from an agricultural stream were compared with measurements conducted in the laboratory on water samples from the identical spot in the stream. A literature review covering the topics of water quality problems in agricultural landscape, runoff of sediments and phosphorus losses is presented to provide a context for this work. Furthermore, evaluation of optical sensors application and their limitations is presented to address the question in the title of this thesis.

Literature review

Water quality

Population growth, shifts in land use and global warming have been the principal factors affecting the freshwater ecosystems and water quality in many places in the world. Activities that increase the level of exposed soil and decrease vegetation cover, as agriculture, forestry, construction and mining contribute largely to water pollution (Ding, *et al.,* 2015). Soil characteristics also influence water quality e.g. through erosion from compacted soils with low organic matter and poor internal drainage (Balasubramanian, 2017) followed by runoff of this suspended material.
Runoff of sediments is associated with phosphorus (P) losses as P binds easily to sediment particles and organic matter in the soil (Busman *et al.*, 2002; Ulén *et al.*, 2007). In Scandinavia, silty and clay soils have an elevated risk of erosion and phosphorus losses (Ulén & Jakobsson, 2005). Through runoff, phosphorus enters agricultural headwaters in upland and arable areas causing eutrophication in many lakes and coastal waters downstream (Ulén *et al.*, 2007). Eutrophication is driven by increased nutrient concentrations, particularly phosphorus from human sewage or fertilizer runoff from agricultural areas (Brönmark and Hansson, 2005) and leads to algal blooms (Conley *et al.*, 2009). This increase in algae growth causes depletion of dissolved oxygen in the bottom of the lakes and seas and in consequence can lead to fish deaths and reduction in biodiversity.

Optical sensors

To monitor the changes that occur in the aquatic environment, it is necessary to have data on chemical compounds and their amounts present in water. Historically, water quality monitoring has been based on discrete samples e.g. taking samples weekly or monthly (Pellerin & Bergamaschi, 2014). Long sampling intervals of this traditional monitoring may underestimate or overestimate chemical compounds concentrations, making it difficult to identify and quantify the true effects of human change in the aquatic ecosystems. The use of modern technologies capa-

ble to monitor water quality at a second time step is therefore of a significant importance. The use of in situ optical sensors to assess water quality is growing considerable in recent years (Bieroza *et al.,* 2014; Rode *et al.,* 2016). Optical sensors are capable to detect the water chemistry changes in lakes, rivers or streams in the real time. These instruments measure absorbance, fluorescence, or scattering properties of the materials which are dissolved or suspended in the water (Pellerin & Bergamaschi, 2014; Kamis *et al.,* 2015).

With the interaction between sensor light and particles or dissolved elements (Figure 1), optical sensors can be used directly or indirectly to detect distinctive parameters of concern to water quality, such as total suspended solids (TSS), chlorophyll-a, turbidity, salinity, total phosphorus (TP), Secchi disk depth (SDD), temperature, pH, dissolved organic carbon (DOC), chromophoric dissolved organic matter (CDOM) (Gholizadeh *et al.,* 2016).

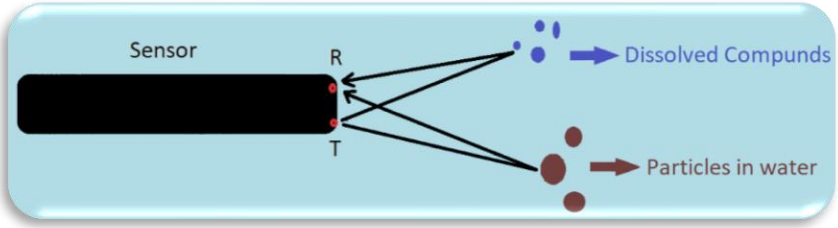

Figure 1. Optical sensor emitting a light from the source (T), the light is absorbed by particles and/or dissolved compounds in water (absorbance) and then emitted (fluorescence). The sensor measures the absorbance and/or fluorescence intensity in the detector (R).

Advantages and disadvantages of optical sensors

There are many considerations to take into account when using sensors. Although the sensors have an exciting potential in its use, little is known about their performance when compared to the traditional methods (Khamis *et al.,* 2015). The sediment properties, as particle size, composition, shape and environmental characteristics, can significantly affect optical measurements (Bunt *et al.,* 1999). Most natural surface waters carry suspended matter that scatters more light than is absorbed (Downing, 2008). Because most natural waters are highly coloured and turbid, sensor calibration is needed to measure fluorescence in situ in water bodies (Downing, *et al.,* 2012). This calibration accounts for correction in variation of the temperature which affects fluorescence and high turbidity that may distort both the fluorescence and absorbance results. High turbidity causes strong light attenuation resulting in very low intensities of raw fluorophores (substances that absorb light and re-emit light at longer wavelengths) (Downing, *et al.,* 2012).

The amount of data collected over an extended period is reliant on the capacity of storage of a sensor and the battery lifetime. These optical measurements are chemical-free (Pellerin & Bergamaschi, 2014; Pellerin *et al.,* 2016.). Sensors can detect

substances with a small particle size (Ahuja & Parande, 2012), but also, sensors should not be used for substances with particle size less than 100 micrometers (Schoellhamer & Wright, 2003). Sensor measurement errors increase if the variability of the size of the particles is high, fouling by biological growth (Schoellhamer & Wright, 2003; Bieroza & Heathwaite, 2016). Sensor measurements based on fluorescence spectroscopy are temperature sensitive. Temperature fluctuations can change fluorescence measurements, reducing the intensity of the light output of the substances (Downing *et al.*, 2012; Bieroza & Heathwaite, 2016). But the signal can also be corrected through the temperature calibration of the sensor. All the advantages and limitations discussed here are present in Table 1 below.

Table 1. Advantages & disadvantages of optical sensors. Collated from Schoellhamer & Wright, 2003; Ahuja & Parande, 2012; Downing *et al.*, 2012; Pellerin & Bergamaschi, 2014; Bieroza & Heathwaite, 2016; Pellerin *et al.*, 2016

Advantages	**Disadvantages**
24/7 data collection	Expensive (>$15,000)
Rapid sampling rates	Invalidate data by particle variation
Time dense data	Slope calibration affected by particle variation
Low detection limits	Should not be used for particles size < 100µm
Low power consumption	Sensitive with high water pollution
Chemical-free	Temperature sensitive (fluorescence)
Easy field servicing	
Long-term deployment capability	

Water quality parameters measured with optical sensors

Since phosphorus and/or dissolved organic matter (DOM) are absorbed to the soil particles surface (Ulén *et al.*, 2007), and phosphorus binds easily to organic matter in the soil (Busman *et al.*, 2002), optical sensors are useful tools to access the information on parameters related to phosphorus dynamics such as organic matter and turbidity.

Organic matter

Dissolved compounds such as dissolved organic matter (DOM), transform absorbed light into other forms of energy, and embody the re-release of energy at longer wavelengths (fluorescence). Fluorescence by humic substances gives valuable information on the type, size and concentration of constituents in water (Pellerin & Bergamaschi, 2014). In many regions worldwide, DOM affects the quality of drinking water (Bieroza *et al.*, 2009), particularly where untreated waters contain high concentrations of chromophoric DOM (CDOM). CDOM comes from non-point source mobilised by rainfall or snowmelt events, transported over the catchment and through the subsurface (Herzsprung *et al.*, 2012). CDOM can

be used to explain events such as a sudden decrease in primary productivity, phytoplankton regime variation, algal blooms and changes in environment (Belzile *et al.*, 2002).

Tryptophan is an amino acid classified as protein-like organic matter, dissolved in water having a specific excitation and emission (λEX ~ 280 nm, λEM ~ 350 nm) (Ghisaidoobe & Chung, 2014). Tryptophan-like fluorescence (TLF) can identify impact of waste water discharge, high biological activity or industrial discharge in the water system (Gray, 2012) or used as an indicator of human impact on surface water and groundwater quality (Khamis *et al.*, 2015). There is a positive relationship between TLF and labile organic carbon and microbial activity (Hudson *et al.*, 2007). Tryptophan-like fluorescence is typical for microbially-produced or processed organic matter (Khamis *et al.*, 2015).

Turbidity

Turbidity is an optical measurement of water clarity (Wetzel, 2001). The quantity of light dispersed from the particles determines the turbidity of the water (Perlman, 2014). The cloudiness in water is associated with soil erosion, turbulence, TOC constituents and primary production. Water turbidity is frequently used as an indicator of water quality and correlates with the concentration of total suspended solids in water. Turbidity levels observed in streams and turbidity classification are presented in Table 2. Turbid waters with high amounts of suspended sediments (SS) are related to reduction of primary productivity due to decrease in light penetration (Sherriff, *et al.*, 2015). According to Pronk *et al.* (2006) TOC and turbidity values can be used as contamination indicators for the bacteria E. coli, since microbial pathogen and similar contaminants cannot be monitored frequently.

Table 2. *Classification of turbidity in streams according to the Swedish EPA (Naturvårdsverket, 1999)*

Classification	**Range (NTU)**
Not turbid	< 0.5
Weakly turbid	0.5 - 1.0
Moderately turbid	1.0 - 2.5
Significantly turbid	2.5 - 7.0
Highly turbid	> 7.0

Methods

Catchment description

This work has been carried out in two catchments in Sweden, Långtora near Uppsala (C6) and Hestad near Norrköping (E23) (Figure 2). These catchments are part of the Swedish Monitoring Programme, which comprises 21 agricultural catchments monitored for the last 20-30 years (Kyllmar *et al.*, 2014).

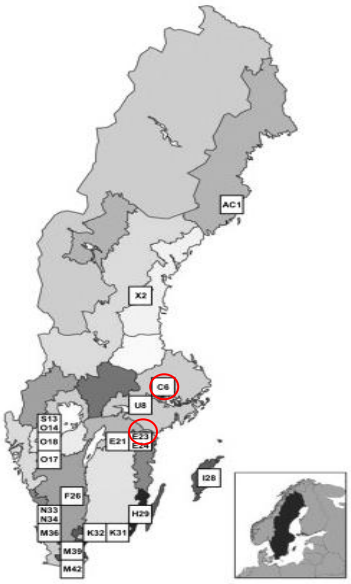

Figure 2. Location of the two catchments studied in this work, marked by the red circles. Adapted from Kyllmar *et al.* (2014).

