Optical and biogeochemical composition of organic and inorganic matter of river Vantaa during ice melt

Metropolia University of Applied Sciences

Bachelors in Engineering

Chemical Engineering

Atte Holm

Bachelor's thesis

10.11.2014

Metropolia

Author	Atte Holm
Title	Optical and biogeochemical composition of organic and inorganic matter of river Vantaa during ice melt
Number of Pages	32 pages + 7 appendices
Date	30 September 2014
Degree	Bachelors in Engineering
Degree Programme	Chemical Engineering
Specialisation Option	Environmental Engineering
Instructors	Kaj Lindedahl PhD Stefan Simis

The purpose of this project was to monitor water quality of river Vantaa during ice and snow melt. Melting of ice and snow increases the rivers discharges for approximately 3 months during spring. Melting waters and increased discharge affect the quality of the river water.

Samples were collected up to 2-3 times during the project. The samples were analyzed in the laboratory of Finnish Environment Institute in Kumpula, Helsinki. Optical measurements were done on sampling day and the rest of the measurements were done at the end of the sampling period.

The results show that the concentration of suspended matter rises when the river discharge increases. The correlation in the results between optical and biochemical measurements was inspected, and it was observed that optical devices can be used to monitor water quality.

Key words	water quality, river, environmental monitoring, melting waters

Metropolia

List of Abbreviations

GF/F:	Glass-fiber filter
INT:	Integrating Sphere. Extra module for the spectrophotometer
STD:	Standard sample compartment of the spectrophotometer
QFT:	Quantitative filter technique
TPTZ:	2,4,6-tri(2-pyridyl)-1,3,5-triazine
DOC:	Dissolved organic carbon
POC:	Particulate organic carbon
TSM:	Total suspended matter

Contents

Metropolia

1 Introduction

This document provides instructions for the determination of optical and biogeochemical properties of organic and inorganic matter of water samples taken from a river. These instructions describe sampling, analysis and data processing techniques. Water samples were collected from the river Vantaa during spring to document the effect of ice and snow melt on water quality.

This project was carried out at the Marine Research Centre of Finnish Environment Institute at Kumpula, Helsinki.

2 Sampling

To obtain a representative series of samples, it is necessary to use the same sampling techniques and equipment every time. Sampling should always be done in the same way in the same place to ensure the comparability of different samples. All sampling equipment needs to be cleaned before and after use to avoid contamination. Duplicate samples reduce the risk of sample loss or contamination and the collected samples should be held in a cooler box to prevent heating and the effects of sunlight.

River water samples are collected from the surface water (0–0.5 m from the surface) with a one-litre glass bottle. The sample should be taken from the middle of the river. If the river is too wide, and it is therefore not possible to use a long pole when collecting the sample, the sample needs to be taken from a bridge or a boat to reach the middle of the current.

Environmental conditions during the sampling must be recorded. Taking pictures of the water and the environment in general, for example pictures describing weather conditions, makes it possible to relate processed results to conditions that were not initially recorded.

2.1 Sampling site

Samples were collected two to three times per week from the river Vantaa at Vanhankaupunginkoski, Helsinki. The river is 101 km long, and its drainage basin is 1685 km^2. Over 1.1 million people inhabit this area. [1]

The site is a historic hydropower plant where the river Vantaa flows to the sea. The river divides into two different streams before the sampling location (Figure 1). The stream where sampling was done is led into a reservoir used to power a hydropower station.

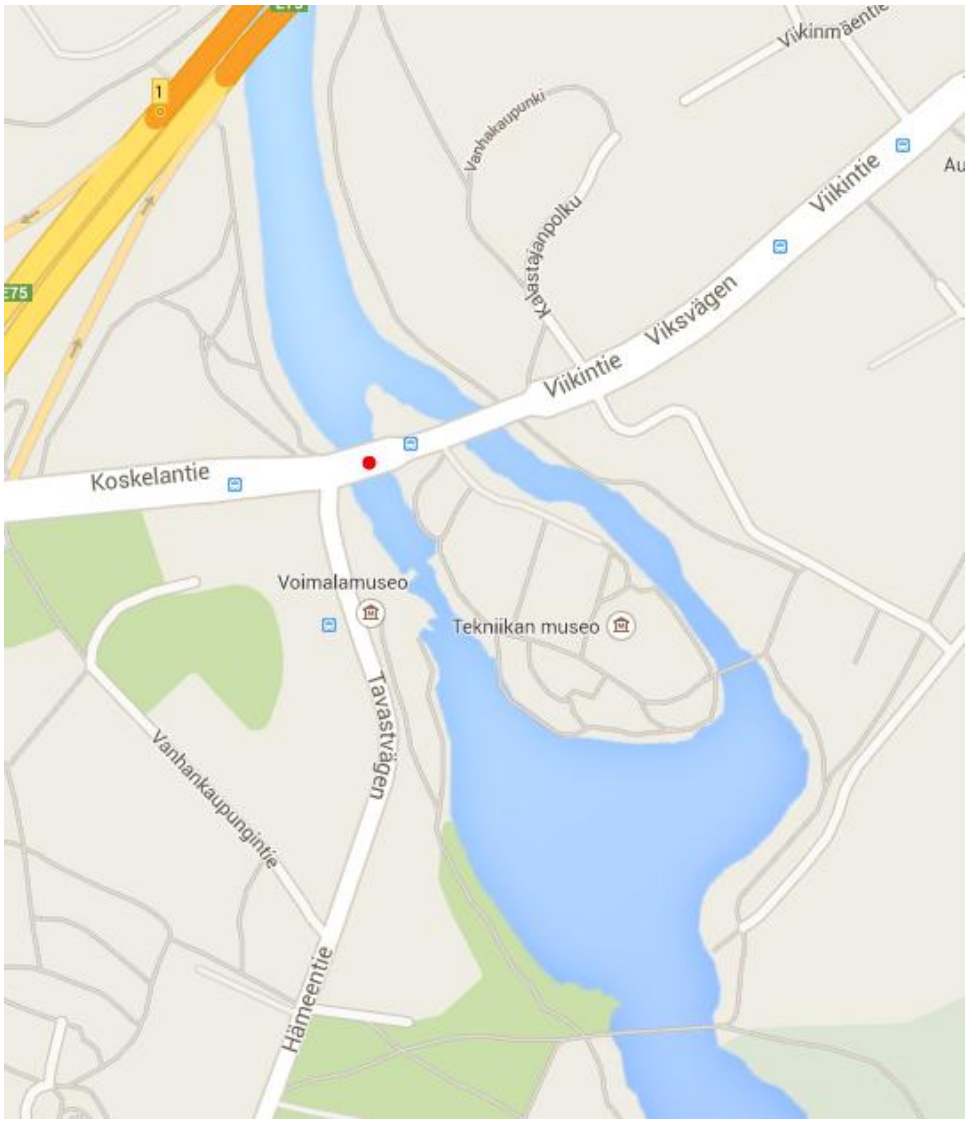

Figure 1. Map of the sampling site. The red dot marks the bridge from where samples were taken.

The river discharge (in units m^3 s^{-1}) increases during spring due to melting ice and snow. Figure 2 presents the river discharge. The average between 1937 and 2011 (red line) shows a peak in the flow during spring months [3]. The river discharge rises significantly from the end of March till the end of April. The discharge reaches approximately four times higher volume during the peak.

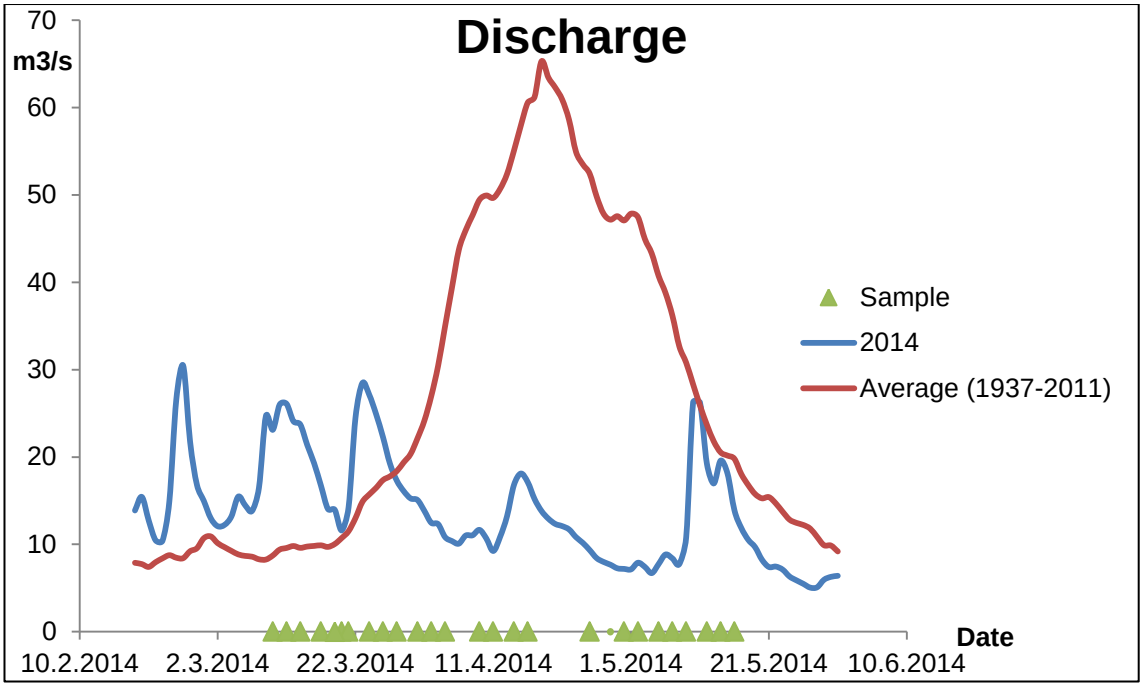

Figure 2. Total flow of river Vantaa. The data is recorded at Oulunkylä, approximately 3 km from Vanhankaupunginkoski.

The blue line represents the discharge at Oulunkylä in 2014. There was little snow during winter between 2013 and 2014; therefore, there was no distinct spring discharge peak. Sampling dates are shown with green markers.

Sampling was done from a bridge with a 10 litre bucket attached to a rope. The collected samples were taken in a cooler box to the laboratory for processing in approximately 30 minutes.

In addition to water sampling, hyperspectral reflectance ('water colour') was recorded with a WISP-3 (Water Insight, Wageningen, The Netherlands) device, in order to relate water colour to the biogeochemical composition of the river, in studies supported by this field work. Samples were taken on mid-day when the Sun was its highest point to

have optimal conditions for the reflectance measurement. The WISP-3 is described in chapter 3.1.

3 Measurements and sample preparations

The samples were processed in the laboratory of the Finnish Environment Institute (SYKE) in Kumpula, Helsinki. Two types of laboratory analyses were made; optical measurements and analyses of the biogeochemical composition of dissolved and particulate matter. Optical measurements were done immediately after sampling while samples were prepared for the remaining analyses. Prepared samples were processed in batches at the end of the field campaign.

This paragraph provides all relevant information of the instruments and instructions of how to make proper measurements and process the data.

3.1 Reflectance

The reflectance measurement characterizes the fate of sunlight upon interaction with the water column. A fraction of the sunlight penetrating the water surface is reflected back towards the surface. The ratio of upwelling over downwelling light is termed Reflectance. The measurement is done from the side of the river with a hand-held WISP-3 device.

