Master Project TVVR 10/5015

Dynamics of Humic Substance in Bolmen

Lake, Sweden



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Lund 2010 Muluneh Ertiro Tumdedo

Abstract

Humic substance (HS) in natural water is a complex compound, and causes problems in the production and distribution of drinking water. In addition to the adverse effect of HS on the aesthetic of water quality, it also causes a health problem. The objective of this thesis was to analyse the dynamics of HS in Bolmen lake. Bolmen lake is the tenth largest lake in Sweden. The lake is situated in the south-western Sweden and used as a drinking water source for the majority of South Sweden (Skåne). In this thesis the long term and short term variation of HS, measured as the water colour, of the lake was analysed. HS in the soil is formed from the microbial degradation of plants and animal matter in the soil, which is affected by the air temperature. HS from the catchment is transported by the runoff. The impact of air temperature on the formation and discharge on the export of HS from the catchment to the lake can be shown by their relation with the water colour correlation. Excel 2007 was used to show the correlation of water colour with air temperature, precipitation and discharge. Storån is the largest tributary river, drains about 40% of the Bolmen catchment. Therefore, the water colour dynamic of Storån river was analysed to show the dynamic of Bolme's water colour dynamics. The 2007 mean annual colour value shows that Storån river contributes the largest portion of water colour to the lake, about 87% with Lillan river. The long term variation shows that there are two ten years; one with smaller annual mean colour value (1988-1997) and the other with higher annual mean colour value (1998-2007). Yearly peak value of water colour mainly occurs in summer and autumn, and the yearly minimum value occurs mainly in winter and spring. The correlation between flow rate and colour value also depends in the season of a year. The correlation was stronger and positive in summer and winter; and it was very weak in the rest of a year. The correlation of water colour with air temperature as well as with precipitation was very weak. The climate change in Sweden is predicted to have increased runoff. Since the discharge has a positive correlation with water colour value, the climate change could have the increasing impact on the water colour of Bolmen lake.

Key Words: Humic Substance, Water Colour, Dissolved Organic Matter, Discharge, Temperature, Precipitation, Bolmen Lake, Storån River.

Acknowledgement

First and foremost I would like to thank God, for the strength that keep me standing and for the grace that gave me enthusiasm to start and finish my study.

I owe my deepest gratitude to Lund University, Department of Water Resources Engineering for allowing me to take part in the International Master Program of Water Resources. I am grateful to my supervisor, Professor Persson, Kenneth M, for his encouragement, guidance and support throughout my thesis work. I would also like to thank the SYDVATTEN AB Company, for the data and keen assistance they gave me. Here I specially would like to thank Britt-Marie Pott, for the data collection from different companies for this work. I would also like to thank all my teachers since my childhood.

Thanks to God, I have lots of exciting friends whom I met in my walk of life. Letters and words limit me to list your names. You all are great. I learnt a lot from you. Those of you I met in Sweden, thank you for those beautiful days we spent together and for the cultures and views we shared. For those in which our friendship extends to Europe, thank you. Our chats and discussions made my stay in Europe very easy. Friends back home, thank you were my courage to go forward. I would like to thank Berekete G., for being such a good friend since childhood. I would also like to thank Yihun Dile and Tseganeh G, for all the constrictive and helpful ideas you shared me on my thesis work.

My deepest gratitude goes to my family for their tireless love and support throughout my life; this thesis work is simply impossible without them. My Father ,Ertiro Tumdedo, thank you for showing me the joy of intellectual pursuit ever since I was a child. My Mother, Amelework Hadero, is the one who sincerely raised me with her caring and gently love. Habtamu, Demeke, Tigist, Mulatu and Tareru, thanks for being supportive and caring siblings.

The last but not the least I would also like to thank all the Lund Ethio-Eritrean fellowship members, for all the fellowship we shared together.

Acronyms

DOC: Dissolved organic carbon DOM- Dissolved Organic Matter FA: Falvic acid HA: Humic Acid HS: Humic Substance HU: Humin POC: Particulate Organic Carbon POM: Particulate Organic Matter SMHI: Swedish Meteorological and Hydrological Institute TOC: Total organic carbon

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1 Introduction

1.1 Background

Organic compounds are found in all natural water bodies including; Oceans, Lakes, Rivers, Bogs and they have the central part in aquatic chemistry. In the boreal region water body due to the cold and wet climate the concentration of natural organic matter is very high (Vogt et al, 2001). The natural water contains considerable amount of dissolved organic matter (DOM), which is considered as the major impurity in drinking water source. In surface water treatment the major processes are designed to reduce the problem such as: disinfectant demand, disinfection by-product formation, and coagulant demand, caused by the presence of natural organic matter (Drewes and Summers, 2006)

The complex organic substance that results yellow to brown colour of bogs or swamps as well as to a lesser extent to some lakes and rivers is called humic substance (HS), and its presence in raw water creates always a problem on water treatment and distribution systems. HS is formed from the decay of bio-matter, and it is the fraction of DOM which has high resistance to further microbial degradation. (Akkanen, 2002).

HS is highly reactive chemical; it can adsorb heavy metals and other organic compounds, which can cause high concentration of metals in the natural water system. During water treatment they also affect the formation of disinfection by-products. (IHSS, 2007). In boreal region's surface water up to 90% of DOM is considered to be HS, while globally HS in average accounts only 50% of the total DOM (Akkanen, 2002). In boreal water region the dynamics of DOC concentration seasonally and regionally is large (Köhler, et al 2008). The most important factors that affect the HS concentration in natural water sources are precipitation, temperature, land use of the catchment and the type and size of natural water. Therefore, the understanding of HS dynamics in drinking water industry can provide important information for the design and operation of water treatment systems.

1.2 The Problem of HS in Drinking Water

Raw water, which contains undesirable chemicals, turbidity and biological contaminates must be purified before distributing to the community. The type and extent of drinking water treatment depends on the quality of raw water, economy and available technologies. For example in USA most of ground water sources are pure enough to drink without applying any treatment, while others sources need additional treatment. Since surface water systems are open to direct runoff and to the atmosphere, to fit the Federal and state regulation requirements the surface water should be treated. (EPA, 1999). The major problems associated with the presence of HS in raw water are described below.

1.2.1 Disinfection by-products

The concept of conventional surface water treatment system is important to understand the formation of disinfection by-products. The major process of conventional water treatment processes are explained below.

Coagulation: during this step aluminium or iron salts, which have positive charges, are added to the raw water. Due to the attraction between the positive charges of the coagulants and negatively charged suspended particles, the suspended particles bind and form bigger particles or flocs.

Sedimentation: Next to coagulation the water is led to the large sedimentation tank, where flocs are settled out at the bottom of sedimentation tank. Coagulation and sedimentation can remove large amount of DOM, suspended particles and some pathogens. While sedimentation and coagulation removes considerable amounts of DOM and suspended particles still some pathogens and suspended materials may remain in the water.

Filtration: it is a process, forcing the water to pass through the porous media and the suspended particles are retained. The filter can pass some contaminates.

Disinfection: The final step in conventional drinking water production from surface water, before distribution, is disinfection. Bacteria, Cholera, Giardia and other microorganisms are among the most known pathogens that are present in surface water. In conventional water treatment to kill the pathogens chlorine is added.

However, chlorination of drinking water is successfully used to inactivate pathogens, it produces canceroginic by-product. In water treatment it has been the bigger challenge to remove HSs from the source water, which lefts large part of population behind the carcinogenic chemicals. The reaction between chlorine and organic matter in water produces different kinds of disinfection by-products (DBPs) such as trihalomethanes, haloketones, haloacetonitriles, haloacetic acids and other chlorinated compounds. DBPs are known to be the cause of cancer or birth defect. (Schäfer, 2001). In water treatment the chlorine consumption and DBPs formation are affected by DOM in the source water (Yee et.al, 2008).

1.2.2 Bacterial Re-growth

As stated in the above section, in conventional drinking water treatment it has been hard to remove all HS from the source water. The deactivated microbes, during disinfection process, can re-grow if they can get favourable conditions. The presence of bio-available nutrients in drinking water distribution system favours the re-growth of bacteria. The fraction of HS, which is not removed during water treatment, can be used as a source of food for bacteria and fungi re-growth in the water distribution system. The presence of excess microorganisms in distribution system causes additional problems such as diseases, unpleasant test and odour. Therefore understanding the dynamics and the factors controlling the formation and transport of HS is very important to manage the water treatment systems, especially when surface water is used as a source.

1.3 Objective

The general objective of this thesis is to analyse the patterns of spatial and temporal variation of HS concentration, measured as water colour, in Bolmen Lake. The main objectives of the thesis are:

- To analyse the pattern of long term and short term variation of water colour in Bolmen Lake.
- To show the impacts of discharge, precipitation and temperature on the water colour of Bolmen Lake.

1.4 Methodology

The concentration of aquatic HS can be measured in many different techniques (see section 3.7). One of the most commonly used techniques of aquatic HS measurement is to measure the water colour (e.g. Löfgren et al., 2003). Because of two reasons the word aquatic HS concentration (measured as water colour mg pt/l) can be used interchangeably with dissolved

organic matter/carbon. The first reason is that in boreal region about 90% of DOM is considered to be HS (Akkanen, 2002). The second reason is aquatic HS and DOC share similar property, including transportation and formation.