The main experimental part of the work, deployment of the optical sensor was conducted in C6 with the intention to test the feasibility of optical measurements in similar agricultural catchments i.e. catchment E23, with clay soils and similar land use. Both catchments are similar in terms of temperature, precipitation, soil texture and agricultural production but C6 is three times larger than E23 (Table 3). Both catchments have modernized drainage system that reduces the risk of diffuse pollution and improves the soil properties. One of the objectives of this work is to

see if the optical sensor can accurately measure water quality in the catchment C6. Positive results would suggest that we could also successfully use optical sensors in r other catchments with similar characteristics, like in E23.

Table 3. *Agricultural catchments characteristics (adapted from Kyllmar et al., 2014)*

	Catchment	
	C6	**E23**
Temperature (°C)	5.5	6.3
Precipitation (mm)	623	587
Area (ha)	33.1	7.4
Soil Texture	clay loam	clay
Arable Land (%)	59	54
Pasture (%)	2	8
Drained area (%)	95	80
Production	cereals	cereals, grass
Livestock density (AUha-1)	<0.1	0.6

The historical data from both catchments were examined and compared to see the differences in concentrations of sediment, phosphorus (total and dissolved P) and flow conditions (Table 4). The mean flow discharge in C6 (1994- 2016) is considerably higher than in E23, corresponding to 238,43 l s^{-1} and 45,13 l s^{-1} respectively. This can be explained by different areas between the two catchments. Despite E23 being smaller and with lower flow discharge, the average P concentration are much higher than in C6, corresponding to 0,29 mg l^{-1} and 0.12 mg l^{-1} respectively. Suspended material concentration is also higher in E23 with an average of 74,79 mg l^{-1} and in C6 58,17 mg l^{-1}.

Table 4. *Statistical analysis of data for catchment C6 and E23 from 1994 to 2016*

Catchment C6			
	N	**Mean**	**S.D.**
Flow (l s^{-1})	8036	238,43	536,04
Suspended Material (mg l^{-1})	737	58,17	89,87
Total P (mg l^{-1})	737	0,12	0,09
Orthophosphate (mg l^{-1})	814	0,04	0,03
Catchment E23			
	N	**Mean**	**S.D.**
Flow (l s^{-1})	8769	45,13	96,76
Suspended Material (mg l^{-1})	664	74,79	83,62
Total P (mg l^{-1})	665	0,29	0,19
Orthophosphate (mg l^{-1})	665	0,15	0,13

Laboratory measurements

Optical measurements are prone to errors when conducted in streams with high suspended sediments content (Downing *et al.*, 2012). Therefore, to evaluate the accuracy of measurements with optical sensors in agricultural streams draining clay catchments with high sediment and phosphorus content, a field experiment was conducted in the outlet of C6. Both the sensor and the autosampler inlet were fixed at the same position in the main stream channel, approximately at ¾ of the stream depth. The experiment was run for one week between 23rd and 30th May 2017. Water samples were collected hourly using ISCO® autosampler (model 2700) and retrieved daily. The samples were transported to the laboratory each day, filtered through 0.45µm (F-45) Sarstedt Filtropur filter and stored in a dark room with a temperature of 4°C for 6 weeks. For each sample, we measured the following:

- Fluorescence: using Aqualog® spectrophotometer in a range absorbance at 240-600 nm and emission at 211-620 nm with 1 s integration time and 2 nm scan width. A high precision sealed quartz cuvette containing distilled water with a light path of 10x10 mm was used to measure the Raman intensity, and used as a reference (blank). This was done to verify the wavelength calibration of the emission detector.
- Absorbance: in addition to absorbance measured with Aqualog, absorbance was also measured with AvaSoft (Avaspec-3648) spectrophotometer at 180-800 nm wavelengths.
- Turbidity: was measured optically using Hach Lange 2100AN turbidimeter, in nephelometric turbidity units (NTU). Standards of 7500, 4000, 1000, 200, 50, 0 NTU were runned first for calibration. To measure turbidity, 40 ml of the water sample was poured into measurement vial and the turbidity recorded. The same 40 ml water sample used to measure turbidity was poured into clean TOC vial for TOC analysis.
- TOC: analyzed using Shimadzu TOC-Vcph analyzer. The unfiltered samples were used to measure TOC and filtered to measure DOC, assuming that when filtering the samples, only the dissolved carbon was present. 100 mg l^{-1} solutions of Phtalate and Ethylenediaminetetraacetic acid (EDTA) standards with were prepared. The samples were acidified with 200 µl of HCl to measure TOC. For each sample, triplicate measurements were performed.
- Orthophosphate**:** using a Hach Lange Dr2800 UV/Vis spectrophotometer at 880 nm. 5 ml of water samples was poured into plastic vials, added 1 ml of color reagent (Sulfuric Acid 2.5M + Ammonium molybdate + Antimony potassium tartrate (Ksb) + Ascorbic acid), and measured after 15 minutes. Blank distilled water was measured first at 880 nm followed by the samples.

Field measurements in C6

An optical sensor, C3 Submersible Fluorometer from TurnerDesigns was placed in the stream collecting data every 15 minutes during the field experiment in May 2017. This sensor measured: turbidity, CDOM, tryptophan-like fluorescence and water temperature. The experiment was conducted in C6 with the goal of testing the usefulness of optical sensors for agricultural streams with high sediment content. The sensor data was compared with laboratory data (see section 3.2 Laboratory measurements) to evaluate its performance.

Sensor Calibration

Stock solution was prepared with tryptophan (TRY) for the calibration of the sensor. The stock solution was prepared with 0,001 g of TRY dissolved in 1000 ml Milli-Q ultra-pure water (1 ppm). Standard solutions for TRY were prepared by diluting stock solution into 1000 ml distillated (DI) water as in Table 5.

Table 5. *Tryptophan standard solutions for sensor calibration*

Tryptophan standard solutions		
Stock solution (ml)	**DI water (ml)**	**(ppb)**
0,01	1000	10
0,05	1000	50
0,2	1000	200
0,5	1000	500
1	1000	1000

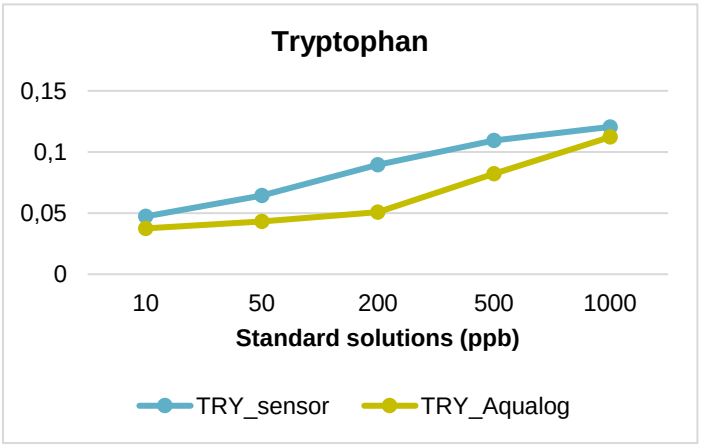

Figure 3. Sensor calibration for tryptophan (blue line). The x-axis corresponds to the standard concentrations having 10, 50, 200, 500 and 1000 ppb. The y-axis corresponds to the ppb concentrations detected by the sensor. The orange line shows the results for the same concentrations in Aqualog.

Table 6. *Sensor and Aqualog readings for Tryptophan*

Standard solution (ppb)	TRY_sensor (ppb)	TRY_Aqualog
10	0,047	0,038
50	0,064	0,043
200	0,090	0,051
500	0,109	0,082
1000	0,121	0,112

100 ppm stock solution was prepared using 0,1207 g of quinine sulfate dehydrated (QSD) and dissolved in 1000 ml Milli-Q ultra-pure water, adding 50 ml of H2SO4 1M. Working standard solutions for quinine sulfate (QS) were prepared by diluting QSD stock solution into 1000 ml distillated water (DI) as in Table 7.

Table 7. *Quinine sulfate standard solutions for sensor calibration*

Quinine sulfate standard solutions		
Stock solution (ml)	**DI water (ml)**	**(ppb)**
0,1	1000	10
0,5	1000	50
2,0	1000	200
5,0	1000	500
10,0	1000	1000
12,5	1000	1250

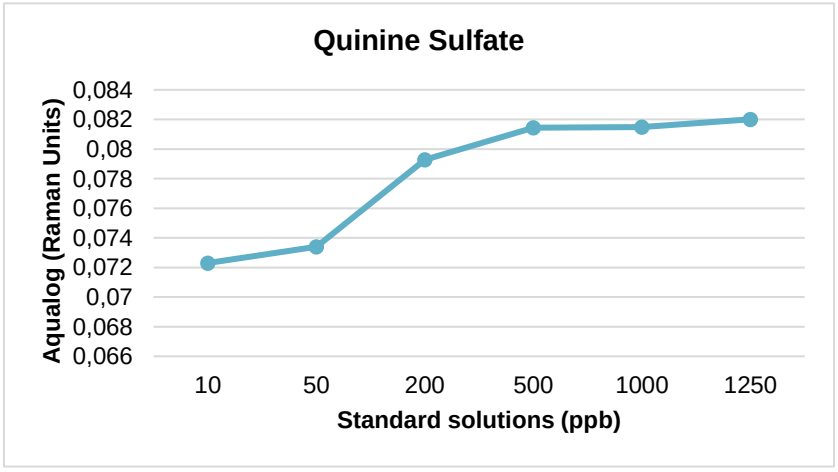

Figure 4. Calibration curve for quinine fluorescence. The x-axis corresponds to the standard concentrations of 10, 50, 200, 500, 1000 and 1250 ppb. The y-axis corresponds to the ppb concentrations detected in Aqualog.

