

How robust is water quality determination with optical measurements for highly polluted agricultural waters?

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Abstract

Optical technology is used to measure and monitor water quality, to date mainly in drinking water treatment, where water is typically much cleaner than in heavily polluted agricultural streams. To characterize suspended sediments (SS) and dissolved organic matter (DOM) in surface water some optical measurements have been used (absorbance and fluorescence spectroscopy). This study aims to use laboratory optical instruments (using turbidimeter and fluorescence and absorbance spectrophotometer) to evaluate how different sediment concentrations measured as turbidity affect fluorescence and absorbance determination of the dissolved organic matter. In the study, ten agricultural catchments located in southern Sweden were analyzed. Clay and sandy soils are most dominant in these catchments with predominant intensive crop production and high livestock in some like F26, E23. Turbidity was measured using a nephelometric turbidimeter to measure the absorption and scatter properties of suspended sediments in the water. Higher turbid waters were found in catchments with clay soil textures (C6, M36, O8, E23, and U8) than sandy soils (E21, F26, I28, M36, and N34). Absorbance and excitation wavelength at 240-600 nm and emission wavelengths at 211-260 nm were used to measure SS and DOC in the water samples. A strong correlation was identified between turbidity and absorbance at 240 and 600 nm range than it was with the fluorescence index vs. turbidity. The result showed a variation in fluorescence index (values range from 1.51 to 1.79) among catchments, these indicate where DOM is coming from. DOM in most catchments is delivered from terrestrial sources, only F26 with a value of FI=1.51 DOM might be derived from a microbial source. The results show a variation among agriculture catchments. UV and FI can be used as a substitute to measure turbidity (SS and DOM) but according to results obtained UV correlates well with turbidity than FI. Implying that UV254 can be a better surrogate parameter to estimate the suspended sediment and DOM in water measured as turbidity for both filtered and unfiltered samples. Additionally, it would be useful to use large quantities of water samples to be able to identify the size effect between turbidity and fluorescence correlations.

Keywords:

Popular science summary

Eutrophication of streams, lakes, and marine ecosystems is an ongoing problem globally and in the Baltic Sea region and it results in a deterioration of water quality. Eutrophication is caused by human actions i.e. bad agricultural practices such as the high rates of fertilizer applications. All these activities in addition to soil erosion and runoff contribute to the transportation of sediments and nutrients in the streams, lakes, and marine ecosystems. Then when the aquatic environments are loaded with suspended sediments, dissolved organic matter and other nutrients affect the water bodies in many ways such as reducing the amount of light penetration in the water. Nutrients loads in water lead to high production of organic matter, a reduction in water transparency (turbidity), algae and plant growth, and change in species composition.

Eutrophication is very pronounced in agriculture areas and the consequence is that there is low water clarity in agricultural streams because of the presence of the dissolved organic matter (DOM) and sediments. At that point, it is important to assess how the quality status of water for better management in the agriculture catchments. For this purpose laboratory, optical technology can be used to monitor water quality. Optical instruments are useful to: describe the clarity in surface water, determine the level and the effect of suspended particles, characterize DOM, and determine the pool of organic carbon in natural water.

In this study, the goal was to use laboratory optical instruments to evaluate how different sediment concentrations measured as turbidity affect fluorescence and absorbance determination of the dissolved organic matter. The study was conducted in 10 agricultural catchments located in southern Sweden. The samples were taken from 10 study catchments and analyzed in the laboratory. Unfiltered (UF) and filtered (F45) 900 samples were analyzed for the following properties: turbidity, absorbance, and fluorescence spectroscopy.

A series of spectroscopic (absorbance and fluorescence) indices to characterize the chemical composition and source of DOM were recorded. But for our study, we used two parameters ultraviolet-visible absorbance at 254 nm and the fluorescence index (FI) because they provide useful information on the characteristics of the water quality. Comparisons were made to evaluate the correlation of different sediment concentrations measured as turbidity with fluorescence and absorbance measurements for both unfiltered (UF) and filtered (F45) samples. The result showed that in some catchments ultraviolet-visible absorbance at 254 nm increase with turbidity for both UF and F45 samples. For the fluorescence index against turbidity, most of the catchments have a negative correlation for both unfiltered and filtered samples. No significant correlations were found between the fluorescence index and turbidity. There is a variation in water quality among the different agricultural catchments. Catchments with clay soils have a higher mean value of turbidity compared to the catchments with sand soil texture. UV and FI can be used as a substitute to measure turbidity but according to results obtained UV correlates better with turbidity than FI. Although further validation is needed to confirm the above mention correlation, there is a potential to use FI and UV as a substitute to measure turbidity. The recommendation for better water quality some measures should be taken to reduce soil erosion and the application methods for trapping sediments. For FI to correlate with turbidity large quantities of water samples may be needed to be able to identify the size effect between them. Also, other water quality data like sediment concentration or phosphorus and nitrogen concentration can be used to improve the study.

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Abbreviations

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1. Introduction

High sediment and nutrient loads to the aquatic ecosystem are considered as the cause of the eutrophication and loss of biodiversity which are the key challenges for water quality management in the countries located in the Baltic Sea basin (HELCOM, 2007). The sediments in the water bodies come from surrounding land use (e.g sewage, agriculture, etc.) or seasonal input from the surrounding catchments, for example; the increase of dissolved organic carbon in the water due to the melting snow (Thurman, 2012). Nutrients enrichment in the streams, lakes, and marine environments deteriorate water bodies by changing species composition, increasing turbidity, clogging benthic habitats, and causing a dangerous elevation in algal and plant growth (HELCOM, 2007).

Intensive agricultural practices and soil erosion are responsible for nutrient losses in the catchments. Erosion and sediment load in the aquatic ecosystem have a significant effect on organisms and the quality of water (Bryan, 2000). Surface runoff erodes soil through rill and rain splash erosion, sediments reach into the streams and other receiving waters by the detachment and transport process (Bryan, 2000). Sediments are not transported as a single particle but as flocculate and aggregate particles, thus the material reaches the river in two forms: solid or in solution (Owens *et al.*, 2005).

Water quality is often affected by land use and is determined by the amount of dispersion of suspended solids (organic matter, clay, algae, etc.) it contains. Water clarity is typically low in many agriculture streams and lakes, due to the presence of dissolved organic carbon and a high amount of phytoplankton (Pérez-Fuentetaja *et al.*, 1999).