To study the dynamics of HS in Bolmen lake the discharge, precipitation and temperature data are used. The temperature and precipitation data are collected from official website of Swedish Meteorological and Hydrological Institute (SMHI). Two sources of discharge data were used for different purposes. One of the discharge data is obtained from SMHI, which is the result of S-HYPE rainfall runoff model. The data obtained from SMHI is the monthly discharge to all sub-basins of Bolmen lake from 1995-2009. The second discharge data is obtained from Ekologgruppen company, which contains the weekly discharge value for the rivers of only Storån and Lillån from 1997 to 2007. The water colour data is collected from Medins-Biologi and SYDVATTEN AB Companies. The colour data collected from Medins-Biologi is measured in different time intervals for Storån and Lillån rivers: once a month for Storån river from 1987 to 2007 and once in two months for Lillån river from 1987 to 2007. The colour data collected from SYDVATTEN contains the 2007 colour data, measured: once a month for Storån and once in two months for Lillån, Unnen, Murån riveres and Skeen. Even if there are other smaller rivers, the major tributaries of Bolmen Lake are Storån, Lillån, Unnen and Murån. To see the relative importance of each tributaries of Bolmen lake in terms of water colour contribution to the lake; the long term colour flux of the inflow rivers should be compared. The colour flux is the product of colour intensity (mg pt/l) and flow rate (m^3/sec) . To show the attenuation impact of the lake that is if the lake has increasing or decreasing impact on the water colour the mass balance of water colour should be done. Since the turnover time of the lake is 2.8 years, to perform the mass balance we need at least 3 years data of colour value both for the inflow rivers and for the outflow river. Unfortunately, the colour data for the inflow rivers Murån and Unnen, and for the out flow river Skeen was available only for the year 2007. Therefore the result obtained is only indicative. To compare the colour contribution of each tributary, the yearly colour flux of each tributary is done using the 2007 water colour data, from SYDVATTAN, and flow rate, from SMHL

The impact of discharge, precipitation and air temperature on the colour intensity of the lake can be shown by their relation with the colour intensity of the lake. Simple linear regression analysis was used to show the correlation of discharge, precipitation and temperature with colour intensity.

1.5 Limitation

The shortage of data was the major problem of this thesis. To study the dynamics of water colour, the long term series of colour value for all tributaries of the lake with high frequency of measurement is required. But the long term data was available only to one river, Storån river, and which was measured sparsely (once a month). The second limitation was the language problem. Most of the available materials including the websites and some important documents were in Swedish, which needed extra time for translation.

1.6 Hypothesis

The concentration of HS varies depending on the land use of the catchment, size and type of the water body, climate and hydrology of the area. For example the DOC concentration in sea water is bellow 0.5 mg/l and in swamps it goes up to 60 mg/l. The boreal region lakes usually contain the highest DOC concentration. The boreal zone lakes receive the highest mass of DOC from the terrestrial sources (Kortelainen, 1999 cited in Tulonen, 2004). Hydrology of a catchment especially runoff plays the major roll on the leaching of HS from the terrestrial source to the lakes. The decomposition rate of organic material on the top layer of the soil by microbes is controlled by temperature. The increase in temperature increases the decomposition rate of soil organic matter (Lützow and Knabner, 2009). The production of DOC in the soil layer, mainly controlled by the hydrological processes (McDowell & Likens, 1988 cited in Clark et al, 2005).

Therefore, it was hypothesized that there would be a strong correlation between the river flow & the natural water colour; and also between the temperature and water colour. It was also assumed that the past flood could affect the present water colour.

2 Description of the Water Shade and its

Management

2.1 Sydvatten AB Company

This research idea was proposed by Sydvatten AB company. Sydvatten is one of the largest drinking water producers company in Sweden, which is a municipal-owned company. The company produces and distributes drinking water about for 750,000 inhabitants in Skåne. The company is managed by the board members, which came from each joint-owner municipalities. The member municipalities and portion of the total water production consumed by each municipality before January, 2010 are: Bjuv (1.91%) , Burlöv (2.11%), Eslöv (4.11%), Helsingborg (16.61%), Höganäs (3.18), Kävlinge (3.53%), Landskrona (5.35%), Lomma (2,53%), Lund (13,97%), Malmö (36.94%), Staffanstorp (2.8%), Svalöv (1.77%), Vellinge (4.33%).

2.2 Water Sources

Sydvatten Company uses three sources to supply drinking water to 14 manicipalites in Skåne. Mainly the company takes raw water from Bolmen lake, located in Småland and Vomb lake , located in southern Sweden. When there is a problem in Bolmen lake and/or Vomb lake the company uses Ring lake as a reserve source, which is situated in Skåne. Sydvatten has a right to withdraw 6000 l/s from Bolmen Lake and 1500 l/s from Vomb lake. But the company draws off far below the allowed quantity of water. Currently the company takes about 1100 l/s from Bolmen lake and 1000 l/s from Vomb lake. The company still has plenty water sources to serve other municipalities of Skåne. Sydvatten owns and manages the 82km long Bolmen tunnel, which is used to convey raw water from the intake of Bolmen Lake to near Perstorp. From the end of the tunnel the water is pumped through 25 km long main to Ringsjöverket and Vombverket treatment plants, and each of them are equipped with emergency power facilities.

2.3 Bolmen Lake

Bolmen is the largest lake in southern Sweden, and the tenth largest lake in Sweden with the area of 184 km^2 . Bolmen basin, with the area of 1640 km^2 , is the largest sub basin of Lagan

watershed, which covers about 6454 km². The lake is elongated in a north–south direction, about 30 km and in east west direction about 10 km wide. The lake is situated in south-western Sweden within three counties, Kronoberg, Jönköping and Halland. From the total Bolmen Lake basin about 48% comprises forest, 22% marsh, 20 % lake and about 9% is cultivated land. The three major tributaries of the lake are Storån river, Lillån river and Unnen Lake. In addition there are a number of other small streams such as: dannäsån, mjösjöbäcken, harasjöbäcke, Murån. The HS concentration or water colour is measured only at the entrance of the lake from the streams Storån, Lillån, Morån and Unnen. The presence of large island in the middle of the lake divides the lake into northern, southern, eastern and western (figure 1). The southern part covers the largest portion of the lake area with the maximum depth of 37 m and average depth of 8m. The maximum depth of the northern part is only 13 m and the average depth is 5-6m. The northern part usually stratified in summer with thermocline between 10-20 meters depth. The retention time of the lake is about 2.8 year.



Figure 1: Bolmen Lake and its main tributaries

2.4 Main Tributaries of Bolmen Lake

2.4.1 Storån River

Storån River is the largest tributary of Bolmen lake's watershed and drains about 40% of the basin. Storån river catchment is situated in the top north-western part of lake. The land use of the catchment is dominated by forest, which shares 64%. Small lakes cover about 4% and the rest of catchment is covered by cultivated land, open land and marsh lands. The cultivate land is mainly situated along the river side of the lower reaches (figure 2). Industrial and municipal treated waste water from Forsheda, Bredaryd, Lanna and Hillerstorp is discharged to Srorån river.

2.4.2 Lillån River

Lillån river is the most intensively cultivated sub-basin of Bolmen lake basin and drains about 10% of the basin. About 51% of the total Lillån river basin is covered by forest; 5% is covered by smaller lakes and the rest is covered by marsh, cultivated and open land. The lower reach of the river is covered by intensively cultivated land use.

2.4.3 Unnen Lake

Unnen drains about 12 % of Bolmen lake basin and which covers about 204 km2. The land use of Unnen is also dominated by the forest (about 62%), 14 % is lakes and the rest is covered by bogs. Municipal treated wastewater from Ldhult and Unnaryd is released to Unnen Lake.



Figure 2: Sturån and Lillån rivers land use (Google earth, 2009)

3 Characteristics and Classification of Humic

Substance

3.1 Dissolved Organic Matter and Particulate Organic Matter

The two broaden classes of organic matter in aquatic environment are Particulate organic matter (POM) and dissolved organic matter (DOM). The common technique used to differentiate the two classes is to use a 0.45 micrometer silver-filter to pass the smaller sized organic matter through the filter and to retain the larger size on the filter. The organic matter which passes through the filter is called DOM, usually measured as dissolved organic carbon (DOC), and the retaining fraction is called POM, usually measured as particulate organic carbon (POC). (Mcknight, 1997). Figure 3 shows the average concentration of DOC and POC for different types of water sources. As shown in the figure there is big variation of DOC concentration for different kinds of water sources. In general, the minimum DOC concentration (0.5 mg/l) are found in ground water & sea water and the maximum DOC concentration (10-60 mg/l) are found in coloured water from swamps, marshes and bogs. In rivers and lakes the concentration varies from 2 to 10 mg/l (Thurman, 1985). Similar to DOC the concentration of POC varies from one water source to the other. In ground water the POC concentration is zero. The majority of POC in lakes caused from algal matter and which ranges from 0.1 to 1 mg/l. The range of POC in sea water is from 0.01 to 0.1 mg/l which is also caused by algal matter. (Thurman, 1985). In aquatic ecosystem POC consists both living biota, such as bacteria phytoplankton and protozoa, and non living materials which includes dead organisms and detritus. The fraction of living biota and non living materials vary depending on the season of the year, size and type of the water body (Tulonen,2004)



Figure 3: Approximate concentrations of DOC & POC in natural waters (Thurman, 1985)

3.2 Humic Substance

HS is a heterogeneous mixture formed from the decay of plant and microbial remains through the process called humification (IHSS, 2008). Even if they share similar properties in common, HS in soil is different from aquatic HS by chemical and structural compositions. (Frycklund 1998). Aquatic humic substance is the largest fraction of natural organic matter in water, which constitutes 40 to 60 % of dissolved organic carbon. And sometimes they are called: Crenic and apocrenic acid, Fulvic acid, Yellow organic acids, gelbstoff and aquatic humus (Thurman, 1985). Elementally the composition of HS is approximately 43-56% carbon, 34-45% oxygen, 3-6% hydrogen, 1-4% nitrogen and less than 1% sulphur (Frycklund , 1998). Functional groups are responsible for chemical binding, UV absorption, charge, hydrophobic interations and other characteristics of HS. The main functional groups in HS are phenolic hydroxyl, carboxylic acids, hydroxyls and carbonyl (Thurman, 1985) Depending on the solubility HS are subdivided into three subclasses.