Table 8. *Aqualog readings for quinine sulfate*

Standard solution (ppb)	QS (Raman Units)
10	0,072
50	0,073
200	0,079
500	0,081
1000	0,081
1250	0,082

Calibration for temperature

Since fluorescence is temperature dependent, the sensor results for CDOM and tryptophan-like fluorescence (TRY) were temperature corrected. The data were adjusted to a reference temperature of 20°C using the following formula (Watras *et al.*, 2011):

$$TRY_c = \frac{TRY_m}{[1+\rho(T_m - T_r)]} \quad \text{Eq. 1}$$

$$CDOM_c = \frac{CDOM_m}{[1+\rho(T_m - T_r)]} \quad \text{Eq. 2}$$

Where:
T = Temperature
m = measured values
r = reference values
ρ = Temperature coefficient ($°C^{-1}$) equivalent to -0,0155, used by Watras *et al.*, 2011

Results and discussion

Experiment

Flow, rain and temperature conditions during the experiment

During the experiment the rainfall was observed only during the last two days (Figure 5). Therefore, the flow was stable, with an average for the period of the experiment of 19,4 l s^{-1} (S.D = 6,58). The mean temperature for the week of the experiment was of 15,8 °C (S.D. = 5,48).

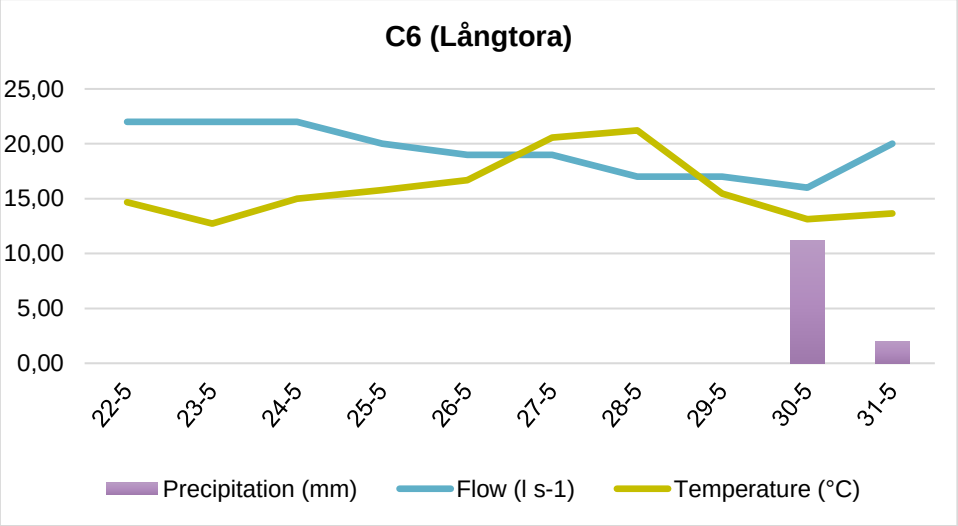

Figure 5. Temperature, precipitation and flow data during the experiments in catchment C6 (Långtora).

Bellow, similarity in terms of a precipitation (Figure 6) and temperature (Figure 7) between the two study catchments during May 2017 is shown. The rainfall amounts are higher in catchment E23 during the days that precede the experiment, becoming more similar during the experiment. The average for this May rainfall was 0,42 mm (S.D = 1,28) in C6 and 0,88 mm (S.D = 1,72) in E23.

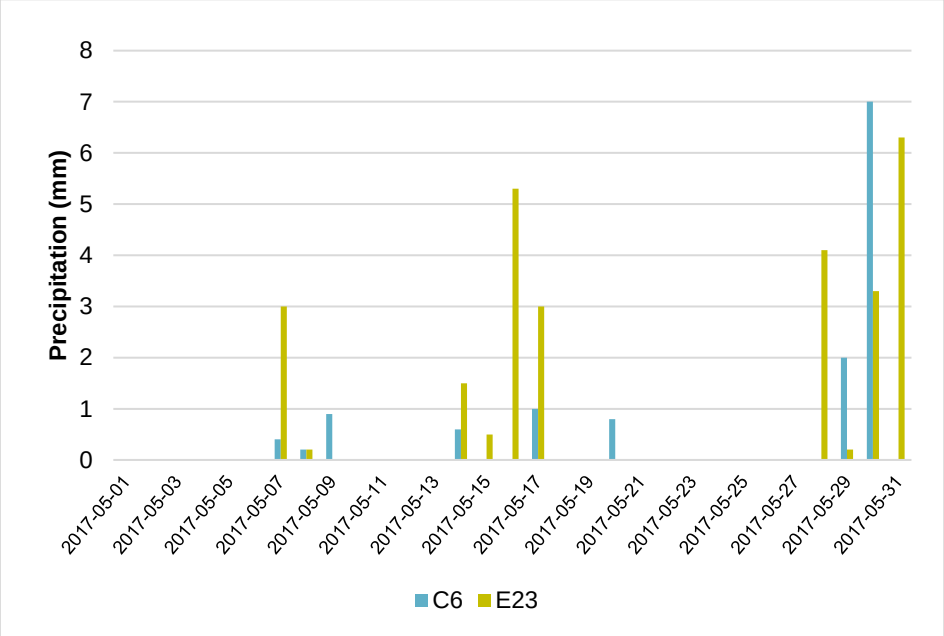

Figure 6. Precipitation for C6 and E23 during May 2017. Antecedent rainfall conditions are important to understand the results of the experiment.

The temperatures were similar in both catchments during May 2017, with an average of 11,00 °C (S.D. = 3,21) in C6 and 12,04 °C (S.D. = 2,58) in E23.

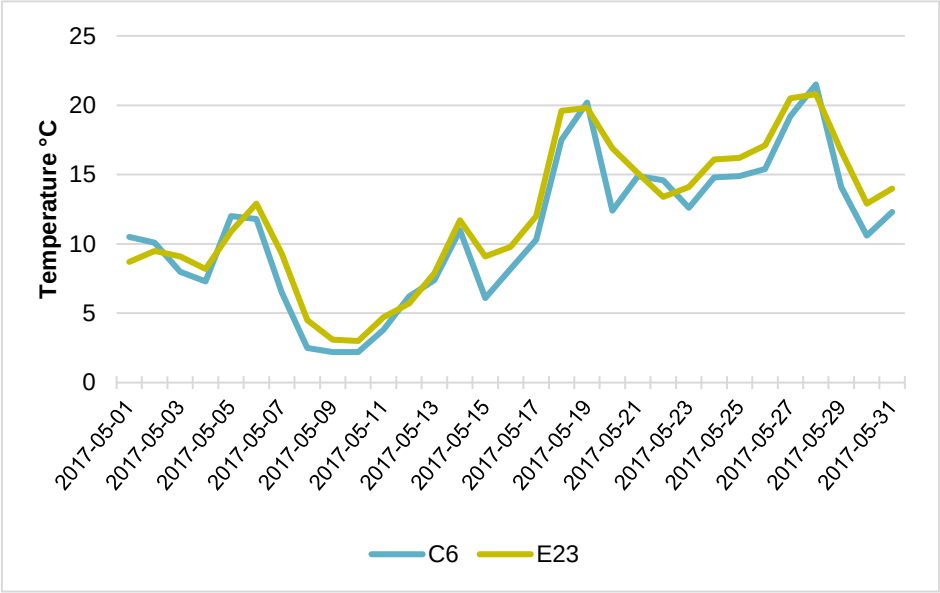

Figure 7. Temperature for C6 and E23 during May 2017. Period that precedes the experiments, to understand if climate may affect physical, chemical and biological process during the experiment.

A summary of all results of the experiment performed at C6 are shown in Table 9. A comparison between the laboratory and sensor results was made to determine if the sensor was able to accurately measure the desired parameters (turbidity, CDOM and tryptophan) in a highly turbid stream. The laboratory results as C intensity (C_int) and T intensity (T_int) (obtained with Aqualog) correspond to CDOM and tryptophan-like, these values will be compared with sensor readings for CDOM and TLF.

Table 9. *Laboratory and sensor measurements from the experiment conducted in catchment C6. C_int corresponds to CDOM and T_int to TLF*

Laboratory data			
Parameter	**N**	**Mean**	**S.D.**
TOC (mg l^{-1})	167	5,73	1,19
DOC (mg l^{-1})	167	6,14	1,09
Fl index	167	1,63	0,03
Fresh index	167	0,74	0,02
Hum index	167	0,88	0,04
C_int (ppb)	167	0,075	2.10^{-4}
T_int (ppb)	167	0,019	4.10^{-6}
Turbidity (NTU)	167	4,8	1,13
Orthophosphate (mg l^{-1})	167	0,016	0,02
Sensor data			
Parameter	**N**	**Mean**	**S.D.**
Temperature (°C)	765	59,57	2,07
CDOM_ (ppb)	765	0,087	0,004
TLF_ (ppb)	765	0,031	0,001
Turbidity (NTU)	765	5,01	1,3

Turbidity measurements

Comparing turbidity results measured with in situ optical sensor and the one measured in laboratory with turbidimeter, we can see similarity in the concentration pattern (Figure 8). The sensor measured every 15 minutes (Figure 9) and autosampler collected samples every hour. Therefore, to be able to compare the turbidity from laboratory and sensor (Figure 8), hourly sensor data was used based on the collection times of the autosampler. Turbidity values from laboratory varied between 2,75 to 8,21 NTU, while turbidity measured by optical sensor varied from 3,11 to 8,49 NTU. This similarity in turbidity between laboratory and field measurements showed that the sensor well captured the turbidity in the stream. Distinctive diurnal pattern was observed in turbidity measurements. The turbidity was high at the dawns, potentially due to flow increase and decrease in evapotranspiration. During the night evapotranspiration decreases and increases during the day

time (Gribovszki *et al*., 2010). During the first days of the experiment the pattern change in turbidity from both laboratory and optical sensor was similar, but a decrease in turbidity from laboratory measurements from the 26th May onwards was detected. Potential reason can be that these samples were analyzed 10 days after collection. Despite having shook each sample before measuring the turbidity, the time which the samples stayed in the storage room can affect the results. Laboratory results showed an average of 4,8 NTU (S.D. = 1,13) and sensor 5,01 NTU (S.D. = 1,3), being classified according to the Swedish EPA as significantly turbid (Table 2) (Naturvårdsverket, 1999).

