

Hydrological catchment analysis from characterisation of organic matter in stream water

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Abstract

Organic matter (OM) in aquatic systems is a complex field which have rapidly developed during the last decade due to the introduction of high resolution mass spectrometers. The composition of OM in the aquatic environment is directly dependent on factors such as oxygen supply, pH and the flow rate in the local system. Furthermore, the OM is closely linked to negative effects on these systems such as eutrophication and brownification, which in many cases are caused by human activity through climate change, water management and changes in land use patterns.

This thesis focuses on the composition of organic matter in the aquatic environment in relation to land use and water management. The aim of this work is characterising of OM from water draining distinctly different sub-catchments and using the internal OM composition as a tracer for different catchment characteristics. Stream water was sampled and analysed for OM using direct-sample-analysis Time-of-flight mass spectrometry (DSA-TOF-MS) and Total-organic-carbon (TOC) analysis from streams draining the different sub-catchments. The results were then linked to the different sampling locations through comparisons of mass spectra, Principle-component statistics and molecular formula correlations. The result show that three different sub-catchments could be distinguished by OM quantification and characterisation. However, it was not possible use characterised mass peaks as a downstream tracer, which can probably be explained by the complex degradation, transformation and sedimentation processes interacting with the OM in the catchment. Improved methodology and further studies to map the processes affecting the OM in the aquatic system is necessary to be able to use the internal organic chemistry as a marker for the status of the system.

Keywords: Organic matter, Time-of-flight mass spectrometry, aquatic chemistry, catchment hydrology.

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1 Introduction

1.1 Background

Previous studies have shown that aquatic systems constitute a major and active role in the carbon cycle. Streams, lakes and wetlands are examples of aquatic environments with distinctly different carbon chemistry due to factors such as oxygen supply and rate of material transport. Further, streams act as transport paths for large quantities of carbon between inland catchments and the sea (Cole et al., 2007). Carbon in the natural environment occurs most commonly as organic carbon (OC) in the form of organic matter (OM). Inorganic carbon (IC) occurs more rarely in the environment and will not be considered further in this study. Many studies use the terminology OC and OM interchangeably when considering organic substances. Both terminologies are closely linked as OM describes different organic substances and their characteristics, whereas OC describes the carbon structure which the organic substances are built around. This study will mainly use OM when discussing the interaction between organic substances in different chemical environments (Cole et al., 2007; Schlesinger & Bernhardt 2013).

Organic matter in aquatic systems are further divided into Particulate-Organic-Matter (POM) and Dissolved-Organic-Matter (DOM). DOM is defined as the Organic-Matter (OM) which remains after filtration of sample water with a 45µm filter. The OM which is trapped in the filter is considered POM and Total-Organic-Matter (TOM) is the sum of DOM and POM (Schlesinger & Bernhardt 2013). The OM chemistry in aquatic environments is extremely complex and not very well understood. This is due to the extreme diversity in composition and degradation and transformation processes of OM which are active in the environment. These processes also contribute to CO₂ emissions from well oxygenated aquatic systems. Carbon budgets developed by Tranvik et al. (2009) estimates that 66% of the total carbon content in a typical Swedish boreal lake consist of Total-organic-Carbon (TOC), and 34% of Total-Inorganic-Carbon (TIC). The study estimates that only 39% of the total amount of carbon will be transported downstream, 19% will be sedimented and 42% will be emitted as CO₂ as a result of degradation and transformation processes in the aquatic system (Tranvik et al., 2009).

The oxygen transport in water is 10⁴ times slower in comparison with air. This means that decomposition of organic matter will be limited and that the degradation processes are different in environments with a low oxygen supply. Mires and peatlands are environments known for a limited supply of oxygen. In these environments oxygen will only diffuse a few millimetres below the water surface (Schlesinger & Bernhardt 2013). The limited decomposition increases carbon storage. In the boreal region, around 15-30% of Soil-organic-matter (SOM) is estimated to be stored in peatlands (Gorham 1991; Limpens et al., 2008). Moreover, the limited supply of oxygen favours chemical reactions with different electron acceptors than oxygen, such as NO₃⁻, Mn⁴⁺, Fe³⁺ and SO₄²⁻. When the supply of these reactants decrease, decomposition through methanogenesis dominates, which results in methane emissions to the atmosphere (Schlesinger & Bernhardt 2013). Of the global methane emissions, a substantial part is estimated to originate from wetlands (Bousquet et al, 2006; Bloom et al. 2010; Ringeval et al. 2010). Furthermore, wetlands are widely considered as a large source of DOM to fluvial systems (Dalva and Moore, 1991; Gergel et al. 1999). The DOM from peatlands are known to mostly consist of humic substances, but composition is to a large extent determined by factors such as pH and ion strength and ion availability in the source material (Thurman, 1985; Schlesinger & Bernhardt 2013).

These systems are further affected by human activity through climate warming, changing land use patterns and hydrological modifications, such as drainage of lakes and wetlands and straightening of streams and rivers. Increased precipitation and temperatures in the boreal region is projected to result in increased terrestrial runoff into the aquatic system, with increased export and burial of DOM and increased emissions of CO₂ and methane (Tranvik et al., 2009). Increased concentrations of coloured-dissolved-organic-matter (cDOM) in aquatic waters impacts the colour of the whole freshwater system. Dark coloured water absorbs light, limiting the light transparency in the water. This effect known as brownification has increased over the last decades and is considered a major problem, causing reduced photosynthesis and primary production in brownified aquatic systems, which eventually can lead to oxygen depletion in the system. Ekström (2013) defines DOM and iron (Fe) as the major causes of brownification, and whether Fe or DOM are the major cause of brownification in the system is closely linked to the pH and acidification history of the water. In the southern parts of Sweden, DOM export and decreased acidification was addressed as the combined main factor for brownification, whereas Fe was considered of higher importance in the northern parts of Sweden (Ekström, 2013).

1.2 Methods for studying organic-matter in aquatic systems

The science of studying organic matter in aquatic systems are generally conducted using three major methodological approaches. The most widely used are the use of optical instrumentation to study the organic matter in water samples taken from the freshwater system of interest. One common optical method is to measure the light absorbance of the water sample, which can result in identification of aromatic character of the organic matter in the sample. This method is especially effective when coupled with DOM concentration analysis, which together is referred to as Specific-UltraViolet-Absorbance (SUVA). Another common optical method is Fluorescence spectroscopy, which studies the emissions from excited organic matter substances in a water sample. This is conducted to identify the characteristics of the organic matter in the sample. This can be coupled with statistical analysis, referred to as parallel factor analysis (PARAFAC) for defining different classes and characteristics of organic matter from fluorescence data (McCallister, Ishikawa & Kothawala, 2018). One way of using PARAFAC with fluorescence spectroscopy data is explained in the article by Murphy et al. (2013).

The second methodological approach is the use of stable isotopes to study organic matter eg. fluxes and turnover times in different pools and systems (McCallister et al., 2018). This will not be further addressed in this study. The third approach which have developed greatly the last decade is the use of techniques to characterise molecules within a sample. This is done through different types of mass spectroscopy or Nuclear magnetic resonance (NMR), the latter being less used in this context. According to McCallister et al. (2018), FTICR-MS (Fourier-transform-ion-cyclotron mass spectroscopy) is today considered the most high-resolution method in this field. Mass spectroscopy is further described below under own heading.

1.2.1 Mass spectroscopy

The general function of mass spectrometers for studying organic matter in water samples are described in this section. The sample substrate is initially ionised and converted into gas phase. The ionisation techniques vary between different instruments and can generally be described as soft or hard. Hard ionisation techniques are used to fragmentise the molecules into smaller constituents, whereas the soft techniques are less prone to produce fragments of the molecules in the sample. Examples of hard ionisation techniques are Electron Ionisation (EI) and commonly used soft ionisation techniques are Atmospheric Pressure Chemical Ionisation (APCI) and Electro Spray Ionisation (ESI) (Hoffmann & Stroobant, 2013).

The sample enters the spectrometer just after ionisation and gas conversion, and the sample content is then sorted in the spectrometer according to its mass and charge. From this data a result consisting of a defined mass-to-charge ratio (m/z), representing a detectable molecular unit, and intensity for each m/z , which is representative of the amount of the detected chemical substance in the sample, is generated as a spectrum. This is achieved with various approaches depending on the type of spectrometer.

Scanning mass analysers is one type of mass spectroscopy which scans the sample for one mass unit at the time and generates results on a time scale for the different masses that is detected in the sample. Other methods such as Time-Of-Flight (TOF) mass spectroscopy generates an electric field in a flight tube and accelerates the molecules through the tube to a detector. The mass to charge ratio m/z is calculated through the time taken to accelerate the ions through electric field in the tube, and a mass spectrum for the whole sample is generated simultaneously. Ion trap techniques such as the Orbitrap mass spectroscopy, which was launched in 2005, traps the ions in orbit around a magnetic field. The disturbances in the field created by each ion generates a sinus-like wave which can be recalculated to a mass to charge ratios using a Fourier-transform calculation. Like the TOF, this method also generates a spectrum for the whole sample simultaneously. FTICR-MS is a further development of the Orbitrap which in many studies is referred to as Ultra-high-resolution mass spectroscopy and the method that is currently capable of producing the highest resolution of all the methods mentioned (Hoffmann & Stroobant, 2013).

1.3 Aim and Hypothesis

The aim of this thesis is to characterise OM from distinctly different subcatchments in the Skogaryd research catchment with the use of Time-of-flight mass spectroscopy. Previous studies in Skogaryd have investigated the DOC export from the sub catchments in relation to water balance (Sandgren 2017), catchment investigation based on geophysical methods (Nyström, 2016) and DOC characterisation based on absorbance (Wallin et al., 2015). Additional studies have been conducted on inorganic carbon in stream water by analysis of stable carbon isotopes (Campeau et al. 2018), and greenhouse gas emissions from stream water (Natchimuthu et al. 2017).

The hypothesis (1) is that analysis of stream water samples with DSA-TOF-MS will be able to characterise OM more effectively and with greater detail in comparison with studies previously committed in Skogaryd. Further (2) the composition of OM from contrasting sub-catchment outlets will be distinguishable, enabling determinations of which molecular masses or OM composition that is characteristic for a specific sub-catchment. The (3) characteristic OM signal from the catchments can be used as an internal standard for tracing the sub-catchment OM contribution to downstream sampling locations.

For this study, the Skogaryd catchment was modified to completely hydrologically separate a forested area on mineral soil from mire water influence, which made it possible to study the organic chemistry of well-defined characteristically differentiated sub-catchments. The modifications are presented in the Results section.

2 Method and site description

2.1 The Skogaryd research catchment

This study was performed with water samples from the Skogaryd research catchment located between Vänersborg and Uddevalla in the south western parts of Sweden (58°23'N, 12°09'E). Skogaryd is part of the national research infrastructure SITES (Swedish infrastructure for ecosystem science) and is located in the hemiboreal climate region (University of Gothenburg, 2017; SITES, 2018).

The Skogaryd Research Catchment

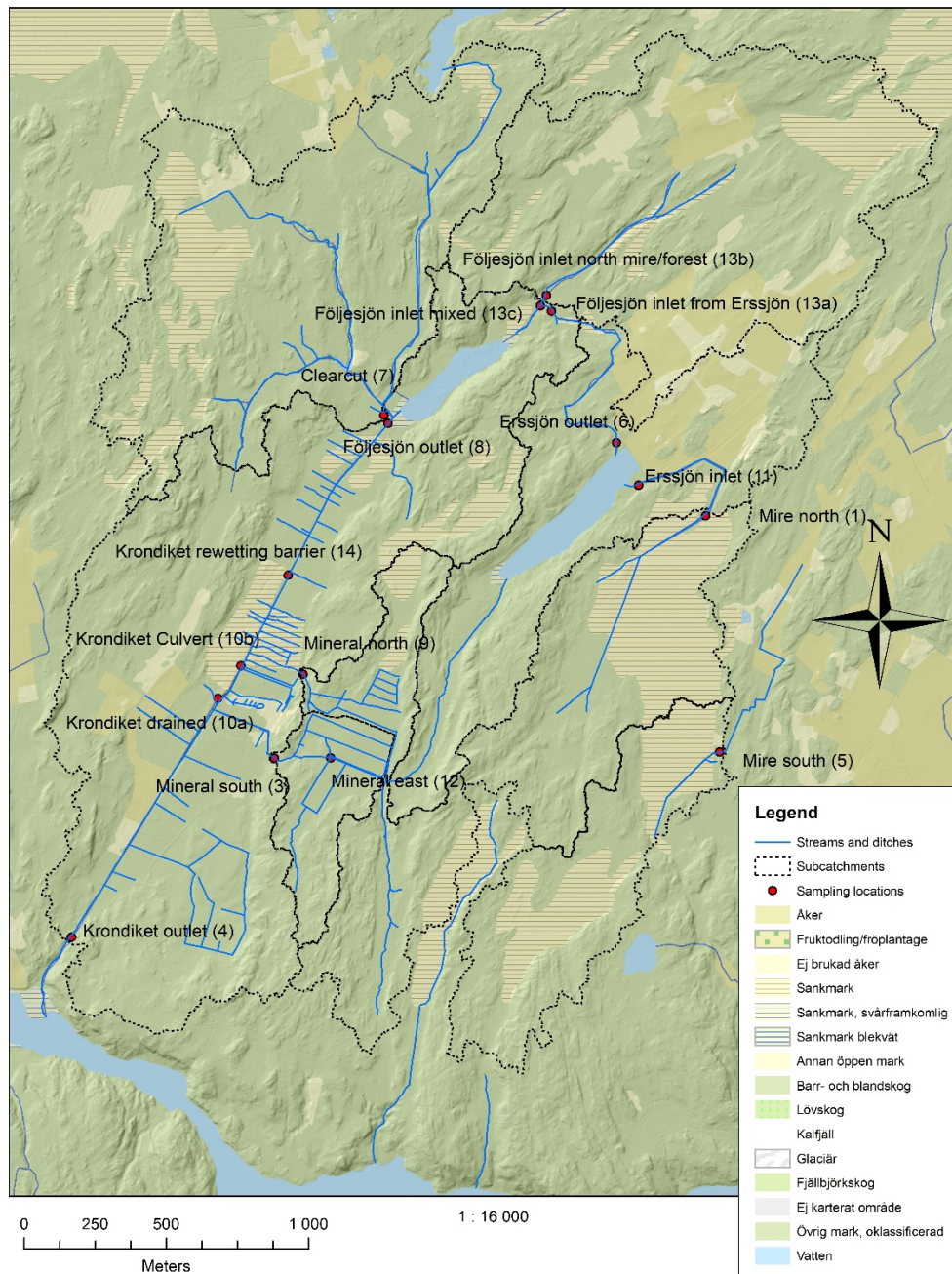


Figure 1 illustrates the Catchment and the vegetation types within the catchment. Sampling locations with name and numbers are also featured in the figure.

2.1.1 Geology

The bedrock in the area is dominated by felsic volcanic and intrusive rocks, with occurrences of mafic equivalents. The landscape is shaped by a north-east to south-western fracture system in the bedrock, which have created elongated valleys and ridges in the directions of the fractures. This continues down to lake Skottenesjön which has an east-western extension. On the ridges the soil depth is thin with large areas of exposed bedrock. The valleys are dominated by glacial and postglacial clay, with inclusions of peat and postglacial sand. Some glacial friction material can be found in the western part of the area and in the northern part, a moraine ridge is propagating in an east-west direction. Geological maps including bedrock, quaternary deposits and soil depth from the Swedish geological survey (SGU) are featured in Appendix 1.

2.1.2 Land use

The Skogaryd area is exposed to hundreds of years of extensive landuse. Forestry, farming and peat harvesting are activities that have been committed or are active in the area. These activities have altered the hydrology in the catchment by drainage operations on peatlands and lakes. Additionally, streams have been straightened to improve drainage which can clearly be seen on the main stream Krongdiket between sampling location 8 följesjön outlet and krongdiket outlet (location 4) in figure 1 and 3. The major landuse activity in the catchment today is forestry, which has increased in the area during the last 50 years as figure 2 shows. The area used for farming in the catchment has during the same period decreased and the peat harvesting has ceased. Changes in hydrology that are occurring today are redirection of streams due to research activities and wildlife, such as beaver dams, causes slight changes to the hydrology.