The aim of this study was to use laboratory optical instruments (turbidimeter and fluorescence and absorbance spectrophotometer) to evaluate how different sediment concentrations measured as turbidity affect fluorescence and absorbance determination of the dissolved organic matter.

2. Literature review

2.1. Importance of turbidity measurements

Suspended sediment concentrations (SSC) or colloidal matter have an impact on the freshwater systems (Schima *et al.*, 2019). To describe the clarity and to determine the level and the effect of suspended particles in freshwater and marine environments turbidity is often used. Turbidity is a measurement of loss of optical transparency of a medium resulting from the presence of suspended solids or other interfering matter in water (Schima *et al.*, 2019; Sinfield & Monwuba, 2014). Ziegler (2002) also defined turbidity as the degree of light scattered by suspended particle size in the water sample. Particle size, the shape and color of suspended sediments (SS), dissolved of organic matter, and dissolved mineral substances may influence turbidity reading (Kitchener *et al.*, 2017; Bilotta & Brazier, 2008; Ankcorn, 2003). Turbidity has been positively correlated with different types of land use and anthropogenic activities (Ryan & research, 1991). In some studies, it was found that increasing SS in the water body is due to natural or anthropogenic perturbations, this can alter its biological, chemical, and physical properties. Therefore some consequences cause the mortality of fish; e.g. the reduction of light penetration, change of temperature, and oxygen reduction in the water (Bilotta & Brazier, 2008). Additional turbidity has a linear relationship with SS and is often used as a surrogate to measure the number of suspended particles in the water body (Bilotta & Brazier, 2008; Downing, 2006). Turbidity has some limitations when used as a surrogate to measure SS; first, it used as a measure of the effects of SS, and the second can answers many factors than SS concentration see Figure 1 (Bilotta & Brazier, 2008).

Figure 1. Diagrams that indicate different components while measuring turbidity (Bilotta & Brazier, 2008)

Turbidity can be quantified in Nephelometric turbidity units (NTU), Foramazin attenuation units (FAU), or Formazin turbidity unity (FTU) depending on the technology or method used. NTU and FTU are specifically used for drinking water assessment while FAU is used for wastewater assessment (Ankcorn, 2003; Ziegler, 2002). There are two basic methods for measuring turbidity; turbidimetry where the degree of transmission of light is determined and nephelometry where the degree of light-scattering is assessed (Kitchener *et al.*, 2017; Rymszewicz *et al.*, 2017; Ziegler, 2002). Different turbidity methods and their characteristics are listed in Table 1. In this study, we used the nephelometry method (USEPA method 180.1) defined as the intensity of light scattered or attenuated at 90[°] angle from the fixed light beam by suspended particles or absorbed in the water column (Saraceno *et al.*, 2017; Ziegler, 2002).

Characteristic	USEPA Method 180.1 (nonratio mode)	ISO Method 7027 (diffuse radiation)	ISO Method 7027 (attenuated radiation)	GLI Method 2
Use of data				
	Drinking water	Drinking water	Wastewater	Drinking water
Range of method	0-40 NTU	0-40 FTU	40-4,000 FAU	0-40 NTU (dilution
	(dilution permitted)	(diluted permitted)		permitted)
Light source	Tungsten Lamp	Photodiode	Photodiode	Photodiode
Wavelength	$400 - 600$ nm.	860 nm	860 nm	860 nm
Spectral bandwidth	Not specified	60 nm	60 nm	60 _{nm}
Detector orientation	$90+/-30$ degrees	$90 + (-2.5$ degrees	$90 +/- 2.5$ degrees	Two sources, two
measurement angle				detectors at $90 +/-$
				2.5 degrees
Aperture angle	Not specified	20-30 degrees	20-30 degrees	unknown
Path length	Less than 10 cm	Less than 10 cm	Less than 10 cm	Less than 10 cm
Primary standard	Formazin polymer	Formazin polymer	Formazin polymer	Formazin polymer
Secondary standards	Polymer	Polymer	Polymer	Polymer
	microspheres	microspheres	microspheres.	microspheres
			cubes, or filaments	

Table 1. Different turbidity methods and units. NTU (Nephelometric turbidity units), FTU (Formazin turbidity units) and FAU (Formazin attenuation units) according toZiegler (2002)

Nephelometry is divided into 3 categories (Figure 2): (1) Side scattering which is measured on 90° angles to the incident beam, (2) back-scattering (referred to as optical back-scattering) has an angle that varies $90^{\circ} < \theta < 180^{\circ}$ and (3) forward scattering has an angle of 0^o $\leq \theta \leq 90^{\circ}$ (Kitchener *et al.*, 2017). In water, suspended particles absorb and scatter light while dissolved compounds absorb the light (Baker, 2005). The concentration of the particles in solution, refractive index, size, shape, and color influence the intensity and direction of light scatter (Sadar, 1999).

Figure 2. Schematic showing the path of light-scattering angle (Kitchener et al., 2017)

2.2. Organic matter in water

Anthropogenic modification of terrestrial ecosystems alters the sources and concentrations of the organic carbon (OC) within streams (Lu *et al.*, 2014). Organic matter in the aquatic and terrestrial environment exists in different forms; colloidal, dissolved, and particulate forms which are complex mixtures of humic substances and other organic compounds (Derrien *et al.*, 2017a; Deb & Shukla, 2011). When measuring the optical properties of samples it's important to distinguish dissolved (filtered), colloidal, and particulate organic matter fractions (Coble, 1996).

In aquatic environments OM controls geochemical processes by acting as pH buffer, proton donor or acceptor, OM affects the transport of pollutants and aids in dissolution and precipitation reactions of minerals (Weishaar *et al.*, 2003). Most present dissolved organic carbon on the molecular are polymeric organic acids known as humic substances(Figure 3) and are polyelectrolytes of carboxylic, hydroxyl, phenolic functional groups, their molecular weight varies between 1000 to 2000 and all anions present 5-10% of dissolved humic substances in streams and river (Thurman, 2012).

