Swedish University of Agricultural Sciences
Faculty of Natural Resources and Agricultural Sciences
Department of Aquatic Sciences and Assessment

Dynamics of color and organic carbon within the Mälaren catchment

– a modeling approach

José Luis Jiménez Ledesma

Master's thesis • 30 hec • Level E
Environmental Pollution and Risk Assessment – Master's Programme
Uppsala 2011

Dynamics of color and organic carbon within the Mälaren catchment – a modeling approach

José Luis Jiménez Ledesma

Supervisor: Stephan Köhler, Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment

Assistant Supervisor: Martyn Futter, Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment

Examiner: Gesa Weyhenmeyer, Swedish University of Agricultural Sciences, Department of Aquatic Sciences and Assessment

Credits: 30 hec
Level: Advanced E
Course title: Independent project in Environmental Science
Course code: EX0431
Programme/education: Environmental Pollution and Risk Assessment

Place of publication: Uppsala
Year of publication: 2011
Picture Cover: José Luis Jiménez Ledesma
Title of series: no:
ISSN:
ISBN:
Online publication: http://stud.epsilon.slu.se

Key Words: TOC, DOC, organic carbon, water color, water treatment, water pollution, modeling, Mälaren, INCA-C, HBV.

Swedish University of Agricultural Sciences
Faculty
Department
Unit/Section (optional)

ABSTRACT

Lake Mälaren, located in eastern Sweden, supplies water for drinking use to more than two million people in Stockholm and the surroundings. Water quality is generally rather good; although concern has been raised in the last years due to observed increasing trends in both color and dissolved organic carbon (DOC) in other surface waters in Scandinavia. This may eventually occur in Lake Mälaren. DOC can carry along contaminants and toxic compounds affecting the functioning of water treatment plants. A better understanding of the DOC dynamics within the catchment is essential. This requires an investigation of the spatial and temporal patterns in DOC quality and quantity. The main aim of this project is to produce the basic knowledge that will be useful to predict DOC quality and quantity in Lake Mälaren. The project is structured in two parts: (1) areal mass transport fluxes of color and total organic carbon (TOC) within the catchment, and (2) simulation of DOC concentrations in Fyrisån subcatchment using the HBV and INCA-C models. TOC concentrations and color show similar dynamics with some differences. Catchments with lower open water proportion present browner waters due to lower retention times. TOC exports are well correlated to discharge in suggesting that TOC concentration is controlled by flow. However, there is a risk of increasing carbon concentrations after peaks in runoff, which are related to wet years. The INCA-C reproduces well the intra- and interannual variation in DOC concentration in Fyrisån, however, the model fails to capture some of the high peaks. Further studies, are needed in order to both understand the new trends in DOC concentration and develop the INCA-C model to predict these trends. Once the new studies based on this report are carried out successfully the model could be used to predict DOC concentrations in the future.

TABLE OF CONTENTS

1. INTRODUCTION

The occurrence of water is may be the reason why it has been possible to develop on the planet Earth what we call life. Human beings, like any other organism, need water and they need it for many different purposes: food, cleaning, hygiene, agriculture, industry, energy, leisure time, etc. The world has an abundance of water, but the amount that we can really use is limited. Besides, it is not equally distributed around the different regions. In that sense, Sweden is one of the luckiest countries, with many water resources. Even so, there is still a need of treat the water for drinking consumption. Contaminants and potential toxic substances have to be removed before water is suitable for human consumption. In this paper the focus is on dynamics of dissolved organic carbon (DOC) concentrations and its influence upon water treatment, especially nowadays since it is increasing in natural waters.

1.1 Characterization of dissolved organic carbon (DOC)

DOC is defined as the broad classification for organic molecules of varied origin and composition in aquatic systems (Sucker and Krause, 2010). Broadly, the organic matter (OM) in natural waters consists of a wide size range of compounds including free monomers, macromolecules, colloids, aggregates and large particles. Traditionally, this material has been divided into two major groups (Spitzy and Leenheer, 1991):

- Particulate organic matter (POM): fraction that upon filtration of a water sample is retained on a 0.45 μm filter. This group is subdivided depending on the element considered in particulate organic carbon (POC), particulate organic nitrogen (PON) and particulate organic phosphorus (POP).

- Dissolved organic matter (DOM): fraction that passes the filtration of a water sample on a 0.45 μm filter. Analogously, this group includes dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP).

Thus, the combination of POC and DOC makes up the total organic carbon (TOC) in a water sample. The OM that can be found in waters has different origins. Natural organic matter (NOM) derives from plants and microbial residues. Besides, we can find an anthropogenic fraction from deliberate or accidental disposal of domestic sewage, agricultural chemicals, medicinal and products of industrial processes (vanLoon and

Duffy, 2005). Therefore, the characterization of the OM present in water is not easy, especially regarding the dissolved part.

Spitzy and Leenheer (1991) suggest that DOC is formed by a defined fraction consisting of carbohydrates, amino acids, hydrocarbons, fatty acids and phenolic compounds; and an uncharacterized fraction consisted mainly of humic (HA) and fulvic acids (FA). HA and FA (from now humic substances) are recalcitrant organic acids derived mainly from detrital plant material and soils, but also from the growth of algae and other microorganisms in the water column or benthos (Miller et al., 2009). HA and FA are differentiated by their solubility at different pH, HA only soluble at pH > 2; and their molecular weight, higher for HA (Vermeer and Koopal, 1998). The majority of DOM consists of the uncharacterized fraction, i.e. humic substances, which may reach more than 80 % in some wetlands (Mladenov et al., 2005). Lakes with high DOC content show a yellow to brown coloration, which is a typical characteristic of humic substances.

1.2 Rising DOC concentrations in recent years

Concentrations of DOC are increasing in surface waters across Europe, especially in Scandinavian countries (Hongve et al., 2004) and in parts of North America (Monteith et al., 2007). The causes for this increasing are still not clear, although some mechanisms have been described as responsible for the trend. According to Futter et al. (2009), the two most important are declines in sulfate (SO_4^{2-}) deposition and changes in climate. These two mechanisms and some others are described next:

- *Decreasing in acid deposition*. It has been observed in the last decades that the deposition of acid compounds such as sulfate (SO_4^{2-}) or nitrate (NO_3^-) has decreased significantly (Fölster & Wilander, 2002), especially in those countries where surface water acidification is an important environmental issue. Skjelkvåle et al. (2005), Monteith et al. (2007) and Futter et al. (2009) found correlations between increasing water DOC concentrations and reduction of sulfate deposition. The reasons for this correlation are still unknown but the hypothesis is that the solubility of DOC increases when sulfate content decreases during recovery.

- *Climate change*. In the international scientific community, it is accepted that the average world temperature will increase in the next decades due to global warming. In the case of Sweden, the annual mean temperature is projected to increase between 2.5 ºC and 4.5 ºC by 2071-2100 compared to the period 1961-1990 (Persson et al., 2007). In the same study, the annual mean precipitation over Sweden is projected to increase during the century by between ~10 to 20 %. The activity of microorganisms that break down organic matter in the soil is enhanced by higher temperatures. Köhler et al. (2008) observed an increase in TOC concentrations during the warm summer months during wet years in forested catchments in an 11-year study in Sweden. Therefore, it is expected that DOC concentrations in Swedish surface waters will be higher in the future due to increasing in both temperature and precipitation.

- *Changes in hydrology*. The spring snow melt period is important for organic matter flow to surface waters. Laudon et al. (2004) monitored TOC concentrations in seven boreal catchments in northern Sweden. They found that the four week long spring period contributed between 50 % and 68 % of the annual TOC export from the seven catchments. Furthermore, the contribution in this period was higher in forested catchments than wetland dominated catchments.

- *Land use*. Land use type and changes on it may affect the quantity and quality of the TOC in the catchments by themselves or by altering hydrological cycles. Mattsson et al. (2005) observed that the TOC export increased with increasing peatland proportion in Finnish main rivers. As it was pointed out earlier, the proportion of forest and wetland is important for the yield of DOC from catchments, being the principal variable in the Northern Hemisphere according to Curtis (1998).

- *Combination of factors*. Despite what has been mentioned earlier, most of the times the change in DOC concentrations in water systems is not a result of one factor but a combination of those. Tranvik and Jansson (2002) suggest that predictions of DOC export based on temperature or any other single parameter may be overly simplistic. In Sweden, the two main factors behind the increasing

concentrations of organic matter in surface waters are decreases in sulphate deposition and flow (Erlandsson et al., 2008).

1.3 DOC, human health and water treatment

One reason concern about the increasing DOC concentrations in surface waters is the possible interaction with human health. When treating water for drinking use, the DOC needs to be removed due to its capability to carry along contaminants and toxic compounds. Moreover, changes in DOC concentrations significantly affect treatment process selection, design and operation (Eikebrokk et al., 2004).

DOC is related to contamination and potential toxicity in aquatic systems in many ways:

- DOC is a precursor of trihalomethanes (THM), which are a group of compounds, including dibromochloromethane, bromodichloromethane, chloroform and bromoform, with potential carcinogenic and mutagenic properties. During the water treatment process the DOM reacts with chlorine forming THM (Chow et al., 2003).

- DOC is important in the fate of mercury in water since there is evidence of strong interactions between DOM and the metal (Ravichandran, 2004). Mercury is mobilized from the solid phase and therefore its bioavailability increases.

- At around neutral pH, the mobility of copper increases due to formation of complexes with DOM, although these complexes are less toxic than the metal itself (Ashworth and Alloway, 2007).

- Lead is transported continuously, but slowly, downward together with colloidal organic matter in soils (Klaminder et al., 2006). They reach water-saturated mineral soil layers and eventually, trough lateral transport, surface waters. Klaminder et al. (2006) suggest that the amount of lead leached from the soil and lost through runoff will increase in the future in boreal catchments.

- DOC structure also allows binding and transport of organic pollutants (Dawson et al., 2009).

- Humic substances belonging to DOC can cause secondary problems such as diseases, taste and odor due to excess microorganism growth (Löfgren et al., 2003).

Surface water treatment comprises a sequence of unit processes in order to produce potable water. The most common unit processes are disinfection, coagulation, rapid mixing/oxygenation, flocculation, fast and slow sand sedimentation, membrane filtration and a final disinfection before distribution. There is a variety of different combinations of such unit processes to achieve this target, and for each unit process different treatment technologies are practiced (Gaulinger, 2007).

Due to the capability of DOC to bind organic and inorganic contaminants and reactive species, it often interferes with treatment processes. There are two measures intimately related with DOC content that have special importance in water treatment: water color and specific ultraviolet absorption (SUVA). Historically, water color was measured by comparison to dissolved platinum standards (mg Pt L^{-1}). Today, color is usually measured by light absorbance at 465 nm and it relates to chromophores in DOC, including conjugated double bonds, aromatic rings and phenolic functional groups (color centers in humic substances). Color can also be measured as light absorption of 0.45 μm filtered water at 420 nm in a 5 cm cuvette (Weyhenmeyer et al., 2004). SUVA is expressed by the ratio of UV absorbance at 254 nm or 280 nm divided by DOC and it is related to the hydrophobicity and aromaticity of DOC respectively (Chen et al., 2004).

For water to become suitable for drinking, water color needs to be eliminated, not only because of DOC can carry contaminants, but also because colored water is regarded to be unpleasant. It has been proved that water color increases with DOC (Weyhenmeyer et al., 2004). In an experiment carried out in Norway, Eikebrokk et al. (2004) found that the required coagulant dose, sludge production, number of backwashes per day and residual TOC increased by 64%, 64%, 87%, and 26% respectively when water color increased from 20 to 35 mg Pt L^{-1}. SUVA also increases when DOC increases and it especially affects the performance of the coagulation process (Eikebrokk, 2009). Therefore, according to these studies it is expected that the treatment costs increase when DOC is higher.

There have been many studies about how to remove DOC from water in the best way. Nishijima et al. (2003) compared a multi-stage ozonation-biological treatment process with the conventional single-stage ozonation-biological treatment process. They found a higher DOC removal in the multi-stage treatment due to larger generation of biodegradable DOC in several ozonation steps, even when the total reaction time was lower. However, traditional removal by ozone may lead to biological regrowth in the distribution network due to formation of biodegradable DOC (Osterhus et al., 2007). This is the basis for developing a biofiltration step. Nowadays, a novel process so-called ozonation, biodegradation and micro or ultra membrane filtration (OBM), has reached importance.

The problem of DOC removal from natural waters is especially important in Sweden, where 50 % of the population drinks water originating from surface waters (Löfgren et al., 2003).

1.4 Problematic of DOC in Lake Mälaren

Lake Mälaren, located in eastern Sweden (Figure 1), supplies water for drinking use to more than two million people in Stockholm and the surroundings. Water quality is generally rather good; although concern has been raised in the last years due to observed increasing trends in both color and DOC in other surface waters in Scandinavia (Hongve et al., 2004). This may eventually occur in Lake Mälaren, with adverse consequences for water treatment.

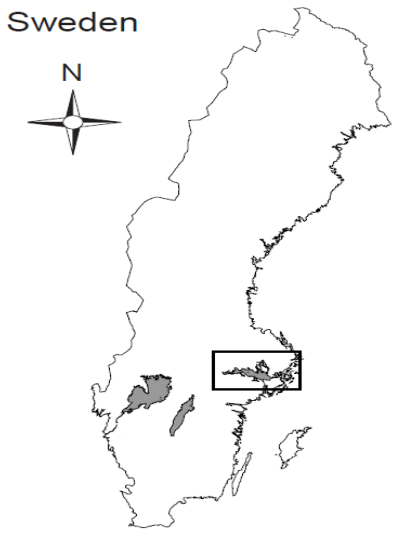

Figure 1. Location of Lake Mälaren in Sweden. Modified from Weyhenmeyer et al. (2004).

Higher water color associated with extreme precipitation events has been already reported in the lake Mälaren (Weyhenmeyer et al., 2004). Since climate change predictions forecast a precipitation increase and more extreme events in the region it is expected that DOC concentrations will increase in the future.

In order to avoid undesirable outcomes in Lake Mälaren water treatment plants, a better understanding of the DOC dynamics within the catchment is essential. This requires an investigation of the spatial and temporal patterns in DOC quality and quantity. The tools commonly used to aid in the understanding of dynamic systems are simulation models.

1.5 DOC modeling in surface waters

Ecosystems are complex systems characterized by an infinite web of interactions and dynamic processes. The integration of these interactions and processes in a simplified way is needed when studying them. Here is where simulation models can help environmental assessors with the ecosystem evaluations. Simulation models are simplified mathematical representations of the functioning of dynamic systems and they are worldwide used in environmental assessment.

According to Futter et al. (2007) a model for simulating fluxes of DOC from headwater streams to outlets in the sea should fulfill six premises:

1. Take into account spatial heterogeneity and land cover types in the catchment.
2. Simulate effects of patterns of precipitation and temperature.
3. Simulate in-soil production and consumption of organic carbon.
4. Incorporate surface water fluxes.
5. Account biological and chemical processes that consume DOC.
6. Be calibrated using monitoring data.

No current models fulfill the above characteristics at a scale greater than at an individual catchment. However, several models of DOC dynamics in both terrestrial and aquatic environments have been developed in the last years. Simple models have been used to simulate the effects of snowmelt on DOC export (Boyer et al., 2000), study carbon processing in lakes (Hanson et al., 2004) and estimate export coefficients of DOC in lakes (Canham et al., 2004). More detailed process-based models have been developed to predict soil water DOC concentrations (Neff & Asner, 2001; Michalzik et al., 2003; Lumsdon et al., 2005).

Recently, a new process-based biogeochemical model, the Integrated Catchments model for Carbon (INCA-C) has been used in similar previous researches (Futter et al., 2007; Futter & de Witt, 2008; Futter et al., 2008; Futter et al. 2009; Oni et al. 2010) in forested, temperate and boreal single catchments with successful results. INCA-C is based on previous versions of INCA which were originally designed to model nutrient patterns in both aquatic and terrestrial environments (Whitehead et al., 1998; Wade et al., 2002a; Wade et al., 2002b). So far, INCA-C has been used in relatively small catchments and subcatchments of lakes and streams in Canada and Scandinavia. In this project, the INCA-C model is applied within a much larger watershed, the lake Mälaren, with a catchment area of 22603 km^2 (Wallin et al., 2000). The model is tested in one of its major tributaries, the river Fyris, with a catchment area of 1982 km^2 (Wallin et al., 2000).

2. AIM

The main aim of this project is to produce the basic knowledge that will be useful to predict DOC quality and quantity in Lake Mälaren by modeling fluxes of water color and organic carbon within the lake catchment.

Some other specific objectives of this project are:

- Calculate and compare the fluxes of different substances (with focus on TOC and color) flowing into the lake Mälaren from its main tributaries and at the outlet.

- Test the applicability of INCA-C model in a large catchment in Sweden: the Fyrisån catchment that contributes to flow into Lake Mälaren.

- Compare the simulated and the observed DOC patterns of the modeled catchment.

3. STUDY SITE: LAKE MÄLAREN AND FYRISÅN SUBCATCHMENT

Lake Mälaren (59º 30´ N, 17º 12´ E) is the third largest lake in Sweden. Located in the southeast, Mälaren catchment area is a large expansion of 22603 km^2 (Wallin et al., 2000) which constitutes about 5 % of the country, with the outlet in the city of Stockholm. The catchment is dominated by forests and wetlands (70 %), arable lands and meadows (20 %) and lakes (10 %) (Wallin et al., 2000). Mälaren has a water surface area of 1120 km^2, a volume of 14.03 km^3, a mean depth of 12.8 m (max depth is 63 m) and water retention time of 2.8 years (Weyhenmeyer et al., 2004). This relatively

short water residence times leads to fast responses to changes in input water quality. The average annual precipitation in the area is about 650 mm and the annual average evapotranspiration about 420 mm (Bergström et al., 2006).

Lake Mälaren receives 80 % of the water from 10 major rivers of the catchment (Wallin et al., 2000). The lake can be divided in six basins (Figure 2) to facilitate the understanding of its functioning.

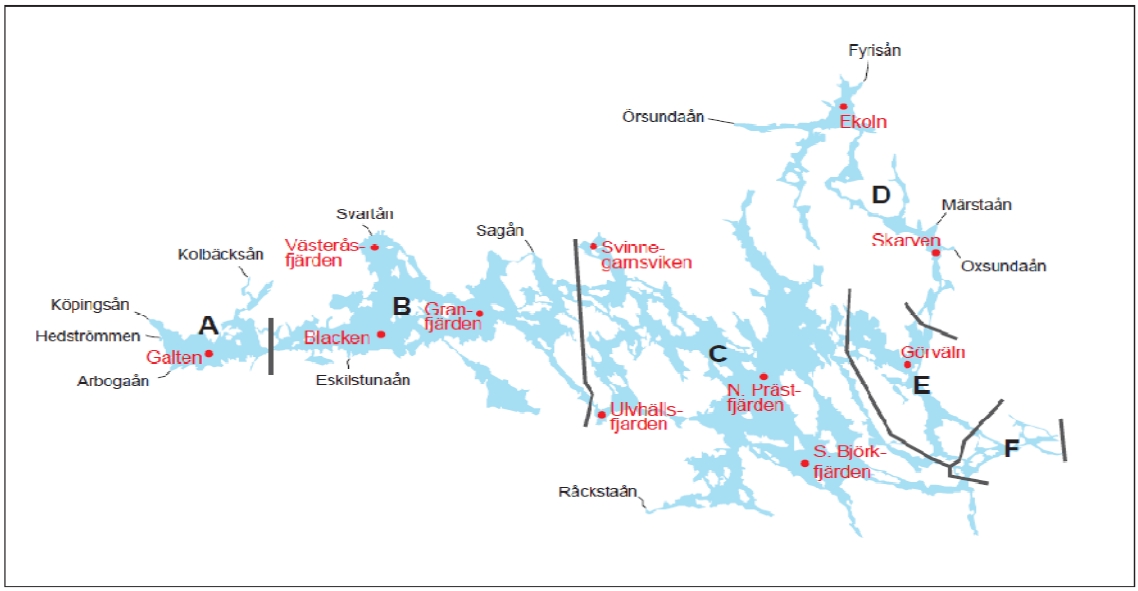

Figure 2. Mälaren basins with sampling stations (red dots). From Wallin et al. (2000).