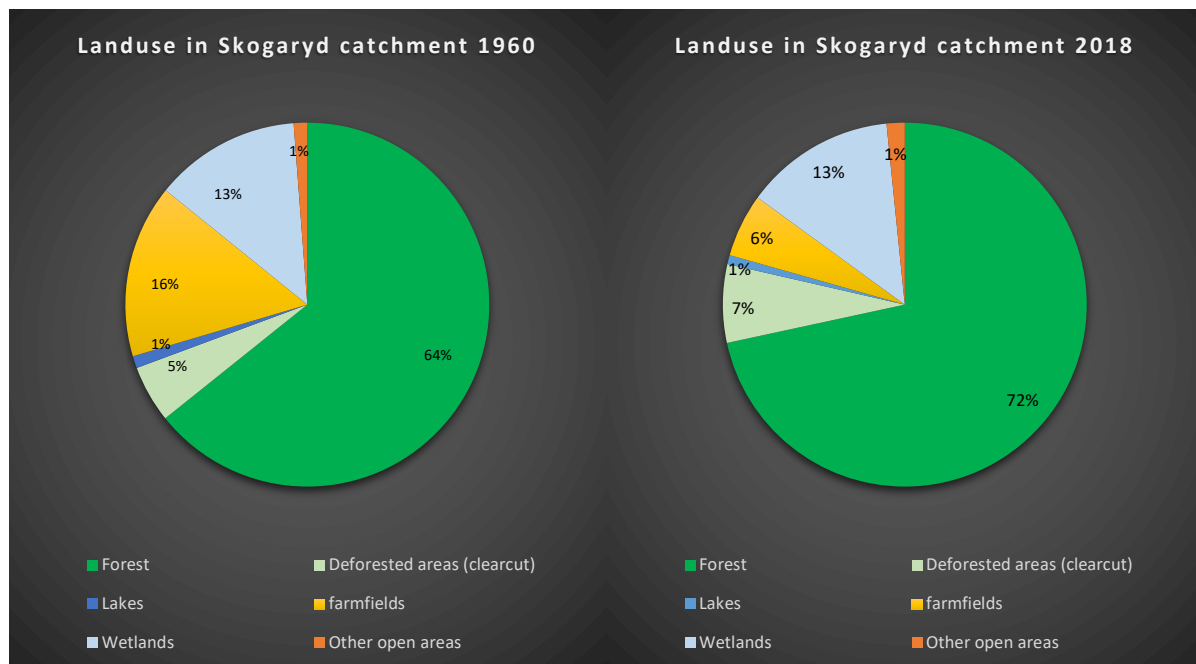


Figure 2 shows an increase in forested areas and a decrease in farmfields in the catchment since 1960. The figure is made from estimations when comparing the orthophotos over the catchment featured in Appendix 2.

The current and historical land use activities along with the geology and the hemiboreal climate has created some characteristic subsites within the Skogaryd catchment, which is illustrated in figure 3. The mire Mycklemossen is located in the eastern part of the catchment. It is the largest mire in the catchment and it is hydrologically divided with two outlets. Along Krongdiket are forested areas which are planted on drained peat soil. There are smaller areas with forest planted on mineral soil, and there are two lakes in the system. Lake Följesjön is an overgrown heavily

eutrophic lake which is slowly turning into a wetland. Lake Erssjön can be described as a more typical hemiboreal forest lake with brownified water from the surrounding forest areas.

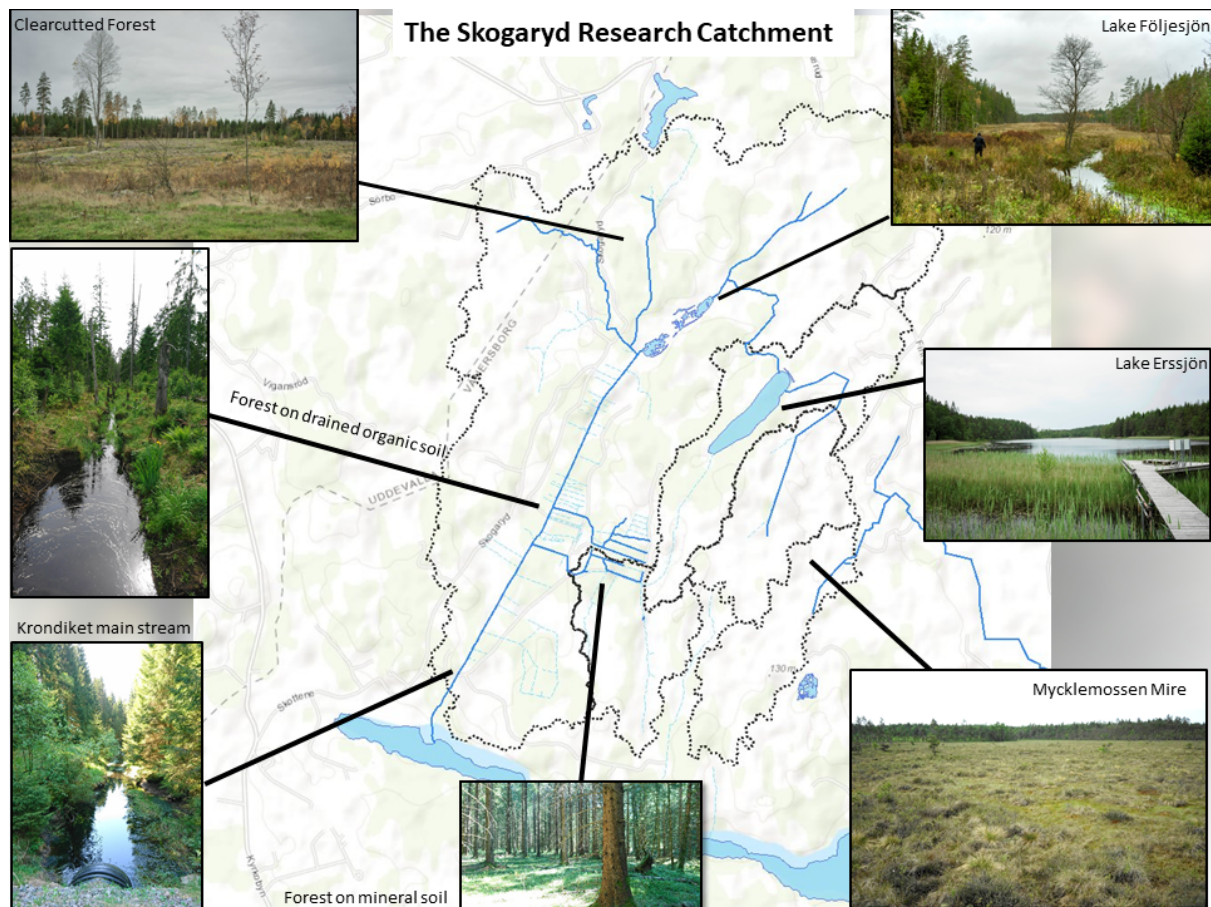


Figure 3 illustrates and marks the location of the characteristic subsites within Skogaryd.

The last 50 years has shown large changes in landuse to the catchment which is visualised in the orthophotos featured in Appendix 2. Furthermore, both lake Följesjön and lake Erssjön show increased vegetation when comparing the images in figure 27-29, while the mire Mycklemossen show only minor differences when comparing the image from 1960 with the image from 2018 in figure 30 in Appendix 2. An estimation of the land use areal coverage was made based on the orthophotos and can be seen in figure 2. The figure shows an increase in forested areas at the expense of farmland areas in the catchment between 1960 and 2018. The estimations was made by creating polygons in ArcGIS over the different land use types and calculating the area for each type of polygon. More information regarding historical land use changes in Skogaryd can be read in Hill (1999) and the study by Fahlgren (2017).

2.1.3 Catchment description

Figure 2 is an overview over the catchment and shows the streams, lakes and outline of the catchment which is defined by the Kron diket outlet into lake Skottenesjön, at sampling **location 4**. The figure also shows the other sampling locations for the SITES water monitoring program, where water samples from the streams for chemical analysis are taken bi-weekly. The sampling is complemented by stream water level measurements and other standard water measurements such as pH, conductivity and temperature. Some sampling sites also have automatic logging equipment installed which logs flow rates and other parameters hourly.

Sampling **locations 1** and **5** represent the northern and the southern outlets of the Mycklemossen mire respectively, which is located towards the eastern border of the catchment. From the northern outlet (**location 1**) a stream extends to the inlet of lake Erssjön, where sampling **location 11** is situated. Lake Erssjön has two outlets, one in the northern and one in the southern ends of the lake. Sampling **location 6** is located at the northern outlet of lake Erssjön from where a stream extends through a forested area in near vicinity of an area dominated by farmlands, and thereafter towards the inlet of lake Följesjön. The stream from the southern outlet extends through forested and wetland areas to the forested mineral areas in the southern parts of the catchment, before entering the main stream Krondiket. North of lake Följesjön the stream from lake Erssjön is joined by a stream from the upper northern areas of the catchment. **Location 13** is situated where the streams join, and three samples are taken at this location, one from the eastern stream, from Erssjön, called **13a**, one sample from the northern stream **13b**, and one sample south of the join where the two streams are mixed **13c**.

The outlet of lake Följesjön is situated in the southern parts of the lake where sampling **location 8** also is located. This is also the inlet to the main stream Krondiket. Just south of **location 8**, Krondiket is joined by a stream from a north-western subcatchment with large areas of clearcutted forest. Small mires and forested areas are also present in the subcatchment. **Location 7** is situated on this stream just upstream the connection to Krondiket. Further south along Krondiket follows forested areas on drained organic soil. Sampling **locations 10a, 10b** and **14** is situated along Krondiket in this area. Two streams with sample **locations 9** and **3** are connecting to Krondiket from the east. These streams originate from forested areas with mineral soil. The stream passing **location 9** is connected to the southern outlet of lake Erssjön and passes a mire before entering the mineral area. The stream passing **location 3** was disconnected from the Erssjön outlet and the mire in May 2018 as part of this study. This was to completely separate the mineral area from mire water influence. **Location 3** and **12** are therefore situated in streams which originates in areas with only forest on mineral soil. The water passing location **12** originates from the southern mineral area, and location **3** covers the entire isolated mineral surface, called Mineral south. As can be seen in Appendix 2, the Mineral areas have previously been used as farmland but is today completely forested. **Location 4** is located in the outlet of Krondiket into lake Skottenesjön.

2.2 Field sampling

Field work with sampling of stream water were conducted during 8 one day occasions with approximate two weeks interval, which will be referred to as F1-F8. These are plotted in figure 4 alongside monthly estimates of precipitation and temperature. The figure also features mean temperature and precipitation for an average year in the area. As seen in figure 4, the summer of 2018 was exceptionally dry and warm in comparison to an average year. Field sampling was therefore paused from May until late September due to low or non-existent water levels in the streams.

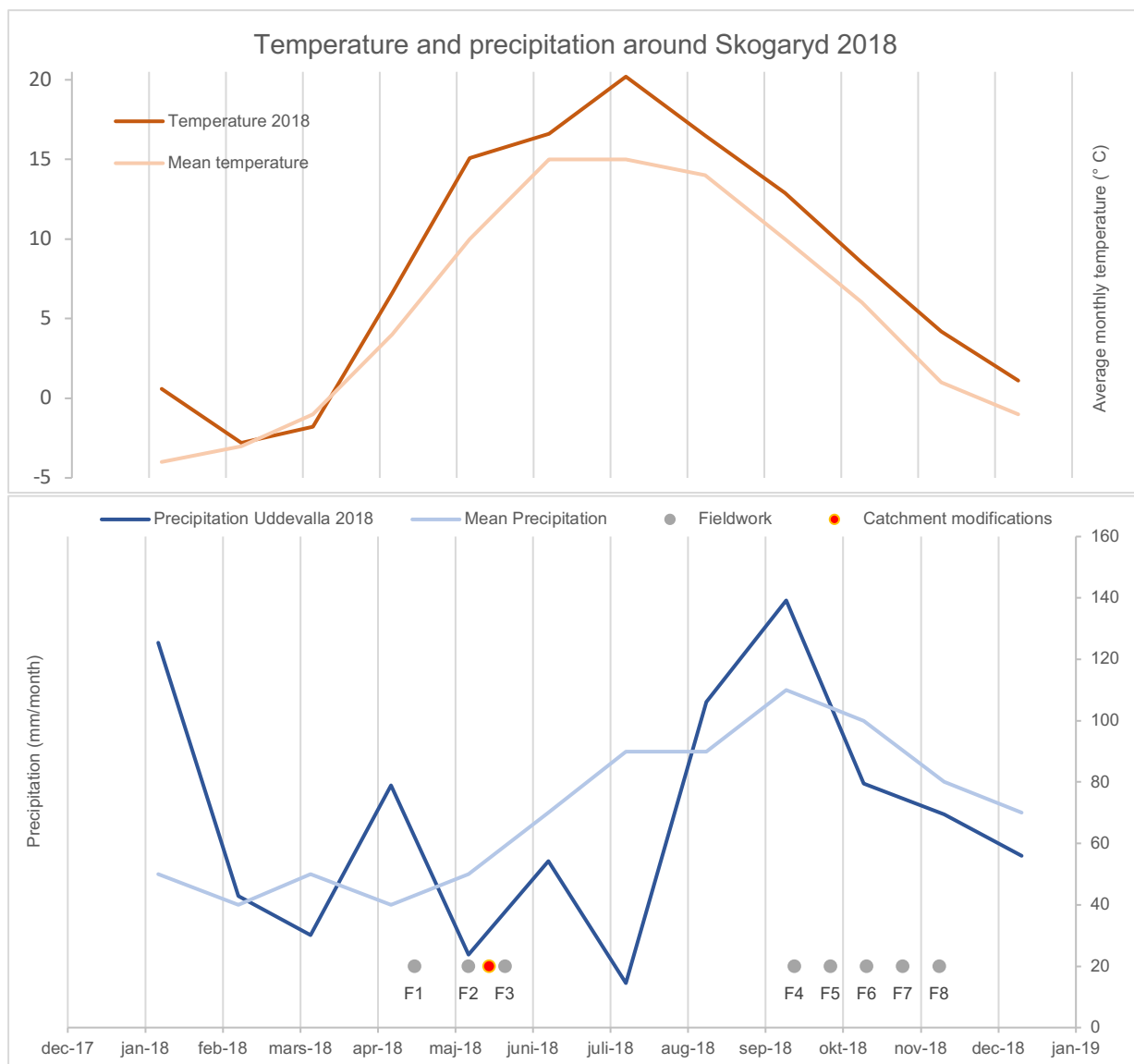


Figure 4, mean precipitation and temperature data for 2018 from weather stations close to Skogaryd are plotted along with similar data for an average year. The summer of 2018 was exceptionally warm and dry which is seen in the figure. The fieldwork occasions are plotted as F1-F8 and the date for when the modifications to the catchment was finished is also featured in the figure.

During field work, 200 ml of stream water was collected from the sampling sites shown in figure 1. Location 14 was not used in this study, and location 13 was sampled from F5-F8. Location 12 and 3 was completely disconnected from the stream originating from the southern outlet of Erssjön, containing mire water, in May 2018, marked as catchment modifications in figure 4. The water from the southern outlet of Erssjön was instead led through the stream passing location 9.

Sampling was performed using a specific procedure to avoid contamination and errors. First, the bottle to be used was rinsed in stream water three times, approximately one meter downstream of the sampling location. During sampling, the bottle was brought into the water with the opening angled downstream. At a depth of approximately 10cm below the surface, the bottle was turned to an upstream angle, to let upstream water enter the bottle. In this procedure, only upstream water is sampled, and surface water is avoided.

Furthermore, glass bottles were used to minimise the use of plastics in the study, which could affect the organic chemistry in the water, and vinyl gloves were used to handle the bottles to reduce possible risks of contamination. Samples cold during the travel from the field area. The samples were then kept in a fridge overnight until the following day when the lab work started.

