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Monitoring dissolved organic carbon in Swedish forest streams after wildfire

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Abstract

In situ water quality monitoring devices (sondes) allow monitoring of dissolved organic matter (DOC) continuously at a high resolution via measurements of fluorescent dissolved organic matter (fDOM). Two sondes were used to test the hypothesis that DOC in local streams would decrease in concentration immediately after forest fire. It was expected that the sondes' measurements would be influenced by turbidity and require post hoc correction. A simple model to predict DOC from fDOM was designed and suggested that DOC inputs were reduced after the fire, but flushing of terrestrial carbon brought values back to normal in following spring. Analysis of fluorescence and absorbance suggested a change in the quality as well as quantity of carbon inputs. Sonde measurements were found to be severely affected by high turbidity events, and varied depending on the stream, but we could partially compensate for this with corrections based on laboratory analysis of samples taken from monitored streams. Future monitoring that relies on fDOM data should be supported by a sampling program to capture natural variation of DOC and turbidity in the monitored stream.

Popular summary

The Västmanland fire in 2014 burned a large area of pine forest in central Sweden. According to research, we think that the fire would have also affected forest streams in the area, so we started monitoring them to see how they were affected. One part of environmental monitoring involves measuring the amount of dissolved organic carbon (DOC) in forest streams. Devices called “sondes” can measure this frequently over long periods of time, but we were not sure how reliable they would be or how to use them most effectively. Beside the amount of DOC, we are also interested in its “quality” (its chemical characteristics) because that can tell us where in the environment the carbon came from.

The main question we wanted to answer was, “What effect did the fire have on the concentration and quality of DOC in streams?” We also wanted to know, “How can we best use our monitoring technology to answer the first question?”

We found that the fire changed the way carbon gets into streams, and the type of carbon that was in them, but the overall amount was only slightly lower than normal. We also found that sondes behave differently depending on the stream they are in. This means that when using sondes, we can get better information by also measuring some samples from the stream in the laboratory, so we can find out more about how the sonde works in that particular stream.

Abbreviations:

DOM – dissolved organic matter (particle size smaller than 0.7 µm).

TOC – total organic carbon.

DOC – dissolved organic carbon (particle size smaller than 0.7 µm).

fDOM – fluorescent dissolved organic matter. The portion of DOM that fluoresces under UV light. Used as a proxy for DOC.

IFE – a phenomenon in fluorescence whereby high concentrations of fluorescing compounds suppress the signal.

QSU – quinine sulphate units. A measurement of fDOM (and fluorescence in general) based on the fluorescing properties of quinine sulphate.

FNU – formazin nephelometric units. A measurement of turbidity based on the light-absorbing properties of formazin.

EEM – excitation-emission matrix. Used to display results of fluorescence analysis.

SUVA – specific ultraviolet absorbance. Fluorescence at the excitation wavelength of 254 nm, normalised against DOC.

Introduction

Dissolved organic matter (DOM) in forest streams is ecologically important for a range of reasons, including water colour (which affects photochemistry), productivity (DOM is a substrate for microbial respiration), and the carbon cycle; changes in DOM also reflect landscape processes. For the purposes of this project, particles smaller than 0.7 μm were considered "dissolved".

Waters in forested catchments typically contain high concentrations of dissolved organic matter, mostly in the form of organic material from the surrounding vegetation and the organic layer of the soil, and the products of decomposition by soil and water microbes. DOM has either a terrestrial source (transported into streams, mostly from organic & surface layers of forest soil (Boyer et al. 1997), or an aquatic (in-stream) source, which may be an independent source or a recycled form of terrestrial DOM. Terrestrial DOM contains a higher proportion of humic substances and aromatic compounds (Fasching et al. 2014); in streams, this is metabolized by microorganisms to less aromatic substances. DOM concentrations are determined by source factors, such as the decomposition of vegetation in the riparian zone, and transport factors such as water flow.

Seasonal variation in DOM is tied to hydrological factors (Pellerin et al. 2011). For example, spring snowmelt increases DOM concentration as water discharge increases; DOM peaks before maximum discharge occurs, and then declines (Boyer et al. 1997). This "flushing" of soils is main mechanism explaining DOM temporal variation in forest streams.

Fluorescence analysis of DOM

A parameter known as Fluorescent Dissolved Organic Matter (FDOM) measures the portion of dissolved organic matter which fluoresces when excited by ultraviolet (UV) radiation, and is used as a proxy for DOM and DOC. Fluorescence occurs when an electron is excited (i.e., absorbs energy from a photon), then this energy is lost as the electron returns to its former state. The lost energy comprises an emission of light (fluorescence) as well as the losses prior to emission (e.g. non-radiative decay of energy). Fluorimeters measure this emission of light. The wavelengths of excitation and emission are specific to the molecule; therefore, the emission at a given excitation wavelength indicates the concentration of the molecule which fluoresces at that wavelength (Hudson et al. 2007).

Laboratory FDOM analysis uses an excitation-emission matrix (EEM), which includes a range of excitation and emission wavelengths. The EEM results can be used to analyse relative

concentrations of substances based on the relative intensity of the signal at different excitation and emission wavelengths (Downing et al. 2012). This phenomenon is used to characterise DOM concentration and composition.

FDOM analysis is complicated by the problem of light attenuation. Dissolved substances can absorb light before or after fluorescence occurs (Downing et al. 2012). This is known as the inner filter effect, and reduces the signal observed at higher concentrations of dissolved material as excited and emitted UV radiation is re-absorbed by molecules in the sample matrix before it is registered by the sensor (Henderson et al. 2009).

Environmental conditions also affect the FDOM signal. Temperature interferes with fluorescence by allowing excited electrons to return to ground state by non-radiative decay (Henderson et al. 2009). Increasing temperature reduces the fDOM signal by ~1% for every degree Celsius (Baker 2005). Although pH effects have been observed in the laboratory, they are variable in the field and less important than other variables such as DOM character. Likewise, the effect of the concentration of metal ions is only predictable under laboratory conditions (Henderson et al. 2009, Hudson et al. 2007).

In unfiltered samples, such as those measured by *in situ* fluorimeters, FDOM signal is also known to be affected by turbidity, as suspended substances absorb and scatter UV light. Saraceno et al. (2009) and Downing et al. (2012) reported a significant reduction in FDOM signal in turbid samples.

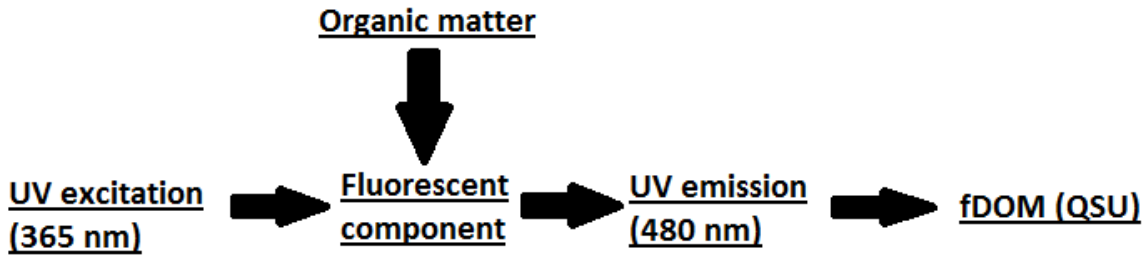

Figure 1: Expected relationship between fDOM (as measured by the EXO2 sondes) and organic matter.

Effects of forest fire

Forest fires can be characterised by intensity (defined by heat transfer and plant mortality) and the type of vegetation burnt (for example, tree crowns, the shrub layer, etc.). These fire characteristics determine the severity of impacts to vegetation, soil and water. In pine forests, crown fires cause higher mortality in large trees; this leads to reduced water uptake from the

soil for several years after the fire, and creates large amounts of woody debris. Fires that burn in the humic layer of the soil can, depending on intensity, completely remove that layer through combustion. Subsequent water erosion can then expose the mineral soil layers below. Soil characteristics are also altered at high temperatures, potentially becoming water-repellent (Shakesby & Doerr 2006).

Vegetation

The most immediate and obvious effect of fire is the combustion of biomass. In Swedish managed forests like those in Västmanland, the vegetation consists of stands of Scots Pine with an under-story of mosses, grasses and shrubs growing in a thick low layer. As it burns, some organic carbon in the form of cellulose is oxidised to CO and CO2; the competing reactions of volatilisation and charring are influenced by fire intensity (Sullivan and Ball 2012). Fire intensity also determines mortality and debris remaining after the event. With increasing fire severity, soil organic matter is slightly volatilized, charred or completely oxidized as the surface and organic layers of the forest are burned (Certini 2005). Burned soils lose carbon as it is mineralized and bound to metals (Fernandez et al. 1997); combustion losses occur in the surface and organic layers (Neff et al. 2005). Burnt organic matter has an increased proportion of humic-like (highly polymerized) and aromatic compounds (Olefeldt et al. 2013). These compounds ("pyromorphic humus"; Gonzalez-Perrez et al. 2004) are hydrophobic and resistant to biochemical degradation (Certini 2005; Gonzalez-Perrez et al. 2005). One year after fire, effects are variable: Neff et al. (2005) found less carbon in burned soils, while Johnson & Curtis (2001) found more (which they attributed to post-fire invasion of N-fixing vegetation). In the long-term, soil organic matter returns with post-fire succession (Certini 2005).

Hydrology & geomorphology

The death of vegetation leads to reduced rainwater interception and water uptake. Severe fires leave exposed soil, which in turn becomes more susceptible to water and wind erosion; physical changes in soil structure that occur at high temperatures can also induce hydrophobicity and erodibility (Shakesby & Doerr 2006). The loss of trees allows more sunlight to penetrate to ground level, which causes faster snow-melt in spring. Similarly, removal of riparian vegetation increases summer water temperature in forest streams (Rhoades et al. 2011).

The hydrological effects typically observed in the weeks and months after fire are increased particle transport into streams; higher rates of overland flow; and reduced movement of water through soil. These effects become apparent during post-fire precipitation events and snow-

melt, as water moving over the landscape into the stream brings debris and eroded material with it (USGS 2012).

Turbidity is often used as a water quality parameter. Turbidity is often observed to increase after fire. This is taken to represent the increased load of particulate matter into the streams. Therefore turbidity is a useful parameter for quantifying hydrological and geomorphological effects of fire in a catchment.

Streamwater chemistry

Turbidity increases due to the particle transport occurring in stream catchments, especially during precipitation events (Rhoades et al. 2011). The concentration of DOC decreases initially to due to the reduced inputs of allochthonous material, but rainfall and snow-melt can "flush" organic debris into streams. Metals and nutrients from burnt vegetation also enter streams in this way and a corresponding increase in concentration of aluminium, iron, phosphates and nitrogen has been observed. Streamwater pH can fluctuate unpredictably as both humic acids and base cations enter the stream (Smith et al. 2011 & 2012).

Forest fire in Sweden

Fire in Sweden's forests has been influenced by human activity since the 14th century or earlier (Niklasson & Granström 2000). Since the 1860s, the forestry industry has suppressed fire across the country, and since the 1950s a seemingly steady state has existed in which roughly 1.7% of total forest area is affected *per annum*. Summer fires typically occur over a few thousand hectares of forest, with a "maximum" (Niklasson & Granström 2004) of 5,000 hectares. However, severe fire weather (hot, dry and windy conditions) allows much more intense and wide-ranging fire, as was observed in the Västmanland fire of 2014, which burned about 14,000 hectares (Länsstyrelsen Västmanland 2014) of pine forest in central Sweden.