Organic substances in the lake are measured as TOC. The highest levels are found in the northeast, in the stations Ekoln and Skarven (Figure 2). In this area, water entering the lake comes from rivers which transport large amounts of organic material from agricultural land. TOC concentrations are high in the western stations. Organic substances are gradually broken down and diluted, leading to lower TOC concentrations in the stations nearby the outlet (S. Björkfjärden and Görväln). Water color is higher at the beginning of the year due to inflows of humic substances in the winter-spring period. The water is significantly less colored in the center (N. Prästfjärden station) and close to the outlet. In these areas there are no large tributaries (Sonesten et al, 2010).

There are 12 main streams which flow into the Mälaren (Figure 3). According to Wallin et al. (2000) the 12 streams altogether contribute about 84 % of the water. The rest of the water comes from the so-called *närområdet* (neighborhood), i.e. small streams within the Mälaren basin. Table 1 shows the contribution of each stream and its catchment area.

Figure 3. Overview of the Mälaren catchment area with boundaries of the largest stream basins. From Wallin et al. (2000).

Table 1. Water contribution of the main streams flowing into the Lake Mälaren with their catchment area. Adapted from Wallin et al. (2000).

Stream	Outflow basin	Area (km^2)	Water contribution to Mälaren (%)
Arbogaån	A	3802	25.1
Kolbäcksån	A	3093	16.9
Hedströmmen	A	1058	7.0
Köpingsån	A	284	1.1
Eskilstunaån	B	4187	14.0
Svartån	B	754	3.5
Sagån	B	865	4.1
Råckstaån	C	239	0.6
Fyrisån	D	1982	7.6
Örsundaån	D	727	2.9
Oxundaån	D	271	0.9
Märstaån	D	71	0.3
Närområdet	A,B,C,D,E,F	-	16.0

One of the most interesting subcatchment to study regarding organic carbon is the Fyrisån basin. According to Sonesten et al. (2010), the Fyrisån is one of the largest contributors of TOC in the whole catchment.

The Fyrisån basin is located in the northwest part of the Mälaren catchment (Figure 3 and Figure 4) and has an area of 1982 km^2. Land use is dominated by forest (mainly coniferous trees) with about 61 %. It has one of the largest agricultural areas in the catchment with 31 % of the total area. The rest, 6 % consists of wetlands and lakes and about 2 % urban areas. The elevation of this lowland catchment ranges from 15 m to 115 m (Exbrayat et al., 2010) with a predominance of clay soils and forest associated with till and croplands (Lindgren et al., 2007). Its main and last contributing subcatchment is Sävjaån, with an own area of 699 km^2 (Exbrayat et al., 2010), approximately one third of the Fyrisån total catchment area.

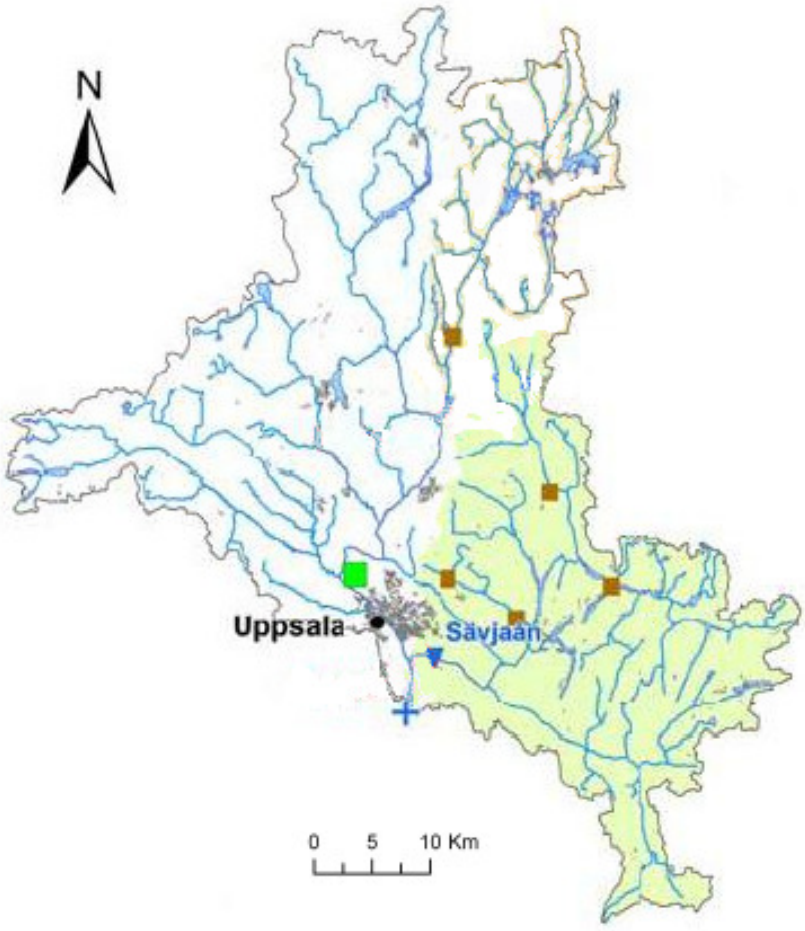

Figure 4. Fyrisån catchment with Sävjaån subcatchment highlighted green. In the map: sewage treatment plants (brown squares), precipitation station (black circle), temperature station (green square), discharge station (blue triangle) and outlet of the catchment at Flottsund (blue cross). Modified from Exbrayat et al. (2010).

Fyrisån, besides to be one of the most interesting subcatchment to study, has one of the largest amounts of data associated. This is why this subcatchment was selected for the INCA-C modeling in this project.

4. MATERIAL AND METHODS

The project was structure in a procedure divided in three main phases, which are summarized next:

1. *Data handling and mass transport calculations*: to calculate fluxes of color (measured as light absorption of 0.45 μm filtered and unfiltered water samples at 420 nm in a 5 cm cuvette), TOC, $KMnO_4$, Ca, Mg, Na, K, NO_2 + NO_3, NH_4, SO_4, Cl, Fe and Al from the 12 major stream catchments (Figure 3) draining into Lake Mälaren and from the outlet.
2. *Use of HBV model*: to estimate soil moisture and hydrologic parameters.
3. *Use of INCA model*: to simulate temporal patterns of DOC in Fyrisån subcatchment using the results from the previous steps and comparison with observed data.

4.1 Data handling and mass transport calculations

The flux estimates were generated using existing data on flow and water chemistry. To calculate a monthly and annual mass export of the different substances, daily flow and daily concentration data are required. Daily flow data are easily available, whereas chemistry data are less frequently recorded and have to be interpolated. Interpolation was done using the Visual Basic program Flownorm 2.1 (Grimvall, 2004).

4.1.1 Data sources

The most suitable data for working in this project were those belonging to the mouth of the 12 major rivers and the outlet in Stockholm. In total, data from 14 stations were used in this project, 12 corresponding to the 12 major streams and 2 corresponding to the outlet of the lake: Arbogaån Kungsör, Kolbäcksån Strömsholm, Eskilstunaån Torshälla, Fyrisån Flottsund, Hedströmmen Grönö, Sagån Målhammar, Svartån Västerås, Örsundaån Örsundsbro, Köping II, Oxundaån Rosendal, Råckstaån Utl., Märstaån Utl., Norrström Stockholm and Stockholm Centralbron. The required information for calculating mass transports was flow data and water chemistry data. Table 2 and Table 3 show a summary of the available data and sources for the different places.

Flow data

There were available flow data from different sources.

- The Swedish Meteorological and Hydrological Institute (*Sveriges Meteorologiska och Hydrologiska Institut*, SMHI) supplies modelled daily flow data from small single subbasins all around Sweden. SMHI has developed the Swedish version of the HYdrological Predictions for the Environment model (S-HYPE) (Lindström et al., 2010). The model provides daily simulations of discharge for more than 17000 subbasins (SMHI, 2010) for the period 1995-2010. Data can be downloaded at the website of the SMHI: http://homer.smhi.se/.

- Besides, another group of flow data at the mouth of the main streams was available. The data in this case came from different sources depending on the stream (Table 2). Some had modelled flow corresponding to either PULSE model, HBM model or a third unknown model. Four of the streams (Hedströmmen, Svartån, Örsundaån and Köpingsån) had measured flow.

Water chemistry data

Water chemistry data were provided by the Department of Aquatic Sciences and Assessment (*Institutionen för Vatten och Miljö*) of the Swedish University of Agricultural Sciences (*Sveriges Lantbruks Universitet*, SLU). The measurements of the different chemical parameters are monthly and the period of available data depends on the station and the substance (Table 2 and Table 3). The substances that had been measured and were used in the calculations of the monthly and annual export by Flownorm 2.1 are: color (measured as light absorption of water at 420 nm in a 5 cm cuvette) in 0.45 μm filtered (AbsF) and unfiltered samples (AbsOF), TOC, permanganate ($KMnO_4$), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), total nitrogen (Tot-N) nitrite and nitrate ($NO_2 + NO_3$), ammonium (NH_4), sulfate (SO_4), chlorine (Cl), iron (Fe) and aluminium (Al). Lists of periods for which data were available are shown in Table 3.

Table 2. List of available data from the main streams flowing into Lake Mälaren. In bold, flow data used.

*: data from either PULSE model, HBM model or a third unknown model.

**: stations corresponding to the outlet of Lake Mälaren in the city of Stockholm

Stream / station	Water chemistry data (IMA)					Flow data (S-HYPE model)			Other flow data			
	X (RAK)	Y (RAK)	Period	Color	TOC	X (RAK)	Y (RAK)	Period	X (RAK)	Y (RAK)	Period	Source
Arbogaån Kungsör	658970	151660	1965-1995	1965-1995	-	**658902**	**151427**	**1995-2009**	658970	151660	1965-2003	*
Kolbäcksån Strömsholm	660069	152632	1965-2010	1965-2010	1997-2010	**660172**	**152589**	**1995-2009**	660069	152632	1965-2008	*
Eskilstunaån Torshälla	659008	153867	1965-1995	1965-1995	-	**659047**	**153876**	**1995-2009**	659008	153867	1965-2003	*
Fyrisån Flottsund	663116	160415	1958-2010	1965-2010	1993-2010	**663275**	**160459**	**1995-2009**	663116	160415	1965-2008	*
Hedströmmen Grönö	659517	151047	1965-1997	1965-1997	1997	659584	150749	1995-2009	**659517**	**151047**	**1965-2008**	**Measured**
Sagån Målhammar	660939	156130	1965-2010	1965-2010	2003-2010	**660949**	**156127**	**1995-2009**	660939	156130	1965-2008	*
Svartån Västerås	660994	154173	1965-1995	1965-1995	-	661001	154176	1995-2009	**660994**	**154173**	**1965-2008**	**Measured**
Örsundaån Örsundsbro	662506	158465	1965-2010	1965-2010	2003-2010	662519	158365	1995-2009	**662506**	**158465**	**1965-2008**	**Measured**
Köping II	659931	151069	1965-1995	1965-1995	-	659966	151056	1995-2009	**659931**	**151069**	**1966-2008**	**Measured**
Oxundaån Rosendal	660657	161572	1968-2010	1968-2010	1997-2010	**660630**	**161568**	**1995-2009**	660657	161572	1968-2008	*
Råckstaån Utl.	657010	157800	1998-2010	1998-2010	1998-2010	**656965**	**157758**	**1995-2009**	-	-	-	-
Märstaån Utl.	661127	161399	1988-1995	1988-1995	-	**661114**	**161384**	**1995-2009**	661127	161399	1988-2004	*
Norrström Stockholm**	658078	162873	1965-2002	1965-2002	1987-2002	**659497**	**157923**	**1995-2009**	-	-	-	-
Stockholm Centralbron**	658065	162841	1996-2010	1996-2010	1996-2010	**659497**	**157923**	**1995-2009**	-	-	-	-

Table 3. List of available period data from 1995 in the different stations for the different substances.

Stream / station	AbsF	AbsOF	TOC	$KMnO_4$	Ca	Mg	Na	K	Tot-N	NO_2 + NO_3	NH4	SO4	Cl	Fe	Al
Arbogaån Kungsör	1995	1995	No data	1995	1995	1995	1995	1995	No data	1995	1995	1995	1995	No data	No data
Kolbäcksån Strömsholm	1995 1997-2009	1995 1997-2009	1997-2009	1995	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1997-2009	No data
Eskilstunaån Torshälla	1995	1995	No data	1995	1995	1995	1995	1995	1995	1995	1995	1995	1995	No data	No data
Fyrisån Flottsund	1995-2009	1995-2009	1995-2009	1995-2002	1995-2003	1995-2003	1995-2003	1995-2003	1995-2009	1995-2009	1995-2009	1995-2003	1995-2003	1995-2003	1996
Hedströmmen Grönö	1995	1995	No data	1995	1995	1995	1995	1995	1995	1995	1995	1995	1995	No data	No data
Sagån Målhammar	1995-2009	1995-2009	2003-2009	1995-2002	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	No data	No data
Svartån Västerås	1995	1995	No data	1995	1995	1995	1995	1995	1995	1995	1995	1995	1995	No data	No data
Örsundaån Örsundsbro	1995-2009	1995-2009	2003-2009	1995-2002	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	1995-2009	No data	No data
Köping II	1995	1995	No data	1995	1995	1995	1995	1995	1995	1995	1995	1995	1995	No data	No data
Oxundaån Rosendal	1995 1997-2009	1995 1997-2009	1997-2009	1995	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	1995 1997-2009	2003-2007	2004-2007
Råckstaåns utl.	1998-2009	1998-2009	1998-2009	No data	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	1998-2009	No data
Märstaån Utl.	1995	1995	No data	1995	1995	1995	1995	1995	1995	1995	1995	1995	1995	No data	No data
Norrström Stockholm	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1995-2002	1996-2002
Stockholm Centralbron	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009	1996-2009

As Table 2 shows, spatial coordinates for chemistry data and the second group of flow data are the same, i.e. the place of measurement was the same. In order to choose the most suitable basin with S-HYPE modelled flow data it was necessary to use the Geographic Information System (GIS) ArcGis 9.3. This task was carried out by overlapping one layer with the spatial location of the known stations with another layer with the boundaries of the basins used by SMHI plus one additional layer with the map of the area. The most suitable basins were placed upstream the known stations. The corresponding flow data were downloaded from the SMHI website.

Since different flow data were available, it was necessary to choose the most appropriate for using in the mass transport calculations. Data were compared for the different places in those years with overlapping information. 11 of the streams had two different sets of flow data. Finally, the decision was to use measured data when available (Hedströmmen, Köpingsån, Svartån and Örsundaån) and S-HYPE modelled data in the other cases (Arbogaån, Kolbäcksån, Eskilstunaån, Sagån, Råckstaån, Fyrisån, Märstaån and the outlet Mälaren). Thus, all the calculations were carried out with a homogeneous group of information when no measured data were available.

4.1.2 Mass transport calculations

Computations of monthly and annual loads from concentration of different substances and flow data for each of the 14 places listed in Table 2 and Table 3 were carried out by using Flownorm 2.1. Flownorm 2.1 consists of five Visual Basic macros, using two Excel worksheets containing concentration (mg/l) and flow (m^3/s) data for an arbitrary number of sampling sites as inputs. When computing color loads, the input units were the measured absorption of 0.45 μm filtered and unfiltered water at 420 nm in a 5 cm cuvette. These units of absorbance per 5 cm were assumed as analogous to the mass concentrations in mg/l used with the other substances. This assumption is justified since the objective was to compare the relative values between the different catchments rather than obtain a specific absolute value. The Flownorm program calculates monthly and annual riverine loads by first expanding the time series of observed concentration and flow data to complete series of daily data and then summing daily values of the product of concentration and water discharge. The expanded values are computed by a linear interpolation between observed values. The units of the outputs are tons per unit of time (month or year) for the monitored substances and $m^3 \cdot 10^9$ per unit of time (month or

year) for the discharge. More intuitive units such as $g \cdot m^{-2} \cdot year^{-1}$ can be easily obtained by dividing the output loads by the area of the specific catchment in km^2. Color outputs, as assumed to be analogous as the others, were also divided by the area obtaining units of $absorbance \cdot m^{-2} \cdot year^{-1}$. Extended information about Flownorm 2.1 can be found in Grimvall (2004).

4.2 HBV model

4.2.1 Description of HBV model

The HBV model (*Hydrologiska Byråns Vattenbalansavdelning*) was developed at SMHI by Sten Bergström (Bergström, 1976). It is a conceptual model for runoff simulations, which has been especially used in Swedish catchments, although it has been also applied in modified versions in many other countries. Some applications of the model have been water balance studies (Graham & Bergström, 2001), forecasting of snowmelt runoff (Şorman et al., 2009), analysis of temporal variability within catchments (Arheimer & Liden, 2000), study of effects of climate change (Beldring et al., 2008) and study of effects of land use change (Seibert & McDonnell, 2010).

Besides, HBV model has been used as a preliminary step in INCA-C model calibrations (Futter et al., 2007; Futter & de Witt, 2008; Futter et al., 2008; Futter et al. 2009; Oni et al. 2010). Two important parameters that are required as inputs in the latter are obtained as outputs from the former. These are the soil moisture deficit (SMD) and the hydrologically effective rainfall (HER). These two parameters are described in the INCA-C model section.

HBV model simulates daily discharge using daily rainfall, temperature and potential evaporation as input. The model consists of four routines or modules and fourteen parameters (Figure 5):

1. Snow routine. Precipitation is simulated as either snow or rain depending on whether the temperature is above or below a threshold temperature TT (ºC). All precipitation that is simulated as snow is multiplied by a correction factor, SFCF (-). Melt of snow is calculated with a degree-day method using a degree day factor, CFMAX ($mm \cdot ºC^{-1} \cdot day^{-1}$). CFMAX varies normally between 1 and 4 $mm \cdot ºC^{-1} \cdot day^{-1}$ with lower values for forested areas. The snowpack retains meltwater and rainfall until it exceeds a certain fraction of the water equivalent of the snowpack, CWH (-).

When temperature decreases below TT, liquid water within the snowpack refreezes again using a refreezing coefficient, CFR (-).