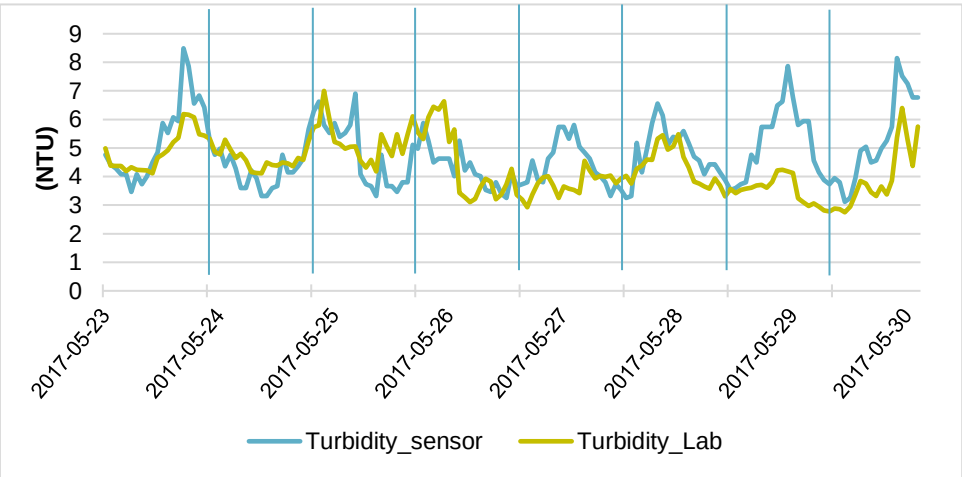

Figure 8. Turbidity results from sensor (blue) and from laboratory (orange) showing similar concentration range and pattern. Vertical lines show samples' retrieval.

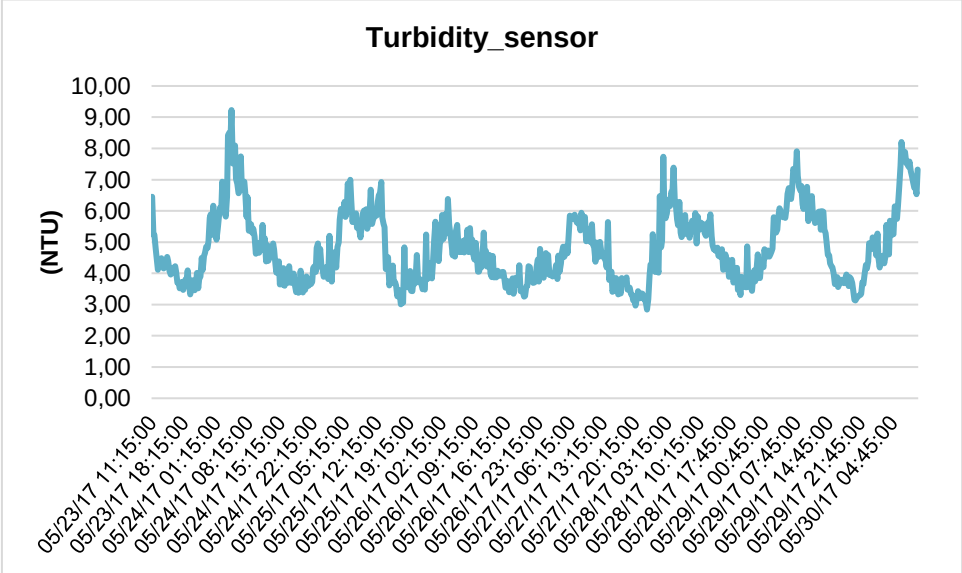

Figure 9. Turbidity measurements with optical sensor every 15 minutes.

Sensor TLF and CDOM measurements

The flow decreased during the experiment and increased in the end of the week due to a rainfall event (Figure 10). Tryptophan-like fluorescence sensor concentrations (Figure 11) decreased between 23/05 and 29/05 and increased again in the end of the experiment. The pattern of changes in TLF concentrations in the stream during the experiment was thus similar to changes in flow, showing that discharge is possibly the main control of TLF dynamics.

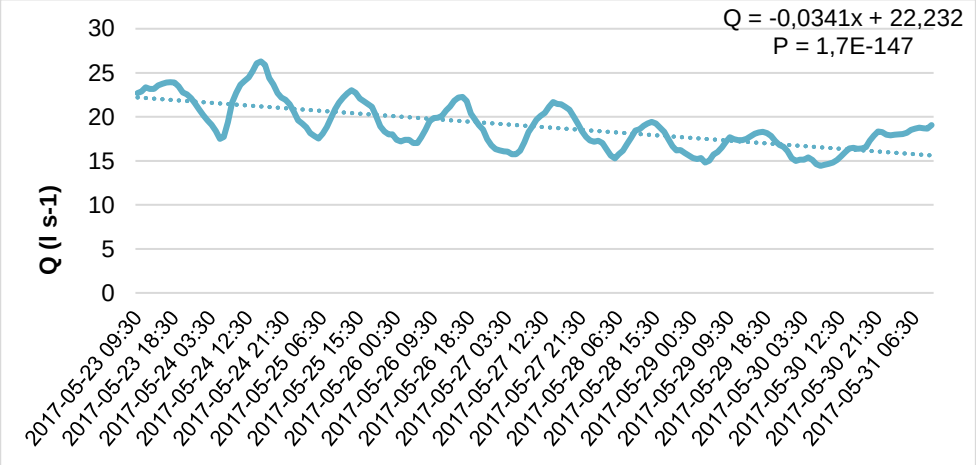

Figure 10. Flow in catchment C6 during the week of the experiment.

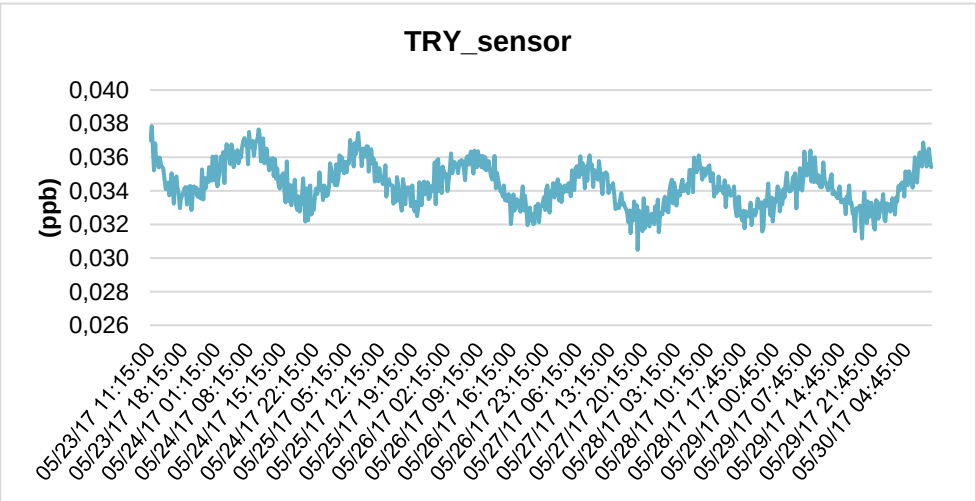

Figure 11. Tryptophan readings from the sensor every 15 minutes.

CDOM readings from optical sensor varied from 0,096 to 0,079 ppb (Figure 12). It was observed that when turbidity was high, CDOM intensity was also high. Peaks in CDOM are prior to peaks in turbidity, but attenuation of CDOM fluorescence intensity could be observed when comparing the peaks in CDOM and turbidity.

CDOM fluorescence attenuation was reported by Downing *et al.*, 2012, in a laboratory study that with a clay loam material having 35 NTU turbidity, 22 % of the signal was lost. Saraceno *et al.*, 2009 reported CDOM attenuation of 8% also for a clay loam material with 50 NTU. This can be explained by the interaction of organic particles with the light beam from the sensor. Some particles absorb more light than they emit.

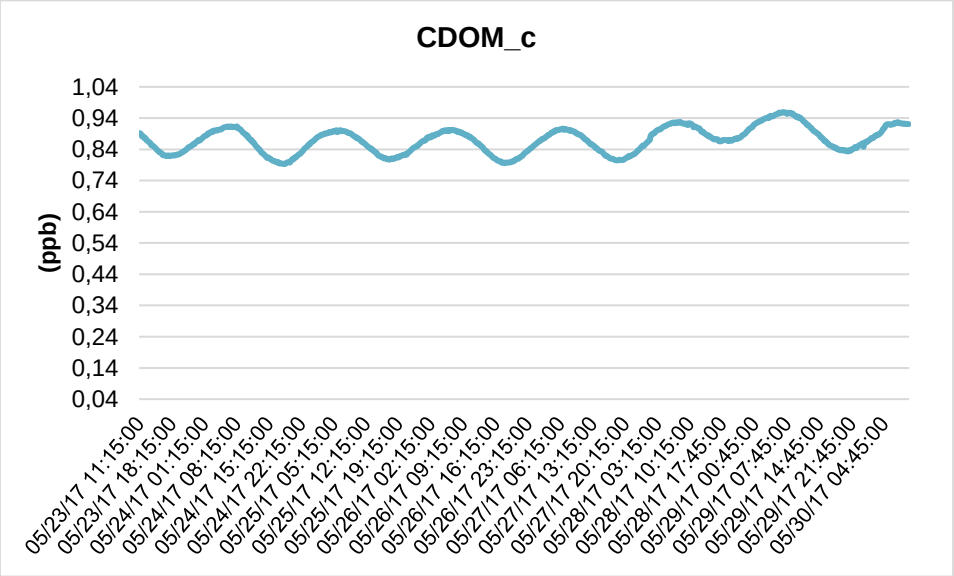

Figure 12. Chromophoric dissolved organic matter (CDOM) results from the optical sensor.

