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# Hydrodynamic modelling of fate and transport of natural organic matter and per- and polyfluoroalkyl substances in Lake Ekoln

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Frida Ekman

# Abstract

## Hydrodynamic modelling of fate and transport of natural organic matter and per- and polyfluoroalkyl substances in Lake Ekoln

*Frida Ekman*

Societies are facing great challenges with obtaining a good quality and quantity of drinking water in the context of climate change. Increases in natural organic matter (NOM) and per- and polyfluoroalkyl substances (PFAS) have been observed in lakes and drinking water the past years, which is of great concern for water treatment plants in Sweden. It is therefore vital to increase the knowledge regarding the distribution of these substances in the environment. The main objective of this project was therefore to further develop a hydrodynamic model for lake Ekoln by including transportation and degradation of NOM. This was to be done by calibrating the model in terms of total organic carbon (TOC) and Water colour (Colour). A second objective was to investigate the requirements to successfully model PFAS in Ekoln for future studies. The study was done using the model MIKE 3 FM, developed by the Danish Hydraulic Institute (DHI).

The two variables TOC and Colour, were calibrated separately for the period of February 2017 to September 2018. For TOC the within-lake processes were decay and sedimentation. These were described using a reference decay constant for 20°C ( $k_0$ ), that was scaled using the Arrhenius temperature coefficient ( $\theta$ ), and sedimentation was represented by a settling velocity ( $v_{sm}$ ). For Colour the included process was photooxidation. This process was described using a maximum photooxidation rate ( $k_{photo}$ ) that was scaled using the Monod relation including parameters for minimum photosynthetically active radiation (PAR) necessary for photooxidation to occur ( $I_{min}$ ) and a PAR half saturation constant ( $I_{1/2}$ ).

The calibration of TOC resulted in the following best fit parameters for  $k_0$  of 0.001 d<sup>-1</sup>,  $\theta$  of 1.07 and  $v_{sm}$  of 0.001 md<sup>-1</sup>. The calibration of Colour resulted in the following best fit parameters for  $k_{photo}$  of 0.0125 d<sup>-1</sup>,  $I_{min}$  of 0  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$  and  $I_{1/2}$  of 4  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$ . Overall it can be concluded that the chosen processes managed to capture the seasonal variations of TOC and Colour, and the calibrated parameter values are in line with similar studies. The assumption of not including autochthonous input proved to be the biggest source of error in the calibration of TOC, but proved to have a minor influence on the calibration of Colour. To achieve a more realistic representation of photooxidation in the vertical profile, for the simulation of Colour, more processes should be considered to be added in the model in future studies.

The limited access to PFAS data for Ekoln, constrained the study of PFAS and only two sources could therefore be studied: The sewage treatment plant Kungsängsverket and precipitation. The results showed that the simulated concentrations of PFAS in Ekoln only accounted for 40 % of the observed concentrations. It could further be concluded that the contribution from precipitation is negligible. For future studies it is judged to be vital to include Fyrisån as a PFAS source, and to look into processes that influence PFAS distribution, such as sedimentation and adsorption to organic matter.

**Keywords:** Ekoln, Natural organic matter (NOM), Total organic matter (TOC), Colour, degradation, sedimentation, photooxidation, PFAS, MIKE 3 FM

# Referat

## Hydrodynamisk modellering av distribution och transport av naturligt organiskt material och per- och polyfluorerade alkylsubstanser i sjön Ekoln

Frida Ekman

Samhällen står idag inför stora utmaningar vad gäller att tillhandahålla god kvalitet och kvantitet av dricksvatten under rådande klimatförändringar. De senaste åren har det observerats ökande halter av naturligt organiskt material (NOM) och per- och polyfluorerade alkylsubstanser (PFAS) i sjöar och dricksvatten, vilket är bekymmersamt för Sveriges vattenreningsverk. Det är därför av största vikt att öka kunskapen om dessa ämnens distribution i miljön. Huvudsyftet med denna studie var därför att vidareutveckla en hydrodynamisk modell för sjön Ekoln så att den även inkluderar transporten och nedbrytningen av NOM. Detta utfördes genom att kalibrera modellen för totalt organisk kol (TOC) och Vattenfärg (Färg). Ett andra syfte var att undersöka vilka förutsättningar som krävs för att kunna modellera PFAS på ett korrekt sätt i Ekoln. Studien utfördes i modellverktyget MIKE 3 FM, utvecklat av DHI.

De två variablerna TOC och Färg kalibrerades separat för perioden februari 2017 – september 2018. Processerna som valdes att påverka TOC var nedbrytning och sedimentation. Dessa processer beskrevs med hjälp av en referens-nedbrytningskonstant för 20°C ( $k_0$ ), vilken anpassades med hjälp av Arrhenius temperaturkoefficient ( $\theta$ ) och sedimentation beskrevs med hjälp av en sedimentationshastighet ( $v_{sm}$ ). Färg påverkades endast av processen fotooxidation vilken beskrevs med en maximal hastighet för fotooxidation ( $k_{photo}$ ) som anpassades med hjälp av Monods relation. Anpassningen skedde med hjälp av parametern för minimal fotosyntetiskt aktivt ljus (PAR) för att fotooxidation ska ske ( $I_{min}$ ) samt en PAR halv mättnads konstant ( $I_{1/2}$ ).

Kalibreringen resulterade i värden för  $k_0$  av 0.001 d<sup>-1</sup>,  $\theta$  av 1.07 och  $v_{sm}$  av 0.001 md<sup>-1</sup>. Kalibreringen för Färg resulterade i värden för  $k_{photo}$  av 0.0125 d<sup>-1</sup>,  $I_{min}$  av 0  $\mu\text{mol fotoner m}^{-2}\text{s}^{-1}$  och  $I_{1/2}$  av 4  $\mu\text{mol fotoner m}^{-2}\text{s}^{-1}$ . Det kan konstateras att de valda processerna lyckas med att beskriva säsongvariationerna av både TOC och Färg och att de kalibrerade parametervärdena stämmer överens med litteraturen. Antagandet om att inte inkludera autoktont tillförsel av organiskt material (NOM från ytvatten), visade sig vara den största felkällan i simulering av TOC, men visade sig ha en mycket liten påverkan på simuleringen av Färg. För en mer realistisk bild av fotooxidations spridning i djupled, för simuleringen av Färg, bör fler processer övervägas att inkluderas i modellen för framtida studier.

Studien av PFAS var begränsad av tillgången till data, vilket medförde att endast två källor av PFAS till Ekoln analyserades: reningsverket Kungsängsverket och nederbörd. Resultaten visade att den simulerade koncentrationen av PFAS endast motsvarade 40 % av den observerade. Vidare kunde det konstateras att tillförsel av PFAS från regn kan antas vara försumbar. För framtida studier av PFAS i Ekoln bedöms det vara avgörande att inkludera Fyrisån som en källa, samt att vidare undersöka processer som påverkar transporten av PFAS så som sedimentation och adsorption till organiskt material.

**Nyckelord:** Ekoln, naturligt organiskt material (NOM), totalt organiskt kol (TOC), färg, nedbrytning, sedimentation, foto-oxidation, PFAS, MIKE 3 FM

## Preface

This master thesis is the final step in my 5 year education in the Master program in Environmental and Water Engineering. This project was done at the Swedish University of Agricultural Sciences. Supervisor is Ekaterina Sokolova, Associate Professor in Water System Modelling at Chalmers University of Technology, and subject reader has been Stephan Köhler, Professor at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences.

I would like to thank my supervisor Ekaterina for being very supportive throughout the whole project, and giving me great insight in the potentials in hydrodynamic modelling. Ekaterina has provided valuable knowledge regarding hydrodynamic modelling that will be of very good use in future projects. I would also like to thank Stephan who has contributed with ideas and great inspiration regarding water quality challenges. You have also put a lot of time into this project, which I really appreciate.

I would also like to thank DHI for providing the student license for the software MIKE 3 FM and Anna Karlsson at Tyréns AB that provided the model set up for the hydrodynamic model for Ekoln. Without DHI and Anna this project would not be possible.

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## Populärvetenskaplig sammanfattning

Vattenkvaliteten i många sjöar runt om i Sverige har försämrats de senaste åren på grund av klimatförändringar och mänsklig aktivitet. Bland annat har det i sjöar i Sverige, och i andra nordligt belägna sjöar, observerats ökade halter av naturligt organiskt material (NOM). Denna ökning är bekymmersam för landets vattenreningsverk då NOM påverkar vårt dricksvatten negativt med färg, lukt och bakterier. Ett annat ämne som fått mycket uppmärksamhet de senaste åren är per- och polyfluorerade alkylsyror som går under det gemensamma namnet PFAS. Dessa ämnen finns i bland annat teflonpannor, impregnerade kläder och brandsläckningsskum. PFAS är klassade som persistenta, bioackumulerande och toxiska och ökade halter av dessa har setts i dricksvatten i både Sverige och globalt.

Med tanke på att Sverige får cirka 70 % av sitt dricksvatten från sjöar är det av största vikt att kunskap om spridning och förändringar i halter av både NOM och PFAS ökar. Huvudsyftet med det här projektet är att kalibrera en modell så att den simulerar säsongsvariationer av NOM. En sådan här studie kan i långa loppet bidra till möjligheter att undersöka hur halter av NOM och PFAS i sjöar påverkas av klimatförändringar. I den här studien undersöks sjön Ekoln som är en delbassäng till Mälaren. Då NOM kan mätas på flera olika sätt används i denna studie två parametrar som är totalt organisk kol (TOC), och vattenfärg (Färg). Ett andra syfte med projektet var att utvärdera vilka förutsättningar som krävs för att kunna modellera PFAS i Ekoln i framtiden. Detta projekt använder modellverktyget MIKE 3 FM som är utvecklat av DHI, och studien bygger vidare på ett projekt som redan kalibrerat modellen för hydrodynamiken för Ekoln.

För att kalibrera modellen för TOC och Färg valdes det att nedbrytning och sedimentation skulle läggas in som processer som påverkar TOC, och fotooxidation för Färg. Det antogs även att enda tillförseln av TOC och Färg var av terrestrialt ursprung (alloktont) och kom från Ekolns fyra huvudinflöden (Fyrisån, Örsundaån, Sävaån och Hågaån). Resultaten från kalibreringen visade att de valda processerna lyckas bra med att fånga säsongsvariationerna av TOC och Färg. För modelleringen av TOC konstateras att antagandet om att inte inkludera tillförsel av TOC från primärproduktionen i sjön (autoktont NOM) hade stor påverkan på simuleringen under sommaren. Det påvisades att simuleringen av Färg skulle ge en mer representativ bild av fotooxidation om även nedbrytning skulle inkluderas som process i framtida studier.

Modelleringen av PFAS var betydligt mer begränsad än den av NOM då mycket lite data finns för PFAS runt Ekoln. Därför bestod modelleringen av PFAS av att endast två källor inkluderades vilket var reningsverket Kungsängsverket samt regn. Modelleringen visade att dessa källor endast kunde förklara 40 % av PFAS halten i sjön, och att tillförseln från regn var försumbar. Detta betyder att Kungsängsverket, om än antagen som en stor källa av PFAS, inte är den enda. Resultaten påvisar att för framtida studier är det mycket relevant att inkludera Fyrisån som källa då denna tros stå för en stor andel av tillförseln av PFAS till Ekoln.

# Abbreviations and definitions

## Abbreviations

**BOD** - Biochemical oxygen demand  
**DHI** - Danish Hydraulic Institute  
**DOC** - Dissolved Organic Carbon  
**DOM** - Dissolved Organic Matter  
**NOM** - Natural Organic Matter  
**OM** - Organic Matter  
**PAR** - Photosynthetically active radiation  
**PFAS** - Per- polyflouroalkyl Substances  
**POM** - Particulate Organic Matter  
**RC-model** - Reactivity Continuum model  
**TOC** - Total Organic Carbon  
**WRT** - Water Retention Time

## Definitions

**Alkalinity** - A fluids ability to buffer against changes in pH  
**Allochthonous** - Terrestrial derived organic matter  
**Autochthonous** - Organic matter created in the lake  
**Bathymetry** - Topography of the beds of water bodies  
**Chlorophyll** - A measurement of the phytoplankton biomass  
**Conservative substance/pollutant** – Pollutants that are not normally physically or chemically transformed to non-toxic substances in the receiving water  
**Water retention time** - is a quantity of the mean time water or a particle spends in a lake  
**Water Colour** - Measurement of the coloured organic matter content in water  
**Epilimnion** - The upper layer of water in a stratified lake  
**Hypolimnion** - The bottom layer of water in a stratified lake  
**Hypolimnetic CO<sub>2</sub>** - Is a way to estimate lake metabolism, i.e. the degradation of organic matter in the hypolimnion. Because the organic matter in the hypolimnion comes from the settling of organic matter from epilimnion, this implies that hypolimnetic CO<sub>2</sub> can also be used as an indirect measure of the production of organic matter in the photic zone.  
**Photic Zone** - The upper top layer in a lake were photosynthesis occurs  
**Thermocline** - A thin layer between epilimnion and hypolimnion that marks a change in temperature

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# 1 Introduction

The water quality in many lakes in Sweden has changed the past years due to climate change and anthropological activities. A brownification of lakes has been observed in Sweden and the northern hemisphere since 1990 which is caused by an increase in natural organic matter (NOM). This increase is believed to be connected effects caused by climate change, such as increased precipitation and rising temperatures (Löfgren & Lundin 2003; Monteith et al. 2007). NOM is a big challenge for water treatment plants because it affects the water quality negatively concerning colour, taste, odour and bacterial growth among many things (Köhler & Lavonen 2015; Leenheer & Croué 2003). Another more recent issue, globally and in Sweden, is the increased levels of per- and polyfluoroalkyl substances (PFAS) in drinking water. PFAS are persistent bioaccumulative and toxic substances that for example are used in fire fighting foam, impregnation of clothes, and pesticides (Swedish Environmental Protection Agency 2019).