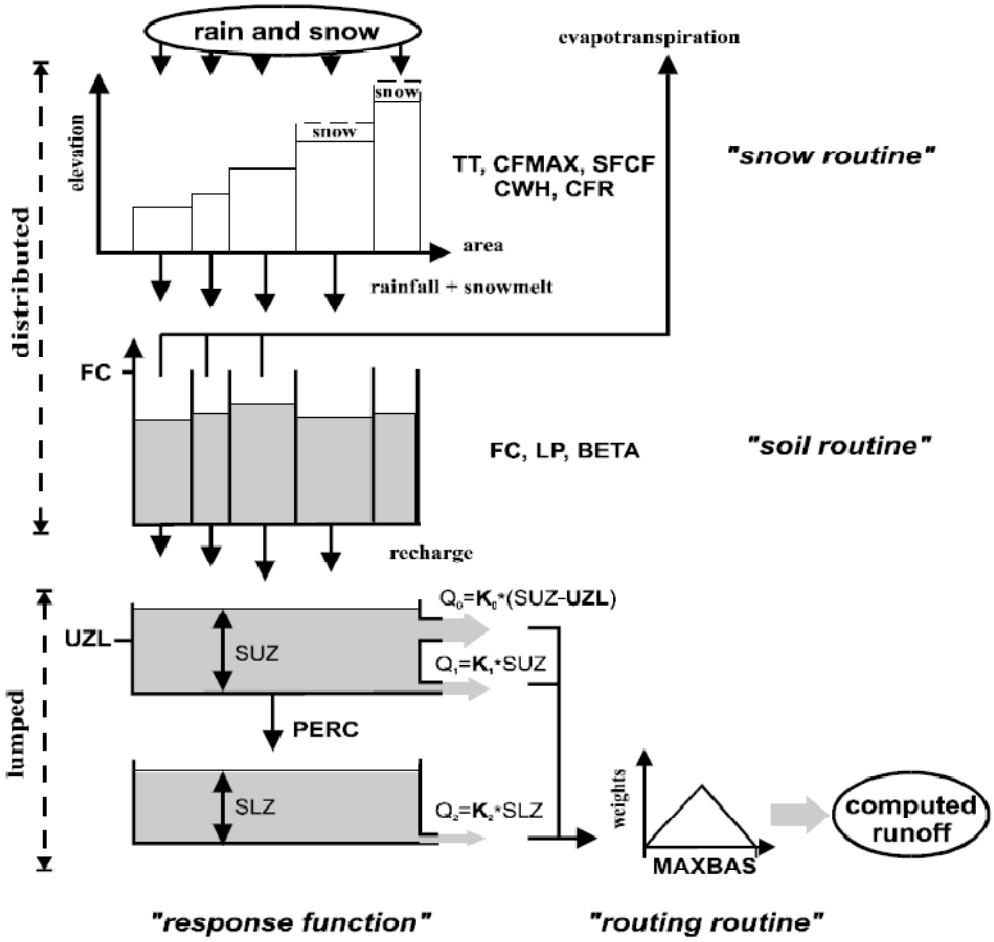

Figure 5. HBV model structure. From Seibert (2000).

2. Soil moisture routine. Rainfall and snowmelt are divided into water filling the soil box and groundwater recharge depending on the relation between water content of the soil box and maximum soil water content, FC (mm). BETA (-) determines the relative contribution to runoff from rain or snowmelt. Actual evaporation is equal to potential evaporation when actual water content divided by maximum water content is above LP (-). Below LP, a linear reduction is used.

3. Response function. SUZ and SLZ define the water storage in upper and lower boxes of the soil respectively. PERC (mm/day) is the maximum percolation from the former to the latter. Runoff from the lower box is calculated as a single outflow, while in the upper box there are two or one outflows depending on whether SUZ is above a threshold value, UZL (mm), or not. To calculate the outflow, three conductivity parameters, K_0, K_1, and K_2 (day^{-1}), are used.

4. Routing routine. The generated runoff is finally transformed by a triangular weighting function defined by the parameter MAXBAS (-) to give the simulated runoff.

4.2.2 Data sources for HBV model

In order to run the HBV model, two files are needed. The first is called a PTQ-file (named as ptq.dat) and contains time series of daily precipitation (mm), temperature (ºC) and flow (mm). The second evaporation-file (named as evap.dat) contains daily values of potential evaporation for the same period of time.

Daily records of rainfall and temperature were available from SMHI at two stations located in the city of Uppsala (Figure 4), where the Fyrisån has its outlet. The available time period consisted of 29 years (1980 to 2008). Unfortunately, no observed flow data for Fyrisån were available. However, measured flow data for the 14 years series 1996-2009 were available for its last and main tributary, the Sävjaån. Sävjaån subcatchment covers more than one third of the Fyrisån catchment (699 km^2 out of 1982 km^2). Parameters SMD and HER obtained by modeling Sävjaån flow can be considered as good estimates for the whole catchment.

Potential evaporation was calculated using the Thornthwaite equation (equation 1) (Shaw, 1994). The formula is based mainly on temperature with an adjustment being made for the number of daylight hours and gives a monthly estimation of the potential evaporation in millimeters per unit of time:

$$PE_m = 16 \cdot N_m \cdot \left(\frac{10 \cdot T_m}{I}\right)^a$$

Equation 1

where PE_m is monthly potential evaporation (mm), m is the months (1,2…12), N_m is the monthly adjustment factor related to hours of daylight, T_m is the monthly mean temperature (ºC), I is the heat index for the year and a is a parameter function of I.

Monthly mean temperature was calculated for the period 1989-2008 with data from the station in Uppsala. Yearly potential evaporation was obtained by summing the monthly results, given a value of 412 mm. This value had to be adjusted since estimation of actual evaporation gave a larger maximum value, 500 mm for the year 1997. The

estimations were made by subtracting annual discharge from annual precipitation. The adjustment consisted of adding 10 mm extra to each month to give a final value of potential evaporation of 532 mm.

4.2.3 Calibration of HBV model

The model was calibrated for the 12 years period 1996-2008, the longest possible with the available data. The HBV model provides the option of doing Monte Carlo runs. The calibration consisted of several Monte Carlo iterations with 100 000 runs each. The different parameters were examined after the simulations by looking at the model efficiency of each run. Only runs with certain minimal efficiency were examined. Therefore, model runs with better fits guide decision making about the upper and lower limits of each parameter for the next Monte Carlo iteration. Every time, the uncertainty of the sensitive parameters is reduced so the range of the parameters was smaller and the new iteration gave better runs. The process was repeated until no improvement in the model efficiency was achieved.

4.3 INCA-C model

4.3.1 Description of INCA-C model

The dynamic, semi-distributed, process-based INCA-C model simulates DOC concentrations, fluxes and water flow in a daily time-step, so the biogeochemical dynamics of organic carbon within a single catchment can be investigated. Recently, the model has been also used to project the effects of climate change and acid deposition on DOC concentrations in surface waters (Futter et al., 2009) and investigate the effects of different land cover uses (Oni et al., 2010).

INCA-C interface is divided in four main groups of parameters which describe the processes represented in Figure 6 and Figure 7:

1. Subcatchment parameters. To specify the areas of the different land cover types (up to six). It includes information about runoff and water flow which is used in a hydrological submodel (Figure 6).

2. Reach parameters. To simulate the transformations in the aquatic phase (Figure 7). It also includes the catchment boundaries and parameters used in the hydrological submodel to simulate water flow (Figure 6).

3. In-stream parameters. To describe the initial conditions in the stream.

4. Land phase parameters. To simulate material fluxes through the soil column and transformations between carbon stocks (Figure 7).

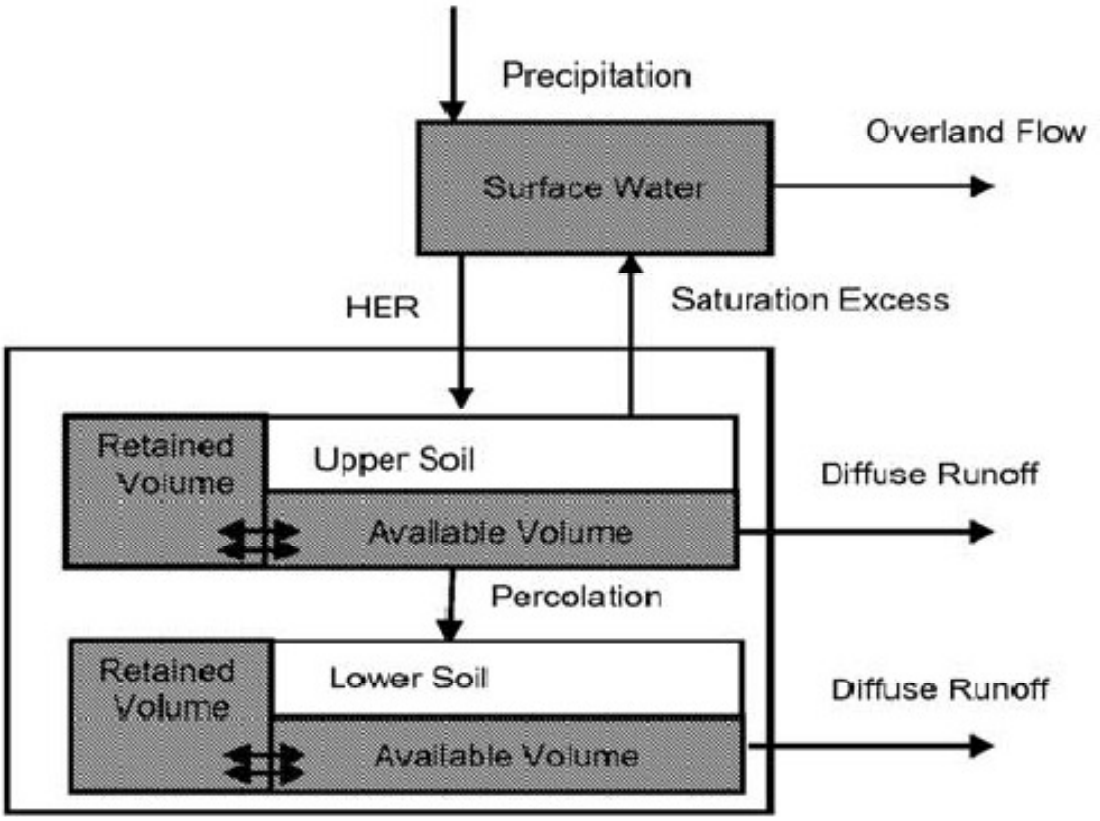

Figure 6. Terrestrial hydrological submodel in INCA-C (from Futter et al., 2007).

The model needs both daily observed time series of air temperature and precipitation, and daily estimates of SMD and HER. Air temperature and a model from Rankinen et al. (2004) are used in INCA-C to simulate both soil and stream water temperatures. The soil moisture deficit (SMD) is an estimate of the difference between the maximum soil water content and the actual amount of water in the soil. The hydrologically effective rainfall (HER) represents the net precipitation, either as rainfall or snowmelt, that can infiltrate after the evapotranspiration effect (Oni et al., 2010). The two estimates can be calculated by an external runoff model, in this case, the HBV model. Besides, time series of observed flow and DOC concentration in the surface water are necessary in the calibration process.

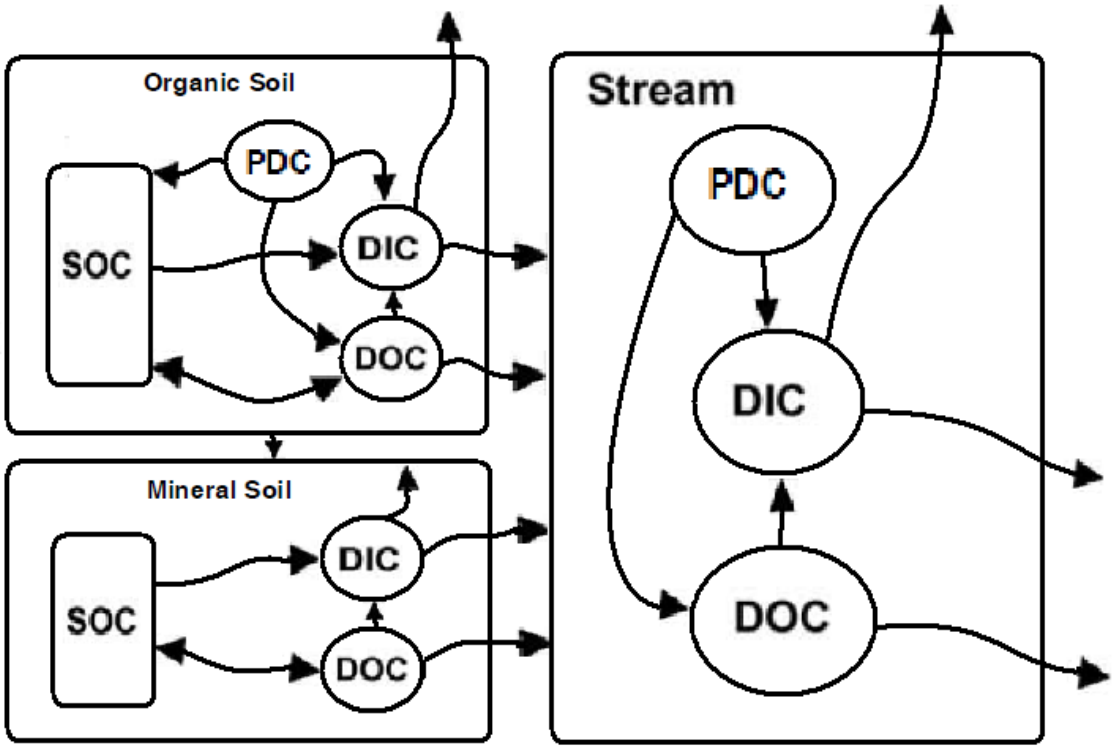

Figure 7. Pools of carbon, fluxes and transformations in terrestrial and aquatic systems in INCA-C (modified from Futter et al., 2007).

INCA-C divides the terrestrial environment into two boxes for each land use considered: the upper organic layer and the lower mineral layer. The modeled catchment can be divided as up to 6 different land cover types. The functioning of INCA-C is divided into two interconnected submodels. On one hand a hydrological submodel simulating the water flows in the soil and to the stream (Figure 6) and on the other hand a carbon model which simulates fluxes and transformations between the different carbon pools in both the terrestrial and the aquatic compartments (Figure 7). A brief description of both submodels is presented next.

Hydrological submodel (Figure 6).

Three water pools are represented in the model: the soil surface water and the water in the upper and lower soil boxes. Precipitation reaches the soil surface and may be accumulated (mostly when is in the snow form) or contributes to overland flow. HER is the only form in which water enters in the soil. Once in the upper soil layer, water may percolate to the lower soil box, return to the surface as saturation excess overland flow or diffuse to the stream as diffuse runoff. All water entering the lower soil horizon will be eventually lost to the stream as diffuse runoff. Water in both soil boxes is divided into drainage water and retention water. The retention volume is fixed and unchanging

and corresponds to the volume of water in the soil at the permanent wilting point (Futter et al., 2007), while the drainage volume includes the water that can eventually reach the stream.

Submodel of carbon transformations and fluxes (Figure 7).

Four different carbon pools are considered in INCA-C: (1) potential dissolved carbon (PDC) which consists of leaf litter, root exudates and soil microflora in the terrestrial system and leaf litter from the terrestrial compartment, particulate organic carbon in the water column and aquatic biota in the aquatic environment (Whitehead et al., 2006); (2) soil organic carbon (SOC) which includes all organic carbon bound to the mineral and clay constituents of the soil and the microbial community attached to the soil substrate (Whitehead et al., 2006); (3) DOC and (4) dissolved inorganic carbon (DIC). In the upper soil box, PDC is the only source for the other three carbon pools SOC, DOC and DIC, so neither DOC nor DIC are directly added in precipitation. DOC and DIC are transported advectively by water movement from the upper to the lower soil box, DOC is the only source of SOC in the lower soil layer. In both layers sorption and desorption processes control the transformation between SOC and DOC and mineralization controls the transformation of SOC and DOC to DIC (Futter et al., 2009). Both DOC and DIC are transported from the soil to the stream through diffuse flow (Futter et al., 2007) and DIC may be lost to the atmosphere through degassing (Futter et al., 2009). In the stream, inflows from upstream and the soil and aquatic PDC contribute to DOC and DIC. DOC is lost by photolytic and temperature-dependent biological mineralization to DIC and in the outflow downstream. DIC is lost to the atmosphere and through biological uptake (both temperature-dependent processes) and in the outflow downstream.

Extended information about INCA-C with model equations is provided in Futter et al. (2007).

4.3.2 Data sources for INCA-C model

INCA-C needs two files when simulating DOC within a single catchment. The first file (.dat file) includes daily time series of SMD, HER, temperature and precipitation. This file is enough to run the model. Another file (.obs file), which contains both measured discharge and measured DOC concentration, is needed in the calibration process.

Temperature and precipitation data were the same that previously were used in the HBV model calibration from the two stations in Uppsala (Figure 4). Daily estimations of SMD and HER for the period 1996-2008 were obtained from the HBV calibration of Sävjaån flow. The Sävjaån subcatchment covers approximately one third of the Fyrisån catchment, so the SMD and HER calculated for Sävjaån are considered as good estimates for the whole Fyrisån catchment.

No measured flow data for Fyrisån were available in this project, although this information is essentially needed in the calibration. The decision was to upscale the input flow by multiplying the observed Sävjaån flow by its corresponding areal fraction (1982 km^2 / 699 km^2 = 2.84) to get an approximation of the actual discharge in Fyrisån. When comparing S-HYPE simulated Fyrisån flow and measured Sävjaån flow (Figure 8) one observes that both inter- and intra-annual flow patterns are very similar in both rivers confirming the approximation made here. No measured DOC were available so TOC concentrations in Fyrisån outlet were used (Table 2 and Table 3). Assuming that particulate organic carbon is not quantitatively important and that both TOC and DOC follow the same patterns during and between the years, we consider that TOC concentrations are a good substitute for the DOC calibration.

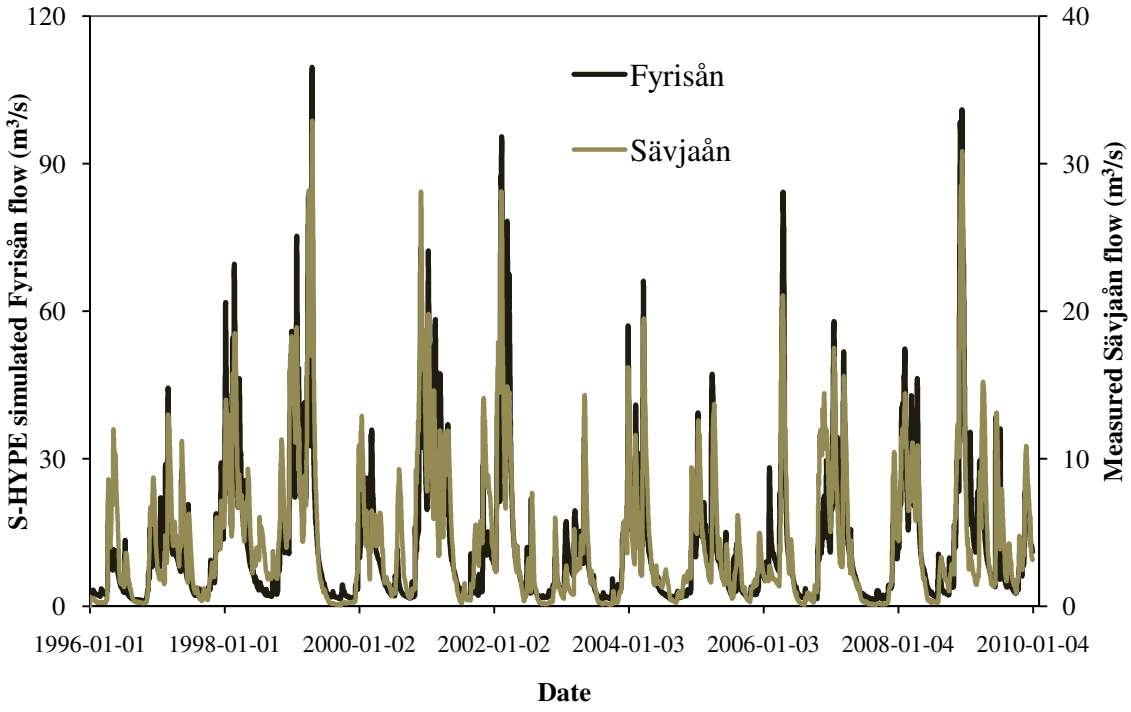

Figure 8. Comparison between observed flow in Sävjaån outlet and simulated flow in Fyrisån outlet for the period 1996-2009.