Forest fires have occasionally occurred in Sweden in recent decades. A few have been significant in size and intensity, causing high vegetation mortality and removing the humic layer. Post-fire studies have reported similar effects on forest streams (Eriksson 2002, Länsstyrelsen Norrbotten 2006, Naturvårdsverket 2006).

It is predicted that climate change will increase the occurrence of these severe fire weather conditions in boreal forests, thus increasing the likelihood of large fires beyond the control of management agencies (de Groot et al. 2012). Most of Sweden's forests occur in the boreal zone. It is therefore important to study the impacts of wildfire on forest catchments in Sweden.

Study area

On the 31st of July 2014 a large wildfire occurred in a managed forest of Scots Pine (*Pinus sylvestris*) in Västmanland län, central Sweden. The fire lasted until the 13th of August, eventually burning about 14,000 hectares of forest (Länsstyrelsen Västmanlands län 2014). This 'fire area' included parts of the courses of several small streams. For the purposes of this study, 7 study streams were selected from within the fire area and 2 reference streams from nearby, similarly managed Scots Pine forests (see **Figure 2**).

Two of the study streams were selected for more detailed monitoring – Gärsjöbäcken & Myckelmossbäcken. These streams each had an EXO2 sonde installed on the stream-bed, which recorded water quality data continuously over its deployment phase. The advantage of this type of instrument over grab samples is the high frequency of measurements – as water chemistry in the streams can change significantly over a day or even an hour, it was expected that with such high-resolution data, we would be able to see changes in DOC accurately and we would not miss any significant changes or trends, which would probably occur if we relied on periodic grab sampling. Furthermore, our review of the literature on fire effects led us to expect significant contributions of DOC from flushing events after rainfall, and *in situ* monitoring was expected to capture this much better than grab samples.

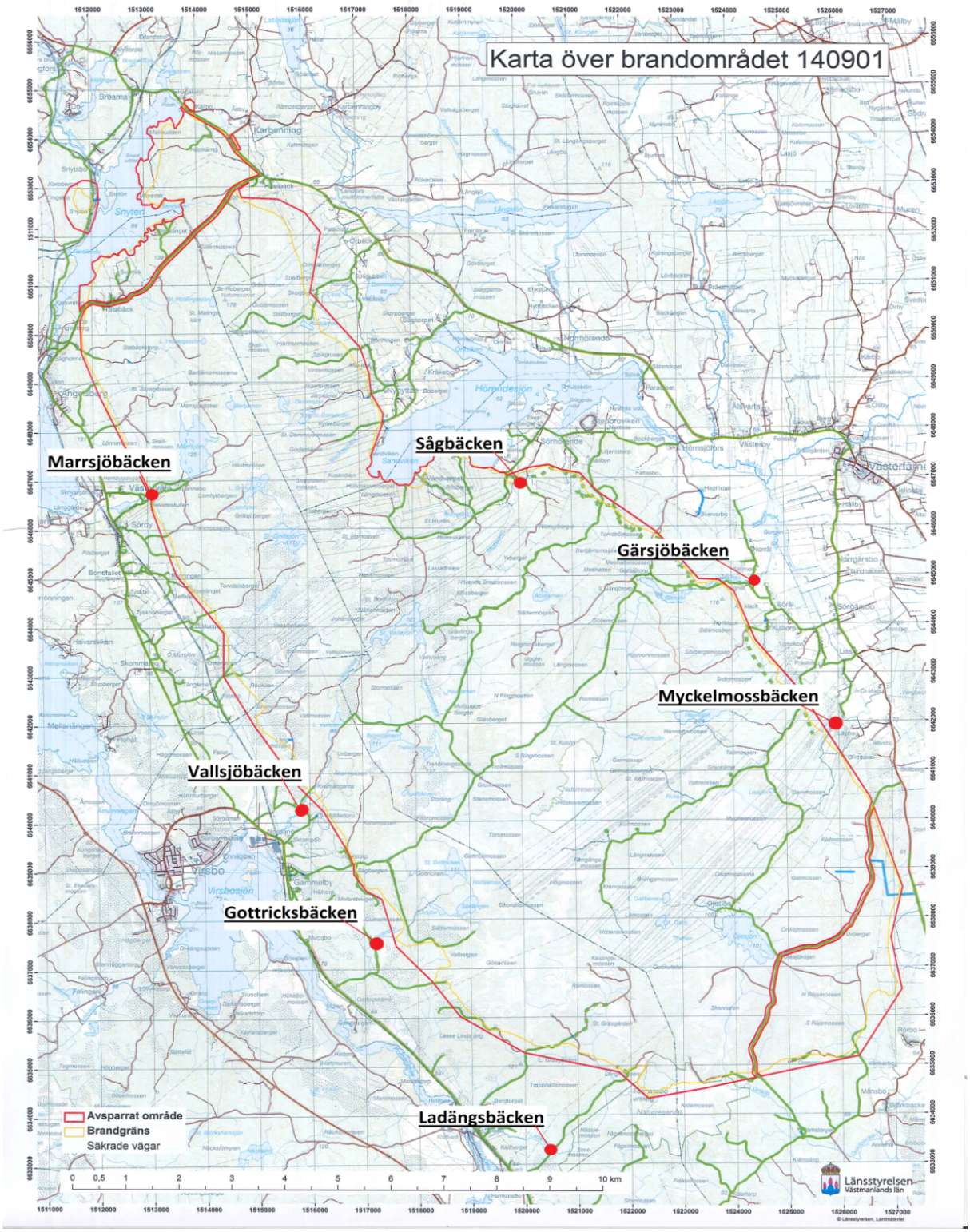

Figure 2: Map of study area, showing sampling sites for each stream and the fire area outlined in red. The reference streams (Säckenbäcken & Solltorpsbäcken) are situated outside the fire area (source: Länsstyrelsen Västmanlands län).

Hypotheses

One objective of this study was to track changes in streamwater DOC quality and quantity in the months immediately following the fire (September 2014 to April 2015). The others were to assess the usefulness of *in situ* florescence measurements as a proxy for DOM in forest streams, and investigate the relationship between florescence and DOM concentration and quality.

DOC mobilisation hypothesis:

It was expected that the fire-driven changes in the sources and transport of DOC into forest streams would produce observable changes in DOC quality and quantity. The theorised new flow regime would have less flow occurring in the soil and organic layer, and more overland flow in peaks directly after precipitation. This, along with the combustion and death of plant material was expected to reduce the overall input of DOC into streams in the fire area; however, overland flow was expected to occasionally flush organic debris, mobilised by the fire, into the streams.

Methods to test this hypothesis:

- Monitoring of DOC concentration from grab samples and sondes. DOC concentration was expected to be lower in streams affected by fire.

- Analysis of DOC quality in the laboratory. It was predicted that quality parameters (see Methods) would reflect a reduction in terrestrial inputs of DOC immediately after the fire.

fDOM calibration hypothesis:

Based on the available literature on fluorescence as a proxy for DOC concentration, it was expected that fDOM would be vulnerable to influences from the inner filter effect, turbidity and temperature.

Methods to test this hypothesis:

- comparison of fDOM values with DOC values

- multiple linear regression of DOC against fDOM, temperature and turbidity.

higher levels of temperature, turbidity and DOC were expected to negatively influence fDOM readings, and so the raw fDOM signal was not expected to provide an accurate estimate of DOC concentration. Experiments were therefore designed to explore the relationship between fDOM, turbidity, temperature and DOC.

Methods

Sampling & monitoring

After the fire area was declared safe for SLU staff to visit in early September, several sampling trips were made to obtain grab samples of streamwater from the study and reference sites. Samples were taken from September 2014 to April 2015; due to time constraints and lack of access, not every stream was sampled on every day (see appendix 1).

One of the study streams, Gärsjöbäcken, was already the subject of monthly sampling for water quality monitoring from July 1995 to December 2013, as part of the regional monitoring program as sampled by the local council of Västmanlands län.

Gärsjöbäcken & Myckelmossbäcken were both selected for monitoring with an EXO2 multi-parameter sonde to provide a 15 minute-step log of water quality in these streams. The sondes were equipped with probes to monitor fluorescent dissolved organic matter (fDOM; see below), turbidity, pH and temperature. The sondes were deployed over two phases: firstly in the autumn (10th September – 3rd December), then in the spring (17th March – 21st April). Winter conditions precluded deployment, and instead this time was used for calibration and experiments in the laboratory.

Water samples were analysed in the laboratory at SLU for a range of parameters; those relevant to this study were DOC, iron and aluminium (in milligrams per litre, mg/l), and sulphate (in milliequivalents per litre, mg/l).

In addition to water chemistry, water flow data was obtained from two sources: Vallsjöbäcken, Sågbäcken, Gärsjöbäcken, Myckelmossbäcken, Ladängsbäcken and Säckenbäcken were monitored for water height with Trutrack pressure transducers, and S-HYPE flow modelling from the Swedish Meteorological and Hydrological Institute (Sveriges Meteorologiska och Hydrologiska Institut, SMHI) was used to estimate flow in Gärsjöbäcken and Myckelmossbäcken.

In order to provide samples with a wider range of DOC concentrations, sub-samples from all samples taken on March 10th and April 16th were diluted with filtered water (assumed to contain no DOC; see appendix 2) in the laboratory. This produced new samples at a known DOC concentration proportional to the dilution. (see appendix 1). These dilutions were then tested for fDOM using an EXO sonde.

Sondes

Two EXO2 sondes were used in the study. Each was equipped with probes to measure fluorescent dissolved organic carbon (fDOM - see below), turbidity and temperature. A pH probe was also available but not attached for most of the deployment phase.

The EXO2 sonde records each parameter at a 15 minute step. At the end of the deployment phase (2-3 months) the sonde is retrieved to charge its battery and extract logged data. Occasionally, errors occur in the log – these represent a failure of the sonde to record correct values on a certain time-step. According to the manufacturer, these errors are caused by power supply problems or the obstruction of probes. These errors only occurred on a few instances out of thousands, and were removed from the dataset.

Turbidity

Turbidity was recorded in Formazin nephelometric units (FNU). The sonde installed in Gärsjöbäcken require a post-calibration with Formazin after the autumn deployment phase (see *Table _*)

fDOM

The EXO sonde fDOM probe measures fluorescence at an excitation wavelength of 365 nanometres and emission wavelength of 480 nanometres.

Post-calibration was performed when the sonde was returned to the laboratory in winter (see *Table 1*). Calibration was performed using quinine sulphate as the fluorescing agent.

Field samples with a known DOC concentration would have been more appropriate for calibration, but those were not available at the time.

Absorbance & Fluorescence

Filtered samples (filter pore size: 0.7 micrometres) taken in September, November, March and April from each site were analysed in a Horiba Aqualog for absorbance and fluorescence using a 1cm cuvette. Samples from the same dates were analysed for DOC in a Shimadzu spectrometer. The excitation-emission matrices for these samples were processed to determine carbon quality characteristics, outlined below.

Freshness – the ratio of β (material fluorescing at 380 nm) to α (material fluorescing at 420-435 nm). Since β is associated with recently produced material, and α is associated with decomposed material, higher freshness values suggest a greater proportion of recently produced material in the sample.

Specific ultraviolet absorption (SUVA) – absorbance at 254 nm, normalised against DOC.