3.1.1 Instrument description: WISP-3

The WISP-3 is a handheld hyperspectral radiometer used to record Reflectance and optionally derive water quality parameters from the colour of the water. The device uses three different collectors for the observation; one on top and two at the front (Figure 3). The collector on top measures irradiance coming from the sky to the surface of water (E_d).

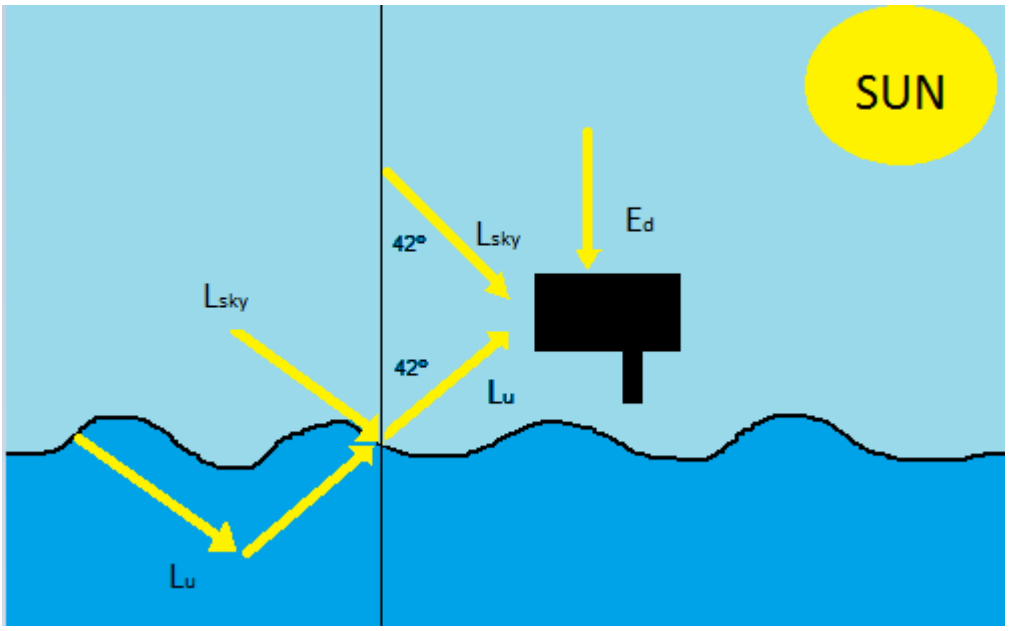

Figure 3. WISP-3 collects data from three detectors.

The two collectors at the front of the device are used to determine radiance coming from the sky (L_{sky}) and the radiance reflected from the substances in the water (L_u). The L_{sky} measurement is used to correct the L_u measurement, which contains some light reflected at, rather than under, the water surface. Both front sensors are pointed 42º away from zenith.

The subsurface irradiance reflectance (R0), or the water colour, is calculated from these three parameters by the WISP-3. A more elaborate processing is done after up-loading the measurements to the manufacturer's website (http://wispweb.waterinsight.nl/).

3.1.2 Performing a WISP-3 measurement

Before the sampling trip it is good to make sure that battery power is sufficient. To see the battery info, start the device, press the hashtag symbol (#) to see the menu, choose *System tools* and then *Battery info*. Use the arrows to scroll up and down and the tick symbol (✔) to select (Figure 4).

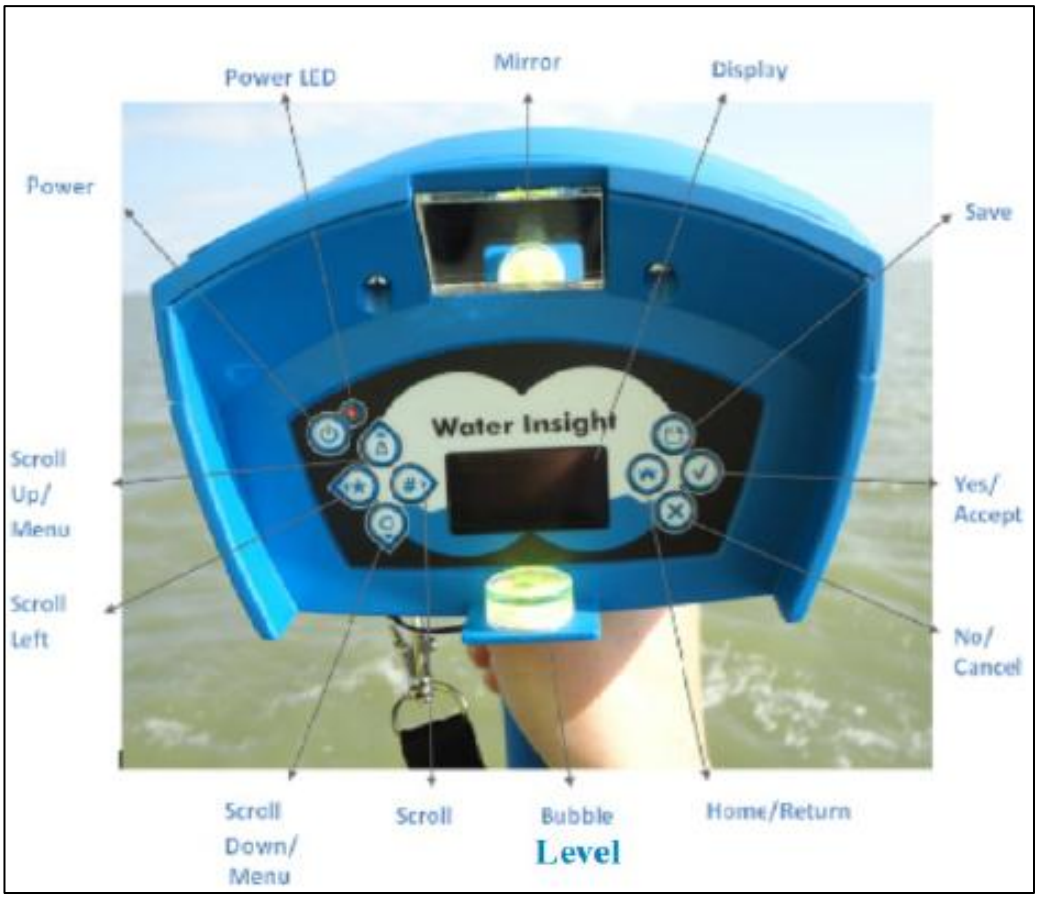

Figure 4. Controls of the WISP-3. [4]

The measurements can be done when the sun is at least 30º above the horizon. With higher sun elevation, more light enters the water, and therefore also the recorded signals will be stronger. Measurements have to be taken at an angle 90° away from the position of the sun to avoid most reflections of sunlight ('sun glint'). The optimal angle is 135° away from the sun.

To measure, start the device and remove the cover. Do not touch the optical parts and make sure the collector on top is free of rain drops or dirt. Point the device in the right direction and use the mirror and bubble level to hold it horizontal. Take three measurements, and after every measurement, check the results to see if the measurement was successful.

The reflectance measurement is sensitive to the condition of the sky and water surface. To be able to trace unrepresentative measurements, pictures of the sky and surface of the water need to be taken (Figure 5). From the pictures it is possible to see if

there is some debris floating on the water or if there are clouds in the sky scattering the sun light. Take pictures in the same angle as the three detectors are during the measurement.

Figure 5. Partly clouded, fully overcast and fully clear sky. Fully overcast and fully clear sky are good conditions for the measurement. Under partly clouded skies, the Lsky measurement may not be representative of reflected sky light recorded along with Lu.

3.1.3 Exporting and processing the reflectance data

Upload the measurement data to www.wetlabs.com/wispweb for processing. The service on the site calculates the results of the measurements. The data are presented in an Excel file. The table contains columns with R0, L_u, L_{sky} and E_d. Sort the four columns of all three replicates on separate sheets for future use.

3.2 Light absorption of dissolved matter and suspended solids

Dissolved and suspended matter influence the transparency and colour of water by absorbing and scattering light. The absorption and scattering thus contain information on the composition of particles and dissolved matter in the water. Light absorption of suspended matter is determined using filters by concentrating particles on filter and measuring its absorbance. Light absorption of dissolved matter is measured with cuvettes.

3.2.1 Filtration system and filtrating

A filtration system is used to separate particulates from filtrate and to concentrate particles. Filter samples are used with absorbance measurements and filtrate for both absorbance and fluorescence measurements. The same system is used to prepare samples for iron, organic carbon and total suspended matter analyses.

The system consists of funnel, glass sinter and vacuum unit. The size of the filtration area should be known to calculate absorption per volume from the absorbance measurements. The diameter of each numbered funnel is measured with a caliper.

Filtration is done over 25-mm GF/F filters. GF/F filters are glass microfiber filters with a nominal pore size of 0.7 µm. When using GF/F filters with vacuum the filtration is done at a maximum pressure of -30 kPa. Higher vacuum must be avoided because cells may get damaged and leak their contents through the filter.

Filters are placed on the sinter under the funnel with clean forceps (Figure 6). The filter must cover the sinter completely to avoid water passing through unfiltered.

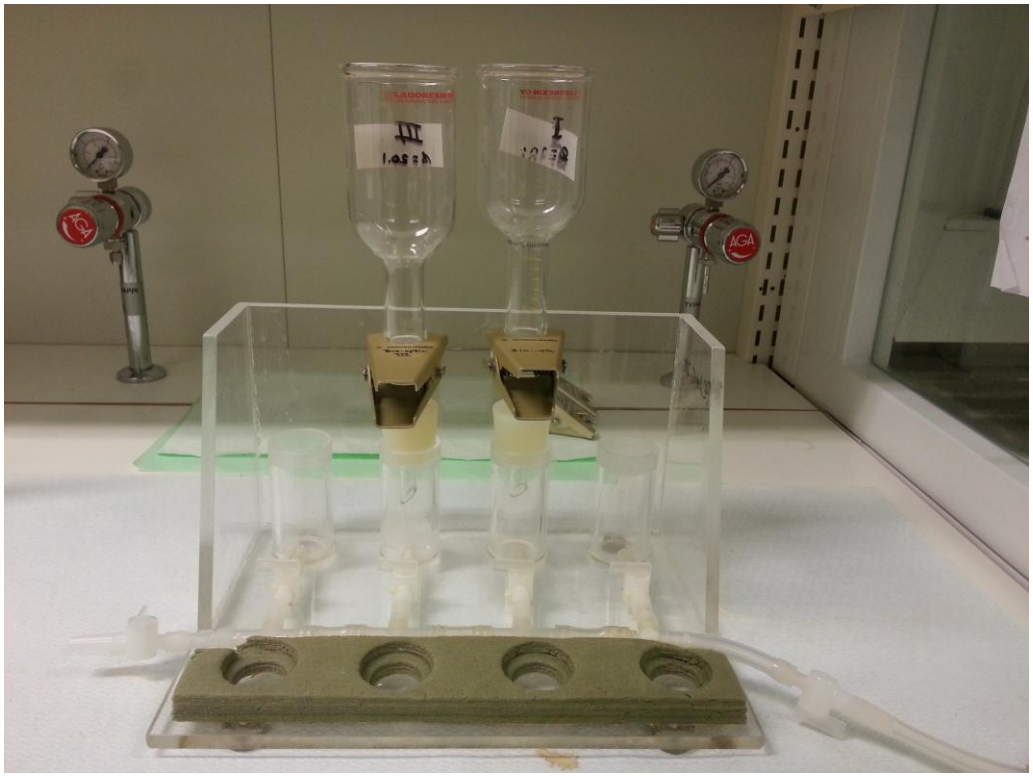

Figure 6. Filtration system. The GF/F filters are placed under the funnel.