Structure of tryptophan, tyrosine, phenylalanine

Theoretical humic acid Stevenson, (1982) cited in Aitken et al., (1985)

Theoretical fulvic acid Buffle, (1977) cited in Aitken et al., (1985)

Figure 3. Aquatic fluorophores: three amino acids (tryptophan, tyrosine, and phenylalanine) structures, humic acid and fulvic acids structures (Hudson et al., 2007)

Amount of dissolved organic carbon varies depending on the type of water; rivers and lakes contain more DOC that typically ranges from 2 to 10 mg $1⁻¹$ and the lowest value of DOC is founded in seawater of an average of $0.5 \text{ mg } l^{-1}$ and last 10 to 60 mg/L concentration of DOC for swamps, marshes, and bogs (Thurman, 2012). Carbon, energy, and nutrients budget are represented in the aquatic ecosystem as a dissolved organic matter (DOM) that can be defined as a portion of organic material that can pass a pore size less than 0.7 μm filter. Dissolved organic compounds have

a molecular weight that ranges from 100 to 100,000 Dalton (Da) and has a role of mediating the availability of dissolved metals and nutrients as well as modifying the optical properties of water bodies in aquatic food webs (Findley, 2003).

2.2.1. Dissolved organic matter

Dissolved organic matter (DOM) is among the form of organic matter in the complex mixture of aromatic (DOM from terrestrial and plant sources) and aliphatic hydrocarbon (DOM from marine and aquatic sources) and plays an essential role in the aquatic ecosystem (Schima *et al.*, 2019; Fellman *et al.*, 2010). It is composed of all dissolved organic compounds in water and has a significant role in the control of light attenuation, biological activity, nutrient availability, and buffering capacity (Schima *et al.*, 2019; Chen *et al.*, 2010; Maie *et al.*, 2005). However DOM may be present in different forms: natural or anthropogenic (e.g. manure), autochthonous (e.g. plankton, macrophytes, dead bacteria, and animal bodies) or allochthonous (e.g. soil organic matter and plant litter) and ecosystem limited or limiting (Zhang *et al.*, 2020; Lozovik *et al.*, 2007; Baker, 2005). Among important DOM constituents, there is colloidal organic matter (COM), described as natural organic matter and its particle size ranges from 1 nm-0.2μm. COM is an important part of DOM and has shown that it makes up a significant amount of up to 73% of organic carbon in aquatic systems (Stolpe *et al.*, 2010).

Colloids are large aggregates of humic acids (Thurman, 2012) produced from natural processes like disturbance and bacterial activity or anthropogenic activities like wastewater treatment plants (Yan *et al.*, 2016)and they are correlated to clay minerals or oxides of iron and aluminum (Thurman, 2012). Higher quantities of COM are founded in shallow lakes, rivers, and estuaries due to the high loading of OM from surrounding environmental (Ren *et al.*, 2010). DOM fractions include chromophoric that only absorbs light and fluorophoric which absorbs and emit light (Gabor *et al.*, 2014).

Chromophoric DOM or colored dissolved organic matter (CDOM) is the fraction of total DOM that absorbs visible and ultraviolet light exponentially (Helms *et al.*, 2008; Kirk, 1994) passes through a submicron filter of 0.2 μm to 0.4 μm (Nelson & Siegel, 2013). Also, CDOM is known as gelbstoff, gilvin and yellow substance, chromophoric dissolved organic matter also absorbs light in the UV-A (wavelength range from 315 to 450 nm) and UV-B (wavelength range from 280 to 215 nm) in the open ocean (Coble, 2007; Del Vecchio *et al.*, 2004). Oceanic CDOM comes from terrestrial runoff and aquatic plant matter, it can be used as a tracer of terrestrial DOC (Mopper & Kieber, 2002; Stedmon *et al.*, 2000). Chromophoric DOM plays important roles in cover biota harmful UV radiation, biogeochemical

and photochemical process (Mopper & Schultz, 1993) and mostly responsible for the optical properties in marine waters (Helms *et al.*, 2008). Chromophoric DOM is usually assessed by its optical properties; absorption or fluorescence properties (Mopper & Kieber, 2002).

2.3. Measurement of optical properties

Different optical measurements have been used to study and characterize DOM; namely fluorescence and absorbance spectroscopy. Dissolved organic carbon measurement is the most and simple measurement in organic geochemistry because this measurement determines the pool of organic carbon in natural water (Mopper & Kieber, 2002).

To characterize OM sources different optical properties of fluorescence DOM and chromophoric DOM can be used (Blough *et al.*, 1993). Chromophoric DOM or colored dissolved organic matter is an important parameter for anticipating the concentration of DOM in the water column (Ferrari *et al.*, 1998). Absorption of CDOM is stronger in the ultraviolet region and reduces to near zero in the red region (Stedmon *et al.*, 2000).

2.3.1. Do you Absorbance spectroscopy

The concentration of natural organic matter (NOM) in water absorbs light over a wide range of wavelengths. The structures that absorb light are referred to as chromophores which are associated with the humic fraction of the NOM (Coble, 2007). The absorbance of UV-visible of CDOM for marine and terrestrial increases exponentially toward shorter wavelengths, with no detectable peaks (Helms *et al.*, 2008). To identify the concentration of the CDOM absorption coefficient on different wavelengths are used for example, like 254, 280, 300, 355, 375, 412, and 443 nm (Coble, 2007; Blough *et al.*, 1993). The absorption degree of CDOM vary seasonally depending on the river input to the near-shore bay waters and inversely to the salinity in the Southern Baltic Sea (Ferrari *et al.*, 1998). CDOM light absorption dominates ultraviolet radiation penetration into the ocean and which has an impact on phytoplankton and bacteria productivity (Mopper & Kieber, 2002).

Studies on composition and concentration of dissolved organic matter in an aquatic system are used for optical properties like fluorescence spectroscopy, specific slope parameter, ultraviolet-visible spectroscopy, and specific UV absorbance (SUVA254)(Helms *et al.*, 2008; Weishaar *et al.*, 2003). Ultraviolet absorbance of light at 254 nm wavelength is used to indicate the presence of carbon content in aquatic ecosystems (Alberts & Takács, 2004) and is typical for the aromatic groups (Korshin *et al.*, 2009).