- > Fulvic acid (FA): This fraction is soluble in aqueous solutions for all range of pH value.
- Humic acid (HA): This fraction is soluble only in the aqueous solution of pH above 2.
- > Humin (HU): It is insoluble in any pH value of aqueous solution.

Since the HU fraction is insoluble at any pH value, the aquatic HS contains only HA and FA. The aquatic HS can be precipitated by lowering the pH of the solution below 2.

3.3 Formation of Humic substances

The formation of HS is complex and only partly understood process. There have been several models suggested about the formation of HS. In all the theories of HS formations fungi and other microorganisms play the central role.

3.3.1 Humic Substance Formation in Soil.

Humic Substances in soil are formed from the microbial degradation of plants and animals remains in the soil. The major four models/pathways of the formation of HS in soil are described by Stevenson (1982). They are discussed below:-

Ligning-degradation model: This model is the oldest theory of the formation of HS. In this theory humic substances are derived from ligning. The theory propose easily degradable organic materials in the soil such as carbohydrates and proteins are totally decomposed and lost from the soil while refractory compounds such as lignings are partially decomposed by soil microbes and the residue forms humic substances (Gary & Stephen, 2005) . The decomposition includes the formation of carboxylic (COOH) groups from the oxidation of aliphatic side chane and loss of methoxyle (OCH3) groups. The first product of the decomposition results HU and further oxidation results HA and then FA (figure 4).



Figure 4: Humic substance formation with the ligning-degradation model (Stevenson, 1982)

Lignin-degradation & polymerization: This model also starts with ligning degradation. Ligning is decomposed by microbes in the soil to make Phenolic aldehydes and acids. Enzymes, which are synthesised by microbes, change the phenolic aldehydes and acids to quinines. Then quinines are polymerized to produce humic substances. The pathway is shown in figure 5.

Non-lignin-polyphenol-polymerization: In this theory microorganisms use other carbon sources (such as cellulose) instead of lignin. Cellulose is decomposed by microorganisms to produce polyphenols. Similar to the model 2, enzymes oxidize polyphenols to quenones, and then quenones are converted to humic substances through polymerization (figure 5).

Suger-amine condensation: This model suggests that the bi-product of microbial metabolism on cellulose and polypeptides produces sugar and amino acid. These simple sugar and amino acid are re-condensed to form humic substances.



Figure 5: Humic substance formation through polymerization theory (Stevenson, 1982)

3.3.2 Aqueous Humic Substance Formation

Aqueous HS can be derived from terrestrial sources (allochthonous) and/or from aquatic ecosystem (autochthonous). Similar with formation of HS in soil the decomposition of plants and animals by microorganisms is the biggest process that produces HS in aquatic environment. The rise of temperature in summer increases the microbiological activity, which facilitates the formation of humic substances. (Schäfer, 2001). HS formation in water is more complex than its formation in soil. Allochthonous humic substances are formed in the same theories that are discussed above. But Autochthonous humic substances have different ways of formation. In addition to the 4 theories of HS formation in soil. Thurman (1985) has described the following 6 composite hypothesis of HS formation in water.

Composite Hypothesis as listed on Thurman (1985)

- 1. leaching of plant organic matter directly into the water
- 2. leaching of plant organic matter through the soil profile with subsequent alteration both chemical and biochemical within the soil,
- 3. leaching of soil fulvic and humic acid into water
- 4. Lysis of algal remains and bacterial action on phytoplankton
- 5. Ultraviolet oxidation of surface-active organic matter in the microlayer of streams, lakes, and seawater, which is followed by polymerization reaction
- 6. Polymerization reactions among phenolic, amine, and aldehyde functional groups from biological products in natural waters. Natural waters that are concentrated in DOC are most likely sources for these reactions. They include dydtrophic and eutrophic lakes, soil waters, and interstitial waters of bottom sediment.

Humic substances can be produced in one or more of the above processes. One method is dominant over the other one depending on the season of the year and type of natural water. For example in streams and rivers allochthonous sources are more important than that of autochthonous sources. That is process (1-3) are the dominant process of HS production in streams and rivers (Thurman and Malcolm, 1983 cited in Thurman, 1985). But for lakes and oceans autochthonous sources are important sources of HS. In this case process 4 and 5 are the most important process for the production of humic substances. In fall season most plants shed off their leaves to prepare for the next winter season. In this season the fallen leaves increase the organic content of the top soil and the rain easily washes the top soil. In this season process 1 & 2 are dominant. In low flow or base flow, when the stream water comes through the ground, some organic substances are retained on the top soil layer. Except in ground waters and wetlands, in aquatic HS formation oxidative process is dominant over polymerization. In reduced condition, where the oxygen concentration is very low, the presence of larger organic matter concentration and phenolic group preservation favours the formation of humic substances through polymerization. Due to cold soil temperature in spring the bacterial decomposition of organic matter is low; the plant leaching increases the carbohydrate and peptide content of the soil, which enables the sugar-amino acid condensation process for HS formation. But for the rest of the year since the carbohydrate and polypeptide concentration in soil is small, sugar-amino acid condensation process for the formation of HS is low. (Thurman, 1985). As shown above HS can be formed through

different processes. But the most important thing on the formation of HS either in aquatic or soil environment is the decomposition of natural organics by microorganisms. In boreal regions, allochthonous sources are the major input of DOC to the lakes organic matter (Dillon and Molot, 1997 cited in Porcal et al, 2009)

3.4 Degradation of Humic Substance in a Lake

The concentration of DOM at the inlet and outlet of the natural water body is usually different. Due to the presence of autotrophic organisms DOC is added to the water ecosystem, while heterotrophic micro organisms consume DOC from the water ecosystem. Figure 6 shows the major controlling factors that affect the concentration of DOM in the lake ecosystem. The processes that increase the concentration DOC in the lake are: the production of DOC within the lake that is manufactured through photosynthesis, DOC import from the terrestrial catchments and water evaporation from the lake. And the major process that decrease the concentration of DOC are: microbial degradation, sedimentation and photomineralizations (which is the conversion of DOC to carbon dioxide or carbon monoxide by the presence of sunlight). Some of the main processes are described below.

Phytoplankton: In aquatic ecosystems the energy sources are either from the terrestrial, which is produced in the catchment and introduced to the aquatic system (Kaushik and Hynes 1971 cited in Young and Huryn, 1999), or from aquatic environment, which is produced within the water body (Minshall 1978 cited in Young and Huryn, 1999). Some plankton community utilize carbon dioxide, sunlight and minerals to produce food and they are called phytoplankton. Autotrophic organisms in the lake prepare their food through photosynthesis process. The availability of minerals, such as nitrate and phosphate, in the lake is the major factor that determines the photosynthesis process. In marine food chain phytoplankton are considered as the food factory of the system.

Microbial degradation: In water column there are some species of bacteria which cannot produce their own food, instead depend on the external source of food and they are called heterotrophic bacteria. These bacteria utilise DOM as the major source of carbon for the energy production. Microorganisms in water can utilize DOC for ATP production or for the production of a new biomass. (Madigan et al. 1997, cited in Tulonen, 2004). In humic lake, a lake with high DOC concentration and common in Boreal region, the bacterial respiration on

the DOC is greater than the organic matte production in the lake. That the heterotrophic bacteria of the lake use extra organic matter form the allochthonous source for their respiration (Salonen et al. 1992, del Giorgio & Peters 1994, Kankaala et al. 1996 cited in Tulonen, 2004).

UV-Radiation: The other process that causes the degradation of HS in natural water is the UV light. When the sun heats the water surface, the sun light is absorbed by DOM. As the DOM absorbs the sunlight the photon energy is changed to the heat energy. The absorbed UV light generates many reactive species of DOM (Canonica, 2009). The UV light makes DOM easily degraded by oxygen and other substances in water and which may cause the depletion of oxygen from the natural water body.



Figure 6: Schematic diagram of DOC production and degradation in the lake (Tulonen, 2004)

3.5 Factors Affecting the Formation of HS in the Catchment

The formation and transport of organic matter from the catchments to the streams are controlled by a number of factors. The climate of the catchment plays the major control both on the formation and transport of humic substances. Among the most important climatic factors are: Temperature, the increasing impact on the formation of organic substance (e.g. Freeman et al., 2001b; Evans et al., 2006 cited on Jennings et al, 2009); soil moisture, accelerates the decomposition process (e.g. Worrall et al., 2006 cited on Jennings et al, 2009); precipitation and snow melt (e.g. Hongve et al., 2004; Erlandsson et al., 2008 cited on Jennings et al, 2009); land use (e.g. Vogt et al, 2001). Some of the factors are explained below.

Temperature: many researchers agree that the production of DOC in the catchment is the result of microbial activity on the soil organic matter (McDowell and Likens, 1988; Guggenberger and Zech, 1993a cited in Christ and David, 1996). Therefore every factor that affects the microbial community in the soil layer has the impact on the production of DOC. Both the laboratory experiments and the field measurements revel that the rise in temperature increases the microbial activity of the soil (Anderson, 1973; Kirschbaum, 1995 cited in Christ and David, 1996). Even if temperature has the increasing effect on the decomposition of organic matter in the soil, due to some factors such as the presence of different microbial community, quantity and type of substrate affect the sensitivities of decomposition rate for temperature (Kirschbaum, 1995; Chapman and Thurlow, 1998; Davidson and Janssens, 2006 cited in Jennings, 2009). It is also stated that as the increase of decomposition rate with the rise of temperature occurs only before optimum temperature is reached. After the optimum temperature is attained the rise in temperature reduces the decomposition rate (Fenner et al., 2005, cited in Jennings et al, 2009).