2.3 Lab work

Two analytical methods were applied in this study for quantifying and characterising organic matter in the water samples. Total Organic Carbon analysis (TOC) were used for estimating the amount of organic matter in each sample, and TOF mass spectrometry were used to characterise the organic matter. How these methods were implemented is described in this section.

2.3.1 Sample preparations

To prepare the samples for TOF and TOC analysis, the samples were filtered with a 45um Sarstedt Filtropur syringe mounted filter, to separate dissolved and particulate organic matter. The samples were then directly inserted and separated into glass vials for the TOC analysis and into smaller glass bottles for mass spectrometry. Approximately 40ml of each sample was inserted to the vials, and the remaining were inserted for TOF analysis. The bottles, vials and syringe were washed one time in sample water, and 10ml of sample water was rinsed through the filter before usage.

Another methodological approach which were briefly tested in this study is to extract the organic matter in the water samples using solid phase extraction. Similar methodology has been successful when studying organic chemistry in natural waters in previous research, for instance in the study by Yang et al. (2011) and by How et al. (2014). When testing this method, SPME PDMS/DVB fibre tips were put in a vial with sample water for approximately 24 hours. The fibre tips were then run on the TOF in a similar way as described for the water droplets below. This method was then completely replaced with the use of water droplets directly, since it proved more difficult to get sufficient signal in the instrument with the fibres in comparison with using droplets.



Figure 5 shows the setup when filtering the water with the water samples directly in the upper left. Vials for TOC in the middle of the picture and glass bottles for mass spectrometry on the right side.

During September both filtered and unfiltered water was tested in the TOC instrument which unexpectedly resulted in higher organic carbon concentrations for the samples that were filtered. To avoid the possibility of contamination by the filters, the analyses were during

October and November performed on unfiltered water. Approximately 80ml of sample water from each sample was transferred to 100ml vials for the TOC analysis. The remaining water were used in the Time of flight analysis as explained under own heading.

2.3.2 Total organic carbon (TOC) analysis

The prepared vials were inserted into a Shimadzu ASI-L auto sampler which is connected to the Shimadzu TOC-L total organic carbon analyser, for TOC analysis. The autosampler adds hydrochloric acid to the sample to dissolved inorganic carbon which is converted into carbon dioxide which is removed. The settings used in the instrument were set to optimize for NPOC (non-purgable organic carbon) and the TOC instrument along with the autosampler were running the samples automatically. The data was then exported as csv. files and the data were imported to Excel where plots were made.

2.3.3 Time of Flight mass spectrometry (TOF-MS)

The other instrument used in the analysis were a Perkin & Elmer Axion TOF 2, which is a Time of flight mass spectrometer. The instrument was coupled with a Direct-sample-analysis system (DSA) and Atmospheric Pressure Chemical Ionisation (APCI). APCI is considered a soft ionisation technique, meaning low levels of fragmentation and that the masses seen in the spectra are relatively comparable to molecular weights. APCI is considered to work well with masses up to approximately 1500 da (Hoffman & Stroobant, 2013).

Initially the water samples were taken out in room temperature for at least one hour before running the instrument. The instrument was tuned in a 5 kV positive ionization mode with a mass range approximately of 50 to 1000 m/z. Before running a new set of samples, the instrument was calibrated using an Agilent Technologies APCI/APPI tuning mix. From October 2018, the mass range was increased to approximately 50 to 2000 m/z. Samples from F6, F7 and F8 was additionally run with a 5 KV negative ionization tuning with a mass range of 50 to 2000 m/z.

Sample were taken from the glass bottles using an automatic pipette approximately 1cm below the water line. The first sample from each bottle was discarded to avoid contamination from the pipette needle. The sample to be used was then applied to the first position of the DSA sample net. Three replicates of each sample were run on each occasion with a space of one sample spot between the samples. On these spots, a droplet of MilliQ water was applied which were run between the samples. A new pipette needle and a new net were used for each sample.

Before running the samples, each new net was sprayed with the instrument nitrogen plasma to clean the net and remove possible contamination. From F5-F8, a protective cover was installed to further reduce risks of contamination from the surrounding air. When running the instrument, the net containing three replicates of one sample was placed In the DSA and the DSA was controlled from a computer to run each replicate separately. The program used to control the process and see the live results is the program that is featured with the instrument. Each sample was saved in one .TOF file and the procedure was repeated for the following samples.

The data was exported from the signal peak, for each individual replicate. The software generated an average spectrum for the signal in the sample peak which can be seen in figure 6. M/z (mass/charge) and intensity data from this spectrum was then copied and saved to an Excel spreadsheet. A baseline was set at the absolute intensity of 1, below which no data was exported. Background noise was also recorded to remove background and noise generated peaks in post processing.

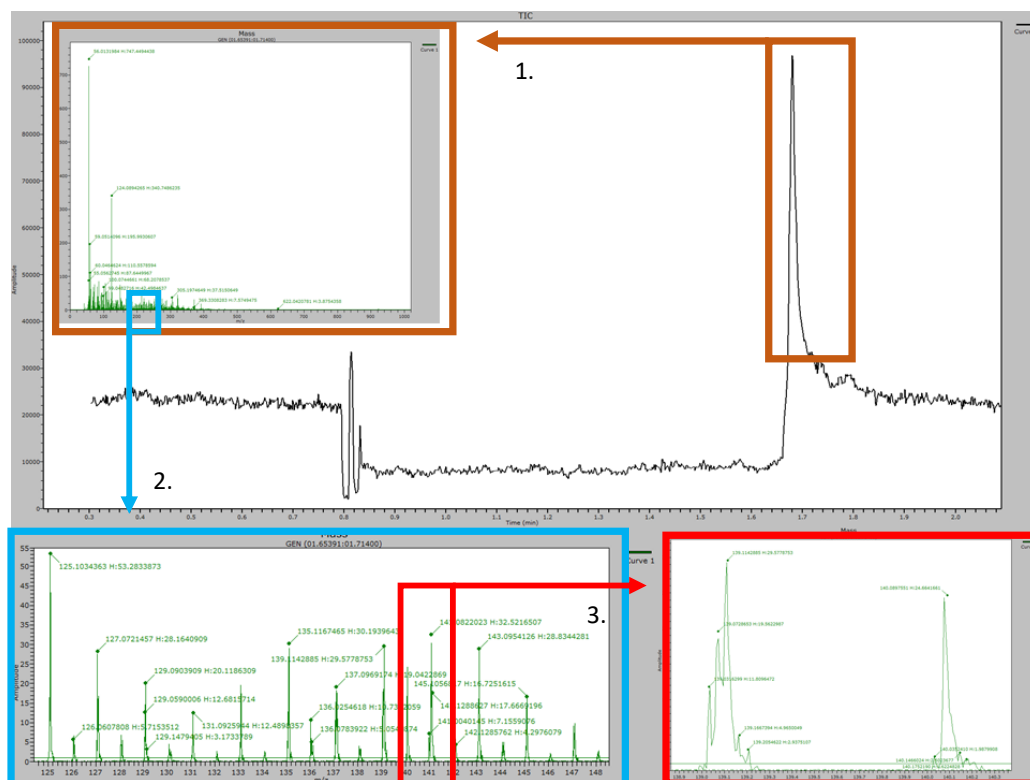


Figure 6, the upper graph is a Total Ion Chromatogram (TIC) representing the total signal of the sample (y-axis) at a given time (x-axis). The large peak in the TIC represents a sample that is run in the TOF. From the peak, a spectrum of the sample (1.) is generated which consist of numerous small peaks, each representing a specific molecular weight. As can be seen when observing the peaks in magnification (2. and 3.), each peak also consist of a number of smaller peaks. In this study these were considered representing the same molecular unit, meaning that only the peaks with the highest amplitude in the red box (3.) were considered in the study.

2.4 Mass spectrometry data management

Several ways of managing the mass and intensity data was tested, including post processing functions in the dedicated Perkin & Elmer software and open source software's for mass spectrometry: Mmass and Massupp. The dedicated software did not have proper functions for comparing samples and removing background noise, which were needed for this study. Additionally, the open source softwares, though including some useful functions, were found to be difficult to use. Instead, two Excel scripts were developed for this study.

2.4.1 Development of Excel scripts

One script were used as a data filter to remove background noise and to group peaks within a 1 da range, which were found to be suitable for this specific data. This can be seen when viewing box 2 and 3 in figure 6, where clusters of peaks are appearing with almost 1 da separation. In this study, the peaks in each cluster has therefore been assumed to be closely linked to each other, and they have therefore been grouped together into the value of the largest peak in the cluster. The second script was made to theoretically create molecular formulas from a set of conditions, using C, H, O and N. The mass of these theoretical formulas was then calculated, and the script matches these masses against the m/z and intensity mass data from the TOF. This script was used to name some of the peaks and can also be used for data filtering. The second script with molecular formula assignments was not very successful in this study, as the resolution of the mass peaks were found to be largely insufficient for accurate molecular assignments. However, one example of formula assignments in a mass spectra is shown in figure 22, and the formulas were used to calculate hydrogen and oxygen ratios in relation to

carbon and plotted as a Van Krevelen plot, figure 23. Van Krevelen plots are a common way of identifying and characterising the type of organic matter found in the material studied. By knowing the relative ratios of elements in different OM classes, a plot can be made to see which OM classes that are the most common in the system. The Van Krevelen plot, figure 23, in this work is based on the classification compiled in figure 1 by D'Andrilli et al. (2015).

The data produced by the first script was assembled in a separate Excel workbook with different spreadsheets for each replicate from one field occasion. This data was then assembled in a matrix with m/z on the first axis, the sample and replicate on the other axis written as 1_2, meaning sample 1 replicate 2. The matrix featured the relative intensity of each replicate on the corresponding m/z. The relative intensity is normalised which enables direct comparisons between samples. The highest peak in the relative intensity is given a value of 100 and smaller peaks in the sample are featured in decreasing order. Mass spectra were plotted from this data and the matrices was used in a Multivariate statistical analysis using the software Canoco5.

2.4.2 Multivariate statistical analysis

For the multivariate statistical analysis, F1 and F2 were run together to represent the late spring 2018. F3 and F4 were used in one run to represent the warm and dry period during the summer of 2018, and F5-F7 was run together to represent the autumn 2018. The negative mode results featured F6-F8 and were run together. The Canoco5 software first runs some initial statistical tests on the dataset to check the standard deviation and the gradient of the dataset. This determines the final method of analysis, where PCA (principle-component-analysis) is used if the dataset has a linear trend, and CA (component-analysis) is preferred if the dataset has a unimodal trend. For the data in this study PCA was preferred in all cases except for the negative mode data where CA was used.

2.5 Hydrological modelling in GIS

Through studies of Muller (2014), Sandgren (2017) and others, the Skogaryd catchment is already well monitored and modelled regarding hydrology. The reason for this additional hydrological modelling is the previously explained redirections of streams and modifications to the Mineral subcatchments, which changed the outlines of the catchments and created new flowpaths within the catchment. The software ESRI ArcGIS was used in the modelling with tools from the hydrology toolset in the spatial analyst toolbox to define the new subcatchments.

The data used in the analysis is collected from the Swedish authorities responsible for geology (SGU), weather and climate (SMHI, Swedish Meteorological and Hydrological Institute) and mapping (Lantmäteriet) as seen in table 1.

Table 1

Data	Source	Retrieved from
Digital elevation model, 2m resolution	Lantmäteriet	Maps.slu.se
Ortophoto 2018 and 1960	Lantmäteriet	Maps.slu.se
Terrain map	Lantmäteriet	Maps.slu.se
Quaternary deposits 1:25000 – 1:100000	Swedish geological survey (SGU)	Maps.slu.se

Bedrock 1:50000 – 1:250000	Swedish geological survey	Maps.slu.se
Soil depth	Swedish geological survey	Maps.slu.se
Precipitation Uddevalla	SMHI	https://www.smhi.se/klimatdata/meteorologi/ladda-ner-meteorologiska-observationer
Temperature Vänernborg	SMHI	https://www.smhi.se/klimatdata/meteorologi/ladda-ner-meteorologiska-observationer

Table 1 features the data and data sources used for all maps in this study.

Almost all streams in the Mineral subcatchments can be defined as drainage ditches or heavily modified streams, which are generally made with a depth of approximately 1 meter. Therefore, one polygon shapefile was created with manually drawn outlines of the streams and ditches which have been closed or filled. A second shapefile was made with the new ditches that were made during the modifications. All polygons in the first shapefile was given a value of 1 and the all polygons in the second shapefile was given a value of -1 to represent a filled and a newly created ditch respectively. These shapefiles are called “dämme” and “dikar” in figure 8. These were merged with the outline of the catchment, which were a polygon shapefile with a value of 0. The merged file was then converted into a raster and added to the 2m resolution digital elevation model from Lantmäteriet, from which the model is based.

The following part of the model follows a standard GIS methodology for developing watersheds and catchment characteristics from a DEM (ESRI, 2016). In summary, a depressionless DEM is created from the Fill tool, from which the tools Flow direction and Flow Accumulation follows to develop flow characteristics and flow paths from each cell. Pour points are added to define the subcatchment outlets, and the pour points used can be seen in figure 9 in the Results section. The tool Watershed is finally used to define the subcatchments from the flow data derived from the DEM and the selected pour points. Additional maps on land use and overviews have been made using data presented in table 1.

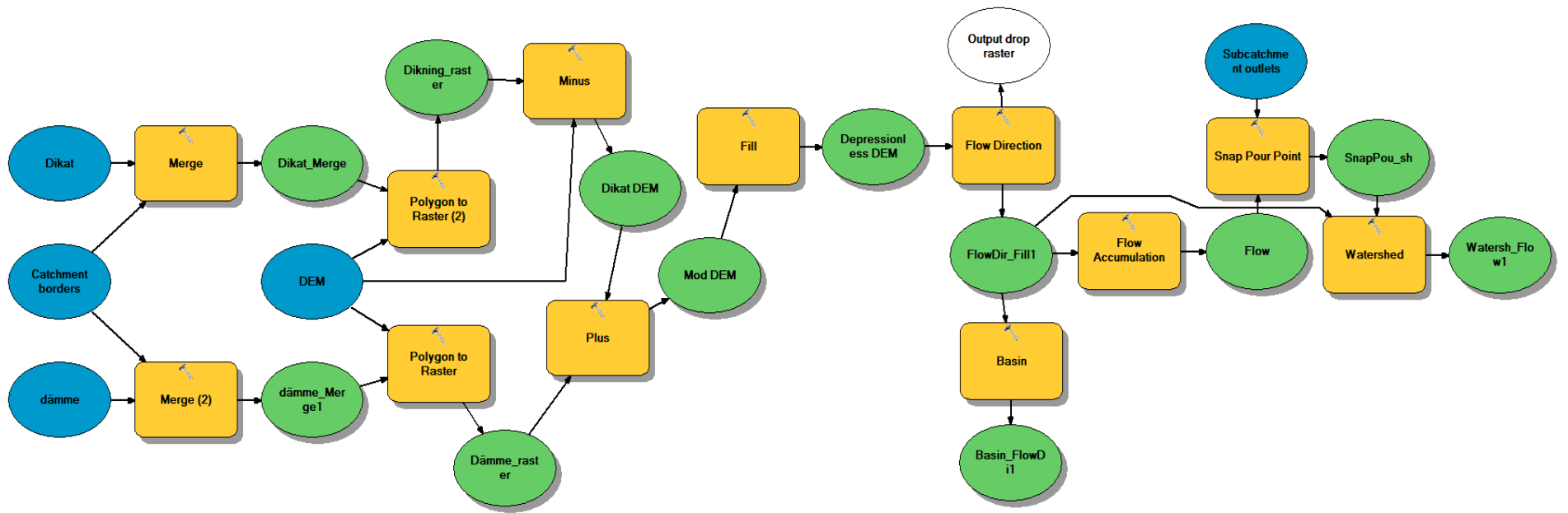


Figure 7 shows the ArcGIS tools and the workflow used to model the hydrology in the catchment.