2.3.2. Florescences spectroscopy

Fluorescence is an easy measurable property of DOM (Coble, 2007) where emission is scanned over a range of wavelengths for known excitation wavelengths (Hudson *et al.*, 2007). Fluorescence spectra are affected by aliphatic structures in DOM through a blue shift (Coble, 1996). On the other hand, fluorescence spectroscopy technique is a method used to study and characterize the light absorption of nature and the source of DOM. Fluorescence is measured in the range of excitation-emission wavelengths using the excitation-emission matrix (EEM) that produces a 3-dimensional dataset. Nowadays fluorescence excitationemission matrix (EEM) spectroscopy is a technique being used to characterizing FDOM in the aquatic system (Hudson *et al.*, 2007; Stedmon *et al.*, 2003; Baker, 2001; Coble, 1996) but it was not in the mid-1990s (Coble, 1996), EEMs have been used to figure out the amount of humification by assessing (quantifying) the amount of shifting of the emission spectra toward longer wavelengths with increasing humification (Derrien *et al.*, 2017b; Krishnarao *et al.*, 2001). In EEMs, excitation, emission, and fluorescence intensity are scanned across a range of wavelengths and plotted on one chart (Figure 4) that shows maps of optical space (Hudson *et al.*, 2007). There is a three-dimensional excitation-emission matrix (EEM) spectroscopy that is used to study fluorescence substances (Mopper & Schultz, 1993; Coble *et al.*, 1990). Excitation emission matrices spectra determined by acquiring emission spectra at a continuously long excitation wavelength and can be used to describe different types of aquatic fluorophores (Kowalczuk *et al.*, 2005). Examples of aquatic fluorophores are shown in figure 3.

Figure 4. Excitation emission matrice of a) Humic acid, b) fulvic acid, c) tryptophan, d) tyrosine adapted in (Hudson et al., 2007)

2.3.3. Fluorescence dissolved Organic matter (FDOM)

Fluorescence dissolved organic matter (FDOM) provides information on the composition and biogeochemical cycling of the organic material. The FDOM is a fraction of CDOM known as the emission after the absorption of UV radiation from organic chromophoric (Del Vecchio *et al.*, 2004; Coble, 1996). Optical properties of fluorescence dissolved organic and chromophoric dissolved organic matter are used for tracing organic matter sources (Coble, 2007) and for distinguishing different classes of organic matter (Senesi, 1990). Fluorescence excitation (Ex) spectra, fluorescence emission (Em) spectra, and three-dimensional excitationemission matrices can be used to identify the spectral characteristic of FDOM. The fluorescence EEM has been introduced as a method to describe different types and sources of naturals waters according to the excitation/emission maxima of fluorescence peaks observed in the soil organic matter, river, and seawater (Coble *et al.*, 1990). In DOM samples fluorescence peaks can be identified with their Ex/Em values and commonly used peaks and their corresponding group of fluorophores are summarized in Table 3 (Coble, 2007). Peak C comes from terrestrial sources and is founded in aquatic ecosystems while peak M dominates in seawater whereas peak T and B can be originated from algal and bacterial activities (Kowalczuk *et al.*, 2003; Coble *et al.*, 1998).

Peak	Excitation (nm)	Emission maximum (nm)	maximum Description of fluorophores	
B	270-280	300-320	Tyrosine –like, protein-like	
T	270-280	330-370	Trytophan-like, protein-like	
A	240-270	380-480	Humic-like	
M	290-320	380-420	Marine Humic-like	
$\mathbf C$	320-360	420-460	Soil fulvic acid	
D	380-400	505-515	Soil fulvic acid	
$\mathbf N$	270-290	360-380	Plankton derived	

Table 2. Fluorescence components and their peak-picking according to Coble et al. (2014)

2.3.4. Spectroscopic indices

A series of spectroscopic (absorbance and fluorescence) indices to characterize the chemical composition and source of DOM are used: (1) Specific ultraviolet absorbance (SUVA $_{254}$) is the absorbance of a water sample at 254 nanometers measured inverse meters (m^{-1}) divided by the DOC concentration in milligram per liter (mg 1^{-1}). SUVA₂₅₄ has been used as a surrogate measurement of DOC aromaticity (Helms *et al.*, 2008; Weishaar *et al.*, 2003) the higher absorbance is the higher aromaticity it is (Dilling & Kaiser, 2002). (2) Humification index (HIX) was calculated by dividing the emission intensity in the 438-480 nm by intensity in the 300-345 nm. HIX is the fluorescence intensity at each wavelength and analyses the amount of humification and tends to increase with a higher degree of humification (Ohno & technology, 2002; Zsolnay *et al.*, 1999). (3) Fluorescence index (FI) is obtained from the ratio of fluorescence intensity at the emission wavelength of 470 nm and 520 nm and an excitation wavelength of 370 nm $(f_{370/520})$ and it has been known as an index differentiating between terrestrial and microbial DOM (Cory *et al.*, 2010; McKnight *et al.*, 2001). (4) Biological index (BIX) is equal to the ratio of fluorescence intensity between wavelengths of 380 nm and 430 nm (emission) and 310 nm excitation (Huguet *et al.*, 2009; Wilson & Xenopoulos, 2009). (5) The absorbance ratio E2:E3 is determined by dividing absorbance at 250 nm to absorbance at 365 nm (Peuravuori & Pihlaja, 1997). (6) And the spectral slope

illustrates a decreasing trend of the absorption with longer wavelengths and be negatively on the same wavelength to the aromaticity and the average molecular weight (Stedmon *et al.*, 2000). For calculating spectral slopes researchers have used a different range of wavelengths values such as 275-295, 290-350, 300-650 nm, etc. (Helms *et al.*, 2008; Blough, 2002; Stedmon *et al.*, 2000). (7) The absorption coefficient is the ratio of absorbance at a specifical wavelength with a concentration unit of organics in the molar unit. In our study, we looked only on absorbance at UV 254 and fluorescence index. To address specific questions about the nature of the organic matter in the ecosystem, for example in lakes and streams (McKnight *et al.*, 2001) and soils and grounds water (Kalbitz *et al.*, 1999), these indices have been applied. Table 4 summarizes the spectroscopic indices and their source. For our study, we used absorbance at 254 nm and the fluorescence index (FIX). FI has been used to differentiate microbial and terrestrial DOM, therefore FI~1.8 indicates that the source of organic is from microbial whereas source from nature or terrestrially has IF~1.2 (Gabor *et al.*, 2014; Cory *et al.*, 2010; Huguet *et al.*, 2009; McKnight *et al.*, 2001).