4.3.3 Calibration of INCA-C model

The calibration process for the period 1996-2008 was carried out in three different phases: (1) selection of fixed values for some parameters, (2) manual calibration of first hydrological submodel and second carbon module and (3) a Monte Carlo simulation.

Selection of fixed values

The Fyrisån catchment was divided in three different land uses: wetlands (6 %), forests (63 %) and agricultural land (31 %) (subcatchment parameters). The boundaries of the catchment (reach parameters) and the initial flow and DOC in the stream (in-stream parameters) were fixed. This information is easily extracted from the observed data but the initial values in the soil (land phase parameters) had to be estimated. Typically, the upper soil horizons (peatlands and forest floors) have higher SOC and DOC concentrations. The SOC and DOC in the upper soil box in wetlands were fixed to $8 \cdot 10^5$ kg/ha and 40 mg/l respectively. We considered that wetlands have double the amount of carbon than forests and forests double the amount of carbon than agriculture and that the upper soil boxes twice as much as the lower horizons in all cover types. Therefore, for instance, the SOC and DOC in the lower box in the agricultural land were 10^5 kg/ha and 5 mg/l respectively. These values were not modified during the calibration.

Manual calibration

This phase is crucial to achieve a good approximation to the observed values before proceeding with Monte Carlo simulations. The strategy was first to establish realistic values for the sensitive parameters such as base flow index (BFI), soil volumes or residence times, until both simulated flow and simulated DOC were in the range of the observed values. Then, the parameters affecting both hydrological and carbon submodels were adjusted until most of the flow and carbon dynamics matched the observed data. Finally, the parameters describing carbon transformation in the soil were adjusted. The objectives of this phase were: (1) to achieve a similar efficiency in the flow model that that obtained previously in HBV model and (2) to get a Nash-Sutcliffe (NS) R^2 statistic (Nash & Sutcliffe, 1970) of at least 0.2 in the carbon model.

Monte Carlo simulation

A Monte Carlo iteration varying the most uncertain parameters with 10000 simulations was carried out in order to get a better calibration. The parameter set with the best NS R^2 statistic was the one finally selected.

5. RESULTS

5.1 Data handling and mass transport calculations results

5.1.1 Flow data comparison

Comparisons for those streams with measured flow data and model data show that S-HYPE underestimated the discharge for the period of overlapping (1995-2008). On average the underestimation is 12 % for Hedströmmen; 2.5 % for Svartån; 22 % for Örsundaån and 3.4 % for Köpingsån. The underestimation can be considered not very important for Svartån and Köpingsån. The pattern is that S-HYPE overestimates the flow during winter time (especially February and March) and underestimates flows during summer (more than 30 % in all cases in July).

Comparisons for those streams with both series of flow data from models show very heterogeneous results, with no general pattern. The worst case is found in Eskilstunaån, where average flow is 37 % larger when using S-HYPE (120 % on average for June). Due to the uncertainty of the source of some information from the second group of flow data and to the fact that S-HYPE is a better and newer model than PULSE and HBM, the second group of flow data were ruled out.

5.1.2 Relative contribution of water from the main streams.

The contribution of water that is discharged into the lake from every catchment in the period 1995-2008 can be calculated easily after computations of loads and flows by Flownorm 2.1 (Table 4). The results are very similar to those presented in Wallin et al. (2000) from the previous decades (Table 1). This may imply two things: (1) the contribution of each catchment remains constant with time and (2) the S-HYPE modeled flow used for some streams is a good approach to simulate the flow dynamics over a relatively long period of time. The exception is Eskilstunaån, in which S-HYPE could be overestimating the flow since the relative contribution increases from 14 % to 18 %.

Table 4. Computed water contribution of the main streams flowing into the Lake Mälaren with their catchment area for the period 1995-2008.

Stream	Outflow basin	Area (km^2)	Water contribution to Mälaren (%)
Arbogaån	A	3802	24.17
Kolbäcksån	A	3093	17.82
Hedströmmen	A	1058	6.67
Köpingsån	A	284	1.31
Eskilstunaån	B	4187	18.48
Svartån	B	754	3.44
Sagån	B	865	3.18
Råckstaån	C	239	0.93
Fyrisån	D	1982	7.66
Örsundaån	D	727	3.07
Oxundaån	D	271	0.84
Märstaån	D	71	0.27
Närområdet	A,B,C,D,E,F	-	12.17

5.1.3 Outlet stations comparison

The Mälaren outlet in Stockholm has two stations (Norrström Stockholm and Stockholm Centralbron) with overlapping data (Table 2 and Table 3) in the seven years period 1996-2002. The two stations are separated by 350 meters and located in two bridges at north of *Gamla* Stockholm with Stockholm Centralbron located upstream. Comparisons of annual areal exports for the computed substances show no significant differences between the two stations. However, the color load as AbsF and the TOC load are 7.1 % and 0.88 % respectively higher on average in Stockholm Centralbron. A special observation is that the calculated ammonium NH_4 loads are 85 % lower in Stockholm Centralbron (200 % lower in 1998). Hereafter all the references to the Mälaren outlet correspond to calculations using Stockholm Centralbron data, except those for 1995 where Norrström Stockholm data are used. The criterion was to use information from the newest station, Stockholm Centralbron. In 1995 only data from Norrström Stockholm were available.

5.1.4 TOC and color fluxes within the catchment

A brief summary of the main results obtained after computing loads of the different substances per unit of area in each station within the Mälaren catchment is presented

next. Tables with all the results are presented in the appendix. Besides, TOC and color fluxes are compared.

Table 5. Subcatchment sizes and land uses within the Mälaren catchment. Other land types include cutting forest and urban areas.

Catchment	Area (km^2)	Wetland (%)	Forest (%)	Agriculture (%)	Open water (%)	Others (%)
Arbogaån	3802	7.07	60.25	14.18	7.11	11.39
Kolbäcksån	3093	7.69	66.32	6.48	8.96	10.56
Hedströmmen	1058	9.69	63.67	9.15	8.27	9.23
Köpingsån	284	7.85	63.05	16.07	5.02	8.00
Eskilstunaån	4187	4.94	44.22	28.70	14.65	7.49
Svartån	754	7.13	54.66	26.20	3.29	8.73
Sagån	865	2.86	45.78	40.88	1.23	9.25
Råckstaån	239	5.45	60.71	19.70	5.30	8.84
Fyrisån	1982	4.13	51.00	30.91	1.56	12.41
Örsundaån	727	2.92	47.37	38.90	1.26	9.55
Oxundaån	271	1.56	33.79	37.73	6.22	20.70
Märstaån	71	0.95	31.01	36.11	0.54	31.39

- *Arbogaån Kungsör*. Only data for 1995 were available. Having as reference this year, Arbogaån shows one of the highest colored waters indicating that a major absolute contribution of carbon comes from this catchment since it is the second largest. Base cations and nitrogen areal exports are slightly below the average of the whole catchment.

- *Kolbäcksån Strömsholm*. The characteristics of Kolbäcksån catchment are similar to Arbogaån regarding land use, leading to similar areal loads. However, data from 1995 indicate less colored waters in Kolbäcksån.

- *Hedströmmen Grönö*. This catchment has similar characteristics to those Arbogaån presents, but shows the lowest loads on base cations and nitrogen in the year 1995. The differences may be due to differences in geology.

- *Köping II*. Köpingsån is included in the same group of catchments as the previous three, which all present similar characteristics and are located next to each other. The main difference here is a higher areal nitrogen flux due to the presence of more agricultural land.

- *Eskilstunaån Torshälla*. It is the largest subcatchment with only data for 1995. Water color in that year was the lowest in the whole catchment together with Oxundaån suggesting a small contribution of carbon per unit of area. On the other hand, the sulfate and base cations inputs are high.

- *Svartån Västerås*. Svartån has only data for 1995 but for color in the filtered samples and permanganate the values are the highest suggesting that this subcatchment could be the largest contributor of carbon per unit of area. The other parameters are about the average of the whole catchment.

- *Sagån Målhammar*. One of the main nitrogen inputs come from Sagån catchment.

- *Råckstaån Utl*. It is a small catchment with areal loads of substances around the average.

- *Fyrisån Flottsund*. Fyrisån is the fourth largest subcatchment and the most important in the east part. Having Kolbäcksån as the representative of the larger forested catchments in the west, Fyrisån contributes with more carbon per unit of area in most of the years in the period 1997-2009 (Figure 9). The nitrogen loads are the highest. Plus, sulfate exports and base cations are high.

- *Örsundaån Örsundsbro*. Örsundaån is smaller but similar to Fyrisån with lower loads per unit of area in general. However, water color is usually higher.

- *Oxundaån Rosendal*. It is the second smallest subcatchment and the lowest contributor of carbon per unit of area. It contributes with large sulfate and base cations inputs. Chlorine is also high.

- *Märstaån Utl*. It is the smallest subcatchment with the largest human influence; two thirds of the catchment corresponds to either agricultural or urban areas (Table 5). Nitrogen and sulfate areal exports are high.

- *Mälaren outlet*. Carbon outputs are low since organic substances are gradually broken down and diluted as they flow to the sea.

Annual TOC areal exports are compared for six of the catchments flowing into Mälaren and the outlet in Figure 9. The highest inputs of carbon per unit of area come from Kolbäcksån, Fyrisån and Örsundaån, while the lowest loads are found in Oxundaån and

the outlet. The interannual patterns are in general very similar in all places. The differences one can see, for instance in the year 2000, come from differences in total modeled runoff. Fyrisån and Oxundaån have less water entering the lake in 2000 compared with that in 1999, while Kolbäcksån, Råckstaån and the outlet shows an increasing in water loads (Figure 11). This suggests a positive relationship between amount of water and mass of carbon exported per unit of area. This relation is studied later in the next section (Figure 12 and Figure 13).

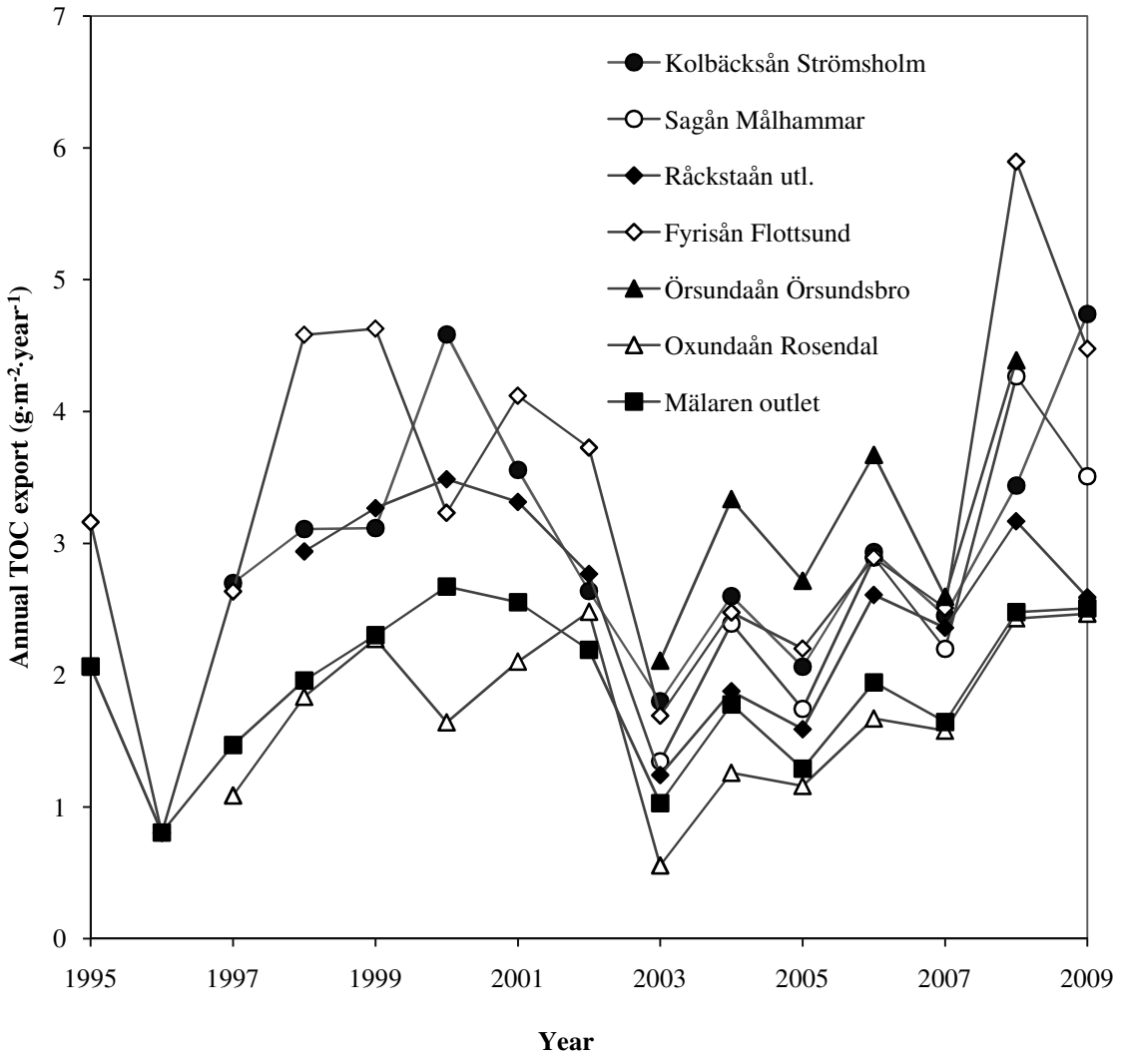

Figure 9. Loads of TOC in $g \cdot m^{-2} \cdot year^{-1}$ in six subcatchments of Lake Mälaren and the outlet.

Color of filtered samples shows similar patterns (Figure 10). Örsundaån shows the highest contribution of color per unit of area, while the lowest are found in Oxundaån and the outlet. These similar results in the dynamics and in the relative importance of both TOC and color loads from the streams indicate that carbon content and water color

are intimately related, although with some slight differences. The relative importance of areal exports from Sagån and Örsundaån are higher for color than for TOC fluxes. For instance, color fluxes are generally higher in Sagån than in Kolbäcksån, while for TOC is the opposite. This indicates that in some streams some different mechanisms or processes might influence the water color, while for some others such as Kolbäcksån or Fyrisån the water color in mainly controlled by the TOC concentration, as Figure 14 shows in the next section.

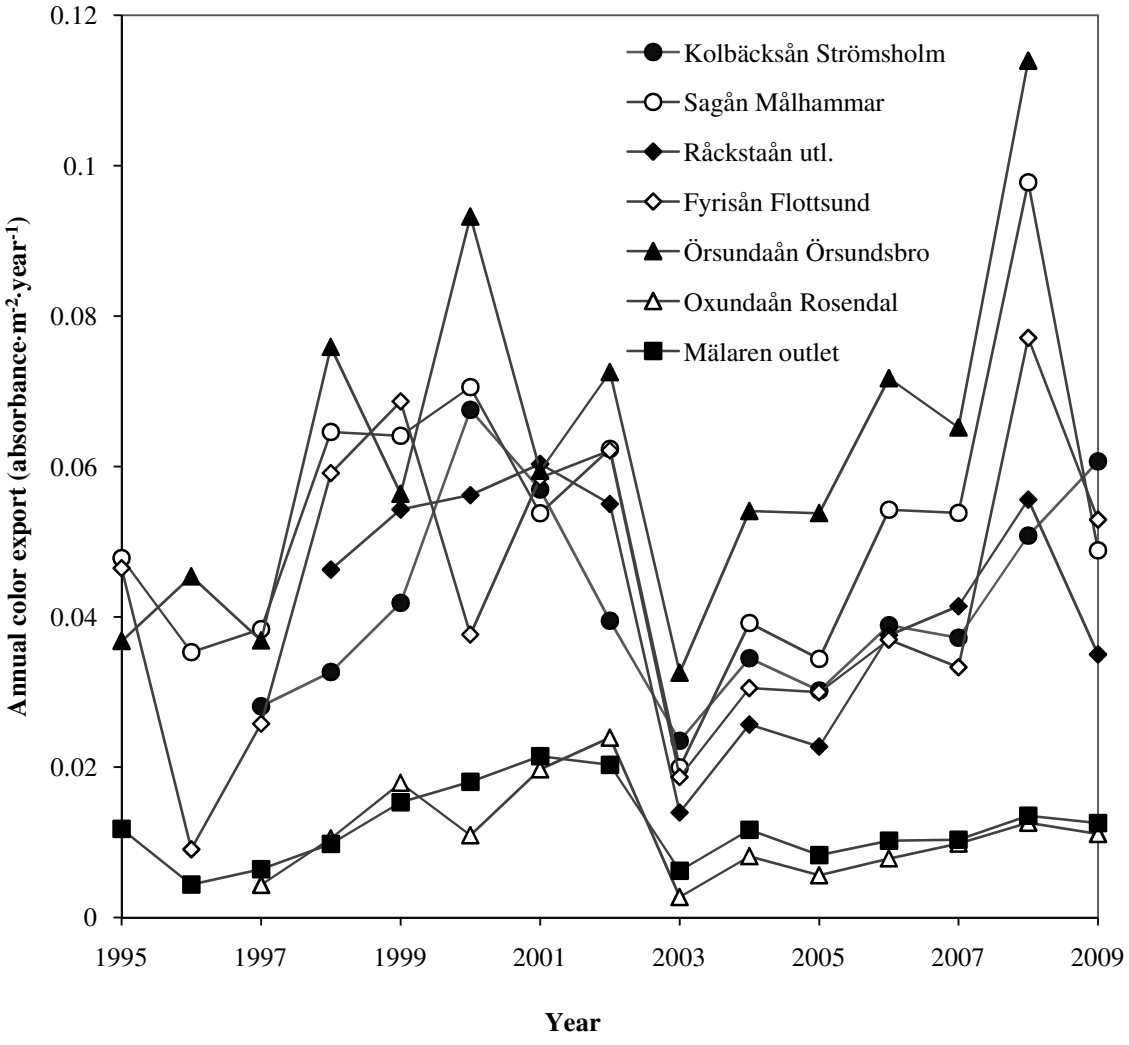

Figure 10. Annual color loads per unit of area from six subcatchments of Lake Mälaren and the outlet. Color is measured in filtered samples.