3 Results

3.1 Remote sensing and hydrological modelling

Figure 9 visualises the result from the GIS modelling with the new subcatchment outlines. The subcatchments was modelled from the subcatchment outlets that are featured in the figure. In comparison with figure 1 it can be seen that the sub catchment *Mineral south* is completely separated from the wetland areas in the northern parts of the Mineral catchment, which is further emphasised in figure 10.

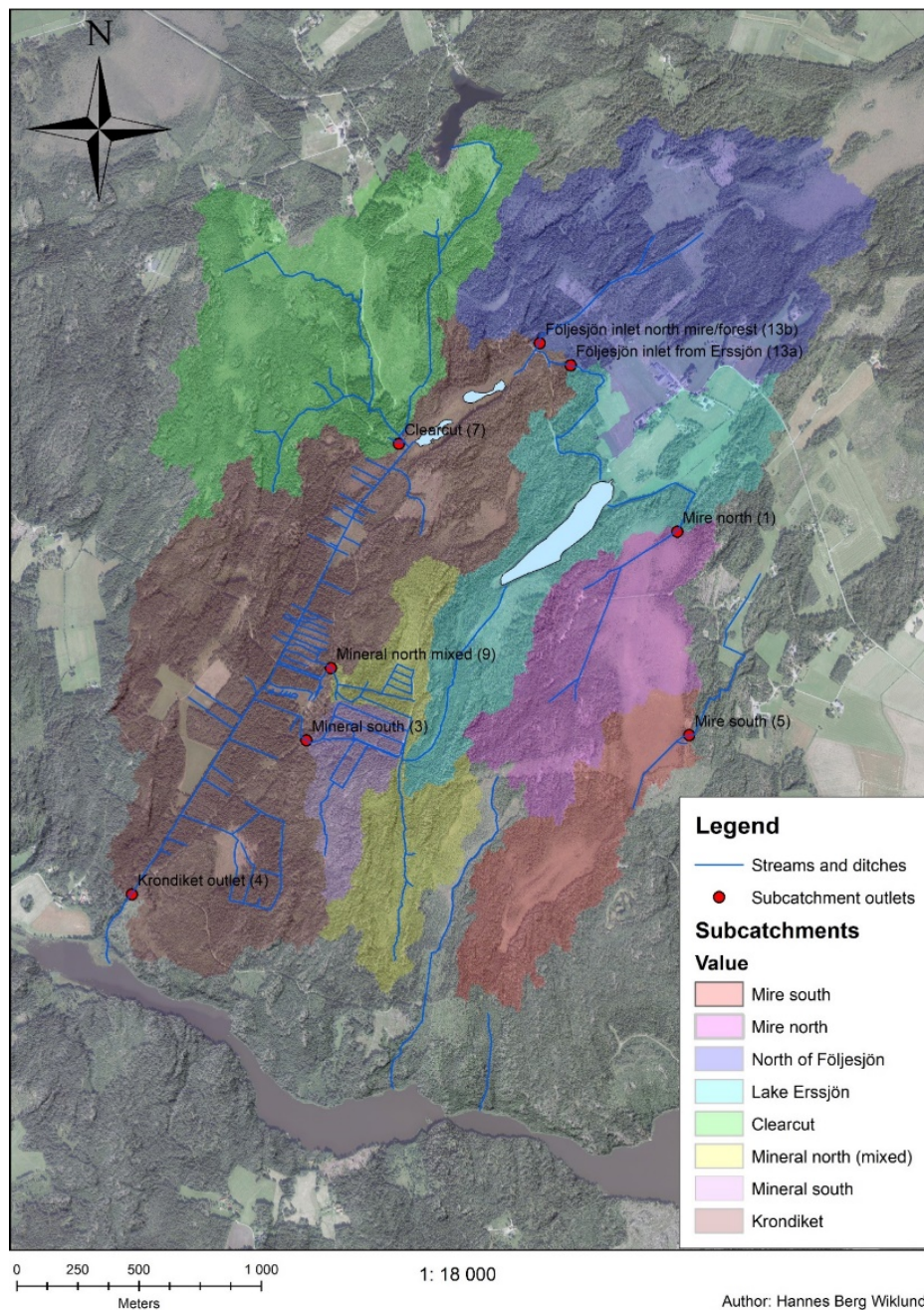


Figure 8 shows the hydrological model of the catchment, with the different subcatchments visualised in different colours. The subcatchments are defined from the subcatchment outlets, and used as pour points in the model in figure 8.

The mineral subcatchments before and after modifications

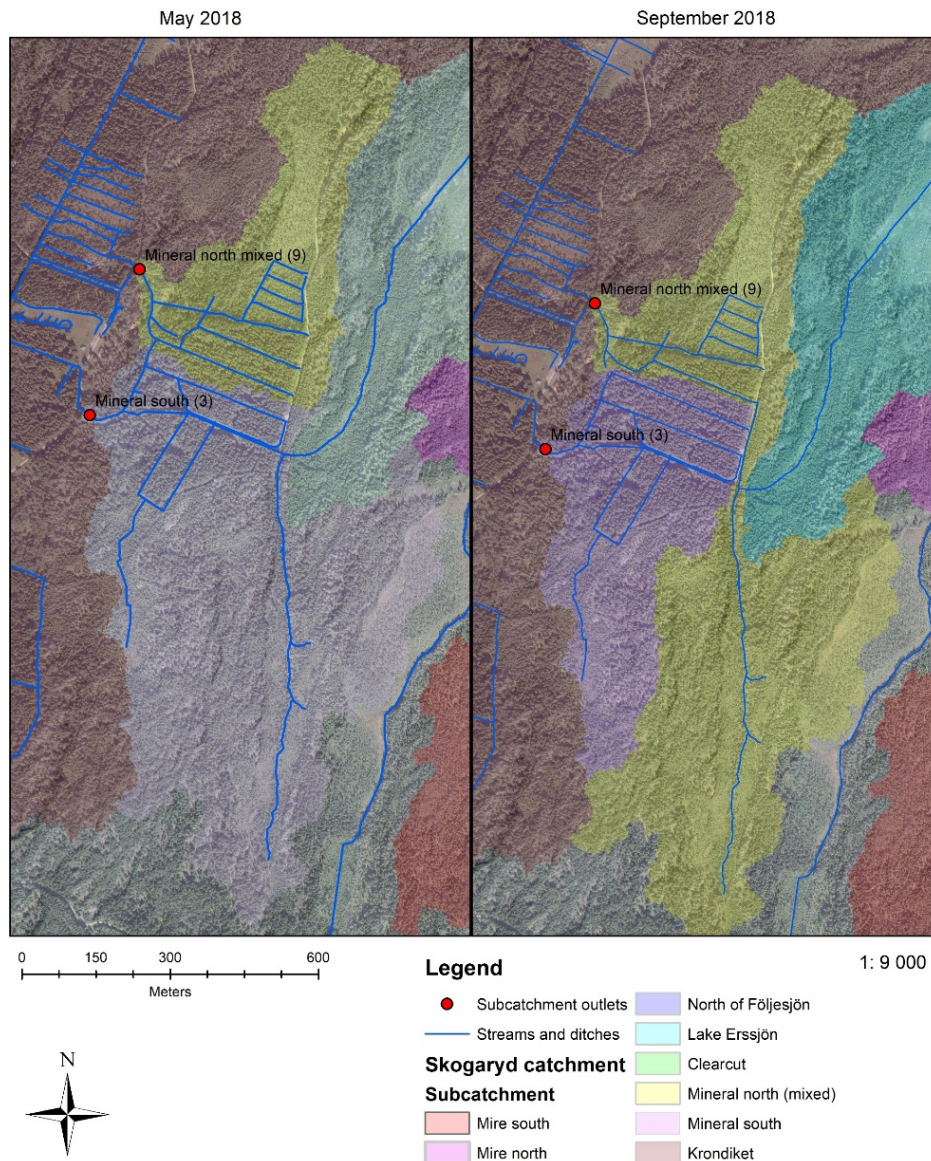


Figure 9 shows the changes to the mineral catchment which was made as part of this study. After the modifications, as can be seen in the map to the right, the mineral south subcatchment was completely hydrologically separated from mire water influence.

3.2 Organic chemistry in stream water

3.2.1 Total organic carbon

The water source can relatively easily be defined by observing the colour of the water samples. In figure 11, bottles H3 and H12 with almost colourless water are samples from the separated forested mineral catchments. H1 and H5 are the Mycklemossen outlets and H11 and H9 are also known of containing mire influenced water. The mire water is clearly the most coloured.



Figure 10 is a photograph of water samples from the different sampling locations in the catchment. The colour of the water correlates well to the concentration of organic carbon. The mire samples, H1, H5 and H11 are the most coloured. H3 and H12 are samples from the mineral south catchment and is almost colourless. The other samples in the photograph are all mire influenced and are all moderately coloured.

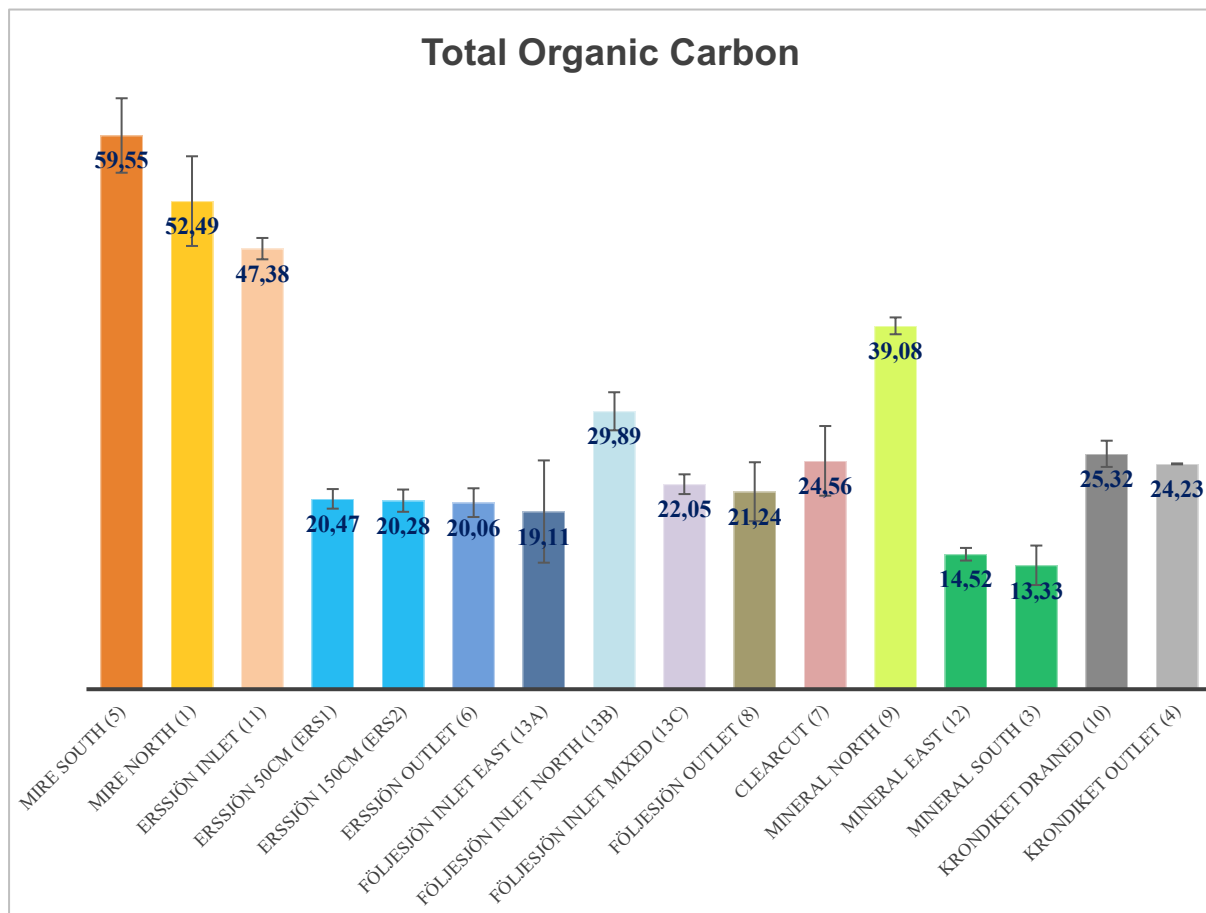


Figure 11 shows the result from the TOC analysis presenting the mean OC concentration (mg/L) for each sampling location. The mire locations (5, 1 and 11) have warm coloured bars whereas the Mineral locations (3, 9 and 12) are shown in green and the locations related to lake Erssjön (ESI, ES2, 6 and 13A) have blue bars. The highest concentrations are seen in the mire influenced locations.

The colour variety shown in figure 10 corresponds well to the measured concentration of carbon in the TOC analysis. Figure 12 show the highest OC concentrations in the mire outlets, 1 and 5, and generally high OC in samples with mire influenced water 11, 13b, 9 and the Kronediket samples 10 and 4. OC decreases drastically when comparing lake inlets 11 and 13b with lake water ERS1 and ERS2 and lake outlets 6 and 8. The lake water and lake outlets show a relatively homogeneous OC content of around 20mg/L. The forested mineral areas, 3 and 12, show the lowest concentrations of OC which is consistent with the almost colourless water on these sites.

The measured OC in this study is considered to correspond directly to the OM content in the water, and the results shown in figure 11 therefore shows some clear trends regarding the

behaviour of OM in the catchment. The results above indicates that the lakes in the study, especially lake Erssjön, acts as a filter for OM in the catchment, where sedimentation and degradation decreases the amount of OM transported to the outlet. This trend is does not correspond to lake Följesjön when comparing the inlet to the outlet OC concentrations. Further, the mineral areas, lake Erssjön and the mire locations have clearly distinct and consistent OC concentration behaviour. The other locations in the catchment all have more distal OM sources and the OM is therefore more influenced by degradation and transformation processes.

With the distinct differences shown in figure 10, the OC concentrations in the water can further be used to roughly estimate the mire influence on each site which is presented in table 2 below. For the northern catchment, north of Följesjön, the OC concentrations for lake Erssjön and the Erssjön outlet was assembled and used as a baseline for water without mire influence. This baseline was compared with the concentrations for the sampling sites to estimate the amount of mire influence on the water, which shows that the northern inlet of Följesjön has a mire influence of approximately 33%. On the southern catchment, the baseline was instead based on the sites in the mineral south catchment after isolation from mire influence. These calculations assumes that all OM above the baselines are originating from mire and wetland areas.

Table 2

Northern catchment

Site	Mean DOC conc.	Mean - baseline	Estimated mire influence on OC	Mean Erssjön DOC	Baseline (based on Erssjön)
1	59,55	39,435	66%	(20,47+20,28+20,6+19,11)/4	20
5	52,49	32,375	62%		
11	47,38	27,265	58%		
13b	29,89	9,775	33%		

Southern catchment

Site	Mean DOC conc.	Mean - baseline	Estimated mire influence on OC	Mean Mineral DOC	Baseline (based on Mineral south + mineral east)
7	24,56	10,56	43%	(14,52+13,33)/2	14
9	39,08	32,375	64%		
10	25,32	25,32	45%		
4	24,23	9,775	42%		

Table 2 shows calculations of mire influence in different locations in the catchment.

The result from the TOC analysis can in a similar way be used to estimate relative flow rates and other hydrological parameters in the catchment. By looking at the OC concentrations from the Följesjön inlet (location 13) with two streams (13a and 13b) that join (13c) before entering the lake, it is possible to estimate by looking at the measured OC concentration that the stream passing 13a has approximately 20% higher flowrate in comparison with 13b. If both streams would have a similar flowrate, the concentration of OC in 13c would have been closer to 25mg/L than 22mg/L which is measured. This means that the stream from Erssjön (13a), with a lower OC concentration of 19mg/L, must have approximately 20% higher flowrate than the northern stream (13b), which has a higher OC concentration (30mg/L). Today, flowrates on the northern area of Följesjön cannot be measured due to that the area is very flat. The organic

content in the water can then with this method be used to roughly estimate the flow contribution from different streams.