Name and index	Calculation	Source	References
Absorbance ratio E2: E3	A250 A365	Aromaticity Molecular weight	(Peuravuori & Pihlaja, 1997)
Specifi UV absorbance at 254 nm $\rm SUVA_{254}$	$\frac{\text{A254}}{\text{DOC}} * 100$	Aromaticity	(Weishaar et al., 2003)
Absorption coefficient (Abs220)		Nitrate signal	
Humification index HIX	$(\Sigma I$ em 436 \rightarrow I em 480) $(\Sigma I \text{ em } 436 \rightarrow \text{ em } 480) + (\Sigma I \text{ em } 300 \rightarrow \text{ em } 346)$	Terrigenous Biological/Aquaticbacterial	(Ohno & technology, 2002; Zsolnay et al., 1999)
Fluorescence index FIX	$(I$ em 450) $(I \text{ em } 500)$	Microbial Terrestrial	(McKnight et al., 2001)
Spectral slope	$a(\lambda)=a(\lambda_0) e^{-S(\lambda_0-\lambda)}$	Aromaticity Molecular weight	(Helms) et al., 2008; Twardowski et al., 2004)
Biological index or Freshness index BIX	$(I$ em 380) $\overline{(max I (em 420 \rightarrow em 436))}$	Allochthonous Biological/Aquaticbacterial	(Huguet et al., 2009)
Humic to tryptophan-like fluorescence A:T ratio	λ excitation(200nm) λ emission (400-500nm)	Degree of humic-like vs fresh- like fluorescence Recalcitrant fulvic-like VS fluorescence	
Humic-to fulvic- like fluorescence C:A ratio	λ excitation(300-350nm) λ emission (400-500nm)	Degree of humic-like vs fulvic- like fluorescence	
Humic-to marine- like fluorescence C:M ratio		Degree of blue-shift in the fluorescence	
Humic to tryptophan-like fluorescence C:T ratio	λ excitation(280nm) λ emission (350nm)	Degree of humic-like vs fresh- (Huguet et al., like fluorescence Recalcitrant fulvic-like VS fluorescence	2009)
Tryptophan- to humic-like fluorescence T:C ratio	λ excitation(300-350nm) λ emission (400-500nm)	Manure/human waste origin vs plant origin	

Table 3. Spectroscopic indices for characterizing the sources for organic matter

**aλ: absorption coefficient at the wavelength λ, λ⁰ is a reference wavelength, S: slope coefficient over a given range of wavelength the absorption spectrum exponential decrease.*

3. Material and method

3.1. Study area and sampling sites

The study catchments are located in the main agricultural areas in the south and the center of Sweden. The catchments C6, E21, F26, I28, M36, M42, N34, O18, E23, and U18 used in this study were chosen depending on their high rate of agricultural land and intensive crop production (Table 5). These ten catchments are part of the Swedish National Agriculture Monitoring Programme, which consists of 21 agricultural catchments see Figure 5 (Kyllmar *et al.*, 2006). Among the catchments climatic conditions; temperature and precipitation vary significantly, where the annual precipitation ranges from less than 600 mm year⁻¹ in the east to more than 1000 mm/year in the west and the annual temperature varies between 5.5 º C to 7.8 º C (Kyllmar *et al.*, 2014; Kyllmar *et al.*, 2006). The catchments are dominated by arable land, the soil texture varies from loamy sand to clay (Kitchener *et al.*, 2017; Bilotta & Brazier, 2008; Kyllmar *et al.*, 2006). These catchments are characterized by intensive crop production with high input of fertilizers and high yield which implies high loading and leaching of nutrients (Kyllmar *et al.*, 2014)

Figure 5. Ten of in total 21 catchments were used for the study (C6, UB, O18, E21, E23&E24, I128, F26, N33&N34, M26 and M42). (Stjernman Forsberg et al., 2015)

Catchm ents code	Soil texture	Area (ha)	Arable land (%)	Precipitation (mm)	Temperature $({}^{\circ}c)$	Drained area $(\%)$	Production	Pasture (%)	Livestock density $(au ha-1)$
C6	Clay loam	33.1	59	623	5.5	95	Cereals	$\sqrt{2}$	< 0.1
E21	Sandy loam	16.3	89	506	6.0	95	Cereals	$\mathbf{1}$	$0.2\,$
F26	Loamy sand	$1.8\,$	70	1066	6.2	\blacksquare	Grass	$\ensuremath{\mathfrak{Z}}$	1.3
I28	Sandy loam	4.8	84	587	6.9	99	Cereals, grass, potato	\overline{c}	0.3
M36	Clay, sand loam	7.8	86	719	7.6	88	Cereals, grass, potato	$\,1$	0.3
M42	Sandy loam, loam	8.2	93	709	7.7	100	Cereals	$\boldsymbol{0}$	0.1
N34	Sandy loam, silt loam	13.9	85	886	7.2	93	Cereals, grass, potato	$\overline{2}$	0.3
018	Clay	7.7	92	655	6.1	100	Cereals	$\boldsymbol{0}$	< 0.1
E23	Clay	$7.7\,$	54	594	6.3	\overline{a}	Cereals, grass	8	0.6
U8	Clay	5.7	56	539	5.9	\overline{a}	Cereals, grass	$\overline{2}$	0.2

Table 4. Agricultural catchments characteristics adapted from (Kyllmar et al., 2014)

3.2. Laboratory procedures

Samples were taken from 10 study catchments and stored in a refrigerated room of 8 ◦C in dark. Samples were delivered biweekly throughout the year of 2017 and 2018. Unfiltered and filtered samples were analyzed for the following properties: turbidity, absorbance, and fluorescence. The samples were divided into two parts: one part was used unfiltered (UF) and the other part of the samples was filtered

using a Whatman glass microfiber filter 0.45 μm membrane filter (F45) before further analyses.

Turbidity of both unfiltered and filtered samples was measured using 2100AN turbidimeter, in nephelometric turbidity units(NTU), and calibrated using reference samples (0, 50, 200, 1000, 4000, 7500 NTU). Simultaneous measurement of absorbance and fluorescence for unfiltered (UF) and filtered (F45) were done using Aqualog (Horriba, US) spectrophotometer. A sealed cuvette containing distilled water was used to perform a validation test, to measure water Raman intensity and then used as reference (blank). Absorbance and excitation wavelength at 240-600 nm and emission wavelengths at 211-260 nm were measured with 1s data integration time and 2 nm scanning interval. Also to measure the absorbance AvaSoft (Avaspec-3648) was used at 180-800 nm wavelengths.

