

Master's Thesis

**The effect of land use on the characteristics of
organic matter load into water bodies**

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In recent years, the amount of natural organic matter (NOM) in Northern lakes has increased and the quality has change. Climate change and anthropogenic activities are one of the major drivers of these alterations. This study was done to assess the applicability of the HPSEC-UV-fluorescence (High Performance Size Exclusion Chromatography with UV and fluorescence detection) method to illustrate the variable nature of NOM among catchments. Water samples from two different catchments in Southern Finland were analyzed. The land use of the catchments was investigated by using Corine land cover (CLC) data from the years 2006-2018. In Tuurujärvi and Joutsijärvi catchment, the share of forests was higher than in Gennarbyviken (GBV) catchment, which was more influenced by arable land and urban fabric. Differences in the characteristics of NOM were also found. In Tuurujärvi and Joutsijärvi catchment, *DOC* concentrations (dissolved organic carbon) in surface waters were 1.3-3.8 times higher than in GBV catchment. *DOC* from the surface waters of GBV showed 1.2 times more specific protein-like fluorescence whereas *DOC* from the surface waters of Tuurujärvi and Joutsijärvi catchment showed 1.4 times more specific humic/fulvic-like fluorescence. From 5 to 7 different fractions were separated from the chromatograms. The HPSEC method proved to be an advanced tool for analyzing the characteristics of NOM. To gain more information about the effects of land use on the characteristics of NOM and to validate the method with statistical significance further research is needed.

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Pohjoisten järvien luontaisen orgaanisen aineen (NOM) määrä ja laatu ovat muuttuneet viimeisten vuosien aikana. Ilmastonmuutoksen ja ihmistoimien osuuden kasvun maankäytössä on katsottu olevan osasyitä muutokselle. Tässä gradussa tutkittiin HPSEC-UV-fluoresenssi (korkean suorituskyvyn kokoekskluusio kromatografia, johon on yhdistetty UV- ja fluoresenssi ilmaisimet) metodin soveltuvuutta kuvaamaan orgaanisen aineen ominaisuuksia valuma-alueilla. Vesinäytteitä analysoitiin kahdelta eri valuma-alueelta Etelä-Suomesta. Lisäksi valuma-alueiden maankäyttöä tutkittiin Corine Land Cover (CLC) aineiston avulla vuosilta 2006-2018. Maankäytön analyysit osoittivat Tuurujärven ja Joutsijärven valuma-alueen sisältävän valtaosin metsää Gennarbyvikenin (GBV) valuma-alueen ollessa enemmän maatalous- ja asutusvaltainen. Eroja löydettiin myös valuma-alueiden orgaanisen aineen ominaisuuksista. Tuuru- ja Joutsijärven valuma-alueella pintavesien liuenneen orgaanisen aineen (DOC) pitoisuudet olivat 1,3-3,8 kertaa suurempia kuin GBV:n valuma-alueella. GBV:n valuma-alueen pintavedet sisälsivät 1,2 kertaa enemmän proteiinin kaltaista fluoresoivaa orgaanista ainetta kuin Tuuru- ja Joutsijärven pintavedet. Tuuru- ja Joutsijärven valuma-alueella pintavesien orgaaninen aines oli puolestaan 1,4 kertaa enemmän humuksen kaltaista GBV:n pintavesiin verrattuna. Pintavesien kromatogrammeista erotettiin 5-7 jaetta. HPSEC-UV-fluoresenssi soveltui hyvin määrittämään orgaanisen aineen ominaisuuksia. Lisätutkimusta tarvitaan, jotta jatkossa saadaan tilastollisesti merkittävää tietoa menetelmän soveltuvuudesta sekä maankäytön vaikutuksesta valuma-alueen orgaanisen aineen ominaisuuksiin.

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TERMS AND ABBREVIATIONS

ABBREVIATIONS

AOM	aquatic organic matter
CLC	CORINE land cover
DOC	dissolved organic carbon
HMW	high molecular weight
HPSEC	High Performance Size-Exclusion Chromatography
IMW	intermediate molecular weight
LMW	low molecular weight
MW	molecular weight
MWF	molecular weight fraction
NOM	natural organic matter
POM	particulate organic matter
PSS	polystyrene sulfonate
SOM	soil organic matter
SUVA	specific UV-absorbance
TN	total nitrogen
TOC	total organic carbon
WWTP	wastewater treatment plant

1 INTRODUCTION

Finnish lakes have naturally high dissolved NOM (natural organic matter) concentrations due to the wet and cold climate (Nordtest 2003). However, since the late 1980s the amount of NOM in Northern hemisphere lakes has unforeseen increased (Forsberg and Pettersen 1990, Freeman et al. 2001). Noteworthy is, that not only the quantity but also the quality of NOM has changed (Nordtest 2003, Eikebrokk et al. 2004). Reasons for this increase are still somewhat unknown; for example, climate change, altered land use and decreased anthropogenic sulfur loadings are suggested (Eikebrokk et al. 2004).

Alterations in land use patterns, such as drainage of peatland and shallow upland soils, and increased forest production have been regarded to reflect the spatial variation of both quality and quantity of NOM (Nordtest 2003). Additional loads from agriculture, peat production and urban and decentralized wastewater disposal are also changing NOM concentrations in receiving waterbodies (Tattari et al. 2015). In Finland it has been forecasted that by the year of 2040 the share of forest area is decreasing while the share of agricultural and built area is increasing (Haakana et al. 2015).

In aquatic environments, NOM has many environmental effects. It also affects the quality of drinking water and the effectivity of the drinking water treatment process (Nordtest 2003). Since, NOM plays important role in water ecology and economics, it is important to investigate the effect of land use and anthropogenic activities on the characteristics of organic matter loads into the water bodies.

The aim of the work was to analyze the properties of NOM ending up in boreal lakes from different land use patterns and anthropogenic activities. The feasibility of a novel characterization method was also tested. Study questions were: How did the land use and anthropogenic activities, such as forestry or agriculture, affect the

quantity and quality of organic matter? Could fluorescence properties and molecule size fractions of NOM indicate a certain land use or anthropogenic activity? Was it possible to trace the sources of NOM by analyzing the water samples with a method based on HPSEC-UV-fluorescence (High Performance Size-Exclusion Chromatography with UV and fluorescence detection)? The hypothesis was that different land use patterns alter the properties of NOM and that these alterations can be analyzed and traced back to anthropogenic activities. The study was based on analyses of water samples collected from two boreal catchments. The characterization of organic matter was based on HPSEC-UV-fluorescence method.

2 THEORETICAL BACKGROUND

2.1 Natural Organic Matter

Natural Organic Matter (NOM) is originated from living matter related to or containing carbon compounds. It includes fractions of living, dead or partially decomposed matter and humus (Tan 2014). NOM is considered as a complex mixture of macromolecules (Nordtest 2003). These macromolecules can be categorized based on their molecular weight distribution (MWD) and water solubility (Thurman 1985).

The size of NOM molecules can vary from a few hundred to 100,000 daltons (Da) (Leenheer and Croué 2003). According to Yue et al. (2004) large fractions of NOM comprise molecules > 3.5 kDa, medium-large fractions 3.5-2.0 kDa, medium fractions 2.0-1.0 kDa and small fractions < 1.0 kDa. High molecular weight fractions (HMW) are mainly comprised of humic and fulvic acids whereas intermediate (IMW) and low (LMW) fractions consist of smaller molecules, such as proteins and carbohydrates (Tan 2014).

Hydrophilic fractions consist mostly of aliphatic carbon and nitrogenous compounds whereas hydrophobic fraction includes mainly humic substances

(Leenheer 1981). Humic substances with acidic and strong binding properties (Nordtest 2003) can be divided into subgroups of humic and fulvic acids and humins with different chemical and physical properties (Tan 2014).

Humic acids are more hydrophobic than fulvic acids and have large aliphatic structures, paraffinic chains and aromatic and polyunsaturated structures (De Paolis and Kukkonen 1997). They are soluble in basics but insoluble in water and below pH 2 (Tan 2014). Fulvic acids (FA), on the other hand, have more hydrophilic functional groups, such as esteric, amine and carboxylic groups. FAs have also lower molecular weight and higher percentage of carboxylic groups, which increases its hydrophilicity (De Paolis and Kukkonen 1997). FAs are soluble at any pH and in water (Tan 2014). Humin is considered less slightly aromatic and has a higher polysaccharide content than humic acid. It is also insoluble both in alkali and in acidic solvents (Tan 2014).

2.2 NOM in aquatic environment

The chemical composition and quality of aquatic organic matter (AOM) differ from soil organic matter (SOM) (Tan 2014). NOM in aquatic ecosystems is either origin from allochthonous or autochthonous sources (Sobek et al. 2007). Allochthonous OM can be considered terrestrial origin whereas indigenous aquatic organisms produce autochthonous OM. The first one resembles SOM in composition whereas the latter one is less aromatic, lignoid and phenolic in nature and has higher nitrogen (N) content. In humic lakes allochthonous OM usually dominates autochthonous OM (Tan 2014).

AOM can be divided into particulate organic matter (POM) and dissolved organic matter (DOM) (Leenheer and Croué 2003). The latter one can be extracted by filtering water sample through 0.45 μm pore filters. DOM comprises only small fraction of the total mass of AOM (Tan 2014). However, according to Lobbes et al. (2000) the fraction of POM generally represents less than 20% of OM in boreal lakes. The molecular weight of aquatic DOM is said to vary from few hundreds up to 100 000 Da (Tan 2014).

Total Organic Carbon (TOC) measurements are widely used to quantify the amount of organic matter in aquatic waters (Leenheer and Croué 2003). However, according to Tan (2014) SOM includes only on average 57% of organic carbon the rest includes the elements, such as oxygen and nitrogen, that are additional components of organic matter. Therefore, conversion factor of 1.72 is used to convert OC to OM (Tan 2014). Humic substances are said to explain over half of the DOM content in water (Thurman 1985). Most of the TOC in boreal surface waters, 94 % according to Mattson et al. (2005), is in dissolved form known as Dissolved Organic Carbon (DOC) (Lobbés et al. 2000, Mattson et al. 2005, Kortelainen et al. 2006).

Recently interest to assess the amounts and sources of nitrogen and phosphorous compounds linked to NOM is increased (Aitkenhead-Peterson et al. 2005, Mattson et al. 2005, Kortelainen et al. 2006) although Mattson et al. (2009) have reported riverine DOM containing mostly DOC and much lower proportions of DON and DOP (Mattson et al 2009). In Finnish rivers on average 90% of total nitrogen (TN) is in dissolved form (Kortelainen et el. 2006). In many cases, the concentration of organic fraction exceeds the concentration of inorganic fraction.

Aquatic DON is similarly to DOM originated either from allochthonous or from autochthonous sources. In case of rivers and lake waters DON from terrestrial leaching and runoff dominates. Nitrogen originated from anthropogenic activities has the potential to stimulate eutrophication. DON can be divided into HMW and LMW fractions. HMW > 1000 Da includes proteins, nucleic acids and humic-like substances whereas LMW fraction includes purines, pyrimidines, amides and aminosugars (Berman and Bronk 2003).

DOM has significant role in aquatic ecosystems, being the most mobile organic fraction affecting both hydrochemistry and ecology of water bodies (Tan 2014). According to Tan (2014) DOM serves as a carbon source to aquatic biota such as algae and phytoplankton. It has also been searched that carbon, nitrogen and phosphorous linked to DOM can serve as nutrient and energy sources to bacterio- and phytoplankton via photochemical transformation (Vähätalo et al. 2003). In addition, DOM affects the mobilization of contaminants and diminish the

penetration of light through photobleaching (Tan 2014) and brownification (Nordtest 2003).

NOM also affects the quality of drinking water and the effectivity of the drinking water treatment process. Besides the aesthetic problems, such as color, taste and odor, it may increase the levels of organic and inorganic pollutants, cause undesired disinfection by-products and provide the medium for microbiological growth in the distribution systems (Nordtest 2003). What comes to the drinking water treatment process, the increase of NOM in the raw water source increases also the coagulant and disinfection doses used in purification process (Jegatheesan et al. 2002, Matilainen and Sillanpää 2010).

Roughly, 25% of the drinking water in Finland originates from surface water and the rest from ground water or artificial ground water recharge (Vesilaitosyhdistys 2020). To ensure the safety and quality of drinking water, efficient NOM removal is needed during drinking water treatment process. The characterization of NOM is essential to ensure the selection of the proper treatment method and treatment efficiency, since molecular size and chemical properties both affect the removal of NOM from raw water (Nordest 2003). Previous studies indicate that HMW fractions remove more readily from raw water than IMW and LMW fractions (Nordest 2003, Szabo et al. 2008). However, latter ones can constitute more health risks (Nordest 2003).

2.3 Variables affecting NOM loads on waterbodies

According to Sobek et al. (2007) the regulation of DOC concentrations in lakes is hierarchical on a global scale. This means climatic and topographic conditions determine the limits on DOC concentrations and variation by regulating hydrology, terrestrial vegetation and soil properties. Precipitation and run off are examples from climatic conditions whereas catchment slope and basin steepness are considered topographic conditions. In addition, lake dynamics, such as internal losses due to mineralization and sedimentation as well as dilution affect the concentrations (Sobek et al. 2007).

Inside the same regional area, local variation of DOC concentration is possible depending on the lake and catchment properties such as drainage ratio, share of peatlands and upstream lakes and water retention times. Since climatic conditions can also vary to some extent annually, temporal variation of NOM loads into the waterbodies is possible (Sobek et al. 2007). Soil properties also affect the loads of organic matter. Aitkenhead and McDowell (2000) showed the soil C:N ratio to be a good predictor of riverine DOC flux at the biome scale. Further research has also found that the soil C:N ratio is linked to DON export from the catchment area in a similar way than DOC (Aitkenhead-Peterson et al. 2005).

Vegetation affects the C:N ratio of soil and thus the loads of both DOC and DON into the waterbodies. According to the research of Smolander and Kitunen (2002) the C:N ratio of the soil has been shown to be higher in the pine stand than in the spruce or birch stands (Smolander and Kitunen 2002). On the other hand, Mattson et al. (2003) have found a positive correlation between the abundance of Norway spruce and both TOC and TN concentrations in undisturbed boreal catchment area (Mattson et al. 2003). In addition, DON concentrations in the organic layers of soil increases if the soils have been fertilized with inorganic N (McDowell et al. 2004) leading to elevated fluxes of organic nitrogen into the waterbodies.

In boreal catchments, the riverine TOC export is best predicted with the proportions of peatland and upstream lakes. The latter one is also predicting TON export together with the percentage of agricultural land. Between TOC and the share of upstream lakes negative correlation is found suggesting organic matter retention in upstream lakes (Mattson et al. 2005). In addition, riverine DOC fluxes are suggested to vary within different biome types, water years and land use (Aitkenhead-Peterson et al. 2005).

The comprehensive study conducted by Mattson et al. (2005) showed that the annual DOM load in Finnish lakes, consisting mostly on organic C, varies between 1300 – 7400 kg (km²)⁻¹. The TOC load ranging from 1200 – 7100 kg (km²)⁻¹ and DON load ranging from 64 to 320 kg (km²)⁻¹ (Mattson et al. 2005). The background leaching, also known as natural leaching, is estimated from unmanaged boreal

catchments by Mattson et al. (2003). The natural load of TOC is on average $62 \text{ kg ha}^{-1} \text{ a}^{-1}$ and TN $1.3 \text{ kg ha}^{-1} \text{ a}^{-1}$. These results suggest the loads of NOM in Finnish lakes are naturally high.

2.4 The effects of land use patterns on NOM

According to Tattari et al. (2015) land use and other human activities affect the loads of nutrients and solids into the waterbodies. Nutrients containing nitrogen or phosphorous increase the eutrophication of lakes. Solids on the other hand may cause turbidity and eutrophication of the lakes.