Societies are facing great challenges with obtaining a good quality and quantity of drinking water in the context of climate change. This makes it vital to be able to predict and monitor changes in water quality. This implies having access to models that simulate the flow patterns of lakes and fluxes of substances. Mälaren is the biggest provider of drinking water in Sweden and is divided into several sub-basins that vary greatly in their chemical properties. Ekoln is one of the sub-basins of Mälaren and was investigated in a modelling study by Lindqvist (2019). The goal with that study was to calibrate the hydrodynamics of the model for Ekoln and study the potential changes in annual patterns of water mixing due to climate change. This was done by using the model MIKE 3 FM, a modelling software developed by the DHI and a model application developed for Ekoln by Tyréns AB (Tyréns AB 2018). The study was important because changes in lake stratification have great impact on water quality because stratification impacts how substances are transported, transformed and stored in lakes.

The study by Lindqvist (2019) opened up for the possibility of investigating the water quality of Ekoln. Both increased concentrations of NOM (Köhler et al. 2013) and the existence of PFAS (Söderholm & Svanholm 2018) have been observed in Mälaren and in Ekoln. Located south of Ekoln, in the Görvåln basin lies a water treatment plant, Görvålnverket, which receives one third of its water from Ekoln. This is one of the reasons for the interest in knowing the transport and degradation processes in Ekoln for NOM and PFAS.

## 1.1 Aim and objectives

The aim with this study was to further develop the model calibrated by Lindqvist (2019) by adding a water quality module, to analyse NOM, in terms of total organic carbon (TOC) and water colour (Colour), and PFAS in Ekoln. This was done by using available data from inflows to Ekoln and compare simulated concentrations with observed measured concentrations in Ekoln. The data available was very different between NOM and PFAS, and the objective with the modelling was therefore different between the two. A lot of data exist for NOM in terms of TOC and Colour, both from inflows to Ekoln, and in Ekoln. For PFAS there is much less data available for the time period in interest and for the inflows. The only source that had PFAS data for the specified time period was the sewage treatment plant Kungsängsverket.

1. The objective with modelling NOM was to calibrate the model for time variations of TOC and Colour. This was to be done by adding different processes to the model that influences TOC and Colour. The study of NOM is the main focus of this project.

2. The objective for the study of PFAS was to look into what is required to successfully model PFAS in Ekoln, and provide important factors to consider for future studies of PFAS in Ekoln.

## **1.2 Limitations**

The development of the model MIKE 3 FM in this project was built directly on the work by Sandra Lindquist, using both her calibration and her model set of parameters and forcing input data for the hydrodynamics. This meant that no new calibration for the hydrodynamics in the model was done for this project.

Due to limited data it was not possible to validate the model with a different time period with data not used for the calibration. This project was therefore focused on finding the right way to model the processes affecting NOM in Ekoln, and can be seen as a first step to fully model and understand the processes of NOM in Ekoln.

## 2 Theory and Background

This section is divided between theory regarding Ekoln, Natural organic matter (NOM), PFAS and the model that is used. The information presented here is later used to judge how complex systems observed in reality is to be simplified in the model environment.

### 2.1 Ekoln

Lake Mälaren is the third biggest lake in Sweden and supplies approximately 2 millions of people with drinking water. This makes it to the water catchment that provides most water to people in Sweden (Mälarens Vattenvårdsförbund 2020a). Ekoln is one of 32 basins in Mälaren and is located in the most northern part of Mälaren and has a surface area of 22 km<sup>2</sup>. There are four major river inflows to Ekoln: Fyrisån, Örsundaån, Sävaån and Hågaån, and one minor inflow from the Uppsala esker (Swedish: Uppsalaåsen). These inflows account for 95 % of the inflow to Ekoln, the rest 5 % is from diffuse sources (Lindqvist 2019). The only outflow from Ekoln is through Erikssund. Ekoln's location in relation to Uppsala and the inflows can be seen in figure 1 where the surrounding basins and inflows are presented. In figure 1 are also the sewage treatment plant Kungsängsverket and the sampling station site Vreta Udd marked. Vreta Udd is the location in Ekoln where all measurements of NOM and PFAS have been done.



**Figure 1:** Map over Ekoln in relation to its location to Uppsala (Ekoln 2020). The blue dots mark the inflows and the outflow. Kungsängsverket lies upstream in Fyrisån, marked as a black diamond. The gauge station Vreta Udd is the red diamond in the centre of Ekoln.

Ekoln is connected through the basins Skofjärden and Skarven with the Görväln basin where the water treatment plant Görvälnverket is situated. The different basins are separated from each other by narrow sounds which gives them very individual characteristics regarding water chemistry depending on the basins' inflow, catchment properties, water retention time and human activities (Wallman, Wallin, & Tjällén 2010). The water retention time has great impact on the water quality since a longer retention time results in more time for pollutants to sediment or possibly degrade (Mälarens Vattenvårdsförbund 2020b).

### 2.1.1 Water chemistry of Ekoln

Currently Ekoln is graded by VISS (2019) as having *Moderate* Ecological status and *Failing to Achieve Good* Chemical status. The bad chemical status is mainly due to high concentrations of mercury (Hg) and polybrominated diphenyl ethers (PBDE). High concentrations of perfluorooctane sulfonates (PFOS) has also been measured. For the Ecological status Ekoln is considered *Moderate* both when it comes to nutrients (in regard of phosphorus) and also moderate in regard of phytoplankton (ibid.).

Wallman, Wallin, & Tjällén (2010) analysed the water chemistry of most of Mälaren's basins, Ekoln being one of them. The results for Ekoln are shown in table 1 where data is presented together with a grade that displays how Ekoln's water quality performed relative other basins in Mälaren (ibid.). In comparison with the rest of Mälaren alkalinity is extra high in the north-east part, where Ekoln lies. Ekoln has a high alkalinity due to the presence of glacially derived calcium rich clay in the catchment area. This also correlates to a neutral pH in Ekoln and in Mälaren in general. Factors that greatly affect the water chemistry of Ekoln are the two inflows Fyrisån and Örsundaån. These deliver high concentrations of organic carbon (OC) and Nitrogen (N) into Ekoln due to farming and the sewage treatment plant Kungsängsverket of Uppsala city that releases water into Fyrisån. In fact Fyrisån and Örsundaån have the highest measurement of Tot-N and nitrite-N and nitrate-N of all the inflows in Mälaren. Nutrients such as nitrogen (N), phosphorus (P) and silicate (Si) are crucial for the primary production by phytoplankton in water ecosystems and high concentrations can cause toxic algae bloom. Chlorophyll is an indirect measurement of the mass of phytoplankton, which was very low for Ekoln compared to the rest of Mälaren. Ekoln also has a very high conductivity, which normally is connected to an easily eroded bedrock (ibid.). The water retention time for Ekoln has been estimated to approximately 1.2 years (Persson et al. 2012; Sonesten et al. 2013).

**Table 1:** The data shown below is taken from Wallman, Wallin, & Tjällén (2010). The grade shown to the right is a comparison between all the 56 gauge stations in the basins, showing how Ekoln is performing in comparison with the rest of Mälaren's basins. The scale is 1-5 where 1 is the lowest concentration/value and 5 is the highest concentration/value.

Parameters		Grade
TOC	13.1-14.8 [mg/l]	5
Chlorophyll	5-10 [ $\mu$ g/l ]	1
Water colour	0.001-0.160 [Abs, 420 nm/5cm]	5
Transparency	2.6-3.3 [m]	4
Alkalinity	1.76-2.24 [mekv/l]	5
pH	7.8-8	3
Conductivity	23.1-36 [mS/m25]	5
Nutrients [ $\mu$ g/l]		Grade
Tot-N	801-1464	5
NO <sub>2</sub> , NO <sub>3</sub> , N	421-777	5
Si	2100 - 3200	5
Tot-P	14-20	2
PO <sub>4</sub> -P	8-13	3

In regard of NOM concentration and variations in Ekoln this can be interpreted in the parameters TOC (Total organic carbon), Water colour (Colour) and Transparency seen in table 1 (Wallman, Wallin, & Tjällén 2010). Ekoln has the highest TOC values in Mälaren due to inflow from Fyrisån and Örsundaån. This part of Mälaren also showed the greatest variation in TOC, which also correlates to similar variations in TOC in Fyrisån and Örsundaån. Colour is strongly affected by the organic matter content in the water, and Ekoln has a very high value there as well. Great variations over the years was also found in Colour for Ekoln. In Ekoln the Colour is highest in the beginning of the year due to high inflows of NOM during winter. The Colour then declines along with the degradation of NOM during summer and dilution with clearer water. The transparency in Ekoln includes both information of water colour, turbidity and phytoplankton. Normally a high transparency (as in Ekoln) would correlate to a low absorbance. This is not the case for Ekoln, where absorbance do not have a clear correlation with transparency (ibid.). This could be because absorbance is not equal to Colour. Colour is sometimes better correlated to absorbance/TOC or Iron/TOC. Therefore, a much clearer correlations is seen between transparency and absorbance/TOC or Iron/TOC in Ekoln.

### 2.1.2 Seasonal changes in Ekoln

As water density changes with temperature, being heaviest at 4 °C, it causes the water masses to either be mixing or to stagnate in lakes depending on the temperature profile. Ekoln is a dimictic lake which implies that the water is mixing twice a year, in spring and fall, when the temperature is constant through the vertical profile. In between the mixing events it is either summer or winter stagnation, which means that the water is separated into epilimnion (the upper water layer in a stratified lake) and hypolimnion (the bottom layer of water in a stratified lake). The epilimnion and hypolimnion are separated by the thermocline, a thin layer that marks the temperature change. The stratification of lakes has great impact on the lake ecosystem and water quality because the stratification minimises the contact between the upper and bottom water layer. This can for example cause very low oxygen levels in hypolimnion in late winter and summer stagnation (Houser et al. 2003; Lindqvist 2019). The periods of mixing, in regard to this, is very important because it will re-oxygenate the bottom water. Because of the great impact that stratification has on the water quality, it is also a very important factor to consider when choosing at what depth to have a raw water intake in a lake. Another effect a dimictic lake have is on the sedimentation of particles. The highest sedimentation velocities are during stable conditions such as winter and summer stagnation, and the lowest are when the water masses are mixing (Stabel 1987).

## 2.2 Natural Organic Matter, NOM

Since 1990 several reports of an increase of natural organic matter (NOM) in surface water around northern Europe and Sweden have been made (Evans, Monteith, & Cooper 2005; Johansson 2003; Löfgren & Lundin 2003; Monteith et al. 2007). The reasons for this are believed to be connected to several effects caused by climate change, for example an increase in precipitation and rising temperatures (Evans, Monteith, & Cooper 2005; Löfgren & Lundin 2003; Norrvatten 2019; Von Einem & Granéli 2009). In the western basins of Mälaren, where 70 % of the water enters Mälaren, a 100 % increase in Colour have been observed over the last 40 years (Köhler et al. 2013). This is alarming considering that NOM is a major issue when it comes to drinking water quality. It effects colour, odour and taste of drinking water and could also produce toxic bi-products from disinfection pro-

cesses and also increase bacterial growth in water pipes (Leenheer & Croué 2003; Norrvatten 2019). The increase of NOM is therefore of great concern for many water treatment plants in Sweden considering that approximately 75 % of the population of Sweden receives their drinking water, directly or indirectly, from surface water (Löfgren, Forsius, & Andersen 2003). Other than the effects on water quality for humans, NOM plays a major part in the ecosystem of lakes as being part of binding and transportation of contaminants, being a carbon source and sink, mediates photo-chemical processes and affecting levels of dissolved oxygen, nitrogen and phosphorus, trace metal and acidity (Leenheer & Croué 2003). It is therefore of great interest, both from drinking water perspective and ecosystem perspective, to know how NOM is transforming and degrading in a lake, the different origins of NOM and the seasonal variations.

### 2.2.1 Chemical properties

Natural Organic Matter (NOM), or also called humic substances, are large complex organic substances and comes from degraded plant- and animal parts or residue (Löfgren, Forsius, & Andersen 2003). Due to the brown/yellow colour of these substances, an indication of NOM can also be to measure colour in water. The long-term increase of NOM can therefore also be mentioned as brownification of surface water. A general formula of the structure of NOM is that they consist of aromatic and aliphatic hydrocarbons with different functional groups attached to them (Leenheer & Croué 2003). A specific chemical structure of NOM cannot be defined because it depends on the origin of the organic matter and several chemical factors of the water it exists in. When studying NOM, several measurements of NOM are used such as total organic carbon (TOC), dissolved organic matter/carbon (DOM/DOC) or particulate organic matter/carbon (POM/POC). TOC is one method used to measure NOM, and tends to be used as a synonym to NOM because the fraction of organic contaminants in TOC is negligible (ibid.). NOM, or TOC, can further be categorised into DOC which is approximately 90 % of NOM, and POC which is approximately 10 % of NOM (ibid.). DOC and POC are separated using a filter size of 0.45  $\mu\text{m}$  in diameter, where DOC are < 0.45  $\mu\text{m}$  in diameter. Considering that DOC is the most abundant part of NOM, many studies focus on studying DOC specifically, instead of NOM or TOC.