3.2.2 Instrument description: PerkinElmer Lambda650 spectrophotometer

A PerkinElmer Lambda650 dual beam spectrophotometer is used to measure light absorption of filter and cuvette samples (Figure 7). The instrument is equipped with an Integrating Sphere (INT). The INT is used to determine the absorbance of solid samples and suspensions. The standard configuration of the spectrophotometer, without integrating sphere, only allows measurements of the absorbance of solutions.

Figure 7. Sample holders are placed inside the sphere from the top. [5]

The main difference between INT and standard spectrophotometer measurement is that INT measures the light field in the sphere, rather than the energy of the light beam. All direct light beams to the detector are eliminated with baffles inside the sphere.

The inside of the sphere is covered with Spectralon, a fluoropolymer with a very high diffuse reflectance. Its reflectance is generally >99% over a range from 400 to 1500 nm. [6]

The sample is set into the sphere with a sample holder. When a light beam is directed to the sample the light scatters around the sphere. The scattered light reflects from the walls creating a light field which is measured by the detector on the bottom of the sphere.

Two different sample holders are used in INT. One holds cuvettes and one filters. These sample holders are coated with Spectralon and barium sulphate. Barium sulphate also has a high reflectance, about 95-98 % over the range of 300 to 1200 nm.

Spectralon and barium sulphate absorb oils from skin and therefore it is necessary to always wear clean cotton gloves when handling the sample holders. If the sample holders get dirty, they will absorb more light which deteriorates the measurement. Recoating the sample holders with barium sulphate is cumbersome thus contaminating the sample holders must be avoided.

3.2.3 Light absorption of particles

The absorption of light is measured according to the quantitative filter technique (QFT). The QFT is used to assess the absorption of light by particles concentrated onto filters.

The method consists of three different measurements: a blank filter, a sample filter and the same filter bleached with a hypochlorite solution. Before starting measurements, let the lamp warm up for 15-30 minutes and perform Autozero with an empty sample holder inside the sphere. Autozero zeroes the light intensity between the sample and reference beams.

First moisten a blank filter and place it in the sample holder using forceps (Figure 8). All filters must be moistened with ultrapure water before the measurement to improve the comparability of the results. Moistening is done by wetting the filter by placing it on top of a few drops of ultrapure water. The filter is then placed on a tissue to absorb some of the moisture before placing it in the filter holder. The tissue helps to have constant moisture levels in all samples.

The filter must always be mounted vertically straight to have the same surface area exposed to the light beam. Place the sample holder into the instrument, carefully not to bump into the sides of the sphere opening. When the sample is mounted in the sphere, turn the sample holder 10 degrees clockwise to prevent light reflecting back out of the sphere. Measure the absorbance from 900 to 300 nanometres. The absorbance value of the blank filter at the end of the measurement should be 0.05 – 0.1.

Figure 8. Filter in sample holder.

After measuring the blank, filter 1 – 10 ml of water sample, depending on the turbidity of the water. Dilute the sample with ultrapure water before filtration to get a homogenous distribution of particles. Moisten the filter with ultrapure water after filtration and perform a measurement like with the blank. The target value of the measurement is 0.20–0.25 at absorption peaks, after subtracting the blank. The absorbance must not exceed 0.30.

After the measurement, bleach the filter to remove pigments. Bleaching is done in the same filtration system as before. Pour 5 ml of sodiumhypochlorite (0.1 - 0.15 % solution of hypochlorite) into the funnel and let it sit for 8 minutes. Cover the funnel with foil to prevent contamination. After 8 minutes, apply the vacuum and rinse the funnel with ultrapure water. Perform the same measurement with the bleached filter as before. Repeat the procedure for replicate samples.

3.2.4 Light absorption in solution

Absorbance with cuvettes is measured in the range 190 – 900 nm, using quartz cuvettes to minimize UV light absorption (Figure 9).

Solutions are measured in the standard sample compartment (STD) and inside the INT. Five different measurements are being done: blank in STD and INT, filtrate (0.2 µm) in STD and INT and untreated sample in INT (Figure 10).

When a solution (filtrate) is measured in the STD, some light will be absorbed and the difference in light intensity between the sample and reference will be recorded. Suspensions (unfiltered samples) also scatter light and thus cannot be measured in STD. When the suspension is set inside the INT, all scattered light will be recorded and the difference between sample and reference beams will be only related to light absorption.

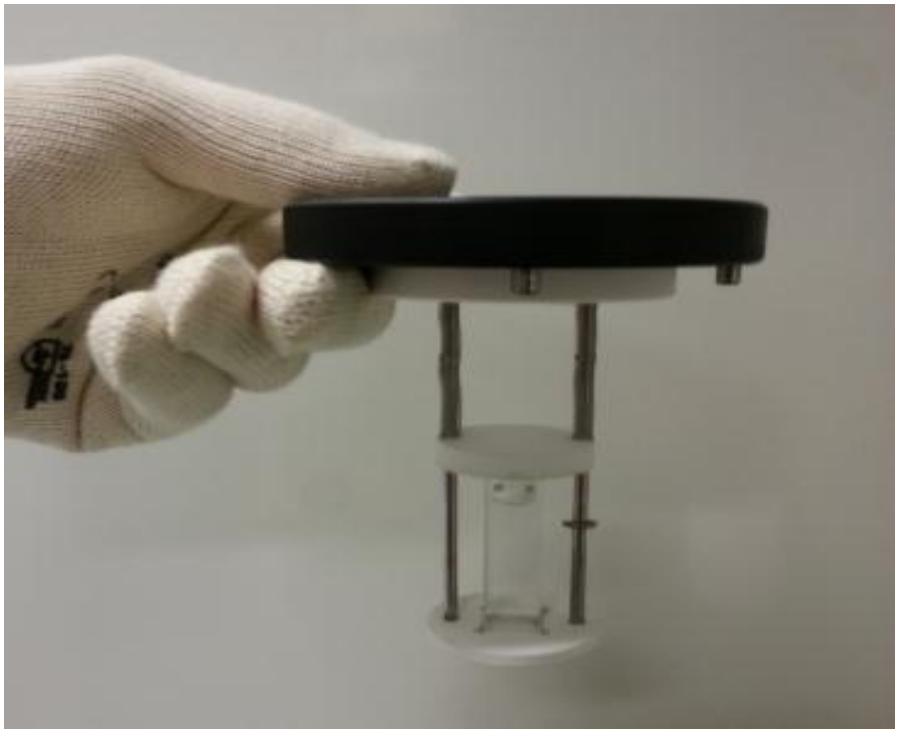

Figure 9. Cuvette set in sample holder.

When using a cuvette, it is important to make sure that it contains no air bubbles or contaminations. A dirty cuvette during one measurement that contributes to an analysis of several measurements, can invalidate the whole set. The sample must be at room temperature because warming up causes bubbles inside the cuvette and the absorption by water itself is slightly temperature dependent.

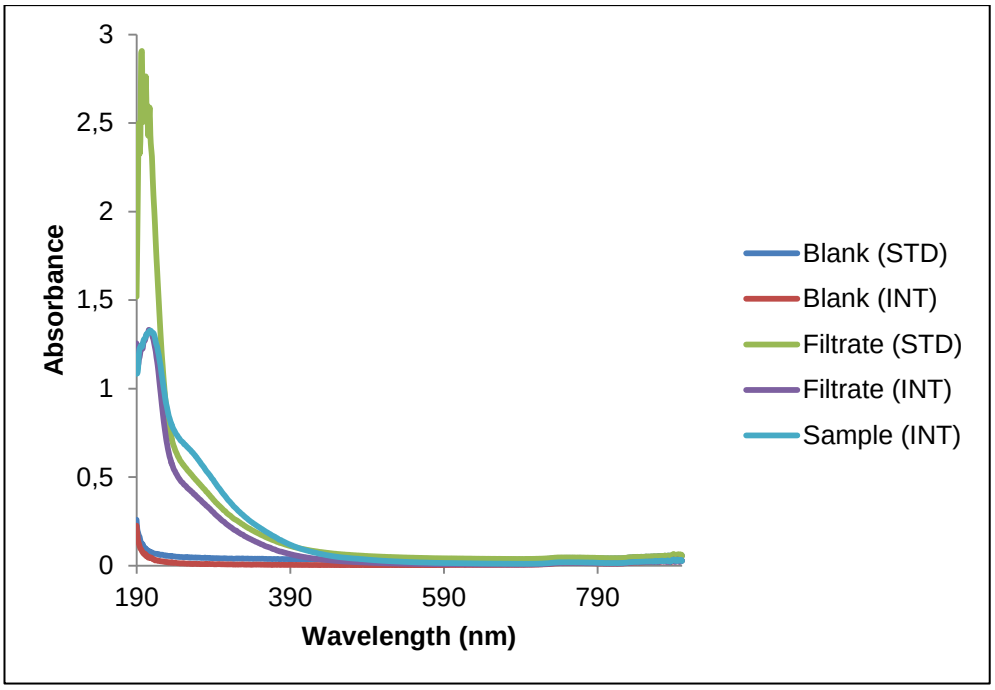

Figure 10 Five measurements of light absorption in solution.

3.2.5 Exporting and processing the absorption data

Export the data from the PerkinElmer Software: click File – Export. There will be one .asc file for every measurement. These files have the data shown in two columns: wavelength and the result of the measurement.

Sort the data of the five filter measurements in different sheets. The absorption is calculated with the following equation:

$$a = \frac{ln[\, pathlength_A \left(A_{\text{sample}} - A_{\text{blank}}\right) + \, pathlength_B \times \left(A_{\text{sample}} - A_{\text{blank}}\right)^2]}{(\, filtrated\ volume \,/\, filtration\ area\,)}$$

where pathlength_A and pathlength_B are path length amplification correction factors, used to remove the effect of the filter on the measurement. For the INT configuration and for absorbance < 0.25, valid values are 0.336 and 0.0869 according to PhD Simis S (conversation May 2014). A_{sample} is the result of the measurement of a solution and A_{blank} is the result of the ultrapure water measurement with the same configuration as the sample.

Sort the data of the cuvette measurements in five different spreadsheets. Add three sheets for calculating the blank corrected values for the filtrate and suspension measurements. Add three more sheets to calculate the absorption from the blank-corrected values. Absorption of the cuvette samples are calculated with the equation:

$$a_{sample} = \frac{ln(A_{ODTSM})}{pathlength},$$

where A_{ODTSM} is the blank-corrected absorbance value and path length is the optical path length of the cuvette, in meters. In this work, cuvettes with 0.1 m path length were used.

3.3 Iron concentration

Iron has the highest concentration of all metals in river water. It can exist in water in colloidal and suspended particulate form, and it is usually associated with humic substances, such as silica and clay. Iron samples were prepared at the sampling day, and all the samples were processed using the 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) method at the end of the sampling period.

3.3.1 Principles of the TPTZ method

Iron concentration is measured with TPTZ method using a spectrophotometer. A calibration curve is produced and the absorbance values of the samples are compared to it. Other metals can influence the measurement when determining iron levels and therefore it is important to use acid-washed glassware.