The percentage of emission signal with wavelength greater than 450 nanometres (%EM>450 nm) can indicate the origin of carbon in the sample, as fluorescence at longer wavelengths is associated with allochthonous material.

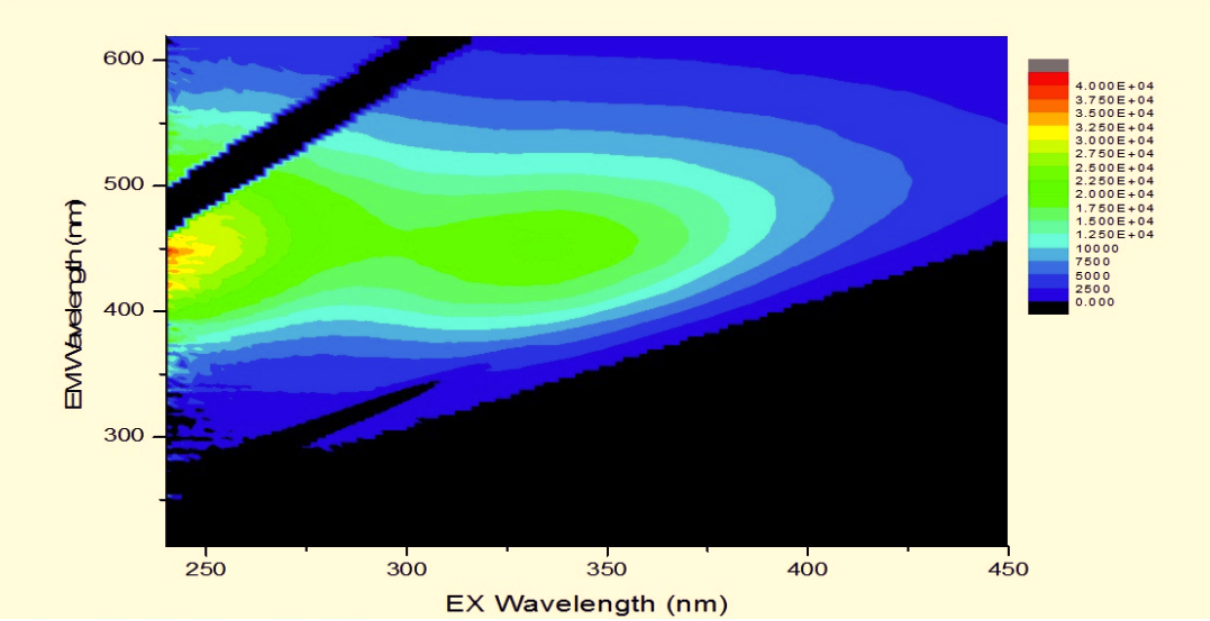

Figure 3: Example of Aqualog output – a contour map display of an excitation-emission matrix. The x-axis plots excitation wavelengths, the y emission wavelengths. Signal intensity is coded by the colour legend on the right.

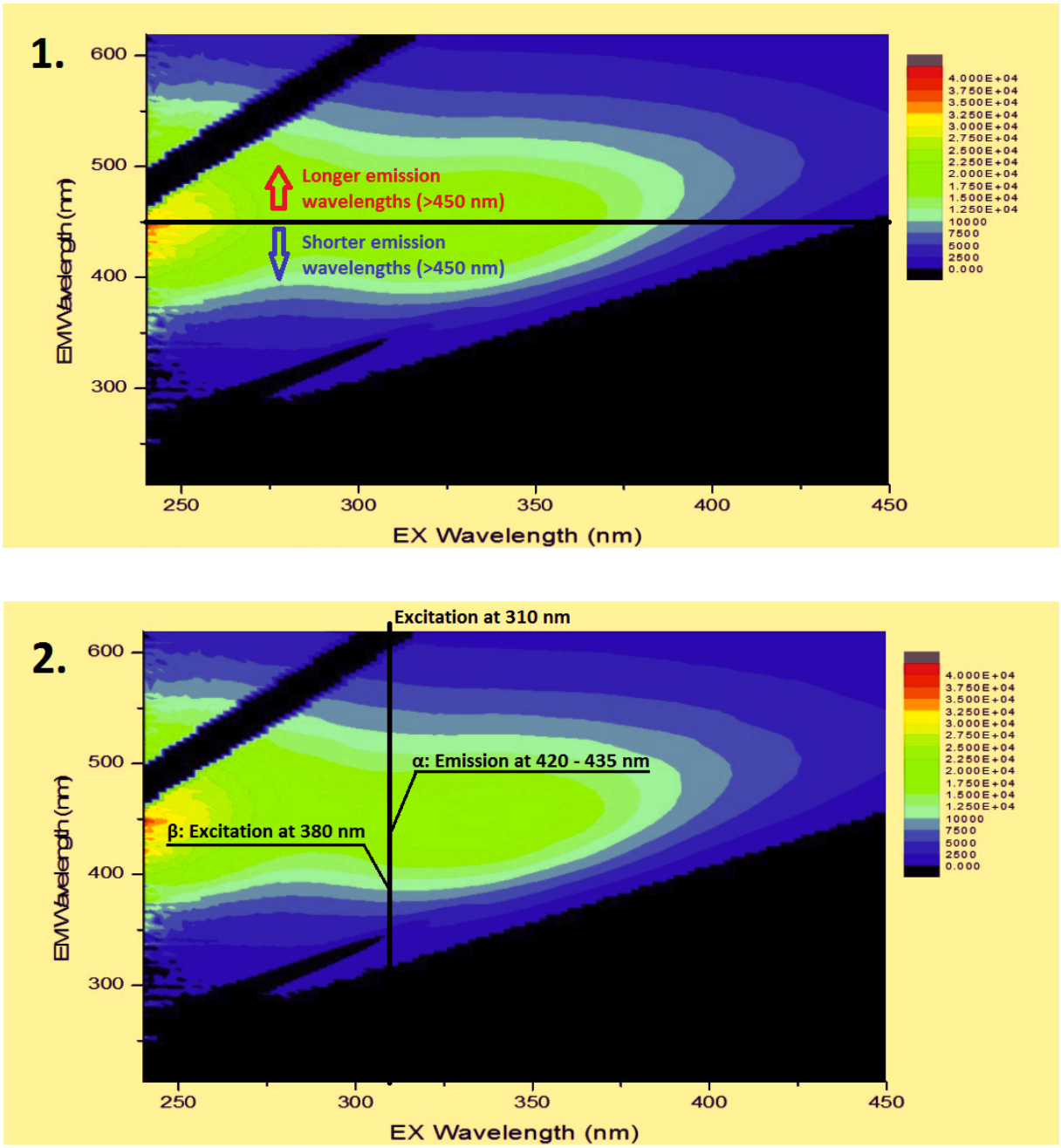

Figure 4: Aqualog output EEM contour maps, showing relevant wavelengths and interpretations for 1) %EM>450 nm, and 2) Freshness.

Results

In order to interpret the fDOM time series recorded by the sondes, it was first necessary to describe the relationship between fDOM and DOC. Based on this relationship, a model was constructed to allow estimation of DOC concentration from sonde data.

Estimating DOC from sonde data

It was predicted that the IFE, temperature and turbidity of samples would influence fDOM measurements. Therefore in order to accurately measure DOC concentrations from fDOM results each of these parameters' relationships with fDOM would have to be tested.

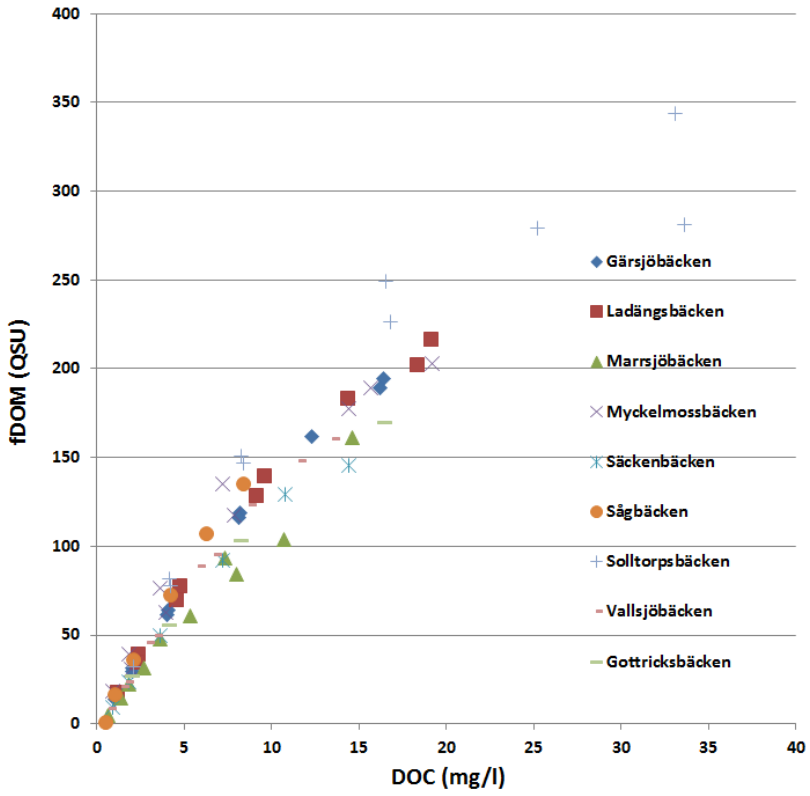

Figure 5: fDOM results in dilution.

Dilution experiments show that in all streams, fDOM decreases non-linearly with decreasing DOC. This effect is listed in the sonde manual, and is attributed to the inner filter effect. Although the EXO sondes have no means of automatically compensating for this effect, the Aqualog fluorometer does. Comparing Aqualog fluorescence before and after IFE correction shows that it increases linearly after IFE correction (see Appendix 3). This suggests that the IFE is responsible for the non-linear trends seen in **Figure 6.**

Therefore, the dilution experiments suggest that although the correlation between fDOM and DOC is strong, if we try to predict DOC from fDOM using a linear model we will underestimate DOC at higher fDOM values. However, this is based on just two samples for each site, under laboratory conditions; it may not be enough to judge the trends in reality. Also, we want to be able to predict DOM at higher concentrations than the starting concentrations of the dilutions.

Therefore, it is beneficial to compare grab samples with sonde data. This is done by linking the results of analysis of grab samples (including DOC concentration) with the data logged by the sondes at the time each grab sample was taken. In this way, we can add more points to the dataset.

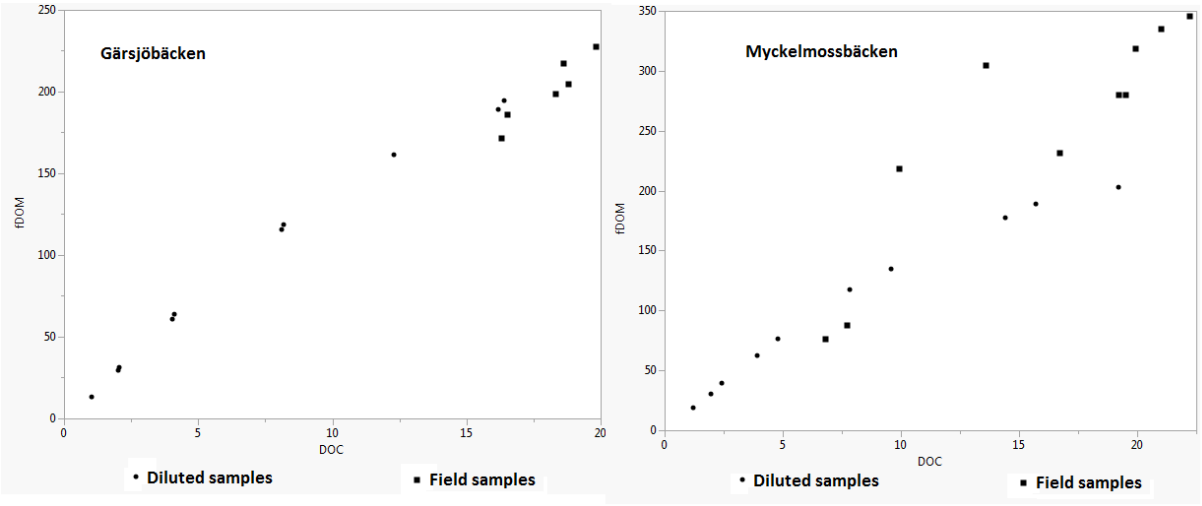

Figure 6: fDOM/DOC plots for Gärsjöbäcken & Myckelmossbäcken.