Soil moisture: The moisture level of soil also affects the microbial activity and therefore, the decomposition rate of organic matter in the catchment (Sommers et al., 1981 cited in Christ and David, 1996). The lowering of water table in dry seasons allows the entrance of oxygen to the anaerobic soil layer, which converts the environment to aerobic (Jennings et al, 2009). The decomposition process in the aerobic condition is much faster than in the anaerobic condition (ENSO Bottles LLC, n.d.). In addition to affecting the decomposition rate, soil moisture also affects the transport rate of DOC from the catchment. In dry season the pH of soil drops down due to the oxidation of organic sulphur to sulphate. The acidification, caused by change of sulphur to sulphate, decreases the solubility of DOC; which lowers the concentration of DOC in streams (Clark et al., 2005 cited in Jennings et al, 2009). Due to different effect of reduced soil moisture on the formation and transportation of DOC, the exact contribution of low moisture content in water DOC concentration is not completely understood (Freeman et al., 2001b; Clark et al., 2005; Worrall et al., 2006 cited in Jennings et al., 2005).

al 2009).

Precipitation: DOC produced in the soil layer is washed out by the precipitation or snow melt, usually the high flow rate corresponds to the maximum DOC concentration (Andersson et al., 1991; Arvola et al., 2004; Worrall et al., 2002; Laudon et al., 2004 cited in Jennings et al 2009). The correlation between precipitation intensity and DOC concentration in the forest dominated catchment is strong. The existence of strong correlation between precipitation intensity and DOC from the upper part of the soil profile (Vogt et al, 2001).

Land use: Land use has significant impact on the production of DOC in the catchment. Usually discharges form peatland, shallow upland soil, and a land with higher land to water ratio, contain higher concentration of NOM (Vogt et al, 2001). In contrary low NOM concentration is associated with the land uses of little vegetation, poorly developed organic soil and a land cover with higher proportion of lakes (Vogt et al, 2001). The presence of drainage facilities also influence the formation of DOC. Drainage creates the aerobic environment by lowering the water table, which increases the aerobic decomposition process for organic matter (Kortelainen, 1999a; Holden et al. Cited in Jennings, 2009).

3.6 Humic Substance Variation and its Pathway

The concentration of DOC in streams, bogs and small water bodies vary wildly from time to time. For the larger water body the variation is smaller compared to the smaller water bodies. The major factor that affect the temporal variation of DOC in streams are runoff, soil wetness and temperature (Urban, 1989 cited in Köhler et al, 2008). The fallen leaves of plants in the top soil layer are degraded by soil microorganisms and enter into the lower soil layer. During the warm and wet season the soil microorganisms activity increases, which increases the decomposition of fresh organic matter into humic substances. The formation of HS in the top soil layer is affected by the soil temperature and soil moistures. The HS formed in the tope soil layer could be either directly carried to the stream by the overland flow (runoff) or it passes through the subsurface. The DOC that comes with the runoff usually contains fresh organic matter and the one that passes through the deeper soil layer contains degraded organic matter. The DOC that passes through the aquifer is subjected for strong sorption in the soil and due to this the base

flow water, the dry season flow, contains smaller fluxes of DOC compared with the surface overland flow. (Hornberger et al, 1994). Figure 7 shows the pathway of water movement from the catchments to the streams. The flow pathway has significant influence on the concentration and type of DOC.



Figure 7: Soil water flow mechanism a) Under low base flow condition, the water passes through the soil horizons b) under high flow condition, the water table is elevated and water table is elevated and water flows toward the stream though upper as well as lower

3.7 Measurement of Aquatic Humic Substances

The direct measurement of aquatic HS has been the most difficult task. The conventional HS concentration measurement requires the isolation of each fraction (HA and FA) from the water, which is tedious and time taking. The three common methods are explained below.

3.7.1 XAD Resin Adsorption Method

The aquatic HS contains only FA and HA fractions. As stated above HS can be precipitated from the aquatic solution by lowering the pH value below 2 and FA is soluble at all pH ranges. XAD resin adsorption method segregates the HA from the FA by lowering the pH of the solution. XAD resin method widely used technique to separate HA from FA. The method has been used in IHSS as standard method after a group of scientists chosen the method in 1981 (IHSS, 2008). The first step of fractionating DOM into hydrophobic and hydrophilic fraction is to pass the solution through XAD-8 resin, which preferentially adsorbs the hydrophobic fraction. Then the hydrophobic fraction is washed out from the XAD-8 resin with NaOH solution. And finally the humic acid is precipitated by lowering the pH of the solution. The complete procedure adopted by IHSS (2008) is listed below.

- 1. Filter water with a $0.45 \,\mu m$ silver or polymer membrane filter
- 2. Lower pH to 2.0 with HCl
- 3. Pass sample through column of XAD-8 resin to retain humic and FA. The preparative cleaning of the resin is described by Thurman and Malcolm (1981).
- 4. Elute HA and FA from the column with 0.1 M NaOH, in the reverse direction. Acidify immediately with HCl to avoid oxidation of humic substances.
- 5. Re-concentrate on a smaller XAD-8 column. Elute with NaOH and acidify. The eluted DOC should contain more that 500 mg C/L
- 6. Adjust pH to 1.0 with HCl. Centrifuge to separate the (HA) from the (FA) fraction. Wash HA with water until wash is negative to the AgNO₃ test for chloride. Add sufficient 0.1 M NaOH to dissolve HA and then acidify by passing through a strong acid resin column
- Adjust FA fraction to pH 2.0 with NaOH and re-adsorb FA fraction on XAD-8. Wash with one void volume of distilled water to remove the salt
- 8. Reverse flow and elute column with 0.1 M NaOH
- Immediately pass FA eluate through cation-exchange resin and hydrogen saturate. Pass HA in 0.1 M NaOH through cation-exchange resin and hydrogen saturate. Repeat until Na⁺ is less than 1 mg/L.

3.7.2 UV Absorbance

Using XDA-resin, to measure the HS concentration is time taking and tidies work. It also requires certain amount of sample; sometimes finding enough volume of sample, spatially when it is from soil and sediment, becomes a problem. Because of the presence of double bonds in aromatic rings hydrophobic fraction of DOC can absorb UV light. The study performed by Dilling and Kaiser (2002) showed that "the light absorption at

260 nm closely related to the amount of hydrophobic DOM in solution while up to 12 times higher concentrations of hydrophilic DOM had no effect on the UV absorption." This shows that UV absorbance can be used as the predictor of the amount of hydrophobic fraction of DOM. The same study shows that the linear relationship, with r2 value of 1, exists between hydrophobic fraction and the light absorbance at 260 nm. The colour and UV absorbance of HS depends on the source of the water. For example bogs and swamps have the biggest UV absorbance and they are the largest coloured water of any other water sources. Streams' and river's HS have the moderate colour per carbon, and the smallest colour per carbon is found in ground waters and eutrophic lakes. In general the colour of HA from any source is much greater than that of FA.

3.7.3 Water Colour (mg pt/l)

The other method used to measure the concentration of HS is measuring the water colour. The colour in water may be produced due to the presence of metallic ions such as iron and manganese, humus and peat materials, plankton, weeds, and industrial wastes (APHA, AWWA and WEF, 1999). In natural surface water the main reason of the water colour is caused by the presence of humic substances, which changes the water to yellow-brown colour. Before using the standard method to measure the water colour the turbidity must be removed. The standard method of measuring water colour is comparing the water colour with the platinum-cobalt standard solution. In this method the unit of the colour is measure by milligram of platinum per litter (mg pt/l) (APHA, AWWA and WEF, 1999).

4 Previous Researches Related to Humic Substance

Dynamics

The environmental and health problems caused by the humic substances in the natural water have drawn the attention of researchers. In drinking water treatment the health hazardous disinfection by-products, formed during chlorination of source water that contains HS, is becoming the centre of attention in many countries. In addition to the health risk the presence of HS in drinking water gives unpleasant test and colour; its presence also serves as the substrate for the microbial re-growth in the water distribution systems. The dynamics of the water colour also affects the transport of heavy metals and other organic materials.

So far the focus of researchers, regarding water colour, have been on the removal techniques of humic substances from drinking water and its health problems. Some of the researches performed on the Boreal HS and other related researches are discussed below.

- Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements (Köhler et al, 2008): This research was performed in Nyänget catchment; situated 60 km northwest of Umeå, Sweden; to show the temporal variation of TOC concentration & fluxes in relation to climate variation and to examine the effect of headwater mixing in two land uses. The research showed that in the forest catchments the concentration of TOC in wet years, where the precipitation (P) is above 350mm, is greater than that of in dry years, where P<350mm; while in the mire site the difference was insignificant. The research also showed that in the snow free season TOC concentration was linearly correlated with precipitation: for forest catchment in the wet years with $R^2 = 0.97$ and for mire catchment in the dry year with $R^2 = 0.83$; while the relation was non-linear in dry years for forest catchment and in wet season for mire catchment.
- Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colourado (Hornberger et al, 1994): The research was carried out in Snake River, Colourado, USA. The runoff and DOC concentration was successfully simulated using TOPMODEL. The dy result also shows that even if their does not exist simple correlation between flow and DOC concentration, the DOC peak in the snow melt period occurs before the runoff flow (in 14 to 33 days gap)

5 Result and Discussion

5.1 Tributaries Flow

The main sub catchments of the Bolmen Lake are Storån, Unnenån, Murån, and Lillån. The water colour in the Bolmen water shade is measured only at the entrance of the lake from the above catchments and just at the outlet of the lake called Skeen. SMHI has used the hydrological model called S HYPE (hydrological Predictions for the Environment set for Sweden) to simulate the runoff from the hydrological sub catchments of Bolmen Lake. According to the model result the yearly average discharge from each catchment vary significantly. From the total out flow of water only some fraction comes in through the measurement station (Storån550, Unnenån 208, Murån 212, and Lillån 540). From the annual average discharge at Skeen the maximum portion of water that passes through the measurement stations (Storån550, Unnenån 208, Murån 212, and Lillån 540) were about 88% in 2004 and the minimum portion was about 56% in 2005, the other values are shown in Table 1. The rest of the discharge could be from the other smaller catchments, direct precipitation on the lake and also from the base flow. Storån is the biggest catchment which contributes the largest fraction of the total out flow from the lake. According to the simulated yearly average flow result, from 1995 to 2009, about 31% in 2005 to 54% of the total out flow from the lake was come in through Storån river. From the tributaries the minimum discharge was measured in Murån river. The inflow to the lake form Murån river is below 2% of the total discharge of the lake. Table 1 shows the percentage of inflow to the lake from the main catchments compared with the total discharge of the lake at Skeen measuring station.