The effects of organic matter on the eutrophication are less straightforward but not meaningless. The decay of organic matter consumes oxygen and this depletion can lead to the release of nutrients from the sediment. In addition, organic matter can silt the banks of the water bodies. (Tattari et al. 2015)

The estimation of annual loads into the waterbodies is difficult due to the multiple factors affecting the amount of the loads and high annual variation between different water years (Tattari et al. 2015). Until very recently Natural resources institute Finland announced that forestry causes much larger annual nitrogen (TN $7\,300 \text{ t a}^{-1}$) and phosphorous (TP 440 t a^{-1}) loads into the waterbodies than previously was thought (TN 3250 t a^{-1} and TP 230 t a^{-1}) (LUKE 2019).

The loads into the waterbodies can originate either from scattered, point or natural sources. Typical scattered sources caused by human activities are forestry, agriculture and wastewaters coming from the area of dispersed settlement. Industry, urban settlement and peat production on the other hand can be considered as point sources. Natural sources containing deposit of the nutrients are considered as background sources. They comprise the natural fraction of nutrient fluxes into the waterbodies (Tattari et al. 2015).

The effect of the load into the water bodies can vary depending on the spatial magnitude of the land use or powerfulness of the human activity. The characteristics of the catchment also affect the extent of the impact. The different

stages of the production for example in forestry or agriculture can also have different impact on the water loads (Tattari et al. 2015).

2.4.1 Natural sources

In Finnish boreal catchments with no anthropogenic activities the background leaching of TOC is best predicted by catchment characteristics; peatland percentage, reflecting topography and site fertility. Nitrogen loads are on the other hand best predicted by climatic conditions and deposition. If the climatic conditions are similar and nitrogen deposition is low, the share of peatland seems to be the best predictor of both TOC and TN (Kortelainen et al. 2006). According to Mattsson et al. (2003) the most important factor controlling TOC and TN loads from unmanaged forested catchments in Finland is temperature.

2.4.2 Agriculture

The share of the arable land from the entire land area in Finland is approximately 7.8% (SVT 2018). The nature of the farming is cyclic and different annual stages follow each other. Therefore, the loads into the waterbodies alter spatially and temporally (Tattari et al. 2015).

Cropping and animal husbandry are the main activities causing loads into the water bodies. The amount of the annual load is affected by the cultivation measures, slope of the field, soil type and water management. The annual variation is also large due to the fluctuations of weather and hydrological conditions. The biggest loads arise typically during the run-off peaks in spring and fall (Tattari et al. 2015).

Without the proper drainage of the arable land, the cultivation of crops is not possible in Finland (Tattari et al. 2015). It has been estimated that 87% of the fields are directly connected to waterbodies by drainage or by location. The average distance from the point of discharge to the nearest water body is 2.3 km (Puustinen et al. 2010). The run-off waters are considered to have both short distances and temporal delays into the water bodies (Tattari et al. 2015).

According to Heikkinen et al. (2013) the stock of TOC in mineral soils that are used in cultivation is decreasing $220 \text{ kg ha}^{-1} \text{ a}^{-1}$. It has been estimated that from 6 to 14 % of TOC is removed as DOC to the water bodies (Tattari et al. 2015). According to Mattsson et al. (2009), among European climatic gradient, a negative correlation between DOC and the share of agricultural land was found. The lower built-up of organic matter into the soils due to intensive agriculture and lower share of peatlands in the catchments may explain the negative relationship (Mattsson et al. 2009). However, the share of agricultural land is reported to increase the export of both TON and DON (Mattsson et al. 2005).

The share of agricultural land is also noticed to affect the molecular weight fractions of NOM. Wilson and Xenopoulos have showed (2009) that DOM from streams contain primarily HMW humic and fulvic acids leached from soil and terrestrial litter, whereas the increasing share of agricultural land reduces these fractions. This leads a proportional increase of lower MW fractions, containing e.g. sugars and proteins, in lakes produced by aquatic microbes.

2.4.3 Urban fabric

Urban fabric comprises on average 3.1% of the total land area in Finland. Settlements, urban run-off and industry are responsible for the organic matter loads into the water bodies.

Wastewaters originated from settlements can be treated in wastewater treatment plants (WWTP) or in decentralized sanitation systems (Tattari et al. 2015). In 2015 approximately 23% of the estates were situated outside the sewerage system (SVT 2019). According to Finnish wastewater act (157/2017) decentralized wastewater system should remove 90% of organic matter, 85% of total phosphorous and 40% of total nitrogen before effluent is released into the environment (Act 157/2017).

Current WWTP can remove 90% of phosphorous and suspended solids but only 50% of nitrogen. The effluent, containing effluent organic matter (EfOM) (Ignatev and Tuhkanen 2019a) is lead to the receiving water bodies (Tattari et al. 2015). According to Sickman et al. (2007) WWTP can be a significant single point source of

TOC into the receiving waterbodies in urban areas. Aitkenhead-Petterson et al. (2009) showed also significantly lower DON concentrations in watersheds without a WWTP compared to those with WWTP. It has been estimated that annually wastewater treatment in Finland causes 8600 - 11000 t. TOC loads into the waterbodies (Tattari et al. 2015).

Non-point urban run-off causes also elevated TOC concentrations compared to less disturbed areas. Impervious surfaces may cause higher volume of run-off leading to higher TOC yields (Sickman et al. 2007). Urban open areas, such as golf courses and parks under turf grass, high-density urban areas and population density are also positively correlated with DOC concentrations whereas urban land use showed no effect on annual DON loads (Aitkenhead-Peterson et al. 2009).

According to Mattsson et al. (2009) DOC is as an overall negatively correlated with the percentage of urban areas in Finland. This is explained by effective water protection measures and lower wetland cover. However, DON concentrations are positively correlated with the share of urban areas and higher population density (Mattsson et al. 2009).

Factories, mining and fertilizer production can be significant point sources locally if the untreated process waters are released directly into the water bodies. Especially pulp and paper industry has been significant discharge source into the water bodies (Tattari et al. 2015). It has been estimated that since 1940 large amounts of chlorinated organic matter is released into the Baltic Sea by pulp industry (Wulff 1993). Annual industrial TOC export into the water bodies is estimated to be 26 000 t. It is originated mostly from paper and pulp industry (Tattari et al. 2015).

2.4.4 Forestry and peat production

Forests cover approximately 86 % of the land area in Finland being the most significant form of the land use (Vaahtera et al. 2018). In agriculture-intensive Southern Finland the share is usually less than 60 %. Swamps cover approximately 34 % of the total forest area and the rest is covered by the coniferous forests. The most common tree species is pine, comprising 50% of the total volume of the forest

cover whereas spruce comprises 30% and birch 17% of the total volume (Tattari et al. 2015).

Logging, ditching and fertilization are the most common activities causing loads into the water bodies (Tattari et al. 2015). According to Nieminen et al. (2017a) the management of harvest residues into piles, drainage and site preparation may increase the nutrient exports into the receiving waterbodies. They also point out that the mitigation procedures to hinder the nutrient loads into water bodies are somewhat controversy. Some procedures, such as establishing a wetland buffer area, may decrease sediment and inorganic nutrient loads but increase the DOC and dissolved organic nutrient exports into the waterbodies (Nieminen et al. 2017a).

The average production cycle in forestry varies from 80 to 100 years. Therefore, the impact of the forestry can be considered temporally restricted (Tattari et al. 2015). However, the influence of the forestry can be spatially significant since it has been showed that clearcuttings can even triple the load of DOC into the water bodies (Schelker et al. 2012). According to Lepistö et al. (2014) clearcuttings in Finland can cause 33% growth on TOC-load leading the total TOC-load of $77 \text{ kg ha}^{-1} \text{ a}^{-1}$. In addition, nitrogen mineralization and nitrification often increase after cutting leading to increased N availability and load into the water bodies (Kreutzweiser et al. 2008).

A recent study of Nieminen et al. (2017b) also suggest that forestry-trained peatlands can affect the catchment nutrient loads considerably longer than previously estimated. They reported TN concentrations over two times higher in 60 years old drainage areas compared to undisturbed and more recently drained areas (Nieminen et al. 2017b).

Peat production area in Finland is 0.19% from the total land area. The annual load of peat production can vary as a sum of production stage and hydrology. However, load is originated from the entire production area. The annual load of peat production is estimated to be 9500 t. TOC (Tattari et al. 2015).

According to Kløve et al. (2013) water released from peat production is darker, more nutrient rich and contains more organic suspended solids compared to the waters

from natural mires. The amount of nutrient load is affected by the quality of peat, climate, the depth and slope of the ditches, production operations and water protection measures. (Kløve et al. 2013)

Drainage and peat mining are showed to increase the mobilization of HMW organic colloids. The loads of inorganic nitrogen are also increasing due to peat mining (Heikkinen 1994). Hulatt et al. (2014) also suggest that the increased DOM production, due to the aeration of peat caused by lowering of the water table by either drought or artificial drainage, may increase the level of DOM release into the waterbodies (Hulatt et al. 2014). The nutrient loads are also increasing due to the removal of plant cover, ditching and drainage and increased erosion of fine organic matter (Tattari et al. 2015).

2.5 The characterization of NOM

The characterization of NOM is important to understand the environmental processes such as carbon cycling and sequestration, soil health, pollutant transport and different water treatment processes (DeLapp and LeBoeuf 2004, Lankes et al. 2009). In addition, the further characterization of humic and fulvic compounds can lead to the development of new agricultural and pharmacological preparatives, improved environmental risk assessment and waste water tracking opportunities (Tuhkanen and Ignatev 2018). However, at the same time the characterization of NOM is challenging due to the variable nature and relatively low concentrations of NOM in natural waters (Sillanpää et al. 2015).

The characterization of NOM includes the identification of chemical groups with similar properties instead of searching individual constituents from thousands of structural elements (Croue et al. 2000). Typical characterization measures of NOM include DOC, chemical oxygen demand (COD), UV₂₅₄, pH, turbidity and color. These, mostly quantitative, procedures however offer only little information about the quality of NOM (Sillanpää et al. 2015).

To gain more information about NOM different isolation and concentration methods and fractionation can be used (Sillanpää et al. 2015). Typical fractionation

methods include resin fractionation, membrane filtration and chromatographic measures. Depending on the characterization method, information about the molecular size distribution, elemental composition, functional groups and hydrophobic properties of NOM can be gained (Tan 2014, Tuhkanen and Ignatev 2018).

A one way to assess the aromaticity of NOM is to calculate the specific UV-absorbance (SUVA) value that is the UV absorbance at a given wavelength divided by DOC concentration. In this way, the UV data combined with DOC results can be used to assess the aromaticity of the NOM (Matilainen et al. 2010). High SUVA value, over 4 ($l\text{ mg}^{-1}\text{m}^{-1}$), indicates hydrophobic, high molecular weight organic matter, whereas the lower SUVA value, under 3 ($l\text{ mg}^{-1}\text{m}^{-1}$), indicates hydrophilic organic compounds with low charge density (Peuravuori and Pihlaja 2007, Sillanpää et al. 2015).

2.5.1 HPSEC

With High Performance Size-Exclusion Chromatography (HPSEC) the molecular weight distribution of NOM can be determined (Tuhkanen and Ignatev 2018). The LMW fractions elute first followed by IMW fractions. HMW fractions have the longest retention times (Sillanpää et al. 2015). HMW fractions contain organic colloids, biopolymers and high MW humics. IMW fractions typically consists of low MW humics and breakdown products of humic substances whereas LMW fractions contain LMW acids and neutrals (Fabris et al. 2008, Huber et al. 2011). The size and the MW (in Daltons, Da) can be determined by comparing the retention times with known molecular mass standards. Polystyrene sulfonate (PSS) and polyethylene glycols standards are used (Tuhkanen and Ignatev 2018).

In NOM studies, both silica and polymer-based columns are used. However, both columns have interactions with NOM. Choice of a right eluent as a mobile phase is also important because pH and ionic strength both affect the results. Phosphate buffer with NaCl that is used for ionic strength adjustment and sodium acetate solution are commonly used (Sillanpää et al. 2015).

Further analysis of the qualitative properties of size distribution can be gained with different detectors combined to HPSEC system. Typical detectors used include on-line DOC analyzers, UV-Vis and Excitation/Emission fluorescence detectors and Fourier transform infrared (FTIR) (Sillanpää et al. 2015). Data collected with these detectors can be used to fingerprinting and tracing the origin of NOM (Szabo and Tuhkanen 2016, Tuhkanen and Ignatev 2018).

Since organic molecules include both light absorbing and emitting fractions, these photochemical properties can be measured with UV and fluorescence detectors (Her et al. 2003). In UV measurements wavelengths between 220- 280 nm are used. Absorbance at 220 nm indicates the presence of both aliphatic and aromatic structures as well as some inorganic ions where as UV_{254} is usually considered as an indicator of aromatic carbon content in aquatic environments. UV_{254} can also be used to calculate the SUVA value as explained in previous chapter (Peuravuori and Pihlaja 2007, Sillanpää et al. 2015). Fluorescence properties of NOM are discussed more detailed in next section.

2.5.2 Fluorescence properties of NOM

When a molecule absorbs certain amount of energy, its outer electron is excited into a higher energy level. When electron returns into its ground state energy is released as light or fluorescence. Fluorophores are organic molecules that absorb and re-emit light. Excitation and emission wavelengths are characteristic to certain molecular structures (Table 1) (Fellman et al. 2010).

Typical raw water exhibits two types of fluorescence: protein- and humic-like (Sillanpää et al. 2015). Protein-like components are considered to include free amino acids and amino acids bound in proteins or in HMW DOM. Humic-like components on the other hand are thought to be aromatic containing many conjugated fluorescent molecules (Fellman et al. 2010).

Fluorescence characterization can give information about the source, redox state and biological activity of DOM (Fellman et al. 2010, Sillanpää et al. 2015).

Table 1. Major fluorescence peaks for aquatic DOM (Adapted from Fellman et al. 2010 and Sillanpää et al. 2015)

Range of excitation (nm)	Range of emission (nm)	Component type	Description and probable sources
270-280	310-320	Tyrosine/protein-like	Fluorescence resembles free tyrosine. Amino acids free or bound in proteins. May indicate more degraded peptide material. Sources: terrestrial (plant or soil OM), autochthonous production, microbial processing
270-285 or 220-235	340-360	Tryptophan/protein-like	Fluorescence resembles free tryptophan. Amino acids free or bound in proteins. May indicate intact protein or less degraded peptide material. Sources: terrestrial (plant or soil OM), autochthonous production, microbial processing
320-350	400-450	Fulvic-like	Fluorescence resembles fulvic acid, Sources: terrestrial (plant or soil OM)
320-390	410-500	Humic-like	HMW humic, widespread, highest in wetlands and forested environments. Sources: Terrestrial (plant or soil OM)

Fluorescence spectroscopy has been used for example to identify natural and anthropogenic DOM inputs into freshwater (Cumberland and Baker 2007). Naturally occurring freshwater is dominated by humic-like NOM. Elevated protein-like fluorescence can be a sign of anthropogenic input and urbanization (Hudson et al. 2007) although protein-like fluorescence can also be considered as a fingerprint of DOM derived from microbial sources (Fellman et al. 2008).

High protein-like fluorescence can be found from waste waters originated e.g. from WWTP, agriculture or industry (Baker 2001, 2002a, 2002b, Ignatev and Tuhkanen 2019a). Fluorescence properties are also used to estimate stormflow sources (Katsuyama and Ohte 2002), forest ecosystem disturbance (Yamashita et al. 2011) and the effect of different soil types on the properties of NOM (Fellman et al. 2010) among other types of implementations.

Compared to more traditional methods, such as UV-Vis, fluorescence is more sensitive and selective. It is a simple method with little sample pretreatment and as such relatively inexpensive (Tuhkanen and Ignatev 2018). However, environmental factors, such as temperature, pH and oxygen concentration may affect results (Fellman et al. 2010).