When determining iron from natural waters, it is important to get all ions of the sample in reactive form. This is done by oxidizing the samples in an autoclave. After autoclaving Fe^{3+} will be reduced to Fe^{2+} with ammonium hydroxide chloride. Fe^{2+} forms a complex ion with TPTZ at pH 3.4 – 5.8. The absorbance of this complex is measured at 593 nm with a spectrophotometer. The measurement needs to be done within 5 - 120 minutes after adding the last reagent.

3.3.2 Sample preparation

Iron concentration was determined from unfiltered and filtered water. The filtration is done with the same filtration system as before using GF/F filters.

Before starting to fill vials, let some water go through the filter to get rid of unwanted particulates. Place an acid-washed vial into the filtration system under the filter, and fill it with filtrate. Lift the vial out with clean forceps, and fill another vial to get a replicate. Pipette 10 ml of filtered water and 10 ml of unfiltered water into acid-washed vials. Acidify samples with 100 µl of 4 M sulphuric acid to keep the ions dissolved. Store the samples at room temperature.

3.3.3 Measuring iron levels with TPTZ method

For the calibration curve, use ammonium iron(II)sulphate to produce solutions with concentrations of 0 µg/l, 100 µg/l, 200 µg/l, 500 µg/l, 1000 µg/l, 1500 µg/l and 2000 µg/l of iron into 100 ml volumetric flasks. Acidify all solutions with 1 ml of 4 M sulphuric acid. After acidification, pipette 10 ml of each solution into 20-ml acid-washed vials.

Oxidizing is done by autoclaving the samples in acidic condition. Oxidize samples and calibration solutions by adding 0.10 ± 0.01 g of potassium peroxodisulfate into the vials. Autoclave vials at 120° for 30 minutes.

Let the vials cool down to room temperature after autoclaving. Add 100 µl of each reagent to every vial in the following order: hydroxyle ammonium chloride (3 M), TPTZ (1 mM) and sodium acetate (3 M). Measure the absorbance from all solutions at 593 nm.

3.4 Backscattering of light

Particulates in water scatter light. Backscattering is the fraction of light scattered in the backward direction. Backscattering contributes to the light that emerges from the water surface and therefore to the light that we observe when we look at a water body. Clear waters have low backscattering, whereas turbid waters have high backscattering and generally appear brighter.

3.4.1 Instrument description: BB-3 and light trap

Backscattering is measured with a scatterometer and a light trap (Figure 11). The scatterometer used here is a Wetlabs BB-3, which measures backscattering of light at three different wavelengths and one fixed (117°) angle. For each waveband, the sensor has light sources and detectors. The detectors are measuring backscattering at a 117 degree angle. This angle is determined as a minimum converge point, and it results in a more concentration-based suspended material measurement, rather than type- or size-based. [7]

The measurement is done right in front of the head of the scatterometer and all other light beams have to be eliminated for a proper measurement. All light that is not scattered to the detector will be faded in the light trap.

The light trap is a completely black box, which volume is approximately 2.7 litres. The diagonal walls and the wall in the middle of the box prevent light beams from reflecting back to the scatterometer.

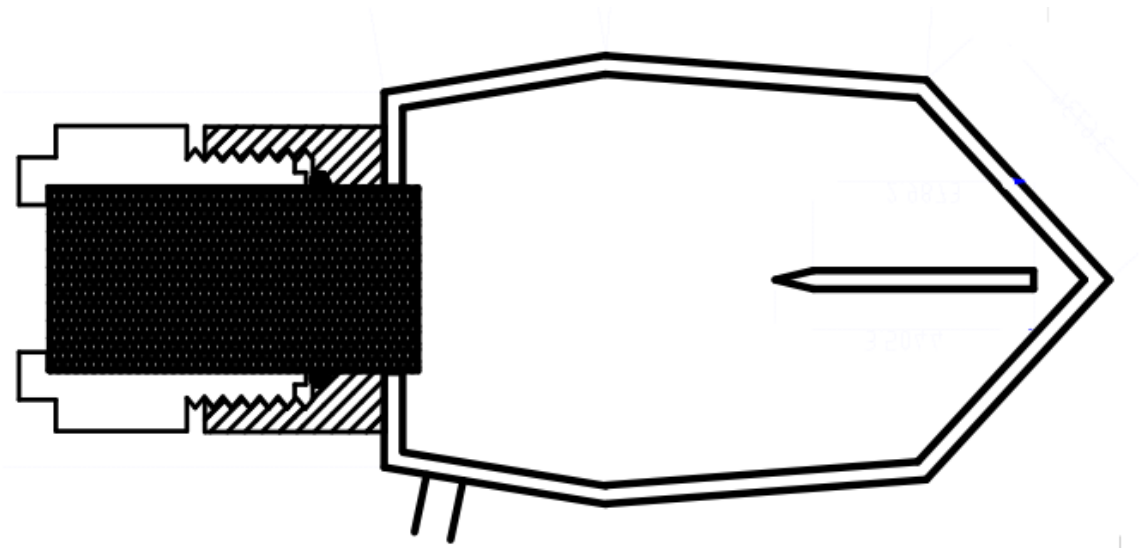

Figure 11. Sketch of scatterometer (black) and light trap. [8]

3.4.2 Performing a backscattering measurement

River water can be very turbid, with strong light scattering. When measuring backscattering, the sample needs to be diluted for a more sensitive measurement. Produce 3 litres of sample suspension diluted with ultrapure water. If the sample is very turbid, the dilution may be in order of 1:50. With clearer river water dilutions up to 1:20 may be possible. A good dilution can be determined by recording backscattering for few minutes. If the result is a very unstable curve, there is too much particles scattering the light and thus, a larger dilution should be used.

Remove the cover of the light trap and make sure both valves are closed. Pour the solution into the light trap until it is completely full. Purge air from both entrance and exit tubes because bubbles will influence the measurement.

Start program EcoView116 and select the right COM port and method. Close the cover and click "Start recording" when the graph has settled. Record for a few minutes and click "Stop record".

Empty the light trap and clean it. Use soft tissue when cleaning the optics.

3.4.3 Data processing

Open the .raw-file in MS Excel and it will be opened in a table of 9 columns. The third, fifth, and seventh columns are the sensor wavelengths, each followed by the measured values. Calculate the average of the measurement on each of the three wavelengths. Gather the calculated averages with the sample name to another sheet.

3.5 Fluorescence of dissolved matter

Fluorescence is a luminescent phenomenon where light is emitted by a substance that has absorbed light or other electromagnetic radiation (Figure 12). The emitted photon has longer wavelength, and therefore lower energy, than the absorbed light. The fluorescence properties of a sample gives information about its molecular composition.

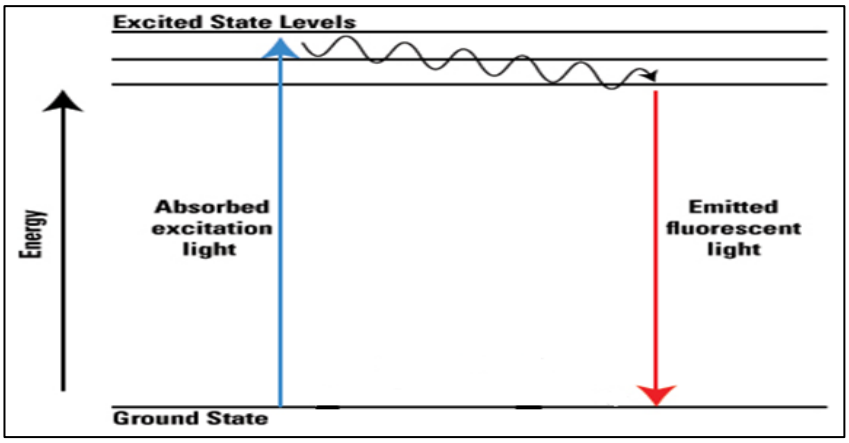

Figure 12. Fluorescence. Short wavelength light (blue arrow) is absorbed and longer wavelength light. [9]

3.5.1 The instrument

Fluorescence is measured with the Agilent Varian Cary Eclipse spectrofluorometer. The device uses a flashing xenon lamp and the light is directed through the sample. Detection is at a 90° angle. The sample is placed in the device in a 10 mm cuvette with clear sides. Open the Cary Eclipse software and create a method with the following settings:

	Range	**Intervals**	**Slit width**
Excitation	220 - 450 nm	5 nm	5 nm
Emission	260 - 600 nm	4 nm	5 nm
Integration time	0.2 s		
PMT Voltage	800 V		

3.5.2 Performing a measurement

Fluorescence is measured from a blank reference (ultrapure water) and from filtrate (0.2 µm) of the water sample. A quartz cuvette is used for measurements in the UV domain.

Having the program and the device set up, pipette 3.4 ml of ultrapure water into the cuvette to act as a blank reference. Place the cuvette inside the device. The markings on the cuvette should always point at the same direction. Press *Start* and name the file and sample. After the blank measurement, empty the cuvette and do the same measurement with the sample filtrate (0.2 µm).

3.5.3 Data processing

Open the .csv files in MS Excel. Select the first column and sort the data in columns by having comma as the delimiter. When in separate cells, wavelength is in the first column and intensity in the second, and so on. Save the first column of the wavelengths and delete the rest of them. Delete also the first two rows and add there the wavelength from 220 to 450 with steps of 5 units. The first intensity value of the table (at 220 / 280) should be in the cell B2.

	220	225	. . .	450
280				
284				
.		INTENSITY DATA		
.				
.				
600				

Figure 13. Example of how to sort the data.

Set the sorted data of the blank to one sheet and the data of the filtrate to another sheet. Make a third sheet for the blank correction of the data set by deleting the blank values from the filtrate. Make a surface plot of the data after blank correction. There are commonly two major peaks in the plot. In Figure 14 the two peaks show in green.

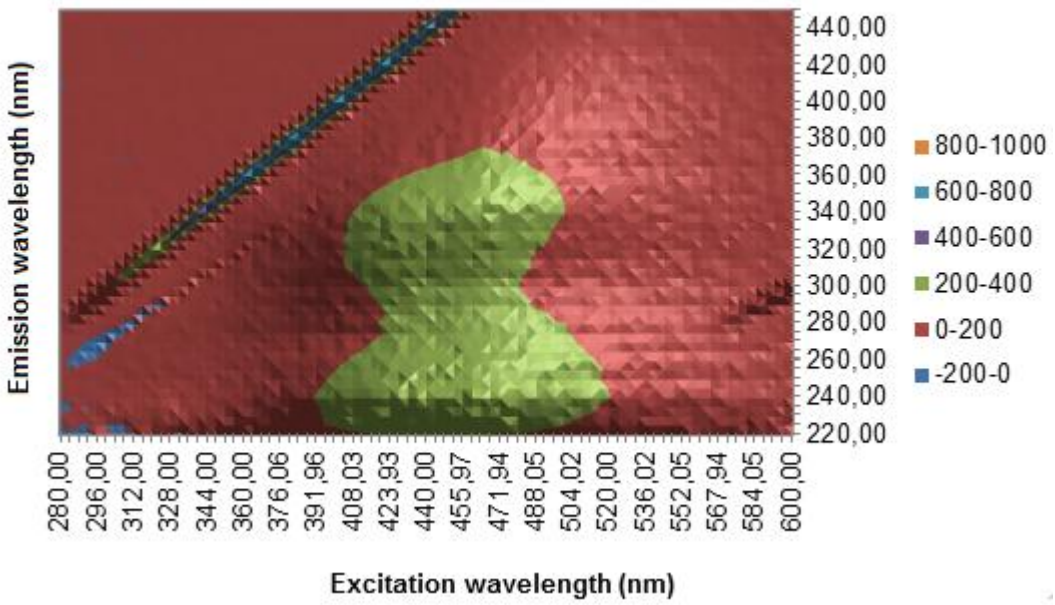

Figure 14. Surface plot of intensity data. The peaks are in green and the cross-talking line can be seen in the upper left corner.

