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The influence of agricultural gypsum additions on the flocculation of dissolved terrestrial organic matter

University of Helsinki
Master's programme in
Environmental Change and
Global Sustainability
Master's thesis
05/2022
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Työn nimi - Arbetets titel - Title
The influence of agricultural gypsum additions on the flocculation of dissolved terrestrial organic matter

Oppiaine - Läroämne - Subject
ECGS – Environmental change

Työn laji/ Ohjaaja - Arbetets art/Handledare - Level/Instructor	Aika - Datum - Month and year	Sivumäärä - Sidoantal - Number of pages
Master's Thesis / David Thomas, Eero Asmala, Hermanni Kaartokallio	**3.5.2022**	**25 pp. + 1 appendix**

Tiivistelmä - Referat - Abstract

Exchanges between DOM and POM play an important role in the carbon cycling of freshwater ecosystems. Flocculation is a process where aggregates of DOM are formed and moved from a liquid phase to a solid phase. For colloids to form flocs, the negative surface charge of the present organic colloids needs to be destabilized. This process is generally dependent on salinity, but other compounds affecting the ionic strength of the solution can influence these processes.

Gypsum is applied to Finnish fields to reduce the amount of nutrient leaching from agricultural soils. Gypsum treatment effectively reduces the runoff of both particulate and dissolved phosphorus from agricultural fields. Gypsum treatments are performed in areas where the soil contains over 30% clay minerals, making gypsum usage highly relevant in the Archipelago Sea area.

This thesis aimed to find out how gypsum additions influence flocculation processes and DOM characteristics of terrestrial organic matter in boreal rivers. The study focused on the implications of gypsum use in waterways from areas with agricultural activities. Three core experiments were conducted to investigate the effects of several variables on flocculation dynamics.

This study provides some preliminary insights into the influence of gypsum on biogeochemical processes in rivers. Gypsum additions were found to influence the flocculation processes of terrestrial organic matter in boreal aquatic environments. The most notable effect of gypsum additions was the enhanced floc formation, creating an increased flux of organic material onto the sediment surface. This has potential implications for microbial and benthic food webs, meaning that gypsum use is something that may need to be considered when assessing the impact of agriculture on the biogeochemical processes of waterways. Gypsum additions were also found the influence the characteristics of the remaining DOM pool. With the current knowledge, the positive aspects of gypsum use heavily outweigh the negative ones.

Avainsanat - Nyckelord
Gips, akvatisk biogeokemi, lantbruk, löst organiskt material, flockulering

Keywords
Gypsum, aquatic biogeochemistry, agriculture, dissolved organic matter, flocculation

Säilytyspaikka - Förvaringsställe - Where deposited
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Muita tietoja - Övriga uppgifter - Additional information

Tiedekunta - Fakultet - Faculty
Bio- och miljövetenskapliga fakulteten

Tekijä - Författare - Author
Jonas Grönroos

Työn nimi - Arbetets titel - Title
Påverkan av gipstilläggningar i lantbruk på flockulering av löst organiskt material från terrestra system

Oppiaine - Läroämne - Subject
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Tiivistelmä - Referat - Abstract

Utbyten mellan löst organiskt material och partikelformigt organiskt material spelar en viktig roll i kolkretsloppet av sötvattensekosystem. Flockulering är en process där olika aggregat av löst organiskt material formas och flyttas från flytande till fast form. För kolloider att forma flockar, bör negativa ytladdningen av negativt laddade organiska kolloiderna neutraliseras. Denna process är i allmänhet beroende av salthalten av lösningen, men andra föreningar som påverkar lösningens jonstyrka kan även påverka dessa processer.

Gips appliceras för tillfället på finska åker för att minska mängden av växtnäringsläckage från jordbruksmark. Gipsbehandling är ett effektivt sätt at minska läckaget från både partikelformig och löst fosfor från åkrar. Gipsbehandlingar utförs i områden där jordens mineralhalt överskrider 30%, vilket gör användningen av gips mest relevant vid Skärgårdshavet.

Syftet med denna avhandling var att ta reda på hur gipstillsatser påverkar flockuleringsprocesser samt egenskaper av återstående terrestriska lösta organiska materialet i boreala floder. Studien fokuserade på följderna av gipsappliceringar i vattendrag från områden med jordbruksverksamhet. Tre experiment utfördes för att undersöka effekterna av flera variabler på flockuleringsprocesser.

Denna avhandling ger preliminära insikter om hur gips påverkar biogeokemiska processer i floder. Tilläggning av gips visade sig påverka flockuleringsprocesserna av terrestrisk löst organiskt material i boreala vattenvägar. Den mest anmärkningsvärda effekten av gipstillsatser var den ökade halten av partikelformigt organiskt material, vilket skapar ett ökat flöde av organiskt material till sedimentytan. Detta har potentiella implikationer för mikrobiella samt bentiska näringsväv, vilket innebär att gipsappliceringarnas effekt är något som möjligen borde övervägas när man bedömer jordbrukets påverkan på biogeokemiska processer i floder. Gippstillsatser visade sig också påverka egenskaperna av den återstående lösta organiska materialet. Med tillgängliga informationen kan det konstateras att de positiva aspekterna av gippsapplicering starkt överväger de negativa.

Avainsanat - Nyckelord
Gips, akvatisk biogeokemi, lantbruk, löst organiskt material, flockulering

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Abbreviations

AA	Amino acids
BIX	Biological index
CDOM	Coloured dissolved organic matter
CLC	Corine Land Cover classes
DOM	Dissolved organic matter
EEM	Excitation-Emission matrix
EEMS	Excitations/emission matrix spectroscopy
FDOM	Fluorescent dissolved organic matter
HIX	Humification index
HS	Humic substances
MML	National Land Survey of Finland (NLS)
OM	Organic matter
PCHO	Polysaccharides
POM	Particulate organic matter
SYKE	Suomen ympäristökeskus (Finnish Environment Institute)
TSS	Total suspended solids

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1 Introduction

The exchanges between dissolved organic matter (DOM) and particulate organic matter (POM) play an important role in the carbon cycling of freshwater ecosystems, as well as coastal waters (He et al., 2016). Flocculation is an important process in estuaries, as aggregates of dissolved constituents potentially sedimentate to the seafloor, functioning as a removal mechanism for organic and inorganic matter (Eero Asmala et al., 2017; Lisitsyn, 1995)**.** In the context of this thesis, the term flocculation is used to describe all kinds of formation of aggregates in aquatic systems. The term floc is used to describe aggregates formed during the flocculation process.

Both hydrophobic and hydrophilic colloids are present in aquatic systems. The requirement for flocculation is the collision of colloids and a specific set of circumstances that allow the colloids to adhere to each other. Inorganic salts are flocculating agents that act by neutralizing the negative surface charge of hydrophobic charge stabilized colloids, such as the constituents that are commonly found in the DOM pool of aquatic ecosystems (Gregory & O'Melia, 1989). The operational definition for DOM is the cut off at a particle size of 0.2 µm. Anything with a larger particle size is considered POM. This is defined by the pore size of the GF/F filters used in the experiment.

Stocks of organic matter in aquatic systems are showing an increasing trend globally, the main increase coming from increased terrestrial inputs (He et al., 2016). Organic matter contributes to aquatic ecosystems by providing energy to microbial food webs and colonization surfaces for various bacteria, protozoa, and metazoa (Zimmermann-Timm, 2002). DOM also plays a significant role in the environmental behaviour of chemicals such as heavy metals and organic pollutants (Artifon et al., 2019). Estuaries and river discharge points are common sites for the flocculation of organic and inorganic colloids, due to the increase in salinity from brackish-water and marine water bodies.

For colloids to form flocs, the negative surface charge of organic colloids needs to be destabilized. The destabilization is generally dependent on the salinity, which is explained by salt-induced flocculation (Gregory & O'Melia, 1989; Sholkovitz, 1976). Flocculation facilitates rapid shuttling of terrestrial material to seafloor estuaries, thus enhancing the nutrient removal functionality of the so-called coastal filter (Eero Asmala et al., 2017). The organic matter derived from terrestrial environments through riverine inputs supports secondary production in estuaries by providing organic carbon to heterotrophic food webs (Wetzel, 1995). However, the importance of allochthonous carbon inputs for secondary production seems to be largely dependent on the level of primary production in the system (Chanton & Lewis, 2002). Suspended flocs act as a favourable substrate for particle-attached bacteria, which degrade organic matter at a higher rate compared to the free-living bacteria of aquatic systems (Chanton & Lewis, 2002).

Currently, gypsum ($CaSO_4$) is applied to Finnish fields to reduce the amount of nutrient leaching from agricultural soils in the drainage basin of the Archipelago Sea (Ollikainen et al., 2018). Based on previous research done in southern Finland, gypsum treatment effectively reduces the runoff of both particulate and dissolved phosphorus from agricultural fields (Ekholm et al., 2012). In addition to the effectiveness of the treatment, from a socio-economic viewpoint, gypsum treatments are perceived positively by farmers (Kosenius & Ollikainen, 2019; Ollikainen et al., 2020). Gypsum is moderately soluble in water, dissolving into Calcium (Ca^{2+}) and sulphate (SO_4^{2-}) ions. Gypsum treatments are done on soil types which contain over 30% clay minerals (Varsinais-Suomen ELY-Keskus, 2020)**.** Based on information from Ollikainen et al. (2018), 4 tons/ha of farmland is enough to get the desired results in protecting aquatic ecosystems. Currently it is estimated that the effect of one gypsum treatment is expected to have an effect lasting 5 years, after which possible future measures may be re-evaluated. The current KIPSI project aims treat 50 000 – 85 000 hectares of agricultural land using gypsum during 2020-2023 (Kokkonen, 2021).

One concern associated with gypsum use is the possible influence on aquatic ecosystems with low sulphate concentrations. However, in a recent study it was determined that the follow-up sulphate concentrations of gypsum amendments are not high enough to be critical for the local biota (Rantamo et al., 2022). The calculated amount of 4 t/ha would amount to an average of 50 000 – 85 000 TPY of applied gypsum in the Archipelago Sea drainage basin. Gypsum is pH neutral when applied, even when dissolved. The specific effects of gypsum on the qualitative changes of DOM and the naturally occurring flocculation processes in waterways are currently unknown and is the subject of this thesis. The study was connected to MAAMERI project 2020-2022, aimed at strengthening the capability observe the effects of gypsum treatment in the Archipelago Sea and funded by the ministry of the environment where The University of Helsinki and SYKE were partners.