3 MATERIALS AND METHODS

Water samples were taken from the catchments of Gennarbyviken and Tuurujärvi and Joutsijärvi. Both serve as a raw water source for artificial ground water production: Gennarbyviken for Hanko Water and Tuurujärvi for Pori Water. The characterization of organic matter was based on HPLC-SEC with UV-fluorescence detection. Some more conventional, quantitative methods, DOC and TN detection, were also used to assess the water quality.

The catchments were determined with VALUE- tool supplied by SYKE (Finnish Environmental Institute). The land use of the catchments was determined with ArcGIS Map-software. The classification was based on the CLC (Corine-land cover) 2006, 2012 and 2018.

3.1 Samples

3.1.1 Catchment description

Lake Gennarbyviken situates in Raasepori, Southern Finland. It has been separated from the Gulf of Finland with a dam in 1957 to meet the water needs of industry (Karonen et al. 2015). It has been classified as strongly altered body of water with satisfying ecological condition (Karonen et al. 2009). Eutrophication and oxygen depletion are the main concerns of Gennarbyviken (Karonen et al. 2015). The Gennarbyviken catchment with total area of 92 km² is represented in Figure 1.

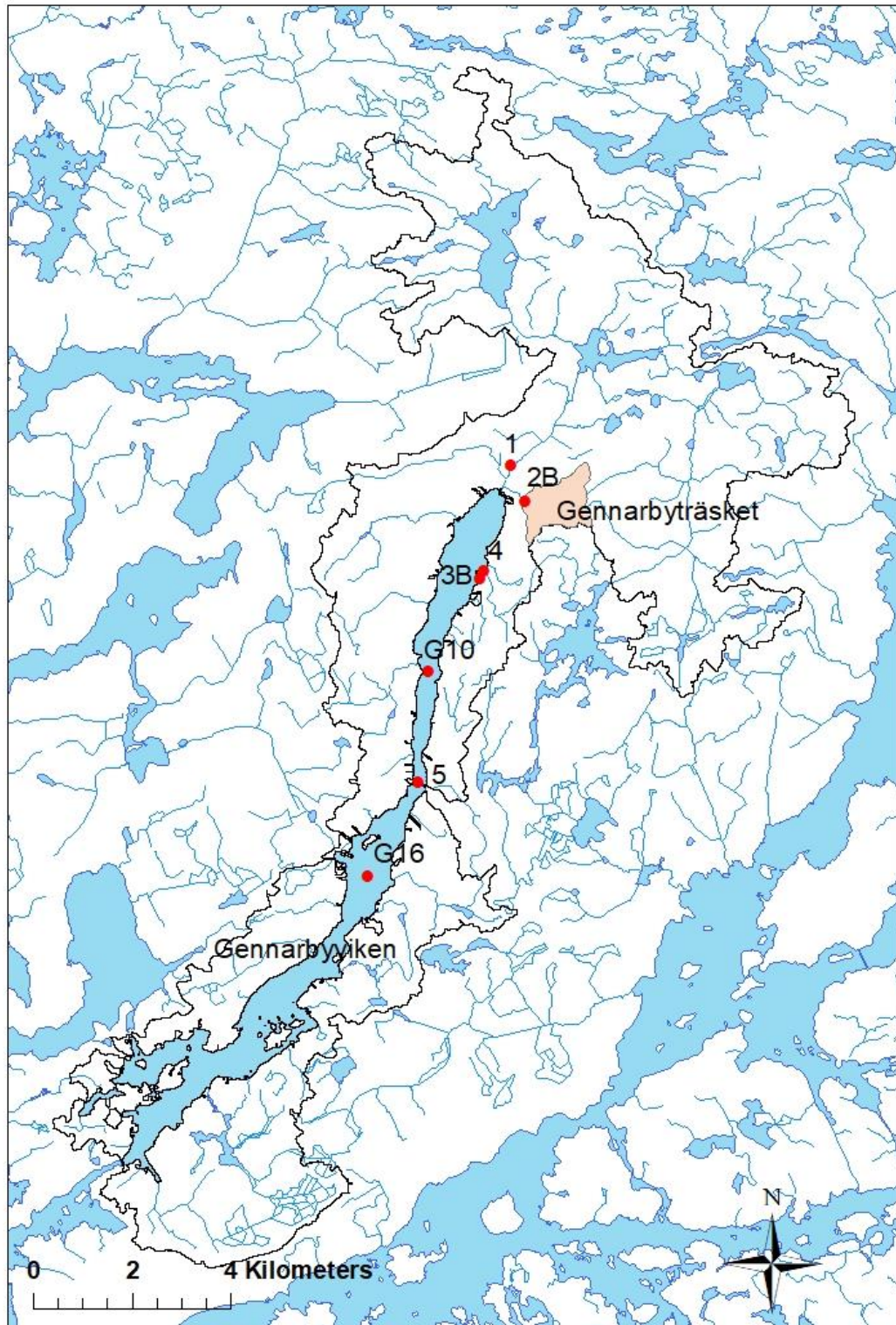


Figure 1. Gennarbyviken catchment and sample places. The brown area represents the catchment of Gennarbyträsket.

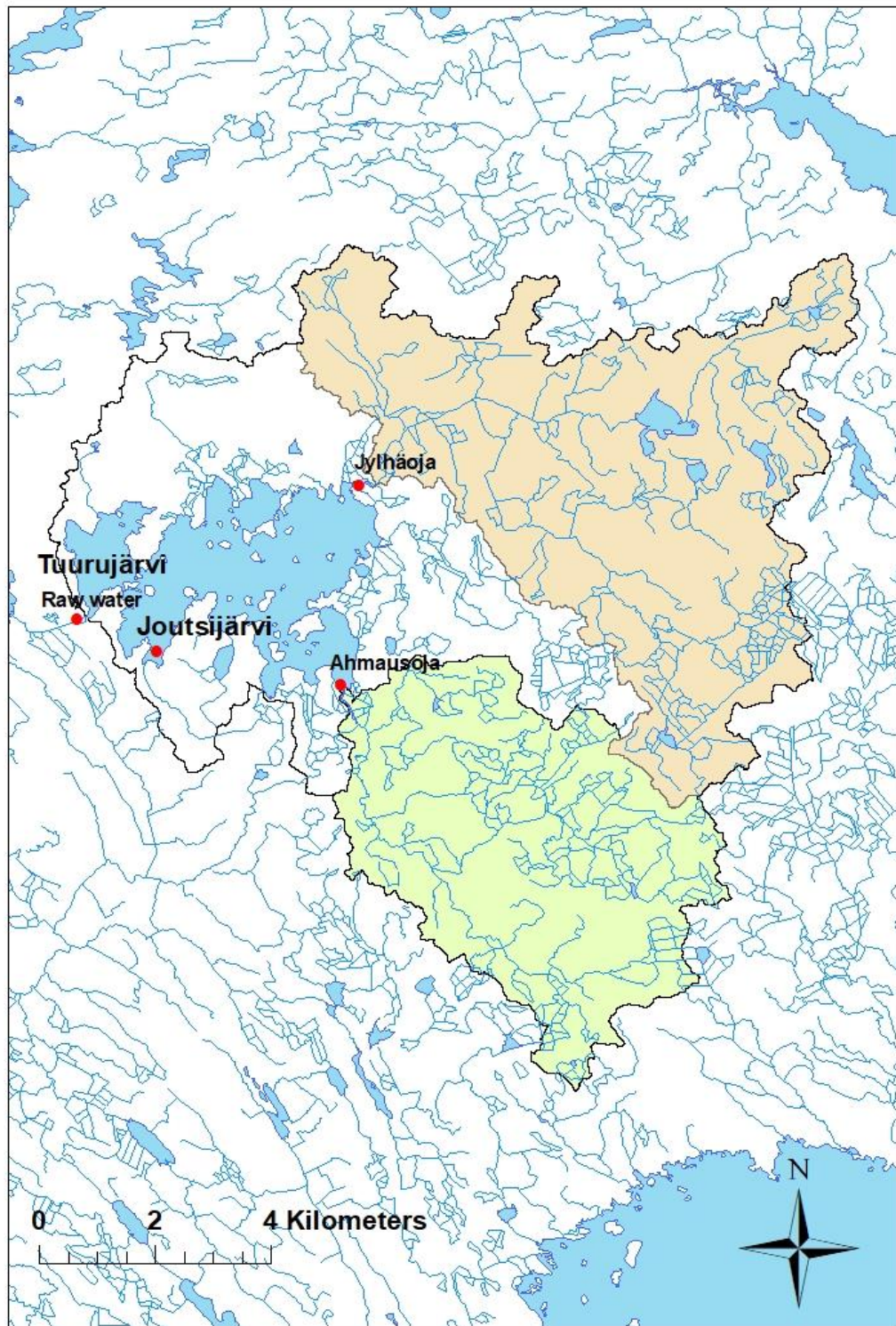


Figure 2. Tuurujärvi and Joutsijärvi catchment and sample places. The green area represents the catchment of Ahmausoja and the brown area represents the catchment of Jylhäoja. These both catchments are part of the entire catchment of Tuurujärvi and Joutsijärvi.

The catchment includes several small lakes. The brown area describes the catchment of Gennarbyträsket, which is part of the entire catchment area of Gennarbyviken.

Lake Tuurujärvi and Joutsijärvi are situated in Ulvila, Southern Finland. These two lakes are connected to each other via small inlets (Salonen et al. 2000). The ecological condition of both lakes is considered good (Ympäristö 2019). Tuurujärvi and Joutsijärvi catchment with total area of 114 km² is represented in Figure 2. The green area in Figure 2. represents the catchment of Ahmausoja and the brown area represents the catchment of Jylhäoja. These both catchments are part of the entire catchment of Tuurujärvi and Joutsijärvi.

3.1.2 Water samples from the catchments

Water samples were collected during the summer 2018 from the lakes and ditches of Gennarbyviken catchment and Joutsijärvi and Tuurujärvi catchment. The sample size from Gennarbyviken was twelve samples. Four samples were taken from lake Gennarbyviken (sample code: G10, G16, 3B and Hanko raw water) and one from lake Gennarbyträsket (2B), three from the ditches of the catchment (1, 4 and 5), three from the wells of the artificial groundwater recharge (ISOK 1-3) and one from the tap water (Hanko drinking water) (Figure 1.).

The sample size from Joutsijärvi and Tuurujärvi area was five samples from which two were from the lakes (sample code: Joutsijärvi and Pori raw water), two from the ditches of the catchment area (Ahmausoja and Jylhäoja) and one from the drinking water (Pori drinking water) (Figure 2.).

3.2 Land use data

To search the effect of catchments' land use on the characteristics of NOM, the catchments were determined with VALUE- tool supplied by SYKE (Finnish Environmental Institute).

The changes in land use were analyzed with ArcGIS Map- software. The alterations in land use of the catchments were investigated by using the land cover data from different years: CLC 2018 (resolution 20 m), 2012 (resolution 20 m) and 2006

(resolution 25 m) supplied by SYKE Open database. The land use classification was based on Level 2 (CLC).

3.3 Methods

3.3.1 DOC and TN measurements

The concentrations of *DOC* and *TN* were measured with TOC-analyzer (Shimadzu TOC-L) with integrated total nitrogen measuring unit (Shimadzu TNM-L, Ordior). Before the analyze 20 ml of sample was filtrated through Cellulose Acetate (CA) membrane filter (0,45 μm , Whatman). Carbon standards with C-content of 3 and 30 mg/l and nitrogen standards with N-content of 0, 15 and 1,5 mg/l were prepared using potassium phthalate and KNO_3 . All samples were acidified with 80 μl of 2M HCl (SFS-EN 1484).

The change of the *DOC* and *TN* concentrations from drains to raw water and from drains to drinking water was calculated (%). Since there were more than one drain in each catchment, the *DOC* and *TN* values used in the calculation were average values of all drain samples of the catchment.

3.3.2 HPSEC-UV-fluorescence analyses

For the *DOC* analyses high performance liquid chromatography unit (Shimadzu) combined with a photodiode array detector (Shimadzu SPD-M20A) and a fluorescence detector (Shimadzu Prominence RF-20A XS) were used. The column was silica-based Yarra SEC-3000. Mobile phase with 5 mM phosphate buffer with $\beta(\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}) = 0.445 \text{ g l}^{-1}$ and $\beta(\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}) = 0.390 \text{ g l}^{-1}$, was used at the flow rate of 1 ml min^{-1} . The phosphate eluent, with ionic strength of 10 mM, was vacuum filtrated before use with CA filter (0,2 μm , Whatman).

Water samples were filtrated with CA filter (0,45 μm , Phenomenex). Injection volume of 50 μl for each sample was used. UVA was measured with detection wavelength of 254 nm. For fluorescence detection different sets of excitation/emission wavelengths were used. For tyrosine/tryptophan- like

detection Ex/Em 220/310 nm and Ex/Em 270/355 nm were used and for fulvic- and humic-like detection wavelengths were Ex/Em 330/425 nm and Ex/Em 390/500 nm respectively. The selection of these wavelengths was based on previous studies (Szabo et. al, 2008, Ignatev and Tuhkanen, 2019a and 2019b).

UVA₂₅₄ and fluorescence chromatograms were divided into fractions and manually integrated in LabSolutions-software. Total area of entire chromatogram and individual areas of different fractions with retention time between 4.5-13 min were determined (mV min or mAU min). Chromatograms of each research site's samples were combined in MATLAB software. Fractions were then divided into different Molecular Weight Fractions (MWFs) according to their elution time. To estimate the MWs calibration curve with polystyrene sulfonate (PSS) standards was used (APPENDIX 1).

Further, relative abundance of MWFs of lake, catchment and drinking water samples (%) and their average values were calculated (1).

$$MWF(\%) = \frac{F_n}{F_{tot.}}, \quad (1)$$

where F_n (mV min) is the fluorescence of a fraction ($n = \text{I-VII}$) and $F_{tot.}$ is the total fluorescence (mV min) on specific Ex/Em wavelengths.

Total UVA₂₅₄ and fluorescence areas were used to characterize the whole water samples.

SUVA₂₅₄ values were calculated as a ratio of the total area of UVA₂₅₄ and DOC to gain information about the aromaticity (2)

$$SUVA = \frac{total\ UVA_{254}}{DOC} \frac{u}{V_{inj}} 100, \quad (2)$$

where *total UVA₂₅₄* (mAU min) is determined from HPSEC-UV₂₅₄ chromatograms, u (l min⁻¹) is the eluent flow, *DOC* is concentration of dissolved organic carbon (mg C l⁻¹) and V_{inj} (l) is the injection volume (Ignatev and Tuhkanen 2019b).

The specific fluorescence was determined by dividing the total fluorescence area with *DOC* concentration.

Correlations between *DOC* and *UVA*₂₅₄ and *DOC* and total fluorescence were also investigated by using IBM SPSS statistic-software and Spearman's correlation.

The comparison of specific fluorescence between the surface waters of the catchments was conducted from the average values calculated from the surface water samples of each catchment. In Gennarbyviken surface waters included samples 1, 2B, 3B, 4, 5, G10, G16, Hanko rw and in Tuurujärvi and Joutsijärvi surface waters included samples Ahmausoja, Jylhäoja, Joutsijärvi and Pori rw.

4 RESULTS

4.1 The land use of the catchments

The catchments of Gennarbyviken and Tuurujärvi and Joutsijärvi were presented in Figure 1 and 2. The total area of Gennarbyviken catchment was 92 km² whereas the total area of Tuurujärvi and Joutsijärvi catchment was slightly bigger, 114 km².

In 2018 the most common land use pattern in both catchments was forests (Figure 3. and 4.). In Gennarbyviken catchment, the share of arable land was notably higher than in Tuurujärvi and Joutsijärvi catchment. Shrub and/or herbaceous vegetation associations, including transitional woodlands, were also common in both catchments. In Tuurujärvi and Joutsijärvi catchment, the share of inland waters as well as wetlands was higher than in Gennarbyviken catchment.