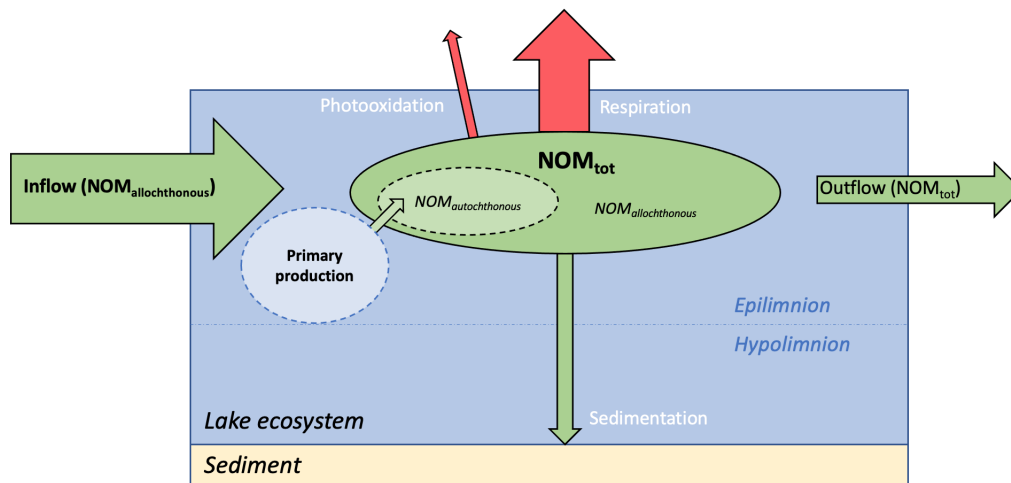
There is not one way to measure organic matter, but several methods and metrics are used (Sepp et al. 2018), some of which have already been mentioned in this report. TOC, as mentioned before is one of them, is the concentration of organic carbon in an unfiltered water sample measured in mg/l (Köhler & Lavonen 2015). Another commonly used measurement is Water colour [Pt mg/l], which in this report will be referred to as Colour. Colour, i.e. the quantitative measurement for brownification, is a measurement of light absorbency. The absorbency is typically measured in a 5 cm cuvette, using a filtered or unfiltered water sample (AbsF or AbsOF) for different wavelength (254 nm, 410 nm, 420 nm, 436 nm), e.g AbsF\_420\_5cm. Colour, measured in unit Pt mg/l, is the colour of water compared to different concentrations of potassium hexachloroplatinate and cobalt chloride solutions (Sepp et al. 2018), and can be calculated from absorbency by multiplying absorbency with 500 (Köhler & Lavonen 2015). The Colour that is referred to here is not only dependent of organic matter, but also depends on iron content, and the origin of the organic matter, pH and nitrate content (ibid.). Terrestrial organic matter tends to be more coloured than organic matter produced in the lake (Köhler et al. 2013). TOC, as being a measurement of the total concentration of organic carbon, is independent on the colour of the organic matter and the correlation between TOC and Colour can

therefore be misleading (Köhler & Lavonen 2015). Colour on the other hand is the fraction of TOC that is coloured, i.e. there can either be TOC high in colour or low colour, depending on for example the origin. TOC and Colour are further the two ways of measuring and estimating NOM that will be used in this report. Other methods that will be used in other studies mentioned in this report is hypolimnetic or epilimnetic CO<sub>2</sub>, which is a way to estimate the lake metabolism, i.e. degradation of organic matter in hypolimnion or epilimnion respectively (Houser et al. 2003; Wetzel 2001).

### 2.2.2 In- and outflows of NOM

As organic matter is being transported from soil to sea through inland freshwater systems, a part of it is mineralized to CO<sub>2</sub> or in other ways transformed or sedimentated. On a global scale roughly 50-60 % of all carbon loaded into lakes evades to the atmosphere, 20 % is buried and only 25-30 % is transported to the oceans (Hararuk et al. 2018). Due to this, organic matter in freshwater systems is playing a major part in the global carbon cycle (Catalán et al. 2016; Koehler et al. 2012). When studying NOM-fluxes in a lake the in- and outflows could be described as below, these processes are also summarised in figure 2.

- *Inflow/creation of NOM*: import of NOM from inlets carrying terrestrial NOM (allochthonous), or creation of NOM (autochthonous) in the lake by algae, macrophyte and bacteria.
- *Outflow/degradation of NOM*: Through export of NOM via outlets, sedimentation, or as degradation of NOM in terms of mineralization through respiration, incorporation of NOM in microorganisms, or photodegradation (e.g. photooxidation).



**Figure 2:** A conceptual picture of the major in- and outflows and transformations of NOM in lakes. The thickness of the arrows can be interpreted as an approximation of the amounts of the flows in relation to each other, these can of course vary greatly depending on the individual lake.

The flux of NOM further depend on physical, chemical and biological characteristics of the lake, such as patterns of water mixing, stratification, water retention time (WRT), the microbial community and the proportions between allochthonous (terrestrial) and autochthonous (produced in the lake) NOM. Generally the autochthonous NOM stands for a minor part of the total amount of NOM in

lakes (Köhler & Lavonen 2015). The bioavailability of NOM has proved to depend greatly on the origin. Autochthonous NOM tends to be more bioavailable (labile) and will therefore be favoured by the microbial community compared to allochthonous NOM, being less bioavailable (recalcitrant) (Koehler et al. 2012; Lambert & Perga 2019; Leenheer & Croué 2003).

Results from Reactive Continuum models (RC-models) indicate that the decay rates, i.e biodegradability, of organic matter changes along with the changes in chemical structure as organic matter degrades. A strong correlation between NOM degradation and the water retention time (WRT) have also been observed in several studies (Catalán et al. 2016; Hanson et al. 2011; Köhler et al. 2013). An increase in WRT (generally larger lakes) means longer time for NOM to be exposed to microorganisms which leads to a higher mineralization of NOM. In a study investigating the reasons behind the increase of DOC in Mälaren it was found that a strong increase in colour was connected with a short WRT (< 1.5 years), being acidic (pH < 6.5) and having a low concentration of dissolved Iron (Fe) (Köhler et al. 2013).

The degradation of NOM may also vary vertically with the stratification in a lake because primary production is limited to the part of epilimnion that is infiltrated by sunlight. This creates a variability in NOM composition with depth, with more degraded organic matter and organic matter from the sediments in hypolimnion (Lambert & Perga 2019). An effect of the summer and winter stagnation is that almost no diffusion of NOM between epilimnion and hypolimnion happens during these periods, which also implies that no new NOM will be added to the hypolimnion until next water mixing event (Houser et al. 2003). Photooxidation of NOM only occur in the upper layer of epilimnion in the photic zone, (approximately at 50 cm or shallower (Haverstock et al. 2012)) where light can penetrate. This process has proved to have a great impact in the NOM flux (Amon & Benner 1996; Köhler et al. 2002), by for example making DOC more labile for bacterial mineralization (Amon & Benner 1996; Houser et al. 2003). In a study of a northern Swedish lake Jonsson et al. (2001), photooxidation accounted for 10 % of the total mineralization of organic matter in the lake, and 20 % of the mineralization in epilimnion.

### 2.2.3 Modelling of NOM in lakes

Although NOM is part of major ecological and global processes and greatly affects the quality of our drinking water, there are many uncertainties when it comes to the flows, mineralization and sedimentation of NOM in freshwater systems (Catalán et al. 2016; Hanson et al. 2011). This creates great challenges when it comes to modelling NOM.

In this section follows a summary of previous studies that are relevant for this project in modelling NOM degradation in lakes. The studies are presented in table 2 and they all model NOM but uses different types of models and include or omit different types of transformation processes, bioavailability and origin of NOM. The conclusions and results from the studies display the great variability in which NOM can be modelled. The studies also show the influence that different assumptions and simplifications have on the models performances, and provide the concluded values for the parameters that have been used in the calibration for their models.



**Table 2:** Summary of previous studies that modelled DOC degradation in water.

Measured variable	Location	Source
epilimnetic DOC and CO <sub>2</sub>	Various	Hararuk et al. (2018)
allochthonous DOC	7 northern lakes	Hanson et al. (2014)
decomposition of DOC	bioassays, 6 swedish lakes	Koehler et al. (2012)
allochthonous DOC	4 northern lakes	Hanson et al. (2011)

**Hanson et al. (2011)** tested several different mineralization rates (0.001-0.01 d<sup>-1</sup>), based on values found in literature, for every lake. Their results showed that the mineralization rate converges towards a value of just below 0.001 d<sup>-1</sup>, which corresponds to what they have seen in literature. The primary factors influencing the fate of DOC proved to be the WRT and the mineralization rates, showing that lakes with a WRT >6 years mineralized approximately 60 % of the DOC, while lakes with WRT < 1 year, exported 60 % of the DOC. Another correlation seemed to exist between the DOC concentration and the mineralization of DOC, where a lake with high DOC concentration, due to a darker colour restrict the light penetration and therefore decrease the mineralization processes of DOC. They emphasise that the importance of photooxidation should be investigated further, since this was not included as a major process in their model, although studies have shown that photooxidation could account for 10 % of the mineralization.

The model used by Hanson et al. (2011) (but also Hanson et al. (2014) - with a few modification between them) is a steady-state solution for the changes of DOC, of the differential equation seen in equation 1. Where the addition of DOC results from the inflow of allochthonous DOC ( $I$ ) and the autochthonous DOC ( $A$ ). The losses of DOC are caused by sedimentation ( $S$ ), mineralization in terms of both respiration and photodegradation ( $R$ ) and export of NOM through an outflow ( $E$ ).

$$\frac{dDOC}{dt} = I + A - S - R - E \quad (1)$$

In **Hanson et al. (2014)** they do not account for the autochthonous DOC but assume that most of the observed DOC is of allochthonous origin. In comparison with Hanson et al. (2011), Hanson et al. (2014) chose to account for sedimentation in their model. They found, as many other studies, that with shorter water residence time, more DOC was exported. When studying the fate of DOC (sedimentation, mineralization or export) the percentage of mineralization and sedimentation of the total load varied from 36-85 %. The mineralization rates were found to be quite similar among the lakes, with the mean being 0.00108 d<sup>-1</sup>.

**Koehler et al. (2012)** uses a reactivity continuum model (RC model) to simulate the degradation of DOC in lakes that either are dominated by allochthonous or autochthonous DOC. What they found was actually that the initial difference in bioavailability between the two DOC pools do not exert a strong force on the long-term (a few months) degradation. In their experiment the first order decay constant  $k$  converges for both lake types after a few month exposed to microorganisms. They even found that allochthonous DOC could be more labile than autochthonous DOC after a few months due to the higher sensitivity to photooxidation of the allochthonous DOC.

A new approach to carbon budget modelling was set in **Hararuk et al. (2018)** that chose to inves-

tigate the accuracy of different model structures, when measuring epilimnetic DOC and CO<sub>2</sub>. They studied the effects of parameters on 102 different models for the same data set. They found that 20 model formulations that significantly performed better than the rest had the following properties in common: they modelled entrainment (mixing), the depth gradient in hypolimnetic CO<sub>2</sub> concentration, the density dependent partitioning of incoming DOC and CO<sub>2</sub> between epilimnion and hypolimnion. Parameters that they found did not seem to impact accuracy as much (since these varied among the top 20 model formulations), was presence or absence of: both recalcitrance and labile DOC or only one DOC pool, photooxidation, depth gradient in hypolimnetic DOC concentration, dependence or independence of labile DOC on recalcitrant DOC decay, and variable or constant incoming DOC quality.

### 2.3 Per- and polyflouroalkyl substances, PFAS

PFAS is a group of about 3000 anthropogenic, per and polyflourinated organic substances that has been widely used since 1950 all over the world (Swedish Environmental Protection Agency [2019](#)). PFAS have typically been used for impregnation of cloth (Goretex-cloth) and non-stick materials (e.g. Teflon) due to their water repellent properties, or in fire extinguishers due to their film-forming and heat-resistance properties (Swedish Environmental Protection Agency [2016](#)). Some of the most well know forms of PFAS are perflourooctanesulfonic acid (PFOS) and perflourooctanoic acid (PFOA). PFOS has since 2008 been prohibited in chemical products in EU, and PFOA is planned to be banned in 2020 in EU (Swedish Environmental Protection Agency [2020](#)). Unfortunately PFOS and PFOA have been replaced in many products by PFAS with a shorter carbon chain which has caused an increase of those in the environment instead. These are also persistent and hard to remove from surface water and the health effects are not as well documented as for PFOS and PFOA (Guo et al. [2020](#)). The challenges with PFAS in our environment is therefore great and we still have a lot to learn about their distribution and the threat they pose to us and the environment.

PFAS are classified as PBT:s meaning being a persistent, bioaccumulative and toxic substance and they are distributed in the environment mainly by water. It was first found in human blood, but has since then been found in animals, drinking water, air and even in animals in the Arctic (Ahrens et al. [2014](#); Swedish Environmental Protection Agency [2016](#)). There is a knowledge gap when it comes to the health effects of PFAS, only a few of the substances have been studied, but there are strong reasons for assuming that most PFAS substances are toxic (Kemikalieinspektionen [2020](#)). PFOS, PFOA and Perfluorononanoat (PFNA) have been classified as having toxic effects on reproduction and are suspected to be carcinogenic ([ibid.](#)). Observations have for example been done on humans that have been exposed to high concentrations of PFAS in their drinking water. These studies have shown a correlation between high amounts of PFOS and PFOA in the blood with negative effects on the immune system ([ibid.](#)).