2 Background

2.1 Flocculation pathways and processes

There are several different types of molecules that typically form the DOM pool of aquatic systems based on several environmental factors, e.g., related to the land-use in the drainage basin. The main constituents for DOM are polysaccharides (PCHO), amino acids (AA), and humic substances (HS) (He et al., 2016). HS include compounds such as fulvic acid, humic acid and humin. HS consists of amphiphilic molecules that are made of separate hydrophobic parts composed of polymers, and hydrophilic parts consisting of carboxylic acid groups (Baalousha et al., 2006). Polysaccharides are molecules that are formed by chains of monosaccharide units. Amino acids are made up of amine and carboxylic acid groups. There are several DOM ↔ POM exchange mechanisms, but only the main pathways relevant for the context of this thesis will be introduced in this chapter. Aggregation and coagulation are DOM ↔ POM exchange mechanisms that are mainly driven by Brownian motion (Zimmermann-Timm, 2002). Certain DOM molecules have characteristics that make them prone for sorption, e.g., onto mineral surfaces that are found in soil (Zielińska et al., 2014). Both aggregation and adsorption are reversible processes, with the counterparts of dissolution and desorption. These two abiotic exchange pathways are the most important ones when considering the tested variables in this study.

2.2 Flocculation processes and aquatic food webs

Bacteria have been found on nearly all types of aggregates that have been studied, with the number of bacteria correlating with aggregate size (Simon et al., 2002). Enriched abundances have been reported compared to free-living bacteria of surrounding waters (Simon et al., 2002). At the POM – water interfaces and on the POM itself, pockets of chemical microenvironments are formed with considerably altered conditions when compared to the surrounding water (Zimmermann-Timm, 2002). One interest in this study is the potential impact of total suspended solids (TSS) changes on the microbial food webs of associated aquatic food webs, including streams, rivers, and estuaries, due to the POM being a site for more active and diverse microbial processes in waterways. DOM characteristics are also known to influence the bioavailability of DOM (Asmala et al., 2013).

3 Research questions

The overarching question for this study was: What is the influence of gypsum additions on the flocculation process and DOM characteristics of terrestrial organic matter in boreal rivers? As gypsum is used as a measure to combat eutrophication caused by nutrient leaching from agricultural land, the study focussed on the implications of gypsum use in waterways from areas with agricultural activities.

To answer the main question, 3 core experiments were conducted to investigate the effects of 1) water movement, 2) effects of salinity and 3) effects of gypsum on flocculation and key DOM characteristics of water from two rivers of contrasting mineral and organic matter loads.

The hypothesis for the experiment to determine optimal RPM of flocculator apparatus used in this study was that increasing mixing speed increases floc formation due to a higher probability of collision between colloids. After a certain speed floc formation will be reduced due to turbulent shear increasing floc breakup.

The hypothesis for the salinity experiment was that increasing the salinity increases floc formation due to lowered colloid stability caused by surface charge neutralisation, increasing the collision efficiency. In addition, a decrease in the humic fraction of DOM in post jar test higher salinity treatments should be seen.

The hypothesis for the gypsum experiment was that floc formation increases due to an increase in salinity and ionic strength with dissolved Ca^{2+} and SO_4^{2-}. Dissolved Ca^{2+} ions are capable of neutralizing negatively charged organic colloids to increase collision efficiency in floc formation.

4 Study sites

Water samples were collected from two rivers, Laajoki (60.6486, 21.8573) and Paimionjoki (60.4217, 22.6542), located in the Archipelago Sea drainage basin (Figure 1.).

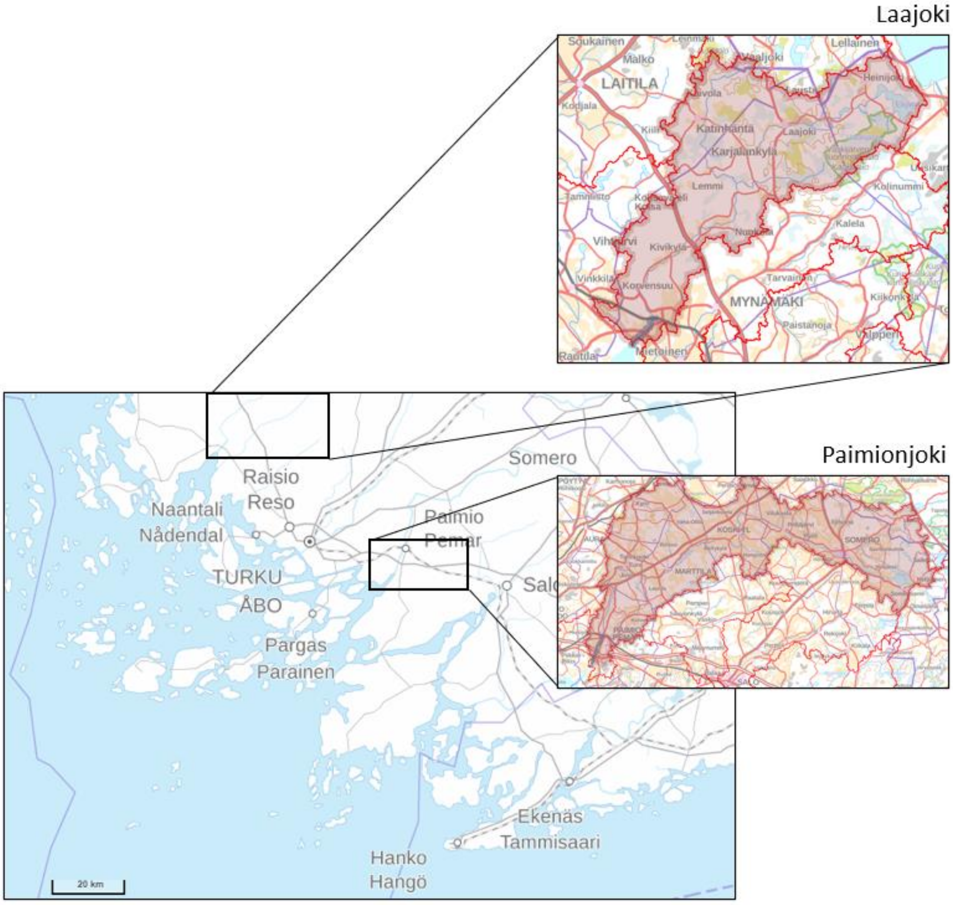


Figure 1. Map of the sampling areas and catchment areas (Modified from SYKE Value tool & MML)

Sampling was conducted at the marked discharge points of the study rivers in early June 2021. Water was collected midstream from a depth of 0.5 m, using a battery driven 12V diaphragm pump. 100 µm pre-screening of river samples was performed on site using a plankton mesh.

The two target river catchments are quite different when looking at the data from SYKE's VALUE-tool that can be used to gain information of drainage basins based on 2018 CLC nomenclature guidelines for land-classes. The greatest difference between the drainage basins for the target rivers were land cover statistics related to agricultural areas as well as forested areas (Table 1.).

River	Laajoki	Paimionjoki
Catchment area (km^2)	398 km^2	1 081 km^2
Land use (%)		
Artificial surfaces	2.8	6
Agricultural areas	16.8	42.2
Forest	70.9	49.1
Inland wetlands	7.6	0.8
Inland waters	1.9	1.9

Table 1. CORINE land cover data for the study rivers

The coverage of Agricultural areas is around 42.2% of the land cover for the Paimionjoki drainage basin, whereas the cover is only around 16.8% for Laajoki. Forest and seminatural areas account for a total of 70.9% coverage of land areas in the Laajoki drainage basin, whereas forest cover accounts for 49.1% of the land cover for Paimionjoki. These two land use classes are the major difference between the target rivers. Laajoki is a typical forest area river which are often associated with humic compounds forming the bulk of the DOM pool (Correll et al., 2001; Cronan et al., 1999). Paimionjoki on the other hand has a significant amount of its drainage basin constituting of arable land, which is typically rich in clay minerals in the study area (Hartikainen, 1982).

Samples were transported to Tvärminne Zoological Station during the same day and subsequently stored in a climate room at 4 °C and double wrapped with plastic bags thereby reducing microbial activity inside the canisters. Quality control was performed daily during the experimental period to ensure that the conductivity was similar inside the canisters throughout the experiments.

5 Materials and methods

The main flocculator experiment was performed using a Velp Scientifica FC6S 6-unit flocculator apparatus (Figure 2.).

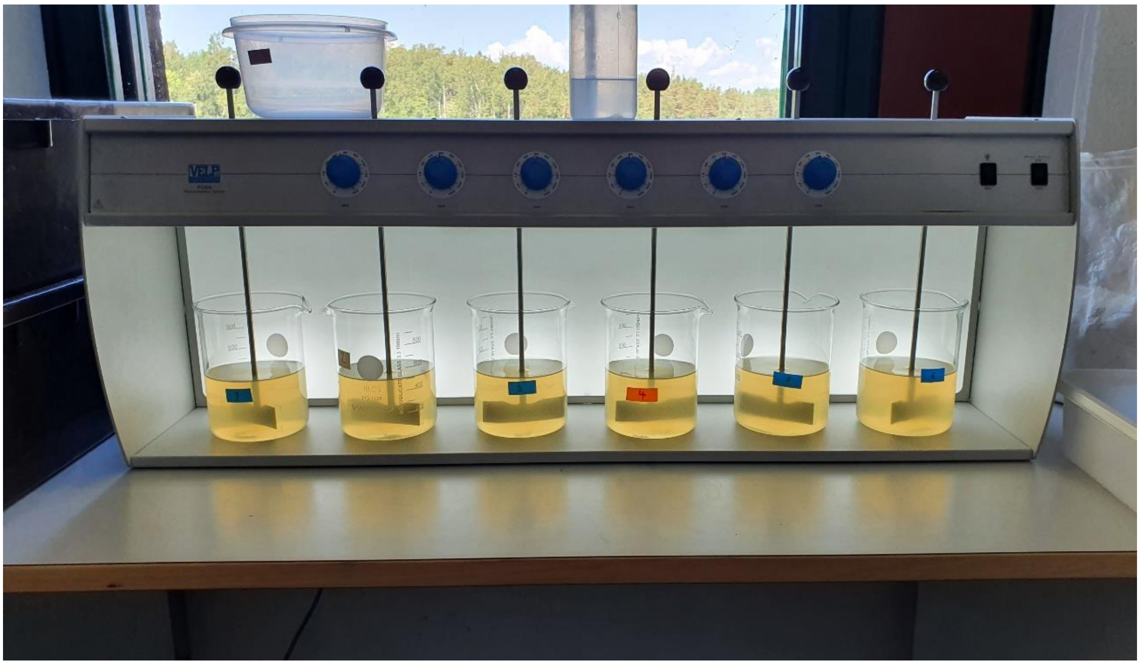


Figure 2. The Velp Scientifica FC6S 6-unit flocculator that was used for the experiment

Artificial seawater was prepared by diluting synthetic sea in ultrapure water. The gypsum solution was prepared by dissolving gypsum ($CaSO_4$*2 H_2O) manufactured by Yara Suomi Oy into ultrapure water, which is intended to be use in agricultural fields to reduce nutrient leaching. The solutions were gently filtered using GF/F filters to avoid particle interference during flocculator test. All experimental units were prepared by diluting target river waters by 10% to keep the conditions as close to natural as possible. The flocculator test duration was 1 hour for each experimental unit, after which the maximum flocculation potential is reached.