Between 2012 and 2018, the largest changes in the land use were among the forests and shrub and/or herbaceous vegetation associations in the Gennarbyviken catchment. The share of forests decreased 6.0 %-points, whereas the share of shrub and/or herbaceous vegetation associations increased 4.2 %-points. In Tuurujärvi and Joutsijärvi catchment, the change was opposite. Since 2006 the share of forests has increased in Tuurujärvi and Joutsijärvi catchment from 73% to 77%.

In the catchment of Gennarbyträsket the share of forest (53%) and arable land (8.5%) was smaller than in the entire catchment area of Gennarbyviken in 2018. On the

other hand, the shares of inland waters (16%), urban fabric (2.9%) and industrial, commercial and transport units (2.1%) were higher than in the entire catchment area.

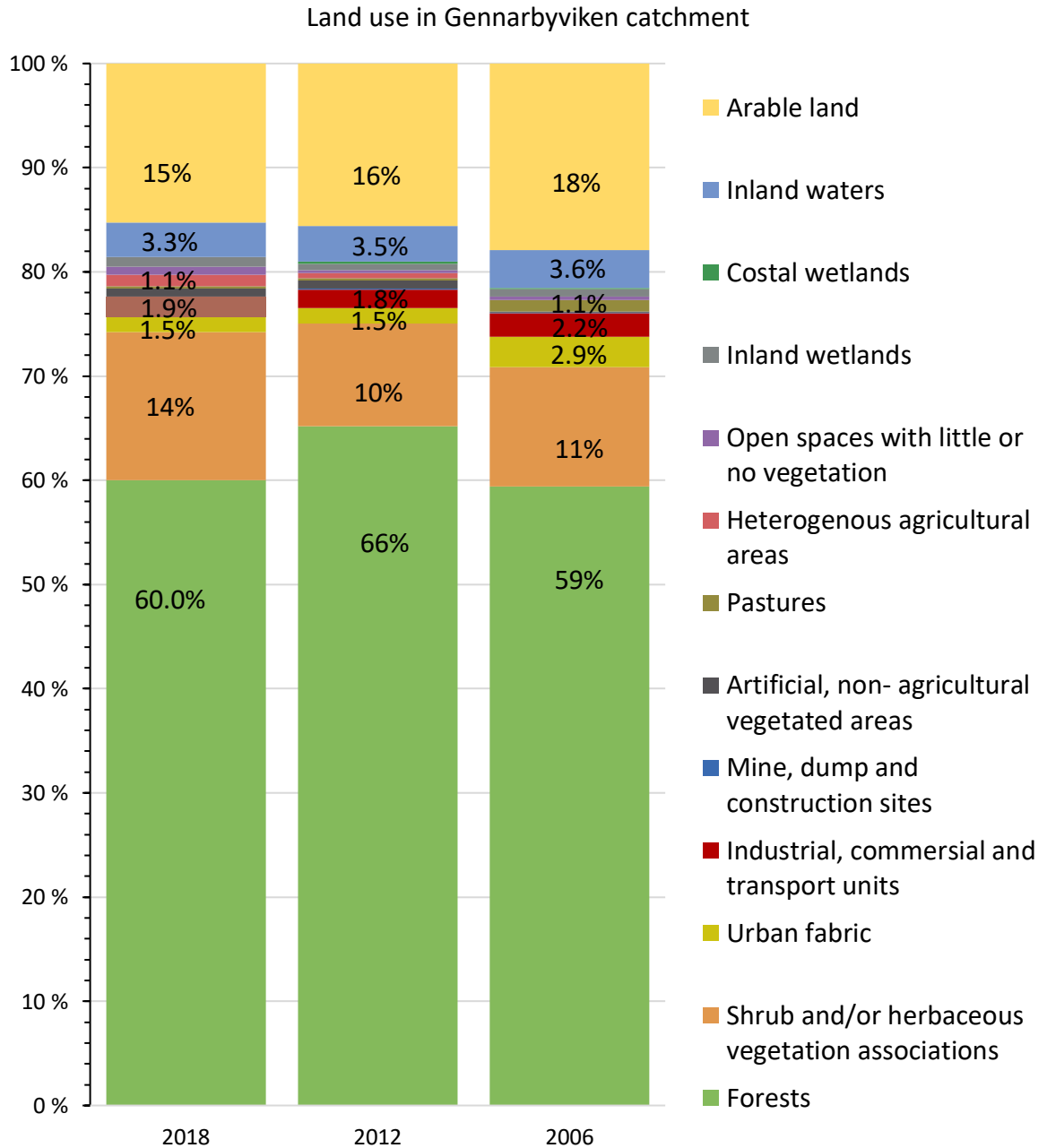


Figure 3. The land use patterns of Gennarbyviken catchment and their change during 2018-2006. Land use patterns < 1.0% are not tagged as numbers in the chart.

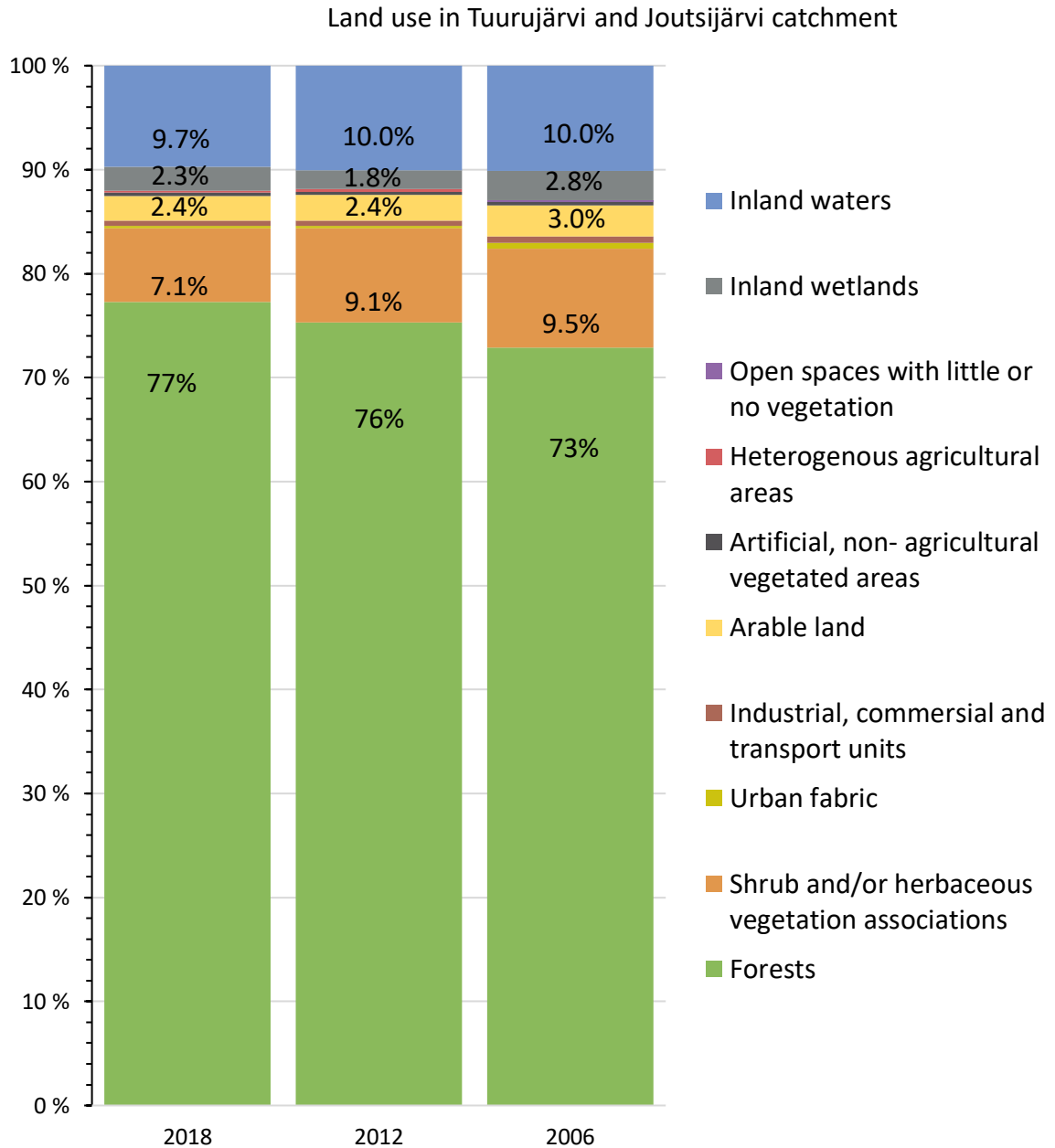


Figure 4. The land use patterns of Tuurujärvi and Joutsijärvi catchment and their change during 2018-2006. Land use patterns < 1.0% are not tagged as numbers in the chart.

When comparing the Ahmausoja and Jylhäoja catchments separately, it was noticed that Ahmausoja catchment had higher share of forests (86%) than Jylhäoja (80%). Jylhäoja on the other hand had higher share of arable land (5.8%) and inland waters (1.3%) than Ahmausoja (arable land 0.8% and inland waters 0.2%).

4.2 DOC and TN

As an overall, ditches had higher *DOC* and *TN* values than lakes (Table 2.), although the standard deviation was high. Among the drains, Ahmausojä's sample had the highest *DOC* and *TN* concentrations whereas sample 4 had the lowest concentrations. In the catchment of Tuurujärvi and Joutsijärvi drains had higher *DOC* and *TN* concentrations than lakes. In the catchment area of Gennarbyviken no such trend was found.

The highest *DOC* concentration among the lakes was measured from Joutsijärvi and highest *TN* from Gennarbyviken (3B). Gennarbyträsket had the lowest *DOC* and *TN* concentrations (Table 2).

Pori's drinking water had higher *DOC* and *TN* concentrations than Hanko's drinking water. The *DOC* concentration of Pori's drinking water was 2.1 mg l⁻¹ and Hanko's drinking water 0.67 mg l⁻¹. The *TN* concentrations were 0.13 mg l⁻¹ and 0,048 mg l⁻¹.

Compared to *DOC* and *TN* concentrations of Tuurujärvi's and Joutsijärvi's drains, lakes had over 50% lower *DOC* and *TN* concentrations. The decrease of *DOC* concentration was 91% and *TN* 84% from the drains to drinking water (Table 3).

In the catchment of Gennarbyviken the *DOC* and *TN* concentrations from drains to lakes increased. However, the change of *DOC* and *TN* concentrations from drains to drinking water was similar than in Pori (Table 3).

When comparing the average values of surface waters' *DOC* concentrations (Table 3.) between the two catchments, it was noticed that the average *DOC* concentrations were 1.3-3.8 times higher in Tuurujärvi and Joutsijärvi catchment.

Table 2. Properties of water samples taken from different parts of the catchments (mean \pm SD).

	Ditches n=5	Max/Min	Lakes n=7	Max/Min	Drinking water treatment n=5	Max/Min
DOC (mg l ⁻¹)	14 \pm 13	37/4.8	8.5 \pm 2.1	12/6.1	1.6 \pm 0.6	2.1/0.67
TN (mg l ⁻¹)	0.51 \pm 0.38	1.2/0.19	0.43 \pm 0.14	0.64/0.29	0.16 \pm 0.07	0.21/0.048
SUVA (l mgC ⁻¹ m ⁻¹)	4.9 \pm 1.5	7.3/3.4	3.4 \pm 0.5	4.1/2.5	1.8 \pm 0.3	2.2/1.4
Tot. UVA ₂₅₄ (mAU min)	42 \pm 54	140/10	15 \pm 6	25/7.6	1.3 \pm 0.4	1.7/0.75
Tot. fluorescence (mV min)						
Tyrosine-like (220/310 nm)	56 \pm 32	110/21	49 \pm 11	66/36	11 \pm 3	15/7.0
Tryptophan-like (270/355 nm)	130 \pm 101	300/38	98 \pm 24	140/39	16 \pm 5	19/6.7
Fulvic-like (330/425 nm)	630 \pm 650	1700/180	310 \pm 120	510/130	45 \pm 18	64/16
Humic-like (390/500 nm)	230 \pm 270	700/62	84 \pm 37	150/31	13 \pm 6	20/4.0
Specific fluorescence (mV min l mg ⁻¹)						
Tyrosine-like (220/310 nm)	5.0 \pm 1.8	7.3/2.9	6.0 \pm 1.7	9.3/4.5	7.4 \pm 2.1	11/5.4
Tryptophan-like (270/355 nm)	10 \pm 2	13/7.9	11 \pm 1	12/11	10 \pm 1	11/8.2
Fulvic-like (330/425 nm)	42 \pm 7	51/32	35 \pm 7	41/21	28 \pm 2	30/24
Humic-like (390/500 nm)	14 \pm 4	19/8.1	9.1 \pm 2.2	12/5.1	8.1 \pm 2.0	11/5.9

Table 3. The *DOC* and *TN* concentrations (mg l^{-1}) and their change (%) compared to the original *DOC* in drains in the catchment of Gennarbyviken and Tuurujärvi and Joutsijärvi.

Gennarbyviken Catchment	<i>DOC</i> (mg l^{-1}) (change %)	<i>TN</i> (mg l^{-1}) (change %)
Drains	6.5	0.31
Raw water	7.6 (+16)	0.46 (+48)
Drinking water	0.67 (-90)	0.048 (-85)
Tuurujärvi and Joutsijärvi Catchment	<i>DOC</i> (mg l^{-1}) (change %)	<i>TN</i> (mg l^{-1}) (change %)
Drains	25	0.79
Joutsijärvi	12 (-51)	0.36 (-55)
Raw water (Tuurujärvi)	10.2 (-59)	0.33 (-58)
Drinking water	2.1 (-91)	0.13 (-84)

4.3 Total UVA_{254} -area

Total UVA_{254} absorbance was highest in the samples collected from the ditches of both catchments (Table 2.) compared to samples from lakes and drinking water treatment. The variation of UV absorbance among the ditch samples was high; Ahmausoja's sample had fourteen times higher absorbance than sample 4 collected from Gennarbyviken catchment.

Lakes had lower UV absorbance than ditches and the variation among the samples was smaller. Joutsijärvi had the highest absorbance and Gennarbyträsket lowest (Table 2.). The absorbance of Joutsijärvi's sample was three times higher than the absorbance of Gennarbyträsket's sample.

What comes to the drinking water treatment process, the highest UVA_{254} absorbance was measured from the sample of ISOK 1. This sample was taken from the well of the artificial groundwater recharge of Hanko Water. Hanko's drinking water on the other hand had the lowest UVA_{254} absorbance (Table 2.) among all the samples.

4.4 SUVA₂₅₄

As an overall samples collected from ditches had higher SUVA values than samples from lakes and drinking water treatment processes. Ahmausoja sample had the highest SUVA₂₅₄ value from all samples. The value was five times higher than the lowest SUVA₂₅₄ value measured from Pori's drinking water and over double compared to the lowest SUVA₂₅₄ value measured from ditches (sample 5).

Among the lakes, Joutsijärvi had the highest SUVA₂₅₄ value and Gennarbyträsket the lowest (Table 2.)

Samples taken from the drinking water treatment process had the lowest SUVA₂₅₄ values among all samples. Pori's drinking water had the lowest SUVA₂₅₄ value of all samples (Table 2.).

4.5 Correlations between DOC and other parameters

Strong monotonic correlation was found between *DOC* and *UVA*₂₅₄ ($\rho_s = 0.95$, $p < 0.01$, $n = 17$) (Figure 5).