In 2012 high concentrations of PFAS was found in the drinking water in Uppsala due to leakage of PFAS into the groundwater from firefighting training sites where firefighting foam had been used. (Uppsala vatten och Avfall [n.d.](#)). Later in 2014 a screening study was done where 44 rivers where tested for PFAS (Ahrens et al. [2014](#)). In that study Fyrisån was found to be the fourth most contaminated river, with approximately 30 ng PFAS/l. This data was sampled down streams Uppsala and downstream the wastewater treatment plant Kungsängsverket.

The current guideline value in Sweden for PFAS-11 in drinking water is 90 ng/l (Livsmedelsverket [2021](#)). PFAS-11 is the sum of 11 PFAS defined as: Perfluorbutansulfonat (PFBS), Perfluorhexansulfonat (PFHxS), PFOS, Fluortelomersulfonat (6:2 FTS), Perfluorbutanoat (PFBA), Perfluorpentanoat (PFPeA), Perfluorhexanoat (PFHxA), Perfluorheptanoat (PFHpA), PFOA, PFNA och Perfluorodekanoat (PFDA) ([ibid.](#)). A new safety threshold for PFAS accumulating in our bodies was set to 4,4 ng/kg body weight per week by the European Food Safety Authority (EFSA) in September 2020 (EFSA [2020](#)). Based on this threshold EU defined new guide line values for PFAS in drinking water to 100 ng PFAS-20/l, and 500 ng PFAS-tot/l. These shall be implemented on a national level the latest in January 2023 (Livsmedelsverket [2021](#)).

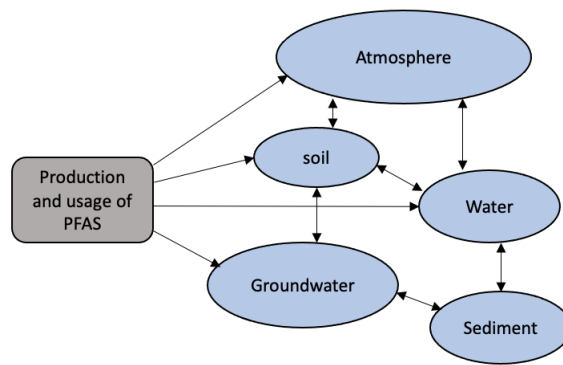
### 2.3.1 Chemical properties

The various use of PFAS are because of their surfactant properties by being both lipo- and hydrophobic (Ahrens et al. [2014](#)). They all have a carbon chain that is either fully (per-FAS) or partly (poly-FAS) flourinated with a functional group at the end. The carbon chain in PFAS is lipophilic which implies it is soluble in fat, and the functional group is hydrophilic, meaning soluble in water (Swedish Environmental Protection Agency [2019](#)). The formula for a per-FAS is  $C_nF_{2n+1}R$ , where R is the functional group that could be for example carboxylic acids or sulfonic acids (Ahrens et al. [2014](#)). The wide range of PFAS is because of the great variation that length and branching of the carbon chain, grade of flourination and type of functional group can be combined (Ahrens et al. [2014](#); Swedish Environmental Protection Agency [2019](#)).

PFAS is classified as persistent because of the strong covalent binding between C and F, which is one of the strongest, due to F having the highest electronegativity in the period table (Ahrens et al. [2014](#)). This makes PFAS extremely hard to degrade naturally and makes it very hard to treat sites contaminated with PFAS. Still, not all PFAS is persistent, but they will eventually partially degrade into a persistent PFAS such as PFOS or PFOA (Swedish Environmental Protection Agency [2019](#)).

### 2.3.2 Distribution of PFAS in the environment

There is still a lack of knowledge when it comes to the distribution of PFAS in the environment. Ahrens & Bundschuh ([2014](#)) raises concerns for this in their review of the fate of PFAS in aqueous environment. They conclude that more research is necessary concerning the interactions of PFAS, other than PFOA and PFOS, and about how they are affected by different stressors in the environment. In figure [3](#) are the many possible ways for PFAS to be distributed in the environment displayed.



**Figure 3:** The figure show a conceptual model over the distribution of PFAS in the environment.

The specific properties of PFAS have a great impact in the way they will persist and spread in the environment. The length of the carbon chain for example, affects their solubility, making a PFAS with longer carbon chain less soluble in water than one with a short carbon chain (Swedish Environmental Protection Agency 2019). In Rosenqvist et al. (2017) the dispersion of PFAS around Arlanda airport is investigated and it is seen that the composition of different PFAS, depending on the length of the carbon chain, varied depending on the distance from the contaminated source. This was shown in the relative amount of longer chain PFAS, of which the concentrations were lower further away from the source, due to hydrophobic properties and their tendency to adsorb to particles and soil (ibid.). This was also shown in Ahrens et al. (2015) who also investigated the distribution of PFAS around Arlanda, they saw that the shorter chain-PFAS ( $C < 8$ ) were mainly transported in the water phase, whereas the longer chain ( $C > 8$ ) had a tendency to accumulate in the food chain or adsorb to particles.

### 2.3.3 Modelling of PFAS in lakes

Considering that many places have been contaminated by PFAS spreading into ground water, typically from fire fighting training sites, many studies covers the modelling of PFAS in ground water, both globally and in Sweden. There are also studies that cover the global and regional distribution of PFAS in oceans (Armitage et al. 2006) or through several compartments (groundwater, sediment, soil, air, freshwater etc.) in a specific area (Su et al. 2018). Kong et al. (2018) conclude on the other hand, from their research of modelling PFAS distribution in a lake in China, that there is a knowledge gap when it comes to modelling PFAS in lakes. The studies found that are of relevance for this project are presented in table 3 and will be described further down below.

**Table 3:** Summary of previous studies that model PFAS distribution in lakes or bays.

Measured variable	Location	Source
PFOS, PFOA	Bay, San Francisco	Sánchez-Soberón et al. (2020)
PFOS, PFOA	Lake, China	Kong et al. (2018)

Sánchez-Soberón et al. (2020) developed a mass balance model to simulate the long-term distribution and concentration of PFOS and PFOA in water and sediment, and tested the model in the sub-embayments in San Francisco bay. It is assumed that the water exchanges PFOS and PFOA with the sediment, atmosphere and the adjacent embayments, and that it receives PFOS and PFOA from

rainwater, rivers and waste water treatment plants. The simulation showed a large difference between PFOS and PFOA when it came to decline in concentration. PFOA concentrations decreased to a stable state after 50 years, while PFOS concentrations first stabilised in sediment and fish after 500 years. This is believed to be an effects of the longer sediment half-life of PFOS. They judge that the limitations with the model is that the model does not take into account the precursors that could be degraded into PFOS and PFOA, and could therefore contribute. The overall most influential and sensitive parameter in determining the concentrations was the sediment half-life.

**Kong et al. (2018)** uses a fugacity-based multimedia fate model to simulate the fate, transport and transformation of PFOS and PFOA in lake Chaohu, the fifth largest freshwater lake in China. In their model they have included four compartments: air, water, soil and sediment. Although they emphasised several factors that could be improved with the model, their study shows an overall behaviour of the contaminant in the environment. They demonstrate for example that the degradation of PFOS was negligible in all compartments, and that the highest degradation of PFOA occurred in the soil and sediment. The water itself proved not to be a big sink for PFOS and PFOA, since they were either transported to sediment or removed via outflows. In their sensitivity analysis of the model they found that the parameters most sensitive were connected to the nonlinear Freundlich sorption to organic carbon, which confirmed their assumption of organic matter playing a major role in the distribution of PFOS and PFOA. To identify the importance of sediment composition (e.g. black carbon) in the sorption of PFAS is something they press on to be investigate further. Other sensitive parameters were connected to the soil, which also confirmed soil as being a big sink and source for PFAS.

## 2.4 MIKE 3 FM

MIKE 3 FM is a 3-dimensional flow model developed by the Danish Hydraulic Institute (DHI). MIKE 3 is typically used for lakes or larger water bodies where stratification due to density or species occur. FM stands for "flexible mesh" and allows to adjust the element size of the grid depending on how much detail is desired in certain parts of the modelled area. This makes the computational time much more efficient without compromising the amount of detail obtained for the areas of special interest. (MIKE powered by DHI [n.d.\[a\]](#)).

For DHI:s MIKE softwares different modules can be used. Two of those that will be used for this project is the Hydrodynamic Module and MIKE ECO Lab Module, these will be described in the following sections.

### 2.4.1 Hydrodynamic Module in MIKE 3 FM

The Hydrodynamic module simulates water level and flows and provides the basic and fundamental information for many other modules. It takes into account bathymetry, density variations and external forces such as for example wind. The hydrodynamic module simulates unsteady flow, and the module solves the numerical 2/3 dimensional incompressible Reynold average Navier Stokes equations. For the model of Ekoln, the settings in this module were calibrated by Lindqvist ([2019](#)), in terms of the temperature profiles for Ekoln.

## 2.4.2 MIKE ECO Lab Module in MIKE 3 FM

MIKE ECO Lab Module simulates water quality and ecological modelling. The module shows the distribution and concentration of the chosen variables, which for example could be organic matter, nutrients or species. It does this based on advective transport, biological, chemical and physical transport processes, and settling, resuspension and sedimentation processes. In difference to the hydrodynamic module the processes and interaction relevant to the variable, is defined and formulated in a template. These formulations can both be accessed, modified and created in ECO Lab. Since the template is independent of the settings done in the hydrodynamic module and of the discretization into a computational grid, it can be used for all model softwares from DHI that supports the ECO Lab module (MIKE powered by DHI [n.d.\[b\]](#)). To describe the processes of physical transport at every grid, ECO Lab is integrated with the advection-dispersion module. The data required, in addition to those defined in the hydrological module, is concentrations at the model's boundaries and flow and concentrations from the pollution sources (DHI [2017d](#)).

In MIKE ECO Lab an ordinary differential equation called  $P_c$  is defined for each variable in interest, see equation [2](#). In the equation below  $c$  is the concentration of the variable,  $n$  is the number of all biological and chemical transformation processes that affects the variable, and  $process$  is a process defined by the user which could be mathematical functions, built-in functions, constants, numbers, forcings and other variables (MIKE powered by DHI [n.d.\[b\]](#)).

$$P_c = \frac{dc}{dt} = \sum_{i=1}^n process_i \quad (2)$$

All processes express how the variable concentration varies in time, and this could both be defined for a certain place in the studied area, i.e bottom or surface, and could also depend on values calculated in the hydrodynamic module such as temperature. In ECO Lab there are two categories of processes: *Transformation* and *Settling*. Transformation includes all processes that transform a variable without the variable having any exchange with neighbouring elements, this could be chemical or degradation processes. Settling includes processes that affects the variable with vertical movements downward towards the bottom, like sedimentation ([ibid.](#)).

## 2.5 Evaluation of the model's performance by Lindqvist (2019)

The model settings for Ekoln in MIKE 3 FM used for this project is originally developed by Tyréns AB. Their purpose were to simulate how the water from Fyrisån, containing water released from the sewage treatment plant Kungsängsverket, spread in Ekoln. The purpose was to use the model to find a suitable place for intake of raw water (Lindqvist [2019](#); Tyréns AB [2018](#)). Their model set up was further developed by Sandra Lindqvist for her master thesis in 2019 (Lindqvist [2019](#)). Her aim was to calibrate the model for the temperature profile, to be able to simulate the patterns of water mixing in Ekoln for future climates scenarios ([ibid.](#)).

Lindqvist ([ibid.](#)) calibrated the hydrodynamics in the model for year 2018, and validated it for year 1989. The calibration went well and the statistical analysis for 150 simulated and observed values gave the following results: NSE 0.96, r 0.99 (p < 0.001) och RMSE 1,05 °C. Where the model lacked

in performance, for the calibration year 2018, was in picking up warming and cooling of the water. Warming too slowly in April, warming too fast in May and June and cooling too fast in September. It also had a difficulty defining the depth of the epilimnion at stratified conditions in August and September.

To investigate the model's sensitivity Lindqvist (2019) tested the model for the reference year 1989 using two sets of meteorological data. Data set 1, which was used for the calibration for year 2018, was collected from Uppsala, while data set 2 was collected from Uppsala Airport. The comparison showed that the model was sensitive to the wind data because of great variation in when summer stagnation happened, and for how long the stagnation was obtained between the two data sets. The discovery of the model's sensitivity towards meteorological data in 1989, could explain why the simulation for 2018 had a difficulty defining the depth of the epilimnion (ibid.). The wind data for the calibration year 2018 was measured at Uppsala University in the city, while temperature data for Ekoln, was measured in the middle of Ekoln. This probably resulted in the model having lower wind velocities (due to the structure of a city reducing wind velocities) than the actual wind velocities in the middle of Ekoln. This could be the reason why the simulated depth of epilimnion was not as deep as the observed measured depth. Higher wind velocities increases the circulations in the lake causing the epilimnion to reach deeper in the lake during summer. Lindqvist (ibid.) therefore emphasises the importance of suitable data used as input in the model, where the optimal of course would be to only use data actually measured at Ekoln.