3.2.2 Timeseries data

Figures 12, 13 and 14 show results from TOC, water temperature, pH, conductivity and flow rates measured during fieldwork. These are plotted together with the distribution of organic masses in the water for the three sampling sites: Mineral south (location 3), Mire north (location 1) and Krondiket outlet (location 4). The organic mass distribution features all masses that were captured by the TOF in the three replicates from each sampling. As can be seen in the graphs, pH, conductivity and TOC show relatively consistent patterns for all locations with slight variations between the sampling occasions. For location 3, OC decreases drastically after the catchment modifications as expected. For the mass distribution, location 1 and 3 show an increase in heavier masses from October. This could be a consequence of increasing the m/z range in F5-F7 from a maximum of 1000 to 2000 m/z. However, the instrument was still tuned at 5KV which is an optimised setting for lighter masses, and the instrument was with this setting in a similar way to before the changes not able to resolve higher masses than 1000 da in decent resolution.

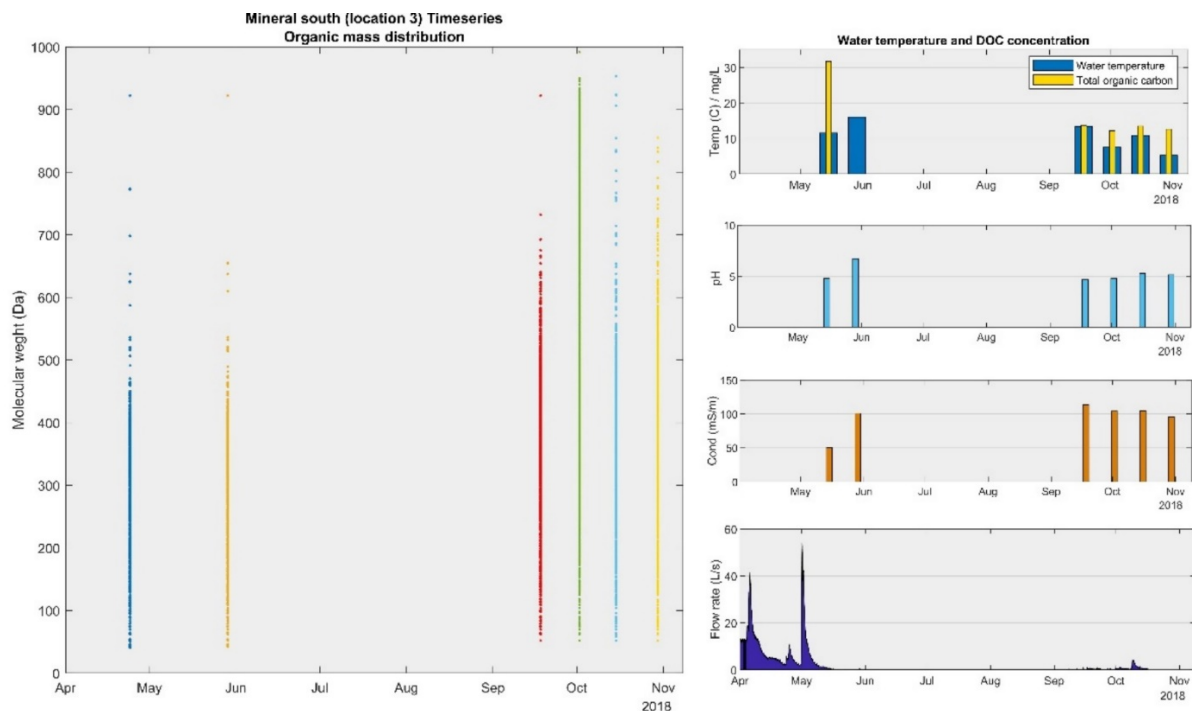


Figure 12, mass distribution for all sampling occasions for location 3 (mineral south) plotted together with TOC, water temperature, pH, conductivity and flowrate, which were measured in connection to fieldwork.

Another explanation for the increase in high masses from October could instead be that increased rain and flowrates after the dry summer increases the amount of high-mass components in the system. This explanation would be consistent with the increase in flow rates during the autumn that is seen in the figures. Further, this trend is not seen in Krondiket (location 4) which have a more consistent mass distribution over the year. This indicates that the trend is not methodological since that would apply to all locations. The absence of the higher mass increase in Krondiket could instead be explained of longer transportation distance from the source of the OM which are expected to be more evenly decomposed closer to the outlet of the catchment.

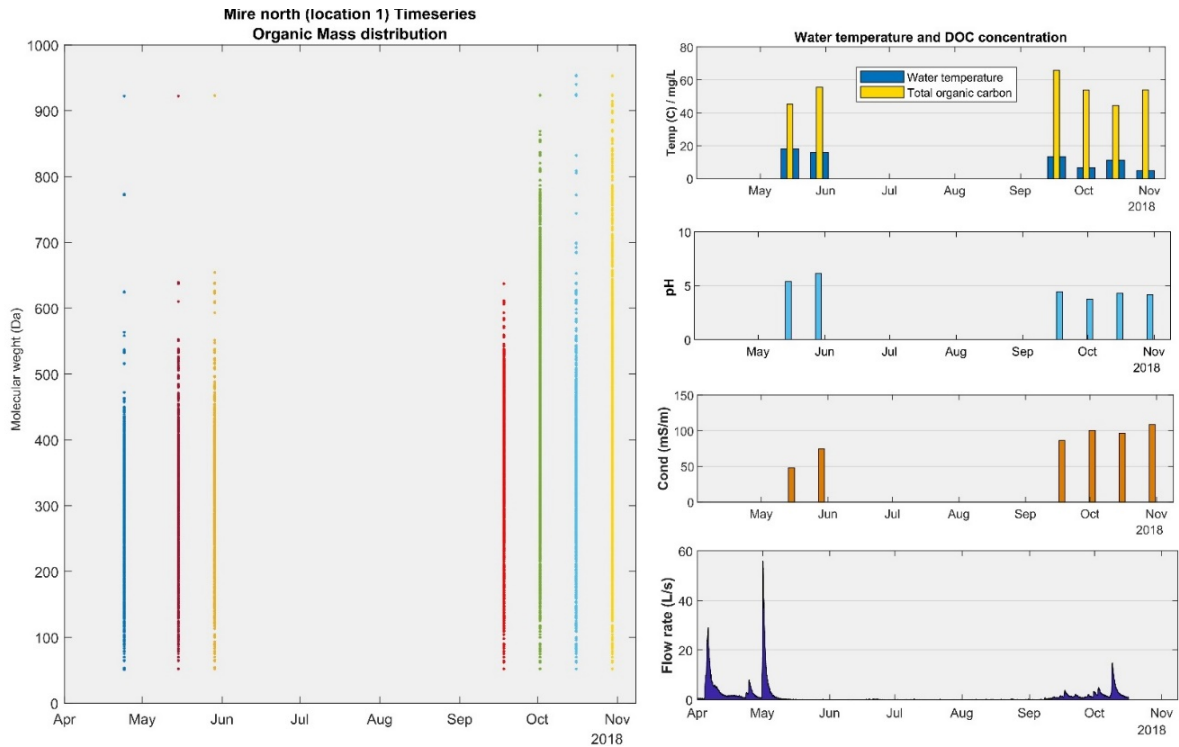


Figure 13 mass distribution for all sampling occasions for location 1 (mire north) plotted together with TOC, water temperature, pH, conductivity and flowrate, which were measured in connection to fieldwork.

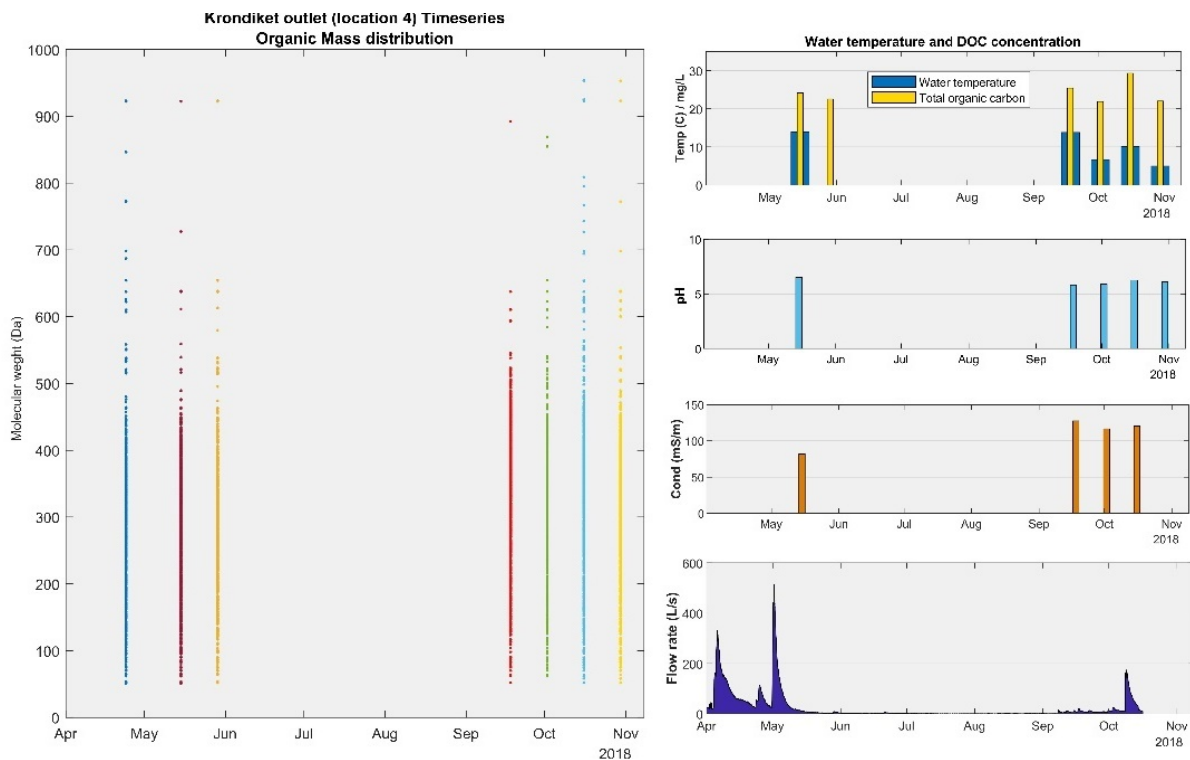


Figure 14 mass distribution for all sampling occasions for location 4 (Krondiket outlet) plotted together with TOC, water temperature, pH, conductivity and flowrate, which were measured in connection to fieldwork.

3.2.3 Mass distribution

This section shows the mass spectroscopy results as mass spectra and statistical plots to visualise differences between the sampling sites over time. Figure 16 is a comparison in composition of OM between mire water, lake water and forest mineral water. The figure shows major differences between the different sites, with higher intensity and wider compositional variety in the mire water in comparison to the other samples. This is consistent with the higher concentration of OM in mire water, figure 11, and with figure 17 which show a decrease in intensity and compositional variety after the redirection of the mire water (green peaks) in comparison with before the catchment modifications (red peaks).

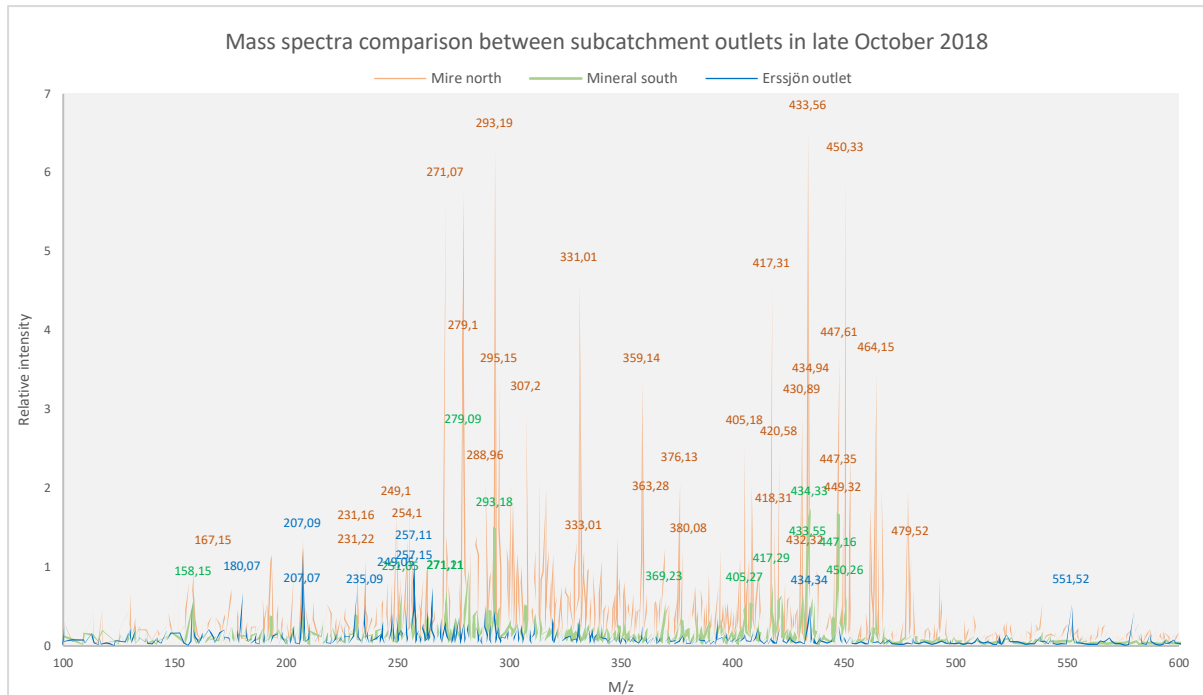


Figure 15, mass spectra comparison showing the OM distribution between sampling sites. Mire location 1 is shown with orange peaks and compared to a forested mineral soil location 3 (green peaks) and the outlet of lake Erssjön (blue peaks). The OM from the mire water has greater diversity and the higher peak amplitudes are indicative of higher OM concentration, which is consistent with the result presented in figure 11.

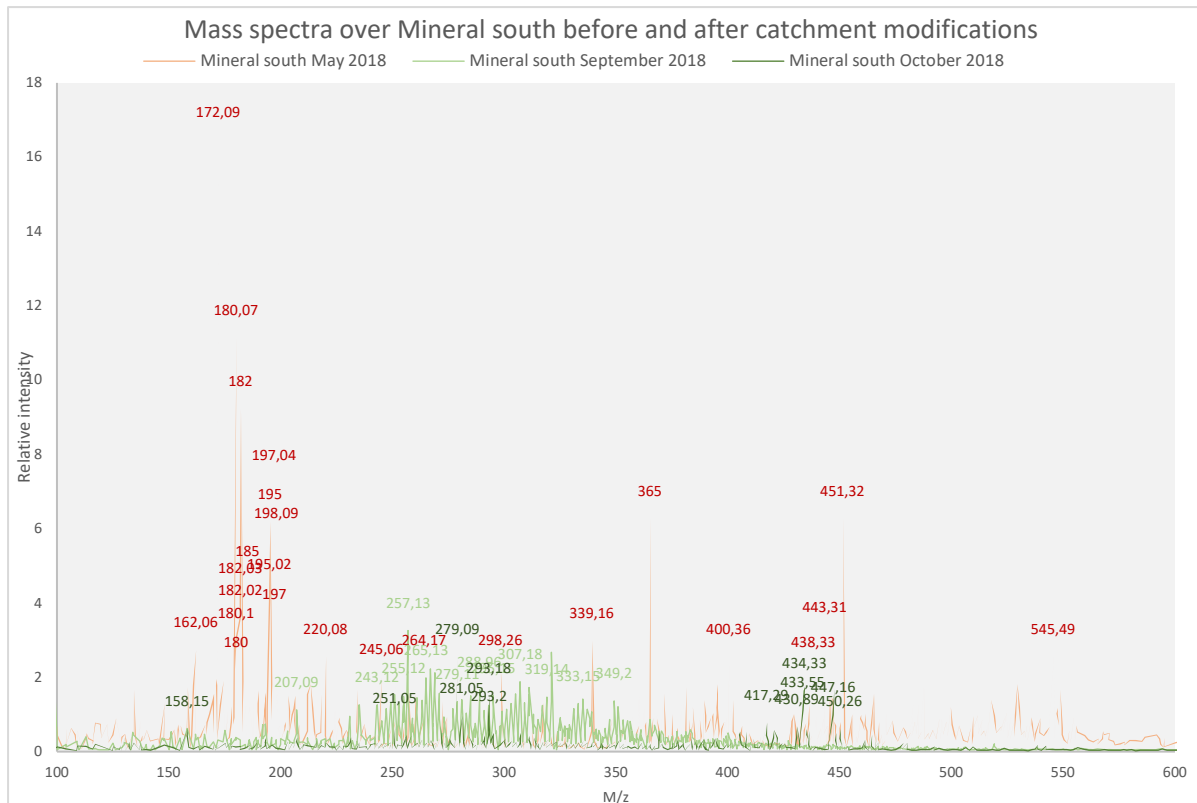


Figure 16, the change in OM distribution to catchment modifications. Greater OM diversity and higher amplitude peaks, indicative of higher OM concentration, is observed before redirecting of mire influenced water from the mineral catchment (red peaks) in comparison to after the modifications (green peaks).