The curved relationship is not apparent in field samples. They seem linear, although the relationship seems somewhat weak and is based on only a few samples. Also, the higher DOC concentrations did not suppress fDOM in the way that the non-linear relationship observed in **Figure 6** would lead us to predict.

Figure 7 suggests that fDOM increases linearly with DOC at realistic values for our streams – not on the same line as at very low concentrations, but for DOC concentrations observed in the field it seems to have a linear correlation. We can therefore conclude that in field conditions, the IFE is not as influential as predicted, and we may ignore it in our model.

In the relationship between fDOM and DOC, the other parameters of interest are temperature and turbidity.

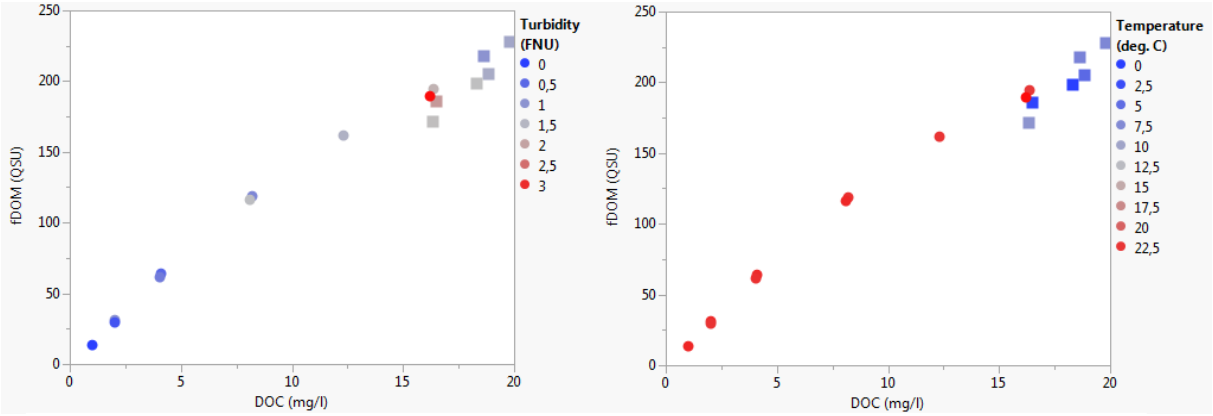

Figure 7: Gärsjöbäcken DOC vs. fDOM, coloured by turbidity (left) and temperature (right).

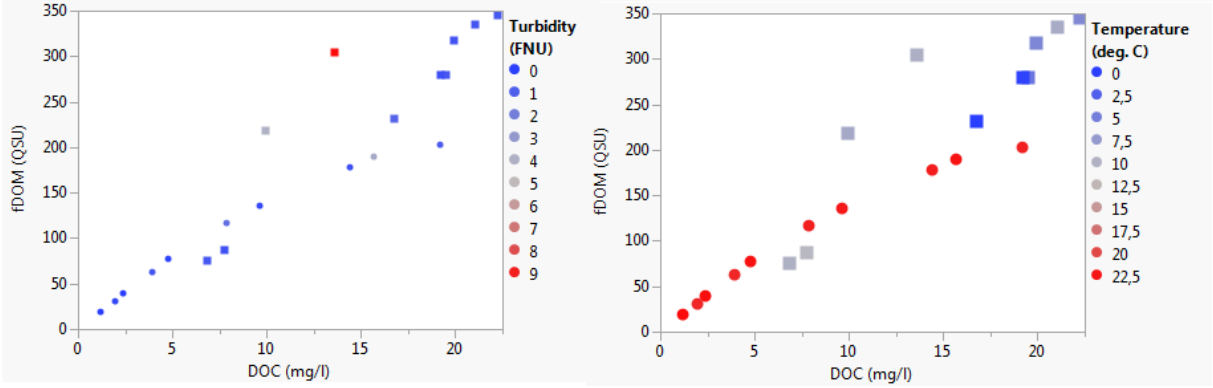

Figure 8: Myckelmossbäcken DOC vs. fDOM, coloured by turbidity (left) and temperature (right).

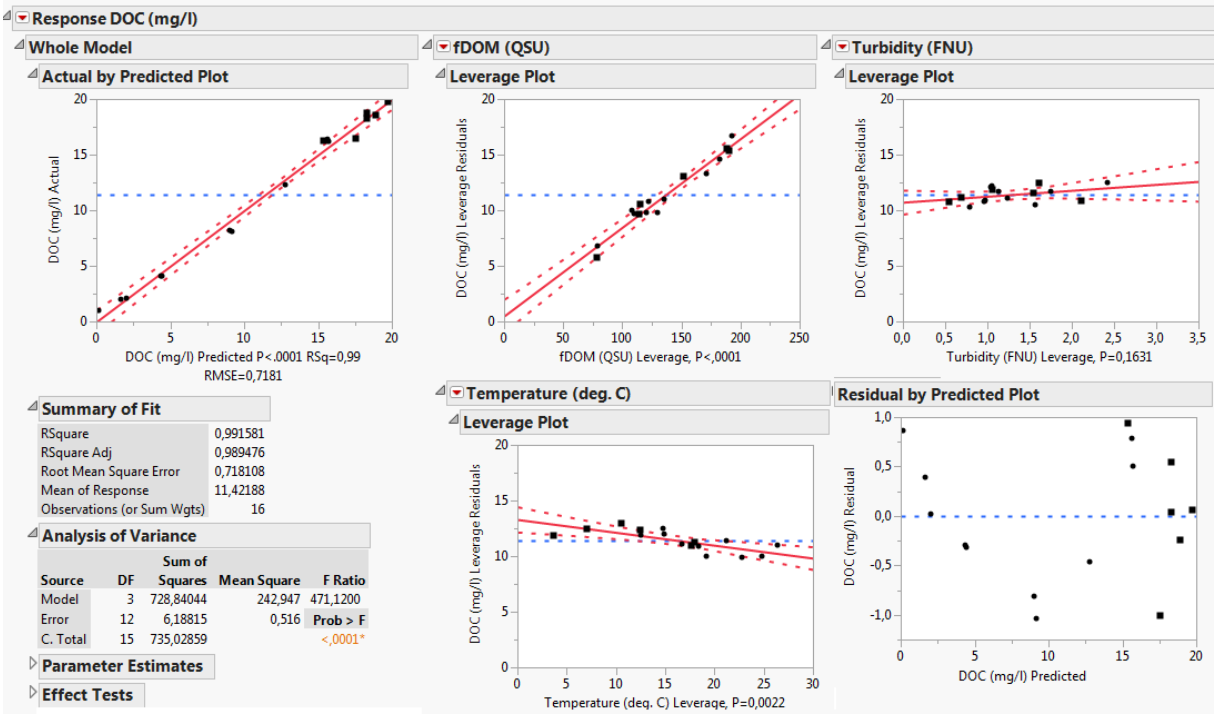

Figure 9: Multiple linear regression of DOC against fDOM, turbidity and temperature for Gärsjöbäcken.

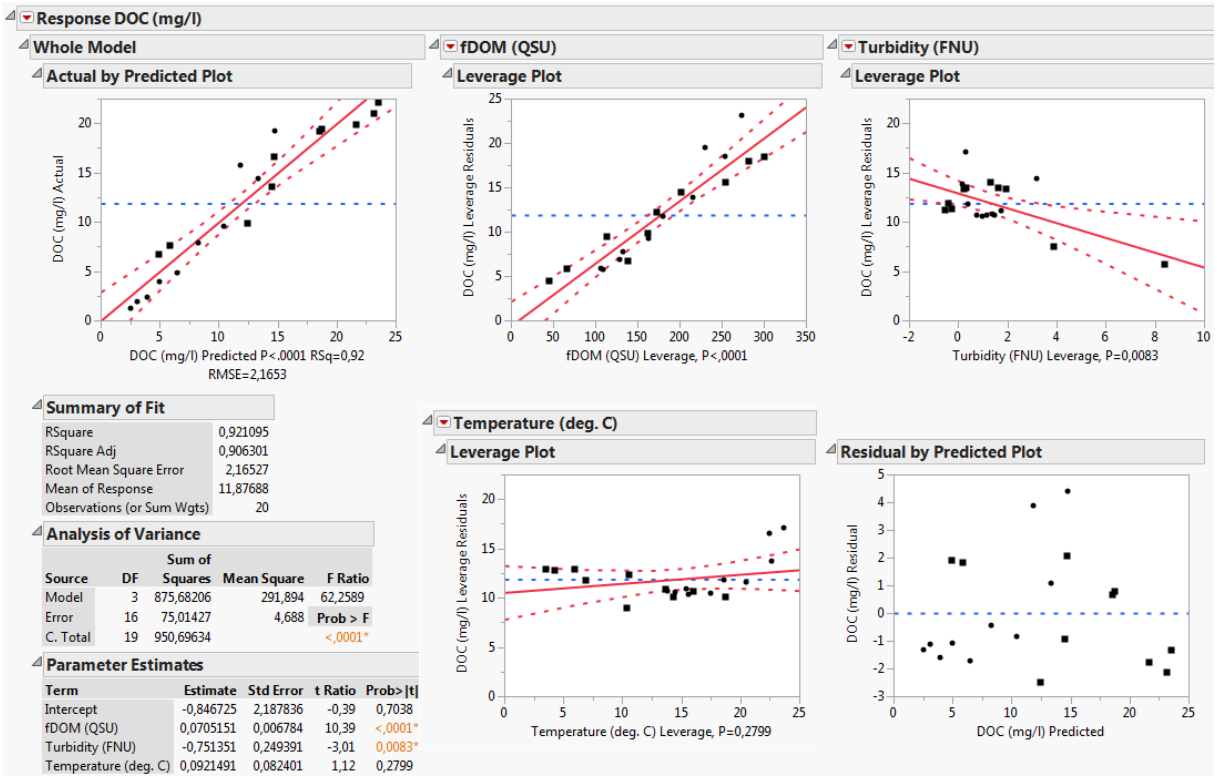

Figure 10: Multiple linear regression of DOC against fDOM and turbidity for Myckelmossbäcken.

Temperature has a slight but significant effect in Gärsjöbäcken samples, but this may be an artefact of the experiment (the lowest concentrations were all warm, the highest cold) or a natural relationship between warmer weather and higher DOC concentration. It is not significant in Myckelmossbäcken.