A total of three types of flocculator experiments were performed to test the relationship of floc formation and the set experimental parameters. The test variable for the first experiment was physical forcing, to determine the effect of physical forcing on floc formation. An ultrapure artificial sea salt solution was used to set the salinity of each experimental unit for the physical forcing experiment to 2. 0, 30, 60, 90, and 120 RPM settings were used for the experiment. Based on the results of the first experiment, it was determined that the 60 RPM setting will be used for the rest of the experiments.

The test variable for the second experiment was salinity, to determine the influence of salinity on floc formation. Ultrapure artificial sea salt solution was used to create a salinity series of 0, 0.5, 1, 2, 3, and 5.

The test variable for the third experiment was gypsum concentration, to determine the effect of gypsum concentration on floc formation. The gypsum solution was used to create a gypsum concentration series of 0, 0.15, 0.30, 0.59, 0.89, and 1.48 mmol/l.

At the end of the flocculator cycle a set volume of each experimental unit was filtered through precombusted GF/F filters, with each filter having a pore size of around 0.2 µm (Nayar & Chou, 2003). TSS were measured by comparing the weight of filters after filtration against the initial pre-combusted filter weight. The concentration of TSS (mg/l) was calculated by dividing the TSS filter results with the volume of filtered sample water used for the experimental unit in question. Samples were stored at 4 °C and further analysed using spectrophotometric and spectrofluorometric analyses, to determine the nature of the coloured dissolved organic matter (CDOM) and fluorescent dissolved organic matter (FDOM) found in the experimental units. Spectrophotometric analyses of CDOM were performed over the range of 200-800 nm after the flocculator experiment.

Excitation/emission matrices (EEM) of fluorescence were constructed for the experimental units using excitation wavelengths 220-450 nm with 5 nm increments after the flocculator experiment. EEM peaks T, A, M, and C were used to further determine the nature of the DOM found in the samples, as well as the humification (HIX) and biological (BIX) indices. Peak T being the tryptophan/protein-like peak, peak A the primary humic peak stimulated by UV excitation, peak M the marine humic-like peak, and peak C the humic-like peak stimulated by visible excitation (Coble, 1996). The fluorescence indices are commonly used to further characterize the DOM present in the samples (Gabor et al., 2014). The spectral slopes $S_{275-295}$ and $S_{350-400}$ were calculated by using linear regression of the log transformed absorption spectra for the corresponding wavelengths (Helms et al., 2008).

For statistics, the Mann-Whitney U test and Kruskal-Wallis one-way analysis of variance were used to test the null hypothesis that the samples from different treatments originated from the same distribution. A Dunn's test of multiple comparisons was performed for significant Kruskal-Wallis tests, where p-values were adjusted with the Benjamini-Hochberg method.

6 Results

The study rivers displayed different initial values for most of the study variables (Table 2.).

River	Laajoki	Paimonjoki
TSS [mg/l]	9.73	36.99
a254 [Absorption coefficient/m]	159.57	161.93
Peak A [R.U.]	0.99	0.77
Peak T [R.U.]	0.05	0.07
HIX	43.27	15.29
$S_{275\text{-}295}$ [nm-1]	0.008	0.007

Table 2. TSS and average DOM variables for Laajoki and Paimionjoki river waters. TSS : Total suspended solids. a254 : CDOM absorption coefficient for 254 nm. Peak A: humic-like fluorescence peak A. Peak T: tryptophan/protein-like fluorescence peak T. HIX : Humification index. $S_{275\text{-}295}$: Nonlinear fit to the absorption spectrum over the wavelength range.

The biggest differences were seen in the initial TSS concentration, as well as the humic-like fluorescence variables. In a previous study related to impacts of land use cover on the DOM export from boreal soils, the proportion particulate matter has been observed to increase with increasing human activity (Mattsson et al., 2005). The $S_{275\text{-}295}$ values indicate that the size of the dissolved molecules is of similar class in both study rivers.

6.1 Salinity experiment

When looking at the flocculator test results for Laajoki and Paimionjoki, a seemingly increasing trend TSS with an increase in salinity can be seen (Fig. 3a & 3b).

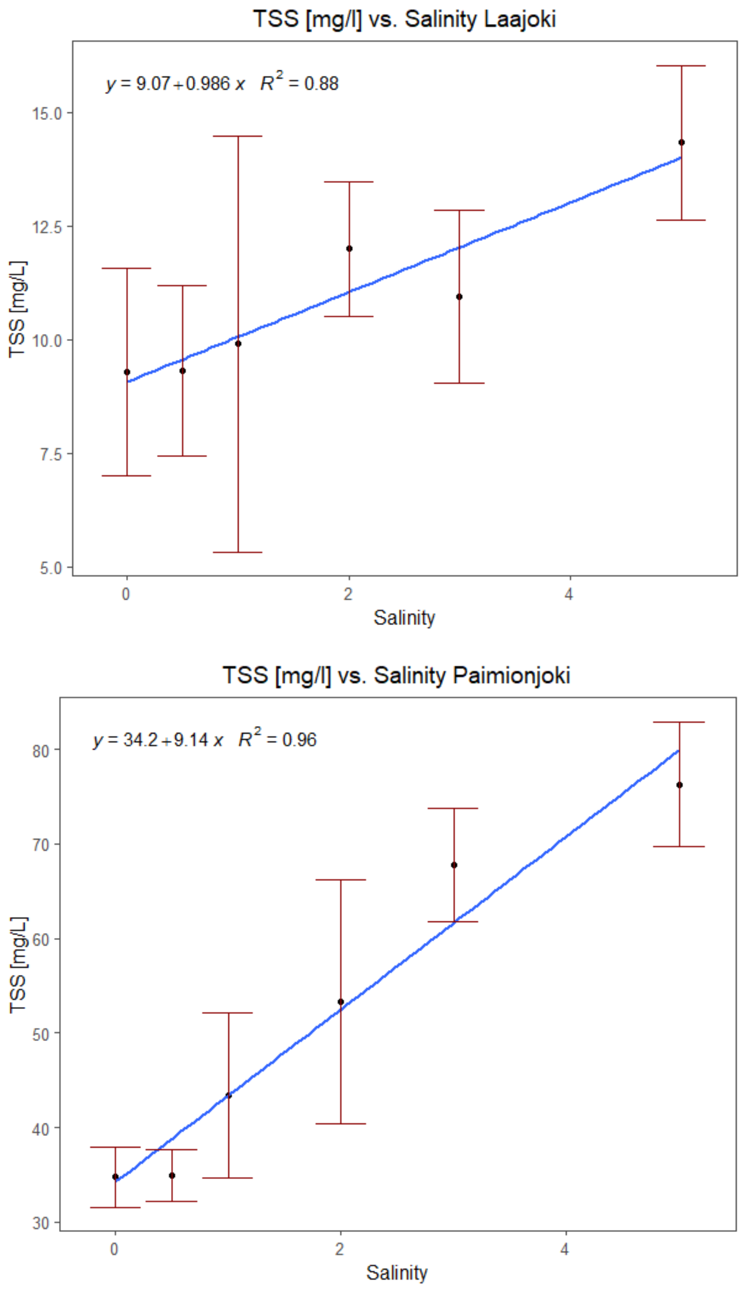


Figure 3a. & 3b. TSS vs. Salinity for Laajoki and Paimionjoki samples for the salinity experiment. Total suspended solids calculated from dried filter masses. Each data point represents the mean of three replicates for each treatment, error bars represent standard deviation.

When comparing the concentrations of TSS between Laajoki and Paimionjoki, the Paimionjoki TSS concentrations are higher for all the treatments. The mean TSS concentrations of the control replicates for Paimionjoki were over threefold higher when compared to Laajoki control treatments. Generally, the Laajoki samples did not behave as expected during the salinity runs, meaning that no salinity thresholds for flocculation could be evaluated based on the experiment. It was also difficult to visually assess the differences in floc formation between the experimental units except between the controls and the maximum salinity treatments. No specific thresholds for salinities were discovered for Paimionjoki samples either, with a strong linear relationship between the salinity and TSS. The variation was however considerably higher for some treatments, especially around salinities of 1-2, making it more difficult to detect thresholds. It can also be seen that TSS values did not increase for the 0.5 salinity treatments when compared to the controls.

The optical analyses of the salinity run samples provided some insights into the CDOM characteristics of each sample. The absorbance coefficient for absorbance at 254 nm was calculated by adjusting the raw data (Fig. 4).

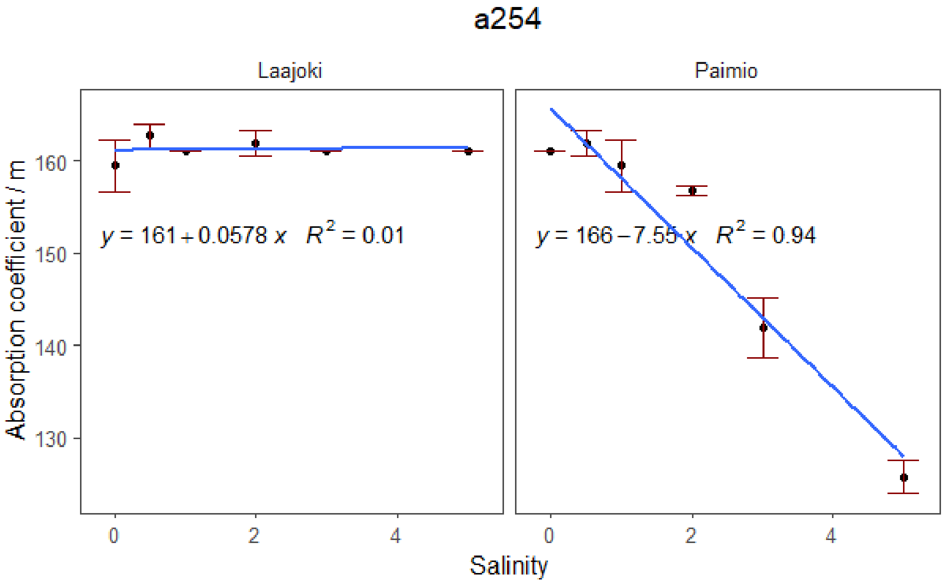


Figure 4. Absorption coefficients for Paimionjoki and Laajoki samples at 254 nm vs. salinity. Each data point represents the mean value of three replicates with error bars showing standard deviation.