## 2.6 Validation of hydrological models

In the article (Biondi et al. 2012) suggestions are presented for how the validation process of hydrological models should be performed. Biondi et al. (ibid.) separates the validation into *performance validation* and *scientific validation*. Performance validation provides a quantitative measurement of the performance of the model, and typically measures the simulated error in some way. This can be done using different statistical tests, or by graphically comparing simulated and observed data (ibid.). Scientific validations are based on the fact that a model's performance should not only be judged by a quantitative measure, which could be misleading. It is often important to evaluate the model, not only by comparing output and observed values, but evaluating what processes the model is supposed to capture (ibid.). The scientific validation is therefore a more qualitative measurement of the model's performance by evaluating the scientific value of the model. Biondi et al. (ibid.) argue that the best validation is done when both performance validation and scientific validation is combined, but the scientific validation is particularly required when performance validation can not be done properly. As presented in Biondi et al. (ibid.) this could be the case when there are few observed measurements to compare simulated values with, or when the goal of the model rather than to make predictions, is to provide knowledge of physical processes.

### 3 Method

*In this section follows a presentation of the process of modelling NOM and PFAS. The first section is focused on a summary of the settings done in the Hydrodynamic module and in ECO Lab. This section also present the data used for the model. This is followed by a presentation of the specific processes used to model time variations of NOM, and then the process of modelling PFAS. Finally, the validation process of the model is discussed.*

There were two objectives with this model study, one was to produce time variations of NOM in terms of Colour and TOC in Ekoln (main focus), and the second was to investigate the necessary requirements to successfully model PFAS. For simplicity, when using the term NOM in the following sections, it refers to both TOC and Colour, and when the observed and simulated concentrations of both PFAS and NOM are discussed, it will always be referring to the concentrations in the centre of Ekoln at the sampling site Vreta Udd. Due to the very different preconditions for NOM and PFAS when it comes to the existing data, the procedure of modelling them was very different. While the procedure of modelling PFAS was very open and explorative, and is discussed further in section [3.3 Modelling PFAS](#), the procedure for calibrating the model for NOM had a more straight-forward approach, which is described further in section [3.2 Constructing within-lake processes of NOM](#). Both simulations however, depend on the same settings in the hydrodynamic and ECO Lab module, which are presented first.

#### 3.1 Model settings

The model settings are separated between those done in the Hydrodynamic module and those done in the ECO Lab module. Lindqvist ([2019](#)) calibrated parameter values for the hydrodynamic module for 2018, and the same settings were therefore used for the hydrodynamic module in this project. What was added in the model for this project was the ECO Lab module which is used to simulate water quality, i.e. NOM and PFAS in this case.

Another factor that was adjusted in this project, compared to the study done by Lindqvist ([ibid.](#)), was the modelled time period. Considering that the water retention time for Ekoln is 1.2 years, that implies that the simulated time period necessary to best capture the full water exchange, should be at least that length. When evaluating for which period all required data overlap, the period of interest was narrowed down to 2017-02-20 to 2018-09-15. The constraining part was the data for PFAS, considering that a lot more data existed for NOM. This specific time period also coincides with a maximum amount of measured concentrations of NOM and PFAS in Ekoln to compare simulated concentrations with. NOM are measured in Ekoln at three depths six times in the period February to September every year. The simulated time period for this project is therefore starting in February 20<sup>th</sup> 2017 and ending in September 13<sup>th</sup> 2018. For PFAS, measurements exist on three depths, seven measurements exist in 2017 from February-November, and one measurement exists in April 2018. Because observed measurements exist for Ekoln for several depths for all variables (Temperature, TOC, Colour and PFAS) at 2017-02-20, this date was chosen as the starting date for all simulations. Another constraining part was the computation time. A simulation running the hydrodynamic module as well as ECO Lab for a period of 19 months, takes approximately two days. When using a decoupled hydrodynamic module (i.e. using pre-recorded results for hydrodynamic conditions) the simulation

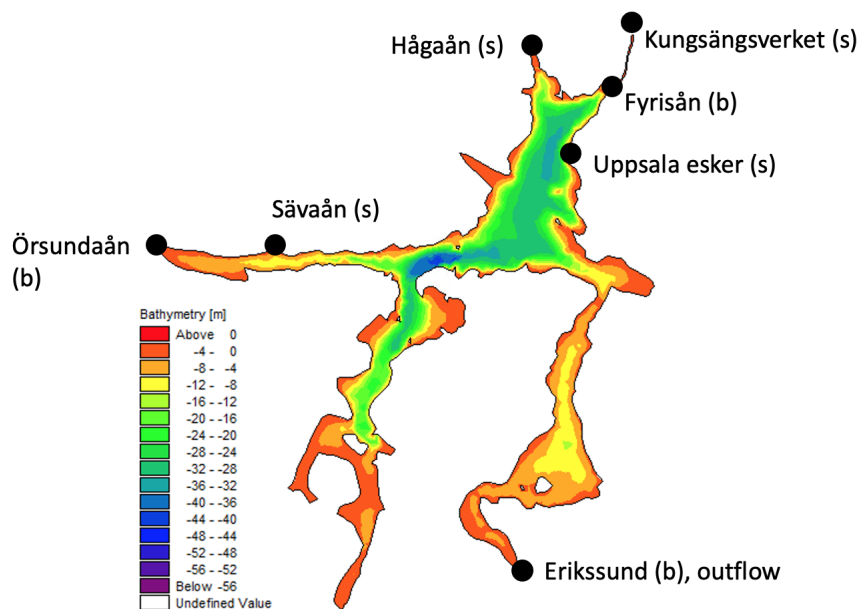


time is reduced to approximately 12 hours.

### 3.1.1 Hydrodynamic module

*The Hydrodynamic module is driven by input data from inflows, meteorological data and initial conditions for Ekoln regarding temperature and water elevation. This is to simulate how water flows in Ekoln, and how water masses either mix or stagnate in the lake.*

Inflows that were accounted for in the model were Fyrisån, Örsundaån, Sävaån, Hågaån, Kungsängsverket (the sewage treatment plant located up streams in Fyrisån) and the Uppsala esker. These account for 95 % of all the inflows to Ekoln. The rest 5 % are from diffuse sources and were not accounted for in the model. The inflow from the esker was set to a constant flow of  $0.05 \text{ m}^3/\text{s}$  (Lindqvist 2019). In figure 4 the model area is shown together with the included inflows and the outflow.



**Figure 4:** The modelled area with inflows and the outflow. Those inflows/outflow that are small enough to be represented as a single point are defined in the model as a source (s), those that have wide outlets are instead defined as boundaries (b). The colours show the depth gradient in the lake. Erikssund is the only outflow.

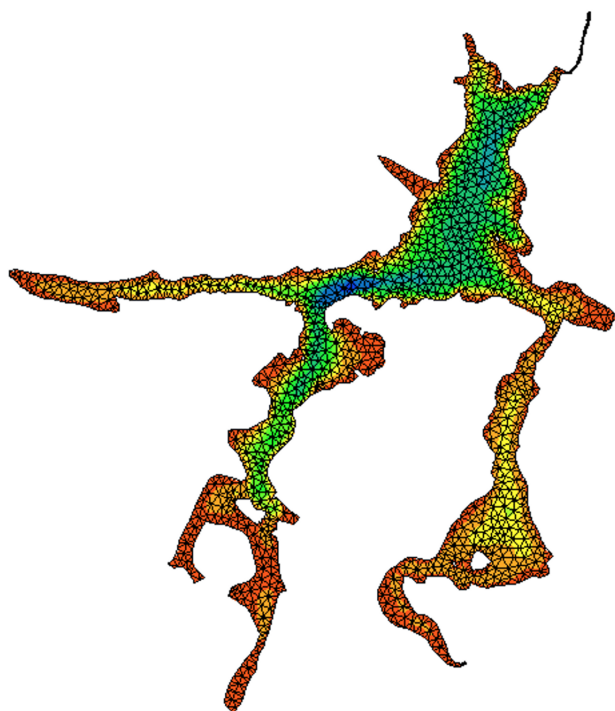
The model is driven by input in terms of meteorological data, and discharge and temperature data from the inflows. The meteorological data included wind speed, wind direction, air temperature, relative humidity and clearness. Included as input was also ice coverage in term of ice thickness, which is set to a constant value of 0.1 m during the periods when the lake is covered in ice. As initial conditions the average water elevation for Mälaren was used. The initial conditions for temperature were based on measured temperatures at 26 different depths at Vreta Udd, measured 2017-02-20. These were estimated to represent the vertical temperature profile in the lake for the starting date. It is only for Fyrisån and Kungsängsverket that temperature input data that varies in time were used, for Uppsalaåsen a constant temperature of  $8^\circ\text{C}$  was set and Örsundaån, Sävaån and Hågaån were assumed

to have the same temperature as the lake. The basic settings for the hydrodynamic module are summarised in table 4. As can be seen in table 4 density in this model is defined as a function of water temperature. The parameterisation of temperature and heat exchange was based on Lindqvist (2019), these are displayed in the end of table 4.

**Table 4:** A summary of the settings for the hydrodynamic module. The parameters that were calibrated by Lindqvist (2019) for Temperature and Heat exchange are presented in the end of the table.

<b>Parameter</b>	<b>Setting</b>
Basic equation	Shallow water equation
Solution Technique	Time integration: higher order Space discretization: higher order
Depth	No depth correction
Flood and Dry	No flood and dry
Density	Function of Temperature
Eddy viscosity	Horizontal: Smagorinsky formulation Vertical: k-epsilon formulation
Bed resistance	Type: Roughness height
Coriolis forcing	Varying in domain
Wind forcing	Varying in time, constant in domain
Ice Coverage	Type: Specified ice thickness
Tidal potential	Not included
Precipitation - Evaporation	Not included
Infiltration	Not included
Wave radiation	Not included
Structures	Not included
Initial condition	Average water elevation in Mälaren
Temperature	Dispersion: Scaled eddy viscosity formulation
<b>Calibrated Parameter</b>	<b>Value</b>
Transfer coefficient for heating	0.0085
Transfer coefficient for cooling	0.0096
Light extinction factor	0.25 m <sup>-1</sup>

The mesh used is an unstructured mesh, which means that the grid size varies in the domain. This mesh was developed by Lindqvist (ibid.) with the aim to decrease computation time without losing resolution vertically for the temperature profile. The mesh together with the bathymetry of Ekoln can be seen in figure 5. The mesh divides the lake into 41 vertical layers, 1 m thick. The number of nodes in the mesh is 1758, number of elements is 2570 and the smallest element is 617 m<sup>2</sup>. Though this mesh was optimal for high resolution vertically, it lost resolution horizontally. To simulate substance transportation it could be argued that a mesh with higher resolution should be used, which was the purpose of the original mesh developed by Tyréns AB. This was considered, but the original mesh would have resulted in a computation time of more than a week for the whole time period, which is not possible for a project this short.



*Figure 5: A map over the unstructured mesh over for Ekoln.*

The data used as input in the Hydrodynamic module are presented in table 5. All data, but the temperature from the inflows, are the same as Lindqvist (2019) used for the calibration of the model for year 2018, only collected for a longer time period, 2017-2018. The exact same temperature data used by Lindqvist (ibid.) could not be found for the longer time period and was therefore taken from SMHI:s modelled data. The only data added is the radiation data and precipitation data. The radiation data was used to calculate a mean annual daily maximum radiation for Ekoln, this is further explained in section 3.2.3 *Photooxidation*. Precipitation was only added in the hydrodynamic module for the modelling of PFAS, to add a PFAS concentration entering Ekoln from precipitation. This is further explained in section 3.3 *Modelling PFAS*. Due to lack of discharge data for the rivers, discharge for all rivers were estimated using SMHI modelled data (SMHI n.d.[e]). Regarding the ice coverage for Ekoln, the data was collected from the same gauge station as in Lindqvist (2019). This data is for Skarven, a sub-basin of Mälaren 13 kilometres south-east of Ekoln (ibid.). Skarven is smaller than Ekoln which implies that Skarven probably has a higher flow through the basin, which could imply that ice might settle sooner and stay longer in Ekoln than in Skarven (ibid.). The surface elevation was based on the average surface level of Mälaren and subtracted by the mean surface level of 0.78 m (SMHI n.d.[d]).

**Table 5: Input data for the Hydrodynamic module.**

	Parameter	Resolution	Location	Source
Meteorology	Air temperature	1 h	Geocentrum	UU <sup>1</sup>
	Relative humidity	1 h	Geocentrum	UU <sup>1</sup>
	Wind velocity	1 h	Geocentrum	UU <sup>1</sup>
	Wind direction	1 h	Geocentrum	UU <sup>1</sup>
	Cloudiness	1 h	Uppsala Airport	SMHI <sup>2</sup>
Discharge	Fyrisån	24 h	Outlet	SMHI <sup>3</sup>
	Örsundaån	24 h	Outlet	SMHI <sup>3</sup>
	Sävaån	24 h	Outlet	SMHI <sup>3</sup>
	Hågaån	24 h	Outlet	SMHI <sup>3</sup>
	Uppsalaåsen	24 h	Uppsalaåsen	Lindqvist <sup>4</sup>
	Kungsängsverket	24 h	Outlet	UVA <sup>5</sup>
Temp.	Ekoln	6 days/year	Vreta Udd, Ekoln	SLU <sup>6</sup>
	Fyrisån	24 h	Outlet	SMHI <sup>3</sup>
	Örsundaån	24 h	Outlet	SMHI <sup>3</sup>
	Sävaån	24 h	Outlet	SMHI <sup>3</sup>
	Hågaån	24 h	Outlet	SMHI <sup>3</sup>
	Kungsängsverket	24 h	Outlet	UVA <sup>5</sup>
Other	Water level	24 h	Mälaren	SMHI <sup>3</sup>
	Ice	24 h	Mälaren Skarven	SMHI <sup>3</sup>
	Radiation	1 h	Vreta Udd, Ekoln	SMHI <sup>7</sup>
	Precipitation	24 h	Uppsala	SMHI <sup>8</sup>

<sup>1</sup> (Uppsala Universitet 2020)

<sup>2</sup> (SMHI n.d.[b])

<sup>3</sup> (SMHI n.d.[e])

<sup>4</sup> (Lindqvist 2019)

<sup>5</sup> (Uppsala Vatten och Avfall AB 2020a)

<sup>6</sup> (SLU n.d.)