Comparison between laboratory and sensor measurements for TLF and CDOM

Tryptophan results (Figure 13) from the sensor and laboratory (T_int) were very similar. Both signals were stable during the experiment. Sensor readings had an average of 0,031 ppb (S.D. = 0,001) and laboratory 0,019 ppb (S.D. = 4.10^{-6}). To be able to compare laboratory and sensor CDOM and TLF concentrations, hourly sensor data was used according to the same time as the samples were taken by the autosampler.

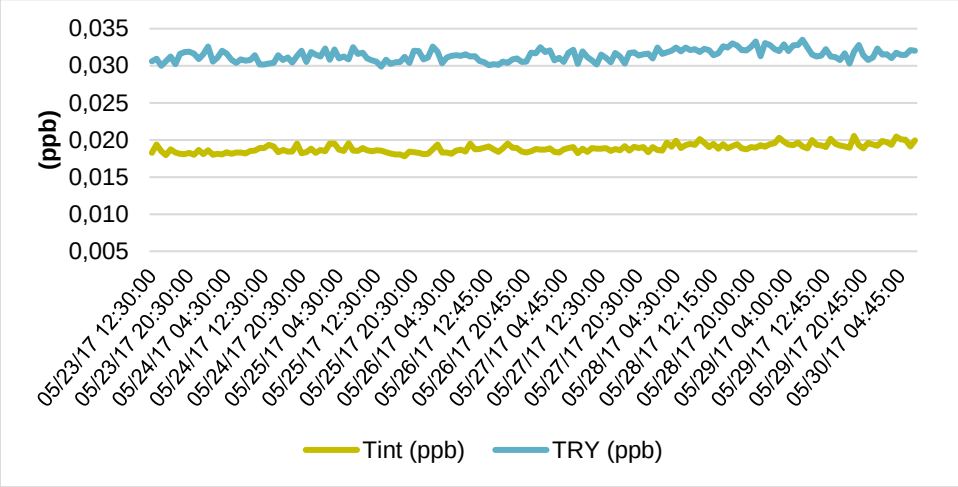

Figure 13. Comparisom between Aqualog and sensor readings for TLF.

The relationship between chromophoric dissolved organic matter results from laboratory (C_int) and sensor (CDOM) is presented in Figure 14. Both parameters had the same fluctuation pattern, but C_int shows an increasing trend during the experiment. CDOM from sensor remained stable in the beginning and increased in the end of the experiment. Laboratory concentrations presented an average of 0,075 ppb (S.D. = 2.10^{-4}) and sensor 0,087 ppb (S.D = 0,004). However, the differences between laboratory and sensor measurements were not significant ($p < 0,05$).

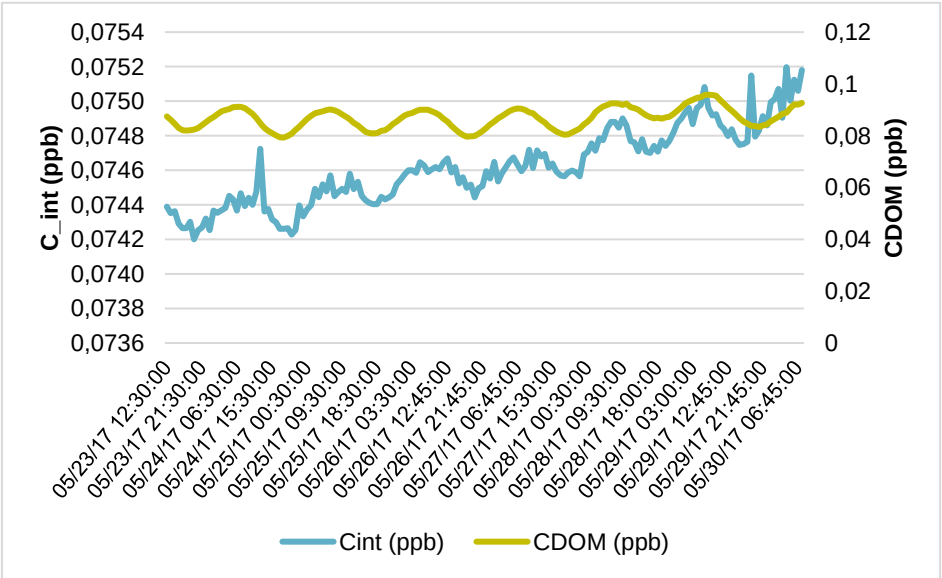

Figure 14. Comparisom between Aqualog and sensor readings for CDOM.

Phosphorus and TOC results

Orthophosphate data showed fluctuations during the week experiment with a minimum value of 0,014 and a maximum of 0,022 mg l^{-1} (Figure 15). Orthophosphate was stable during the experiment, having a mean value of 0,016 mg l^{-1}, but presented an increase in the end of the trial. The pattern of change in this parameter did not reflect changes in flow, but the increase in concentrations in the end of the experiment could be due to increase in flow. This increase in orthophosphate due to increase in flow is possibly related to phosphorus delivery to the stream from diffuse agricultural sources.

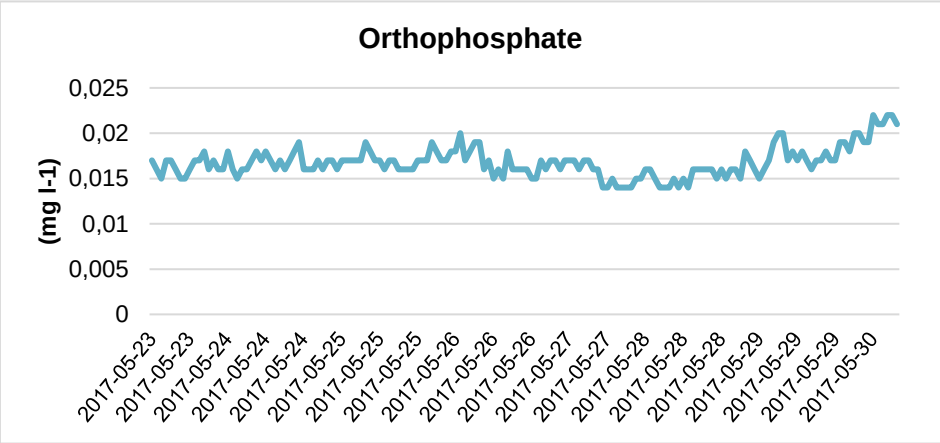

Figure 15. Orthophosphate concentrations in the stream based on autosamples analysed in the laboratory.

TOC concentrations varied between 4,65 to 7,2 mg l^{-1}, having a mean value of 5,73 mg l^{-1} (Figure 16). In the first three days of the experiment, fluctuations in TOC concentrations followed the same pattern as the streamflow. This pattern changed in the last days of the experiment, which could be related with the longer storage time of samples prior to analyses.

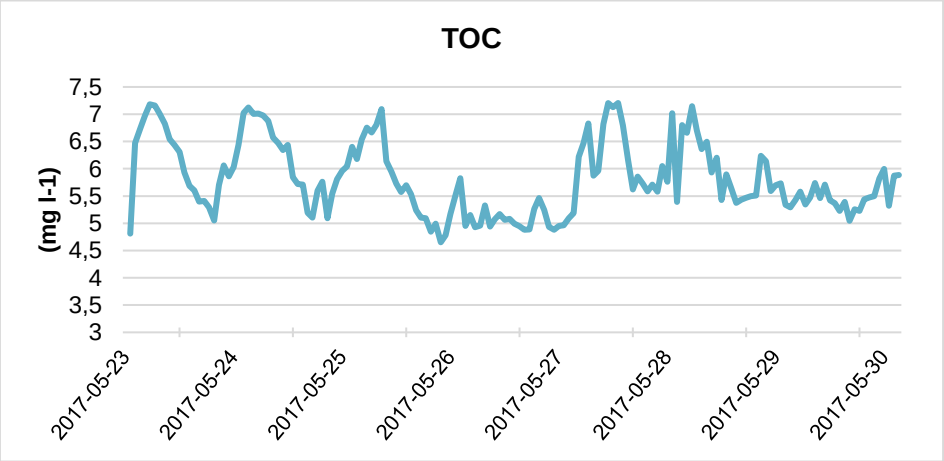

Figure 16. TOC concentrations in the stream during the week of experiment.

Organic matter fluorescence measured with Aqualog

To better understand the composition of the sediment material in C6, the following spectroscopic indices based on data from Aqualog have been calculated from the fluorescence data: humification index, fluorescence index, freshness index and spectral slope. According to Baker (1998) C_int provides useful information about the overlying soil type and degree of humification. We can see that both C_int and humification index (Figure 17) were increasing during the week of experiment indicating increase in humic substances in stream water (Zsolnay, 2002). Humification index is used to identify the compounds with higher molecular weight (large aromatic compounds) compatible with humic material (Gabor *et al.*, 2014). Humification is the process in which low molecular weight compounds are transformed to higher molecular weight compounds (Wickland *et al.*, 2007).

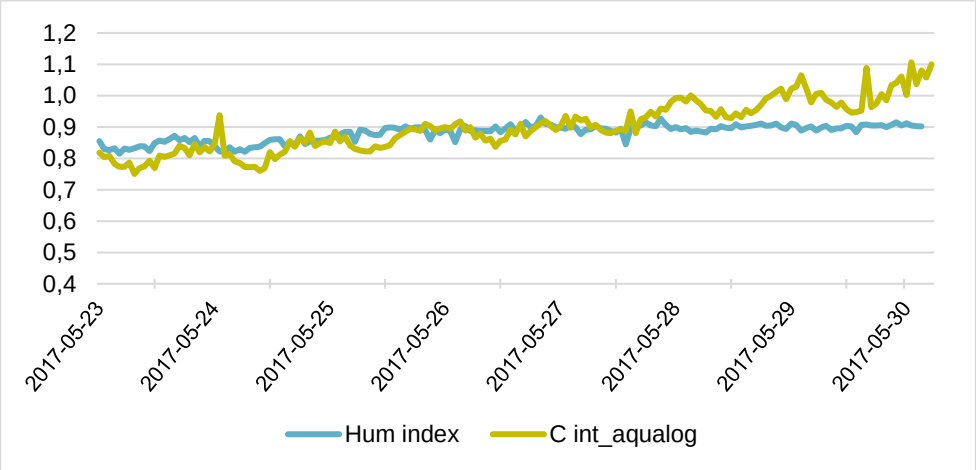

Figure 17. Humidification index, C and T intensity measured with Aqualog.