The absorption coefficient at 254 nm represents the fraction of the DOM pool that absorbs UV-light. In this study the absorption coefficient is used as proxy for the concentration of this DOM fraction. Paimionjoki samples show a clear decreasing trend in absorption coefficient values with increasing salinity at 254 nm, no clear trend found for Laajoki treatments. When Paimionjoki 254 absorption coefficient results are observed closer, there seems to be a salinity threshold at 1.5-2 whereafter the absorption coefficient decrease rate increases. However, a linear trend line gave the best fit.

From the commonly used fluorescence peaks, peak A was chosen as a study variable as it functions as a proxy for humic-like terrestrially derived matter in the DOM pool. For the primary humic peak A, there was a clear increase in the values with increasing salinity of experimental units (Figure 5.).

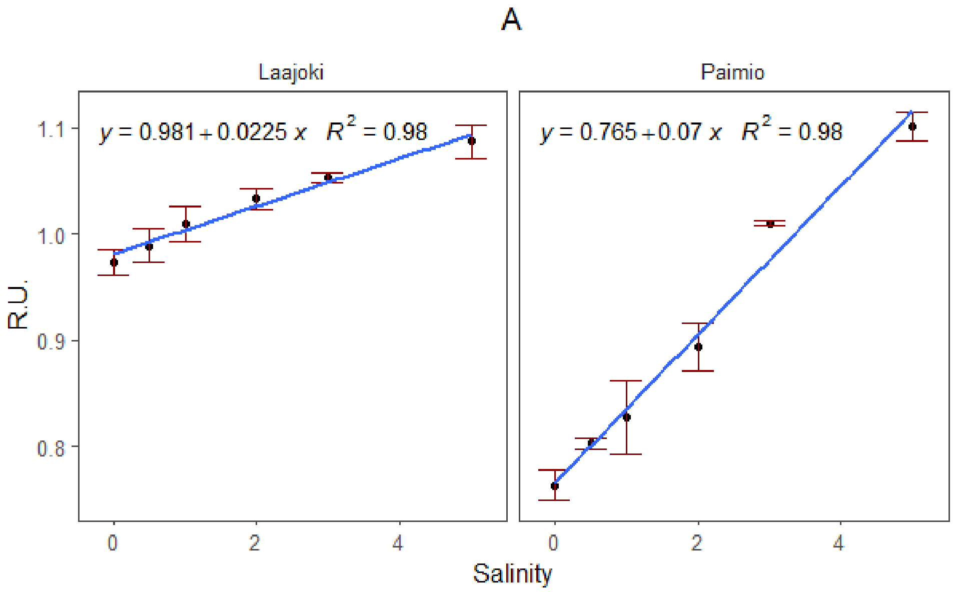


Figure 5. EEM A peak values vs. salinity. The unit for the fluorescence peak values is measured in Raman units (R.U.). Each data point represents the mean value of three replicates with error bars showing standard deviation.

It can be observed that the proportional increase of A values was higher for Paimionjoki treatments, as the Laajoki values where higher for control treatments. The difference in the initial values aligns with the information about the drainage basins of the rivers, and Laajoki can be expected to have a higher concentration of terrestrially derived humic content due to the higher occurrence of forested areas and wetlands.

The protein-like peak T was chosen as a study value, and functions as a proxy for the lability of the DOM pool in this study. For the protein-like peak T, seemingly opposite trends were found for the two target rivers (Fig 6.).

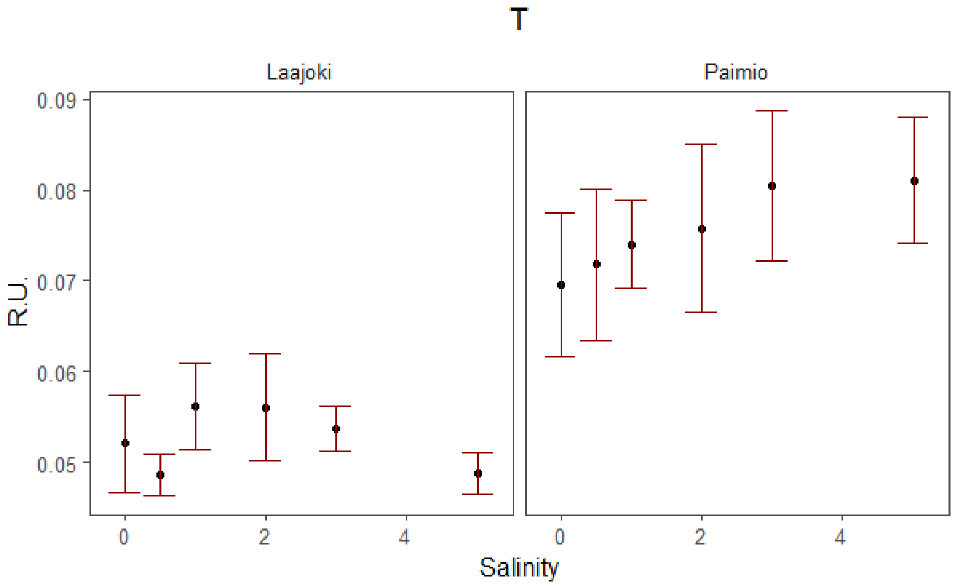


Figure 6. T peak values vs. salinity. The unit for the fluorescence peak values is measured in Raman units (R.U.). Each data point represents the mean value of three replicates with error bars showing standard deviation.

For Laajoki samples, there is an initial decrease followed by an increase in the T values. However, for the highest salinity treatment the values were lower than for the control units. For Paimionjoki samples, there is a clear increasing trend of T values with increasing salinity.

The HIX values had a very different slope for the target rivers, with Paimionjoki samples displaying twice the HIX value increase compared to Laajoki samples (Fig. 7).

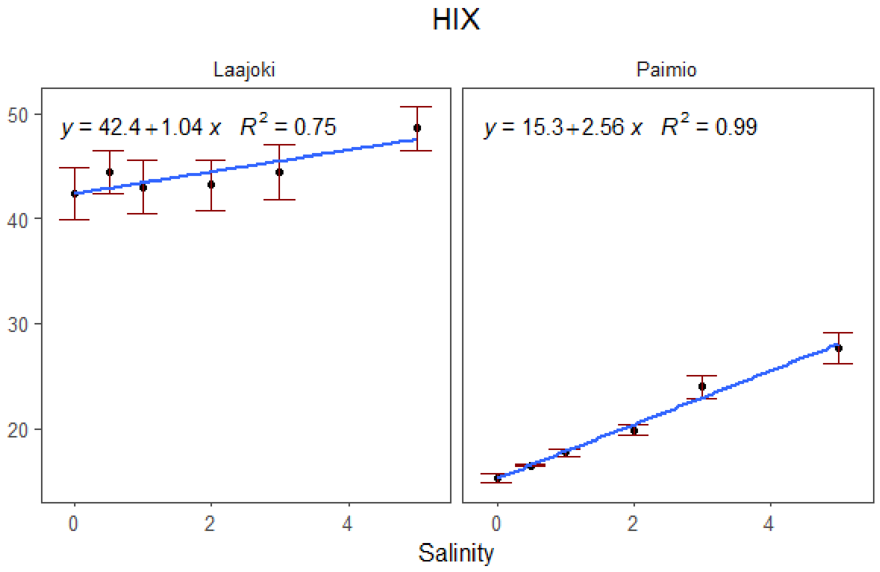


Figure 7. Humification index values vs. salinity. Each data point represents the mean value of thee replicates with error bars showing standard deviation.

HIX values showed an increasing trend with salinity for both target rivers. The increase for Laajoki samples is not as prominent as for Paimionjoki, but the initial values are considerably higher for Laajoki samples.

The $S_{275-295}$ slope was chosen as a study variable, as it functions as a proxy for molecular weight. The $S_{275-295}$ values showed a clear increasing trend for Paimionjoki samples, with no seemingly clear trend for Laajoki samples (Fig. 8).

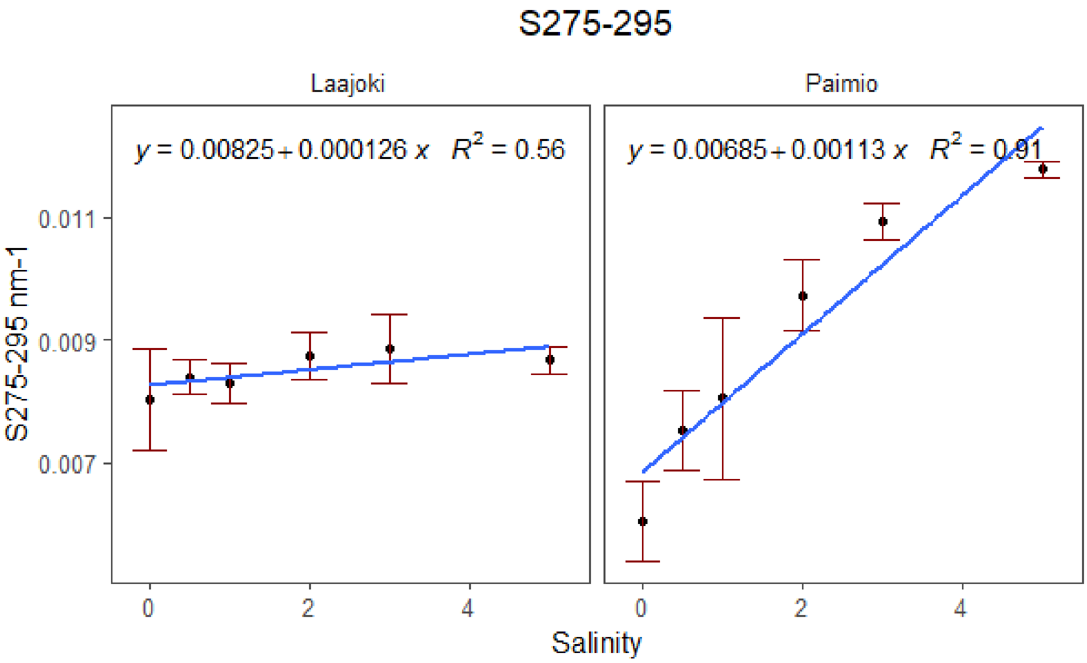
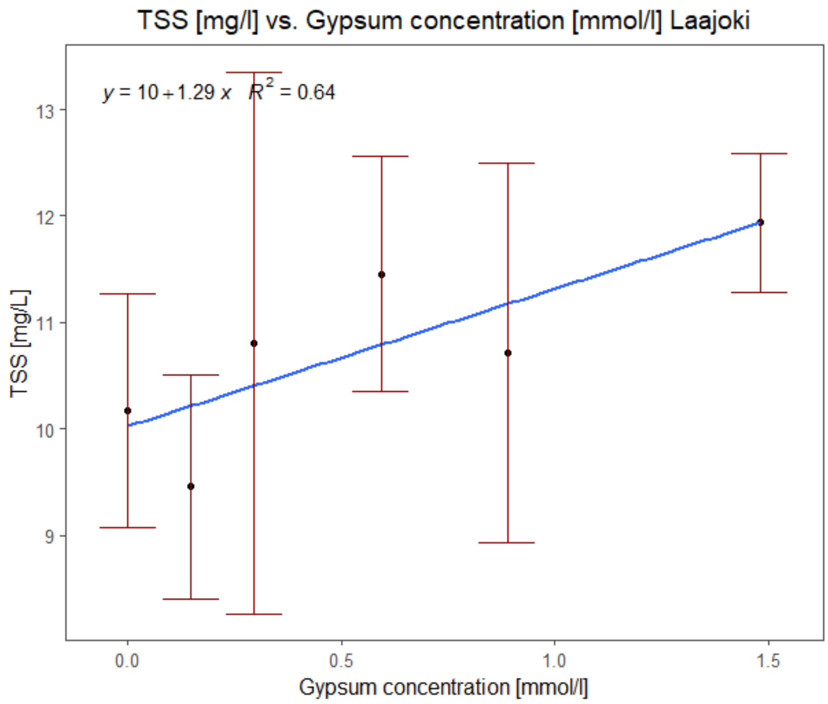