The northern inlet of lake Följesjön (13b) contains approximately 33% of mire water according the estimates in table 2 and the flowrates of joining streams are can be estimated from the OC concentrations. A more accurate measure would be to identify mass peaks which are indicative of mire water. In figure 17, the mass composition of the stream water OC in location 13b is compared to the composition in water from the mire outlets. Location 13b show a generally different mass distribution in comparison to the mire outlets. Peaks with m/z approximately 258 da, 301 da, 344 da and 407 da show high intensities in the water of location 13b and can be correlated with peaks from the mire outlets. Since the general mass distribution is different from the mire samples, the above-mentioned peak correlations must be replicated and proven absent in lake and mineral forest stream samples to prove a robust correlation. The general decrease in TOC and compositional variety of OM is expected and can be explained by the longer transport distance from the source of the OM, since degradation and sedimentation processes will decrease the amount and variety of OM with longer transportation. This however makes it more difficult to use specific molecular weights as markers and tracers in the catchment.

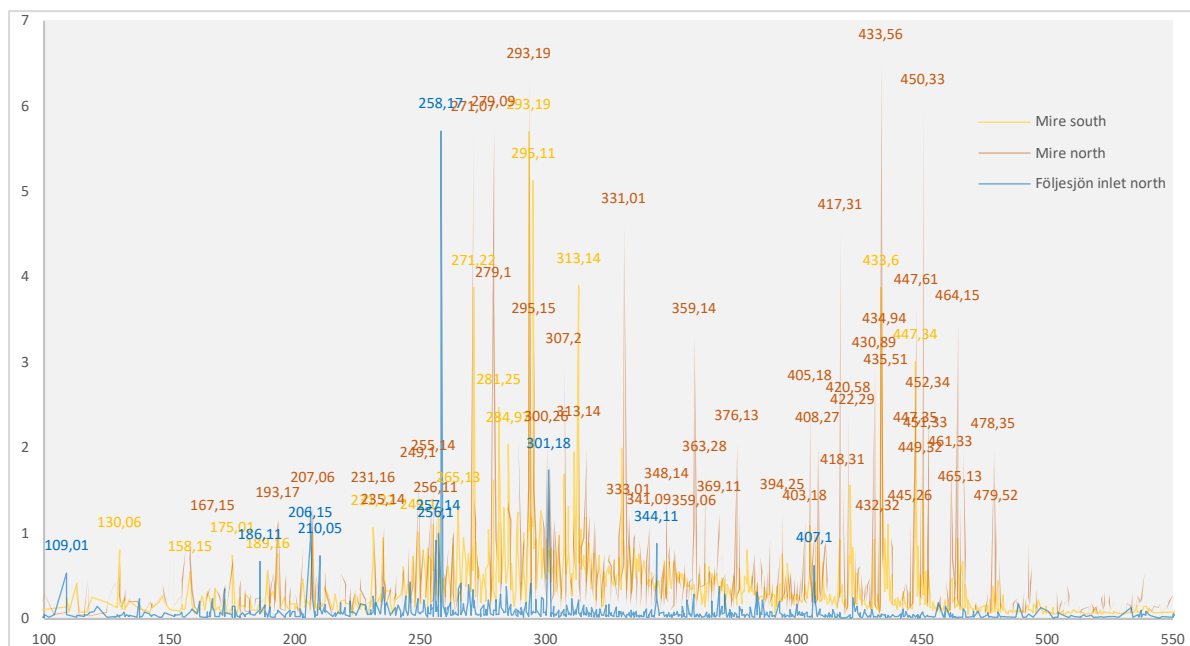


Figure 17, mass spectra comparison between the northern inlet of Följesjön, a mire influenced location (blue peaks), and the Mycklemossen mire outlets (yellow and orange peaks). The clear difference between the sites can possibly be explained by longer water transport from the source material in the Följesjön location, and that the OM in the Följesjön inlet is more influenced by decomposition processes in comparison to the water from the mire outlets.

3.2.4 Mass distribution through multivariate statistics

Figure 18-20 are multivariate statistical plots (principle-component-analysis) based on positive mode mass distribution and intensity data for each sample during each sampling occasion. Figure 21 is a CA-plot (component analysis) based on negative mode data from the autumn 2018. The negative mode data are probably not as accurate as the positive mode data due to tuning issues with the instrument. This is reflected in that the software Canoco5 detected a unimodal trend in the negative dataset in comparison to linear trends in the positive data. Further, the OM trends in figure 21 are not as clear as in the positive mode plots.

For figures 18-21, the numbers which are plotted represent the sampling location and differences in colour represent different sampling occasions. Each data point is a mean of the three replicates which are run in the TOF for each sampling occasion. Standard deviation and confidence intervals for the replicates are calculated with alpha 0,15, and the error bars in the plots shows the confidence interval calculated for each data point. Each figure 18-21 represent one statistical analysis in the Canoco5 software. Figure 18 shows two datasets from the spring 2018, and figure 19 also consist of two datasets, one from late May and one from September. Figure 20 and 21 consist of three datasets each, from the autumn of 2018, with figure 21 being a CA-plot with the negative ionisation mode data.

Figure 18 show that the samples taken in May 2018 (blue) and the samples taken in September 2018 (orange) have plotted along the first axis. Erssjön related data points (6, ES1 and ES2) can generally be said to have negative values on the first axis, whereas the mire related data points (1, 5 and 11) generally have positive values on the first axis in both datasets. The datasets are comparable on the first axis but almost completely separated on the second axis.

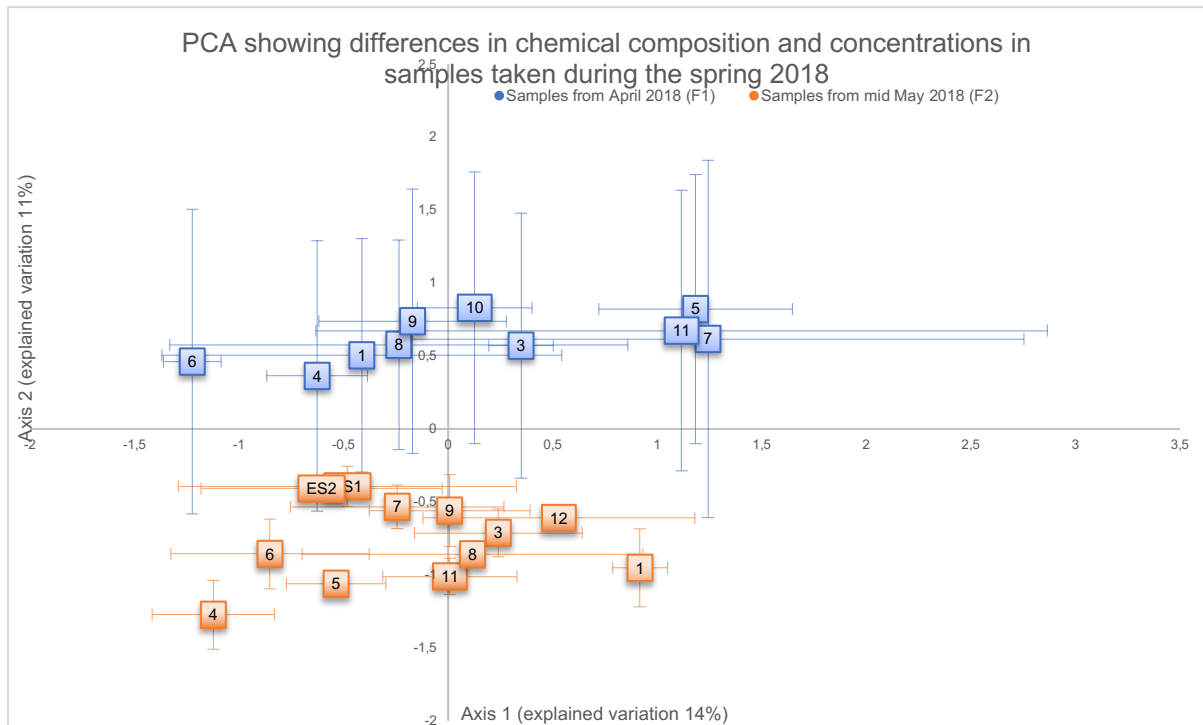


Figure 18, Principle Component Analysis (PCA) based on mass spectra peak from the sampling locations sampled during F1 (blue) and F2 (orange).

Figure 19 shows a similar trend as figure with the mire related tend to cluster at higher values, both in the first and second axis, and the Erssjön related sampling points are clustering at the other end of the datasets. In this figure the general trend is diagonal rather than horizontal for both datasets, but the late spring and early autumn data is also in this plot completely separated.

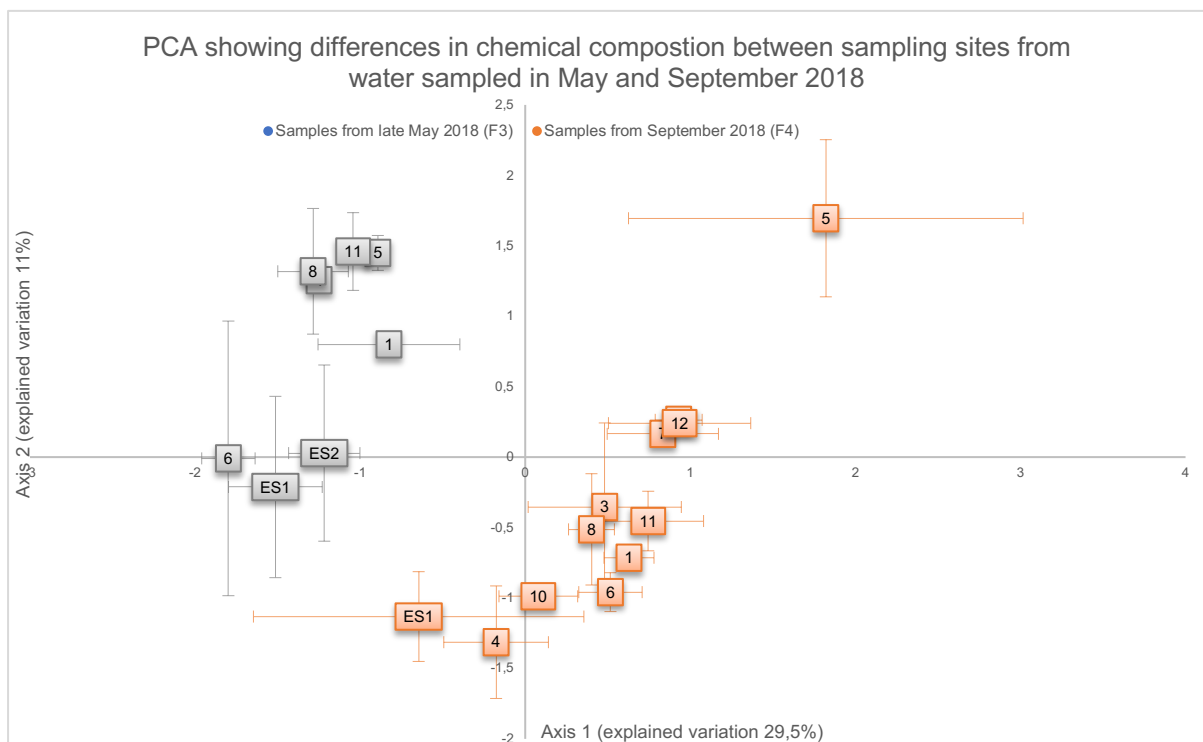


Figure 19, PCA based on mass spectra data comparing the OM composition and concentration differences between the sampling locations sampled in May 2018 (grey) and September 2018 (orange). No sampling was conducted between these occasions due to the exceptionally dry summer.

The autumn datasets, figure 20 and 21, are not as clearly separated in comparison to the plots above. This is possibly due to that these datasets feature more sampling points and that three datasets are plotted together instead of two. For the positive data, figure 20, a similar trend as the previous plots can be observed with some separation between the sampling occasions, especially between F5 (blue) and the other two datasets. Additionally, there is a clear cluster of the mire related sampling points (1,5 and 11) at approximately 1 on the first axis in figure 20. Similarly as the previous plots, the Erssjön related sampling points also group on the negative side in figure 20. These trends are not as obvious in the negative mode data, which is probably due to the previously mentioned tuning issues. This is further reflected when viewing the error bars in figure 21, which shows large variety between replicates.

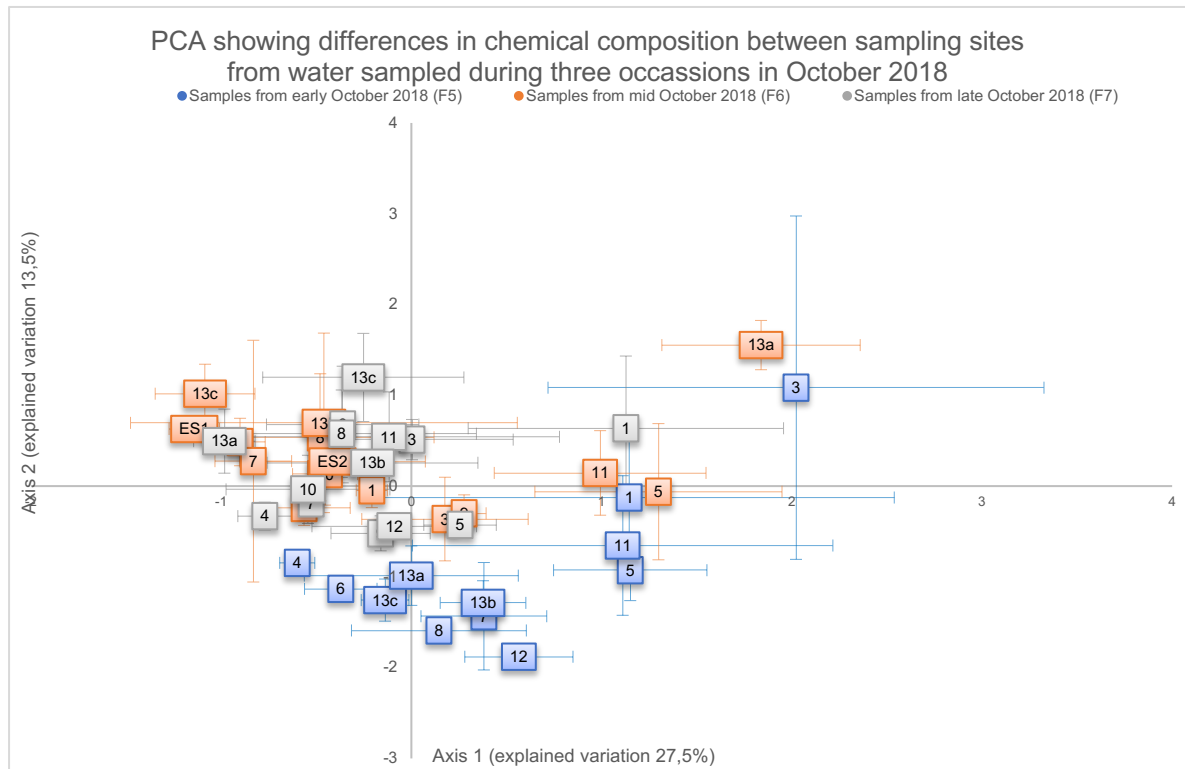


Figure 20, PCA based on mass spectra data from sampling conducted in early October (blue), mid-October (orange) and late October 2018 (grey).