	Storån		Unnen		Storån+Lillån+Unnen+Muren
Year	(%)	Lillån (%)	(%)	Murån (%)	(%)
1995	36.7	9.7	12.8	1.4	60.6
1996	42.7	11.1	12.8	1.6	68.2
1997	41.9	11.2	13.9	1.7	68.7
1998	49.0	13.6	16.7	2.1	81.5
1999	40.5	11.7	13.7	1.6	67.6
2000	39.4	11.1	14.2	1.6	66.4
2001	39.3	11.0	14.0	1.6	65.9
2002	35.5	10.3	13.4	1.6	60.8
2003	38.8	10.4	11.4	1.4	61.9
2004	53.5	14.7	17.5	2.1	87.9
2005	30.8	9.9	13.6	1.5	55.8
2006	49.5	13.7	16.0	2.0	81.2
2007	38.3	11.2	15.1	1.8	66.3

Table 1: Mean annual inflow fraction (%) from the main rivers to the lake compared to the mean annual outflow from lake, measured at Skeen.

5.2 Catchment Contribution of Colour

From the rivers that flow to the lake, the water colour is measured only at four of them. The 2007 mean annual colour value was used to compare the colour contribution of rivers. The major factors that affect the water colour of rives are the climate, precipitation and land use. Even if different catchments are situated in the same climatic zone they respond differently for the water colour. Boges and Marshes are known for producing brown to tea coloured water and ground water contains the lowest water colour. From the four stations the biggest

colour value is obtained from Muråne river, Table 2. The 2007 mean water colour of Murån rivere, as measured at Murån 212 station, is about 363 mg pt/l. However, the colour value of Murån river is very large, due to its low flow rate the contribution of the colour to the lake is insignificant. The 2007 mean flow of Murån river to the lake is about $0.52 \text{m}^3/\text{s}$, which is only about 2.5% of the total inflow through the four measurement stations, Table 2. Murån catchment in 2007 contributes about 4.9% of the total colour flux that passes through the four stations. This shows that the colour contribution of Murån to the lakes is very small. According to the 2007 mean colour values, next to Murån, Lillån river is the most coloured water of the Bolmen tributary. The 2007 mean colour of Lillån river is about 280 mg pt/l, and its contribution is about 20% of the colour flux that pass through the four measurement stations. Ståren river, the biggest tributary of the lake, contributes the largest portion of the lake colour. Dispite of its low colour content, Storån river contributes the largest percentage of water colour to the lake. From the 2007 mean annual incoming colour flux to the lake, measured at four stations, about 66% comes in through Storån river. The water that comes from Unnen catchemetn contains the lowest colour content of all other tributaries. Because of its lowest content of water colour, from the total flux of colour in 2007 that pass through the measuring sations only about 10% comes from Unnen.

Table 2: The 2007 mean annual water colour intensity (mg pt/l) and the percentage fraction of the measured inflow colour value.

				colour
		2007		Contribution of
Sub-	Measureme	mean annual	2007 mean	Sub-catchment
catchment	nt station	colour(mg pt/l)	Flow(m3/s)	(%)
Storån	Storån 550	262	12.23	66
Lillån	Lillån 540	280	3.57	21
Murån	Murån 212	363	0.52	4
Unnen	Unnen 208	96	4.83	9

According to the measured value of water colour at four inlet stations and at the main outlet station, out flow water (skeen) has lower colour value than all inflow rivers. As shown in Figure 8, the 2007 mean water colour at the outlet of the lake is only 70 mg pt/l, while the water colour at the inlet of Murån is about 363 mg pt/l. The colour value at the inlet of biggest river, Storån, is about four times greater than the out flow colour value. The smaller colour value at the outlet could be, due to the microbial degradation of organic matter in lake is greater than the phytoplankton production of organic matter or the dilution of water colour in the lake due to either by direct precipitation on the lake or the inflow from other streams and base flow directly to the lake.



Figure 8: The 2007 mean annual colour value at inlets (Storån 550, Lillån 540, Murån 212 and Unnen 208) and at the outlet of the lake (Skeen 14)

5.3 The Relationship between Colour values of Storån River and Lillån River

The yearly average colour values (1991-2004) at the inlets from Storån and Lillån sub catchments to the lake are displayed in Figure 9. The figure shows that the yearly average colour values, measured at stations of Lillån 540 & Storån 550, have similar trends. The correlation between the two rivers' colour value is positive and strong (r=0,9). As shown in

the figure the mean annual colour value of Lillån river for all of the year (1991-2004) is greater than the Storån's river colour value. According to the mean 2007 colour value, measured at the four inlets of the lake, Storån and Lillån catchments contributed about 87% of the measured colour value to the lake. The colour value at Lillån 540 station was measured only once in two months, which is very sparse to really on the data for the anal



Figure 9: The trand of water colour of Storån and Lillån rivers

Most DOC and HS dynamics study are based on daily, weekly and at most on the monthly data of DOC, water colour and other related data (Grieve, 1994; Pettine et al. 1999; Köhler et al, 2008; Hornberger et al, 1994). The poor frequency of measurement of water colour may result a non representative data of the stream colour dynamics. Due to its sparse frequency of colour measurement of Lillån river and the strong positive correlation between Lillån and Storån water colour values (r=0.9), to understand the dynamics of water colour in Lillån river the analysis will be based on the Storån river water colour values. The water colour of Storån river is measured once every month, which is good frequency for the analysis of colour dynamics in the river. Toming et al (2009) have also used the monthly water colour data to study "Spatial and temporal variations in coloured dissolved organic matter in large and shallow Estonian waterbodies". Since the monthly data is available only for Storån river and it contributes the largest portion of water colour to the Bolmen lake (about 87% of the measured incoming colour to the lake with Lillån River in 2007), to study the behaviour of colour dynamics of the Lake, the Water colour of Storån river is analysed.

5.4 Long Term Dynamics of Water Colour in Storån River

The mean annual colour value is used to show the long term variation of water colour in Storån river. Figure 7 shows the normalized mean annual colour value of Storån (1987 to 2007); the graph is drawn by assigning the average value of all the years, which is 176 mg pt/l, as zero. The figure exhibits that there is a clear difference in the mean annual colour values between the first 10 years (1988 to 1997) and the second 10 years (1998 to 2007).



Figure 10: The mean annual normalized colour value of Storån river (1987-2007). The normalized value is calculated by subtracting the total mean value from the yearly mean value.

In the first 10 years, except in 1993, all the colour values are below the base line. That is all the mean annual colour values for the first 10 years are below 176 mg pt/l. Only in 1993 the mean colour value was above the base line, which is 180mg pt/l. In contrast to the first 10 years most of the second 10 years mean annual colour values are above the base line. In 2002, 2003 and 2006 the annual mean values are below the base line, which is only 3, 2 and 10 mg pt/l below the base line respectively. The mean colour value for 1988-1997 was 145 mg pt/l while for 1998-2007 was 205, this reflects the two different categories of the 10 year regarding the colour value of the stream.

Most studies performed in the boreal region especially in Nordic countries indicate that there is an increase in water colour (Vogt et al, 2001 and Haaland et al 2010). Many researches also showed the increase of long term DOC and water colour in Europe and North America catchments (Freeman et al., 2001a; Skjelkvåle et al., 2001; Löfgren et al., 2003; Hongve et al., 2004; Evans et al., 2005; Worrall et al., 2005; Vuorenmaa et al., 2006 cited in Jennings et al, 2009). The colour and DOC increase in boreal regions has been discussed for long time and different ideas and theories have been suggested. One of the popular suggestions is the increasing trend of DOC and water colour are caused by climate change (Freeman et al., 2001b cited in Jennings et al, 2009 and Vogt et al, 2001). The cause of climate change is explained by the increase of temperature which accelerates the organic matter decomposition process in a soil (Chapman and Thurlow, 1998; Davidson and Janssens, 2006 cited in Jennings et al, 2009). The other widely accepted cause of water colour increase is the decrease in SO_4^2 and Cl ions. Some studies show that water colour is negatively correlated with the deposit of SO_4^2 and Cl anions. The recent decrease in sulphur deposition is beloved to be the cause of water colour increase in natural water system (Vogt et al, 2001). Despite of long term water colour increase theories, explained above, the long term water colour trend is explained in the periodic change in Nordic countries. The research performed in river Lyckebyån (south Sweden), Lake Rogsjön (central Sweden) and Lake Görveln (east central Sweden), indicated that the change in water colour follow a cyclic trend (Löfgren, n.d). Which is in line with the cyclic change of water colour in Ståren river. This indicates that in addition to the recent increase the water colour long term change could be explained by its cyclic trend.