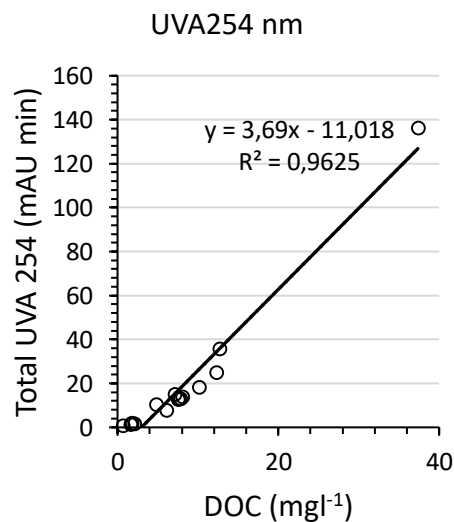


Figure 5. Total *UV*₂₅₄ absorbance (mAU min) against *DOC* concentrations (mg l⁻¹) of all water samples. Strong monotonic correlation was found between *DOC* and *UVA*₂₅₄ ($\rho_s = 0.95$, $p < 0.01$, $n = 17$).

Strong monotonic correlation was also found between *DOC* and total fluorescence: tyrosine-like ($\rho_s = 0.82$, $p < 0.01$, $n = 17$), tryptophan-like ($\rho_s = 0.94$, $p < 0.01$, $n = 17$), fulvic-like ($\rho_s = 0.83$, $p < 0.01$, $n = 17$) and humic-like ($\rho_s = 0.89$, $p < 0.01$, $n = 17$) (Figure 6).

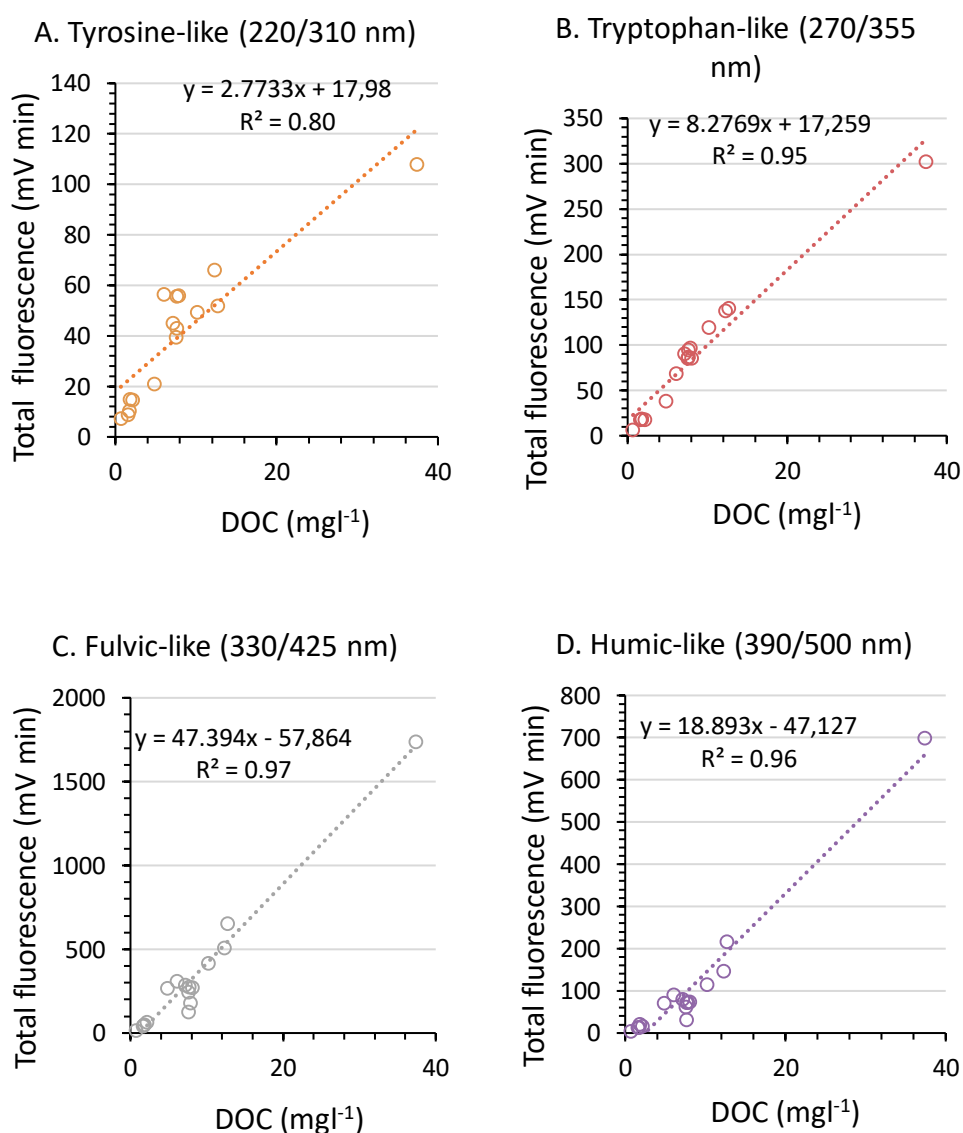


Figure 6. Diagrams A-D. present the total fluorescence of different Ex/Em wavelengths against *DOC* concentrations (mg l⁻¹) of each sample. There were found strong monotonic correlation between the *DOC* and total fluorescence.

4.5.1 Differences in correlation between the catchments

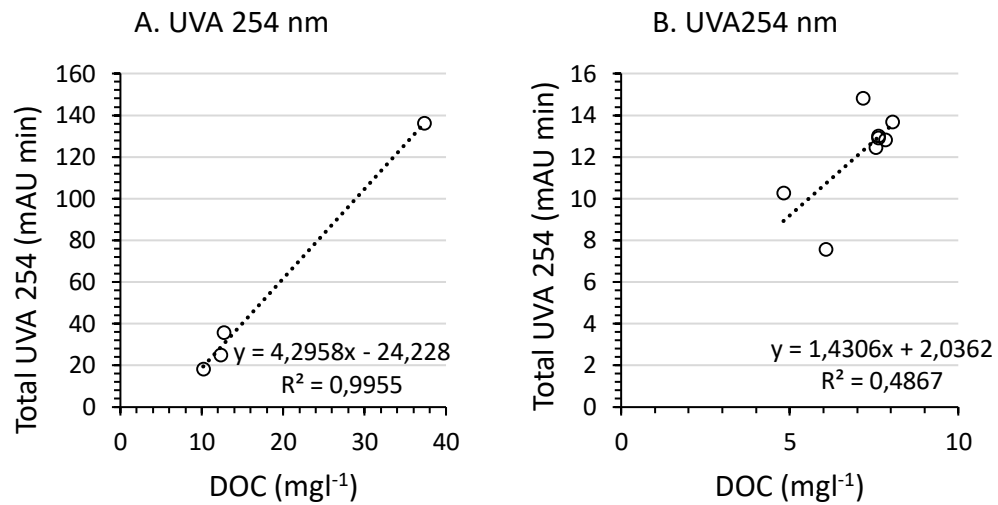


Figure 7. Total UV_{254} absorbance (mAU min) against DOC concentrations (mg l⁻¹) of water samples from Tuurujärvi and Joutsijärvi catchment (A.) and Gennarbyviken catchment (B.).

When comparing the correlations between the catchments, it was found out that in Tuurujärvi and Joutsijärvi catchment DOC correlated strongly with UVA_{254} ($\rho_s = 1.0$, $p < 0.01$, $n=4$) (Figure 7.), total tryptophan-like fluorescence ($\rho_s = 1.0$, $p < 0.01$, $n=4$), total fulvic-like fluorescence and total humic-like fluorescence ($\rho_s = 1.0$, $p < 0.01$, $n=4$). However, DOC did not correlate however tyrosine-like fluorescence. (Figure 8)

What comes to Gennarbyviken catchment correlation between DOC and other parameters was not found (Figure 7, 8 and 9). Especially sample taken from Gennarbyträsket showed divergent values in all cases, whereas the sample collected from a ditch (5) showed deviant values in DOC correlations with fulvic-like and humic-like fluorescence.

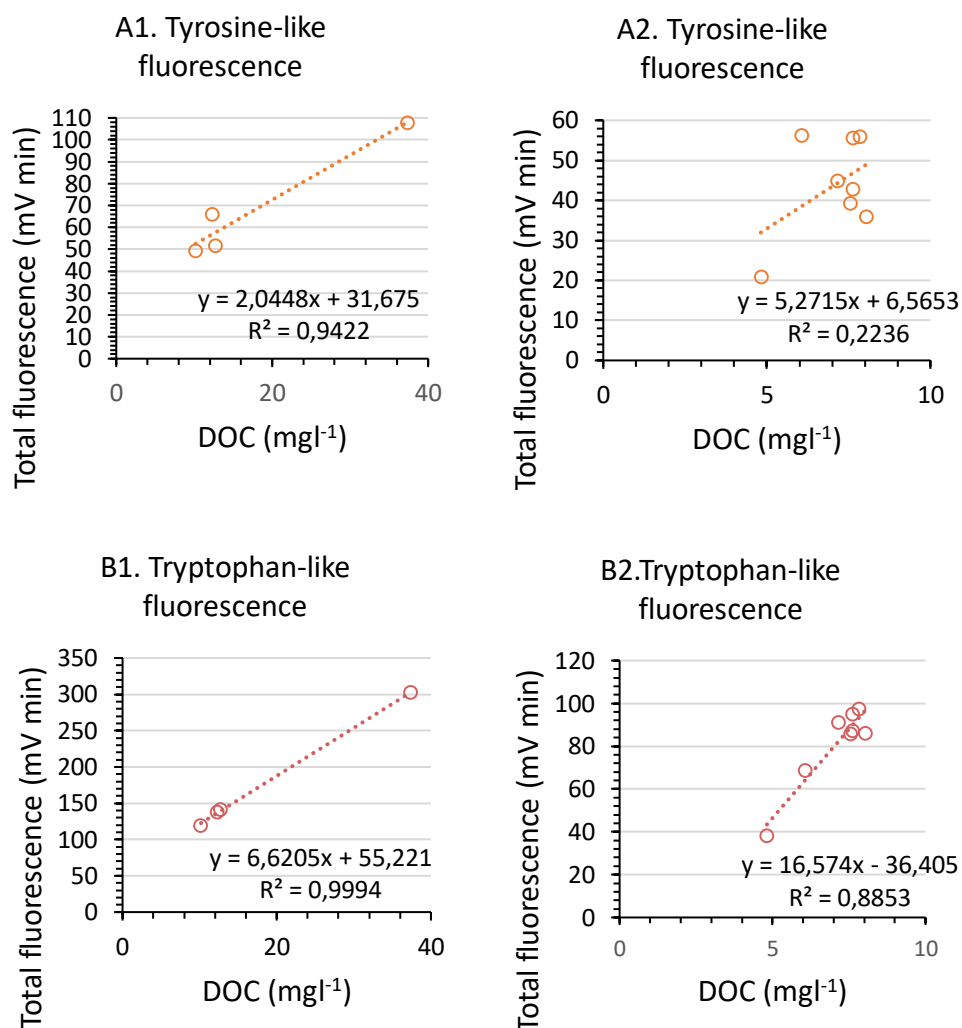


Figure 8. Diagrams A-B. present the total protein-like fluorescence of different Ex/Em wavelengths against DOC concentrations (mg l⁻¹). A1. and B1. present the samples from Tuurujärvi and Pori catchment and A2. and B2. present the samples from Gennarbyviken catchment.

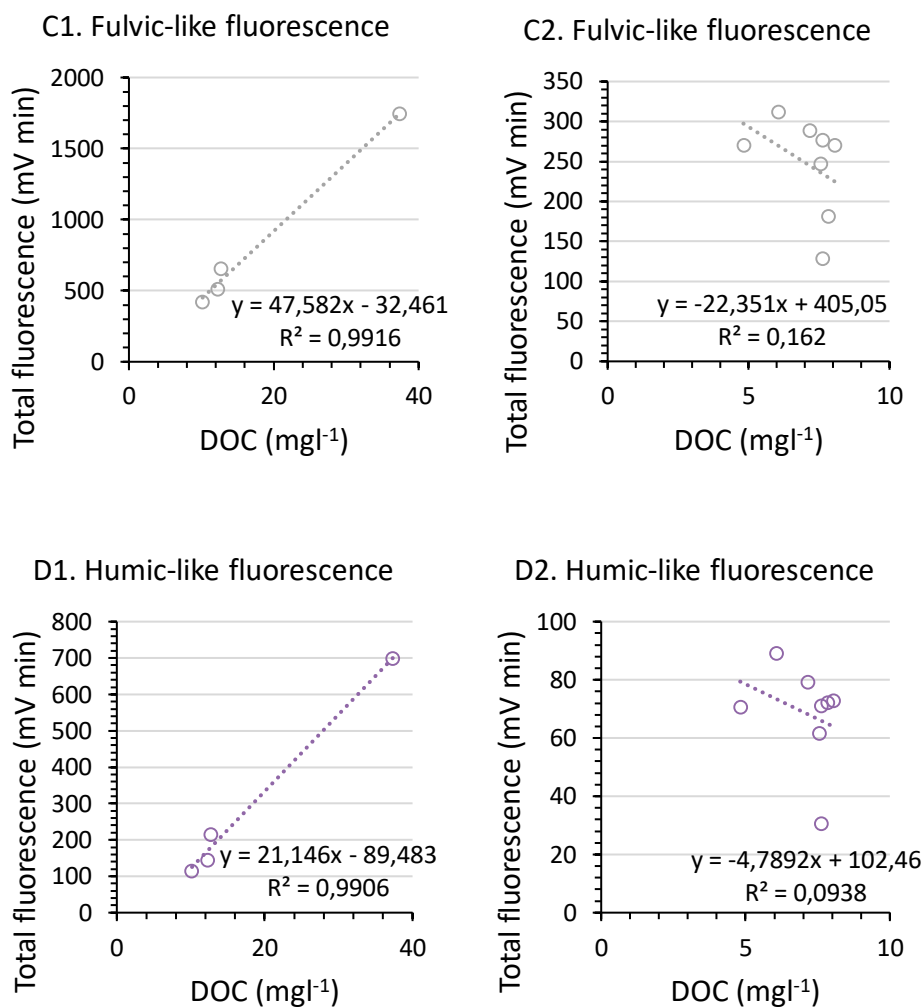


Figure 9. Diagrams C-D. present the total humic/fulvic-like fluorescence of different Ex/Em wavelengths against DOC concentrations (mg l⁻¹). C1. and D1. present the samples from Tuurujärvi and Pori catchment and C2. and D2. present the samples from Gennarbyviken catchment.

4.6 Molecular Weight Fractions

Peaks of the fluorescence chromatograms (APPENDIX 2) were combined from five to seven different molecular weight fractions (I-VII) (Figure 10, 11 and 12).

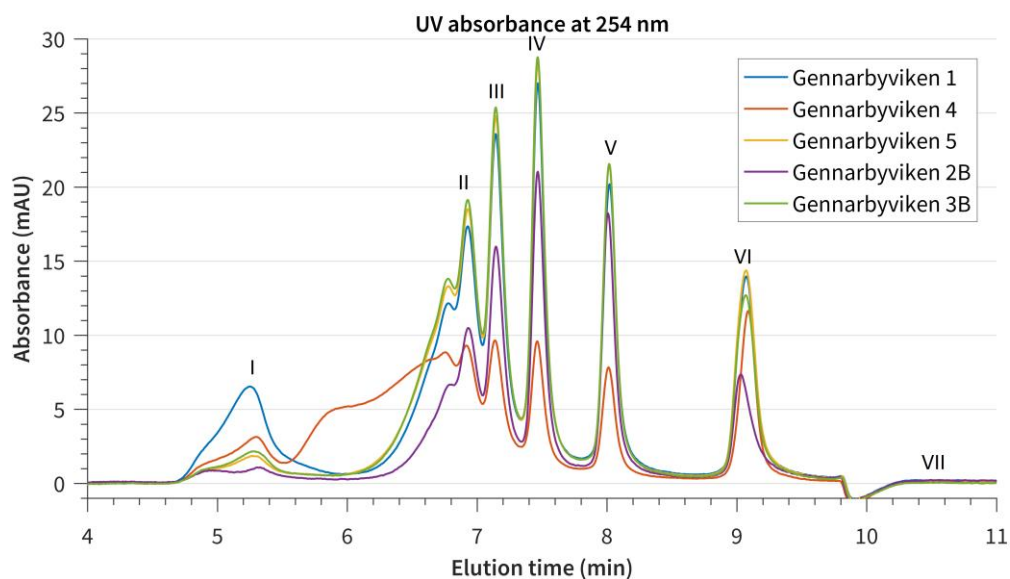


Figure 10. An example of fluorescence chromatogram. Seven different molecular weight fractions (I-VII) were identified from the UV₂₅₄ chromatograms of surface waters.