The straight line in the plot where intensity reaches extreme values is due to cross-talk of the instrument, observed when the wavelength of the light source and the detector overlap.

3.6 Organic carbon

The yellow or brown colour of the river water is related to dissolved organic matter. This originates from leaching of humic substances from plants and soil. Organic carbon is determined from water samples because it is an important part of the carbon cycle of aquatic ecosystems. It also increases light absorption, which decreases light penetration in water, making it unavailable for phototrophs.

Organic carbon is in the water in dissolved and particulate form. Dissolved organic carbon (DOC) is the organic matter in the water sample that is able to pass through a filter. Particulate organic carbon (POC) is the counterpart of DOC i.e. all the carbon matter that retained on the filter.

POC and DOC samples were stored for external analysis. Only sample preparations were made.

3.6.1 Sample preparation for POC

Particulate organic carbon (POC) is measured from filters. Use pre-combusted QF/F filter and the standard filtration system. Filter a small amount of the sample, for example 10 ml, to get a light-coloured filter. After the sample is filtered, rinse the funnel with ultrapure water to get all the particulates from the funnel to the filter. Remove the filter with clean forceps, and store it in a plastic petridish. Write the sample name to the petridish and close it with tape. Write the sample name also to the tape. Store the samples at room temperature.

3.6.2 Sample preparation for DOC

Dissolved organic carbon (DOC) is measured from a 0,2 µm filtrate. Filtration is done with stacked filters and a syringe (Figure 15). GF/F filter (0.7 µm) needs to be used to avoid the syringe filter (0.2 µm) from getting blocked. The filtration is done straight into a DOC vial to prevent any extra carbon to contaminate the sample.

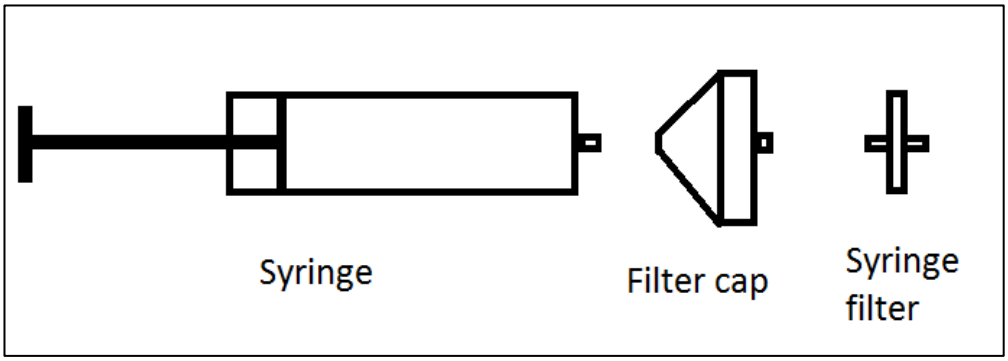

Figure 15. DOC filtration setting. The GF/F filter is placed inside the filter cap.

Fill the syringe with water sample. Place GF/F filter into filter cap and add a syringe filter with nominal pore size of 0.2 µm to it. Let a few drops through the filters to ensure they are clear from any extra particulates. Filter about 20 ml of sample into a vial

and add 80 µl of HCl (2M). Use acid-washed and combusted vials to avoid unwanted carbon getting in the sample. Store the sample at 4 ºC.

3.7 Total suspended matter (TSM)

River water often carries a high concentration of suspended organic and inorganic matter. Usually river waters gain high concentration of suspended solids due to eroded soil, carried by rain and melting snow run-off. TSM absorbs and scatters sunlight.

3.7.1 Sample preparation of TSM

To determine the organic and inorganic dry weight, concentrate the sample onto GF/F filters. The filters must be pre-combusted to have them clean from any organic matter. The dry weight of the filter without sample must be determined before use. The same filtration system as earlier is being used.

The more there are particles on a filter, the accurate the measurement will be. Therefore the idea is to get as much matter to the filter as possible. After approximately 5 minutes of filtration, filtration will have slowed down as the filter gets increasingly blocked, so the volume of water to be filtered must be chosen accordingly. When the sample is filtered, rinse the funnel with ultrapure water to get all particles from the surface of the funnel onto the filter.

When the filtration is done, reduce the vacuum and remove the filter with clean forceps. Touching the coloured area of the filter must be avoided. Filters are stored at -80 ºC in small plastic petridishes.

3.7.2 Measurement of organic and inorganic dry weight

Weigh the filters with a micro balance before and after combustion to determine the difference between organic and inorganic dry weight (Figure 16). Filters can be moist after being stored at -80 ºC so they need to be dried and at room temperature before the weighing. Take care that filters do not stick to the surface on which they are drying as this can tear glass fibre off, reducing their weight.

During the combustion process, filters cannot be held in plastic petridishes and therefore all the filters have to be put on large glass petridishes. Organize them by placing them in a spiral on the dish, with slight overlap between filters. When filters are in a form of a spiral, it is possible to trace them in order. It is recommendable to take a picture of the dish before the combustion to make it easier to identify them afterwards.

Figure 16 Filters being weighed.

Combust filters at 450 ºC for 240 minutes. After the combustion, let the oven cool down to prevent the air flow when opening the door of the oven. The air flow can move the filters and mix them up, making it impossible to identify them.

After weighing the combusted filters, calculate the fraction between organic and inorganic matter with following formulas:

$$TSM = \frac{Dry\ weight - Filter\ weight}{Filtered\ volume}$$

$$Organic\ TSM = \frac{Dry\ weight - Weight\ after\ combustion}{Filtered\ volume}$$

$$Inorganic\ TSM = \frac{Weight\ after\ combustion - Filter\ weight}{Filtered\ volume}$$

4 Results

The results of organic carbon were not analysed during this project. Other results were inspected to illustrate the correlation between river discharge and matter composition. Also, some correlations between optical and biogeochemical measurement methods were inspected.

4.1 Reflectance

Back scattering is the result of suspended matter reflecting the light beams back to detector. Figure 17 shows a strong correlation (R^2 = 0.86) between the TSM measurements and back scattering measurements. Backscattering measurement is a lot faster than TSM measurement thus it can be used to determine TSM.

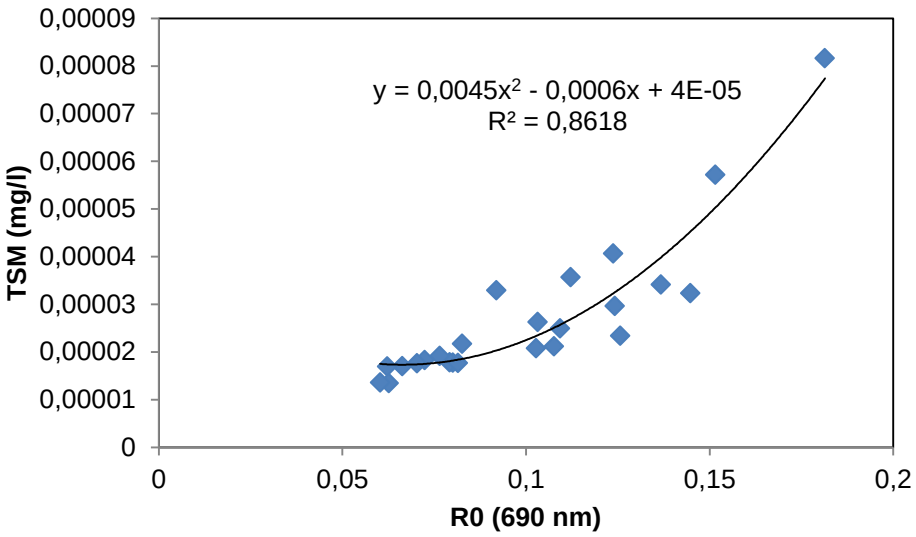

Figure 17. TSM and Reflectance peak. The figure shows a strong correlation between water colour and total suspended matter measurements.

Figure 18 presents normalized reflectance data. According to the figure, the reflectance measurement is noisy between 350 – 400 nm. However, only the peak is inspected, which is the least noisy part.

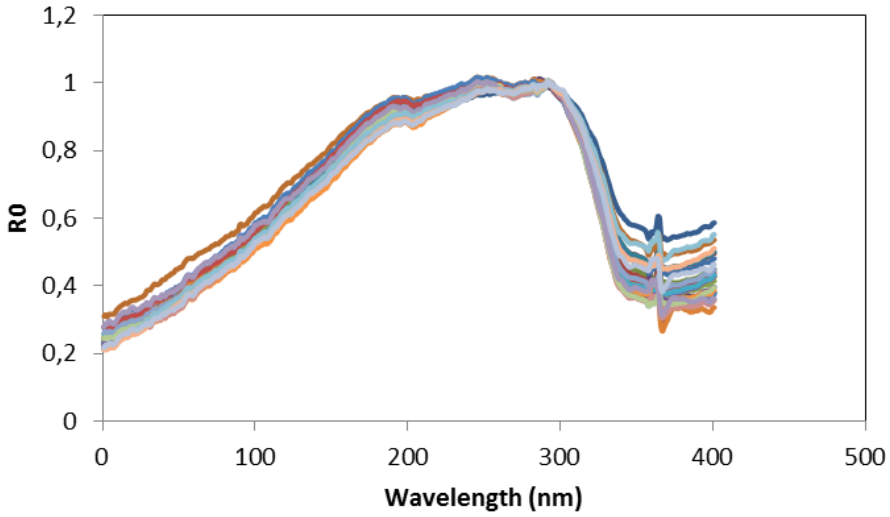

Figure 18 Normalized reflectance data. The peaks at 690 nm were used to normalize the data.

4.2 Light absorption

Results of the light absorption results were inspected at four wavelengths. Wavelengths 350 nm and 850 nm are rear ends of the measurement range. Wavelengths 412 nm and 532 nm are inspected because many of the optical monitoring devices operate with these wavelengths.

4.2.1 Light absorption of particles

Light absorption measurement is very noisy at higher wavelengths because of the high, almost complete, transparency. Light absorption had a low correlation at 850 nm when plotted against backscattering data.

Relatively a lot more light was absorbed at the end of the measurement (350 nm) which led to a lot less noise-sensitive results (Figure 19).