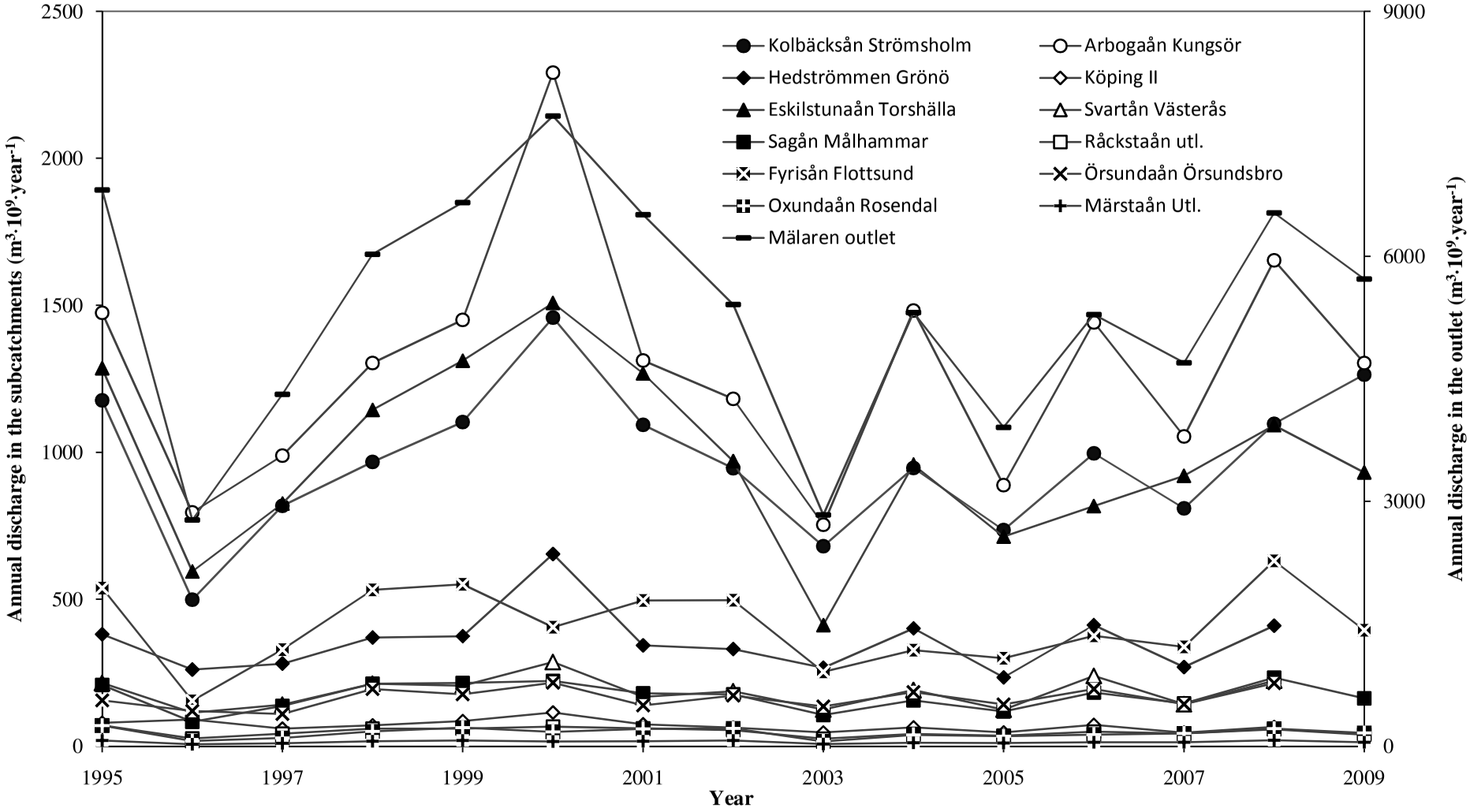

Figure 11. Annual runoff export from the different subcatchments of the Lake Mälaren and from the outlet.

5.1.5 Exported TOC correlations at Fyrisån Flottsund and Mälaren outlet

TOC exported per unit of area is well correlated to runoff in both Fyrisån subcatchment (r^2 = 0.820) and the Mälaren catchment (r^2 = 0.868) (Figure 12 and Figure 13). This indicates that the TOC concentration is mainly controlled by flow. The interannual value remains stable since the carbon exported is proportional to the discharge per year. Therefore, only big changes in flow may affect the TOC concentration. However, this tendency seems to change in the two catchments in the last two years of the time series (2008 and 2009), where the ratio exported carbon/discharge increases and so does the concentration. The period 1996-2000 of increasing discharge is follow by a decreasing in 2000-2003 in the outlet. On the other hand, the carbon follows the same pattern but the decrease is more gradual, suggesting a risk of prolonged increased TOC concentrations after periods with peaks in runoff.

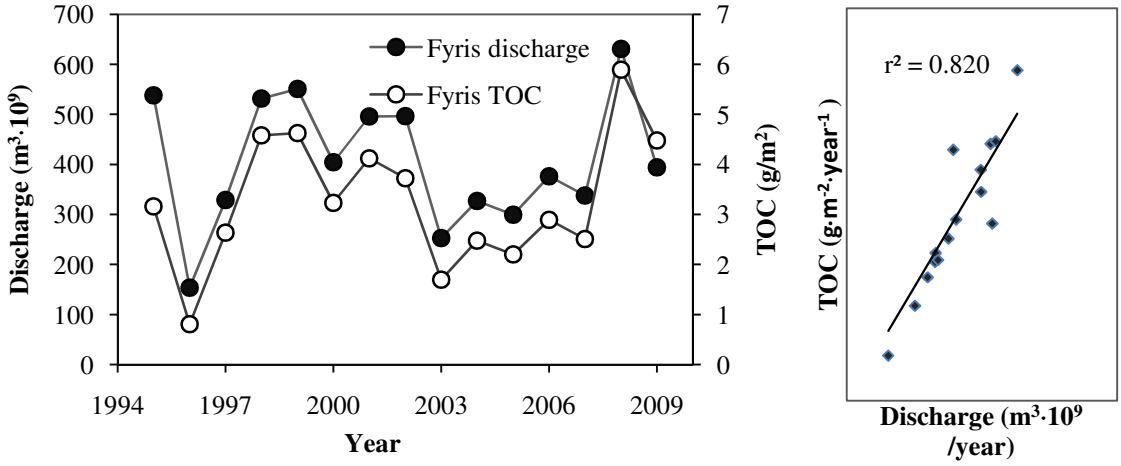

Figure 12. Correlation between mass of TOC per unit of area and volume of water transported from Fyrisån catchment

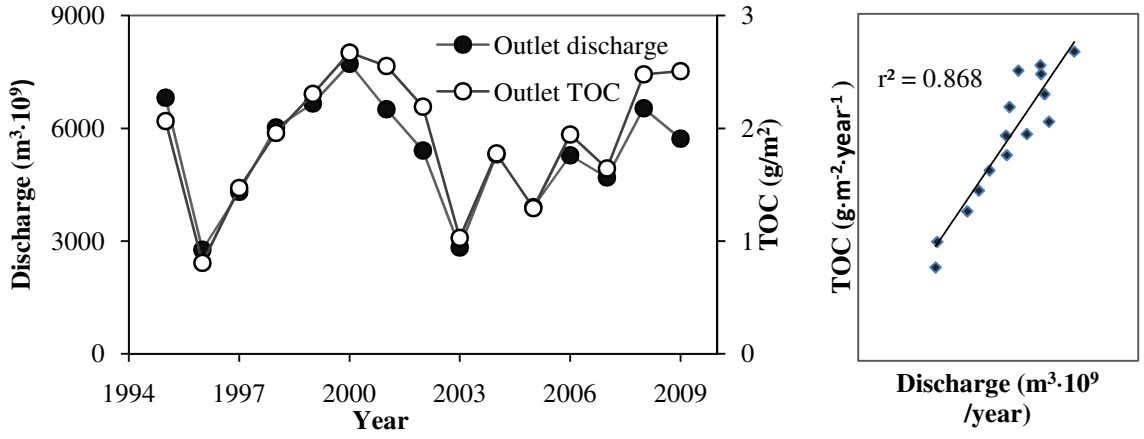

Figure 13. Correlation between mass of TOC per unit of area and volume of water transported from Mälaren outlet

The correlation between color and TOC export is marked and stronger in Fyrisån (r^2 = 0.919) than in the outlet (r^2 = 0.694) (Figure 14 and Figure 15). The good correlation in Fyrisån shows the strong relationship between organic carbon and the color of water in the catchment. The lowest peak corresponds to a very dry cold year while the highest peak corresponds to a very wet and warm year supporting the idea that warmer and wetter soils produce more organic carbon. The year 1999 was significantly drier than 1998 but discharge, color and carbon increased indicating that for some years the conditions of the previous year are important. The opposite happens in 2000, where despite of being wetter than 1999, the discharge, color and carbon all decrease. The lake shows several signs of poor color-TOC correlation at the outlet. For example, the relative importance of color decreases from 2003 onwards.

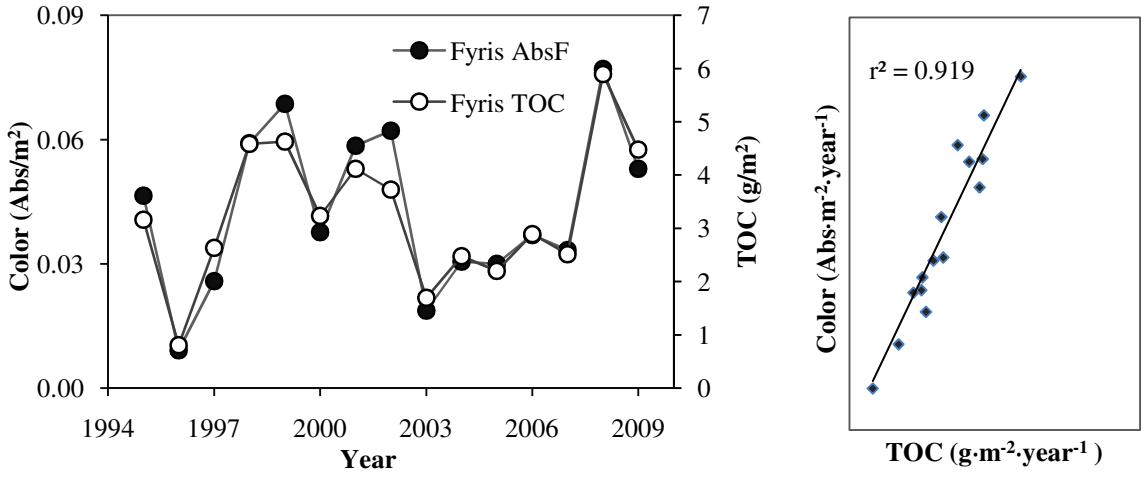

Figure 14. Correlation between mass of TOC and color of water transported per unit of area from Fyrisån catchment.

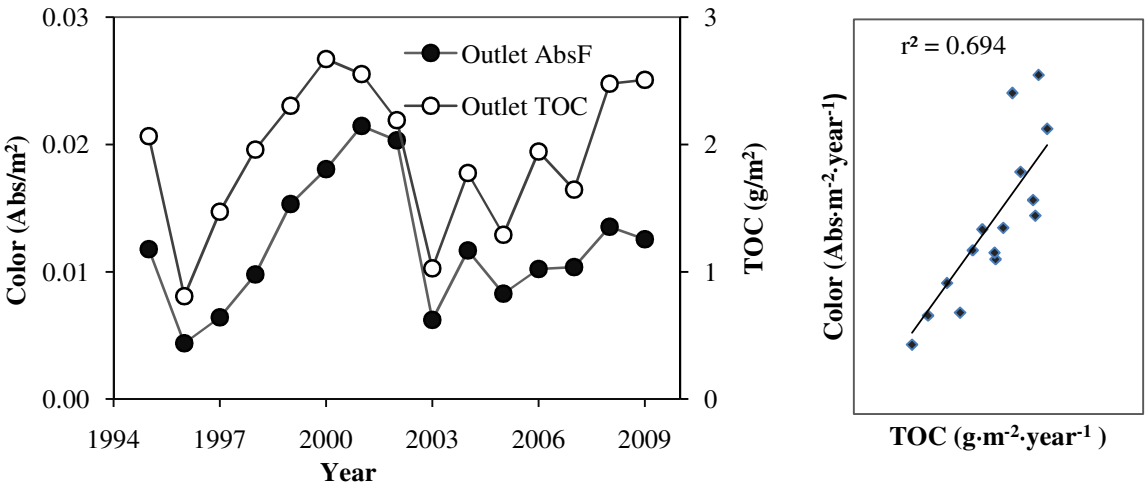

Figure 15. Correlation between mass of TOC and color of water transported per unit of area from Mälaren outlet.

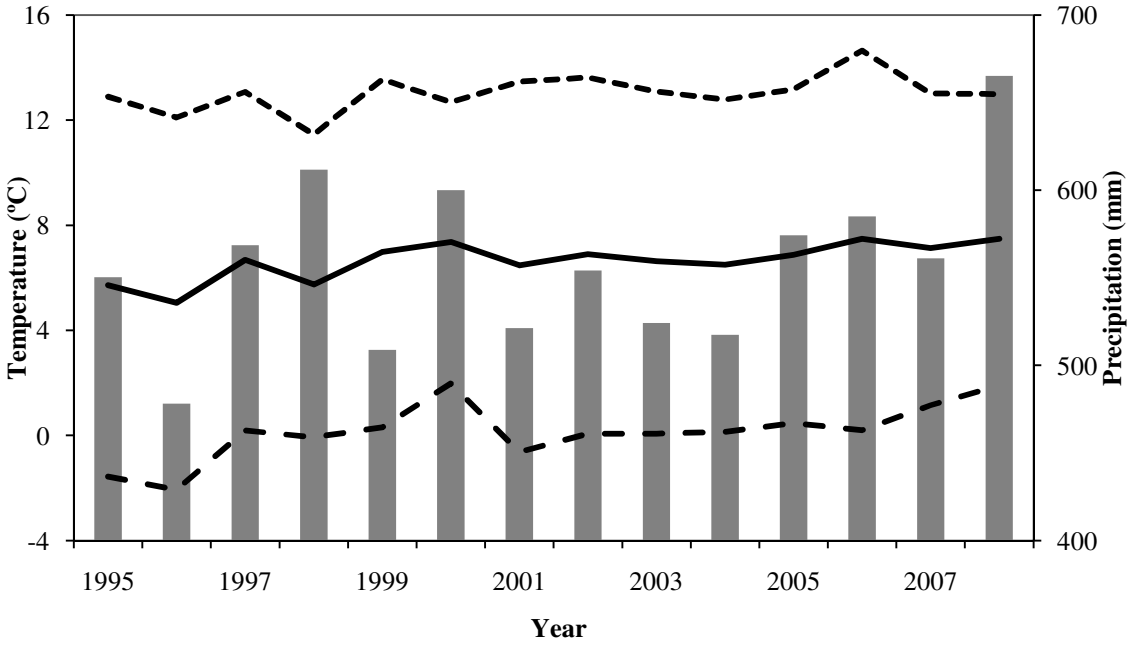

Figure 16. Climate data at Uppsala (1996-2008). In the figure: total precipitation (bars), mean temperature (continuous line), mean temperature during growing season May-October (upper dotted line) and mean temperature during no growing season January-April and November-December (lower sparse dotted line).

Sulfate and iron are two interesting compounds to look at regarding organic carbon. Sulfate competes with carbon for places in the soil (Kaiser and Zech, 1996), and the simulated correlation TOC-SO_4 suggests a bad relationship between them (r^2 = -0.09, Figure 17). Iron is theoretically co-transported with DOC (Maloney et al., 2005) and the similar dynamics and relative good correlation (r^2 = 0.731) showed in Figure 18 support this idea.

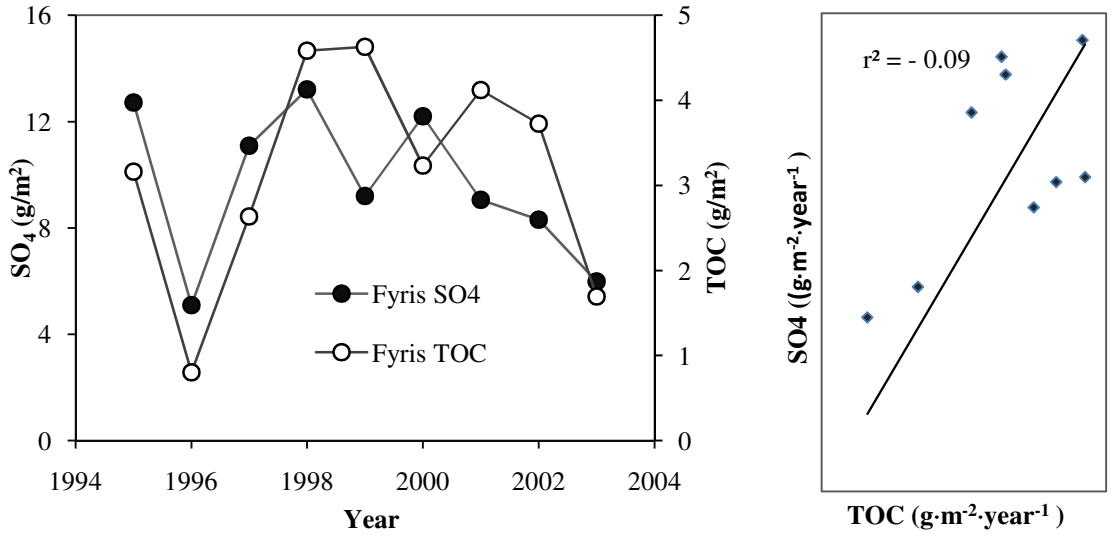

Figure 17. Correlation between mass of TOC and mass of sulfate transported per unit of area from Fyrisån catchment.

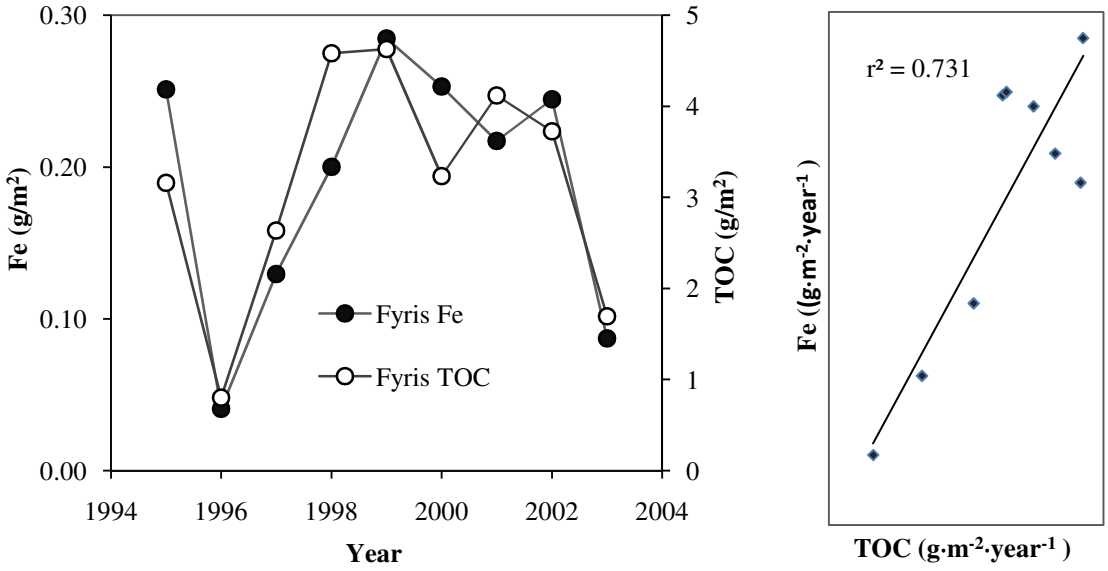

Figure 18. Correlation between mass of TOC and mass of iron transported per unit of area from Fyrisån catchment.