Turbidity is not significant in Gärsjöbäcken (there was very little difference between turbidity values). In Myckelmossbäcken it was significant, in an interesting way: two slightly elevated turbidity values caused higher than expected fDOM readings. This suggests that turbidity at slightly elevated levels may actually increase fluorescence, contrary to expectations. Perhaps at this NTU level some non-target particles are fluorescing, and the water is still clear enough for a strong signal to come through.

We must therefore decide whether or not to use these parameters in the model. Although two parameters (temperature in Gärsjöbäcken and turbidity in Myckelmossbäcken) were statistically significant in linear regression, it was decided that they could not be used in designing a model for two reasons: Firstly, the sample size was low, and secondly, the trends are slight and go against stronger trends observed in more robust datasets (see below).

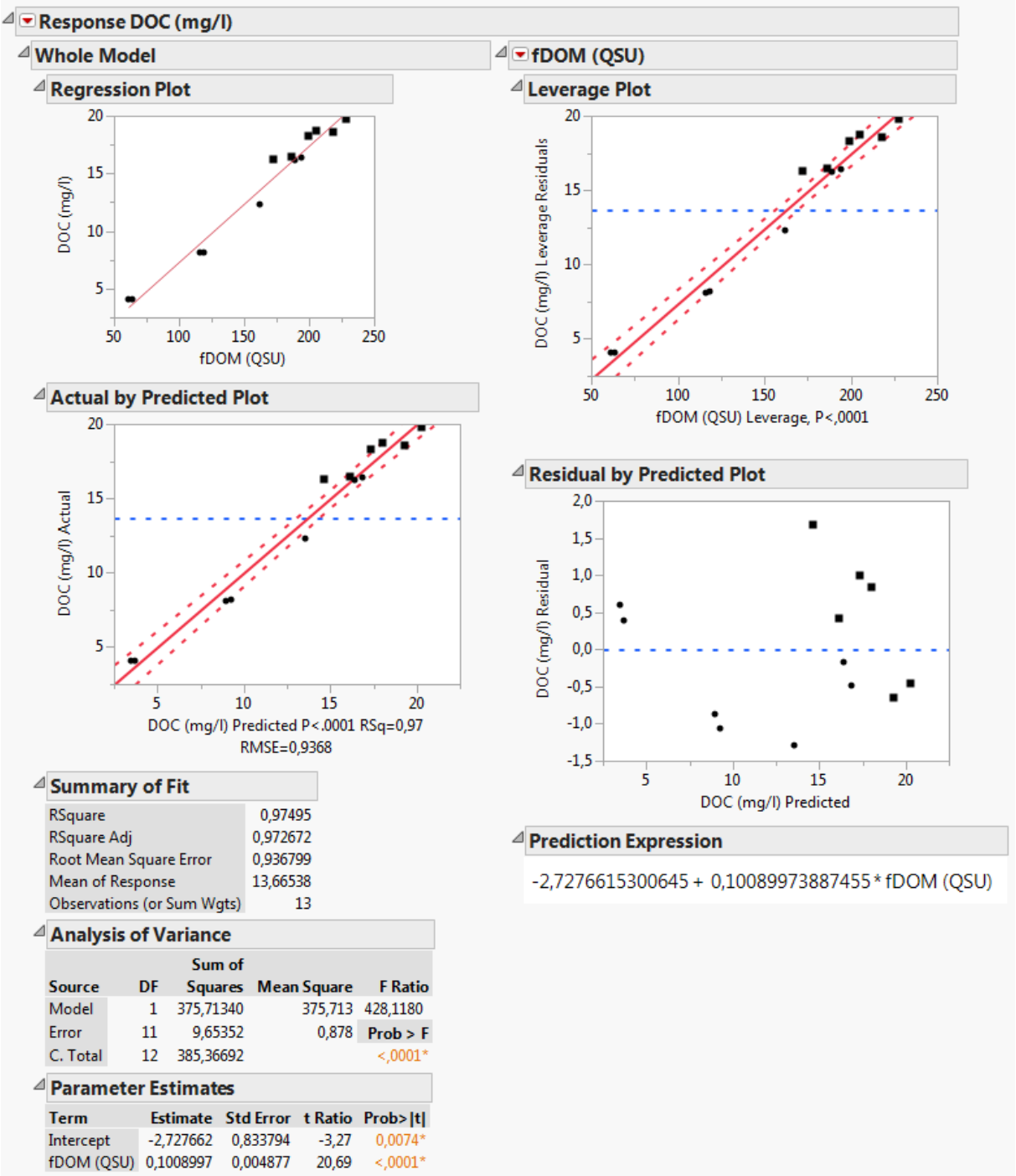

Figure 11: Model for predicting DOC from fDOM in Gärsjöbäcken.

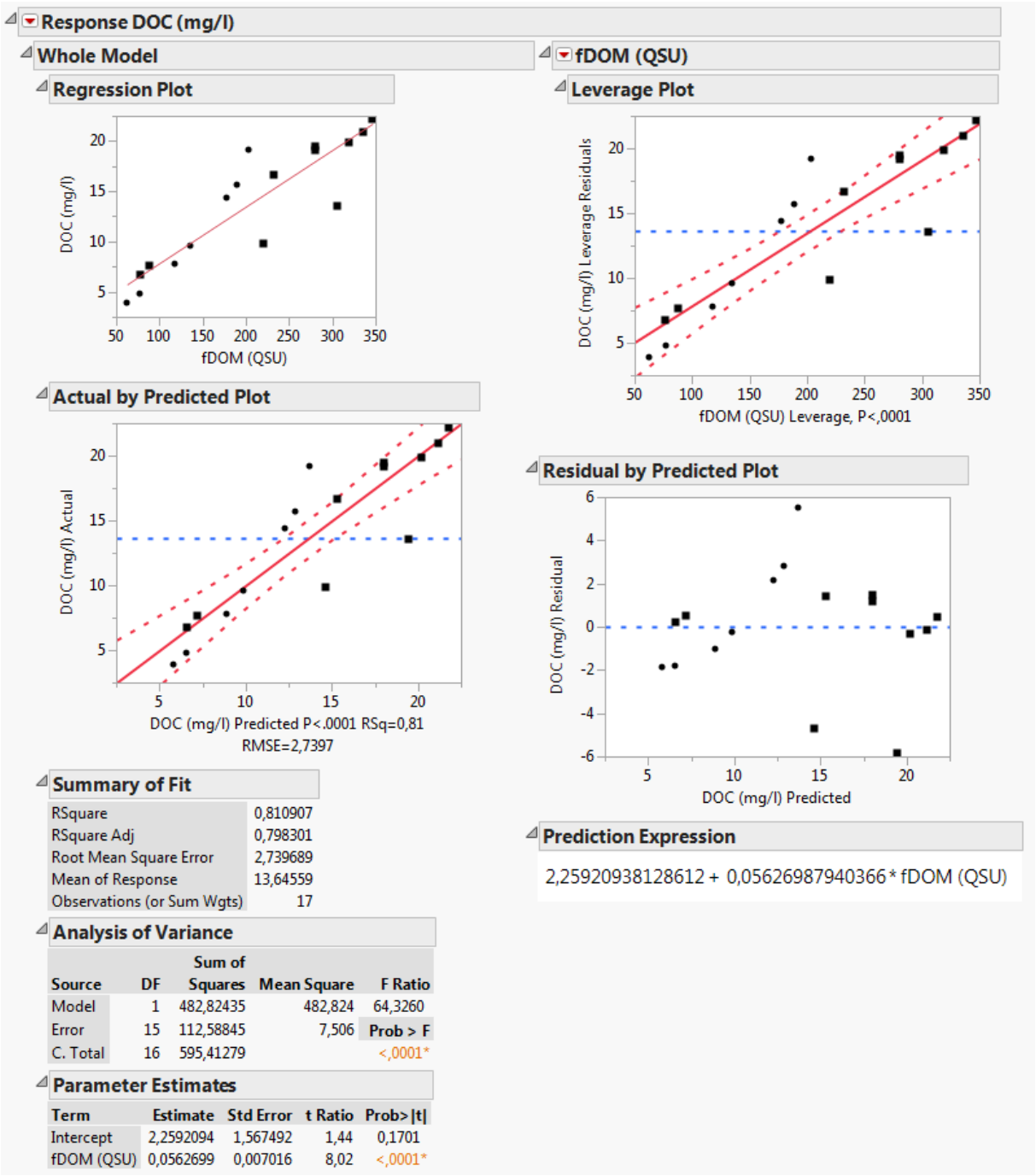

Figure 12: Model for predicting DOC from fDOM in Myckelmossbäcken.

With the IFE, temperature and turbidity excluded from the model, the only remaining parameter is fDOM. It is still necessary to decide which dataset to use in building the model: field values only, or dilutions as well. In the Gärsjöbäcken data, adding the dilution results into the model improves the fit and increases the range of both axes, but also introduces its characteristic curve to lower values. In the Myckelmossbäcken data, including dilution results introduces two high residuals as undiluted lab samples report less fDOM than expected. On balance, it was decided to

use field data plus dilutions with a DOC concentration over 3 mg/l, as the observed range of DOC in the field was never lower than this.

The resulting models show different relationships between DOC and fDOM in each stream.

Turbidity influence on sonde data

Logged data from both EXO sensors show that turbidity was usually low, but on some days increased briefly to high levels. Almost all significant turbidity levels occur during a few episodes lasting 6-12 hours (see **Figures 14 & 15**).

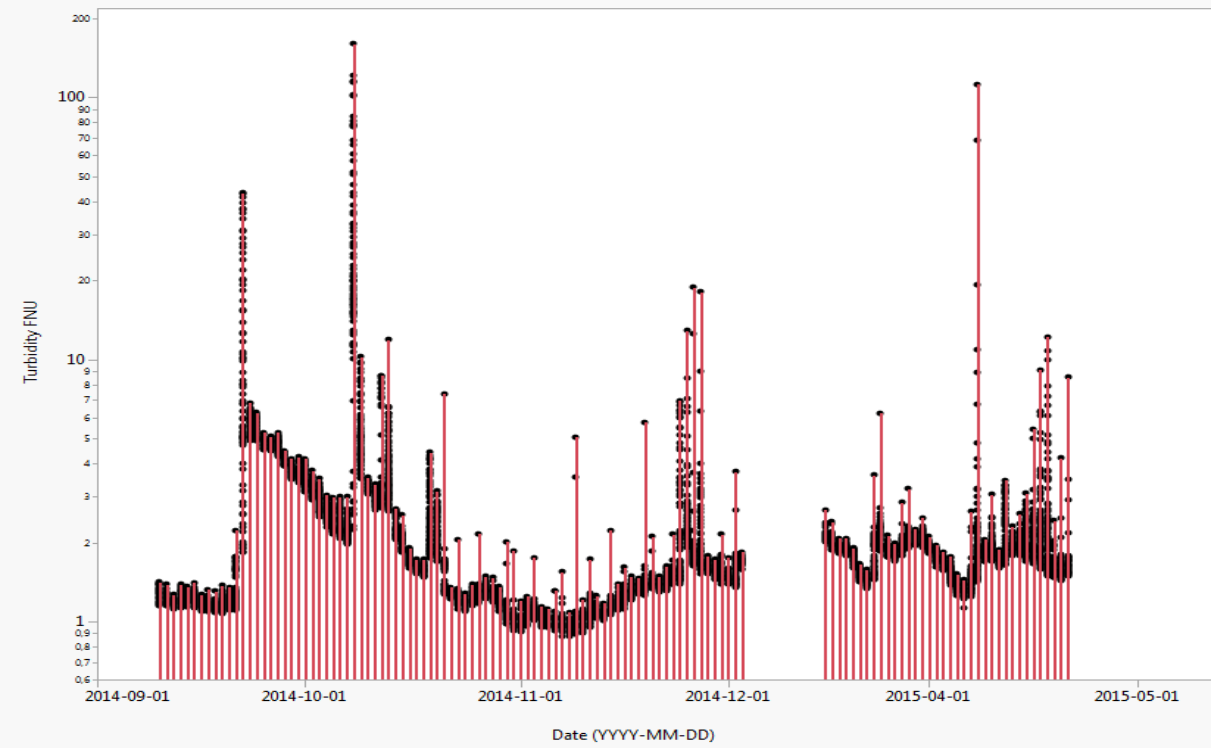

Figure 13: Gärsjöbäcken turbidity by date.