5.5 Interannual Variation of Storån River Water Colour

However there is a long term, significant increment and variation of organic matter in many rivers, the interannual variability, which is caused by flow, is usually large (Erlandsson et al, 2008). The yearly variation is best explained by the monthly and mean annual HS, measured as water colour. The yearly change of water colour is highly variable at Storån river. For example the mean annual water colour in 1999 was 265 mg pt/l, while the mean value in 2003 was about 175 mg pt/l. The peak value of water colour in the river also varies from year to year. For example in 1999 the peak value was 500 mg pt/l, just the next year it was only

275 mg pt/l. This shows that there is a big interannual variation of water colour in Storån river. The difference between yearly peak and minimum values of water colour were also used as the indicator of interannual variation. The variation between the yearly peak value and the minimum value is large (Table 3). In all the years (1987-2007) the peak value is more than double of the minimum value, except in 1991 where the peak value is only 1.6 times the minimum value. The standard deviation of the water colour value varies from 118.3 in 2007 to 17.8 in 1991. The large variation of yearly mean value is also the indicator of the existence of high interannual variation of water colour in the river. The yearly mean value varies between 265 in 1999 to 109 mg pt/l in 1992. It can be easily observed the existence of large interannual variation of water colour value in the river.

					Standard
Year	Average	Maximum	Minimum	Factor=max/min	Deviation
1987	185	350	100	3.5	87.0
1988	161	250	120	2.1	41.3
1989	157	250	120	2.1	32.1
1990	176	300	100	3.0	53.6
1991	132	175	110	1.6	17.8
1992	109	150	60	2.5	25.5
1993	180	350	85	4.1	95.1
1994	127	200	85	2.4	27.8
1995	146	200	75	2.7	36.9
1996	134	170	80	2.1	25.1
1997	141	230	85	2.7	34.8
1998	216	400	125	3.2	85.5
1999	265	500	150	3.3	105.3
2000	181	275	100	2.8	56.9
2001	206	450	125	3.6	84.9
2002	174	300	85	3.5	75.0
2003	175	250	100	2.5	55.9
2004	209	400	120	3.3	89.0
2005	193	400	125	3.2	71.5
2006	167	260	100	2.6	44.6
2007	261	500	150	3.3	118.3

Table 3: The yearly average, maximum and minimum values of water colour from 1987 to 2007; the yearly standard deviation and the factor between the yearly peak and minimum values in Storån river

5.6 Occurrence of Peak and Minimum Values of Water Colour in Storån River

The amount of coagulant and disinfectant requirement mainly depends on the raw water HS

content. The coagulation process is also depends on the season and temperature. Due to low temperature in winter: the water viscosity will increase, the solubility of coagulant will decrease and flocculation process is also affected. Due to these reasons, in winter the coagulant demand will increase (Pernitsky, n.d.). So understanding the seasonal pattern and variation of water colour in the source water, will help to plan the treatment process and coagulant requirement. Usually the water treatment plants are designed based on the worst scenario of water impurities, which is the peak value of water colour. In Storån river the peak values occur in different months and seasons of a year. In Storån river both the yearly maximum and minimum values can happen in most of the months. As shown in Table 4 in 21 years (1987-2007) except 4 months of the year; January, March, April and June; the yearly peak value occurred in all other months of the year. In the mentioned 21 years peak value occurred about 8 times in July and about 4 times both in August and November. Most of the peak values occurred either in summer (12 occasions) or in autumn (8 occasions). The peak yearly value occurred only once in spring and three times in winter season. While most of the yearly minimum values occurred in spring (16 occasions), and 5 times both in summer and autumn, and three times in winter.

Table 4: Number of occasions	that the yearly maxim	um and minimun	n value of	water of	colour
occurred in Storån river, for the	e year 1987-2007				

	Maximum value	Minimum value	
Month	occurrence	occurrence	
January	0	0	
February	1	2	
March	0	4	
April	0	6	
May	1	6	
June	0	4	
July	8	1	
August	4	0	
September	1	1	
October	3	4	
November	4	0	
December	2	1	

To understand more clearly the occurrence of extreme values a threshold range was set using average and standard deviation of water colour. Since the average value of the first 10 years (1988-1997) is very small compared to the second 10 years (1998-2007), only the second 10 years data was chosen to show the occurrence of extreme values. The upper and the lower limits of the threshold were delineated using the formula: Upper limit= mean value +1/2 Standard deviation

Lower limit= mean value - 1/2 Standard deviation

The average value = 205 mg pt/l The standard deviation =88 mg pt/l The upper limit =205+88 \approx 250mg pt/l The lower limit= 205 - 88 \approx 160 mg pt/l

Table 5 and 6 show the number of occasions where the water colour values are above and below the thresholds respectively, for the year 1998-2007. As shown in the Table 5 most of maximum values (above 250 mg pt/l) occurred in summer (16 occasions) and in autumn (14 occasions). In winter and spring the occurrences of maximum values were only in 3 and 1 occasions respectively. And as shown in Table 6 most of the minimum values occurred in winter (13 occasions) and in spring (18 occasions). The occurrence of minimum values in summer (7 occasions) and in autumn (6 occasions) is considerable. The dominance of peak values in summer and autumn is in line with many research results (Löfgren et al, n.d.; Köhler, et al 2008 and Pettine et al. 1999).

Table 5: Number of occasions, where the colour values exceed the threshold limit (250 mgpt/l). For Storån river (1998-2007).

	Occurrence
	above the above
Season	upper limit
Winter	3
spring	1
Summer	16
Autumn	14

Table 6: Number of occasions, where the colour values are below the threshold limit (160 mg pt/l). For Storån river (1998-2007).

Season	Occurrence below the lower limit
Winter	13
spring	18
Summer	7
Autumn	6

The seasonal variation of water colour in Storån river is quite significant. Figure 11 shows the Storån river's seasonal mean value of water colour. As shown in the figure the seasonal mean value varies from 433 mg pt/l in 1999 summer to 116 mg pt/l in 2002 spring. The yearly seasonal peak values occurred 7 times in summer and 3 times in autumn. And in 10 years (1998-2007) the mean seasonal values for winter, spring, summer, and autumn were 176, 151, 258 and 232 mg pt/l respectively. These all results indicate the dominance of peak values in summer. The rate of HS production in soil layer increases with the rise in temperature (Chapman and Thurlow, 1998; Davidson and Janssens, 2006 cited in Jennings et al, 2009). The most probable reason for the rise of water colour in summer is, the production of DOC stimulated by high temperature (Christ and David, 1996b, cited in Köhler, et al 2008). The DOC solution in the stream is affected by the temperature of the previous months (Grieve 1994, Köhler, et al 2008). Part of the HS flushed in summer is produced in spring season and part is produced in summer. So the mild temperature of spring has a positive contribution for the peak summer colour values. Autumn is the second season in the occurrence of maximum values. This is because part of the HS flushed in autumn is produced in summer season and the rest is produced in autumn. The dominance of peak value in summer and autumn season could also be due to lowering of water level, which facilitates the formation and transport of fresh organic matter (Naden and McDonald, 1989 cited in Worrall et al, 2002). Generally the lowest water colour occurred in spring season. Since the temperature of winter is the lowest of the year, the production of HS in winter is very low. The lowest colour value in spring is probably due to the cold temperature in winter because part of the HS produced in winter is transported in spring.



Figure 11: The mean seasonal water colour value of Storån river. The red colour represents the season with the peak value of the year and the lighter Chocolate colour represents season with the minimum seasonal value of the year (1998-2007)

5.7 The Impact of Discharge on Water Colour of Storån River

The water that passes through the catchment picks up minerals, nutrients, organic substances and other chemicals. Once after the HS is produced in the catchment, it is washes out by the runoff to the river. The washing out is an important process of HS transport from the catchment to the river, which might be revealed by the positive correlation between the colour value and flow (Naden, 1989). To show the correlation between flow and HS (measured as water colour), the water colour and flow data are used. The water colour value is measured once a month and flow is measured once a week. These days mostly the monthly, weekly or sometimes daily data of water colour may vary within an hour or even below in response of the peak discharge (Jennings et al, 2009). Sparse interval of measuring the water colour may not capture the peak values. Due to the low frequency of colour measurement the result may be considered as indicative instead of being conclusive. To show the relation between flow rate and colour value, simple linear regression analysis performed using the monthly colour value and the mean monthly flow rate for years 1997-2007. The excel regression result reveals that even if flow and colour is positively correlated, the

correlation is very weak (r=0.17), Figure 12. Even if the runoff is responsible to carry the water colour from the catchment, the relation is not linear. The weak correlation between flow rate and colour value reveals that discharge rate is not the only factor that controls the value of water colour in Storån river.



Figure 12: The linear regression analysis result using the monthly colour value and the monthly mean discharge for Storån river using the data from 1997 to 2007

Temperature is the other factor that affects the water colour in a river, because it affects the formation of HS in the soil layer. The temperature varies widely throughout the year. In general each month in Sweden has a unique average temperature. For example, in Sweden February is generally the coldest month while July is the warmest month. To account the temperature variation of each month the correlation was analysed for each month separately (Appendix 3). Simple linear regression analysis was done using excel 2007. The correlation between flow and water colour is different for all the months, Table 7. The result shows that there are two categories of correlations: one stronger and the other weaker correlation. The stronger and positive correlation exists from June to December, summer and autumn. During the rest of a year the correlation is very week and even negative in February. The variation in correlation coefficients revels that the catchment's response for each month is different. The study of Köhler et al (2008) shows that the correlation between flow and organic matter concentration depends on the season of the year. Depending on the hydrologic, biological and geochemical processes, the correlation between flow and DOC could be positive (Meyer & Tate 1983 cited in Hinton et al, 1997), negative (Hornberger et al. 1995 cited in Hinton et al, 1997) or there may exist no association between DOC and flow. During June, July, August, September and December the correlation is strong and positive. Generally the increase in runoff dilutes the major ions (Likens et al. 1977 cited Hinton et al, 1997). In contrast to the major ions the increase of runoff increases the concentration of HS, which is revealed by its positive and stronger correlation with water colour. The positive correlation also indicates that the flushing effect of runoff on the soil organic substance (Thurman, 1985). The positive correlation also suggests that the rise in flow increases the HS concentration, measured as water colour, instead of lowering the concentration.