When observing all plots it can be seen that the error bars at times indicate large variety between the replicates. One possible explanation to this phenomena is that the replicate droplets evaporate differently when using DSA, which leads to concentration and intensity differences on similar peaks between replicates. In addition to tuning issues in negative mode, another explanation could be carry-over effects between different samples.

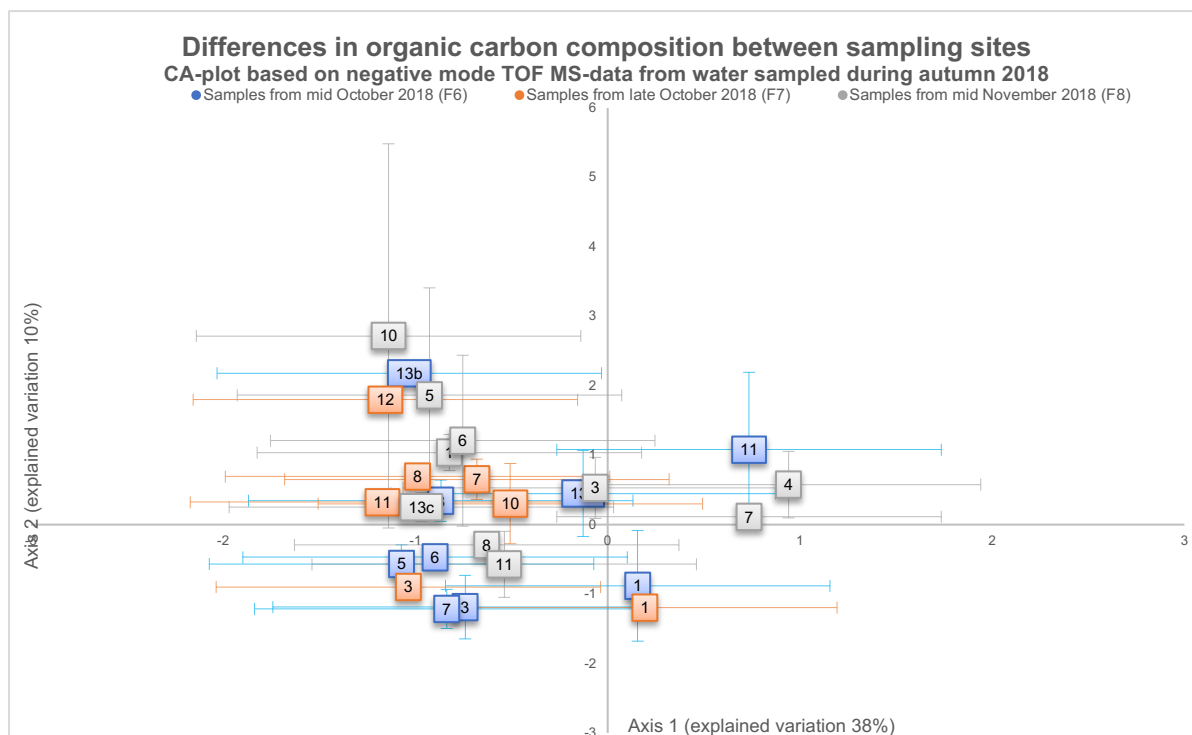


Figure 21, Component analysis based on mass spectra data using negative mode in the TOF, from sampling conducted during the autumn 2018.

3.2.5 Formula assignments

Figure 22 is a spectrum comparison between three sampling sites in Krondiket. The mass spectra data have been matched to the theoretical formulas generated by the second Excel script. The formulas have been labelled to the corresponding peak in the figure and the mass for each formula match the corresponding peak with a maximum mass difference of 10ppm.

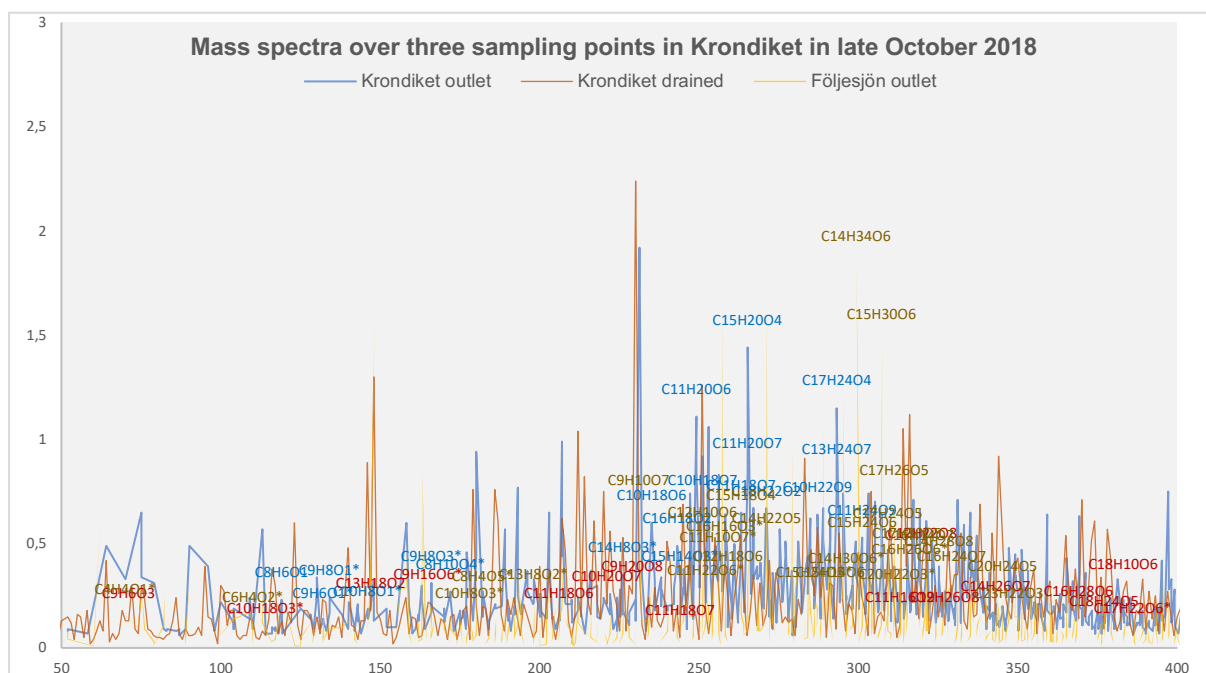


Figure 22, mass spectra comparing three sampling locations along stream Krondiket from sampling occasion F7, featuring formula assignments on a selection of matching peaks.

As can be seen in figure 22, the composition of peaks from the three sites show a similar pattern with some differences in certain parts of the spectrum. However, the formula assignments were only matching to a few of the higher peaks due to greater mass difference than 10ppm. This is probably due to limitations in the methodology which is further discussed in the discussion.

From the formula assignments, ratios of the included elements can be used to group the formulas to which type of organic material that is studied. One common plot which is based on hydrogen-carbon and oxygen-carbon ratios is called the Van Krevelen plot. A Van Krevelen plot based on the theoretical formulas assigned with a mass difference of 10ppm from correlated peak is shown in figure 23. The data in the figure has been grouped according to the water source e.g. Mire outlets including location 1 and 5 is marked with a red dot. In a similar way, the mineral locations 3 and 12 are marked in green, the Krondiket locations (4 and 10) is shown in brown colour and lake Följesjön in yellow.

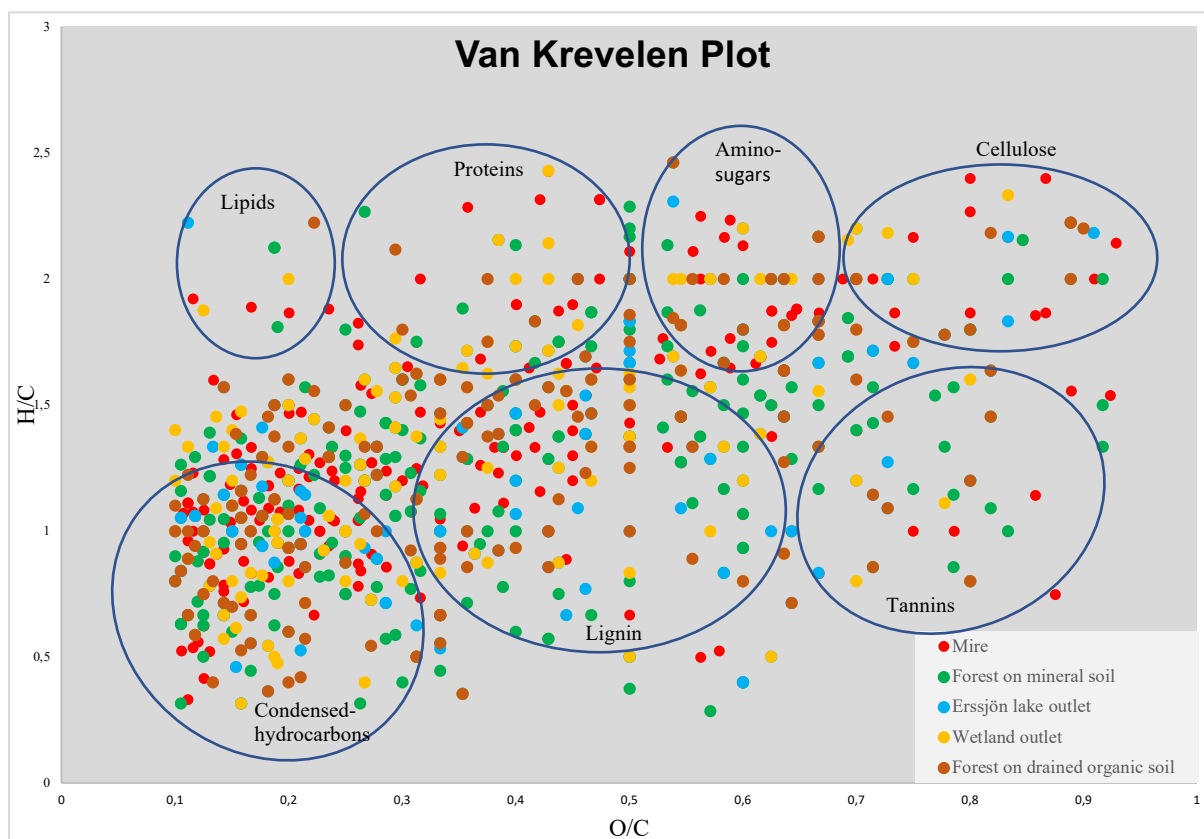


Figure 23, Van Krevelen plot with defined organic classifications (classifications after the compilation in figure 1 by D'Andrilli et al. (2015)). The plot is based on hydrogen/carbon and oxygen/carbon ratios from formula assigned peaks.

The figure shows a domination of condensed hydrocarbons and lignin in the material studied, with lower occurrences of lipids, amino-sugars, tannins, proteins and cellulose in the catchment. However, differences and specific trends for the different subsites cannot be observed in the figure. The trend towards lignin and condensed hydrocarbons could possibly be explained with that the OM is dominated by secondary products that have been decomposed or degraded from its source material. Although it should also be mentioned that the plot in figure 23 might not be completely reliable due to that the method used was not able to resolve the peaks to the extent of reliable formula assignments.

4 Discussion and conclusions

4.1 Results

The result show that it is possible to distinguish certain subsites within the Skogaryd research catchment from comparing TOC concentrations and the molecular weight distribution of stream water from the different sites. The mire sites were clearly distinguishable due to significantly higher OC concentration and a greater OM diversity. The Erssjön lake sampling locations and the forested mineral locations were also distinguishable based on OC concentration and to some degree from the mass distribution, although not as clearly as the mire sites. Also visible in the data is the filter effect or decrease in OM concentration from the inlet to the outlet of a lake, which is important in the discussions regarding brownification problematics and water regulations. Another note is that this effect is not replicated when observing the inlet and the outlet of a wetland, as in the case of the overgrown lake Följesjön. This result emphasises the risks that vital ecosystem services are lost due to eutrophication and changes in water management. From the above it can be concluded that the results of this study has added greater insights to the hydrology of the Skogaryd research catchment.

Although the three main vegetation and landuse types could be distinguishable with this method, this study was not able to find mass peaks which specifically originated from a specific subsite. Therefore it was not possible to use the internal chemistry as a tracer as expected. This is probably due to the not fully understood degradation, transformation and sedimentation processes which are affecting the OM during transport through the catchment. Further, the study of these processes probably require a higher resolution instrumentation or coupled methodological approaches. A scanning mass spectrometry coupled with a simultaneous spectrum generating mass spectrometer might be able to replicate the findings in studies like Adamczyk et al. (2016), Adamczyk, Kitunen & Smolander (2009), Kanerva. et al. (2006), Kanerva & Smolander (2008) and Smolander et al., (2012) which have shown linkages between specific OM components and vegetation types by chemical extraction analysis. However, the study by Hawkes et al. (2018a) showed that the complexity of the OM from natural environments was greater than expected and that the HPLC-MS/MS instrumentation used in the study was, in a similar way as the result from this thesis, not sufficient to identify individual isomers.

Another way of studying the processes affecting the OM in the water would be to incubate stream water samples and run incubated water in the TOF. Additionally, the result from the statistics further indicate changes to the OM between sampling occasions. How the OM responds to seasonality, changes in weather and climate are other factors that needs to be surveyed and considered in future studies, and that is likely to have great impact on the result.

4.2 Methodology: limitations and future improvements

Despite the complexity of studying OM there are several ways the accuracy of this method could be improved. The use of sample droplets with the direct-sample-analysis approach is a quick and simple method but it also comes with problems. One issue is that the droplets are evaporated to some degree before injection into the spectrometer. This probably leads to concentration differences between the samples and the replicates. Along with carry-over effects and high contamination risks, this could be one explanation for the great variety between replicates, shown in the error bars, in the statistical plots. One way of improving the consistency would be to use an automated syringe system, or LC-MS approach, which feeds the spectrometer with sample at a constant rate. This would remove the need for replicate runs and

reduce the risk of contamination and carry-over effects as well as increasing the control over the procedure.

This method was also not very successful in matching molecular formulas to the observed peaks. One limitation is that only carbon, hydrogen and oxygen was considered when generating the formulas and that some of the peaks might include other elements. Furthermore, most studies applying formula assignments to mass spectra have been conducted using higher resolution equipment. The study by Hawkes (2018b) on water samples from Swedish headwater streams have been conducted on an Orbitrap which generates higher resolution peaks, more accurate formula assignments and more reliable Van Krevelen plots. This study showed similarities in the DOM composition from a variety of forested hemiboreal catchments, and that river DOM in many cases is reflected by the headwater catchment, as also shown to some degree in this study.

4.3 Conclusions

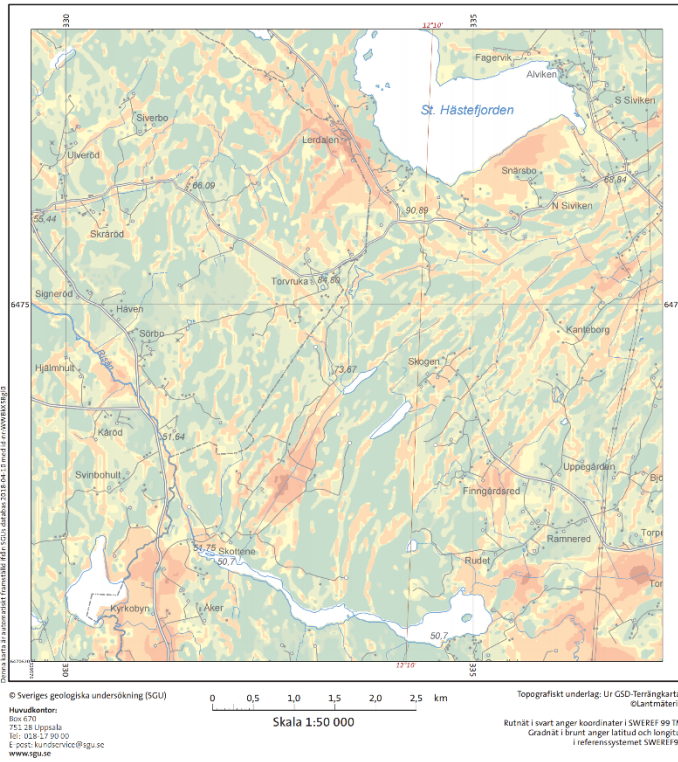
In conclusion, this study shows that characteristic sub-catchments can be distinguished based on the OM concentration and distribution from the stream water draining the specific sub-catchment. However, it was not possible to identify and use specific molecular weights from mass spectra as a downstream tracer for water originating from a specific sub-catchment. This is probably due to degradation, transformation and sedimentation of OM occurring in the transport of OM through the aquatic environment. Improving the methodology with coupled methodological approaches and studies covering longer time periods are necessary to improve the understanding of OM behaviour to seasonality and the complex processes affecting the OM in the aquatic environment.