Fluorescence index (Fl index) is associated with microbial organic matter. The mean Fl index (Figure 18) value during the experiment was 1,7, which shows that the precursor material of DOM at that time was microbial (FI ~1.8) in nature (McKnight *et al.*, 2001).

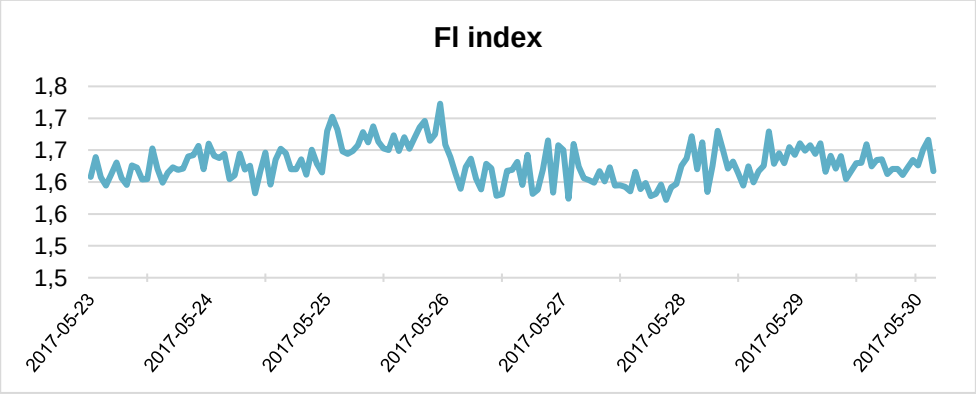

Figure 18. Fluorescence index from Aqualog.

Freshness index (Figure 19) decreased during the experiment, indicating that proportion of newly produced DOM decreased (Parlanti *et al.*, 2000).

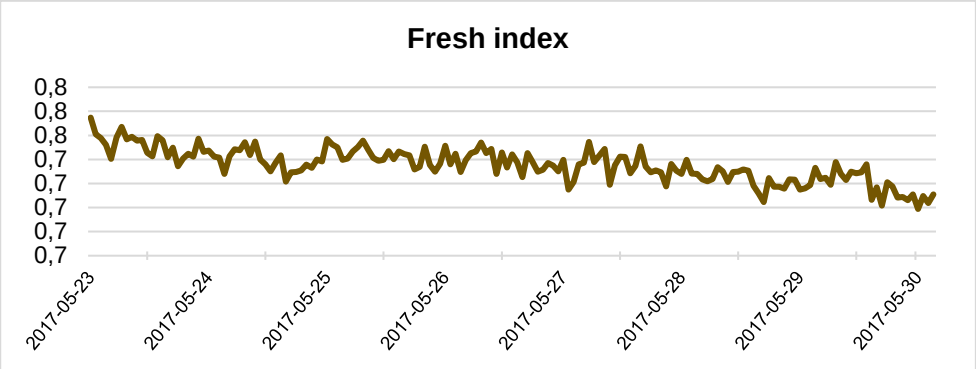

Figure 19. Freshness index readings from Aqualog.

Spectral slope (Figure 20) gives information about the molecular weight and aromaticity of DOM (Helms *et al.*, 2008). Higher slope means a lower molecular weight. Spectral slope is used to measure trends in the relative size of DOM molecules, being a useful tracer of DOM source transformations and humification. During the experiment the spectral slope was quite stable showing that DOM source did not change. If the result had shown the slope increasing, we would affirm that new fresh material was entering the stream (Helms *et al.*, 2008).

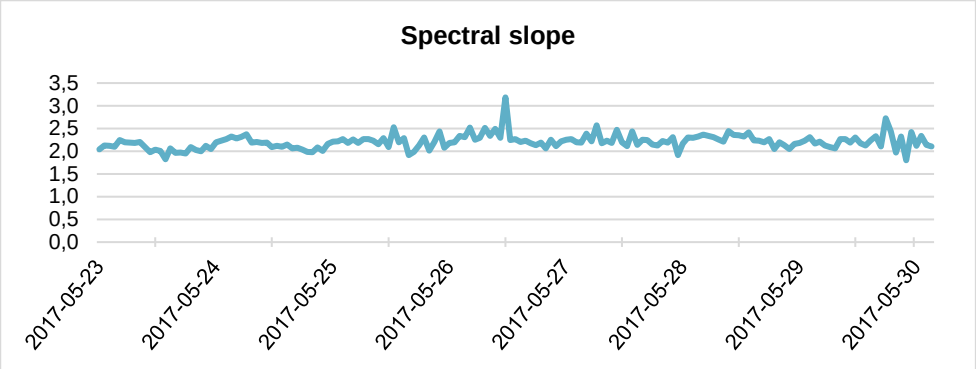

Figure 20. Spectral slope results from Aqualog.

Conclusions and Recommendations

The aim of this work was to test the performance of optical sensors in highly turbid waters. The results from this experiment show that laboratory measurements agreed mostly with sensor readings, which will be discussed hereafter for each parameter analysed.

CDOM: chromophoric dissolved organic matter readings from optical sensor showed similar concentrations and daily fluctuations when compared to the laboratory results, apart from an increasing trend present in laboratory measurements but not in sensor measurements.

Turbidity: outcomes from sensor and laboratory measurements had strong similarity, both in concentration and pattern over time. Readings had lower daily fluctuations after the third day for laboratory measurements. The time in the storage room can affect the natural characteristics of the sample. Sediments get stuck to the bottom of the sample bottle, despite being shaken before measuring.

TLF: tryptophan readings from the sensor also matched with tryptophan measured in laboratory, both in terms of concentration and trend over time. This study has highlighted the potential utility of optical sensors to measure tryptophan-like fluorescence, being a useful tool to monitor surface and ground water quality.

Organic matter: investigated through fluorescence by Aqualog in laboratory, humic substances in stream water increased during the experiment and fresh DOM decreased. The precursor of DOM was found as being microbial and not terrestrial. Trends in DOM size were stable during the experiment, which means that DOM source was the same and new material did not enter the watercourse. No pollution from point sources into the stream during the period of the experiment has been observed.

Phosphorus: laboratory findings showed that orthophosphate (dissolved phosphorus) in the stream was stable and increased in the end of experiment due to increase in discharge.

TOC: concentrations presented similar fluctuation in the first three days as stream flow, but started to differ in the end of the experiment. A possible explanation for this could be because the analysis of the samples from the last 4 days got delayed.

With all the findings we can conclude that optical sensors are able to measure accurately parameters regarding water quality in high turbid waters. Although the results are encouraging, more research is needed to explore the full ability of optical sensors in highly turbid waters. One basic requirement to improve accuracy is to account for conditions that may influence spectral readings, performing the necessary calibration to convert from DOM reflectance into DOM concentrations. Another important procedure is to correct the data for temperature quenching, since temperature is sensitive to fluorophore DOM. Biofouling corrections is another question that need to be considered when using optical sensor. It was not an issue in this study since the experiment was only 1 week, but it can be a problem for longer deployments. For a better laboratory results, if possible, samples should be analysed immediately or within 24 hours. The time in the storage room can affect sample properties, underestimating the concentrations.

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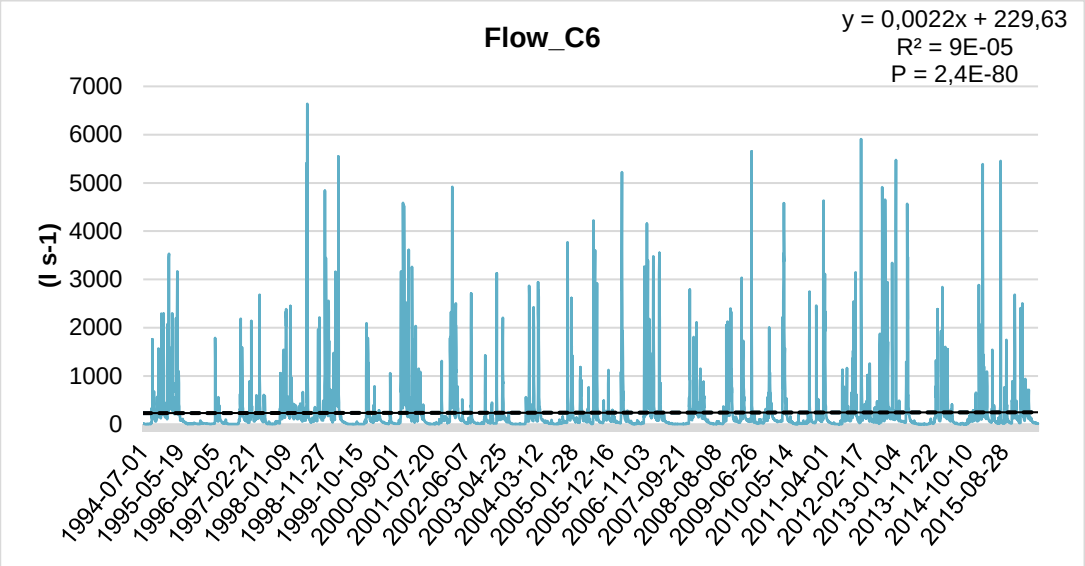
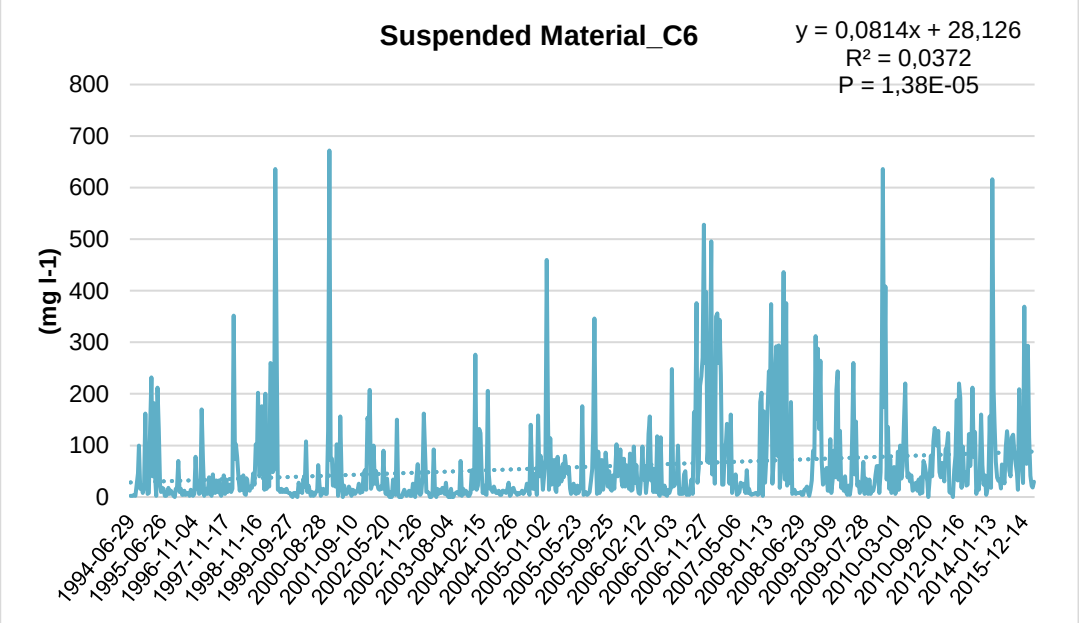
Appendix 1