<sup>7</sup> (SMHI, Naturvårdsverket, & Strålsäkerhetsmyndigheten n.d.)

<sup>8</sup> (SMHI n.d.[c])

### 3.1.2 ECO Lab module

The ECO Lab module requires input data of the specified variable, i.e. NOM and PFAS, which is defined in the ECO Lab template. This information is added into the calculated flows from the hydrodynamic module to simulate how substances spread in water masses.

For NOM all rivers act as sources and the contribution from the Uppsala esker was assumed to be negligible. The concentration of NOM from Kungsängsverket is already accounted for in data from Fyrisån. For PFAS the only source used was Kungsängsverket. This was due to limited data of PFAS from other sources. The outflow of TOC, Colour and PFAS is through Erikssund and no data exists for this point, therefore the condition for the outflow is set to "zero gradient", i.e. same concentration

as the lake.

Below are the data used for ECO Lab presented. In table 6 and 7 the data for NOM and PFAS respectively are presented for the inflows used and for observed data in Ekoln. No TOC data exists for Sävaån, the TOC data for Sävaån is therefore estimated with the same TOC concentrations as for Hågaån. Colour, unit Pt mg/l, is measured using a filtered water sampled in a 5 cm cuvette at wavelength 420 nm (AbsF\_420\_5cm). AbsF\_420\_5cm is converted to the unit Pt mg/l by multiplication with 500 (Köhler & Lavonen 2015). For NOM and PFAS the initial conditions for Ekoln were set using the observed measurements in Ekoln for 2017-02-20. The vertical variation from those measurements at Vreta Udd were approximated to represent the vertical variation in the whole lake, i.e. no horizontal variation. For dispersion, scaled eddy viscosity formulation is used, and the default value of 1 is used for horizontal dispersion, and 0.01 is used for vertical dispersion. The settings for dispersion were used for both PFAS and NOM. The time step for the model calculations was defined as 30 s, and output data for NOM and PFAS were stored for every hour.

The PFAS that are included in this study are: FOSA, PFBS, PFHxA, PFDA, PFDoDA, PFOS, PFHpA, PFNA, PFPeA, PFOA, PFHxS, PFUnDA. These are the substances referred to when the term "PFAS" is used in the following sections in this report. The substance PFTeDA is also measured in Ekoln but is not included in this study because it is not measured at Kungsängsverket.

**Table 6:** Data used for modelling NOM for the period February 2017 - September 2018.

	Parameter	Resolution	Depth [m]	Source
Ekoln	Colour [Pt mg/l]	6 days/year	0.5, 15, 30	(SLU 2020)
	TOC [mg/l]	6 days/year	0.5, 15, 30	(SLU 2020)
Fyrisån	Colour [Pt mg/l]	day		(SLU 2020)
	TOC [mg/l]	1 time/month		(SLU n.d.)
Örsundaån	Colour [Pt mg/l]	day		(SLU 2020)
	TOC [mg/l]	2 time/month		(SLU n.d.)
Sävaån	Colour [Pt mg/l]	day		(SLU 2020)
	TOC [mg/l]	–		(SLU n.d.)
Hågaån	Colour [Pt mg/l]	day		(SLU 2020)
	TOC [mg/l]	1 time/month		(SLU n.d.)

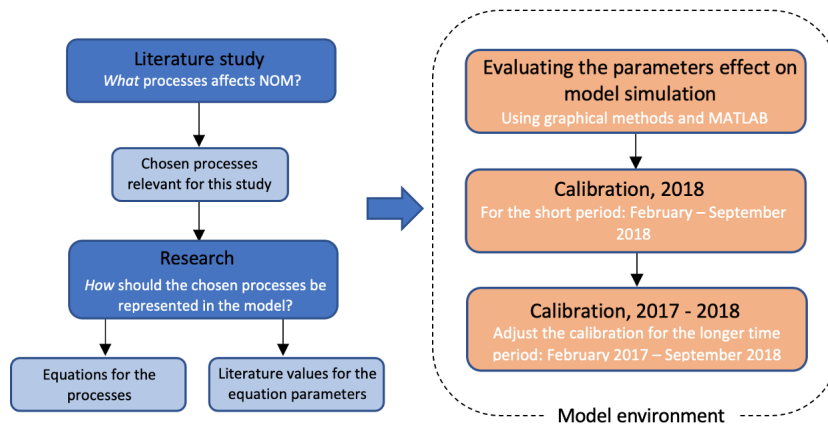
**Table 7:** Data used for modelling PFAS for the period February 2017 - September 2018.

	Parameter	Resolution	Depth [m]	Source
Ekoln	PFAS	7 times	0.5, 15, 30	(SLU 2020)
Kungsängsverket	PFAS	1 time/month	-	(Uppsala Vatten och Avfall AB 2020b)

### 3.2 Constructing within-lake processes of NOM

The ambition with modelling NOM was to calibrate the model for within-lake processes affecting NOM. This was judged to be possible considering the amount of data that exists for NOM from both

inflows and for Ekoln. The process, seen in figure 6, can be divided into two parts: theory/research and model calibration (in the figure showed as blue boxes versus red boxes). The theory and research for NOM was built up by the results from the literature study presented in section 2.2 *Natural Organic Matter; NOM*, this information was used to decide how the processes observed in reality should be represented and simplified in the model. Further research was done to decide what equations should be used to represent the chosen processes based on previous studies. When the equations were defined and literature values were found for the equation parameters, the equations were implemented in the model using ECO Lab. To make the process of calibration more precise, some parameters were investigated by using MATLAB, to deepen the understanding of their effect on the simulation. To be more time efficient the calibration was done in two steps: first the parameter values were calibrated on a shorter time period, and secondly, when the simulation was "good enough" (based on visual interpretation), the calibrated parameter values were applied on the longer time period, and if needed were calibrated further.



**Figure 6:** A flowchart over the process of calibrating the model for degradation of NOM.

For the modelling of TOC and Colour three processes were chosen to influence the variables in the lake (other than inflows and outflow), which can be seen in equation 3. Where  $S(z)$  is sedimentation dependent on depth  $z$ ,  $D(T)$  is decay dependent on temperature  $T$  and  $P(I, z)$  is photooxidation dependent on irradiation  $I$  and depth  $z$ . The term decay refers in this case to mineralization through respiration which stands for the majority of the mineralization of organic matter (Jonsson et al. 2001), i.e. do not include mineralization caused by photooxidation.

$$\frac{d(TOC)}{dt} = -S(z) - D(T) \quad \frac{d(Colour)}{dt} = -P(I, z) \quad (3)$$

As can be seen in equation 3, TOC is only affected by decay and sedimentation, and Colour is only affected by photooxidation. The differentiation is because TOC and Colour have different properties and are not influenced in the same degree by different processes. It is known that Colour (i.e. the fraction of TOC high in colour) is effectively degraded through photooxidation, while this is not as effectively on TOC low in colour (Koehler et al. 2012; Köhler & Lavonen 2015). This is the reason why the dominating process influencing degradation of Colour was chosen to be photooxidation and why it was not included as a major process influencing TOC. A process that was not included for

neither TOC nor Colour is the input of autochthonous NOM, i.e the production of NOM in the lake. This is due to lack of knowledge of the proportions between allochthonous and autochthonous NOM in Ekoln. Considering that autochthonous NOM often can be assumed to stand for a smaller part of the total NOM concentration in lakes (Jonsson et al. 2001; Köhler & Lavonen 2015) it is not unreasonable for a simplified model to only account for NOM of allochthonous origin, as has also been done in Hanson et al. (2014). This further implies that the model only models one pool of NOM considering biodegradability, meaning that it considers all TOC and Colour equally recalcitrant/labile. This assumption is based on the results from Hararuk et al. (2018) and Koehler et al. (2012) that both showed that the inclusion of pools of DOC with different bioavailability did not have a substantial impact on the performance of the model. Sedimentation was chosen to be included as a process influencing TOC considering that many studies show that sedimentation stands for a major part of the NOM flux in lakes (Hanson et al. 2014; Sobek et al. 2006).

Below follows a description of how these processes, seen in equation 3, are described in the ECO Lab template. For each process, i.e. decay, sedimentation and photooxidation, also follows a section presenting literature values for the relevant parameters based on previous studies.

### 3.2.1 Decay

The process of decay in ECO Lab is described in equation 4, where  $TOC_{decay}$  is the amount of decayed TOC [mg/l/d],  $[TOC]$  is the original amount of TOC in the water,  $k_0$  is a reference decay constant at 20 °C [ $d^{-1}$ ] and  $\theta$  is the Arrhenius temperature coefficient for a reference temperature of 20 °C and  $T$  is temperature.

$$TOC_{decay} = [TOC] \cdot k_0 \cdot \theta^{(T-20)} \quad (4)$$

There are many ways to calculate temperature sensitivity, a common way is to use the Van't Hoff-Arrhenius equation that describes the relation between a reaction constant and temperature (Myszograj 2018; Sierra 2012). The equation is commonly expressed using temperature coefficients such as  $Q_{10}$  or  $\theta$ . These are two common ways to express the scaling of an experimental reaction rate ( $k_0$ ) to an actual reaction rate on ecosystem scale that depends on temperature ( $k$ , see equation 5) (Hanson et al. 2011). The equations for  $Q_{10}$  or  $\theta$  is presented in equation 5 where  $T_{ref}$  is a reference temperature. In ECO Lab the expression for  $\theta$  exists as a built in function and is also used in the scaling of decay of biochemical oxygen demand (BOD) in DHI (2017d).  $\theta$  is also used by Hanson et al. (2011) in their modelling study for the scaling  $k_0$ . For this study  $\theta$  will therefore be used for the scaling, but  $Q_{10}$  is also presented here because it is often mentioned in the same context as  $\theta$ .

$$k = k_0 \cdot Q_{10}^{\left(\frac{T-T_{ref}}{10}\right)} \quad k = k_0 \cdot \theta^{(T-T_{ref})} \quad (5)$$

$k_0$ : From Hanson et al. (2014) the mean mineralization rate was  $0.001 d^{-1}$ . This rate is also used by Hanson et al. (2011) that test rates in the range  $0.01-0.001 d^{-1}$ . In the study Sobek et al. (2006) their carbon budget for a small lake in Sweden shows that on average 43 % of all carbon (C) are mineralized, which equals to a decay rate of approximately  $0.0012 d^{-1}$ .

$\theta$ : For the scaling of  $k_0$  a value of  $\theta$  is typically in the range of 1.0-1.12 for different biochemical processes (Myszograj 2018). For biological respiration a value of 1.07 is commonly used (Hararuk

et al. (2018). In (Hanson et al. (2011)) a value of  $\theta = 1.073$  is used for a  $T_{ref}$  of 20°C (which equates to a Q10 value of 2.0 when using the same reference temperature of 20°C). And Hanson et al. (2014) uses a  $\theta$  of 1.07.

### 3.2.2 Sedimentation

The process of sedimentation is described in equation (6). Where  $TOC_{sed}$  is the amount of sedimentated TOC [mg/l/d],  $vsm$  is the settling velocity [m/d],  $[TOC]$  is the original amount of TOC in the water [mg/L] and  $dz$  is the thickness of the layer in the computational grid [m] (DHI (2017b)).

$$TOC_{sed} = \frac{vsm \cdot [TOC]}{dz} \quad (6)$$

**vsm:** Little literature, to the best of my knowledge, were found regarding a settling velocity expresses in m/s as it is ECO Lab. Therefore a theoretical settling velocity is used to estimate the settling velocity, as was also used in Stabel (1987). A theoretical settling velocity is calculated using Stokes relation as can be seen in equation (7) (ibid.).

$$vsm = \frac{(\rho_s - \rho)gd^2}{18\mu} \quad (7)$$

$vsm$  = settling velocity [ $ms^{-1}$ ]

$\rho_s$  = density of the particles [ $kgm^{-3}$ ]

$\rho$  = density of the water [ $kgm^{-3}$ ]

$g$  = acceleration of free fall [ $9.81 \text{ m s}^{-2}$ ]

$d$  = particle diameter [m]

$\mu$  = coefficient of viscosity of the lake water [ $kgm^{-1}s^{-1}$ ]

Using equation (7) with:

$\rho_s = 1500 \text{ kgm}^{-3}$  (assumed as bulk density of a particle in Stabel (ibid.)),

$d = 0.225 \cdot 10^{-6} \text{ m}$

$\mu = 8.9 \cdot 10^{-4} \text{ kgm}^{-1} \text{ s}^{-1}$ ,

the value for  $vsm = 0.00134 \text{ md}^{-1}$ .

Based on the definition of DOC being particles less than  $0.45 \mu\text{m}$  in diameter and stands for 90 % of TOC, the value of  $d$  is set to half that value to represent a diameter for the most abundant particle of organic matter.