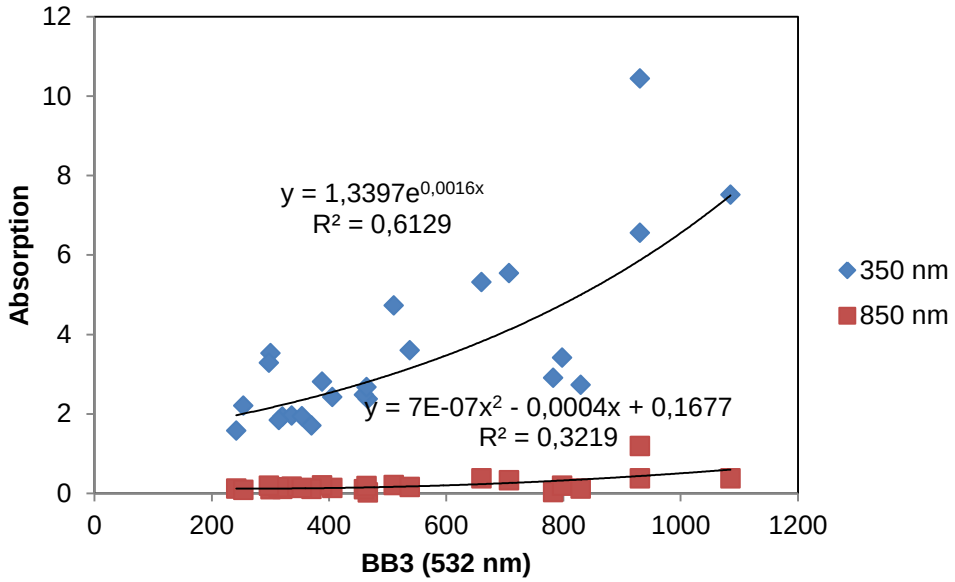

Figure 19. Correlation between backscattering (532 nm) and pigment absorption at 350 nm and 850 nm. Some correlation at 350 nm. At 850 nm the measurement is very noisy and thus there is a low correlation.

In Figure 20 there can be seen a connection between material concentration and pigments. Correlations at 412 nm and 532 nm are at the same scale as it was at 350 nm.

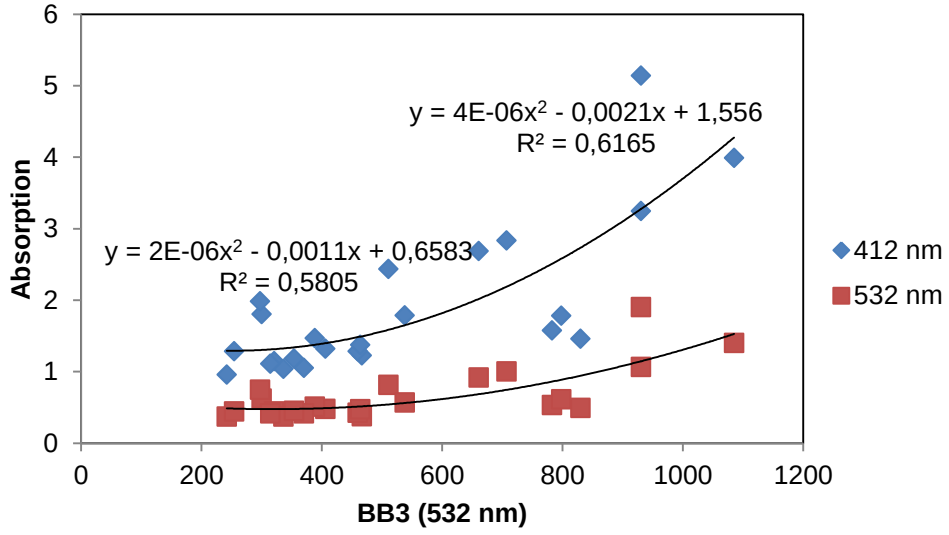

Figure 20 Correlation between backscattering (532 nm) and pigment absorption at 412 nm and 532 nm.

Metropolia

4.2.2 Light absorption in solution

The results of the absorption in solution measurements had also a correlation over 50%, except at 850 nm, which is the noisiest part of the measurement range (Figure 21 and Figure 22).

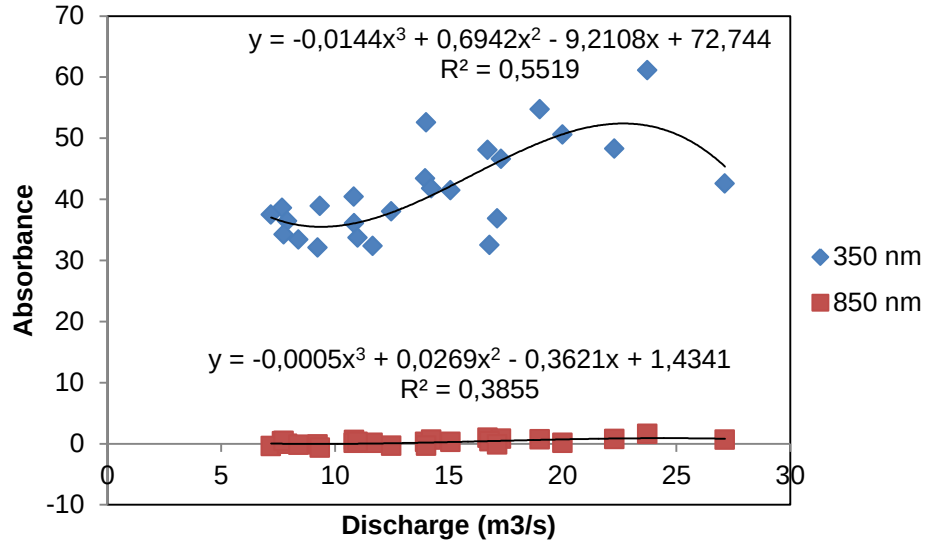

Figure 21 Absorption of untreated samples at 350 nm and 850 nm plotted against river discharge.

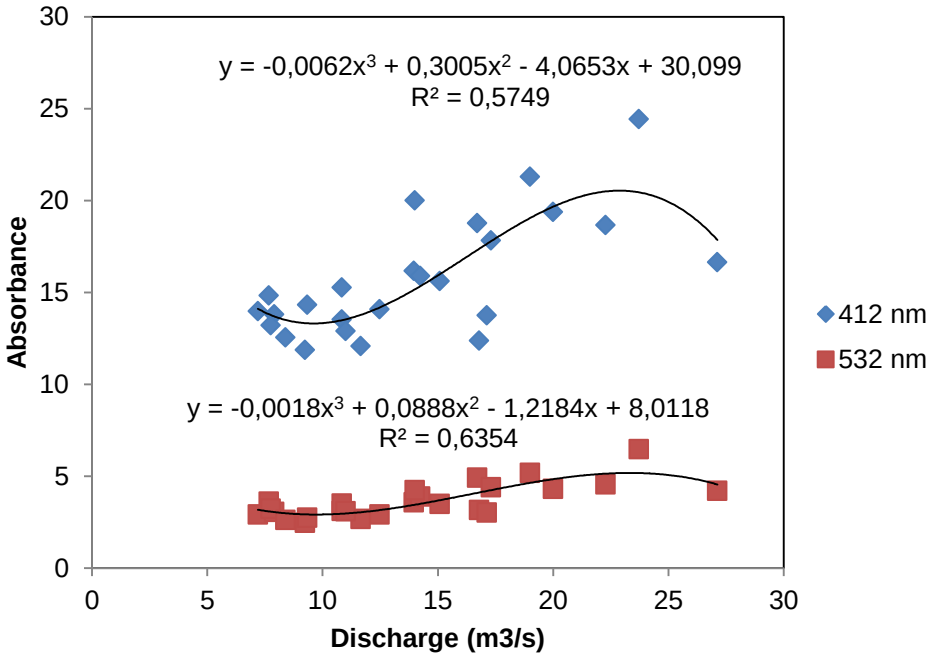

Figure 22 Absorption of untreated samples at 412 nm and 532 nm plotted against river discharge.

Metropolia

4.3 Iron

Filtered iron samples and discharge had a 0.50 % correlation (Figure 23). Unfiltered iron samples had a lot stronger correlation (Figure 24). Iron is in a floc form in natural waters and thus the unfiltered samples had better correlation.

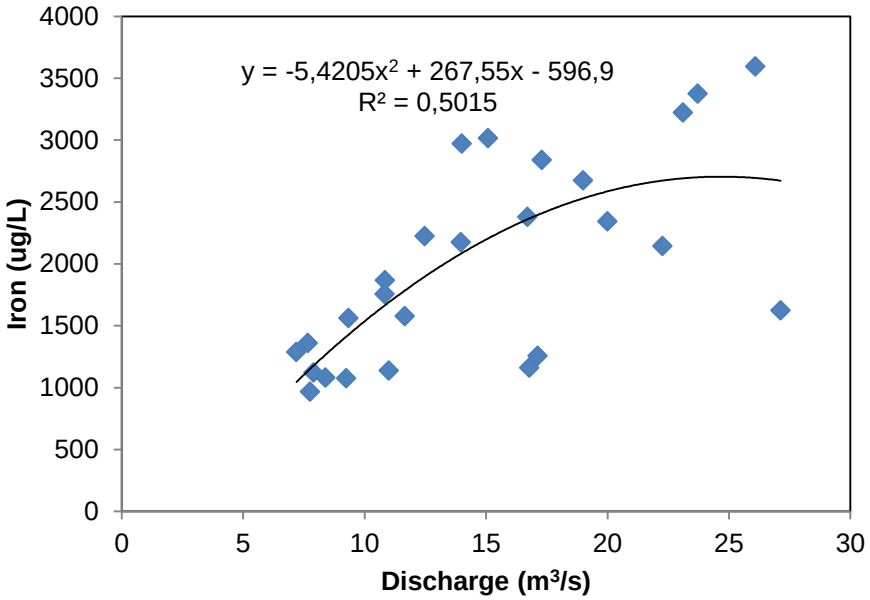

Figure 23 Filtered iron samples as a function of river discharge.

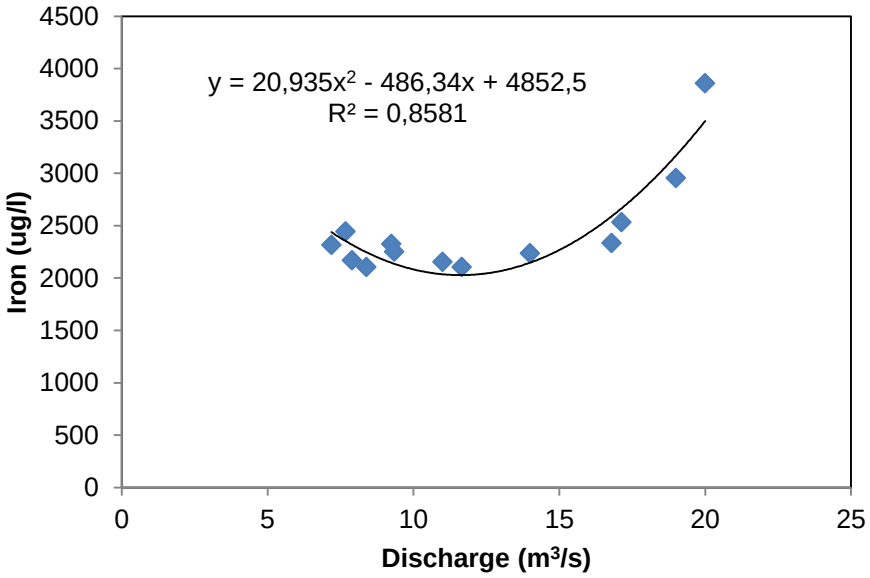

Figure 24 Unfiltered iron samples had a strong nonlinear correlation (R^2 = 0.86) with river discharge. The results of the first 12 sampling days exceeded the detection range of the measurement and thus only the last 15 samples are plotted.

4.4 Back scattering

Figure 25 reveals the correlation between reflectance and back scattering measurements. This suggests that instead of collecting a sample, WISP-3 can be used for this measurement.