Figure 8. $S_{275-295}$ values vs. salinity. The values are measured in nm^{-1}. Each data point represents the mean of three replicates with error bars showing standard deviation.

For the Paimionjoki treatments, it seems that the trend follows a relatively linear increase in the values with increasing salinity. The molecule sizes are larger for Paimionjoki in the control treatments but the increasing values with higher salinities suggest that larger molecules are selectively being removed from the dissolved phase.

6.2 Gypsum experiment

For Laajoki samples, a visual difference for the experimental units during the flocculation experiment, when compared to the control treatments, was only detected for the 1.480 mmol/l gypsum concentration treatment. The TSS values were also higher for the highest gypsum treatments when compared to the controls, but no strong correlation between gypsum concentrations and TSS was found. For Paimionjoki samples, a clear linear trend was found between the gypsum concentration and TSS (Fig. 9a. & 9b.).



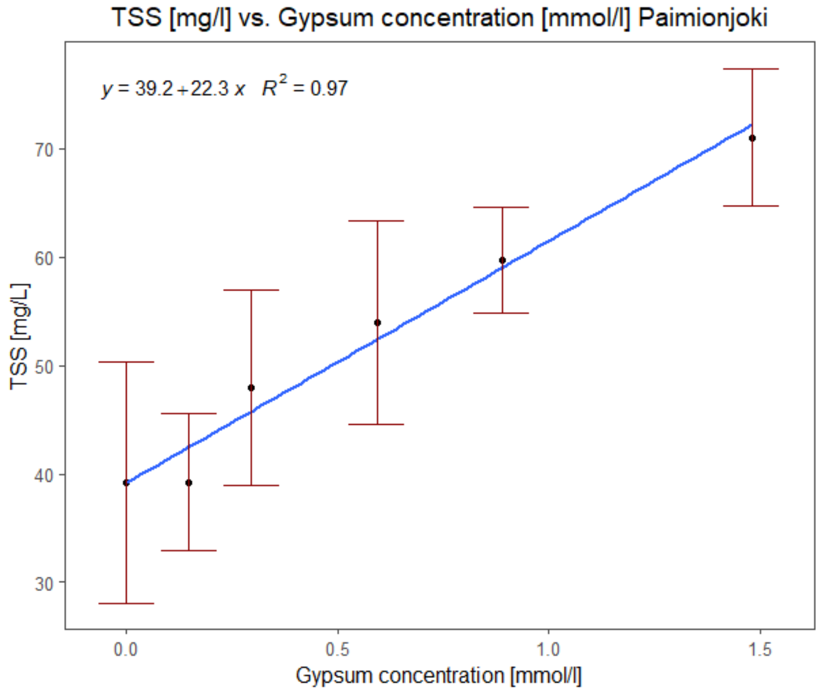


Figure 9a. & 9b. TSS vs. Gypsum concentration for Laajoki and Paimionjoki samples for the gypsum experiment. Total suspended solids calculated from dried filter masses. Each data point represents the mean of six replicates for each treatment, error bars represent standard deviation.

Most variance was detected in the lower concentration treatments, which might be most volatile and dynamic conditions where there is not a great difference between floc breakup and formation in the used RPM setting.

Based on the optical analyses, different trends were recognised when looking at the different CDOM parameters used for this experiment the absorbance coefficients for absorbance at wavelengths 254 nm was calculated as a proxy for the concentration of UV absorbing DOM (Fig. 10).

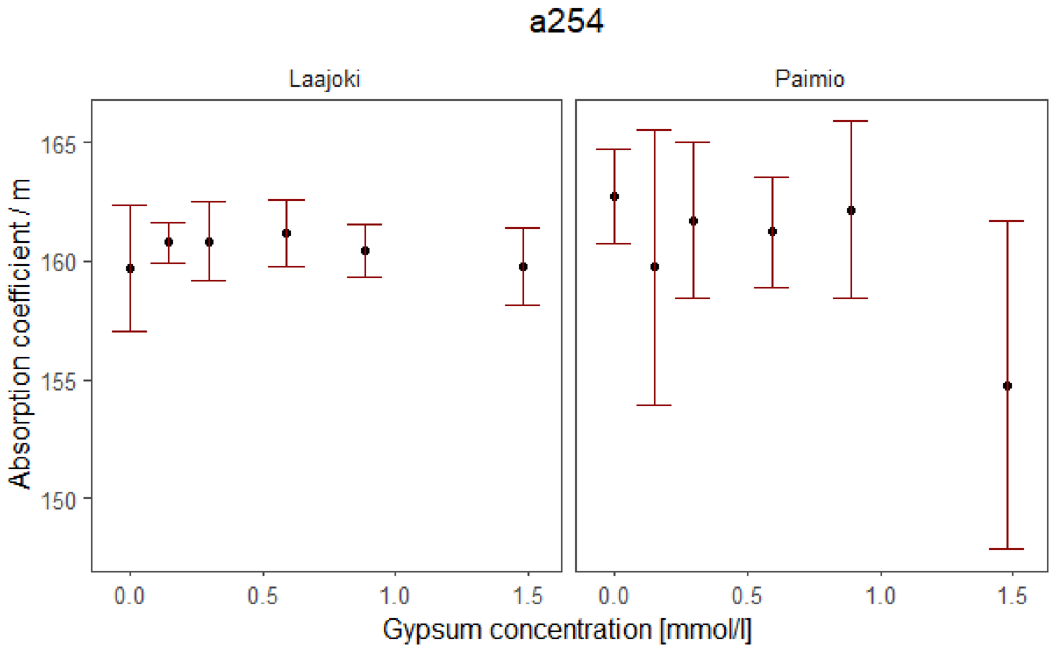


Figure 10a. & 10b. Absorption coefficients for Paimionjoki and Laajoki samples at 254 nm vs. salinity. Each data point represents the mean value of six replicates with error bars showing standard deviation.

As in the salinity experiment, selective flocculation of UV absorbing components was not detected. For the Paimionjoki samples, the variance was higher than for the salinity treatments, but there was a difference between the control units and the 1.48 mmol/l gypsum concentration replicates.

As expected, the primary Cobble peak A values were higher for the samples from Laajoki, due to the strong humificating effect of the surrounding forest areas (Fig. 11).

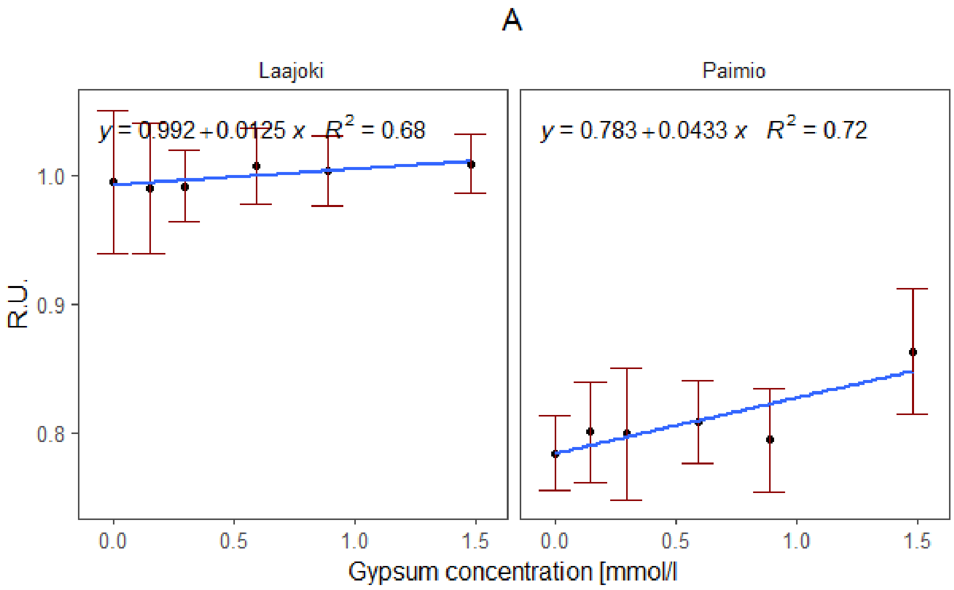


Figure 11. EEM A peak values vs. gypsum concentration. The unit for the fluorescence peak values is measured in Raman units (R.U.). Each data point represents the mean value of six replicates with error bars showing standard deviation.

In general, an increase in the value of A peaks correlated with an increase in the gypsum concentration of the samples, suggesting an increase in the humic-like fluorescence with increasing gypsum concentration.

For the protein-like peak T, no strong correlation can be seen with increasing gypsum concentrations in the Laajoki samples, suggesting that there is no strong relationship between the lability of the DOM and gypsum concentrations with the used experimental setup (Fig. 12).