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Kartans syfte är att ge en generell bild av jordtäckets måttighet. Kartan grundas på analys av jorddjupsinformation från brunnborrings-, undersökningsberriggar-, schakter och seismiska undersökningar. För att identifiera områden där jordtäckets är mycket tunt eller saknas helt har information om berg från SGUs jordartskartor använts. Jorddjupet har beräknats genom att interpolera kända jorddjupsdata. Eftersom vissa jordarter uppvisar betydligt större jorddjup än andra har jordartskartan använts som stöd vid denna interpolering. Information om sprickzoner i bergsunden har använts för att ta fram områden med speciellt stora jorddjup.

Osäkerheten i beräkningarna ökar med avståndet till punkter med uppmätta jorddjup. Om avståndet exempelvis är flera hundra meter till närmaste observation är osäkerheten i det beräknade jorddjupet betydande.

Ny information om jorddjup tillkommer hela tiden vilket gör att kartan successivt kan förbättras. Kartan kommer därför att uppdateras ungefär en gång per år.

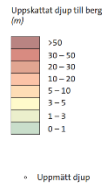


Figure 26 Map showing soil depths in the area around Skogaryd (Swedish geological survey, SGU)

7 Appendix 2: Historical landuse changes over Skogaryd

The Skogaryd Research Catchment 2018

The Skogaryd Research Catchment 1960

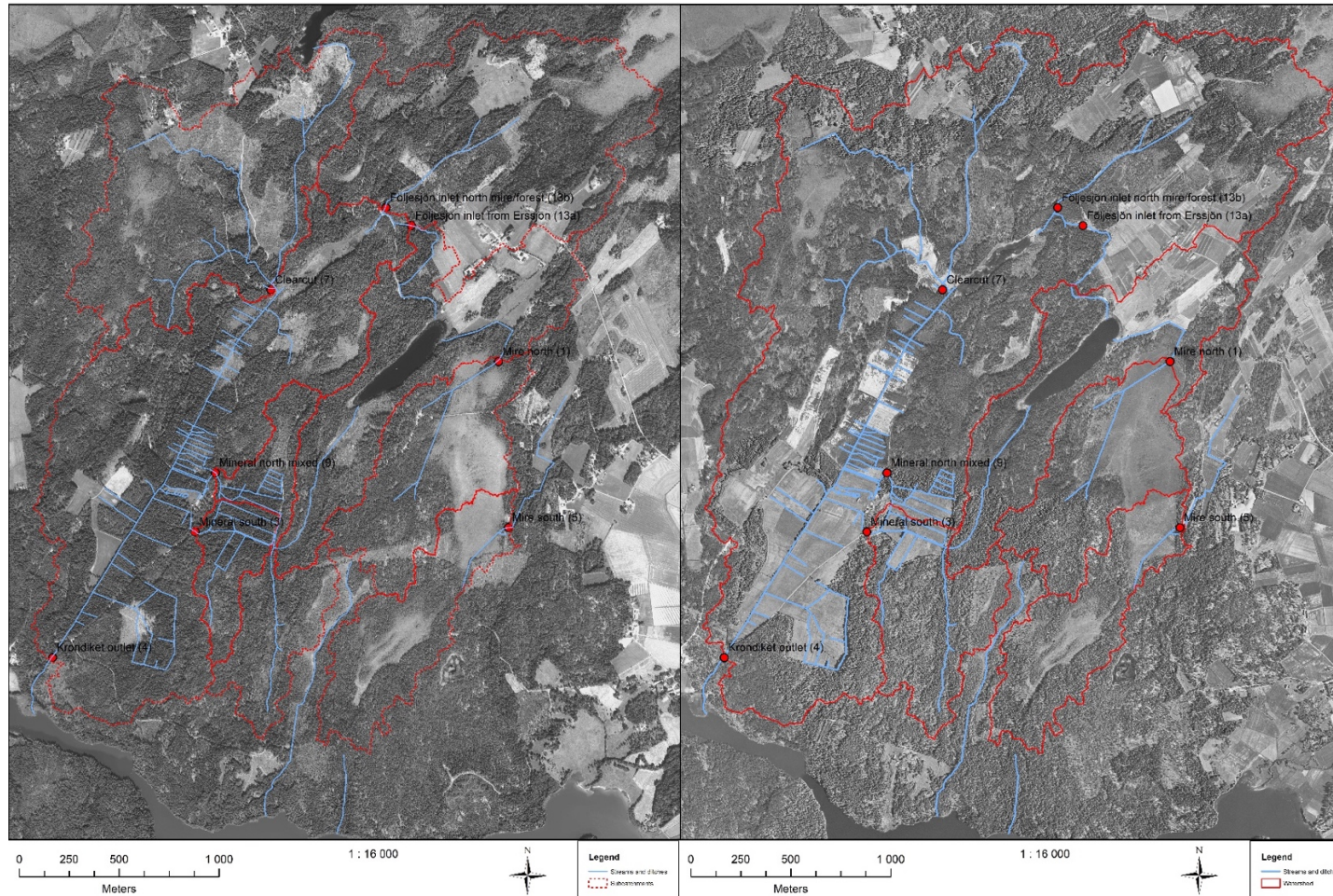


Figure 27 Maps showing two orthophotos over the Skogaryd research catchment to visualise changes between 1960 and 2018 (data source: Lantmäteriet)

Lake Erssjön 1960 and 2018

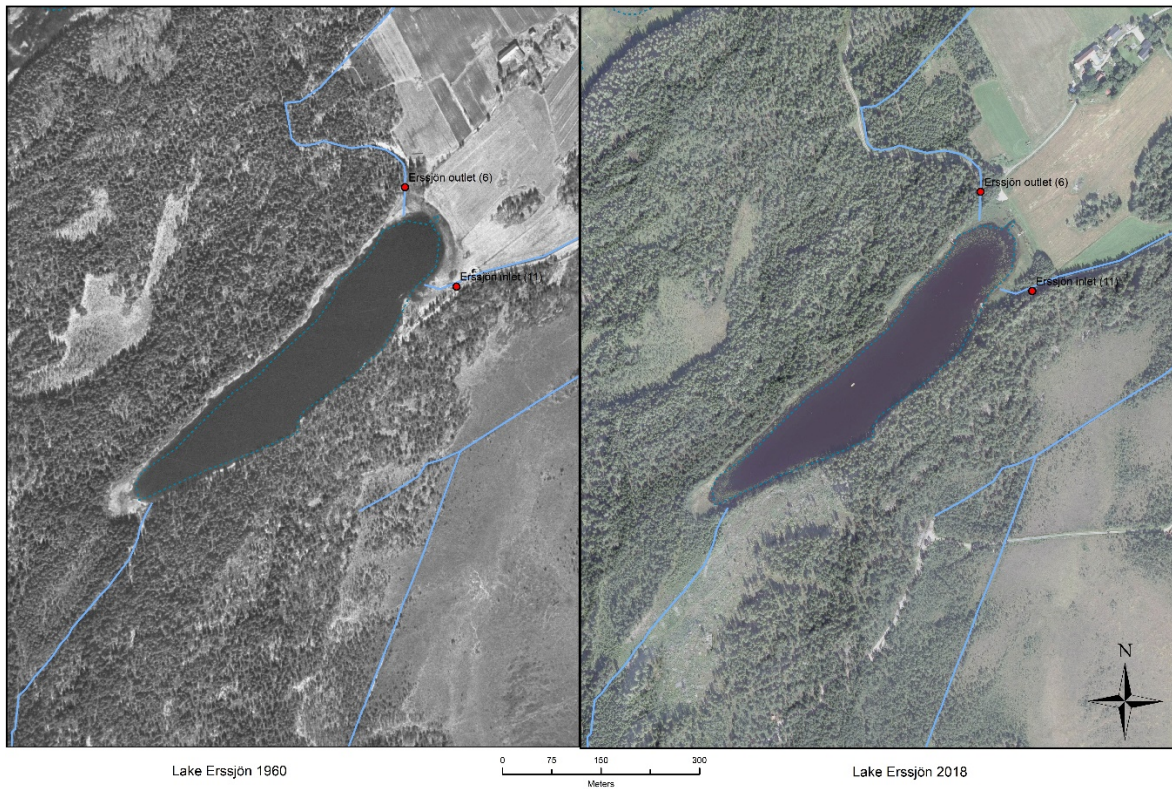


Figure 28 Lake Erssjön 1960 and 2018 (data source: Lantmäteriet)

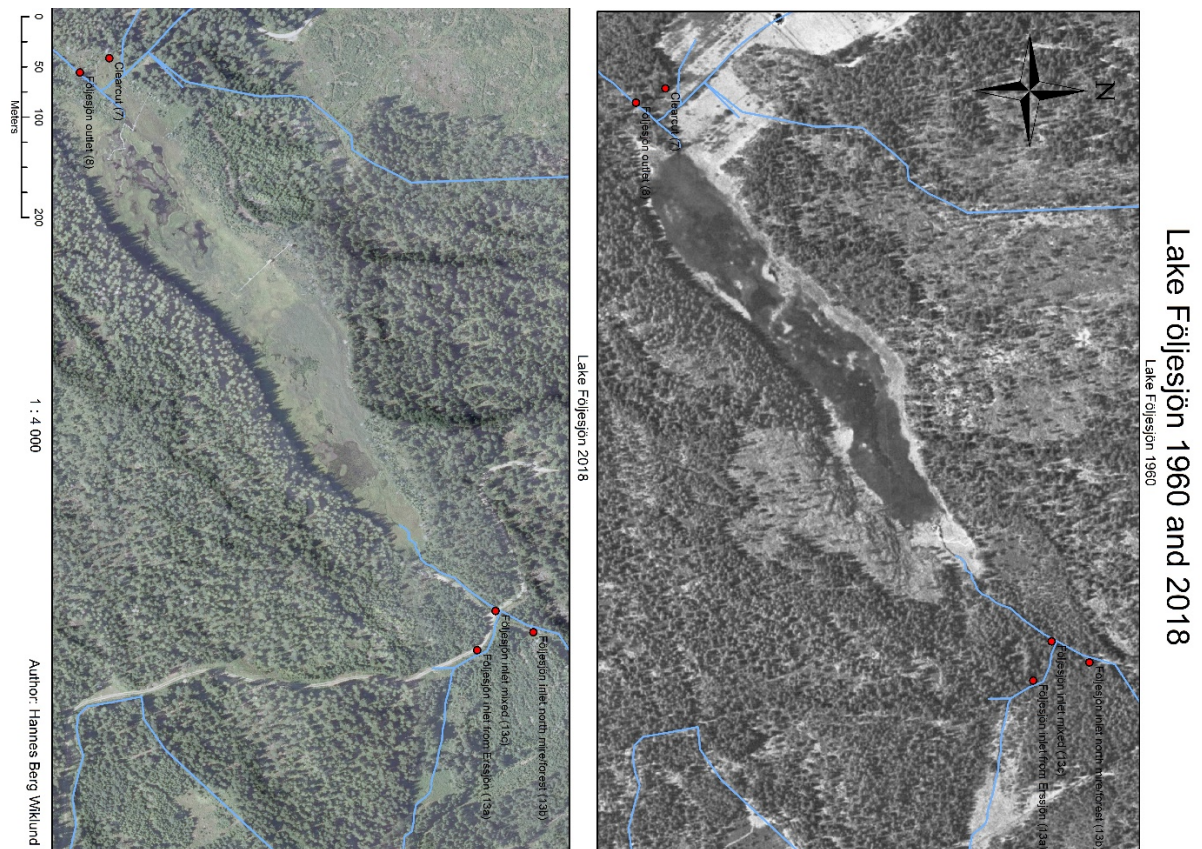


Figure 29 Lake Följesjön 1960 and 2018 (data source: Lantmäteriet)

Mycklemossen 1960 and 2018

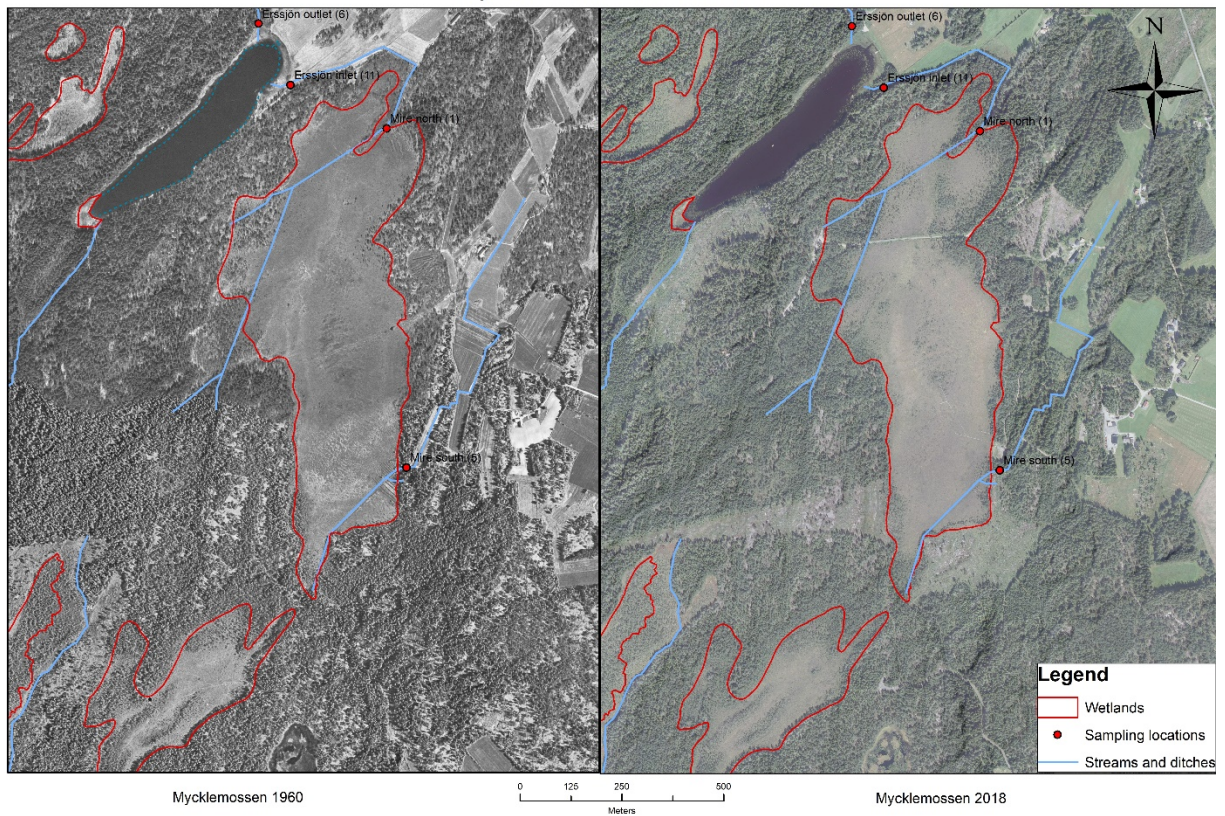


Figure 30 Map over the mire Mycklemossen 1960 and 2018