### 3.2.3 Photooxidation

The photooxidation process can be described as presented in equation (8) where the expression is taken from the DHI ECO Lab template for Algae and Sediment Model (DHI (2017a)).

$$Colour_{photo} = [Colour] \cdot rd \cdot k_{photo} \cdot M_{photo} \quad (8)$$

$Colour_{photo}$  = Photooxidated Colour [Pt mg/l/d]

$[Colour]$  = Amount of Colour in the water [Pt mg/l/d]

$rd$  = Relative day length, f(latitude, day, month, year)

$k_{photo}$  = max relative photooxidation rate [ $d^{-1}$ ]



$M_{photo}$  = UV radiation Monod relation for photooxidation

The relative day length ( $rd$ ) is calculated using ECO Lab built in function for relative day length that depends on latitude, day, month and year (DHI 2017c). The UV Monod relation ( $M_{photo}$ ) scales the maximum photooxidation rate ( $k_{photo}$ ) depending on the access to light. Originally the Monod equation is an empirical relation between the growth rate of microorganisms and the concentration of an essential substrate (typically nutrients) (Monod 1949). In the case for photooxidation rate the limiting factor is light and the expression for the correction factor  $M_{photo}$  is therefore expressed as presented in equation 9 (DHI 2017a).

$$M_{photo} = \frac{(I - I_{min})}{(I - I_{min}) + I_{1/2}} \quad (9)$$

$I$  = Solar radiation, photosynthetically active radiation (PAR) in actual water column layer [ $\mu\text{mol photon m}^{-2}\text{s}^{-1}$ ]

$I_{min}$  = minimum PAR light necessary to achieve photooxidation [ $\mu\text{mol photon m}^{-2}\text{s}^{-1}$ ]

$I_{1/2}$  = PAR half saturation, PAR light at which the photooxidation rate is half its maximum rate [ $\mu\text{mol photon m}^{-2}\text{s}^{-1}$ ]

The solar radiation in the water column,  $I$ , can be calculated as presented in equation 10 which calculates an average radiation in the water column. This is calculated using Lambert Beer's law that calculates the radiation,  $I_{top}$ , reaching the top of a certain water layer  $dz_{0-j}$ . Lambert Beer's law exists as a built in function in ECO Lab and is presented in equation 11 (DHI 2017c). The radiation at the surface,  $I_{surface}$  in equation 11, is here a constant and can for example be set as an annual mean of daily maximum radiation (Haverstock et al. 2012).  $dz$  stands for the length of a water layer which is 1 meters in this model. The light extinction coefficient ( $\eta$ ) is a percentage of how much light is absorbed or scattered in a 1 m column of water. This factor depends on the turbidity and colour of the lake water and ranges from 0-1, where clear water lakes have low values, and more turbid lakes a value closer to 1.

$$I = \frac{1 - e^{-\eta \cdot dz}}{\eta \cdot dz} \cdot I_{top} \quad (10)$$

$$I_{top} = I_{surface} \cdot e^{-\eta \cdot dz_{0-j}} \quad (11)$$

$\eta$  = Light extinction coefficient

$dz$  = Water layer height [m]

$I_{top}$  = Surface light at the top of the water layer [ $\mu\text{mol photon m}^{-2}\text{s}^{-1}$ ]

$I_{surface}$  = Surface light [ $\mu\text{mol photon m}^{-2}\text{s}^{-1}$ ]

$dz_{0-j}$  = Water column height between layer 0 and j [m]

Considering that less radiation will reach the water when the lake is covered in ice, two conditions are set in ECO lab. If the temperature is below 0.2 °C an ice coverage is assumed and radiation reaching the water surface ( $I_{surface}$ ) is reduced by 90 %, otherwise  $I$  is calculated according to equation 10 (DHI 2017a).

$k_{photo}$ : In Amon & Benner (1996) they compare the relative degradation of DOC by photooxidation and bacterial respiration. From their experiment using water from the Amazon river system they find that under the same time period photooxidation consumed 15 % of DOC, while bacterial mineralization only consumed 1.2-2.7 % (ibid.). This was when comparing the two processes in water layers penetrated by light, when compared over the whole water column bacterial mineralization were the dominating process (ibid.). Applying this to Ekoln, based on the assumption of the mineralization rate ( $k_0$ ) being approximately  $0.001 \text{ d}^{-1}$  (Hanson et al. 2011, 2014) this gives a photooxidation rate ( $k_{photo}$ ) of approximately  $0.006 - 0.013 \text{ d}^{-1}$ . This can be compared to the default value for the photooxidation rate in DHI's template of 0.02 (DHI 2017a).

$I_{min}, I_{1/2}$ : In the DHI template DHI (ibid.), the default value for both  $I_{min}$  and  $I_{1/2}$  is  $5 \mu\text{mol photons m}^{-2}\text{s}^{-1}$ . To my best knowledge no other literature values specifically addressing these to parameters were found for photooxidation.

$I_{surface}$ : For the value of  $I_{surface}$  Haverstock et al. (2012) chose to calculate that from the mean annual maximum of daily radiation. Using radiation data for Ekoln from SMHI, Naturvårdsverket, & Strålsäkerhetsmyndigheten (n.d.), the annual mean of 2017 of daily maximum is  $51 \mu\text{mol photons m}^{-2}\text{s}^{-1}$ . The radiation data was for the location of Vreta Udd, and the radiation collected was photosynthetically active radiation (PAR) for every hour, in  $\text{Wm}^{-2}$ . A conversion factor of 0.22 was used to convert  $\text{Wm}^{-2}$  to  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$ . This is in the same scale as the default value for  $I_{surface}$  for June being  $60 \mu\text{mol photons m}^{-2}\text{s}^{-1}$  in DHI (2017a).

$\eta$ : The light extinction factor for Ekoln is already defined as 0.25 in the hydrodynamic module, a value that was calibrated for Ekoln by Lindqvist (2019).

### 3.3 Modelling PFAS

The main goal for modelling PFAS was to pin point critical factors concerning how to successfully be able to model PFAS in Ekoln. The ambition is that the results from this study can be of help for future studies when modelling and analysing PFAS in Ekoln. Two simulations were made for PFAS in Ekoln:

1. Assuming that PFAS enters Ekoln only with discharges from Kungsängsverket
2. Assuming that PFAS enters Ekoln with discharges from Kungsängsverket and with precipitation

For the modelling of PFAS the only source that data existed for was for the sewage treatment plant Kungsängsverket. When simulated concentrations of PFAS in Ekoln from the first simulation were compared to observed data at Vreta Udd, it could be concluded that the simulated values were much lower than the observed concentrations. This implied that Kungsängsverket, although assumed to be a major source of PFAS to Ekoln, could not account for all the PFAS entering Ekoln. This first simulation led to thoughts of how the model could be improved, considering the limited access to data from other sources.

It is known that PFAS can be transported in the atmosphere and is spread by precipitation (Fredricsson et al. 2018). Another source that was added specifically for the modelling of PFAS was therefore

precipitation. Data for precipitation was added in the hydrodynamic module using daily data from SMHI (n.d.[c]) measured at Uppsala city. A constant concentration of PFAS was set to 1.1 ng/l, which is based on data collected by Fredricsson et al. (2018) for 2017 at Norunda, a location approximately 4 miles north of Ekoln. By doing a mass balance calculation it could be concluded that the addition of PFAS in precipitation most likely would not explain the differ between simulated and observed concentrations, but for future modelling of PFAS in Ekoln it would still be a source that should be accounted for. For these two simulations all other sources were set to contribute with 0 concentrations of PFAS to Ekoln.

### 3.4 Validation

In accordance to the suggested process of validation done by Biondi et al. (2012), a great focus was on the scientific validation of the model used in this project. This is because the goal with this study was mainly to reproduce physical processes (decay, sedimentation and photooxidation) and because few observed measurements exists to compare simulated concentrations with. For each of the three depths measured in Ekoln there are only 12 observed measurements, which is few in comparison with the time span of 19 month that they cover. Also, the optimal performance validation is done for a new time period using a different data set than that used for the calibration (ibid.). This was not possible for this project either, due to limited data. Despite this a performance validation was done, considering that it can still be used as an additional tool in analysing the model together with a scientific validation.

#### 3.4.1 Performance validation

For the performance validation two commonly used validation methods for hydrological models was used: Nash-Sutcliffe efficiency coefficient (NSE) and Root mean square error (RMSE) (ibid.). The equations used can be seen in equation 12 and 13 respectively.  $s_i$  and  $o_i$  are the simulated and observed value respectively at time step  $i$ .  $e_i$  is the difference between  $s_i$  and  $o_i$ . From equation 12 it can be seen that NSE is unitless and that a perfect fit, when the error variance equals zero ( $s_i - o_i = 0$ ), is when  $NSE = 1$ . If  $NSE = 0$ , it means that the model's error variance equals the variance of the observed data. RMSE is a measurement of the average error between simulated and observed values, meaning it has the unit of the measured variable. For RMSE a perfect model fit is  $RMSE = 0$ .

$$NSE = 1 - \frac{\sum_{i=1}^n (s_i - o_i)^2}{\sum_{i=1}^n (o_i - \bar{o}_i)^2} \quad (12)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n e_i^2} \quad (13)$$

#### 3.4.2 Scientific validation

This validation method was the main focus for this project. For the scientific validation the suggested steps as presented in Biondi et al. (ibid.) was applied. They suggest using the SWOT analysis, which stands for Strengths, Weaknesses, Opportunities and Threats. This type of analysis focuses on spending an equal amount of time on the evaluation for each of the four SWOT steps. In addition to SWOT

Biondi et al. (2012) further present a list of steps for the scientific validation focusing on evaluation of: the model's purpose, the assumptions made, the theoretical fundamentals, alternative hypothesis, potential developments and applications and uncertainty in output and input data. It is also important to make material and results available for the scientific community to reproduce the results.

## 4 Results

*In this section the simulated time variations of NOM and PFAS are presented in comparison to observed measurements in Ekoln. First comes a presentation of the calibration done for NOM in terms of TOC and Colour, focusing on the performance of the model and the impact of the processes (decay, sedimentation and photooxidation). This is followed by the results from the modelling and investigation of the PFAS-situation in Ekoln.*

### 4.1 Simulation of temperature profiles for the period of 2017-2018

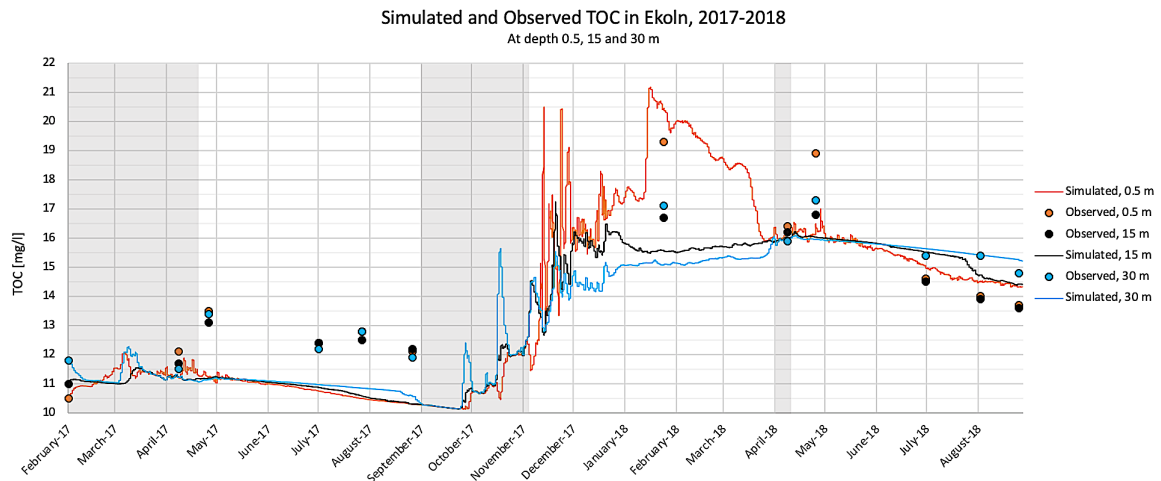
Before analysing the results for NOM and PFAS, the temperature profiles were analysed to make sure that the simulated water mixing patterns in the lake were close enough to those observed. The hydrodynamics in the model were originally calibrated for year 2018 using initial temperature conditions for 2018-02-12 (Lindqvist 2019). For this project the time period starts in 2017, and uses initial temperature conditions for 2017-02-20. The temperature profiles were compared to observed measurements of temperature in Ekoln, and with the results from 2018 by Lindqvist (ibid.). The profiles showed that the model lacked in timing the water mixing event in September for both 2017 and 2018. For all the other dates the model matched observed temperatures very well. The temperature profiles for 2018 from this project were also compared to the temperature profile from the calibration of the model done by Lindqvist (ibid.), these are not identical, but very close to each other. The temperature profiles for this model can be seen in Appendix section 8.1 in figure 13a and 13b, together with calibration results for 2018 by Lindqvist (ibid.) in figure 14.