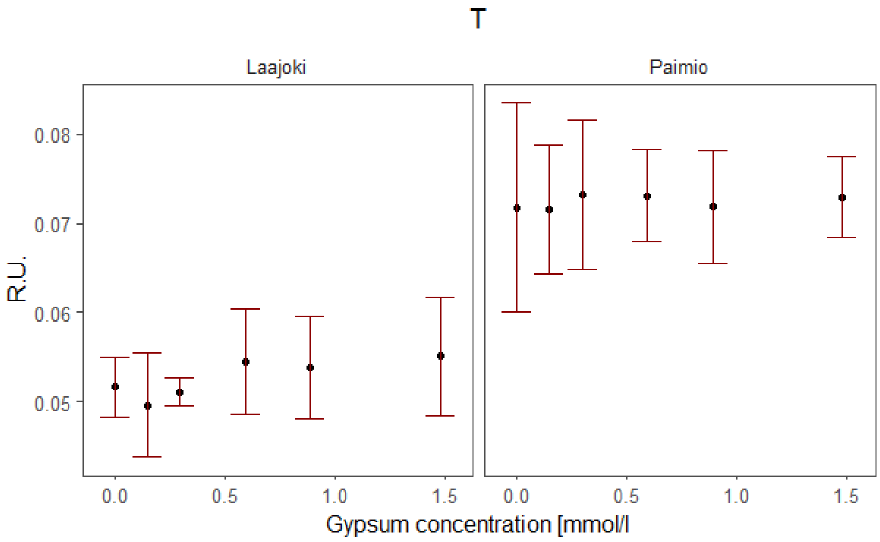


Figure 12. EEM T peak values vs. gypsum concentration. The unit for the fluorescence peak values is measured in Raman units (R.U.). Each data point represents the mean value of six replicates with error bars showing standard deviation.

The HIX values displayed an opposite trend when comparing the values for the target rivers, no strong correlation was found for the Laajoki samples (Fig. 13).

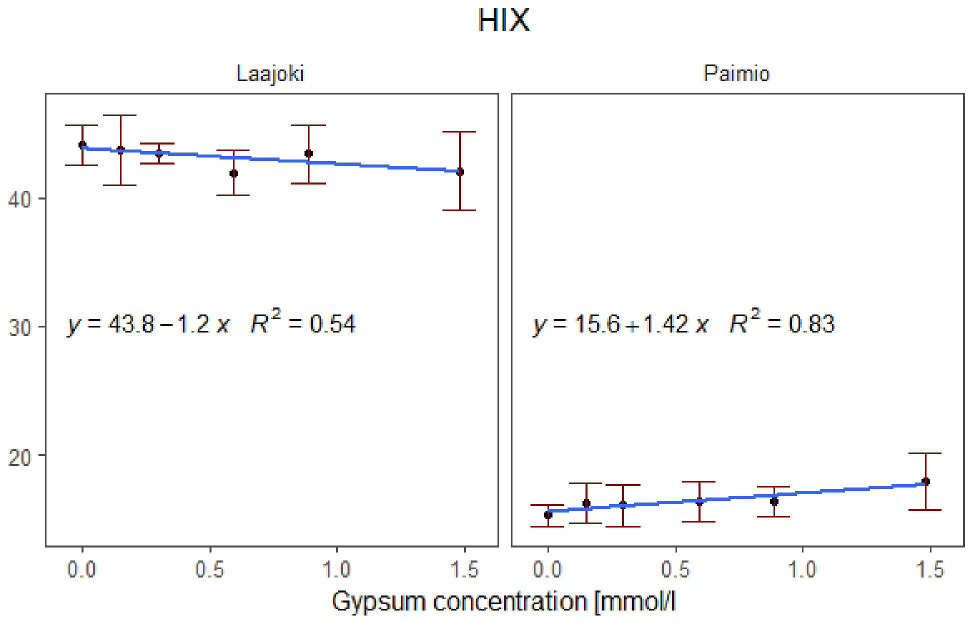


Figure 13. Humification index values vs. gypsum concentration. Each data point represents the mean value of six replicates with error bars showing standard deviation.

The values were higher for the Laajoki samples, which is to be expected due to the humic nature of the river. A decreasing trend of the HIX can be seen with increasing gypsum concentrations. For Paimionjoki samples, an increase in the HIX can be seen with increasing gypsum concentrations.

In addition to individual Cobble peaks and the relevant indices, a response was detected in some relevant spectral slope variables. For $S_{275-295}$, both target rivers showed increasing values in response an increased gypsum concentration (Fig. 14). For Paimionjoki samples, it should be noted that the variation between replicants was considerable.

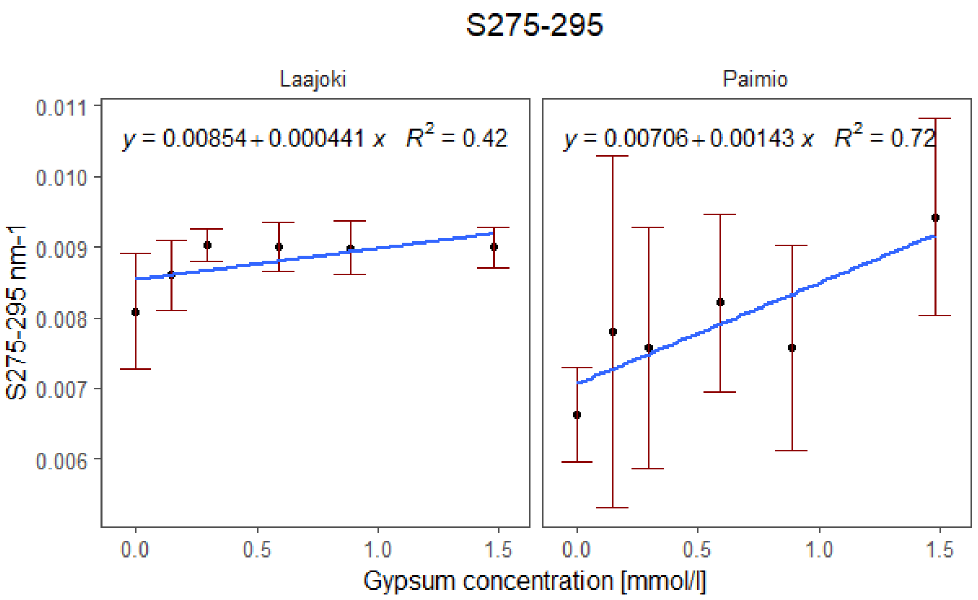


Figure 14. $S_{275\text{-}295}$ vs. gypsum concentration. Each data point represents the mean value of six replicates with error bars showing standard deviation.

7 Discussion

The results of the experiments the two study rivers present two different types of narratives in response to salinity and gypsum concentration changes, as well as displaying the differences observed in landscapes. The particulate matter content was almost fourfold higher in initial Paimionjoki water samples, and the CDOM profiles of the study rivers were quite different. Laajoki samples showed more humic-like characteristics to Paimionjoki, but the humic-like fluorescence response to gypsum was more noticeable in Paimionjoki gypsum samples.

The first hypothesis was that increasing the salinity of the experimental units will increase the floc formation due to lowered colloid stability. For both study rivers, the general trend was that increasing the salinity increased the TSS, in a relatively linear fashion. This is in line with studies related to salt-induced flocculation, but the trend for the Paimionjoki samples differs from the Laajoki samples and the results of other studies (Asmala et al., 2014), showing a constant increase in TSS starting at salinity 1. For Laajoki samples the highest variance among replicates occurred in the salinity 1 treatments, suggesting a salinity where equilibrium reactions are most prone to carry out to both directions and the formed flocs are least stable. Similarly, for the Paimionjoki samples the highest variance in the samples occurred in the salinity 1 and 2 treatments.

From the CDOM absorption coefficient differences in the salinity experiments it can be determined that the observed change in the remaining DOM pool varied considerably between Laajoki and Paimionjoki. The absorption coefficient at 254 nm remained relatively stable in the Laajoki samples, indicating that the concentration of CDOM remains in a similar range independent of the salinity. For Paimionjoki, increases in salinity decreased the concentration of UV absorbing compounds in the samples, suggesting that this fraction of the DOM pool is rapidly flocculating and removed from the dissolved phase as a response to increases in salinity. When comparing the CDOM absorption coefficients values to other studies the values are quite high (Asmala et al., 2018). The study sites in the Asmala et al. 2018 study are however from Denmark, which may be slightly different from more northern boreal areas in terms of the humic content of DOM. Other studies from Finnish rivers have however found 254 nm absorbance coefficients in the similar range, with a trend of decreasing values with increasing salinity (Asmala et al., 2014).

When comparing the protein-like T peak values to Asmala et al. 2018, the stream values are considerably higher in the Asmala study. The results are closer to values gathered from the outer estuary areas, suggesting low lability of DOM in both study sites. The results point out that there is an increase in the humic fluorescence (peak A) in the samples, which suggests a physical change in the remaining DOM pool altering the electrochemical properties of the fluorophores. Fluorescence emission spectra from humic substances is known to be very broad and unstructured, with complex charge-transfer interactions (Sharpless & Blough, 2014). When compared to Asmala et al. 2018, the HIX values are in the same magnitude as values recorded from streams in mid-May. As HIX is acquired by dividing the emissions intensity between 435-480 region by the intensity in the 300-345 at an excitation wavelength of 254 nm (Ohno, 2002), the results show that the proportion of the 435-480 compared to the 300-345 nm region is increasing with increasing salinity .

As $S_{275-295}$ values have an inverse relationship to the molecular weight (Helms et al., 2008), the results from the salinity experiments for the Paimionjoki samples display that larger molecules are more prone to flocculation. The slope ratio values for Paimionjoki seem to follow a relatively linear increase for the tested salinities. When comparing the results to Asmala et al. 2013, the initial values are around 4 μm^{-1} lower, even when compared to values acquired from river endmembers. This suggests that the molecular size for the DOM in both target rivers is relatively large, consisting mainly of higher complexity/aromaticity organic compounds.

The second hypothesis was that increasing the gypsum concentration will increase floc formation due to increased ionic strength. The target rivers responded very in very different ways to the gypsum treatments. A considerable increase in the TSS for the Laajoki samples was only detected in the highest gypsum concentrations, with a very high variability in the lower gypsum concentration treatments. For the Paimionjoki samples, a clear linear increase of TSS was found as a response to increasing gypsum concentration. A possible explanation for the drastic differences in the responses between the two rivers is the difference in the landscape. It seems that gypsum has a higher influence on the flocculation processes of soils rich in clay minerals, such as agricultural land**.** Agricultural land is a major constituent of the Paimionjoki drainage basin, whereas Laajoki drainage basin is mainly constituted of forested areas. When comparing to the TSS values of the salinity experiment, the TSS values for the control treatments of both study rivers had around 10 % higher values. Overall, the general trend for both experiments were similar, but with higher variability in the gypsum experiments.

The CDOM absorption coefficient results for the gypsum treatments were similar in Laajoki samples, however, the variance was higher for the gypsum experiment. For the Paimionjoki samples the nonlinear trend is not as pronounced as for the salinity experiments, and the variance was also higher for the gypsum experiments. For the protein-like peak T, no significant trend was detected in the gypsum experiment. Peak A results display a similar trend to the results of the salinity experiment, suggesting a physical change in the remaining DOM pool.