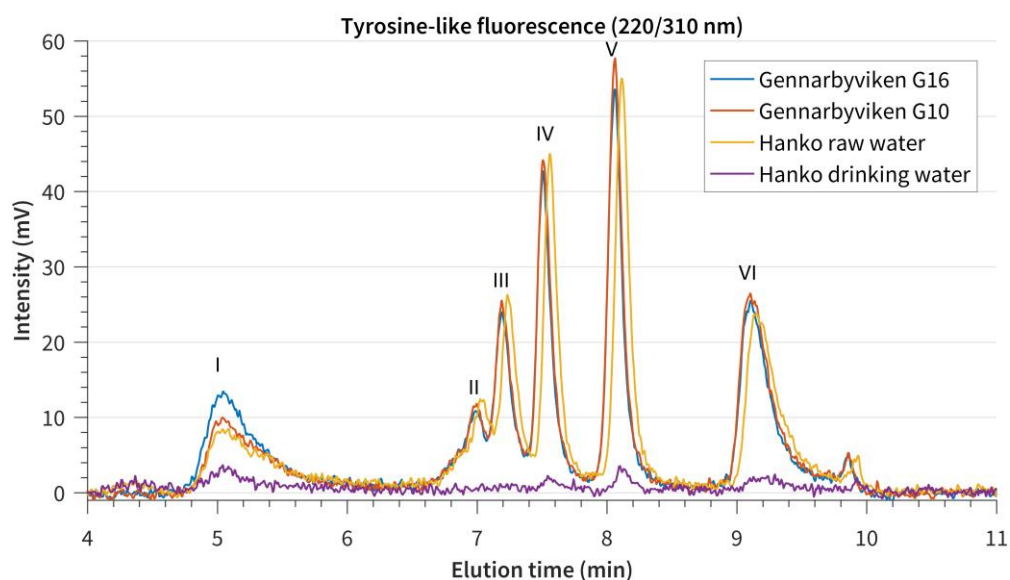


Figure 11. In tyrosine-like fluorescence of Gennarbyviken's surface waters six different fractions (I-VI) were identified.

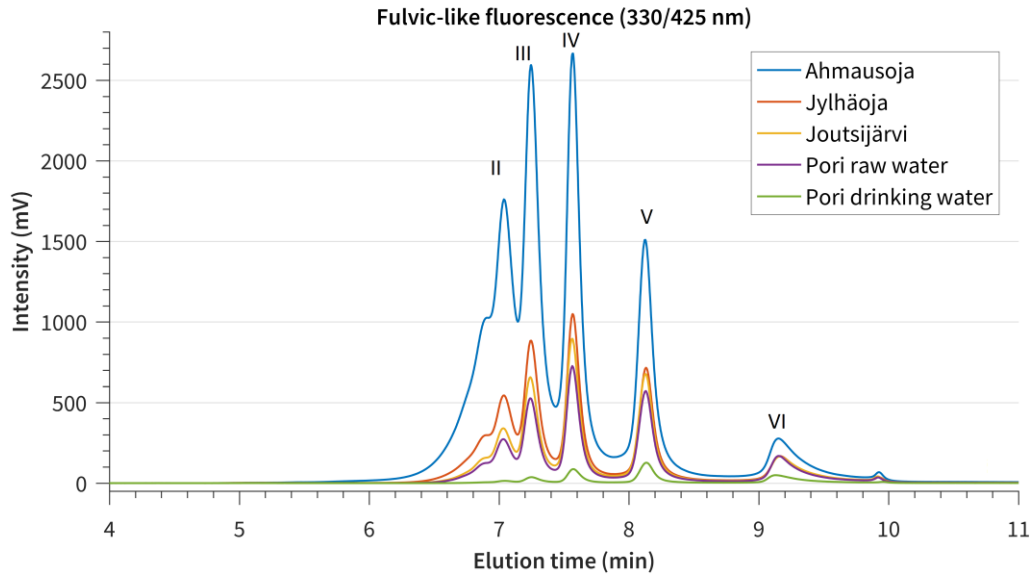


Figure 12. In fulvic-like fluorescence of Tuurujärvi and Joutsijärvi only five fractions (II-VI) were identified.

Fractions were classified into high molecular weight (HMW) fraction (I and II), intermediate molecular weight (IMW) fractions (III and IV) and low molecular weight fractions (V-VII). Molecular weights were calculated based on PSS standards (APPENDIX 1). Fraction I consist molecules about 4.7 kDa on size. Fraction II includes molecules 3.3 kDa on size, fraction III molecules 1.4 kDa on size and fraction IV 1.0 kDa on size. Fraction V consist molecules 520 Da on size, fraction VI molecules 240 Da on size and fraction VII molecules 55 Da on size.

4.7 Ditches

4.7.1 Total and specific fluorescence

Ahmausoja's sample had the highest total fluorescence intensity in all Ex/Em wavelengths compared to other samples (Figure 13). Especially fulvic- and humic-like intensity (330/425 and 390/500 nm) showed large difference compared to others. In tyrosine-like fluorescence, the difference was smallest. Jylhäoja had also higher total fluorescence, except tyrosine-like (220/310 nm), compared to ditches located in Gennarbyviken catchment.

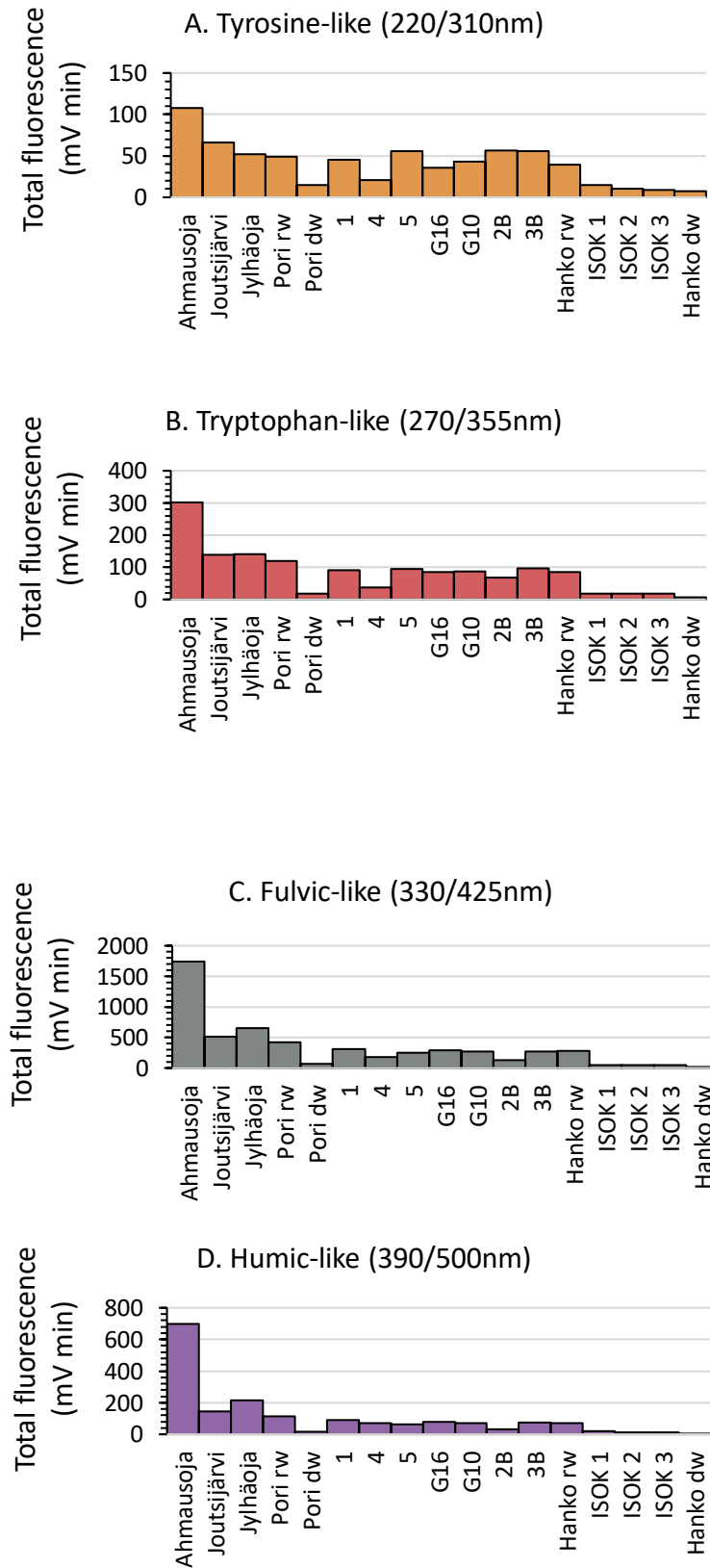


Figure 13. Total fluorescence area (mV min) measured in protein-like (Ex/Em: 220/310 and 270/355 nm) A.-B. and fulvic/humic-like (Ex/Em: 330/425 and 390/500 nm) C.-D. wavelengths. Samples Ahmausoja-Pori dw represents the

Tuurujärvi and Joutsijärvi catchment and samples 1-Hanko dw represents the Gennarbyviken catchment.

Among the ditches of Gennarbyviken the highest protein-like total fluorescence was found from samples 1 and 5, which differed from sample 4 remarkably. In humic/fulvic-like fluorescence the differences were small.

When normalized with *DOC*, specific fulvic-like fluorescence was highest in ditch samples of Jylhäoja, Ahmausoja and 1 (Figure 15.). The variation among samples was smallest in this type of fluorescence. Specific humic-like fluorescence showed highest values in ditch samples collected from Ahmausoja, Jylhäoja and 4 but the variation among individual samples was notably higher than in fulvic-like specific fluorescence.

Among the protein-like specific fluorescence ditches showed also high variation; the highest specific tryptophan-like fluorescence was measured from sample 1 whereas the lowest from sample 4 (Figure 15.). These both samples were collected from the Gennarbyviken catchment. In addition, Jylhäoja had higher protein-like fluorescence compared to Ahmausoja among Tuurujärvi and Joutsijärvi catchment.

4.7.2 Relative abundance of MWFs

In ditch samples, the relative abundance of fraction I was high in protein-like fluorescence compared to humic/fulvic-like fluorescence, in which the fluorescence was near zero.

As an overall IMW and HMW fractions dominated humic/fulvic-like fluorescence in Tuurujärvi and Joutsijärvi catchment. In Gennarbyviken catchment humic/fulvic-like fluorescence was dominated by LMW and IMW fractions. The trend was also same in tryptophan-like fluorescence. (Figure 14.)

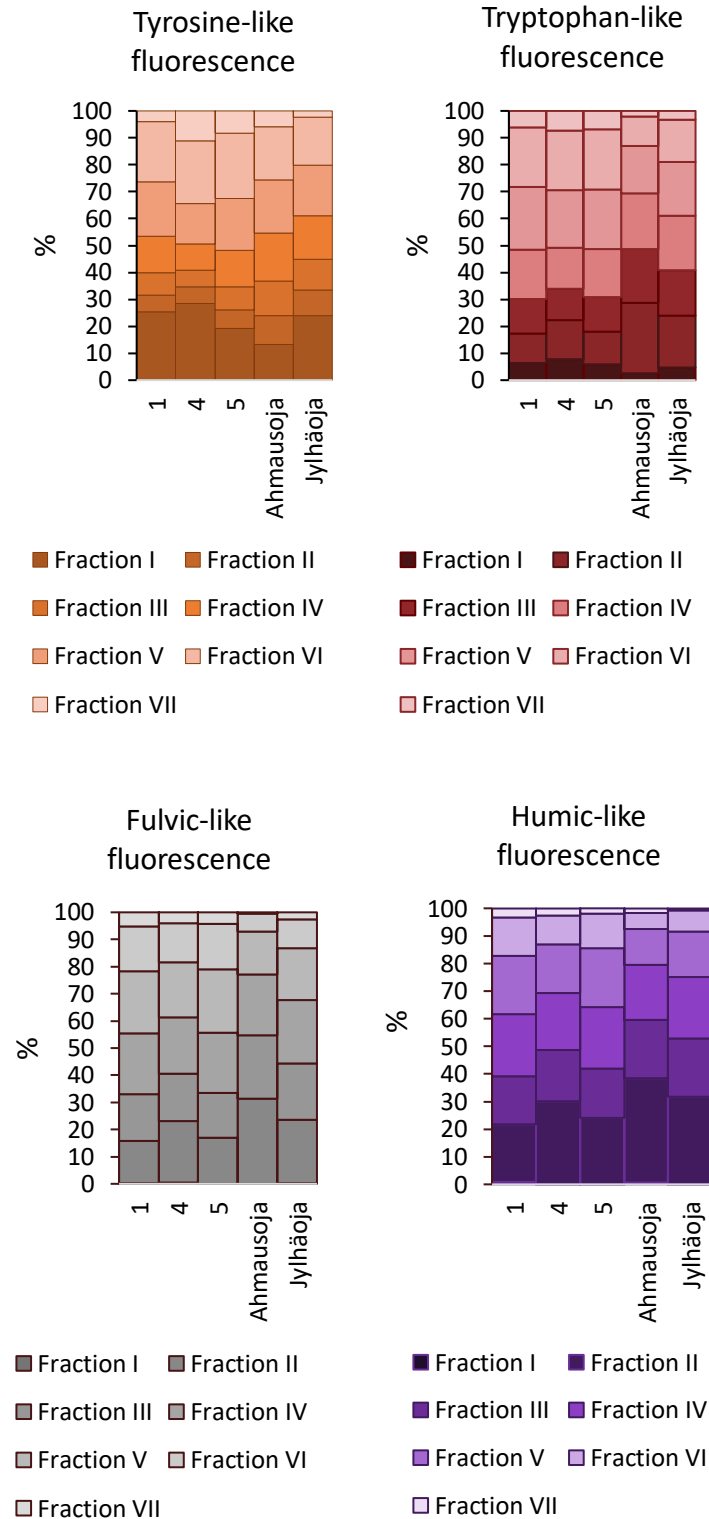


Figure 14. Relative abundance (%) of fluorescent fractions (I-VII) in ditches. Samples 1-5 represents the Gennarbyviken catchment and samples Ahmausoja and Jylhäoja represents the Tuurujärvi and Joutsijärvi catchment.

4.8 Lakes

4.8.1 Total and specific fluorescence

Joutsijärvi had the highest total fluorescence in all wavelengths among the lakes. Tuurujärvi showed also higher total fluorescence than lakes in Gennarbyviken catchment Gennarbyviken (G10, G16 3B and Hanko rw) and Gennarbyträsket (2B). Among all lakes Gennarbyträsket showed lower total fluorescence in all but tyrosine-like fluorescence. (Figure 13.)

Specific protein-like fluorescence showed no distinctive trends between lakes, except the tyrosine-like fluorescence, which was notably higher in Gennarbyträsket (2B) than in other lakes. On the other hand, fulvic/humic-like specific fluorescence was remarkably lower in Gennarbyträsket and slightly higher in Joutsijärvi and Tuurujärvi (Pori rw) compared to other lakes. (Figure 15.)

The *DOC* from the surface waters of Gennarbyviken showed 1.2 times more specific protein-like fluorescence whereas the *DOC* from the surface waters of Tuurujärvi and Joutsijärvi catchment showed 1.4 times more humic/fulvic-like specific fluorescence.