5.2 HBV model results

During the calibration process, some unexpected relations between precipitation and observed flow were found. Specifically, two extreme precipitation events in two summer days in 1997 and 2001, 108 mm and 78.5 mm respectively, did not produce any response in the observed flow. Two arguments could explain this: (1) errors in the precipitation measurements or in the data handling for those days and/or (2) very local storms occurred in the surroundings of the weather station but not in the place where flow is measured. In the near station of Västerås (80 km from Uppsala) the measured precipitation in the same two days was 0 mm and 15 mm respectively. The decision was to delete the event with 108 mm and reduce by half the event of 78.5 mm. These changes helped to improve the model fit. The changes were kept in the subsequent INCA-C modeling.

One advantage of working with Monte Carlo simulations is the possibility of decreasing the uncertainty of the most sensitive parameters. No specific analysis on parameter uncertainty or sensitivity was carried out. However, simple plots of parameter values against model efficiency gave an idea of how the parameters are related to each other and helped to decide the ranges in following iterations. Table 6 shows the final parameter set. SFC, CFR, CWH and LP were given standard values in the first iteration and were unchanged during the calibration. TT has a low uncertainty, while the

uncertainty of CFMAX is higher. The final value of CFMAX is 1.0 $mm \cdot ºC^{-1} \cdot day^{-1}$, a low value which usually corresponds to forested areas. Sävjaån catchment can be considered as mainly forested with 65 % of the total area with this land type. FC shows a credible value of 135 mm with low uncertainty and BETA is more uncertain with a final value relatively high indicating important contributions of precipitation and snowmelt to runoff. The uncertainty of UZL is the largest, although it is also the less sensitive parameter. UZL uncertainty can be related with the low value of K_1. PERC is uncertain and so is K_0, while K_1 and K_2 has very low uncertainty. MAXBAS is somewhat uncertain. The fact that K_0 shows a final value significantly high, specially comparing with the low K_1 and K_2, indicates that the largest contribution of flow to the stream is from the upper soil, having the lower layers higher retention times. Nevertheless, this parameter is very uncertain.

Table 6. Final parameter set in HBV model calibration of Sävjaån flow. The model efficiency with these parameters is 0.766 for the period 1996-2008.

Parameter	Value	Units	Module
TT	-0.3	ºC	Snow routine
CFMAX	1.03	$mm \cdot ºC^{-1} \cdot day^{-1}$	Snow routine
SFCF	0.692	dimensionless	Snow routine
CFR	0.02	dimensionless	Snow routine
CWH	0.014	dimensionless	Snow routine
FC	135.13	mm	Soil moisture routine
LP	0.867	dimensionless	Soil moisture routine
BETA	7.087	dimensionless	Soil moisture routine
PERC	0.54	mm/day	Response function
UZL	70.84	mm	Response function
K_0	0.857	day^{-1}	Response function
K_1	0.0624	day^{-1}	Response function
K_2	0.0596	day^{-1}	Response function
MAXBAS	3.51	day	Routing routine

The efficiency of the best run with HBV model was 0.766 with an R^2 of 0.787, which can be considered as high. The HBV model performed well when describing flow patterns at Sävjaån for the period 1996-2008 (Figure 19). However, simulated average runoff was somewhat lower: 171 mm/year, compared with the observed one, 203 mm/year. Average precipitation is 559 mm/year given a simulated mean annual evapotranspiration of 388 mm, which is higher than the observed 356 mm/year. The assumptions used when calculating potential evapotranspiration could have lead to an

overestimation of the evaporation in the region, producing the slightly lower simulated average runoff. Some of the peaks from both simulated and observed flow do not match properly. This might be due to very local precipitation events, although the distance between the station where precipitation is measured and the station where flow is measured is only 5 km (Figure 4). Even so, the final parameter set used in HBV (Table 6) simulates properly the temporal patterns of Sävjaån discharge to the Fyrisån, reproducing well the general trends.

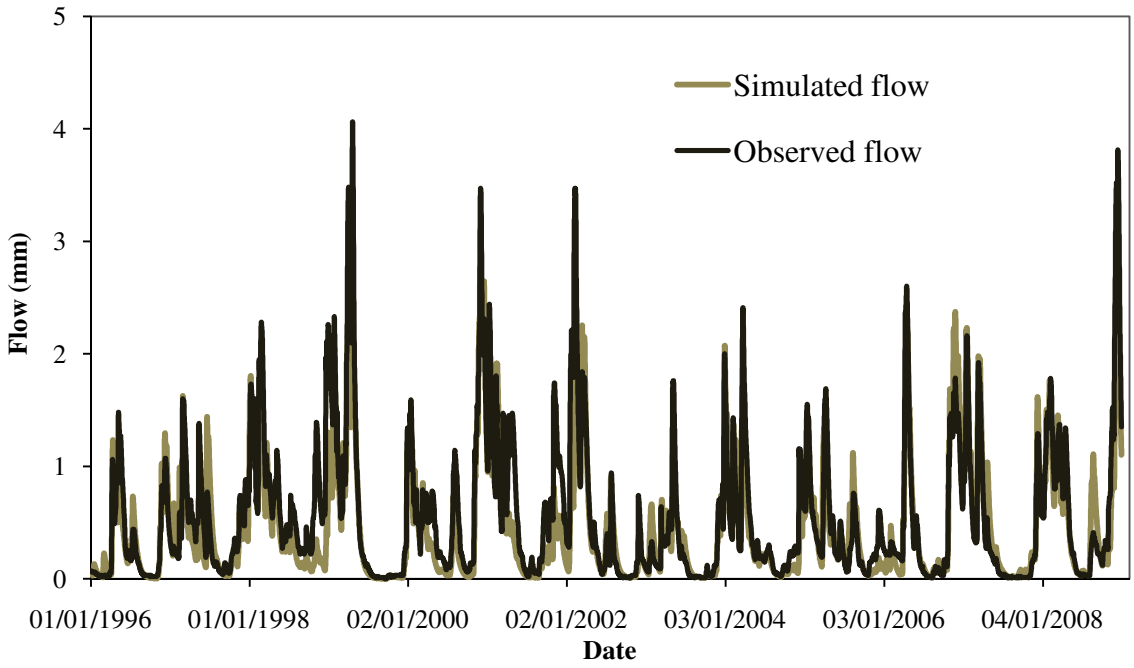

Figure 19. Observed and HBV simulated flow at Sävjaån for the period 1996-2009.

5.3 INCA-C model results

The results from the manual calibration of the model were very encouraging, achieving the objectives in both flow model (r^2 = 0.757, N-S = 0.745) and DOC model (r^2 = 0.245, N-S = 0.218). After the Monte Carlo simulation, the best parameter set improved significantly the DOC model (r^2 = 0.432, N-S = 0.392), with a similar efficiency in the flow model (r^2 = 0.752, N-S = 0.719). With these results we consider that the simulated hydrology is very good and the simulated carbon is good.

The INCA-C simulation reproduces well the intra- and interannual variation in DOC concentration (Figure 20). The model fails to capture some of the high peaks (especially "0008" and "0606" in Figure 20), although the timing is correct. The high concentration in summer 2000 that the model fails to capture corresponds to a year where the non-

growing season, i.e. winter and early spring, was especially warm (Figure 16). Also, the peak in the summer of 2006 that the model is unable to reproduce corresponds to a year when the growing season, i. e. spring and summer, is especially warm. Two conclusions can be draw from these results: (1) peaks in DOC are linked to especially hot periods and (2) the model is unable to predict high concentrations related to warm conditions. Although the model does a better job in reproducing the lower concentrations, in some cases there is an overestimation. Despite a good reproduction in the general trends, these problems on capturing both high and low concentrations make the model consider DOC more stable that it really is, not covering all the range of observed variation.

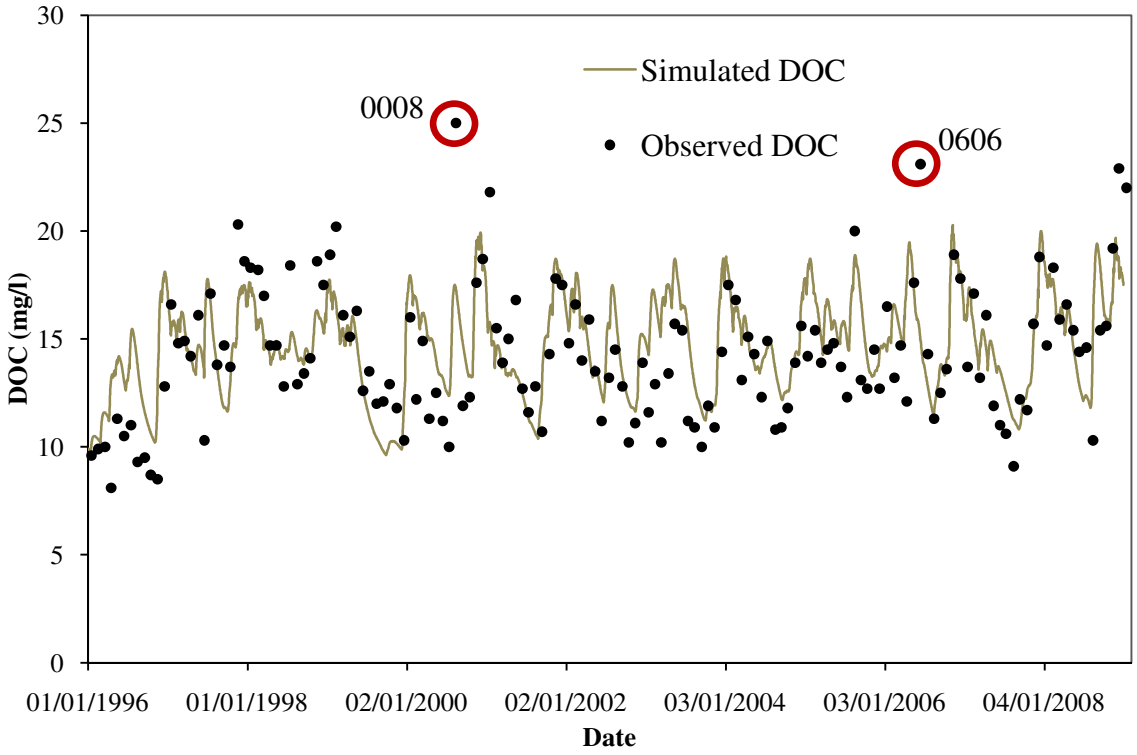

Figure 20. Observed and INCA-C simulated TOC at Fyrisån for the period 1996-2008. The two most deviated values are marked as "0008" and "0606".

6. DISCUSSION

A considerable amount of data was handled during the course of this project. Only part of the information could be subject of investigation, but future researches are necessary to complete the task given here.

In the first phase of this project, comparisons of areal export of substances were done in an annual scale despite the tool Flownorm 2.1 calculates also the monthly values. For some subcatchments of the Mälaren flow data were S-HYPE modelled. Lindström et al.

(2010) conclude that S-HYPE model provides good simulations of discharge. However, it was shown after comparisons with measured data in four subcatchments that the model works well over annual periods but have serious mismatches in the individual months. Thus, it was more convenient to work in the annual scale to avoid possible significant errors in the monthly calculations despite this information could be less relevant from the managing point of view.

There are differences in the carbon inputs per unit of area flowing into the Lake Mälaren from the different subcatchments. For example, the eastern Fyrisån and Örsundaån contribute with more carbon and color per unit of area than the large forested catchments in the west. According to Löfgren et al. (2003) high concentrations of humic substances, which are the main cause of water color, occur mainly in peat and forest covered areas with few lakes. Less open water leads to less water retention times so the humic substances are rapidly mobilized with lower mineralization. The results suggest more rapid responses in the Fyrisån and Örsundaån catchments due to lower retention times. The opposite example is the Eskilstunaån catchment which contributes with very low carbon per unit of area. Here, there is a significant proportion of open water (15 %) which increases the retention time of water in the catchment leading to mineralization and dilution of carbon. Besides, the forest proportion in Eskilstunaån is lower than in other subcatchments so the carbon sources are reduced. The high color found in Sagån could be caused for the same reason since open water comprises 9.0 % of the area in Kolbäcksån catchment, while the proportion in Sagån is only 1.2 %. But some other mechanisms could explain differences in water color. Higher open water also tends to higher photobleaching and loss of color (Reche and Pace, 2002). Fyrisån and Örsundaån are very similar catchments with similar carbon contributions but different water color: Örsundaån has browner waters. In this case we speculate on hypothetical higher iron content in the soil which is usually related to browner waters (Forsberg, 1992) and/or more sedimentation of organic material from erosion processes.

Nitrogen, sulfate, base cations and chlorine were also subject of a small investigation. High nitrogen inputs are intimately related with larger agricultural land, see for example Fyrisån (31 %) and Sagån (41 %). Small catchments such as Oxundaån and Märstaån show high sulfate and base cations loads. The urban area here is significantly important leading to higher sulfate deposition from industrial activity. In Sweden sulfur deposition shows a pronounced gradient, with decreasing deposition from south to north (Fölster &

Wilander, 2002). Eskilstunaån is may be more influenced than other catchment by this phenomenon and that is why it presents higher sulfate inputs. The high content of base cations is intimately related to acid deposition since the environment needs them to buffer the sulfate. High chlorine is more related to sea influence as the catchments close to the coast show higher loads of this element.

Annual TOC exports are well correlated to discharge in both Fyrisån and Mälaren outlet suggesting that TOC concentration is controlled by flow. However, after annual peaks in runoff the ratio TOC/discharge increases in the following years, meaning that TOC concentration increases in those years. Besides, these peaks in runoff are related to wet years. The year 2008 was very wet in the Fyrisån catchment which might explain the increase in TOC concentration in 2009. If we assume that the climate change will bring more precipitation, the expectations are higher carbon concentrations. The TOC concentration in the lake is also very high in 2009. What happens in Fyrisån could be very important on what happens in the Mälaren. More studies are needed in order to relate TOC dynamics in the Fyrisån with TOC dynamics in the lake.

There is an important concept to be considered when modeling complex environmental systems, the so-called equifinality. According to Beven & Freer (2001), the equifinality is produced when several or many different parameters sets within a model may be behavioral or acceptable in reproducing the observed behavior of that system. The causes are the overparameterization and the compensatory effects across the parameter space. The Monte Carlo simulations during the HBV model calibration give thousands of different parameter sets with similar efficiency. Although the uncertainty can be minimized by reducing the parameter ranges, there is still an important degree of equifinality in the last iteration where thousands of parameter sets are close to the best simulation with the parameter measuring conductivity in the upper layer having values varying between 0.1 and 0.9 day^{-1}. This variability is compensated with the variability in the two related parameters PERC and UZL. Thus, different combinations of these three parameters produce the same result, leading to equifinality. Signs of equifinality were also noticed during the manual calibration of INCA-C model. For example, the model efficiency was the same when considering a low retention time in the mineral layer with low rates of DOC production than high retention times with high productions. Since the experience let us know that retention times are usually higher in mineral layers than in organic layers, the second possibility is considered better. This

point out the importance of a first manual calibration to produce more realistic parameter sets.

INCA-C is used in this project in a significantly bigger catchment that it was used before. The experience can be considered as successful, but the combination of different land types and the large range of conditions that can be found in an 80 km stream within a 1982 km^2 catchment might be too big for a single model. Furthermore, some processes are different in the headwaters than in the outlet such as the DOC mineralization, which is more important upstream (Köhler et al., 2002). Therefore the longer the stream the larger the chance to have different conditions and omit information with one single model. In this sense, an intentional omission of information was done when dividing the catchment in land uses. The 2 % urban area of the Fyrisån catchment was not considered in the model. This was done to simplify the inputs and make the calibration easier. Besides, among all the previous projects in which INCA-C was used, only in one of them (Oni et al., 2010) the urban land type was introduced. The results in that project were good. However we preferred to share the small 2 % urban area between the other more studied land types: wetlands, forest and agriculture.

Two approximations were used in the Fyrisån input data to INCA-C: (1) estimates HER and SMD from HBV model and subsequent water flow upscale from the tributary Sävjaån and (2) TOC concentration measurements considered as DOC. There is no possibility to estimate to what extent the error from these considerations could influence model simulations. Nevertheless, Sävjaån is big enough to represent the whole catchment. Plus, TOC concentration has been described as effectively equivalent to DOC concentration in previous studies. Laudon et al. (2004) suggested that POC contributed insignificantly to the TOC in a study based in seven boreal catchments in northern Sweden. Balogh et al. (2003) found that 82-96 % of the TOC in a Hungarian lake was in the form of DOC.

Further work in parameter sensitivity would improve the understanding of the important parameters and thus, the model calibration itself. However, typical sensitive parameters in previous INCA-C applications such as base flow index, in-soil DOC transformations, residence times and retention volumes were found as sensitive here as well. Special concern rises from two parameters describing stream velocity. INCA-C uses Equation 2 to calculate the water velocity in the stream, with the dimensionless “a” and “b” as

model parameters. They both show high sensitivity. Considering a spring peak flow of 80 m^3/s and a stream velocity of 1 m/s in Fyrisån, "a" and "b" should have values around 0.05 and 0.7 respectively (the model responded better with "b" values around 0.7). However, these values produce very good flow simulations but lead to a very poor simulation of DOC concentration. The simulated signal is faster than the observed data. In order to reproduce a good pattern the "a" value needed to be reduced one order of magnitude. The simulated flow is still good but the result is a slower flow than in reality. TOC is sampled monthly so it is not possible to catch a lower time-scale variation which could be more accurate to represent the velocity in the model.

$$v = a \cdot Q^b$$

Equation 2

Most of the parameters in the INCA-C had to be calibrated manually since no data on actual conditions were available. This lack of information leads to a high uncertainty in the values. For instance, no inventories of carbon content in the soil were available and the initial values used were only estimations that did not change during the calibration. There is a risk of missing accuracy by unchanging parameters. However, we believe the values fixed are adequate to represent reality, giving higher values to wetlands and upper layers than forest and agricultural land and lower layers. Besides, the calibration is easier when some parameters are kept unchanged. Even so, better results would have been obtained with more data.