When looking at the fluorescence indices of the gypsum experiment, there is a clear difference in the trend for the Laajoki samples. HIX increased with increasing salinity but decreased with increasing gypsum concentration. $S_{275-295}$ values for the Laajoki samples suggest a logarithmic relationship between the gypsum concentration and $S_{275-295}$ values.

The $S_{275-295}$ values for the Paimionjoki samples display a relatively linear increase, with changes in the values throughout the whole concentration series. This suggests some degree of selective flocculation where larger molecules are being flocculated at a higher rate than smaller ones.

7.1 Effect of gypsum use on flocculation and DOM quality

When assessing the use of gypsum for reduced nutrient loading of aquatic ecosystems, the most important thing to consider is the influence of gypsum use and its alignment with the goals of gypsum usage in agricultural lands. As the main goal is to reduce nutrient leaching from agricultural soils, the accelerating effect of gypsum concentrations on the aggregate formation in fluvial systems that are under the influence of agriculture. One key characteristic of fluvial systems under agricultural influence could be the presence of clay minerals. The heterogenous flocculation processes involve minerals, different particulate colloids and constituents of the OM pool, leading to a larger range of active flocculation mechanisms when compared to the Laajoki samples. When comparing the optical data for the target rivers, the difference in the 254 nm absorbance coefficients indicates a higher rate of flocculation for humic substances for the Paimionjoki samples. As mentioned, amphiphilic compounds such as HS and AA have a wide array of adsorption forms due to having both hydrophobic and hydrophilic parts. The TSM values are trifold for Paimionjoki compared to Laajoki, indicating that there is more material both dissolved and particulate, readily available for flocculation. The initial thought was that Laajoki samples have a higher humic content due to the nature of the drainage basin. Based on the 254 nm absorbance coefficients for the samples the controls for both target rivers have very similar values, indicating a similar concentration of DOC. Wilson and Xenopoulos discovered that changes in the quality of terrigenous DOC is partially related to agricultural land use, indicating that the structural complexity of OM decreased with decreasing wetland/cropland ratios. Laajoki samples have a higher percentage of wetlands in the riparian zone, which would imply higher complexity/aromaticity of DOM.

It should be noted that in shallow turbid environments, strong hydrodynamic forcing creates a different type of environment for aggregate formation and breakup when compared to pelagic systems. In general, the suspended matter load is much higher for riverine systems when compared to marine and estuarine ones, combined with a higher proportion of the production being supported by aggregates (Simon et al., 2002). The movement of DOC and POC is in general very different in fluvial networks, where the OM is subject to hydrodynamic lift and drag forces in addition to gravitational settling (Battin et al., 2008). In terms of transport processes, horizontal transport is considerably more significant than vertical transport in fluvial networks (Zimmermann-Timm, 2002).

7.2 Variance and errors

When considering the experiment, there are several notes to make related to possible errors and large variances in some of the results, especially for the low and mid concentration replicates. This is possibly hinting that at the lower gypsum concentrations and salinities the conditions are most chaotic, meaning the reversible exchange processes between DOM and POM are preceding both ways in a more balanced equilibrium than the controls or highest concentration/salinity treatments. In addition to this, the variance is quite high for some of the absorbance parameters, where for some instances it is difficult to conclude significant trends with changes in the experimental treatments. The scope of the methods comes with a specific limitation, mainly related to the method not being capable of characterizing the non-chromophoric fraction of DOM. However, as flocculation is known to be a selective process, it does not limit the interpretation of results as much as one might expect (Forsgren et al., 1996).

8 Conclusions

Gypsum additions influence the flocculation processes of terrestrial organic matter in boreal aquatic environments, with Paimionjoki samples showing a strong correlation between gypsum concentration and TSS concentrations. Gypsum use is something that needs to be considered when looking at flocculation processes in agricultural waterways where gypsum is applied to the fields in the catchment area. The clearest relationship discovered in the study was the relationship between TSS and gypsum concentrations for the Paimionjoki samples and this river is the more interesting one due to the high abundance of agricultural land in the drainage basin of the river. Based on the optical analyses conducted for the samples, gypsum concentrations influence the characteristics of the remaining DOM pool as well. Absorbance data for 254 suggests some degree of selective flocculation, as well as the $S_{275-295}$ data. As previously stated, the humic-like fluorescence increased for all the samples, which is an indication of physical changes in the present

DOM. As the experimental method included filtering of the samples, it is not possible that the concentration of humic-like molecules could have increased.

As the goal of the gypsum used in agricultural lands is to reduce eutrophication and other environmental impacts from agriculture, this study provides some preliminary insights into the effects of gypsum on biogeochemical processes in rivers. Based on the acquired results, gypsum use is something that needs to be considered when looking at the biogeochemical processes of waterways under the influence of agricultural gypsum use. The TSS results from Paimionjoki show an increase in the flocculation rate as a response to increasing gypsum concentrations. Based on the optical analysis, the DOM pool is altered by gypsum additions, this however requires further analysis to determine the specific mechanisms involved. Compounds that were not included in the study, such as NO_3, NO_2 and iron concentrations, are known to absorb light at UV-specific wavelengths (Weishaar et al., 2003).

The concerns related to the results of this study involve enhanced flocculation processes leading to the increased availability of micro- and macroaggregates in streams. Enhanced sedimentation of these aggregates would create an increased flux of organic material onto the sediment surface, with possible implications for microbial and benthic food webs (den Meersche et al., 2009; Yoshimura et al., 2010). Essentially this would mean an increase in the geophysical opportunity and microbial capacity to increase the secondary productivity of waterways.

Based on the results and studies related to the use of gypsum in the Archipelago Sea drainage basin it can be concluded that with the current knowledge the positive aspects of gypsum use heavily outweigh the negative ones. There is however one question that is left open when considering the sampling method for this study. Sampling was conducted at river endpoints, but gypsum additions occur from all over the catchment area. This is of significance as in these long waterways the DOM is greatly altered by biological and photolytic degradation processes
(Fichot & Benner, 2012; Hansen et al., 2016; Mayer et al., 2011). This highlights one of the fundamental differences between gypsum and sea salt, being the spatial dimension of the DOM and POM exchange processes for these two flocculants.

9 Acknowledgements

The study was connected to the MAAMERI project funded by the ministry of the environment where The University of Helsinki and SYKE were partners. I would like to acknowledge and give my warmest thanks to my supervisors Prof. David Thomas, Dr. Eero Asmala, and Dr. Hermanni Kaartokallio, who made this work possible. I also want to thank Walter and Andrée de Nottbeck Foundation for their invaluable financial support, as well as Tvärminne Zoological Station for their material support and expertise.

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Appendices

Appendix A. Results for each experimental unit

ID	Site	RPM	Exp. Type	Salinity	Gypsum	TSM	Abs 254	A	T	HIX
007	Paimio	0	RPM	2		42.40	152.97	0.92	0.08	19.97
008	Paimio	10	RPM	2.1		44.40	153.75	0.92	0.10	18.35
009	Paimio	30	RPM	2.1		47.80	159.05	0.92	0.08	20.35
010	Paimio	60	RPM	2		60.40	153.75	0.94	0.08	20.75
011	Paimio	90	RPM	2.1		56.20	149.60	0.96	0.09	20.41
012	Paimio	120	RPM	2.1		38.80	152.97	0.96	0.09	21.29
013	Laajoki	0	RPM	2		16.14	157.11	1.04	0.06	43.59
014	Laajoki	10	RPM	2		9.43	157.11	1.02	0.05	46.87
015	Laajoki	30	RPM	2		11.14	159.05	1.02	0.05	46.03
016	Laajoki	60	RPM	2		13.00	159.05	1.01	0.06	43.21
017	Laajoki	90	RPM	2		11.86	163.47	1.00	0.05	47.04
018	Laajoki	120	RPM	2		14.14	163.47	0.99	0.05	48.32
019	Laajoki	0	RPM	2		10.40	163.47	1.01	0.05	43.68
020	Laajoki	10	RPM	2		9.00	161.12	0.98	0.06	42.43
021	Laajoki	30	RPM	2		9.20	166.09	0.98	0.05	48.24
022	Laajoki	60	RPM	2		13.60	166.09	1.00	0.05	49.04
023	Laajoki	90	RPM	2		13.60	161.12	1.00	0.05	47.90
024	Laajoki	120	RPM	2		15.80	163.47	0.97	0.04	50.18
025	Paimio	0	RPM	2		40.80	159.05	0.90	0.07	20.79
026	Paimio	10	RPM	1.9		43.60	161.12	0.92	0.08	20.50
027	Paimio	30	RPM	2		50.60	155.36	0.99	0.08	22.97
028	Paimio	60	RPM	2		61.00	157.11	1.00	0.09	21.38
029	Paimio	90	RPM	2		57.60	155.36	1.00	0.09	20.55
030	Paimio	120	RPM	2.1		48.20	161.12	1.00	0.08	21.20
031	Paimio	0	RPM	2		43.40	161.12	0.94	0.09	18.68
032	Paimio	10	RPM	2		41.60	163.47	0.94	0.07	20.19
033	Paimio	30	RPM	2		43.60	157.11	0.95	0.07	21.03
034	Paimio	60	RPM	2		42.00	163.47	0.91	0.08	19.97
035	Paimio	90	RPM	2.1		35.60	159.05	0.97	0.09	19.72
036	Paimio	120	RPM	2.1		42.80	161.12	0.96	0.07	20.80
037	Laajoki	0	RPM	2		15.60	159.05	1.07	0.05	44.15
038	Laajoki	10	RPM	2.1		14.00	159.05	1.07	0.05	50.48
039	Laajoki	30	RPM	2		11.40	159.05	1.04	0.05	48.40
040	Laajoki	60	RPM	2		12.80	159.05	1.07	0.05	47.53
041	Laajoki	90	RPM	2		11.40	159.05	1.06	0.06	40.52
042	Laajoki	120	RPM	2		11.80	161.12	1.08	0.05	48.09
043	Laajoki	60	Gypsum	0	0	10.14	161.12	1.05	0.05	43.02