3.3. Data analysis

Nine hundred fluorescence data points were collected and modeled using MatLab and Microsoft Excel 2016. Exported Matlab data, turbidity, UV254, and fluorescence index (FI) were compiled together for statistical analysis. For each catchment, a linear regression analysis was used to see the correlation between spectroscopic indices: fluorescence index (FI) and absorbance at 254 nm and with suspended sediments quantified as turbidity. Descriptive statistics were also considered for the dataset and the mean and standard deviation values were reported.

4. Results

The detailed results for all experiments are in Appendix 1. Comparisons were made to evaluate how different sediment concentrations measured as turbidity correlates with fluorescence and absorbance measurements. Correlations of the absorbance at 254 nm (UV254) vs. turbidity and fluorescence index vs. turbidity (NTU) for both unfiltered (UF) and filtered (F45) samples are shown in Figures 6 and 7. Descriptive statistics of all parameters can be found in Table 5 and Appendix 2.

In Table 5 values for mean and standard deviation (SD) are presented for turbidity, ultraviolet absorbance at 254 nm, and fluorescence index. When observing the mean values of turbidity before and after filtration, the values after filtration are lower because the turbidity has been removed by filtration, e.g. mean values for turbidity range from 2.6 to 50.9 NTU and the standard deviation (SD) from 1.5 to 84.5 NTU for UF samples; for F45 samples concentrations are lower: mean values are between 0.82 to 31.04 and SD=0.51 to 68.72 in all catchments. The UV254 have values that range between 0.19-0.64 (UF) and 0.16 to 0.58 (F45). The reported values in Table 4 show that the fluorescence index has a mean that varies from 1.51- 1.71 for UF and 1.51 to 1.69 for F45, standard deviation varies between 0.02 to 0.40 (UF) and 0.03 to 0.06 (F45).

By plotting absorbance spectra (UV254) vs. turbidity (Figure 6), generally, the graphs show a significant positive trend in most of the catchments for both unfiltered (UF) and filtered (F45) samples. The O18 catchment has the highest mean value of turbidity before and after filtration (UF= 50.8 NTU and F45=31.0 NTU) and the lowest value of turbidity is found in F26 and E21 catchments see table 4. The highest average value of UV254 was found in catchment F26 for both UF and F45 (0.64 nm and 0.58 nm) and E21 catchments have a lower value of 0.2 nm for both. UV254 remains constant in E21 catchment for UF samples and slightly increasingly for F45 samples. In catchment M42 the value of UV254 remains constant for both unfiltered and filtered samples but the turbidity is increasing (Figure 6).

When looking at the most graphs (Figure 6) the R^2 is much stronger in samples after filtration than for unfiltered samples, the R^2 ranges between 0.00-0.90 for the unfiltered samples and from 0.00 to 0.97 for filtered samples. Observing catchment M42 the correlation between turbidity and UV254 is relatively poor 0.00, UV254 range from 0.1 to 0.7 nm, and turbidity cluster range from 0 to 30 NTU for UF samples. The distribution in the graph found in the catchment O18 shows a positive

trend and a good correlation of $R^2 = 0.90$ in UF and $R^2 = 0.97$ in F45, where UV254 varies from 0 to 2.5 nm and turbidity between 0 to 400 NTU for UF samples and F45 samples UV254 varies between 0-3 nm and turbidity between 0-300 NTU. The filtered samples show higher slopes than for unfiltered samples, the highest value of the slope is observed in C6 and E23 catchments for F45 samples.

Figure 7 shows data for the fluorescence index against turbidity analyzed for all catchments with most of them having a negative correlation for both unfiltered and filtered samples. For the fluorescence index, the E23 has a higher value ($FI = 1.71$) and the lower value is 1.51 in F26 catchment. The correlation is poorer for filtered samples (R^2 = 0.00 to 0.20) compared to unfiltered samples (R^2 = 0.00 to 0.26). For catchment E21 the correlation between turbidity and fluorescence index is relatively poor $R^2 = 0.0082$ and the fluorescence index range from 1.4 to 1.6 and the turbidity cluster range from 0 to 60 NTU for UF samples. The distribution in the graph found in the catchment C6 shows a negative trend and a good correlation of 0.20 (UF samples) with fluorescence index that varies from 1.45 to 1.80 and turbidity between 0 to 100 NTU for UF samples and F45 samples fluorescence index varies between 1.55-1.85 and turbidity between 0-30 NTU. The linear regression between the fluorescence index and turbidity has an \mathbb{R}^2 of 0.26 for F45 samples in catchment U8.

Figure 6. UV254 vs turbidity concentration for all 10 catchments, the graph shows a positive trend.

Figure 7. Plot illustrating fluorescence index vs turbidity for 10 study catchments, the graph shows a negative trend between turbidity and absorbance.

Turbidity (NTU)								
Catchment code	Mean UF	SD UF	Mean F45	SD F45				
C6	27.1	28.1	6.5	11.6				
E21	10.7	14.0	0.8	0.9				
F26	2.6	1.5	0.8	0.5				
I28	14.7	59.0	1.4	2.3				
M36	37.3	50.5	18.7	38.6				
M42	15.7	21.1	1.3	1.2				
N34	14.0	11.4	2.5	3.9				
O18	50.8	84.4	31.0	68.7				
E23	29.1	32.1	17.2	25.6				
U8	38.7	56.2	16.7	33.1				
	$UV254$ (nm)							
Catchment code	Mean UF	SD UF	Mean F45	SD F45				
C ₆	0.3	0.1	0.3	0.1				
E21	0.2	0.1	0.2	0.1				
F26	0.6	0.3	0.6	0.3				
I28	0.3	0.1	0.2	0.1				
M36	0.5	0.4	0.4	0.4				
M42	0.3	0.1	0.3	0.1				
N34	0.3	0.1	0.3	0.1				
O18	0.5	0.5	0.4	0.6				
E23	0.5	0.2	0.4	0.3				
U ₈	0.5	0.4	0.4	0.3				
	Fluorescence index							
Catchment code	Mean UF	SD UF	Mean F45	SD F45				
C6	1.64	0.1	1.64	0.1				
E21	1.68	0.1	1.69	0.1				
F26	1.51	0.1	1.51	0.1				
I28	1.68	0.0	1.68	0.0				
M36	1.63	0.0	1.64	0.0				
M42	1.60	0.0	1.61	0.0				
N34	1.62	0.0	1.62	0.0				
O18	1.69	0.0	1.69	0.0				
E23	1.71	0.4	1.64	0.0				
U8	1.64	0.1	1.65	0.1				