Despite all the aforementioned sources of uncertainty, INCA-C does a good job modeling the DOC in the Fyrisån catchment. However it fails to what is one of the main objectives of the model: predict high concentrations of DOC. Related to this problem, new results were obtained close to the end of this project. Data of precipitation and temperature in Uppsala in the year 2009 were lately available. The final parameter sets obtained before were used again to rerun both HBV and INCA-C models with the new climate data. The observed DOC concentrations suffered a significant increase in the year 2009. Again, INCA-C reproduces well the intra-annual pattern but it clearly underestimates the DOC concentration during the whole year (Appendix 17).

7. CONCLUSIONS AND FURTHER INVESTIGATIONS

This report is a good first step for more specific project studying the color and DOC dynamics in Lake Mälaren. Further studies, especially after the late results obtained for 2009, are needed in order to both understand the new trends in DOC concentration and develop the INCA-C model to predict these trends. Once the new studies based on this report are carried out successfully the model could be used to predict carbon content in the future. These investigations can be very useful to the Mälaren water treatment plants since they will be aware of future changes and thus apply the proper solutions before the problems come.

8. REFERENCES

- Arheimer, B., & Liden, R., 2000. Nitrogen and phosphorus concentrations from agricultural catchments – influence of spatial and temporal variables. *Journal of Hydrology* 227: 140-159.

- Ashworth, D. J., & Alloway, B. J., 2007. Complexation of copper by sewage sludge-derived dissolved organic matter and plant uptake. *Water, Air and Soil Pollution* 182: 187-196.

- Balogh, K. V., Vörös, L., Tóth, N., & Bokros M., 2003. Changes of organic matter quality along the longitudinal axis of a large shallow lake (Lake Balaton). *Hydrobiologia* 506 67:74.

- Bergström, S., 1996. Development and application of a conceptual runoff model for Scandinavian catchments. *SMHI RHO 7.* Norrköping, 1-134.

- Bergström, S., Hellström, S., & Andréasson, J., 2006. Nivåer och flöden i Vänerns och Mälarens vattensystem – Hydrologyskt underlag till klimat och sårbarhetsutredningen. *SMHI Reports Hydrology* 1-55.

- Beldring, S., Engen-Skaugen, T., Forland, E. J., & Roland, L. A., 2008. Climate change impacts on hydrological processes in Norway based on two methods for transferring regional climate model results to meteorological station sites. *Tellus* 60A: 439:450.

- Beven, K., & Freer, J., 2001. Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology. *Journal of Hydrology* 249: 11-29.

- Boyer, E. B., Hornberger, G. M., Bencala, K. E., & McKnight D. M., 2000. Effects of asynchronous snowmelt on the flushing of dissolved organic carbon: A missing model approach. *Hydrological Processes* 18: 3291-3308.

- Canham, C. D., Pace, M. L., Papaik, M. J., Primack, A. G. B., Roy, K. M., Maramger, R. J., Curran, R. P., & Spada, D. M., 2004. A spatially explicit analysis of watershed scale dissolved organic carbon in Adirondack lakes. *Ecological Applications* 14: 839-854.

- Chen, D., He, Z., Weavers, L. K., Chin, Y., Walker, H. W., & Hatcher, P. G., 2004. Sonochemical reactions of dissolved organic matter. *Research on Chemical Intermediates* 30: 735-753.

- Chow, A. T., Tanji, K. K., & Gao, S., 2003. Production of dissolved organic carbon (DOC) and trihalomethane precursor (THM) from peat soils. *Water Research* 37: 4475-4485.

- Curtis, P. J. Aquatic humic substances: Ecology and Biogeochemistry. Hessen, D. O., & Tranvik, L. J. (eds). 1998. *Springer*, Berlin, 93-105.

- Dawson, J. J. C., Malcolm, I. A., Middlemas, S. J., Tetzlaff, D., & Soulsby, C., 2009. Is the composition of dissolved organic carbon changing in upland acidic streams? *Environmental Science and Technology* 43: 7748-7753.

- Eikebrokk, B., Vogt, R. D., & Liltved, H., 2004. NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Science and Technology: Water Supply* 4: 47-54.

- Eikebrokk, B. Water treatment: optimization with respect to what? in Techneau 2009: safe drinking water from source to tap. Van den Hoven, T., & Kazner, C. (eds). 2009. *IWA Publishing*, London, 253-268.

- Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G. A., & Bishop, K. H., 2008. Thirty-five years of synchrony in the organic matter

concentrations of Swedish rivers explained by flow and sulphate. *Global Change Biology* 14: 1191-1198.

- Exbrayat, J. F., Viney, N. R., Seibert, J., Wrede, S., Frede H. G., & Breuer, L., 2010. Ensemble modelling of nitrogen fluxes: data fusion for a Swedish meso-scale catchment. *Hydrology and Earth System Sciences* 14: 2383-2397.

- Forsberg, C., 1992. Will an increased greenhouse impact in Fennoscandia give rise to more humic and coloured lakes? *Hydrobiologia* 229: 51-58.

- Futter, M. N., Butterfield D., Cosby, B. J., Dillon, P. J., Wade, A. J., & Whitehead, P. G., 2007. Modelling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resources Research* 43: W02424, doi:10.1029/2006WR004960.

- Futter, M. N., & de Witt, H. A., 2008. Testing seasonal and long-term controls of streamwater DOC using empirical and process-based models. *Science of the Total Environment* 407: 698-707.

- Futter, M. N., Starr, M., Forsius, M., & Holmberg, M., 2008. Modelling the effects of climate on long-term patterns of dissolved organic carbon concentrations in the surface waters of boreal catchment. *Hydrology and Earth System Sciences* 12: 437-447.

- Futter, M. N., Forsius, M., Holmberg, M., & Star, M., 2009. A long-term simulation of the effects of acidic deposition and climate change on surface water dissolved organic carbon concentrations in a boreal catchment. *IWA Publishing. Hydrology Research* 291-305.

- Fölster, J., & Wilander, A., 2002. Recovery from acidification in Swedish forest streams. *Environmental Pollution* 117: 379:389.

- Graham, L. P., & Bergström, S., 2001. Water balance modelling in the Baltic Sea drainage basin – analysis of meteorological and hydrological approaches. *Meteorology and Atmospheric Physics* 77: 45-60.

- Grimvall, A., 2004. Flownorm 2.0 – a Visual Basic program for computing riverine loads of substances and extracting anthropogenic signal for time series of load data (User's manual). *Department of Mathematics, Linköping University.*

- Gaulinger, S., 2007. Coagulation pre-treatment for microfiltration with ceramic membranes. *Techneau* 3-21.

- Hanson, P. C., Pollard, A. I., Bade, D. L., Predick, K., Carpenter, S. R., & Foley, J. A., 2004. A model of carbon evasion and sedimentation in temperate lakes. *Global Change Biology* 10: 1285-1298.

- Hongve, D., Riise G., & J. F. Kristiansen, J. F., 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water: A result of increased precipitation? *Aquatic Sciences* 66: 231-238.

- Kaiser, K., & Zech, W., 1996. Nitrate, sulfate, and biphosphate retention in acid forest soils affected by natural dissolved organic carbon. *Journal of Environmental Quality* 25: 1325-1331.

- Klaminder, J., Bindler, R., Laudon, H., Bishop, K., Emeteryd, O., & Renberg, I., 2006. Flux rates of atmospheric lead pollution within soils of a small catchment in Northern Sweden and their implications for future water quality. *Environmental Science and Technology* 40: 4639-4645.

- Köhler, S. J., Buffam, I., Jonsson, A., & Bishop, K. H., 2002. Photochemical and microbial processing of stream and soilwater dissolved organic matter in a boreal forested catchment in northern Sweden. *Aquatic Sciences* 64: 269-281.

- Köhler, S. J., Buffam, I., Laudon, H., & Bishop, K. H., 2008. Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscapes. *Journal of Geophysical Research* 113.

- Laudon, H., Köhler, S., & Buffam, I., 2004. Seasonal TOC export from seven boreal catchments in northern Sweden. *Aquatic Sciences* 66: 223-230.

- Lindgren, G., Wrede, S., Seibert J., & Wallin, M., 2007. Nitrogen source apportionment modeling and the effect of land-use class related runoff contributions. *Nordic Hydrology* 38: 317-331.

- Lindström, G., Pers, C. P., Rosberg, R., Strömqvist, J., & Arheimer, B., 2010. Development and test of the HYPE (Hydrological Predictions for the Environment)

model – A water quality model for different spatial scales. *Hydrology Research* 4: 295-319.

- Lumsdon, D. G., Stutter, M. I., Cooper, R. J., & Manson, J. R., 2005. Model assessment of biogeochemical controls on dissolved organic carbon partitioning in an acid organic soil. *Environmental Science and Technology* 39: 8057-8063.

- Löfgren, S., Andersen, T., & Forsius, M., 2003. Climate induced water color increase in Nordic lakes and streams due to humus. *Nordic Council of Ministry brochure* 1-12.

- Maloney, K. O., Morris, D. P., Moses, C. O., & Osburn, C. O., 2005. The role of iron and dissolved organic carbon in the absorption of ultraviolet radiation in humic lake water. *Biogeochemistry* 75: 393-407.

- Mattsson, T., Kortelainen, P., & Räike, A., 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. *Biogeochemistry* 76: 373-394.

- Michalzik, B., Tipping, E., Mulder, J., Gallardo Lancho, J. F., Matzner, E., Bryant, C. L., Clarke, N., Lofts, S., & Vicente Esteban M. A., 2003. Modeling the production and transport of dissolved organic carbon in forest soils. *Biogeochemistry* 66: 241-264.

- Miller, M. P., McKnight, D. M., & Chapra, S. C., 2009. Production of microbially-derived fulvic acid from photolysis of quinine-containing extracellular products of phytoplankton. *Aquatic Sciences* 71: 170-178.

- Mladenov, N. M., McKnight, D. M., Wolski, P., & Ramberg, L., 2005. Effects of annual flooding on dissolved organic carbon dynamics within a pristine wetland, the Okavango delta, Botswana. *Wetlands* 25: 622-638.

- Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., & Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450: 537-540.

- Nash, J. E., & Sutcliffe, J. V., 1970. River flow forecasting through conceptual models, part I – a discussion of principles. *Journal of Hydrology* 10: 282-290.

- Neff, J. C., & Asner, G. P., 2001. Dissolved organic carbon in terrestrial systems: Synthesis and a model. *Ecosystems* 4: 29-48.

- Nishijima, W., Fahmi, Mukaidani, T., & Okada, M., 2003. DOC removal by multi-stage ozonation-biological treatment. *Water Research* 37: 150-154.

- Oni, S. K., Futter, M. N., & Dillon, P. J., 2010. Landscape-scale control of carbon budget of Lake Simcoe: A process- based modelling approach. *Journal of Great Lakes Research*, doi:10.1016/j.jglr.2010.05.003.

- Osterhus, S. W., Azrague, K., Leiknes, T., & Odegaard, H., 2007. Membrane filtration for particles removal after ozonation-biofiltration. *Water Science and Technology* 56: 101-108.

- Persson, G., Bärring, L., Kjellström, E., Strandberg, G., & Rummukainen., 2007. Climate indices for vulnerability assessments. *SMHI* 111: 1-64.

- Rankinen, K., Karvonen, T., Butterfield, D., 2004. A simple model for predicting soil temperature in snow-covered and seasonally frozen soil: model description and testing. *Hydrology and Earth System Science* 8: 706-716.

- Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter – A review. *Chemosphere* 55: 319-331.

- Reche, I., & Pace, M. L., 2002. Linking dynamics of dissolved organic carbon in a forested lake with environmental factors. *Biogeochemistry* 61: 21-36.

- Seibert, J., 2000. Multi criteria calibration of a conceptual runoff model using a genetic algorithm. *Hydrology and Earth System Science* 4: 215-224.

- Seibert, J., & McDonnell, J. J., 2010. Land-cover impacts on streamflow: a change-detection modelling approach that incorporates parameter uncertainty. *Hydrological Sciences Journal* 55: 316-332.

- Shaw, E. M., 1994. Hydrology in practice. 3rd edition. Chapman & Hall, London, 259-260.

- Skjelkvåle, B. L., Stoddard, J. L., Jeffries, D. S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D. T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J.,

Wieting, J., Wilander, A., & Worsztynowicz, A., 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. *Environmental Pollution* 137: 165-176.

- SMHI, Sveriges Meteorologiska och Hydrologiska Institut, http://www.smhi.se/en/Research/Research-departments/Hydrology/hype-in-sweden-s-hype-1.7891, 2010-10-19.

- Sonesten, L., Wallin, M., Vrede, T., & Wallman, K., 2010. Miljöövervakning I Mälaren 2009. *Mälarens vattenvårdsförbund* 1-32.

- Şorman, A. A., Şensoy, A., Tekeli A. E., Şorman, A. Ü, & Akyürek, Z., 2009. Modelling and forecasting snowmelt runoff process using the HBV model in the eastern part of Turkey. *Hydrological Processes* 23: 1031-1040.

- Spitzy, A., & Leenheer, J. Dissolved organic carbon in rivers in Biogeochemistry of major world rivers. Degens, E. T., Kempe, S., & Richey, J. E. (eds). 1991. *SCOPE 42* Chapter 9.

- Sucker, C., & Krause, K. (2010). Increasing dissolved organic carbon concentrations in freshwaters: what is the actual driver? *iForest* 3: 106-108.

- Tranvik, L. J., & Jansson, M., 2002. Climate change-terrestrial export of organic carbon. *Nature* 415: 861-862.

- vanLoon, G. W., & Duffy, S. J. (eds). 2005. Environmental chemistry, a global perspective. 2nd edition. *Oxford University Press* 254-272.

- Vermeer, A. W. P., & Koopal, L. K., 1998. Adsorption of humic acids to mineral particles. 2. Polydispersity effects with polyelectrolyte adsorption. *Langmuir* 14: 4210-4216.

- Wade, A. J., Durand, P., Beaujouan, V., Wessel, W. W., Raat, K. J., Whitehead, P G., Butterfield, D., Rankinen, K., & Lepisto, A., 2002a. A nitrogen model for European catchments: INCA, new model structure and equations. *Hydrology and Earth System Sciences* 6: 559-582.

- Wade, A. J., Whitehead, P. G., & Butterfield, D., 2002b. The Integrated Catchments model of Phosphorus dynamics (INCA-P), a new approach for multiple source

assessment in heterogeneous river systems: model structure and equations. *Hydrology and Earth System Sciences* 6: 583-606.

- Wallin, M., Andersson B., Johnson R., Kvarnäs, H., Person G., Weyhenmeyer, G., & Willén, E. 2000. Mälaren miljötillstånd och utveckling 1965-98. *Mälarens vattenvårdsförbund* 1-94.

- Weyhenmeyer, G. A., Willén, E., & Sonesten, L., 2004. Effects of an extreme precipitation event on water chemistry and phytoplankton in the Swedish Lake Mälaren. *Boreal Environment Research* 9: 409-420.

- Whitehead, P. G., Wilson, E. J., & Butterfield, D., 1998. A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchments (INCA): Part I – model structure and process equations. *Science of the Total Environment* 210: 547-548.

- Whitehead, P. G., Futter, M. N., & Wilby, R., 2006. Impacts of climate change on hydrology, nitrogen and carbon in upland and lowland streams: assessment of adaptation strategies to meet Water Framework Directive Objectives. *BHS 9th National Hydrology Symposium*, Durham.

9. APPENDIX

Appendix 1. Deviation in % in the measurements from the outlet station Stockholm Centralbron with respect to Norrström Stockholm.

Year	AbsF	AbsOF	TOC	$KMnO_4$	Ca	Mg	Na	K	Tot-N	$NO_2 + NO_3$	NH4	SO4	Cl	Fe	Al
1996	6.99%	-7.92%	-5.46%	-4.27%	-0.51%	0.22%	-2.54%	-1.59%	-6.60%	-16.54%	-10.36%	0.83%	-0.88%	-28.91%	-17.58%
1997	5.96%	-0.19%	-1.51%	1.09%	-0.16%	-1.03%	-5.61%	-3.32%	-5.11%	-12.17%	-172.69%	0.09%	-7.40%	-35.02%	-20.43%
1998	-0.61%	-9.53%	2.29%	-0.39%	-0.96%	-0.94%	-4.70%	-1.82%	5.43%	-1.62%	-204.40%	-21.36%	-13.20%	-59.97%	-32.93%
1999	6.01%	-3.61%	-0.04%	-1.56%	-0.23%	2.07%	-4.05%	0.17%	1.11%	3.48%	-138.81%	1.57%	23.82%	-45.28%	-24.64%
2000	15.56%	0.74%	1.97%	3.13%	-2.01%	-0.73%	-2.07%	-0.88%	-7.12%	-2.54%	20.75%	-0.21%	29.19%	-2.22%	8.48%
2001	5.62%	2.10%	1.94%	1.56%	-1.12%	0.40%	-3.11%	-0.76%	3.49%	0.40%	-88.24%	0.79%	28.06%	-10.03%	-14.37%
2002	6.23%	3.30%	1.94%	5.36%	1.30%	0.38%	-1.09%	-1.27%	4.34%	10.20%	-97.65%	1.48%	26.68%	-5.89%	5.27%
Average	7.13%	-0.69%	0.88%	1.35%	-0.62%	0.10%	-3.34%	-1.21%	0.21%	1.09%	-84.70%	-2.45%	16.37%	-19.25%	-9.77%

Appendix 2. Annual export of color in filtered samples (**AbsF**) per unit of area ($m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	0.066														
Kolbäcksån Strömsholm	0.036		0.028	0.033	0.042	0.068	0.057	0.039	0.023	0.034	0.030	0.039	0.037	0.051	0.061
Hedströmmen Grönö	0.058														
Köping II	0.065														
Eskilstunaån Torshälla	0.016														
Svartån Västerås	0.070														
Sagån Målhammar	0.048	0.035	0.038	0.065	0.064	0.071	0.054	0.062	0.020	0.039	0.034	0.054	0.054	0.098	0.049
Råckstaån utl.				0.046	0.054	0.056	0.060	0.055	0.014	0.026	0.023	0.038	0.041	0.056	0.035
Fyrisån Flottsund	0.046	0.009	0.026	0.059	0.069	0.038	0.059	0.062	0.019	0.031	0.030	0.037	0.033	0.077	0.053
Örsundaån Örsundsbro	0.037	0.045	0.037	0.076	0.056	0.093	0.059	0.073	0.033	0.054	0.054	0.072	0.065	0.114	
Oxundaån Rosendal	0.016		0.004	0.011	0.018	0.011	0.020	0.024	0.003	0.008	0.006	0.008	0.010	0.013	0.011
Märstaån Utl.	0.036														
Norrström Stockholm	0.012	0.004	0.006	0.010	0.014	0.015	0.020	0.019							
Stockholm Centralbron		0.004	0.006	0.010	0.015	0.018	0.021	0.020	0.006	0.012	0.008	0.010	0.010	0.014	0.013