044	Laajoki	60	Gypsum	0	0.148	8.43	159.05	1.08	0.05	42.75
045	Laajoki	60	Gypsum	0	0.296	7.86	159.05	1.03	0.05	43.46
046	Laajoki	60	Gypsum	0	0.592	10.29	159.05	1.04	0.06	41.37
047	Laajoki	60	Gypsum	0.1	0.888	10.14	161.12	1.05	0.06	42.28
048	Laajoki	60	Gypsum	0.1	1.48	11.71	161.12	1.03	0.07	37.48
049	Paimio	60	Gypsum	0	0	42.00	163.47	0.81	0.07	15.47
050	Paimio	60	Gypsum	0	0.148	35.29	163.47	0.75	0.07	13.96
051	Paimio	60	Gypsum	0	0.296	46.71	163.47	0.80	0.08	14.93
052	Paimio	60	Gypsum	0	0.592	51.00	163.47	0.84	0.08	16.02
053	Paimio	60	Gypsum	0.1	0.888	53.29	163.47	0.82	0.08	15.77
054	Paimio	60	Gypsum	0.1	1.48	68.14	159.05	0.90	0.08	18.66
055	Laajoki	60	Gypsum	0	0	11.14	161.12	1.08	0.06	42.03
056	Laajoki	60	Gypsum	0	0.148	10.86	161.12	1.02	0.05	42.86
057	Laajoki	60	Gypsum	0	0.296	12.86	161.12	1.02	0.05	42.60
058	Laajoki	60	Gypsum	0	0.592	12.14	163.47	1.05	0.06	40.00
059	Laajoki	60	Gypsum	0.1	0.888	13.86	161.12	1.02	0.06	40.19
060	Laajoki	60	Gypsum	0.1	1.48	11.43	161.12	1.04	0.06	41.90
061	Paimio	60	Gypsum	0	0	51.00	161.12	0.81	0.09	14.57
073	Paimio	60	Gypsum	0	0	53.00	161.12	0.78	0.06	16.26
062	Paimio	60	Gypsum	0	0.148	51.14	149.60	0.78	0.07	16.33
074	Paimio	60	Gypsum	0	0.148	39.86	161.12	0.81	0.08	15.94
063	Paimio	60	Gypsum	0	0.296	48.57	159.05	0.86	0.08	17.24
075	Paimio	60	Gypsum	0	0.296	63.00	157.11	0.86	0.08	18.79
067	Laajoki	60	Gypsum	0	0	11.57	161.12	0.99	0.05	44.50
068	Laajoki	60	Gypsum	0	0.148	9.29	161.12	0.98	0.06	40.00
069	Laajoki	60	Gypsum	0	0.296	13.29	159.05	0.98	0.05	43.73
070	Laajoki	60	Gypsum	0	0.592	13.14	161.12	1.00	0.06	40.55
071	Laajoki	60	Gypsum	0.1	0.888	11.29	159.05	0.99	0.06	42.30
072	Laajoki	60	Gypsum	0.1	1.48	13.00	157.11	1.01	0.05	43.87
064	Paimio	60	Gypsum	0	0.592	59.71	161.12	0.80	0.08	16.21
076	Paimio	60	Gypsum	0	0.592	68.71	161.12	0.76	0.08	14.51
065	Paimio	60	Gypsum	0.1	0.888	66.43	159.05	0.83	0.07	18.14
077	Paimio	60	Gypsum	0.1	0.888	61.14	157.11	0.84	0.08	17.13
066	Paimio	60	Gypsum	0.1	1.48	67.00	159.05	0.82	0.07	16.29
078	Paimio	60	Gypsum	0.1	1.48	81.57	148.41	0.91	0.07	20.96
079	Laajoki	60	Salinity	0		9.71	161.12	0.99	0.05	44.94
080	Laajoki	60	Salinity	0.5		7.43	161.12	0.99	0.05	45.96
081	Laajoki	60	Salinity	1		13.71	161.12	1.02	0.05	45.00
082	Laajoki	60	Salinity	2		10.83	161.12	1.03	0.06	43.22
083	Laajoki	60	Salinity	3		8.83	161.12	1.05	0.06	44.68
084	Laajoki	60	Salinity	5.1		14.00	161.12	1.08	0.05	47.25
091	Paimio	60	Salinity	0		33.83	161.12	0.78	0.08	15.19
092	Paimio	60	Salinity	0.5		32.17	161.12	0.81	0.08	16.59
093	Paimio	60	Salinity	1.1		52.00	161.12	0.86	0.08	17.69
094	Paimio	60	Salinity	2		67.83	156.19	0.92	0.08	20.53

095	Paimio	60	Salinity	3.1		73.83	142.79	1.01	0.09	22.87
096	Paimio	60	Salinity	5.1		77.50	123.81	1.12	0.08	28.00
097	Paimio	60	Salinity	0		38.33	161.12	0.76	0.06	15.72
098	Paimio	60	Salinity	0.5		37.67	163.47	0.80	0.08	16.43
099	Paimio	60	Salinity	1		43.67	156.19	0.84	0.07	18.07
100	Paimio	60	Salinity	2		43.17	157.11	0.89	0.08	19.64
101	Paimio	60	Salinity	3		67.67	138.36	1.01	0.07	25.04
102	Paimio	60	Salinity	5.1		82.17	125.97	1.09	0.09	26.05
103	Paimio	60	Salinity	0		32.17	161.12	0.75	0.07	14.84
104	Paimio	60	Salinity	0.5		34.83	161.12	0.80	0.06	16.45
105	Paimio	60	Salinity	1		34.50	161.12	0.79	0.07	17.35
106	Paimio	60	Salinity	2		49.00	157.11	0.87	0.07	19.44
107	Paimio	60	Salinity	3.1		61.83	144.67	1.01	0.08	24.17
108	Paimio	60	Salinity	5.1		69.17	127.40	1.10	0.07	28.89
109	Laajoki	60	Salinity	0		6.83	161.12	0.97	0.06	40.01
110	Laajoki	60	Salinity	0.5		11.17	163.47	0.97	0.05	42.05
111	Laajoki	60	Salinity	1		4.83	161.12	0.99	0.06	43.88
112	Laajoki	60	Salinity	1.9		11.50	163.47	1.03	0.06	40.82
113	Laajoki	60	Salinity	3		12.50	161.12	1.05	0.05	46.87
114	Laajoki	60	Salinity	5		12.83	161.12	1.07	0.05	47.56
115	Laajoki	60	Gypsum	0	0	8.50	161.12	0.96	0.05	46.21
121	Laajoki	60	Gypsum	0	0	9.67	154.53	0.94	0.05	45.55
127	Laajoki	60	Gypsum	0	0	10.00	159.05	0.95	0.05	43.37
116	Laajoki	60	Gypsum	0	0.148	10.67	161.12	0.94	0.05	42.99
122	Laajoki	60	Gypsum	0	0.148	8.67	161.12	0.95	0.04	46.79
128	Laajoki	60	Gypsum	0	0.148	8.83	161.12	0.96	0.05	47.15
117	Laajoki	60	Gypsum	0	0.296	7.50	163.47	0.99	0.05	44.83
123	Laajoki	60	Gypsum	0	0.592	10.67	161.12	0.98	0.05	42.68
129	Laajoki	60	Gypsum	0	0.592	11.83	161.12	0.98	0.05	44.73
118	Laajoki	60	Gypsum	0	0.296	11.00	161.12	0.96	0.05	42.80
124	Laajoki	60	Gypsum	0	0.296	12.33	161.12	0.97	0.05	43.37
130	Laajoki	60	Gypsum	0	0.592	10.67	161.12	0.99	0.05	42.40
119	Laajoki	60	Gypsum	0.1	0.888	9.17	159.05	1.00	0.05	44.61
125	Laajoki	60	Gypsum	0.1	0.888	10.83	161.12	0.97	0.05	46.37
131	Laajoki	60	Gypsum	0.1	0.888	9.00	161.12	0.99	0.05	44.87
120	Laajoki	60	Gypsum	0.1	1.48	11.17	161.12	1.00	0.05	39.76
126	Laajoki	60	Gypsum	0.1	1.48	12.17	159.05	0.98	0.05	43.61
132	Laajoki	60	Gypsum	0.1	1.48	12.17	159.05	1.00	0.05	45.79
133	Paimio	60	Gypsum	0	0	32.17	166.09	0.74	0.06	15.14
139	Paimio	60	Gypsum	0	0	27.67	163.47	0.76	0.08	14.20
145	Paimio	60	Gypsum	0	0	29.33	161.12	0.79	0.06	16.30
134	Paimio	60	Gypsum	0	0.148	35.33	166.09	0.79	0.06	16.08
140	Paimio	60	Gypsum	0	0.148	34.17	161.12	0.81	0.07	16.58
146	Paimio	60	Gypsum	0	0.148	39.50	157.11	0.87	0.08	18.69
135	Paimio	60	Gypsum	0	0.296	41.67	166.09	0.74	0.06	15.34

141	Paimio	60	Gypsum	0	0.296	36.50	163.47	0.76	0.06	15.79
147	Paimio	60	Gypsum	0	0.296	51.17	161.12	0.77	0.07	14.44
136	Paimio	60	Gypsum	0	0.592	48.33	163.47	0.79	0.07	15.60
142	Paimio	60	Gypsum	0	0.592	41.67	161.12	0.81	0.07	16.94
148	Paimio	60	Gypsum	0	0.592	54.17	157.11	0.85	0.07	19.06
137	Paimio	60	Gypsum	0.1	0.888	58.67	166.09	0.74	0.07	14.89
143	Paimio	60	Gypsum	0.1	0.888	55.67	161.12	0.75	0.07	15.89
149	Paimio	60	Gypsum	0.1	0.888	63.17	166.09	0.79	0.06	16.27
138	Paimio	60	Gypsum	0.1	1.48	68.00	163.47	0.80	0.08	15.40
144	Paimio	60	Gypsum	0.1	1.48	65.50	145.69	0.84	0.07	16.62
150	Paimio	60	Gypsum	0.1	1.48	76.00	152.97	0.90	0.07	19.72
151	Laajoki	60	Salinity	0		11.33	156.19	0.97	0.05	42.31
152	Laajoki	60	Salinity	0.5		9.33	163.47	1.01	0.05	45.31
153	Laajoki	60	Salinity	1		11.17	161.12	1.02	0.06	40.23
154	Laajoki	60	Salinity	2		13.67	161.12	1.04	0.05	45.67
155	Laajoki	60	Salinity	3.1		11.50	161.12	1.06	0.05	41.66
156	Laajoki	60	Salinity	5.1		16.17	161.12	1.10	0.05	50.96

Appendix A. Results for each experimental unit and the study variables. ID = Sample id. Site = Study site, either Paimionjoki or Laajoki. RPM = RPM setting used on the flocculator. Exp. Type = Experiment type, split to RPM, salinity, and gypsum. Salinity = Salinity. Gypsum = Gypsum concentration in mmol/l. TSM = Total suspended solid concentration in mg/l. Abs 254 = Absorption coefficient at 254 nm / m. A = Cobble Peak A, R.U. T = Cobble Peak T, R.U. HIX = Humification index.