Table 5. Means and standard deviations (SD) values for all catchment

5. Discussion

5.1. Effects of turbidity on UV254 measurements

Figure 6 illustrates the optical measurement for absorbance spectra (UV254) in nm and corresponding turbidity NTU for 10 catchments. Of all possible correlations of UV254 against turbidity, only M36 and O18 catchments showed a strong statistically significant relationship for both filtered and unfiltered samples with $(R² > 0.80)$. For the filtered and unfiltered samples absorbance increases with turbidity. Some catchments show a linear increase in absorbance with turbidity for both filtered and unfiltered samples e.g. C6, F26, M36, O18, E23, and U8. Increasing ultra-violet absorption at 254 nm among catchments is proportional to the number of sediments in the water samples (Hoorman *et al.*, 2008). Other catchments like I28, show constant UV254 throughout the experiment for UF samples and show a small trend after filtration. The UV254 measurements vary in different water samples with varying degrees of turbidities before and after filtration. Often a reduction of color in the strongly colored samples after filtration is observed, this is due to the adsorption of colloidal or dissolved substances in the filter and thus cause the decrease in turbidity (Karanfil *et al.*, 2005).

As in Figure 6 the absorption increases in all catchments after filtration as well as the turbidity decreases. An exception is catchment F26 where the UV254 for samples after filtration remains constant but the range of turbidity decreased from 0-8 NTU to 0-2 NTU. It appears that there was an appreciable amount of suspended sediment higher than 0.45 μm was retained by the filter. In catchments E21and M42, there is a significant decrease in turbidity between before and after filtration (Figure 6). In all catchments, the effect of turbidity was significant because after filtration the turbidity decrease and UV254 increase, moreover one catchment showed a higher significance effect of turbidity on UV254; catchment I28 where the absorption increases from 0-0.3 nm to a range of 0-0.5 nm after filtration and turbidity decreased. The higher residual turbidities in water samples influence the UV254 measurements reported by Karanfil *et al.* (2005). Some research suggests measuring the turbidity of filtered water is a simple way to assess the role of organic matter on the measurement of UV254 and the characteristic of turbidity e.g. particle size distribution and characteristic of a membrane filter may influence in UV254 measurements (Karanfil *et al.*, 2005). In spectrophotometric measurements, relatively constant attenuation of light through the visible part of the spectrum is caused by suspended particles in natural water. Suspended sediments contribute little to nephelometric turbidity because they cause little scattering (Hongve & Åkesson, 1996). When the particle size is almost equal to the wavelength of the incident light although there arise of maximum scattering of light for a given weight of sediments. Then the degree on which turbidity affects the ultra-violet absorbance at 254 nm might depend on the size and number of SS in the water (Dobbs *et al.*, 1972).

5.2. Effects of turbidity on fluorescence index measurements

The source of DOM can be described using the fluorescence index (Huguet *et al.*, 2009) and FI is often used as a proxy for DOM origin means from allochthonous or autochthonous (McKnight *et al.*, 2001). For this study, we focused on the fluorescence index describing origin from terrestrial and microbial DOM (Cory *et al.*, 2010; McKnight *et al.*, 2001). The different correlations between fluorescence index versus turbidity plot (Figure 7) for all 10 catchments show that there is a pronounced significant negative trend in C6, F26, I28, and U8 catchments and small significance in E21, M36, M36, N34, and E23. In catchment E21, M36 and E23 there is slightly different for UF samples and F45. Interesting in catchments M42 there is a positive trend for UF and a negative trend for F45. While a significant positive trend is shown in catchment O18 for both filtered and unfiltered samples.

The turbidity affects the fluorescence index when observing the graph (Figure 7), the overall variation of FI was constantly decreasing with high turbidity for UF samples and high FI with low turbidity values. According to (McKnight *et al.*, 2001) fluorescence index is a technique being used to characterize the change in FDOM in the aquatic system and analyzing of the fulvic acid source. Higher FI is delivered from microbial precursor whereas low FI is derived from a terrestrial precursor material. Higher turbidity can affect the calculation of the fluorescence index (Karanfil *et al.*, 2005). Low intensities of fluorophores may be resulting in high turbidities that cause light attenuation (Downing *et al.*, 2012).

5.3. Effects of turbidity on optical properties measurements

The turbidity and spectroscopic indices were correlated (Figure 6 and 7). The effect of turbidity on optical measurements is that it differed depending on the concentration of sediments and particles size. Optical measurements tend to have errors when done in streams with high suspended sediment content (Downing *et al.*, 2012).

The mean values of turbidity after filtration were lower because the suspended sediments that were higher in size than 0.45 μm were removed by filtration (Table 4). The O18 catchment had the highest mean value of turbidity before and after filtration (UF= 50.8 NTU and F45=31.0 NTU) this might be the result of soil texture (clay), and high precipitation (655 mm) that contribute to erosion (Table 4). The effect of inner-filter might influence the increase in turbidity in this catchment, caused by sediments and colloids that pass through a 0.45 μm membrane filter and organic carbon present in the dissolved form (Karanfil *et al.*, 2005). Also, higher turbidities indicate a higher level of organic particles and suspended sediments in and around the stream (Lenhart *et al.*, 2010) due to agriculture practices and livestock production. Some studies showed that suspended solid can pass through a filter of 45 μm (Karanfil *et al.*, 2005). The lowest value of turbidity was found in the F26 catchment (2.57 NTU).

The highest average value of UV254 was found in catchment F26 for both UF and F45 (0.64 nm and 0.58 nm) which may indicate that this catchment has more organic carbon-absorbing light at 254 nm than other catchments. Lower ultraviolet absorbance at 254 nm of E21 (UF &F45) varying between lower value reflects that samples from this catchment have few particles that absorb light (Alberts & Takács, 2004). These results could be correlated with soil texture and structure in this catchment reported by Kyllmar *et al.* (2014) also the source of CDOM. CDOM has different absorbtivities depending on the degree of UV (Coble, 2007; Blough *et al.*, 1993).