Appendix 3. Annual export of color in unfiltered samples (**AbsOF**) per unit of area ($m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	0.189														
Kolbäcksån Strömsholm	0.090		0.054	0.061	0.075	0.142	0.093	0.067	0.042	0.056	0.054	0.075	0.074	0.125	0.099
Hedströmmen Grönö	0.157														
Köping II	0.265														
Eskilstunaån Torshälla	0.057														
Svartån Västerås	0.206														
Sagån Målhammar	0.252	0.131	0.216	0.229	0.257	0.339	0.371	0.201	0.089	0.165	0.156	0.219	0.270	0.594	0.144
Råckstaån utl.				0.101	0.150	0.129	0.136	0.118	0.027	0.062	0.077	0.097	0.105	0.152	0.096
Fyrisån Flottsund	0.109	0.021	0.070	0.111	0.139	0.132	0.130	0.124	0.046	0.074	0.071	0.097	0.112	0.203	0.100
Örsundaån Örsundsbro	0.143	0.189	0.229	0.281	0.206	0.402	0.363	0.248	0.179	0.217	0.262	0.378	0.435	0.754	
Oxundaån Rosendal	0.051		0.012	0.029	0.068	0.027	0.048	0.083	0.007	0.028	0.013	0.017	0.028	0.036	0.032
Märstaån Utl.	0.386														
Norrström Stockholm	0.021	0.007	0.011	0.018	0.028	0.027	0.037	0.029							
Stockholm Centralbron		0.007	0.011	0.016	0.027	0.028	0.038	0.030	0.009	0.016	0.013	0.016	0.019	0.024	0.021

Appendix 4. Annual export of **TOC** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör															
Kolbäcksån Strömsholm			2.699	3.108	3.116	4.585	3.556	2.637	1.802	2.598	2.063	2.933	2.452	3.437	4.738
Hedströmmen Grönö															
Köping II															
Eskilstunaån Torshälla															
Svartån Västerås															
Sagån Målhammar									1.346	2.390	1.744	2.893	2.199	4.267	3.509
Råckstaån utl.				2.938	3.267	3.486	3.314	2.767	1.242	1.878	1.590	2.608	2.359	3.167	2.589
Fyrisån Flottsund	3.161	0.803	2.635	4.583	4.629	3.232	4.120	3.726	1.693	2.475	2.201	2.891	2.509	5.895	4.476
Örsundaån Örsundsbro									2.109	3.334	2.715	3.670	2.595	4.387	
Oxundaån Rosendal			1.086	1.836	2.274	1.642	2.103	2.480	0.556	1.259	1.159	1.670	1.578	2.431	2.466
Märstaån Utl.															
Norrström Stockholm	2.065	0.851	1.493	1.914	2.305	2.620	2.504	2.149							
Stockholm Centralbron		0.807	1.471	1.959	2.304	2.672	2.553	2.192	1.028	1.777	1.291	1.945	1.644	2.478	2.507

Appendix 5. Annual export of **$KMnO_4$** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	16.924														
Kolbäcksån Strömsholm	13.082														
Hedströmmen Grönö	15.655														
Köping II	16.709														
Eskilstunaån Torshälla	9.534														
Svartån Västerås	20.603														
Sagån Målhammar	12.767	6.805	10.356	16.083	18.217	18.095	13.467	11.764							
Råckstaån utl.															
Fyrisån Flottsund	15.966	3.885	9.818	18.993	21.504	13.689	17.907	16.252							
Örsundaån Örsundsbro	10.748	10.825	9.194	18.088	16.104	21.045	11.379	14.561							
Oxundaån Rosendal	9.386														
Märstaån Utl.	16.028														
Norrström Stockholm	7.464	3.145	4.304	6.304	8.102	9.278	9.069	7.789							
Stockholm Centralbron		3.016	4.352	6.280	7.978	9.578	9.213	8.230	3.831	6.485	4.548	5.675	5.281	7.929	7.192

Appendix 6. Annual export of **Ca** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	2.904														
Kolbäcksån Strömsholm	2.765		2.027	2.342	2.310	2.869	2.132	1.979	1.422	1.912	1.552	2.092	1.802	2.322	2.515
Hedströmmen Grönö	1.642														
Köping II	2.122														
Eskilstunaån Torshälla	7.704														
Svartån Västerås	3.393														
Sagån Målhammar	6.543	3.275	4.783	8.247	7.442	7.049	4.253	5.198	3.498	4.666	4.118	5.223	4.421	6.895	5.517
Råckstaån utl.				4.189	3.926	4.404	3.499	3.347	1.853	2.756	2.328	3.231	2.711	3.604	2.470
Fyrisån Flottsund	16.060	5.217	11.705	17.154	16.317	13.115	13.552	13.399	7.405						
Örsundaån Örsundsbro	6.534	5.480	4.728	8.475	6.409	8.302	4.087	6.502	5.425	7.620	5.809	6.691	5.060	7.608	
Oxundaån Rosendal	13.404		6.317	10.892	12.407	10.145	11.793	10.577	3.212	7.737	7.389	8.226	8.776	12.293	9.384
Märstaån Utl.	13.673														
Norrström Stockholm	7.181	2.923	4.294	6.785	7.469	7.547	5.967	5.250							
Stockholm Centralbron		2.909	4.287	6.721	7.452	7.398	5.901	5.319	2.543	4.942	3.720	4.974	4.390	6.323	5.418

Appendix 7. Annual export of **Mg** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	0.962														
Kolbäcksån Strömsholm	0.694		0.497	0.570	0.547	0.749	0.571	0.511	0.350	0.476	0.396	0.522	0.458	0.603	0.648
Hedströmmen Grönö	0.547														
Köping II	0.755														
Eskilstunaån Torshälla	1.762														
Svartån Västerås	1.046														
Sagån Målhammar	1.871	0.997	1.421	2.448	2.020	2.105	1.243	1.550	0.954	1.318	1.167	1.456	1.276	2.072	1.530
Råckstaån utl.				1.189	1.103	1.299	0.995	0.945	0.482	0.760	0.634	0.888	0.748	1.078	0.701
Fyrisån Flottsund	1.847	0.685	1.481	1.951	1.760	1.640	1.576	1.571	0.886						
Örsundaån Örsundsbro	1.524	1.378	1.265	2.019	1.401	2.126	1.043	1.617	1.292	1.812	1.415	1.601	1.275	2.033	
Oxundaån Rosendal	2.371		1.214	2.149	2.274	1.879	2.198	1.897	0.622	1.530	1.380	1.509	1.631	2.407	1.754
Märstaån Utl.	2.053														
Norrström Stockholm	1.673	0.690	1.058	1.510	1.662	1.747	1.372	1.115							
Stockholm Centralbron		0.691	1.047	1.496	1.697	1.735	1.378	1.119	0.576	1.060	0.803	1.090	0.968	1.391	1.211

Appendix 8. Annual export of **Na** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	2.580														
Kolbäcksån Strömsholm	1.906		1.405	1.627	1.682	2.182	1.612	1.596	1.210	1.592	1.270	1.614	1.317	1.761	1.704
Hedströmmen Grönö	1.286														
Köping II	1.261														
Eskilstunaån Torshälla	3.246														
Svartån Västerås	1.731														
Sagån Målhammar	2.382	1.122	1.604	2.568	2.568	2.421	1.640	1.861	1.331	1.688	1.546	1.840	1.469	2.216	2.077
Råckstaån utl.				2.325	2.380	2.820	2.293	2.310	1.236	1.924	1.707	2.318	1.781	2.264	1.521
Fyrisån Flottsund	4.618	2.068	4.092	4.315	3.778	4.036	3.746	4.064	2.866						
Örsundaån Örsundsbro	2.320	2.040	1.757	2.856	2.249	3.066	1.509	2.462	2.188	2.927	2.168	2.346	1.774	2.694	
Oxundaån Rosendal	5.443		2.852	4.733	5.084	4.711	5.399	4.819	1.809	4.289	3.926	4.512	4.212	6.025	4.553
Märstaån Utl.	8.656														
Norrström Stockholm	4.201	1.749	2.777	3.601	3.975	4.173	3.472	2.737							
Stockholm Centralbron		1.705	2.629	3.440	3.820	4.089	3.368	2.707	1.646	2.835	2.397	3.002	2.822	3.639	3.042

Appendix 9. Annual export of **K** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	0.628														
Kolbäcksån Strömsholm	0.425		0.328	0.350	0.327	0.499	0.369	0.350	0.263	0.333	0.285	0.405	0.376	0.459	0.425
Hedströmmen Grönö	0.328														
Köping II	0.475														
Eskilstunaån Torshälla	0.989														
Svartån Västerås	0.531														
Sagån Målhammar	0.777	0.436	0.624	0.846	0.895	0.893	0.620	0.731	0.457	0.598	0.595	0.816	0.785	1.038	0.628
Råckstaån utl.				0.604	0.619	0.708	0.573	0.535	0.265	0.421	0.346	0.544	0.489	0.647	0.366
Fyrisån Flottsund	0.917	0.397	0.799	0.973	0.950	0.887	0.832	0.878	0.588						
Örsundaån Örsundsbro	0.664	0.769	0.654	0.821	0.635	1.075	0.635	0.862	0.728	0.903	0.828	1.122	0.783	1.276	
Oxundaån Rosendal	1.253		0.601	1.045	1.162	0.989	1.179	1.135	0.356	0.870	0.776	0.908	0.947	1.257	0.970
Märstaån Utl.	1.740														
Norrström Stockholm	0.901	0.376	0.584	0.822	0.886	0.965	0.787	0.651							
Stockholm Centralbron		0.370	0.565	0.808	0.888	0.957	0.781	0.643	0.339	0.640	0.499	0.655	0.601	0.814	0.686

Appendix 10. Annual export of **Total nitrogen** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör															
Kolbäcksån Strömsholm	0.378		0.293	0.241	0.242	0.304	0.284	0.253	0.164	0.227	0.158	0.225	0.223	0.269	0.296
Hedströmmen Grönö	0.217														
Köping II	0.366														
Eskilstunaån Torshälla	0.435														
Svartån Västerås	0.434														
Sagån Målhammar	0.554	0.300	0.441	0.729	0.727	0.551	0.425	0.474	0.290	0.493	0.312	0.462	0.419	0.696	0.408
Råckstaån utl.				0.346	0.302	0.339	0.307	0.231	0.108	0.199	0.107	0.185	0.189	0.257	0.161
Fyrisån Flottsund	0.726	0.293	0.650	0.917	0.796	0.537	0.581	0.608	0.321	0.453	0.362	0.565	0.506	0.837	0.452
Örsundaån Örsundsbro	0.434	0.532	0.440	0.785	0.511	0.567	0.380	0.472	0.451	0.578	0.408	0.535	0.441	0.678	
Oxundaån Rosendal	0.354		0.118	0.283	0.429	0.216	0.353	0.331	0.063	0.228	0.117	0.164	0.247	0.272	0.210
Märstaån Utl.	0.795														
Norrström Stockholm	0.215	0.087	0.117	0.182	0.267	0.253	0.232	0.195							
Stockholm Centralbron		0.082	0.112	0.193	0.270	0.236	0.241	0.204	0.097	0.149	0.099	0.128	0.113	0.181	0.156

Appendix 11. Annual export of **$NO_2 + NO_3$** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	0.134														
Kolbäcksån Strömsholm	0.186		0.114	0.140	0.124	0.133	0.165	0.138	0.090	0.117	0.101	0.127	0.118	0.151	0.128
Hedströmmen Grönö	0.075														
Köping II	0.145														
Eskilstunaån Torshälla	0.187														
Svartån Västerås	0.197														
Sagån Målhammar	0.357	0.221	0.278	0.483	0.358	0.379	0.249	0.372	0.192	0.325	0.250	0.380	0.282	0.482	0.192
Råckstaån utl.				0.163	0.149	0.136	0.107	0.103	0.039	0.092	0.058	0.078	0.103	0.123	0.050
Fyrisån Flottsund	0.435	0.168	0.267	0.466	0.473	0.421	0.425	0.452	0.215	0.330	0.286	0.496	0.399	0.624	0.239
Örsundaån Örsundsbro	0.321	0.344	0.258	0.463	0.266	0.383	0.256	0.345	0.329	0.402	0.329	0.413	0.333	0.489	
Oxundaån Rosendal	0.172		0.033	0.175	0.247	0.117	0.229	0.217	0.020	0.150	0.062	0.069	0.182	0.128	0.079
Märstaån Utl.	0.585														
Norrström Stockholm	0.054	0.022	0.020	0.056	0.101	0.086	0.096	0.083							
Stockholm Centralbron		0.019	0.018	0.055	0.104	0.083	0.096	0.093	0.024	0.034	0.031	0.033	0.048	0.064	0.048

Appendix 12. Annual export of **NH_4** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	2.79E-02														
Kolbäcksån Strömsholm	2.26E-02		2.02E-02	1.03E-02	1.39E-02	1.75E-02	1.98E-02	2.55E-02	1.90E-02	1.98E-02	1.52E-02	2.02E-02	2.23E-02	1.71E-02	2.54E-02
Hedströmmen Grönö	1.48E-02														
Köping II	2.11E-02														
Eskilstunaån Torshälla	5.24E-02														
Svartån Västerås	2.17E-02														
Sagån Målhammar	3.32E-02	8.85E-03	3.07E-02	3.27E-02	5.74E-02	3.37E-02	2.84E-02	3.19E-02	4.12E-02	4.49E-02	2.95E-02	3.51E-02	2.66E-02	4.27E-02	5.56E-02
Råckstaån utl.				1.39E-02	1.42E-02	1.82E-02	2.33E-02	1.90E-02	9.64E-03	6.90E-03	7.48E-03	1.30E-02	7.16E-03	1.11E-02	6.37E-03
Fyrisån Flottsund	9.11E-02	7.68E-02	2.00E-01	1.66E-01	7.89E-02	2.82E-02	3.15E-02	3.02E-02	2.31E-02	3.02E-02	2.10E-02	2.34E-02	1.71E-02	3.72E-02	3.47E-02
Örsundaån Örsundsbro	1.64E-02	2.59E-02	1.47E-02	2.17E-02	2.80E-02	1.87E-02	2.35E-02	3.23E-02	4.23E-02	4.05E-02	2.73E-02	3.50E-02	2.57E-02	4.22E-02	
Oxundaån Rosendal	9.34E-03		3.13E-03	1.72E-02	1.58E-02	1.01E-02	1.18E-02	1.82E-02	5.96E-03	1.61E-02	9.04E-03	1.21E-02	7.33E-03	1.41E-02	8.94E-03
Märstaån Utl.	1.12E-01														
Norrström Stockholm	6.08E-03	2.21E-03	5.81E-03	9.40E-03	9.04E-03	5.05E-03	8.00E-03	6.74E-03							
Stockholm Centralbron		2.00E-03	2.13E-03	3.09E-03	3.79E-03	6.37E-03	4.25E-03	3.41E-03	1.68E-03	3.08E-03	5.12E-03	3.69E-03	1.59E-03	3.02E-03	5.00E-03

Appendix 13. Annual export of **SO_4** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	5.730														
Kolbäcksån Strömsholm	3.653		2.639	3.046	2.826	3.466	2.408	2.232	1.686	2.184	1.656	2.188	1.866	2.478	2.258
Hedströmmen Grönö	2.688														
Köping II	2.940														
Eskilstunaån Torshälla	12.454														
Svartån Västerås	3.480														
Sagån Målhammar	6.211	4.807	6.149	9.003	6.990	8.593	4.175	5.248	3.684	4.793	3.595	4.242	3.518	6.766	4.171
Råckstaån utl.				4.765	4.022	5.616	3.727	3.359	1.784	3.287	2.334	3.127	2.793	4.244	2.135
Fyrisån Flottsund	12.720	5.095	11.092	13.209	9.198	12.199	9.055	8.315	5.988						
Örsundaån Örsundsbro	6.391	7.019	6.204	8.888	5.326	9.493	3.646	6.013	6.264	8.628	5.271	5.770	4.043	7.427	
Oxundaån Rosendal	14.311		7.483	14.753	14.113	12.955	15.239	10.953	3.584	10.314	9.084	8.952	10.729	15.665	10.557
Märstaån Utl.	8.857														
Norrström Stockholm	9.213	3.571	5.530	8.518	9.166	9.522	7.594	5.834							
Stockholm Centralbron		3.600	5.535	7.019	9.313	9.502	7.655	5.922	2.959	5.821	4.531	5.910	5.022	6.983	6.015

Appendix 14. Annual export of **Cl** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör	2.461														
Kolbäcksån Strömsholm	2.387		1.795	1.978	2.089	2.427	1.724	1.734	1.288	1.741	1.431	1.820	1.510	1.972	1.974
Hedströmmen Grönö	1.706														
Köping II	1.274														
Eskilstunaån Torshälla	4.170														
Svartån Västerås	2.035														
Sagån Målhammar	2.480	1.465	2.010	2.808	3.129	2.792	1.821	1.905	1.604	1.872	1.681	2.109	1.760	2.406	2.548
Råckstaån utl.				3.081	3.295	3.540	2.918	3.060	1.554	2.504	2.393	3.274	2.547	2.717	1.910
Fyrisån Flottsund	6.024	3.297	6.040	6.502	5.900	5.953	5.125	5.504	4.337						
Örsundaån Örsundsbro	2.191	2.846	2.086	3.097	2.769	3.401	1.506	2.450	2.495	3.108	2.286	2.581	1.962	2.860	
Oxundaån Rosendal	6.981		4.093	6.828	7.633	7.037	7.226	6.421	2.497	6.207	5.754	6.686	6.098	8.294	6.322
Märstaån Utl.	12.481														
Norrström Stockholm	5.199	2.368	3.876	4.820	5.237	4.966	4.064	3.205							
Stockholm Centralbron		2.348	3.609	4.258	6.874	7.014	5.650	4.371	2.184	4.297	3.344	4.362	3.707	5.154	4.440

Appendix 15. Annual export of **Fe** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör															
Kolbäcksån Strömsholm			0.110	0.123	0.155	0.299	0.190	0.138	0.096	0.121	0.116	0.201	0.189	0.255	0.228
Hedströmmen Grönö															
Köping II															
Eskilstunaån Torshälla															
Svartån Västerås															
Sagån Målhammar															
Råckstaån utl.				0.270	0.378	0.300	0.346	0.299	0.060	0.146	0.175	0.267	0.355	0.505	0.189
Fyrisån Flottsund	0.251	0.041	0.129	0.200	0.285	0.253	0.217	0.245	0.087						
Örsundaån Örsundsbro															
Oxundaån Rosendal									0.007	0.054	0.015	0.022	0.074		
Märstaån Utl.															
Norrström Stockholm	0.032	0.008	0.015	0.024	0.029	0.025	0.061	0.035							
Stockholm Centralbron		0.006	0.011	0.015	0.020	0.024	0.056	0.033	0.008	0.014	0.013	0.013	0.024	0.023	0.021

Appendix 16. Annual export of **Al** per unit of area ($g \cdot m^{-2} \cdot year^{-1}$)

Stream/station	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009
Arbogaån Kungsör															
Kolbäcksån Strömsholm															
Hedströmmen Grönö															
Köping II															
Eskilstunaån Torshälla															
Svartån Västerås															
Sagån Målhammar															
Råckstaån utl.															
Fyrisån Flottsund		0.026													
Örsundaån Örsundsbro															
Oxundaån Rosendal										0.045	0.013	0.021	0.088		
Märstaån Utl.															
Norrström Stockholm		0.006	0.011	0.016	0.021	0.020	0.059	0.032							
Stockholm Centralbron		0.005	0.009	0.012	0.017	0.022	0.051	0.034	0.008	0.013	0.013	0.015	0.021	0.020	0.022

Appendix 17. Observed and INCA-C simulated DOC at Fyrisån for the period 1996-2009.