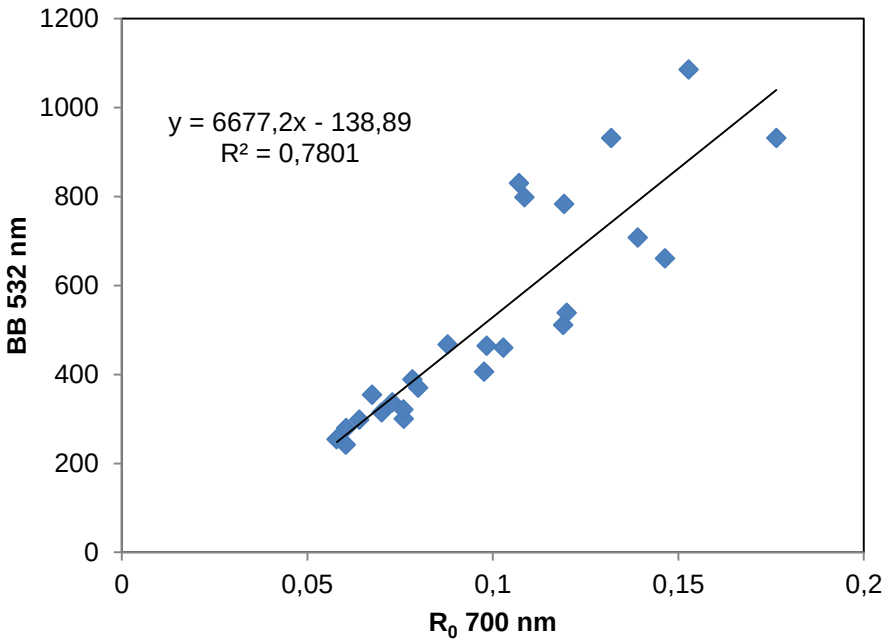

Figure 25 Figure shows data of back scattering and Reflectance peak. According to this model there is a correlation between the material concentration and water colour.

4.5 Fluorescence

Figure 26 shows that the molecular composition of the water does not change when the discharge rises. No correlation with other parameters was discovered.

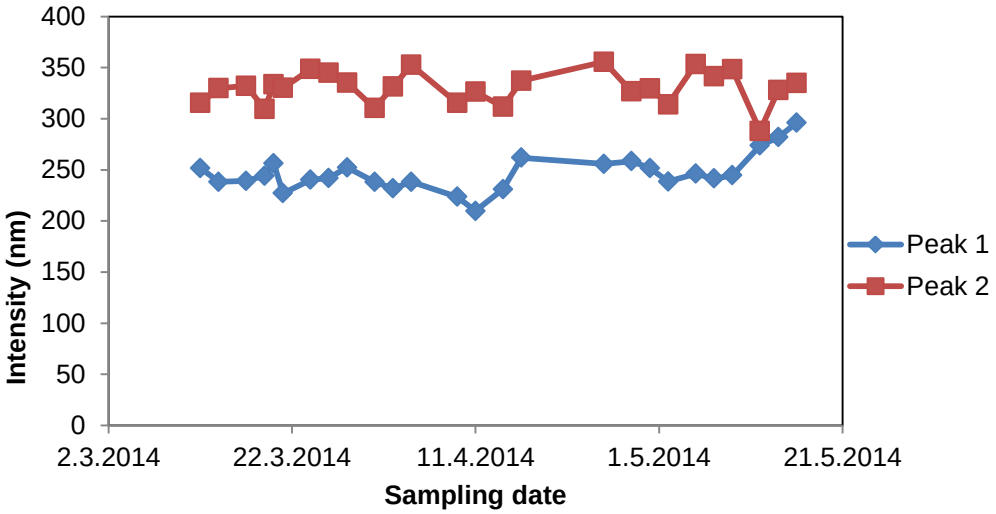

Figure 26 Fluorescence measurements had no notable difference during the sampling period.

4.6 Total suspended matter

As it was expected, the levels of total suspended matter have a high correlation with river discharge (Figure 27).

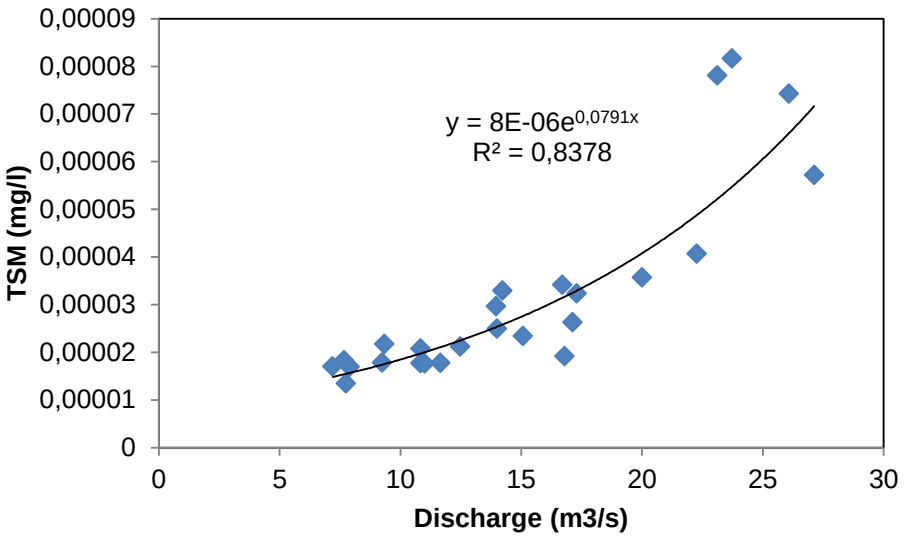

Figure 27. TSM plotted against river discharge.

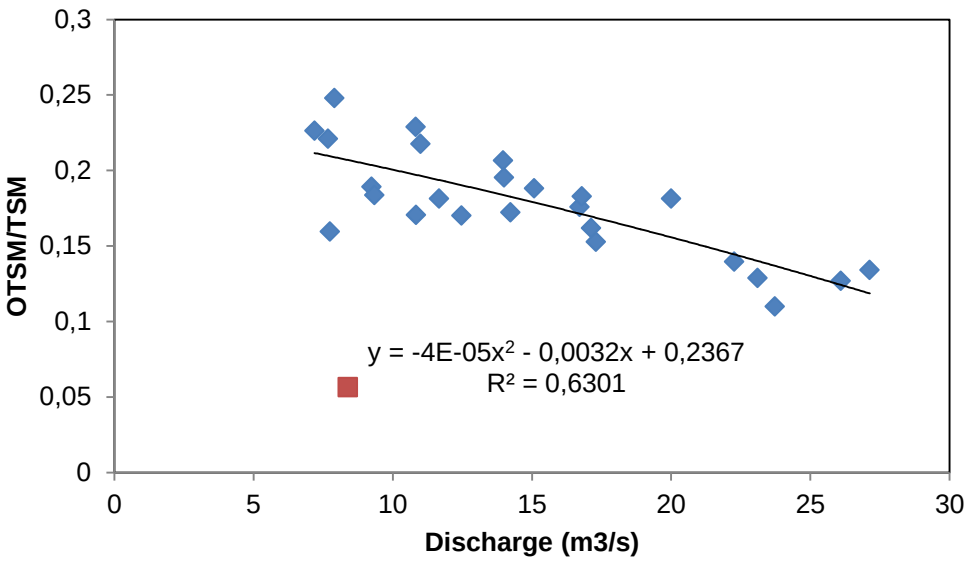

Figure 28. The relation of organic TSM and TSM plotted against river discharge. One excluded sample marked with red square.

According to Figure 28, more inorganic matter ends up to the river when the discharge rises. The organic suspended matter concentration decreases as the river discharge increases. This can be a result of strong floods when the inorganic matter from the banks and bottom of the river gets mixed into the water.

5 Discussions and conclusions

As it was expected, the material concentration of the river water increases when discharge increases. All the results of optical and biogeochemical measurements showed an increase of the matter in water during higher discharge volumes.

Reflectance measurements had reliable results and high correlation with other parameters. The WISP-3 instrument turned out to be a useful tool in water quality monitoring due to the on-site accessibility.

A lot of problems turned out during the iron analysis, which led to excluding of a series of samples. The sensitivity of the method did not reach the highest concentrations, although the samples were diluted. Because of this, the highest concentrations in the plot can have a significant error and thus are not the most reliable results. In order to improve the reliability, the samples should have been diluted in a relation of 1/3 instead of 1/2.

Sources

1. Vantaanjoki pähkinänkuoressa [Internet] 2014 [cited 2014 May 23] Available from: www.vantaanjoki.com

2. "Vanhankaupungginkoski" 60.216995 N, 24.980364 E. Google Maps. Retrieved on 26.5.2014

3. Discharge data [Internet] 2014 [cited 2014 June 12]] Available from: http://www.ymparisto.fi/fi-FI/Kartat_ja_tilastot/Hydrologiset_havainnot

4. Water Insight B.V. WISP-3 User Guide [booklet]. Wageningen(NL): Water Insight B.V; 2013.

5. PerkinElmer. Applications and Use of Integrating Spheres With the LAMBDA 650 and 850 UV/Vis and LAMBDA 950 UV/Vis/NIR Spectrophotometers [booklet]. Shelton CT(USA): PerkinElmer; 2004.

6. Spectralon Targets [Internet] 2014 [cited 2014 May 26] Available from: http://www.labsphere.com/products/reflectance-standards-and-targets/reflectance-targets/spectralon-targets.aspx

7. ECO BB. [Internet] 2014 [cited 2014 May 26] Available from: http://www.wetlabs.com/eco-bb

8. Image courtesy of Giorgio Dall'Olmo. E-mail from S. Simis, PhD (Stefan.simis@ymparisto.fi) to Atte Holm (atte_h@hotmail.com) 2014 July 16 [cited 2014 July 21]

9. Fluorescence image. [image on the Internet] 2014 [cited 2014 May 23] Available from: http://www.piercenet.com/method/fluorescent-probes

Environmental conditions during sampling

Date	Time	Sky	Visibility	Temp
	Local			°C
10.3.2014	9:07	clear	hazy	-0,3
12.3.2014	11:08	partly overcast	clear	0,8
14.3.2014	11:28	clear	clear	1,2
17.3.2014	12:08	partly overcast	hazy	0,5
19.3.2014	11:35	partly overcast	clear	0
21.3.2014	12:26	partly overcast	foggy	0,8
24.3.2014	12:15	partly overcast	hazy	1,2
26.3.2014	12:20	partly overcast	clear	2,4
28.3.2014	12:13	partly overcast	clear	2,9
31.3.2014	12:10	partly overcast	clear	3,8
2.4.2014	12:15	fully overcast	foggy	3,1
4.4.2014	12:20	partly overcast	clear	3,4
9.4.2014	12:30	partly overcast	clear	4,7
11.4.2014	13:14	fully overcast	foggy	4,2
14.4.2014	12:25	fully overcast	foggy	6,2
16.4.2014	13:04	clear	clear	7,1
23.4.2014	12:27	clear	clear	9,6
25.4.2014	12:08	clear	clear	10,1
28.4.2014	12:48	clear	hazy	11,5
30.4.2014	12:09	partly overcast	clear	11,9
2.5.2014	13:26	fully overcast	foggy	10,9
5.5.2014	12:53	fully overcast	foggy	8,9
7.5.2014	12:47	partly overcast	hazy	8,9
9.5.2014	13:08	fully overcast	foggy	9,6
12.5.2014	11:54	fully overcast	foggy	10,2
14.5.2014	11:23	partly overcast	clear	11,1
16.5.2014	11:02	fully overcast	hazy	11,5