Table 7: The linear regression analysis result for each month (1997-2007) between flow and colour value, and the correlation coefficient (r value). Water colour is considered as the dependent variable

Month	r value	y=mx +c
January	0.26	y = 0.0537x + 3.8695
February	-0.07	y = -0.2256x + 150.19
March	0.27	y = 2.12x + 118.64
April	0	y = 0.01x + 150.31
May	0.2	y = 3.5305x + 118.99
June	0.8	y = 31.914x - 48.233
July	0.68	y = 12.03x + 148.45
August	0.76	y = 20.199x + 130.51
September	0.78	y = 19.62x + 108.93
October	0.6	y = 12.519x + 115.74
November	0.19	y = 1.0294x + 201.73
December	0.8	y = 5.7185x + 125.46

In addition to the flow rate, the availability of HS or leachable organic carbon in the soil affects the DOC concentration in streams (Nelson et al. 1993, cited in Hinton et al., 1997). The stronger

positive correlation between discharge and water colour starts in June, the beginning of summer and high temperature. The rise in temperature in June stimulates biotic activity, which increases the production of HS in the soil layer. The most probable reason for the start of stronger positive correlation between discharge and colour in June is the availability of HS in the soil layer, which is affected by temperature. Except in November, the discharge and water colour correlation in summer and autumn seasons seems stronger and positive. The production of HS in the previous month also affects the concentration and its correlation with flow of the present month. For example, generally the May's temperature is comparable with the September's temperature; but since the temperature of August is higher than the temperature of April, the correlation is stronger in September. The weak correlation in November is unexpected. The weak correlation between discharge and water colour intensity in winter and spring seasons indicate that in those seasons runoff does not have strong influence on the intensity of water colour. The weak correlation in winter could also be explained by the dominance of snow precipitation in Sweden (Jennings et al, 2009). The negative correlation in February indicates the dilution impact of flow and low organic matter storage in the soil layer

(Jennings et al, 2009)

5.8 Relation between Yearly Average Discharge and Water Colour Value in Storån River

Using the mean annual value of discharge and water colour is the most widely used technique to show the association between discharge and water colour. The association between flow rate and colour value could be used to predict the impact of flow change on the export of water colour (Hinton et al., 1997). Figure 13, shows the normalized yearly flow rate and colour value of Storån river. The normalized value is obtained by dividing each year's mean value by the average value of all the years (1997-2007). The graph shows there is some similarity in the trend of flow rate and colour value of Storån river. The correlation coefficient between yearly mean flow rate and water colour value is positive and significant (r= 0.76). From the correlation coefficient we can see that flow is the important driving factor of water colour export from the catchment to the stream.



Figure 13: The non-dimensional yearly average flow rate and colour value variation trend for Storån river

The colour value of Storån river is measured only once a month, which is very sparse frequency because the colour value can change below an hour time interval. The presence of strong correlation between discharge and colour value inspite of sparse measurement, indicates the future change in flow rate could affect the water colour value of Storån river.

5.9 The Impact of Temperature on Water Colour of Storån River

Temperature is the major factor which affects the formation of HS in the soil layer. Many researchers explained the importance of temperature on the formation of HS (e.g. Vogt et al, 2001). The influence of temperature on the formation of HS can be revealed by the direct relation with water colour. Table 8 shows the correlation between mean monthly temperature and monthly water colour value; the equation in the table is the result of linear regression analysis using colour value as the dependent variable. Even if the correlation between monthly mean temperature and monthly colour value for most years is positive, the correlation was not strong. Stronger correlation exits only in 1999, 2002 and 2007. In 1997 temperature and colour value are negatively correlated.

Year	r value	Y=mx +C
1997	-0.226	y = -1.0899x + 148.75
1998	0.3	y = 4.7214x + 180.54
1999	0.76	y = 12.768x + 169.03
2000	0.32	y = 3.5666x + 151.91
2001	0.23	y = 2.8732x + 186.26
2002	0.59	y = 6.3347x + 124.39
2003	0.36	y = 2.8248x + 154.9
2004	0.53	y = 7.439x + 157.4
2005	0.3	y = 3.445x + 169.62
2006	0.12	y = -0.6924x + 172.27
2007	0.6	y = 12.548x + 162.96

Table 8: The linear regression result using the mean yearly temperature and water colour value of Storån river

The result of linear regression analysis between mean annual temperature and mean annual water colour value, for the years 1997-2007, indicates that the correlation is very weak (r=0.13). Contrary to the hypothesis, the result indicates temperature has low impact on the formation of HS in the catchment. It is not surprising to see the negative correlation in 1997 and weak correlation in most of the years because it happened in other catchments as well. The study performed by Erlandsson et al (2008) on 28 boreal region rivers indicated that the correlation between temperature and water colour is either positive and very weak or negative. Figure 14 shows the trend of mean annual temperature follow different trends. As stated in section 3.5, the sensitivity of organic matter decomposition for variation of temperature depends on the availability and type of substrates and the existence of different microbial community. The most probable reason for existing low correlation between temperature and water colour is, the water colour is more dependent on the availability of substrate than the decomposition process.



Figure 14: The non-dimensional yearly average temperature and colour value variation trend for Storån river

5.10 Relation between precipitation and Water colour value in Storån River

Precipitation is also considered to be the other factor that affects the export of DOC from the soil layer. Eighteen years data (1990-2007) of average monthly precipitation and monthly value of water colour is used to show the relation between precipitation and water colour in Storån river. Figure 15, shows the linear regression analysis result using 18 years data. Even if the correlation between mean monthly precipitation and water colour value was positive, it was very weak (r=0.29).



Figure 15: Plot of monthly colour value and mean monthly precipitation with the result of linear regression analysis using 18 years data (1990-2007) for Storån river

To consider the monthly variation of temperature the linear regression was performed for each month separately. The result of linear regression analysis for all moths, except December, shows the correlations between colour value and precipitation is very weak (Table 9). Generally for Storån river the correlation between flow rate and water colour is much stronger than the correlation of water colour with precipitation. The most probable reason for the weaker correlation of water colour with precipitation is, the evaporation and snow fall. Evapotranspiration from the catchment does not involve in export of DOC and snow does not have any impact on the export of DOC before it melts.

Table 9: The result of linear regression analysis and correlation coefficient (r value) using mean monthly precipitation and monthly colour value of Storån river. Colour value is considered as the dependent variable

	_	
Month	r value	y=mx +b
January	-0.05	y = -0.0238x + 169.21
February	0.095	y = 0.0692x + 139.55
March	0.31	y = 0.2511x + 116.73
April	0.42	y = 0.5013x + 105.91
May	0.33	y = 0.5016x + 108.24
June	0.15	y = 0.1603x + 128.1
July	0.5	y = 0.8638x + 144.16
August	0.27	y = 0.8128x + 152.18
September	-0.02	y = -0.0348x + 195.4
October	0.37	y = 0.6265x + 116.52
November	-0.42	y = -0.5224x + 244.58
December	0.74	y = 0.4899x + 121.65

6 Conclusion and Recommendation

The formation and transport of HS in Bolmen lake watershed is complex and controlled by many factors, including temperature and runoff. Storån River contributes the largest fraction of both water and HS to Bolmen Lake. Due to the existence of strong positive correlation between the colour value of Storån river and Lillån river (r=0.9) and their colour contribution is very big, about 87% in 2007, any change of colour value of Storån could affect the lake"s colour value.

Both the intra-annual and interannual variation of water colour of Storån river is very large. Summer and autumn season are dominated by peak value of colour intensity, while spring and winter are dominated by the minimum water colour values.

Despite the sparse measurement interval of colour value, there is positive and strong correlation between mean annual discharge and colour value (r=0.76). During summer and autumn season the influence of discharge is high relative to spring and winter seasons, in terms of contribution to HS concentration, measured as the water colour. The direct influence of both air temperature and precipitation on the variation of water colour is very small.

In Sweden particularly in northern and southern Sweden, climate change is predicted to have increased runoff (Andréasson, 2007). Due to the existence of positive correlation between discharge and water colour it can be concluded that the climate change will increase the water colour of Bolmen Lake, particularly in Storån river.

It is recommended to do further study on the dynamics of HS in the lake using: colour, discharge, temperature and precipitation data with high frequency of measurement for all the tributaries. As stated in the literature review (Section 3.5) in addition to climate there are other factors which affect the dynamics of HS concentration in the natural water body. Therefore, it is recommended to consider other factors such as soil moisture and sulphate content of the tributary rivers, to further study the dynamic of HS in the lake.

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APPENDEX

Appendix 1: The yearly average discharge that passes through the measuring points in m^3/s : Skeen 14 is the outflow from the lake and all rest are the inflow to the lake.