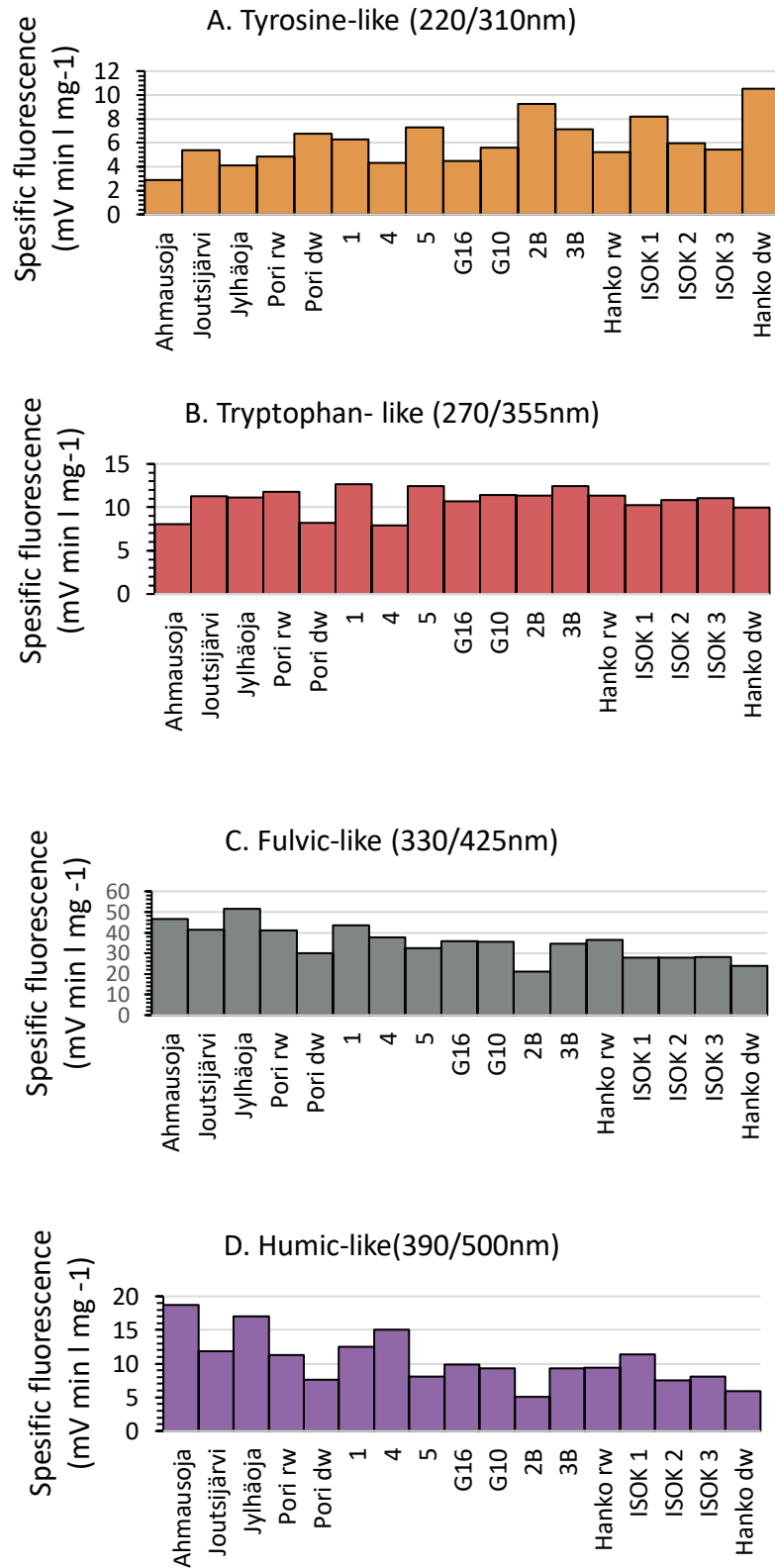


Figure 15. Specific protein-like fluorescence A-B. and humic/fulvic-like fluorescence C-D. (mV min l mg^{-1}) in catchments. Samples Ahmausoja-Pori dw represents the Tuurujärvi and Joutsijärvi catchment and samples 1-Hanko dw represents the Gennarbyviken catchment.

4.8.2 Relative abundance of MWFs

In lake samples, protein-like fluorescence was dominated by LMW fractions (Figure 16). Although, the relative abundance of Fraction I in protein-like fluorescence was high compared to fulvic/humic-like fluorescence. On the other hand, in fulvic/humic-like fluorescence IMW and LMW fractions dominated (Figure 16). The fractionation was similar in all lakes except Gennarbyträsket (2B) where the share of LMW fractions was slightly higher in all wavelengths compared to other lakes.

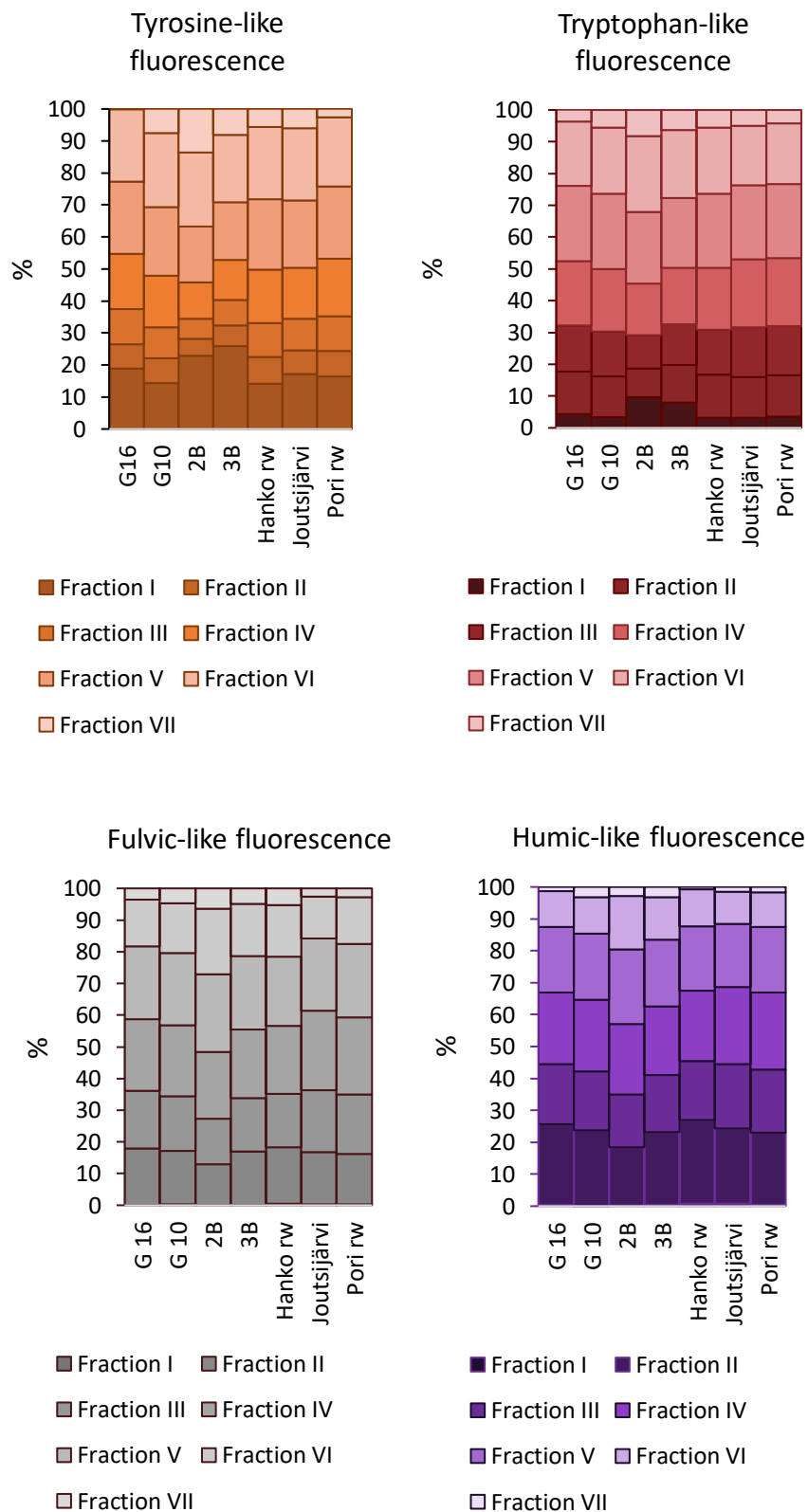


Figure 16. Relative abundance (%) of fluorescent fractions (I-VII) in lake waters. Samples G16-Hanko rw represent the Gennarbyviken catchment and samples Joutsijärvi and Pori rw represent Tuurujärvi and Joutsijärvi catchment.

4.8.3 Comparing the MWFs of ditches and lakes

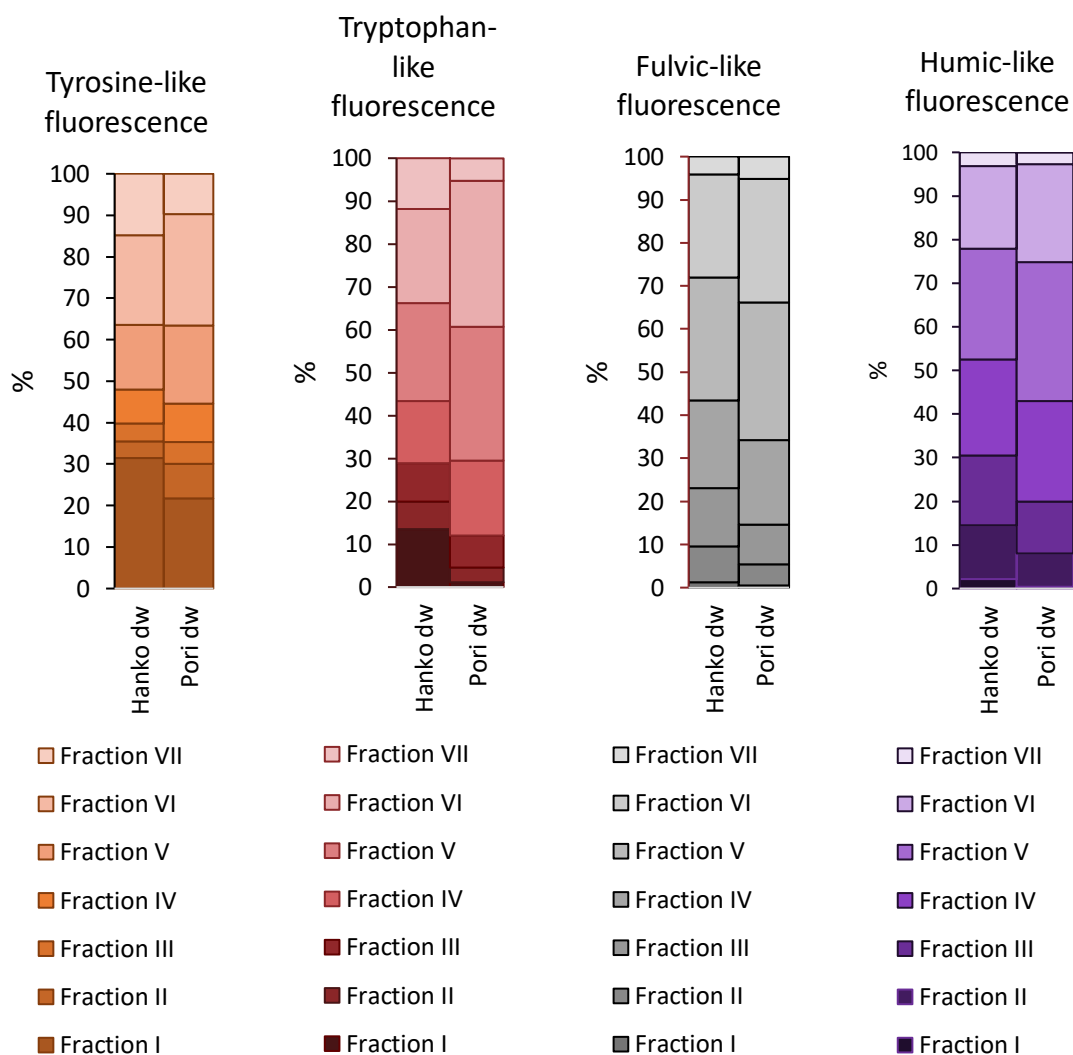


Figure 17. The average molecular weight fractions (%) of ditches and lakes.

When comparing the average molecular weight fractions of ditches and lakes it was noticed that the abundance of Fraction I is high in protein-like fluorescence both in lake and ditch samples. On the other hand Fraction I was somewhat missing in humic- and fulvic-like fluorescence. LMW and IMW fractions dominated the protein-like fluorescence both in lakes and ditches. In fulvic-like fluorescence the LMW and IMW fractions dominated whereas in the humic-like fluorescence HMW and LMW fractions were approximately equally abundance. Ditches had an overall slightly higher abundance of HMW fractions whereas lakes had slightly higher share of LMW fractions in all wavelengths (Figure 17.).

4.9 Drinking water treatment plants

4.9.1 Total and specific fluorescence

Lowest total fluorescence intensities were found from drinking waters of both catchments (Table 2.). The difference was multiple compared to samples from ditches and lakes. Pori dw had slightly higher total fluorescence in all wavelengths compared to Hanko's dw (Figure 13.)

The highest specific tyrosine-like fluorescence among all samples was found in Hanko's drinking water. Hanko's dw had also higher tryptophan-like fluorescence than Pori's dw. On the other hand Pori's dw had slightly higher fulvic- and humic-like specific fluorescence. (Figure 15.)

4.9.2 Relative abundance of MWFs

Both drinking water samples were dominated by LMW fractions (Figure 18.), except humic-like fluorescence of Hanko dw, which was dominated by HMW and IMW fractions. The relative abundance of Fraction I in tyrosine-like fluorescence was high in both drinking waters (Figure 18.) and the relative abundance of Fraction I was high tryptophan-like fluorescence of Hanko's dw.

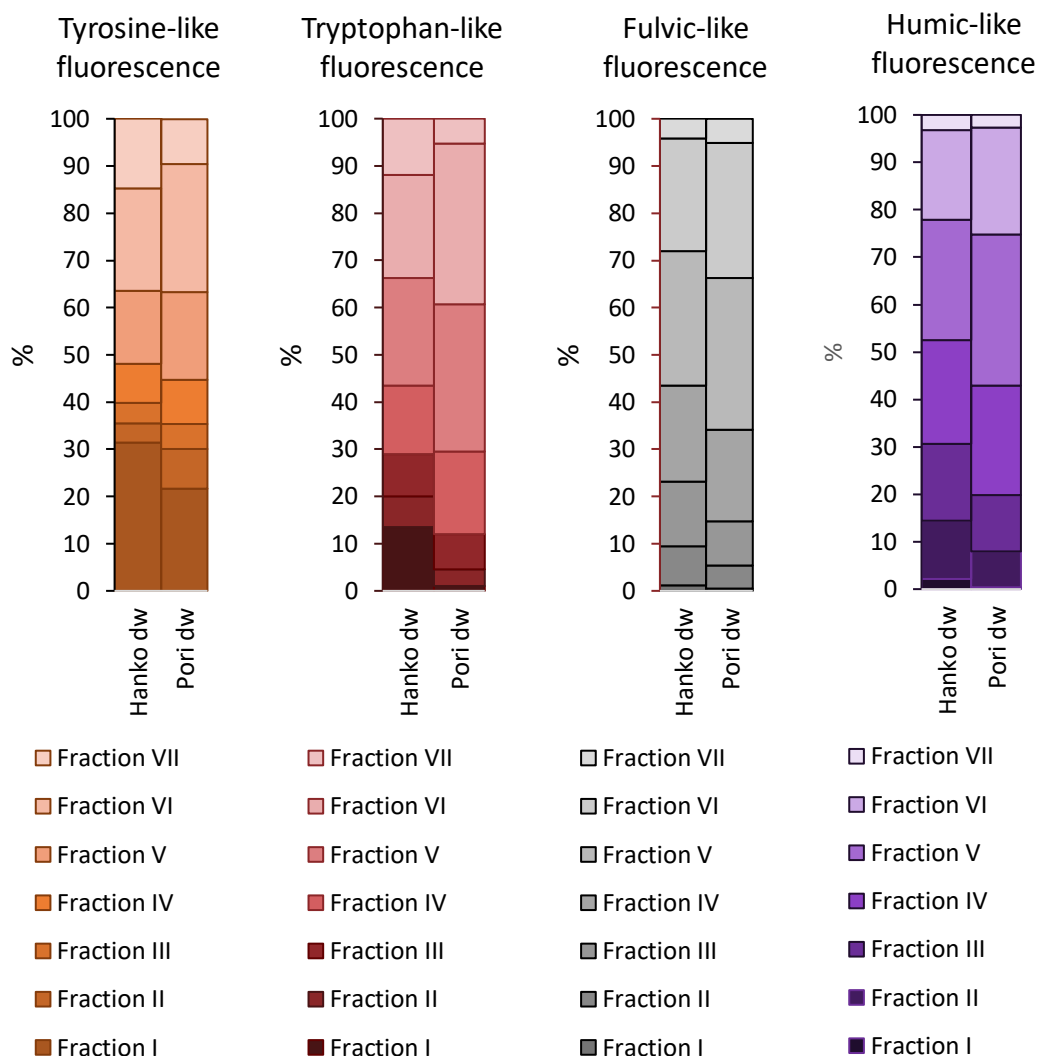


Figure 18. Relative abundance (%) of fluorescent fractions (I-VII) in drinking waters.