Back scattering and fluorescence results

Date	Back scattering			Fluorescence	
	Average			Average	
	470 nm	532 nm	715 nm	Peak A	Peak B
10.3.2014	509	864,34	1637,5	#N/A	#N/A
12.3.2014	576,07	960,91	1768,24	251,68746	315,4328
14.3.2014	563,85	930,69	1695,54	238,24333	329,8843
17.3.2014	331,248	520,784	930,888	239,12835	332,1111
19.3.2014	272,464	408,768	729,672	244,25952	309,6981
21.3.2014	246,28	373,344	707,848	256,19299	333,6112
24.3.2014	336,416	528,424	986,432	227,10973	330,0787
26.3.2014	391,072	626,16	1136,536	240,2964	348,6087
28.3.2014	359,608	565,848	1002,8	242,02893	344,8644
31.3.2014	285,96	430,424	760,248	252,35666	335,3287
2.4.2014	245,04	367,944	642,808	238,29068	310,346
4.4.2014	223,624	324,608	566,496	231,88562	331,5553
9.4.2014	174,032	240,208	422,208	238,17936	352,7476
11.4.2014	181,72	256,616	462,624	223,69061	315,452
14.4.2014	190,808	269,2	481,728	209,67421	326,3957
16.4.2014	246,264	371,36	672,248	231,05732	311,639
23.4.2014	215,92	310,56	550,456	261,95383	337,144
25.4.2014	208,616	296,12	516,416	255,70808	355,7023
28.4.2014	187,624	251,736	446,8	258,38233	326,7005
30.4.2014	173,512	238,048	420,176	251,71081	329,6282
2.5.2014	159,232	223,048	387,472	238,62294	314,0621
5.5.2014	153,816	193,48	342,256	246,20587	353,5341
7.5.2014	154,208	203,28	350,344	241,51743	341,5196
9.5.2014	152,358	212,256	373,872	244,70991	348,2694
12.5.2014	405,306	651,054	1232,73	273,7836	287,9662
14.5.2014	300,348	478,83	879,648	281,94789	328,0152
16.5.2014	305,208	497,868	867,768	296,17263	334,8154

Light absorption in solution (untreated samples) results

Date	Light absorption in solution			
	Untreated sample			
	350 nm	412 nm	532 nm	850 nm
10.3.2014	#N/A	#N/A	#N/A	#N/A
12.3.2014	#N/A	#N/A	#N/A	#N/A
14.3.2014	61,1044	24,4224	6,46819	1,59086
17.3.2014	48,0432	18,7635	4,91533	0,94107
19.3.2014	43,3855	16,1697	3,58259	0,27792
21.3.2014	41,7714	15,8904	3,89252	0,64518
24.3.2014	42,5619	16,6392	4,20015	0,61065
26.3.2014	48,2845	18,6565	4,55037	0,71357
28.3.2014	46,5965	17,8335	4,40738	0,79969
31.3.2014	41,444	15,6194	3,49417	0,26411
2.4.2014	37,9956	14,0817	2,9153	-0,3884
4.4.2014	36,0737	13,5286	3,11217	0,5966
9.4.2014	32,3248	12,0787	2,67791	0,12112
11.4.2014	32,0462	11,8657	2,46561	-0,1319
14.4.2014	32,4964	12,3796	3,16168	0,37187
16.4.2014	36,8292	13,7593	3,02399	-0,1319
23.4.2014	40,4048	15,2754	3,51996	0,12941
25.4.2014	38,8978	14,3216	2,7433	-0,6862
28.4.2014	38,5874	14,8245	3,6192	0,35805
30.4.2014	37,4633	13,9877	2,91761	-0,3958
2.5.2014	36,4129	13,8081	3,05023	-0,0297
5.5.2014	34,2137	13,2083	3,22661	0,42598
7.5.2014	33,3564	12,5567	2,61896	-0,1842
9.5.2014	33,6691	12,9023	3,09214	0,24684
12.5.2014	54,6875	21,2968	5,17874	0,6666
14.5.2014	50,5894	19,3763	4,30791	0,10339
16.5.2014	52,574	20,0062	4,23906	-0,3728

Light absorption in solution (filtrate) results

Date	Light absorption in solution			
	Filtrate			
	350 nm	412 nm	532 nm	850 nm
10.3.2014	#N/A	#N/A	#N/A	#N/A
12.3.2014	#N/A	#N/A	#N/A	#N/A
14.3.2014	33,6481	15,3714	7,64136	6,0132
17.3.2014	30,3902	10,6069	2,13749	-0,0366
19.3.2014	31,4512	10,9944	2,12506	0,07967
21.3.2014	29,941	10,538	2,16029	0,09832
24.3.2014	27,2064	9,31327	1,81237	-0,2056
26.3.2014	27,6499	9,63079	1,99634	0,30855
28.3.2014	28,1991	9,81914	1,94407	0,11628
31.3.2014	25,1378	8,27089	1,13702	-0,4656
2.4.2014	23,4311	7,97569	1,26596	-0,5485
4.4.2014	22,2672	7,63031	1,283	0,09878
9.4.2014	22,3397	7,77491	1,47757	-0,0808
11.4.2014	20,7491	7,14423	1,05458	-0,5119
14.4.2014	20,8518	7,30679	1,44648	-0,1246
16.4.2014	21,5531	7,38071	1,31639	-0,1264
23.4.2014	26,7731	9,31994	1,66316	-0,4789
25.4.2014	26,3757	9,23636	1,55309	-0,6086
28.4.2014	28,3032	9,99852	1,99496	0,00046
30.4.2014	26,897	9,49103	1,74122	-0,242
2.5.2014	26,2433	9,40951	1,84829	0,035
5.5.2014	24,2858	8,62295	1,75526	0,02625
7.5.2014	24,4811	8,68512	1,54849	-0,1448
9.5.2014	24,3372	8,55963	1,71289	0,10224
12.5.2014	27,978	9,15047	1,18031	-0,872
14.5.2014	27,2433	9,27297	1,3979	-0,5436
16.5.2014	32,3198	11,0255	1,57888	-0,8446

Light absorption of particles (untreated) results

Date	Light absorption of particles			
	Untreated			
	350 nm	412 nm	532 nm	850 nm
10.3.2014	#N/A	#N/A	#N/A	#N/A
12.3.2014	#N/A	#N/A	#N/A	#N/A
14.3.2014	20,6388	9,65554	3,21943	0,7151
17.3.2014	9,62907	4,74266	1,52511	0,32704
19.3.2014	8,42253	3,88931	1,31236	0,31467
21.3.2014	5,79157	2,85916	1,05378	0,26968
24.3.2014	11,4867	5,50585	1,83179	0,21075
26.3.2014	14,1922	6,95567	2,27063	0,61187
28.3.2014	7,62314	3,66462	1,22931	0,35428
31.3.2014	7,72362	3,67261	1,21056	0,31043
2.4.2014	5,84226	2,77789	0,91653	0,27836
4.4.2014	5,69277	2,66945	0,85069	0,25033
9.4.2014	5,70682	2,81723	1,03998	0,31769
11.4.2014	5,51177	2,62355	0,85857	0,27965
14.4.2014	5,03334	2,5655	0,89455	0,32785
16.4.2014	5,23944	2,52328	0,80688	0,23869
23.4.2014	5,26145	2,61235	0,89003	0,31511
25.4.2014	7,07444	3,55599	1,18362	0,29245
28.4.2014	3,8844	1,91324	0,60831	0,20742
30.4.2014	4,14819	2,1266	0,6649	0,17071
2.5.2014	#N/A	#N/A	#N/A	#N/A
5.5.2014	3,73925	2,01375	0,71456	0,17545
7.5.2014	3,92612	2,04976	0,68286	0,19877
9.5.2014	4,59924	2,50334	0,90236	0,28189
12.5.2014	12,6392	6,17628	2,11382	0,63324
14.5.2014	9,92559	4,88079	1,67532	0,48673
16.5.2014	6,75183	3,43869	1,16664	0,25441

Light absorption of particles (bleached) results

Date	Light absorption of particles			
	Bleached			
	350 nm	412 nm	532 nm	850 nm
10.3.2014	#N/A	#N/A	#N/A	#N/A
12.3.2014	#N/A	#N/A	#N/A	#N/A
14.3.2014	8,55038	3,57013	1,10184	-0,144
17.3.2014	3,81758	1,73791	0,5163	-0,0286
19.3.2014	3,32743	1,40535	0,54462	0,08788
21.3.2014	3,23798	1,56359	0,60102	0,11915
24.3.2014	7,89225	3,68101	1,25935	0,08911
26.3.2014	6,0045	2,83307	0,95182	0,28485
28.3.2014	4,92458	2,30912	0,7996	0,32802
31.3.2014	4,25443	2,0345	0,72818	0,2212
2.4.2014	3,71768	1,51409	0,47136	0,12189
4.4.2014	3,52892	1,5627	0,45075	0,10006
9.4.2014	3,51724	1,67379	0,61877	0,2024
11.4.2014	3,46228	1,45267	0,44271	0,17019
14.4.2014	2,7293	1,34176	0,44101	0,11637
16.4.2014	2,66772	1,15887	0,27713	-0,0165
23.4.2014	2,70705	1,23645	0,39059	0,16577
25.4.2014	3,06253	1,32246	0,37731	0,07126
28.4.2014	1,88606	0,80239	0,20015	0,01841
30.4.2014	2,17889	1,01936	0,34686	0,09906
2.5.2014	#N/A	#N/A	#N/A	#N/A
5.5.2014	1,87932	0,93881	0,31755	0,08578
7.5.2014	2,03146	0,951	0,27937	0,05567
9.5.2014	2,39136	1,16445	0,3979	0,1404
12.5.2014	6,27658	2,89296	0,84396	0,13581
14.5.2014	5,29573	2,4222	0,77815	0,25069
16.5.2014	3,82718	1,71245	0,49884	0,0875

Iron and Reflectance results

Date	Iron		Reflectance
	Filtered	Unfiltered	Peak
			690 nm
	µg/l	µg/l	
10.3.2014	3221,33	3963,33	#N/A
12.3.2014	3593,33	#N/A	#N/A
14.3.2014	3374,33	#N/A	0,18141
17.3.2014	2378	3993,33	0,13674
19.3.2014	2174,33	#N/A	0,12417
21.3.2014	#N/A	4024,67	0,09191
24.3.2014	1624	1828,67	0,1516
26.3.2014	2144,33	2165,33	0,12373
28.3.2014	2840	4034,33	0,14475
31.3.2014	3015,67	#N/A	0,12565
2.4.2014	2222,67	#N/A	0,10759
4.4.2014	1866	3675,33	0,10279
9.4.2014	1577,33	2104	0,08007
11.4.2014	1074,67	2324	0,07919
14.4.2014	1160,67	2334	0,0765
16.4.2014	1255	2530,67	0,10318
23.4.2014	1754,33	#N/A	0,08148
25.4.2014	1562	2250,33	0,08263
28.4.2014	1358,67	2443,33	0,07239
30.4.2014	1287	2314	0,06627
2.5.2014	1121,33	2169,33	0,06221
5.5.2014	966	#N/A	0,06266
7.5.2014	1081,33	2104	0,06026
9.5.2014	1138	2151,33	0,07035
12.5.2014	2672,67	2952,33	0,15682
14.5.2014	2342	3857,33	0,11215
16.5.2014	2971	2235,33	0,10927