The variation among catchment could be related to the source of FDOM and its origin which can be determined by the fluorescence index. A higher mean value of FI= 1.7 was found in E21, I28, O18, and E23 catchments which may correspond to the DOM derived from a plant litter and soil. A lower mean value $(FI=1.51)$ is observed in F26 catchments of dissolved organic matter which may result from both microbial and terrestrial sources. Emission intensity at 450-500 nm has a ratio from 1.5 to 1.7 (Table 4) for both microbial and terrestrial samples. The slight change in FI can be related to the age of DOM, from more recently to more decomposed (Parlanti *et al.*, 2000) or interpreted depending on FDOM origin (McKnight *et al.*, 2001). This ratio represents a decline in emission with increasing turbidity and it is referred to as fluorescence index. Many of the DOM in all catchments are delivered from terrestrial sources.

The lower value of the fluorescence index $(FI_{\sim}1.2)$ indicates a low contribution of DOM from the microbial origin and FI~1.8 indicates DOM derived from the autochthonous sources (Cory *et al.*, 2010; Huguet *et al.*, 2009; McKnight *et al.*, 2001). The FI was developed to study the source of humic substances more particularly fulvic acids.

The catchment properties also might contribute to the observed difference (Table 4). The soil texture differs between catchments, for example, catchments with clays soils texture have a high mean value of turbidity (C6, M36, O8, E23, and U8) compared to the catchments with sandy soils texture (E21, F26, I28, M36, and N34). This is because clay colloids that are being dissolved in water and increase the color in the water than sandy soils (Bilotta & Brazier, 2008). Also, it implies that turbidity has a strong relationship with SS. For all catchments, very small trends could be observed for UV254 and FI (Table 4) for both unfiltered and filtered samples. For UV254 mean values ranged between 0.2-0.6 nm and 1.5-1.7 for FI. The effect of turbidity on fluorescence measurements increased linearly with decreasing fluorescence index and been applied to understand the control of DOM and sediments. The absorption degree of CDOM vary seasonally depending on the river input to the near-shore bay waters and inversely to the salinity in the Southern Baltic Sea (Ferrari *et al.*, 1998).

In some catchments there is no significant temporal trend according to p-value as it is shown in Appendix 2, e.g. F26, I28, M42 have p-value greater than 0.05 for UV254 against turbidity. And in most of the fluorescence index versus turbidity catchments, there is no significant trend C6, E21, F26, I28, M36, M42, etc. The reason for not showing significance for these cases it might be because samples were not enough, and there is a, therefore, need to increase samples to be able to detect if there are the effect sizes. For catchments that show a significant temporal trend based on p-value obtained ($p<0.05$, $p<0.001$, and $p<0.001$), a low p-value indicates a higher statistical significance. The R-square value increase as the pvalue decreases.

Suspended particles and DOM can affect optical measurement significantly (Downing *et al.*, 2012; Bunt *et al.*, 1999). Even both absorbance and fluorescence measure the fraction of dissolved organic matter that is most similar and optically active, they have some differences in particles that absorb and fluoresce light efficiently (Korak *et al.*, 2015). Absorbance measures the degree of chromophores that absorb light at a certain wavelength (Coble, 2007). While fluorescence measures fluorophores which absorb and emit light at long wavelengths (Gabor *et al.*, 2014; Downing *et al.*, 2012). Turbidity scatters light along the optical path length affects both UV254 and fluorescence measurement, where turbidity (a proxy of suspended concentration) less than 50 NTU affects more ultraviolet absorbance than fluorescence (Yoo *et al.*, 2014).

6. Conclusion

This work aimed to use laboratory optical instruments; turbidimeter and fluorescence and absorbance spectrophotometer to evaluate how different sediment concentrations measured as turbidity affect fluorescence and absorbance measurements of dissolved organic carbon. SS and DOC are important pollutants in the water bodies, and environmentalists are using turbidity and spectroscopic indices analysis to monitor water quality in the water ecosystem. Absorbance and fluorescence measure the optically active fraction of DOM.

The results showed a variation in water quality among the different agricultural catchments. Factors such as particle properties of SS (size, composition, color, and shape), dissolved of organic matter and soil characteristics may influence the measured value of turbidity and it's a correlation with UV254 and fluorescence index. Catchments with clay soils have higher turbidity and absorbance compared to the catchments with sandy soils. This is because of the clay colloid in the water.

However, UV254 vs. turbidity measurement showed a higher linear correlation compared to the fluorescence index vs. turbidity. UV and FI can be used as a substitute to measure turbidity (SS and DOM) but according to results obtained UV correlates better with turbidity than FI. This implies that UV254 can be a better surrogate parameter to estimate the suspended sediment and DOM in water measured as turbidity for both filtered and unfiltered samples. Of all possible correlations of UV254 against turbidity, only M36 and O18 catchments showed a strong statistically significant for both filtered and unfiltered samples. The results of FI indicates that the source of suspended sediments and dissolved organic matter in the catchments mostly come from terrestrial sources.

The results of this study show that some agriculture catchments are loaded with suspended sediments and DOM in their water. The recommendation for better water quality is good to advise farmers to reduce erosion and apply methods for trapping sediments before they get to the water bodies. Additionally, it would be useful to use large quantities of water samples to be able to identify the size effect between turbidity and fluorescence.

This study can be considered as the potential to use UV as a substitute to measure SS and DOM. Although further validation is needed to confirm the above mention correlation.

To improve this work further studies can be carried out:

- by measuring also other water quality data like phosphorus and nitrogen concentrations in addition to suspended sediment concentrations.
- Correlating suspended sediments and turbidity.

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Appendix 1

Catchment C6 (CLAA, UP1)

Catchment E21 (EMAA, OG6)

Catchment F26 (FDRA, JK1)

Catchment I28 (IBAA, BA1)

Catchment M36 (LKAA, LKA1)

Catchment M42 (MVEA, UT10)

Catchment N34 (NDAA, DA1)

Catchment O18 (RUVA, RUVI)

Catchment E23 (EHE, EHEA)

Catchment U8 (UF1, UFIA)

Appendix 2