5 DISCUSSION

5.1 The land use of the catchments in 2018

The share of forests in both catchments is lower (< 86%) than usually in Finland (Vaahtera et al. 2018). However, this is typical to the more agriculture intensive Southern Finland where the share of forest is commonly around 60% (Tattari et al. 2015).

Gennarbyviken catchment has higher share of agricultural land than in Finland on average (7.8%) (SVT 2018). In Tuurujärvi and Joutsijärvi catchment the share of arable land is on the other hand lower than on average.

In Tuurujärvi and Joutsijärvi catchment the share of wetlands and inland waters is higher than in Gennarbyviken catchment, which can increase the natural load of NOM into the water body (Mattson et al. 2005) and explain the higher humic-like fluorescence compared to Gennarbyviken catchment.

Urban fabric comprises typically around 3% of the total land area in Finland (SVT 2019). In Gennarbyviken the share of urban fabric and industrial, commercial and transport units is around 3.4%. However, in Tuurujärvi and Joutsijärvi catchment the share is less than one percent. Based on these results, it can be said that Gennarbyviken catchment is more influenced by agriculture, industry and urban fabric than Tuurujärvi and Joutsijärvi catchment.

5.2 DOC and TN results

The average concentration of *DOC* in the ditches is somewhat lower than typically in Finnish brooks (*TOC* 20 mg l⁻¹) (Mattson et al. 2003). Especially the ditches of Gennarbyviken catchment have lower *DOC* concentrations than 20 mg l⁻¹ whereas Ahmausoja's *DOC* concentration is notably higher than the average. The average *TN* value is higher than usually in Finnish brooks (*TN* 430 µg l⁻¹) (Mattson et al. 2003). This higher average, however, can be explained by a single notably higher *TN* concentration measured from Ahmausoja.

The higher share of forests and inland waters in Tuurujärvi and Joutsijärvi catchment may be the reason for higher concentrations of *DOC* and *TN* compared to Gennarbyviken catchment. Since the summer of 2018 was exceptionally dry, many ditches of Gennarbyviken were desiccated. Perhaps the drought has also lowered the runoffs from the land to the ditches.

In previous study, the average *DOC* concentration of Ahmausoja has been 20.87 mg l⁻¹ and Jylhäoja 18.61 mg l⁻¹ (Szabo et al. 2008). Also, in this study, Ahmausoja

showed higher *DOC* concentration than Jylhäoja. However, the *DOC* concentration of Ahmausoja (*DOC* 37 mg l⁻¹) measured in this study is remarkably higher than the highest *DOC* concentration measured in previous study by Szabo et al. (2008) (*DOC* 24.97 mg l⁻¹). On the other hand, the *DOC* concentration of Jylhäoja was lower in this study than in previous study (Szabo et al. 2008).

The share of forest in Tuurujärvi and Joutsijärvi catchment has increased since the previous study, which could explain the elevated *DOC* concentration of Ahmausoja. On the other hand, the exceptionally dry summer in 2018 may have affected the Jylhäoja *DOC* concentrations if the loads from inland waters have been significantly lower due to the drought. The same may not be seen Ahmausoja because the lower share of inland waters in Ahmausoja catchment compared to Jylhäoja catchment.

Typically, Finnish lake waters contain on average 7.7 mg l⁻¹ *DOC* and 430 µg l⁻¹ *TN* (Rantakari et al. 2004). In southern coast where both catchments are situated the average concentrations are slightly higher 8.7 mg l⁻¹ *DOC* and 490 µg l⁻¹ *TN* (Rantakari et al. 2004). The average results of this study correspond well to these previous results. In addition, the *DOC* concentrations of Joutsijärvi and Tuurujärvi are in line with the previous study (Joutsijärvi 13.5 mg l⁻¹ *DOC* and Tuurujärvi 9.55 mg l⁻¹ *DOC*) (Szabo et al. 2008).

Typically, the *DOC* concentrations decrease from brooks to lakes. However, in Gennarbyviken catchment the trend was opposite. Perhaps in Gennarbyviken the in-lake processes have significant role in *DOC* formation. In addition, the dry summer may have affected the results.

In case of drinking water, *DOC* concentration is not usually determined. However, in Norway average concentration of 2.2 mg l⁻¹ *DOC* in drinking water has been reported (Keinänen-Toivola et al. 2007). The average *DOC* concentration is in line with this result, although the *DOC* concentration of Hanko's drinking water is notably lower than Pori's drinking water.

The removal of both *DOC* and *TN* from ditches to drinking water was similar kind in both catchments. Since the *DOC* and *TN* concentrations were higher in the ditches and lakes of Tuurujärvi and Joutsijärvi catchment compared to Gennarbyviken

catchment, also the *DOC* and *TN* concentrations in drinking water left higher. In this case, the raw water quality has straight effect on drinking water quality.

5.3 HPSEC results

5.3.1 UVA₂₅₄-area

Total UV₂₅₄ absorbance area of lakes and drinking water is in line with previous studies (11.6 mAU min and 1.1 mAU min, respectively) (Ignatev and Tuhkanen 2019b). However, previous knowledge from ditches was not found.

5.3.2 SUVA

Both Ahmausoja and Jylhäoja ditches contain high aromatic and complex heterogeneous macromolecular organic matter. Especially Ahmausoja has high SUVA value compared to previous results from surface waters SUVA 4.3-5.2 l mg⁻¹ m⁻¹ (Szabo and Tuhkanen 2016) and SUVA 3.4 l mg⁻¹ m⁻¹ (Ignatev and Tuhkanen 2019b).

Lakes and drinking waters in this study show typical SUVA values to surface waters and drinking water (3.4 and 1.1 l mg⁻¹ m⁻¹, respectively) (Ignatev and Tuhkanen 2019b). OM of lakes and drinking water can therefore be considered less aromatic and more homogenous in nature than OM of ditches.

5.3.3 Correlations between *DOC* and other parameters

Strong correlation between *DOC* and UV₂₅₄ absorbance has also been found in previous studies (Szabo et al. 2008). Because of the strong correlation, UVA₂₅₄ could be considered as an indicator of the content of organic carbon in the water samples.

Previous studies show variable correlations between *DOC* and humic- and fulvic-like fluorescence. Stronger correlations are found at natural sites where natural DOM dominates the carbon pool whereas the correlation is poorer at sites with more anthropogenic activity (Baker 2002c, Cumberland and Baker 2007). This trend can also be seen in this study; the correlation is strong in Tuurujärvi and Joutsijärvi

catchment whereas correlations between *DOC* and other parameters cannot be found in Gennarbyviken catchment.

5.3.4 Total and specific fluorescence

Total fluorescence of lakes is more intensive in all Ex/Em wavelengths than measured from Lake Tuomiojärvi in previous study (Ignatev and Tuhkanen 2019b). Differences are largest in humic/fulvic-like fluorescence, where the average fulvic-like fluorescence is 16% and humic-like fluorescence is 20% higher compared to Lake Tuomiojärvi. In protein-like fluorescence, the difference is around 10%.

In addition, compared to previous study from Jyväskylä drinking water treatment plant (Ignatev and Tuhkanen 2019b) drinking waters in this study show more intensive total fluorescence in all Ex/Em wavelengths. The difference is again highest in humic-like fluorescence meaning 54% higher intensity. The differences among other wavelengths are around 30%.

Ahmausoja's high total fluorescence in all Ex/Em wavelengths can be explained by the overall high *DOC* concentration. When normalized with *DOC* Ahmausoja has highest specific humic-like fluorescence and high fulvic-like fluorescence, which could indicate the main source of *DOC* in the catchment is forests. Jylhäoja has also high fulvic- and humic-like specific fluorescence, which is in line with the high share of forest in the catchment. In addition, Jylhäoja has higher protein-like specific fluorescence compared to Ahmausoja. This could be due to the notably higher share of arable land in Jylhäoja catchment. In addition, the increased nutrient inputs from human activities may stimulate the algal growth, which is another source of protein-like organic matter (Fellman et al. 2010).

Among the ditches Gennarbyviken drains have an overall higher protein-like specific fluorescence than Tuurujärvi and Joutsijärvi ditches and lower humic- and fulvic-like specific fluorescence. The higher share of agriculture, industry and urban fabric and lower share of forest in the Gennarbyviken catchment could explain this.

Lakes show no difference among the specific tryptophan-like or humic- and fulvic-like fluorescence. On the other hand, Gennarbyträsket has notably higher specific

tyrosine-like fluorescence than other lakes. This could indicate the human activities, such as agriculture and industry, being a considerable source of organic matter into the lake especially when the other like specific fluorescence is small. On the other hand, tyrosine indicates more degraded peptide material (Fellman et al. 2010). This can be considered as a sign of biological activity and could indicate autochthonous DOM rather than anthropogenic DOM.

Hanko drinking water shows elevated tyrosine-like fluorescence. However, since the overall *DOC* concentration of the Hanko dw is small can the lowest detection limit be reached and produce bias to the result.

5.3.5 MWFs and their relative abundance

Surface waters typically contain from six to eight MWFs (Vuorio et al. 1998, Nissinen et al. 2001, Ignatev and Tuhkanen 2019b) which is consistent with the findings of this study.

HMW and IMW humic fractions are considered the most dominant fractions of surface waters whereas IMW and LMW humic fractions dominate ground waters (Nissinen et al. 2001). This overall trend cannot be seen in this study. However, the abundance of LMW fractions is highest in both drinking waters.

Among the drains tryptophan-, humic- and fulvic-like fluorescence are dominated by HMW and IMW fractions in Tuurujärvi and Joutsijärvi catchment. In Gennarbyviken however IMW and LMW fractions dominate these fluorescences.

The abundance of Fraction I is high in protein-like fluorescence compared to humic/fulvic-like fluorescence in both catchments. This fraction typically consists organic colloids and biopolymers, e.g. polysaccharides with a little proteinic matter and amino sugars (Fabris et al. 2008, Huber et al. 2011), which could explain the high relative abundance in protein-like fluorescence.

Among the lakes humic/and fulvic-like fluorescence is dominated by IMW and LMW fractions whereas protein-like fluorescence is dominated with LMW fractions. In addition, the relative abundance of Fraction I in tyrosine-like

fluorescence is high compared to other type fluorescence. These trends are also seen in previous studies (Ignatev and Tuhkanen 2019b).

In drinking waters LMW fractions dominate although again the abundance of Fraction I, especially in Hanko dw, is high in protein-like fluorescence. Nissinen et al. (2001) have showed that the drinking water treatment process removes the two largest humic fractions shifting molecular size distribution towards smaller molecular size, which can also be seen in this study (Nissinen et al. 2001).

Wilson and Xenopoulos have showed (2009) that DOM from streams contains primarily HMW humic and fulvic acids leached from soil and terrestrial litter, whereas the increasing share of agricultural land reduces these fractions. This leads a proportional increase of lower MW fractions in lakes produced by aquatic microbes. This could explain the observations of this study; higher share of HMW fractions in ditches compared to the lakes and the differences between the two catchments in molecular weight distributions.

6 CONCLUSIONS

In this study, correlations between the catchments land use and NOM characteristics were found. It seems that the organic matter load from the catchment dominated by forest is quantitatively larger and its fluorescence properties are more humic/fulvic-like, whereas the load from the catchment containing more arable land and urban fabric shows more protein-like fluorescence. Based on this research it can be said that the used method, HPSEC with combined UV and fluorescence detection, provides valuable information about the characteristics and origin of organic matter and is therefore suitable analysing organic matter from the catchment to drinking water.

The complex nature of NOM and its dynamics in water bodies brings uncertainty to the interpretation of the results. To gain more information about the effects of

land use on the characteristics of NOM and to validate the method with statistical significance further research is needed. More samples from different catchments and from longer time scales are required so that annual variations and differences between the catchment characteristics can be better taken account. Standard reference samples containing e.g. algal bloom, fertilizers or effluent organic matter could be collected and analysed with HPSEC-UV-fluorescence to get valuable information about the nature of NOM origin from different anthropogenic activities and land use.

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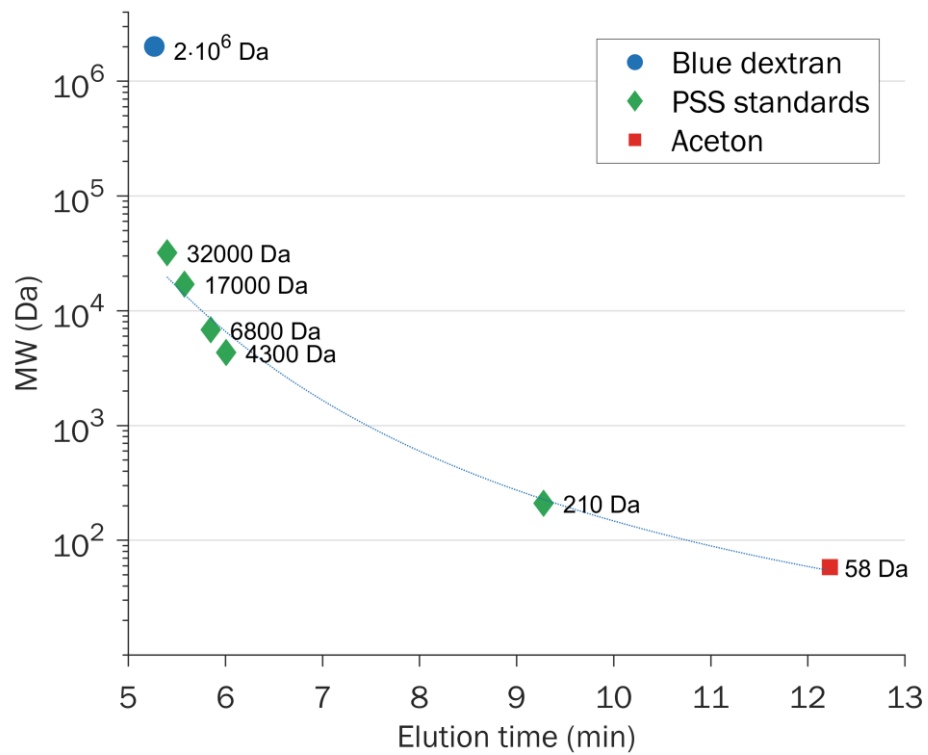
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APPENDIX 1. PSS standard curve



APPENDIX 2. Chromatograms