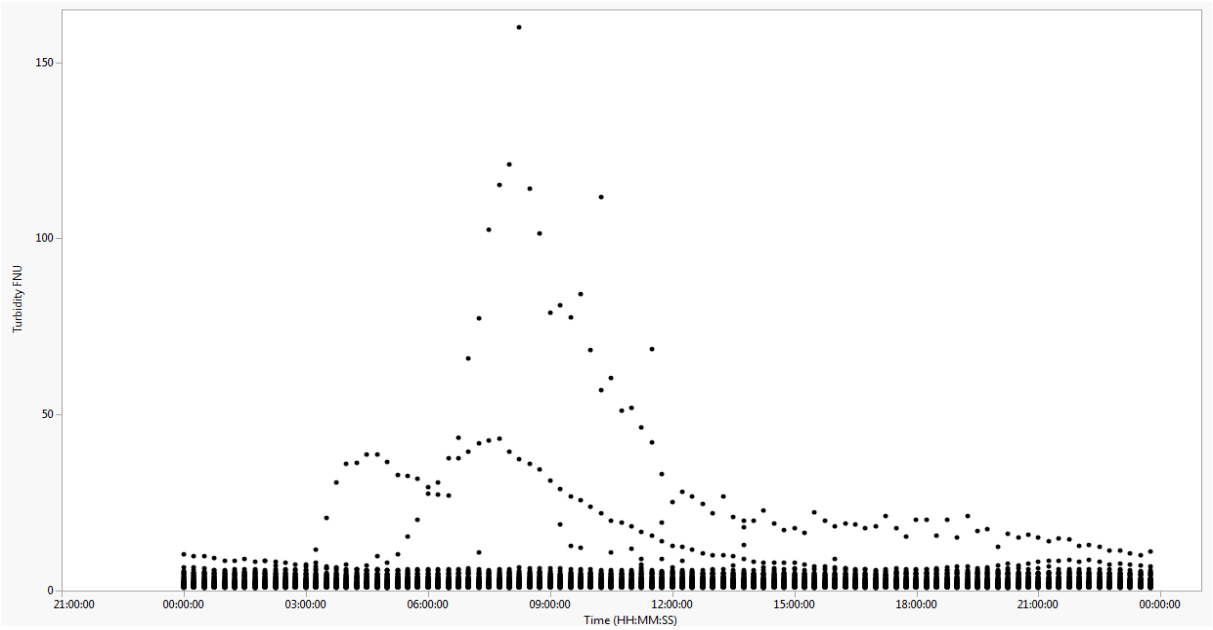

Figure 14: Gärsjöbäcken turbidity by time.

EXO logs also indicate that turbidity has an effect on fDOM readings (see **Figure 15**).

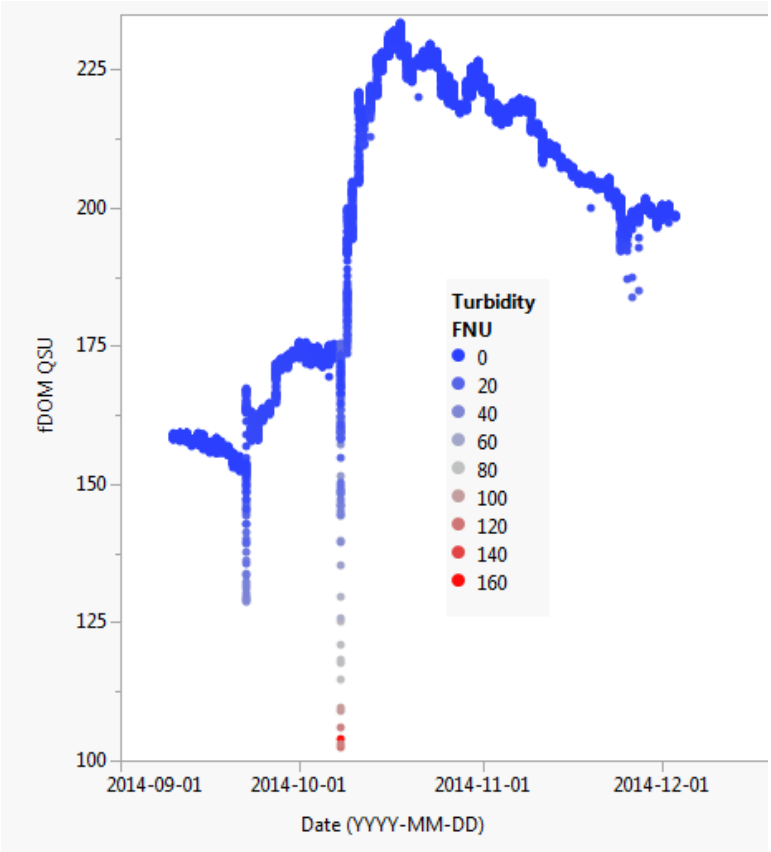

Figure 15: Low fDOM readings are associated with spikes in turbidity.

This relationship means that we need a way to estimate fDOM during high turbidity events. These events seem to have a roughly similar effect on fDOM:

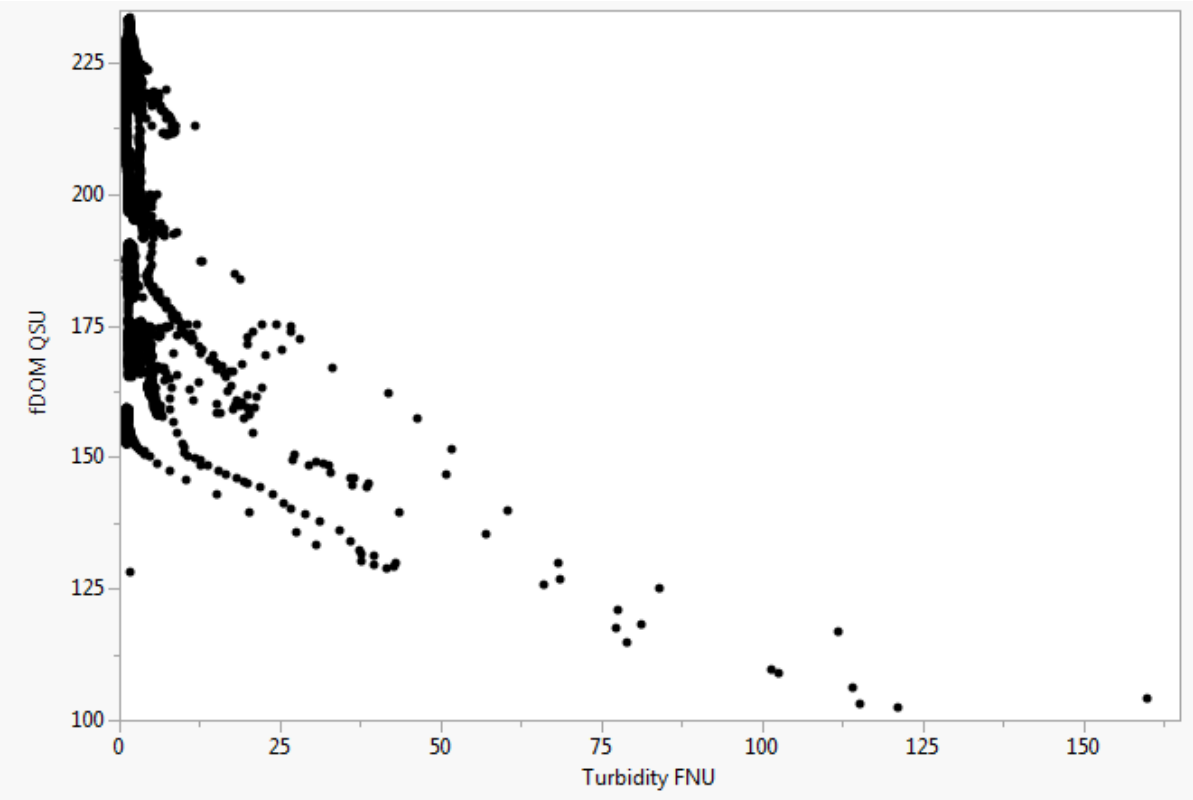

Figure 16: Different high-turbidity events have similar effects on fDOM.

The linear regression equation describing the relationship between high turbidity (over 20 FNU) and fDOM suggests that for each unit of turbidity over 20 FNU, fDOM decreases by 0.51 QSU. This equation was used to correct suppressed fDOM readings in the data.

We can then plot this estimate of DOC over time, along with modelled flow data created with the HYPE model (SMHI 2015):

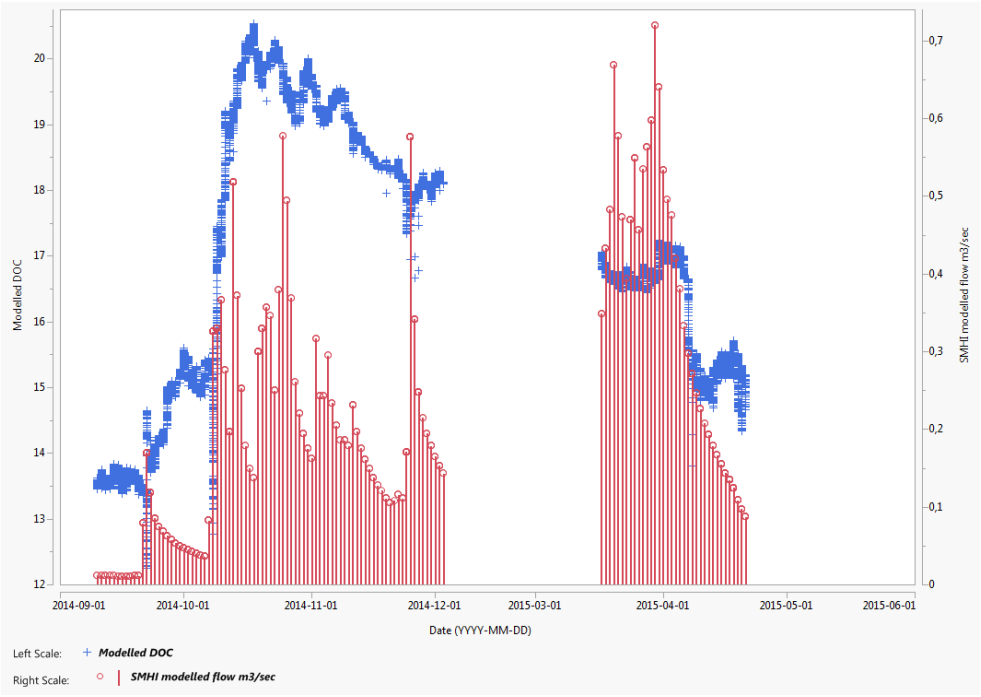

Figure 17: Estimated DOC and modelled flow over sonde deployment phases in Gärsjöbäcken.