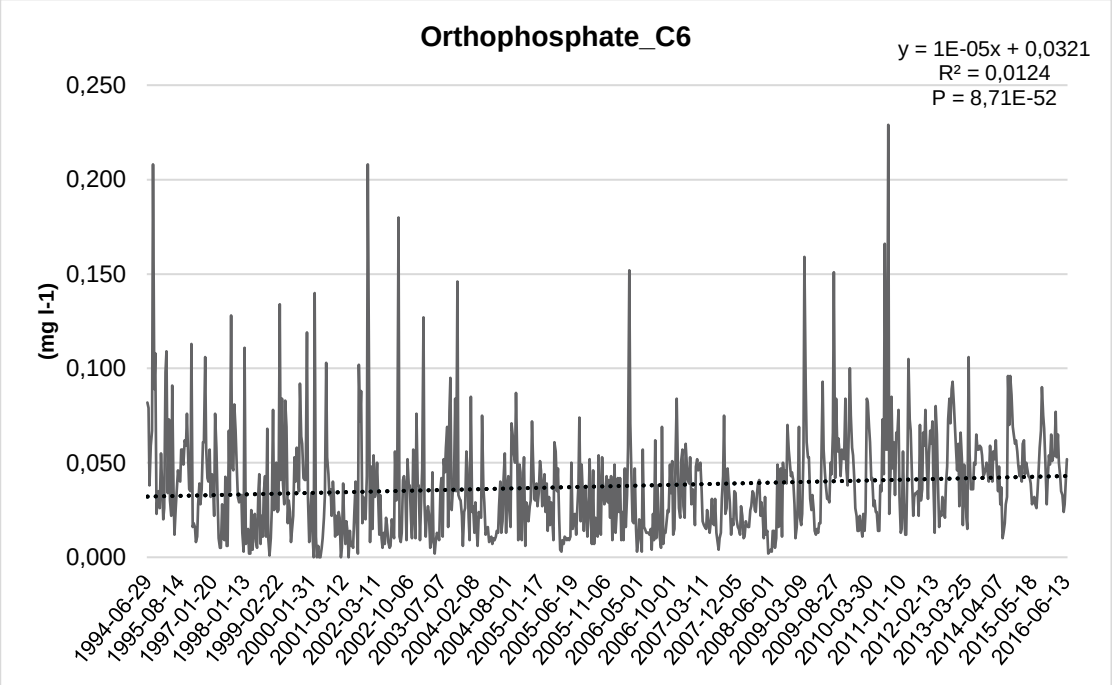
Historical data information for catchment C6 (Långtora):



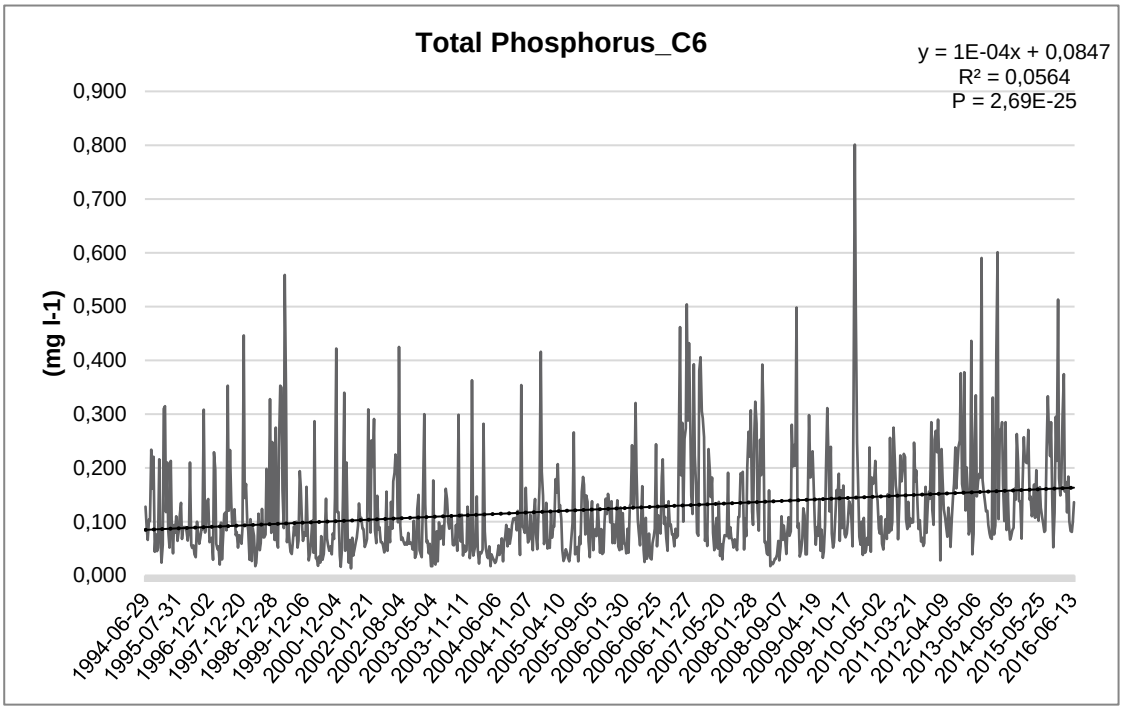
Flow data for Catchment C6 from 1994 to 2016



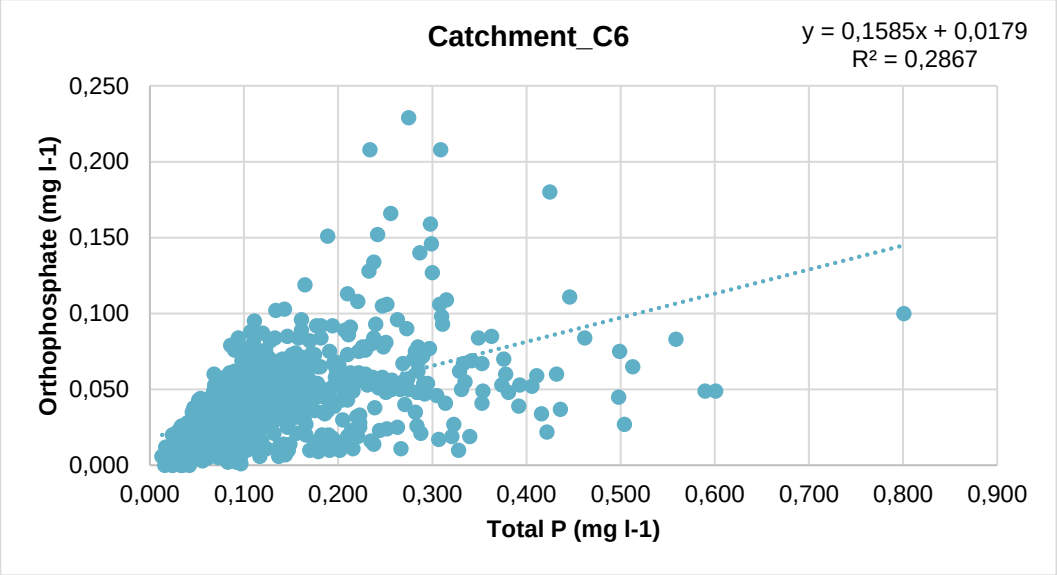
Sediment data for Catchment C6 from 1994 to 2016



Orthophosphate (dissolved P) data for catchment C6 from 1994 to 2016



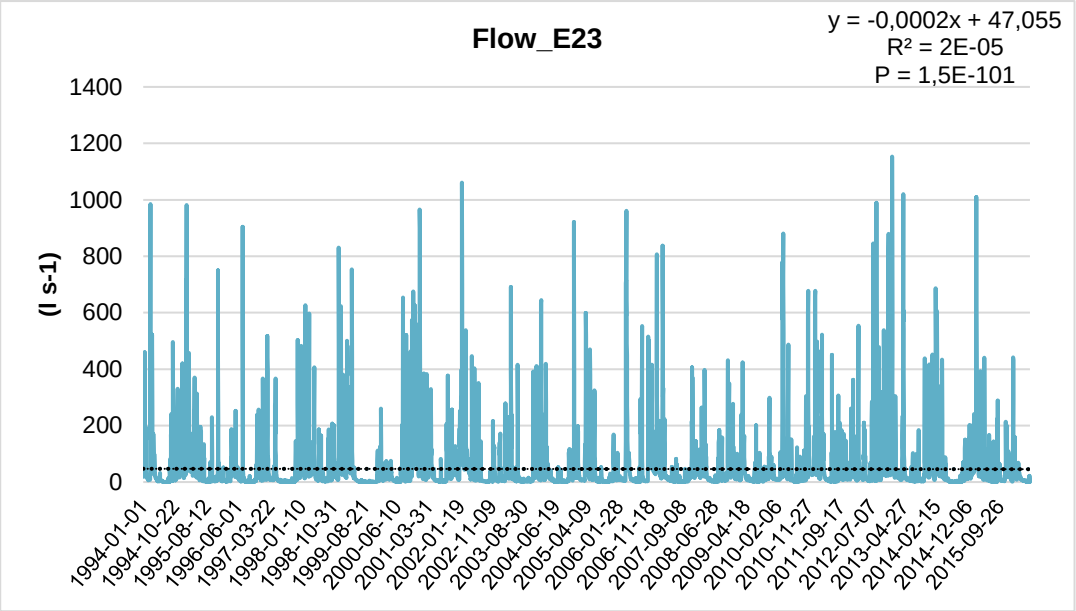
T*otal phosphorus for catchment C6 from 1994 to 2016*