	Storån	Lillån	Unnenån	Muren	
Year	550	540	208	212	skeen 14
1995	11.64864	3.07137	4.05938	0.45975	31.75632
1996	5.67839	1.47883	1.70772	0.21877	13.31155
1997	7.22576	1.93315	2.39640	0.28719	17.24063
1998	12.51634	3.4748	4.27245	0.53417	25.52863
1999	11.99748	3.46122	4.05875	0.48654	29.59786
2000	10.74781	3.03418	3.87300	0.43439	27.25052
2001	8.0733	2.2618	2.87590	0.32490	20.54682
2002	9.85862	2.86354	3.73894	0.44117	27.80522
2003	6.11898	1.64351	1.79685	0.21669	15.78252
2004	12.38427	3.4097	4.04163	0.49584	23.13455
2005	7.13422	2.30335	3.15768	0.35562	23.18914
2006	10.62461	2.93567	3.44692	0.43991	21.48108
2007	12.24157	3.56836	4.83427	0.56502	31.99074
2008	13.04562	3.60682	4.49980	0.53052	31.38240
2009	7.20979	1.92809	2.44562	0.28874	19.01757

		Min (mg	Factor=	Annual Average
Year	Max (mg pt/l)	pt/l)	max/min	(mg pt/l)
1987	350	100	3.5	185.5
1988	250	120	2.1	160.8
1989	250	120	2.1	157.1
1990	300	100	3.0	176.3
1991	175	110	1.6	132.1
1992	150	60	2.5	109.2
1993	350	85	4.1	179.6
1994	200	85	2.4	127.1
1995	200	75	2.7	146.3
1996	170	80	2.1	133.8
1997	230	85	2.7	141.3
1998	400	125	3.2	215.9
1999	500	150	3.3	264.6
2000	275	100	2.8	181.3
2001	450	125	3.6	206.3
2002	300	85	3.5	173.8
2003	250	100	2.5	175.0
2004	400	120	3.3	209.2
2005	400	125	3.2	193.3
2006	260	100	2.6	167.1
2007	500	150	3.3	260.8

Appendix 2, the yearly maximum, minimum and average value of water colour for Storån river.

Appendix 3,	The mean	monthly	value	of flo	w rate,	temperature	and	the
monthly value	e of water c	olour, for	Storår	n River				

	colour			
	(mg	Average	Average	Average
Month	pt/l)	flow(m3/s)	Temprature(0C)	precipitation(mm)
Jan-97	160	3.98	-4	22.7
Jan-98	150	13	0.3	98
Jan-99	175	20.35	-0.1	168.1
Jan-00	150	22.5	1	134.8
Jan-01	200	14.3	0.3	57.4
Jan-02	250	12	0.9	193.5
Jan-03	175	4.92	-2.5	86.4
Jan-04	140	9.29	-4.2	111.7
Jan-05	180	22.4	1.1	188
Jan-06	175	4.225	-4.2	45.3
Jan-07	250	23.1675	2.6	251
Feb-97	13.35	160	0.9	162
Feb-98	11.0125	175	3.3	125.5
Feb-99	14.05	175	-1.3	85.6
Feb-00	21.15	125	1.9	153.6
Feb-01	11.1825	150	-1.9	62.3
Feb-02	27.1	125	2.9	195.5
Feb-03	4.39	100	-4.2	28.1
Feb-04	11.05	150	-0.3	56.1
Feb-05	9.44	150	-1.8	73.8
Feb-06	2.775	150	-2.3	48.7
Feb-07	16.84	160	-0.6	58

	colour			
	(mg	Average	Average	Average
Month	pt/l)	flow(m3/s)	Temprature(0C)	precipitation(mm)
Mar-97	13.75	110	1.9	56.7
Mar-98	13.475	125	1.1	92.7
Mar-99	15.38	150	2.5	59.3
Mar-00	17.14	125	2.1	101.5
Mar-01	8.47	125	-0.5	42.7
Mar-02	7.806	125	3	88.8
Mar-03	3.695	100	2.1	34.9
Mar-04	10.4125	200	2.1	96.4
Mar-05	7.29	180	-1.4	64.7
Mar-06	3.614	110	-3.9	76.3
Mar-07	14.516	200	4.6	85.4
Apr-97	8.62	85	4.1	76
Apr-98	13.06	125	5.8	85.7
Apr-99	15.24	175	7.3	137.3
Apr-00	13.48	100	8.4	72.5
Apr-01	9.414	225	4.8	80.5
Apr-02	6.735	125	6.9	35.3
Apr-03	3.37	200	5.8	104
Apr-04	12.318	120	7.1	31.9
Apr-05	9.756	150	6.2	40.2
Apr-06	18.475	200	4.8	108.1
Apr-07	8.845	160	7.5	48

	colour			
	(mg	Average	Average	Average
Month	pt/l)	flow(m3/s)	Temperature(0C)	precipitation(mm)
May-97	11.32	130	9	99.7
May-98	9.6	125	11.6	44.9
May-99	12.55	225	9.6	80.8
May-00	6.855	150	12	88.1
May-01	9.31	125	11.3	56.8
May-02	7.806	100	13	117.1
May-03	11.012	250	11.1	100.2
May-04	5.635	120	11.3	78.5
May-05	5.4675	175	10.2	61
May-06	12.925	100	10.7	76.1
May-07	6.966	160	11.3	107.4
Jun-97	5.2	110	15.4	99.7
Jun-98	6.735	200	13	44.9
Jun-99	10.606	400	13.9	80.8
Jun-00	7.04	150	14	88.1
Jun-01	6.478	125	13.1	56.8
Jun-02	11.62	250	15.4	117.1
Jun-03	6.745	125	15.7	100.2
Jun-04	5.422	120	13.1	78.5
Jun-05	4.754	150	13.3	61
Jun-06	7.028	160	15.3	76.1
Jun-07	7.352	200	16.2	107.4

	colour	Average	Average	Average
Month	(mg pt/l)	flow(m3/s)	Temprature(0C)	precipitation(mm)
Jul-97	5.12	160	17.4	54.1
Jul-98	9.91	225	14.4	159.7
Jul-99	6.866	400	17.1	83
Jul-00	5.174	275	15.3	49.9
Jul-01	6.47	250	17.5	63.5
Jul-02	10.818	300	17.6	100.8
Jul-03	16.88	250	17.8	128.4
Jul-04	17.924	300	14.6	197.8
Jul-05	3.114	125	17	172.4
Jul-06	2.81	130	18.9	47
Jul-07	21.4875	500	14.9	203.4
Aug-97	2.875	130	19.3	6.5
Aug-98	10.95	300	13.7	106.4
Aug-99	4.66	300	15.2	135.6
Aug-00	4.3525	250	14.4	112
Aug-01	5.636667	175	16	164.1
Aug-02	5.83	300	18.8	66.9
Aug-03	7.748	200	16.2	63
Aug-04	11.015	400	17.1	141.6
Aug-05	6.92	400	14.7	129.8
Aug-06	3.176	140	15.7	189.8
Aug-07	16.514	450	15.6	126.4

	colour			
	(mg	Average	Average	Average
Month	pt/l)	flow(m3/s)	Temprature(0C)	precipitation(mm)
Sep-97	2.175	140	11.7	89.2
Sep-98	8.92	300	12.7	99.6
Sep-99	5.836	250	14.4	140.9
Sep-00	3.588	175	10.7	76.2
Sep-01	5.114	350	11.7	116
Sep-02	2.68	150	11.9	21.4
Sep-03	3.215	125	12.7	37.4
Sep-04	10.584	300	11.8	122.8
Sep-05	5.54	225	12.2	27.6
Sep-06	4.916	160	14.2	66
Sep-07	13.38	400	11.3	151.8
Oct-97	2.36	130	4.4	110.9
Oct-98	13.63	400	7.2	269.5
Oct-99	14.95	250	7.4	108.2
Oct-00	4.8	175	10.4	176
Oct-01	6.8975	225	10.6	134.7
Oct-02	2.324	85	4.5	110.4
Oct-03	2.308	125	3.5	67.6
Oct-04	11.156	300	7.1	150.8
Oct-05	3.5725	260	7.6	86
Oct-06	7.37	220	9.8	228.1
Oct-07	11.595	300	5.4	36.3

	colour	Average		Average
	(mg	flow(m3/	Average	precipitation
Month	pt/l))	Temprature(0C)	(mm)
Nov-97	3.375	230	2.3	46.6
Nov-98	16.0725	250	-0.7	51.8
Nov-99	7.1625	225	4.2	63.1
Nov-00	15.45	250	6.2	126.9
Nov-01	9.172	225	2.6	85.4
Nov-02	4.1875	150	1.8	77.5
Nov-03	3.07	250	5.1	114.3
Nov-04	12.55	200	1.8	88.8
Nov-05	7.492	150	3.7	120.2
Nov-06	22.1	200	5.8	116.5
Nov-07	6.354	200	2.2	87
Dec-97	6.35	150	0.2	129.7
Dec-98	9.6	210	-1.6	123.7
Dec-99	20.666	250	-0.4	284.3
Dec-00	17.22	250	2.3	147.5
Dec-01	7.6525	200	-2	66.7
Dec-02	4.1175	125	-3.2	35.3
Dec-03	6.64	200	2.1	143.6
Dec-04	16.08	180	2	115.6
Dec-05	6.416	175	-0.2	47.2
Dec-06	21.36	260	5.1	232.6
Dec-07	10.668	150	2.6	124.9

	colour			
	(mg	Average	Average	Average
Month	pt/l)	flow(m3/s)	Temprature(0C)	precipitation(mm)
Jan-97	160	3.98	-4	22.7
Jan-98	150	13	0.3	98
Jan-99	175	20.35	-0.1	168.1
Jan-00	150	22.5	1	134.8
Jan-01	200	14.3	0.3	57.4
Jan-02	250	12	0.9	193.5
Jan-03	175	4.92	-2.5	86.4
Jan-04	140	9.29	-4.2	111.7
Jan-05	180	22.4	1.1	188
Jan-06	175	4.225	-4.2	45.3
Jan-07	250	23.1675	2.6	251
Feb-97	13.35	160	0.9	162
Feb-98	11.0125	175	3.3	125.5
Feb-99	14.05	175	-1.3	85.6
Feb-00	21.15	125	1.9	153.6
Feb-01	11.1825	150	-1.9	62.3
Feb-02	27.1	125	2.9	195.5
Feb-03	4.39	100	-4.2	28.1
Feb-04	11.05	150	-0.3	56.1
Feb-05	9.44	150	-1.8	73.8
Feb-06	2.775	150	-2.3	48.7
Feb-07	16.84	160	-0.6	58