Similar influences were observed in Myckelmossbäcken. The estimated DOC and modelled flow show similar patterns:

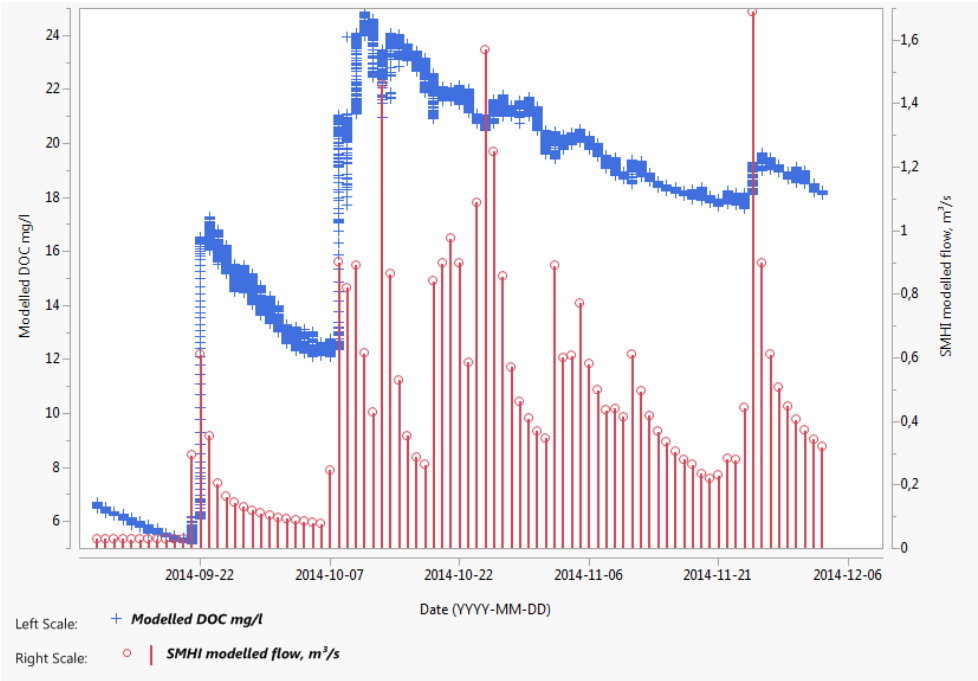

Figure 18: Estimated DOC and modelled flow over sonde deployment phases in Myckelmossbäcken. No spring flow data was available.

A clear pattern is apparent is these time series: high flow events have corresponding peaks in DOC (and turbidity), followed by a gradual decline. Flow events earlier in the season are associated with larger increases.

Gärsjöbäcken historical data

In order to understand these results we can compare post-fire Gärsjöbäcken data to those observed in pre-fire conditions during the 18.5 years of monitoring of that stream.

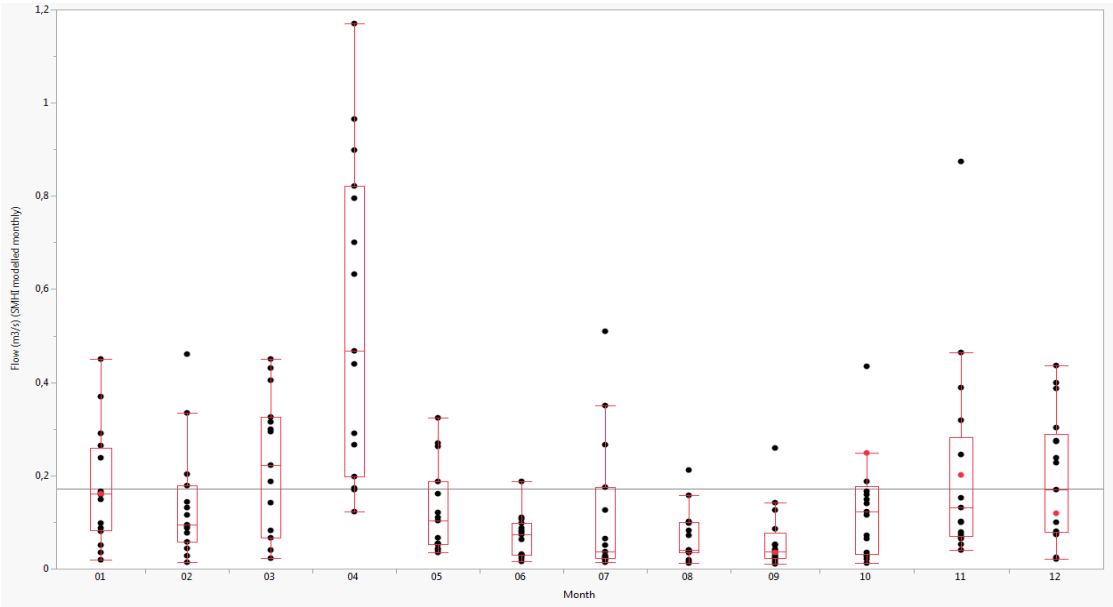

Figure 19: Monthly modelled flow in Gärsjöbäcken, 1999-2013. Post-fire values are marked in red.

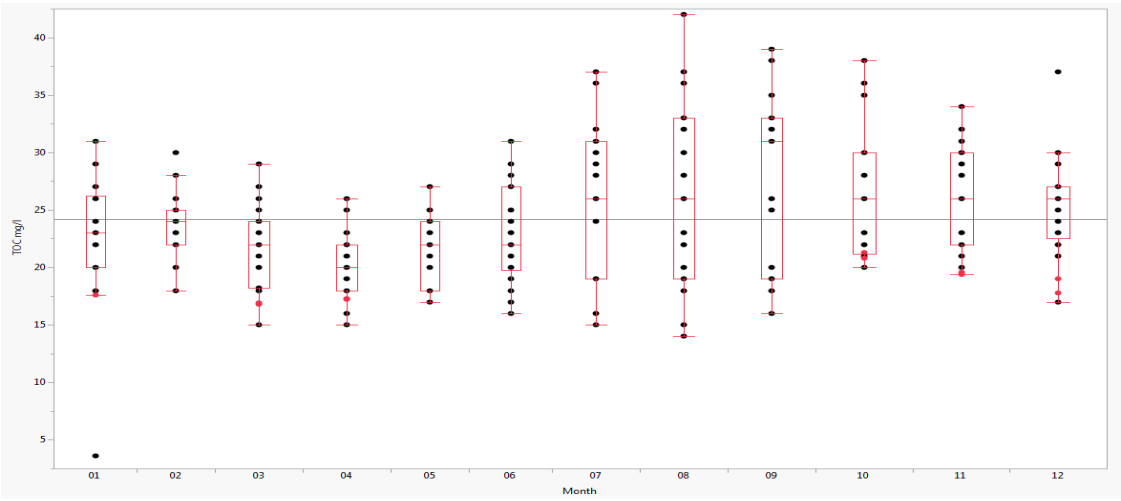

Figure 20: Monthly TOC in Gärsjöbäcken, 1995-2013. Post-fire values are marked in red.

These show that TOC values were lower than average after the fire, despite normal flows.

Carbon quality data

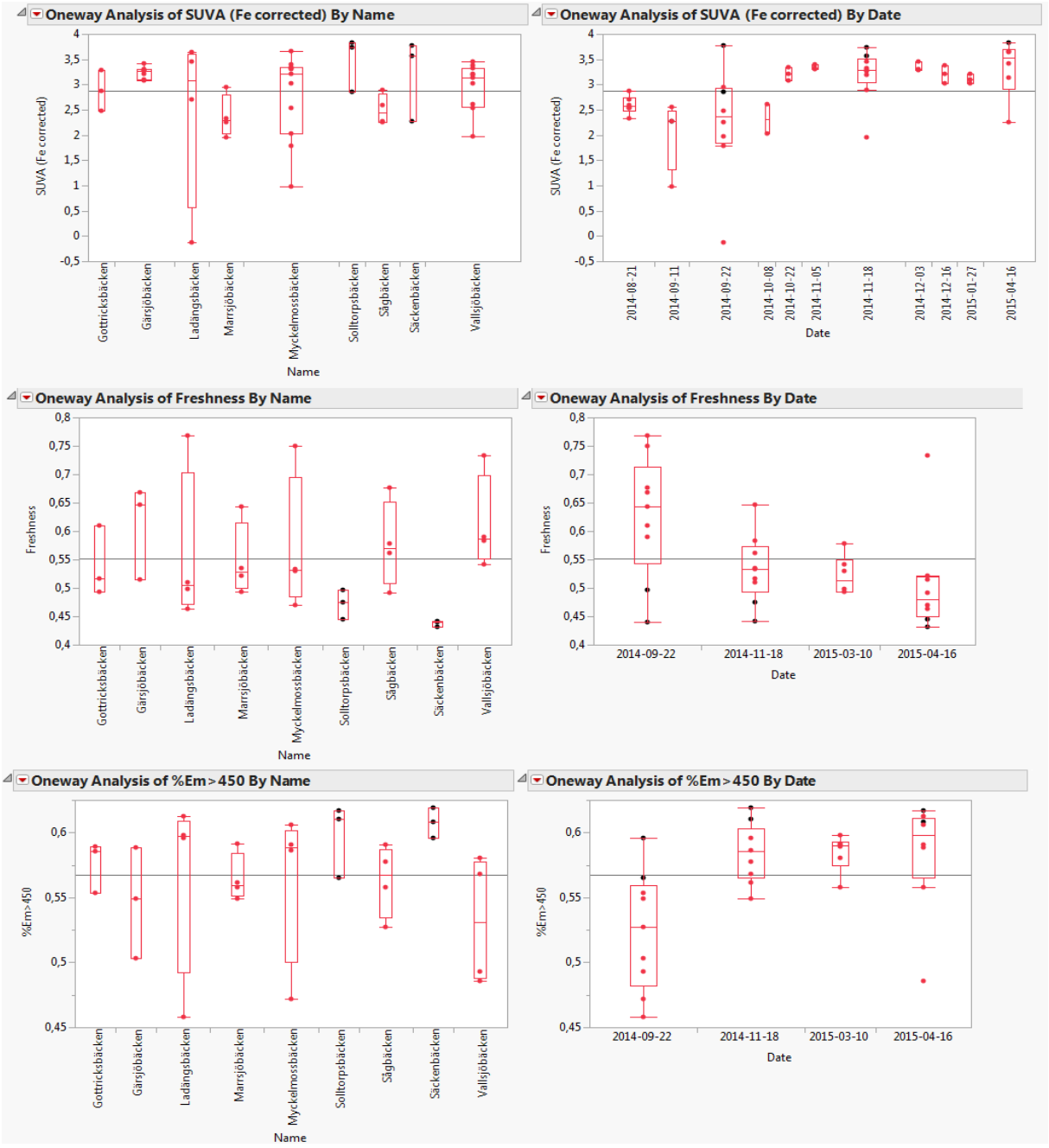

Figure 21: Carbon quality data for each sampling date and each stream. Values from fire streams are marked in red.

In terms of freshness, reference streams show lower freshness scores and are less variable, suggesting that they have lower proportions of recently-produced material than fire streams.

The %EM>450 is higher in reference streams, with decreasing variability from autumn to spring. This suggests that allochthonous origin of carbon is less prevalent in fire streams.