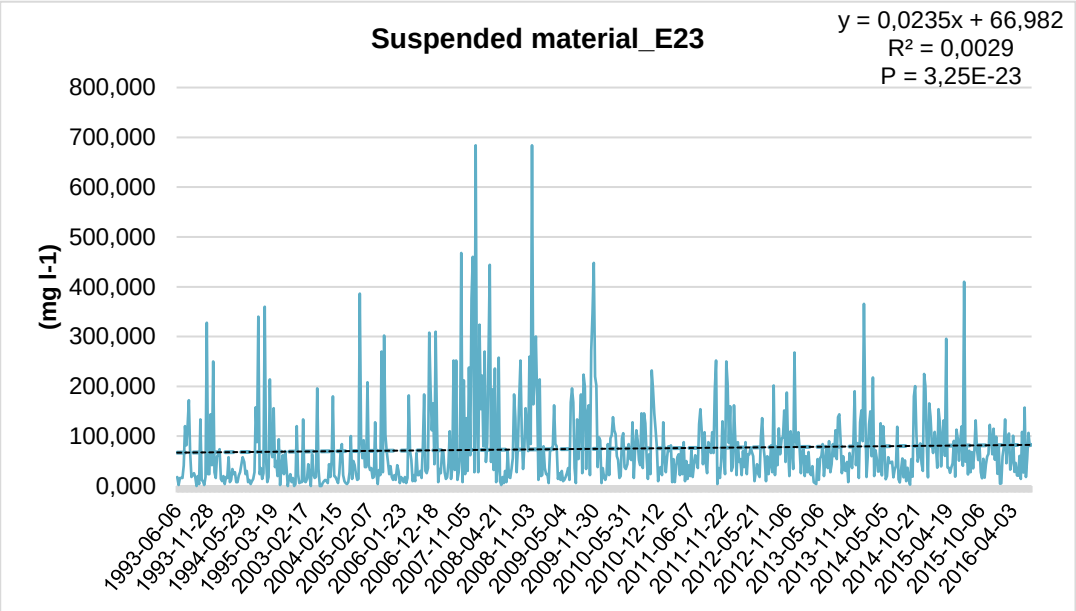
Linear correlation between historical Orthophosphate and total Phosphorus data for catchment C6

Appendix 2

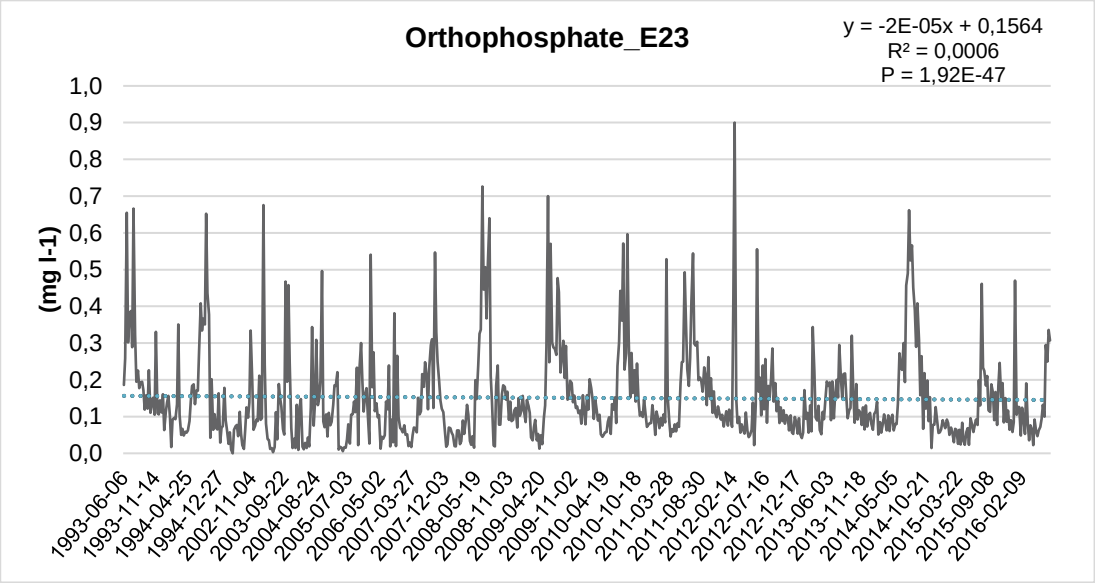
Historical data information for catchment E23 (Norrköping):



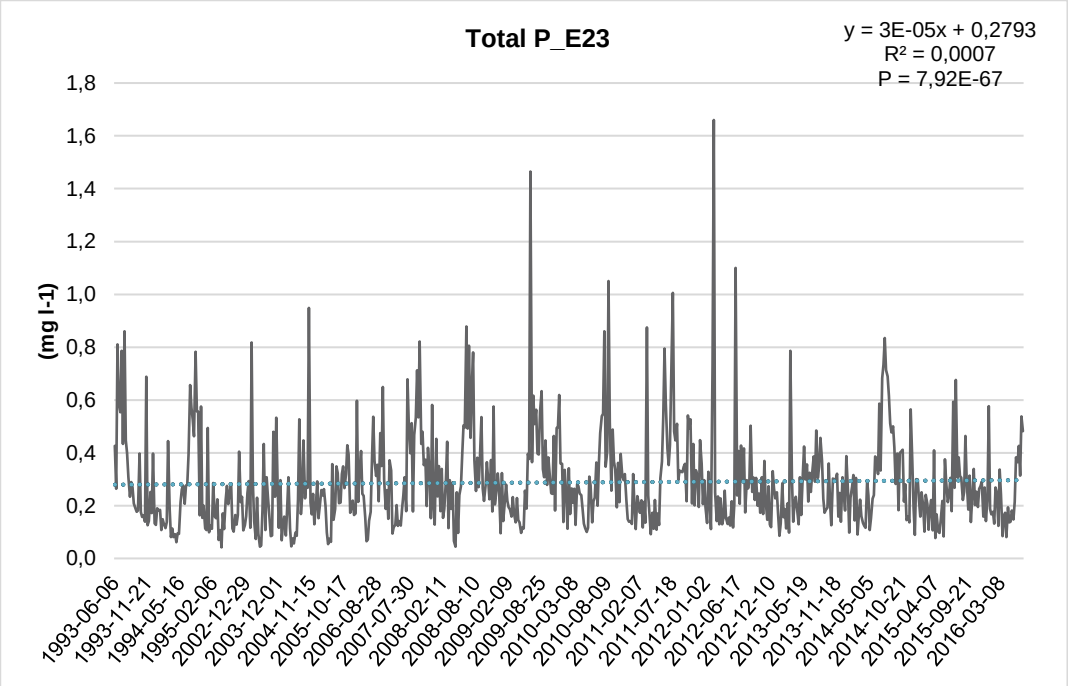
Flow data for catchment E23 from 1994 to 2016



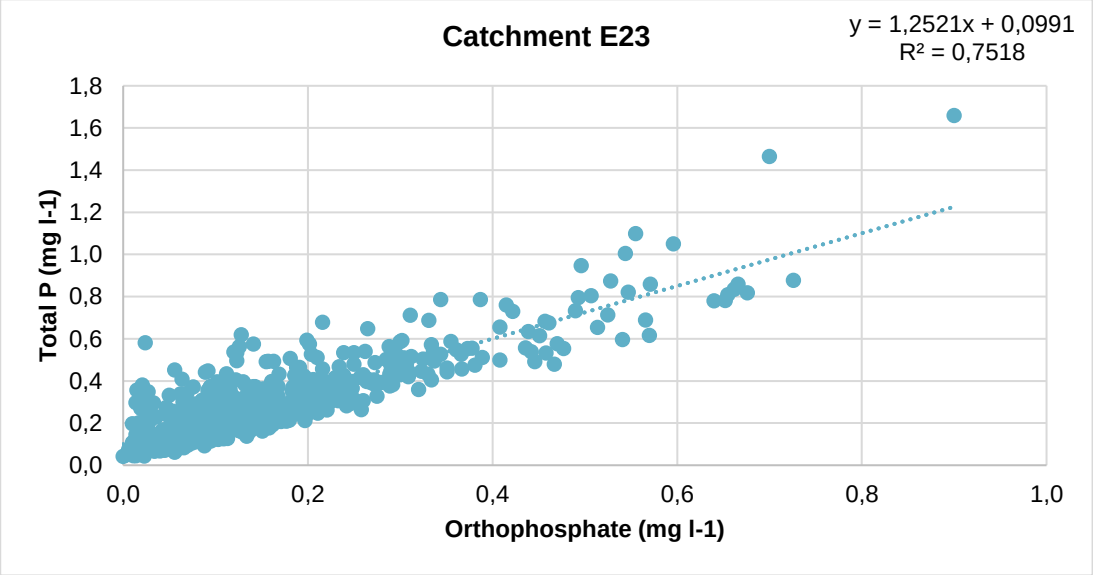
Suspended material data for catchment E23 from 1993 to 2016



Orthophosphate data for catchment E23 from 1993 to 2016



Total phosphorus data for catchment E23 from 1993 to 2016



Linear correlation between historical phosphorus and orthophosphate data for catchment E23