The lowest SUVA values were observed in autumn, with SUVA generally lower in fire streams.

Discussion

Tracking changes in DOC concentration

The high resolution data obtained from the EXO sondes allow us to observe variation in DOC concentration over short times (15 minutes) – much faster than would be possible with traditional grab samples. The advantages of in situ monitoring are clear from the results – without this kind of sampling, it would be practically impossible to capture the true range of values. Since these streams are such a fast-changing habitat, an attempt to study them using only grab samples would probably miss out on the most important changes in DOC concentration.

Of the three hypothesised influences on fDOM, only turbidity had a significant effect on field samples.

Although laboratory experiments suggested that the inner filter effect was influencing fDOM measurements, this was not borne out by field samples. A possible explanation is that in the field, natural variations in fluorescence occur unpredictably and are not determined solely by DOC concentration (as was the case in the dilutions). There were not enough samples to test this hypothesis, however, so the IFE was ignored as a factor in the relationship between fDOM and DOC.

Another possible explanation is that the comparatively high temperatures of the samples in the laboratory (each was at room temperature, 21 degrees C) increased the strength of the IFE. This could be tested in future research by measuring the fDOM signal of a sample with known DOC at different temperatures.

Turbidity had a strong negative effect of fDOM at high levels, which would probably make raw fDOM data unreliable in sites with consistently high turbidity. In the sites studied here, high turbidity only occurred on a few occasions; the water was usually very clear and so most of the time series was unaffected. If possible, researchers and managers working with more turbid water bodies should plan a sampling program to support *in situ* data; it is important to know the relationship of fDOM and turbidity in the monitored site.

It was possible to reduce the errors caused by turbidity with a simple correction; however, the observed relationship doesn't completely account for the drop in fluorescence. Samples with a medium level of turbidity (5-20 FNU) had a less predictable effect on fDOM, and may even have increased it. A possible explanation could be that, at medium turbidity levels, some of particles which contribute to the slightly elevated turbidity also fluoresce, and since the sample is still fairly clear this is picked up by the fDOM probe. At high levels the cloudiness of the sample reduces fluorescence as expected. The relationship is, however more complicated than we can

explain with our limited samples; more sampling would have been beneficial, although given the short amounts of time (less than 1 day) that turbidity spikes lasted for, it would have been difficult to capture the full range of turbidity.

fDOM also behaved differently in different streams. The model created for Gärsjöbäcken suggests that that stream has a different environment for fluorescence than Myckelmossbäcken (and, presumably, other streams). This suggests that in order to use sonde data more accurately, one should independently analyse enough samples from the monitored water body.

Post-fire trends in carbon transport

Combining EXO time series data for turbidity, temperature and fDOM allows us to create a realistic estimate of DOC concentration at high resolution (15 minutes). By combining this with flow modelling, we can link high flow events with drastic changes in DOC concentration.

Timing and intensity of water flow into the stream determines the DOC and turbidity response. The biggest changes in both monitored streams were observed in the first high flows after the fire (September 22 and October 10). Later, higher-volume flows caused smaller increases in DOC and turbidity, suggesting that the early flushes had already deposited the bulk of local organic and particulate material into the streams by mid-autumn. Each peak in TOC was followed by a gradual decline, until a new high flow event occurred and brought more organic matter into the stream.

One seemingly obvious conclusion is that these flushing events are bringing terrestrial organic matter, left over from the fire, into the streams. This would also be consistent with the hypothesis that DOC inputs from other sources, such as soil water moving through the organic layer, have been reduced since the fire removed the organic layer and redirected water flow over the soil rather than through it. However, the results have slightly different implications depending on the landscape position of each stream. Gärsjöbäcken, situated downstream from Gärsjön (a small forest lake in the fire area), would have received an input of lake-water in the autumn, possibly contributing material which had been decomposed over summer. On the other hand, Myckelmossbäcken, receiving water from the Myckelmoss bog, would receive less standing water. This makes it difficult to generalise about the sources of DOC during flushes – further study on lake and soil water in the catchments of these streams is required.

Although the overall patterns are consistent with the altered catchment characteristics we would expect after fire (flushing by rain in autumn and spring), historical data from Gärsjöbäcken shows this pattern in years before the fire, and all of the measured parameters fell within the range of variability established by the last 18 years of monitoring. Therefore, we cannot claim to observe fire impacts purely in terms of stream inputs – there is not enough

evidence to say that DOC input has changed after the fire. This is inconsistent with the findings of researchers in the field of fire science (see introduction), despite the fact that the fire location and intensity was comparable to those studied in North America.

Changes in DOC sources

Analysis of carbon quality shows that (need to test this in R) SUVA and %EM>450 were lower in fire streams, while freshness was higher. Although this is to be expected in streams draining a lake (as lake-water is chemically influenced by microbial activity over summer), these effects seemed to occur irrespective of landscape position. This suggests that the proportion of terrestrial carbon entering streams was lower for those with burned catchments, supporting the hypothesis that fire reduces DOC inputs through terrestrial processes. Change in freshness could be caused by sulphates released by the fire impeding transport of terrestrial carbon through the soil.

Despite these results, sampling only in surface water limits the scope of the study. If soil water samples had also been taken, they could have provided better insight into the hypothesised changes in carbon transport in riparian soils.

The duration of the study (8 months) is much shorter than the predicted duration of impacts from fire. It is possible that much of the effects of the fire have not yet been observed, so further monitoring would be required to fully test the hypotheses identified here. It is clear that in future monitoring we will need modelling to read data, that modelling has to be done on a per site basis, and that accurate modelling requires grab samples. Therefore, despite the advantages of *in situ* monitoring technology, monitoring still benefits from frequent field visits.

Conclusions

Different streams have different fluorescence characteristics, which should be accounted for when using fluorescence analysis to monitor them.

Future studies should be supported by water sampling in soil and surface waters, with the aim of accounting for variability in fluorescence.

The hypothesised effects of fire seemed to occur as expected, although the time taken to improve the usefulness of fluorescence measurements meant that the study was limited in its conclusions.

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Appendices

1. Study sites & sampling

Stream name	Source	Sampling point coordinates
		X RAK
Gärsjöbäcken (Gär)	Gärsjön (lake)	6644770
Gottricksbäcken (Got)	Gottricken (lake)	6637575
Ladängsbäcken (Lad)	Långmossen (bog)	6633297
Märrsjöbäcken (Mär)	Märrsjön (lake)	6646753
Myckelmossbäcken (Myc)	Myckelmossen (bog)	6642045
Sågbäcken (Såg)	Acktjärnen (tarn)	6647453
Vallsjöbäcken (Val)	Vallsjön (lake)	6639795
Säckenbäcken (Säc)	Säcken (lake)	6643094
Solltorpsbäcken (Sol)	Not marked on map	

Table: Sample and reference streams (source: Länsstyrelsen Västmanland 2014)

Land cover	Gärsjöbäcken	Myckelmossbäcken
Agriculture	0.18%	12.8%
Bog	12.66%	9.72%
Forest	85.64%	76.04%
Lake	1.52%	0.73%
Marsh	0%	0.72%

Table: Proportional land cover in the catchments of Gärsjöbäcken and Myckelmossbäcken (Source: SMHI 2014)

	8/21	9/11	9/16	9/22	10/08	10/22	10/29	11/05	11/18	12/03	12/16	1/27	2/17	3/10	3/17	4/16	4/21
Gär				x		x		x	x	x		x		x	x	x	x
Got	x			x					x					x			
Lad	x			x					x					x		x	
Mär	x			x					x					x		x	
Myc	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Såg	x	x		x					x					x		x	
Val	x	x		x	x	x		x	x	x	x	x	x	x		x	
Säc		x		x					x					x		x	
Sol				x					x					x		x	

Table: Sampling history.

Sampling date	Dilution series
10th March 2015	50% (equal parts sample and filtered water), 25%, 12.5%
16th April 2015	75% (3 parts sample to 1 part filtered water), 50%, 25%, 12.5%, 6.25%

Table: Dilution experiments

2. Equipment

***EXO2* multiparameter sonde - http://www.exowater.com/exo2**

Horiba *Aqualog* fluorospectrometer - http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Fluorescence/Aqualog-Nov13.pdf

Merck Millipore *Millipak 20* filter - http://www.merckmillipore.com/SE/en/product/Millipak%C2%AE-20-Express-Filter,MM_NF-MPGP02001

Shimadzu Coorporation *TOC-V CPH* analyzer - http://www.ssi.shimadzu.com/products/literature/toc/toc-v-series.pdf

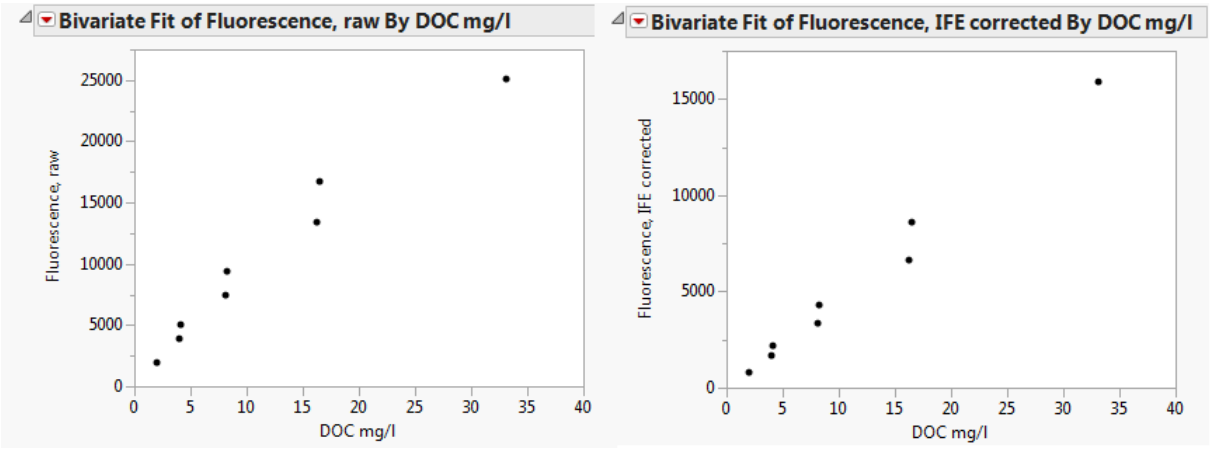
Whatman glass microfiber grade GF/F filters - http://www.sigmaaldrich.com/catalog/product/aldrich/z242519

3. Calibration & experiments

Calibration	Calibration standard	Pre-calibration value	Post-calibration value	Correction
Sonde 33 fDOM (Myckelmossbäcken)				
	300 QSU	139.24 QSU	299.94 QSU	y = x * 2.154
Sonde 34 fDOM (Gärsjöbäcken)				
	300 QSU	214.46 QSU	296.84 QSU	y = x * 1.384
Sonde 34 turbidity (Gärsjöbäcken)	0 FNU	-6.29 FNU	4.53 FNU	
	12.4 FNU	0.01 FNU	12.39 FNU	y = 1.1442 * x + 7.2069

Table _: post-calibrations for EXO sonde probes after autumn deployment phase. Pre-calibration error was due to errors in the previous calibration (before the autumn deployment phase).

Correction for Fe influence on SUVA: A* = A (@ 254nm, over 1m) – 0.01 * Fe (ppb)



Aqualog measured fluorescence before (left) and after IFE correction.