### 4.2 Modelling time variations of NOM

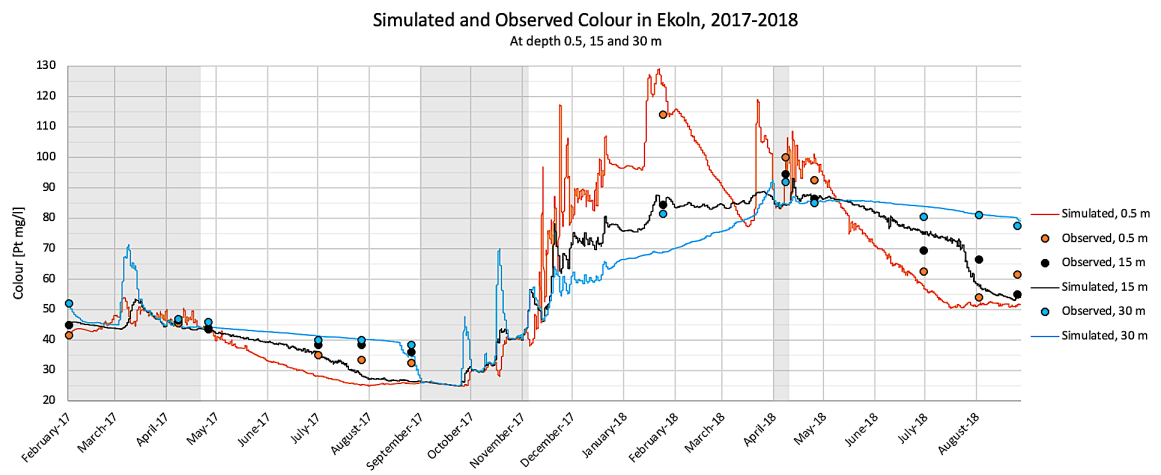
*In the following sections the results from modelling time variations of NOM are presented. First the simulations are presented, showing how the model managed to capture time variations of TOC and Colour. This is followed by a sensitivity analysis and a presentation of results from the calibration. Finally the impact from the processes decay, sedimentation and photooxidation is analysed.*

#### 4.2.1 Time variations and comparison of simulated and observed concentrations of NOM

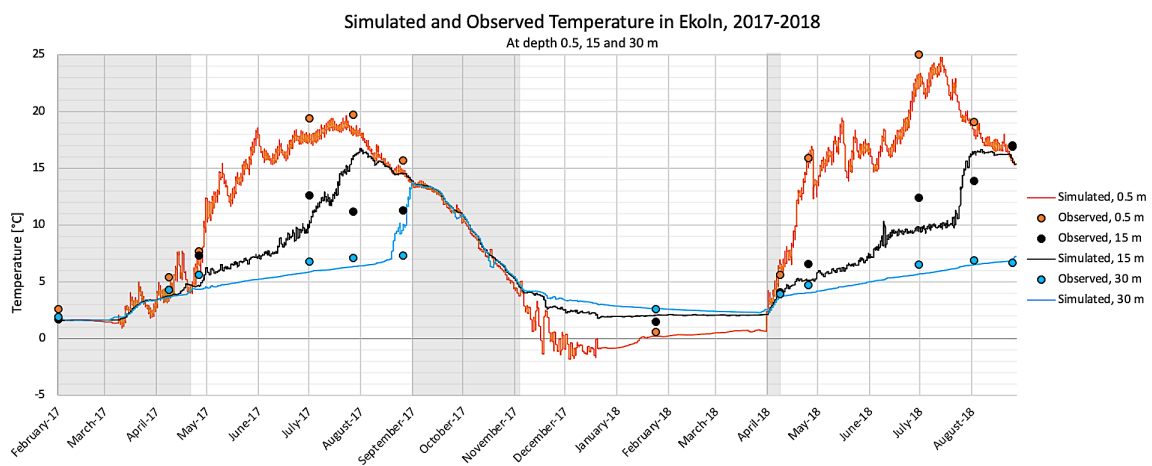
The study of the within-lake processes of NOM was divided into the processes affecting TOC: decay and sedimentation, and those affecting Colour: photooxidation. These two variables, TOC and Colour, were investigated and calibrated separately. The results from the simulation of TOC and Colour concentrations compared to observed concentrations at Vreta Udd in Ekoln are presented in figure 7a and 7b. NOM concentrations are greatly influenced by the seasonal patterns of water mixing in the lake, which is why the water temperature at the three depths (figure 7c) is presented together in figure 7 too. Figure 7c shows when the lake water is either stratified or mixed. Mixing events occur in spring and fall when water temperatures are homogeneous at all depths, these periods are marked as grey in figure 7. During the rest of the year the water temperature is different between the epilimnion and hypolimnion, which implies stratified conditions (winter and summer stagnation). For a more detailed graph over temperature variation for 15 different depths in Ekoln, see Appendix section 8.2 figure 15.



(a) Simulated and observed concentrations of TOC.



(b) Simulated and observed concentrations of Colour.

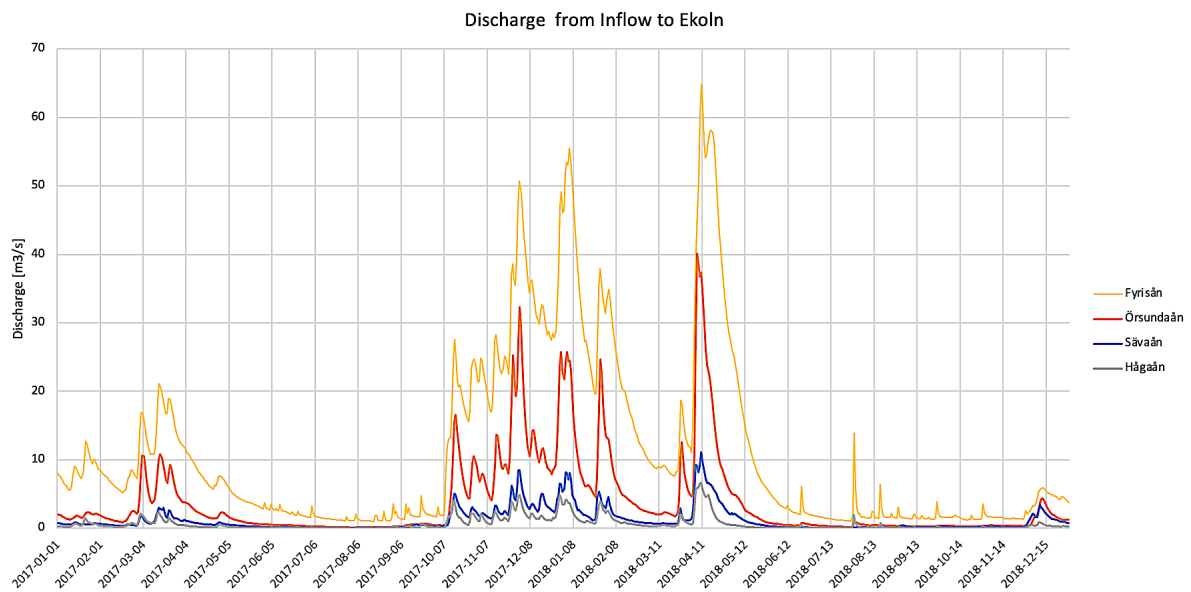


(c) Simulated and observed water temperatures.

**Figure 7:** The three graphs show the simulated and observed concentrations of TOC and Colour, and water temperature for the period 2017-02-20 to 2018-09-15 at Vreta Udd. The red, black and blue lines (simulated) and dots (observed) represent values at depths 0.5, 15 and 30 meters respectively. The vertical lines mark the 20<sup>th</sup> for every month and the grey areas mark when the lake water is mixed.

The water mixing patterns, seen in figure 7c, can be observed regarding variations in concentrations of TOC and Colour in figure 7a and 7b. During the mixing events the simulated concentrations of TOC and Colour at all depths tend to converge to the same value, while during stratified conditions the concentrations vary the most between the depths. During winter stagnation (approx. Dec 2017 - April 2018) the concentrations for both TOC and Colour (simulated and observed) are highest at the surface, but during summer due to the primary production being concentrated to the epilimnion and the photic zone, the concentrations are generally lowest at the surface and highest at 30 meters depth. These variations are very similar for both TOC and Colour during the winter stagnation. During summer stagnation the variation is the most clear for Colour (simulated and observed), while for TOC no clear vertical differences could be observed. For TOC during the first summer stagnation, the concentration appears to be homogeneous through the water profile from the mixing event in the spring to that in the fall for both observed and simulated concentrations. For Colour it can be observed that both simulated and observed values follows the expected overall decline in concentrations during the summer, due to degradation and dilution with clearer water (Wallman, Wallin, & Tjällén 2010). Overall, the observed trends for the simulated concentrations for TOC and Colour follow the trends of the observed concentration when it comes to the variation between the depths, although the simulated and observed values are not exactly the same.

The winter and spring of 2018 were extreme in terms of very high water levels and discharge (SMHI n.d.[a]), which is most likely the reason behind the much higher concentrations of both TOC and Colour in February and into the summer of 2018, compared to 2017. The discharge for Fyrisån, Örsundaån, Sävaån and Hågaån can be seen in figure 8. It can be observed that high flows in figure 8 correlate with high concentrations of TOC and Colour in figure 7a and 7b. During normal years the spring floods carry loads of organic matter from the autumn, which causes a rapid increase of organic matter in lakes during that period. This phenomena can be observed in the end of March of 2017 for TOC and Colour for the simulated values, and correlates with a peak flow in March 2017 in figure 8. The extreme flow event that happened in middle of April in 2018 (figure 8) can also be observed in the graph for Colour, but can not be observed in the graph for TOC.



**Figure 8:** Discharge for the inflows to Ekoln, from 2017 and 2018. The year 2018 was an extreme year with very high water levels in lakes, and discharge in rivers (SMHI [n.d.\[a\]](#))

It could be observed from figure [7](#) that the simulated concentrations of TOC and Colour generally match the fluctuations and trends compared to the observed concentrations. The model also simulates correct vertical variation between the depths for both TOC and Colour. Only for TOC concentrations measured in February 12<sup>th</sup> 2018, have the model simulated a vertical variation that does not correlate to observed concentrations.

For TOC, the major difference between simulated and observed concentrations is found during the summer of 2017 (approx. May to October) for all depths, and during the winter for depth 15 and 30 meters. During the summer of 2017 there is an underestimation of the concentrations, and this underestimation continues for depth 15 and 30 meters until April 2018. The model also did not manage to match the sudden increase in TOC occurring for both years in the beginning of May. These events can not be correlated to a similar flow peaks in figure [8](#) for discharge nor peaks in concentration of Colour in figure [7b](#) (in neither simulated nor observed concentrations). In the end of the summer of 2018 the model overestimated the concentrations at the surface and at 30 meters depth.

For Colour the simulated concentrations during the first summer are much better estimated than for TOC, still slightly underestimated for depths 0.5 and 30 meters. These concentrations are back in line with observations by February 2018, but for depth 15 meters it is first in line with observations by April 2018. For the summer of 2018, simulations match observations well for depth 15 and 30 meters but underestimates the concentrations slightly for 0.5 meters.

#### 4.2.2 Sensitivity analysis and calibration of the model for NOM concentrations

*The sensitivity analysis is performed before the calibration is done and has the purpose of finding the most sensitive parameters to make the calibration process more efficient. In this process the RMSE*



and NSE values was used to support the visual interpretation to determine the sensitivity of the parameters.

For the modelling of decay for TOC, two parameters were calibrated:  $k_0$ , the reference decay constant at 20°C, and  $\theta$ , the Arrhenius temperature coefficient. Additionally sedimentation was chosen to influence TOC and for this the settling velocity,  $v_{sm}$ , was calibrated. The equation for decay can be seen in equation 4 presented in section 3.2.1 Decay and sedimentation in equation 6 in section 3.2.2 Sedimentation. The scaled decay rate ( $k$ ) depends on  $k_0$  and  $\theta$  according:  $k = k_0 \cdot \theta^{T-20}$ . How  $k$  varies depending on temperatures lower (or higher) than the reference temperature of 20°C depends on  $\theta$ . In general a high value of  $\theta$  implies a stronger temperature dependency (large differences in  $k$  at low and high temperatures), and low values of  $\theta$  little temperature dependency ( $k$  values close to  $k_0$ ). The calibration and sensitivity of  $\theta$  were investigated using MATLAB, calculating  $k$  for different values for water temperatures and  $\theta$  (with a constant value of  $k_0 = 0.001 \text{ d}^{-1}$ ), this can be seen in Appendix section 8.4.

Values for  $\theta$  of 1.06, 1.07 and 1.08 were tested in the model based on a reasonable interval of  $\theta$  being around 1.07 (Hanson et al. 2011, 2014). Visually the difference is very small and the change of +/- 0.01 only changed RMSE and NSE values of 3 % each. Because literature point towards 1.07 or lower values it is concluded that 1.07 most likely can be judged to represent the overall variation of TOC over the year. For decay, a higher decay rate was tested using a  $k_0$  of 0.0012, this resulted in a 7 % change in RMSE, and a 14 % change of NSE. Considering that a reasonable interval for  $k_0$  is 0.001-0.01  $\text{d}^{-1}$  (Hanson et al. 2011) it can be concluded that changes in  $k_0$  have a notable effect on the performance of the model, which is supported by a visual interpretation.  $k_0$  is judged to be the most sensitive parameter when it comes to decay, which is in accordance to Hanson et al. (ibid.) sensitivity analysis.

A change of  $v_{sm}$ , from 0.001 (based on a diameter of 0.225  $\mu\text{m}$ ) to 0.005 (based on a diameter of 0.45  $\mu\text{m}$ ), affects RMSE and NSE with approximately 20 %. A change in the fourth decimal only resulted in a change of 1 % in RMSE and NSE. Considering that sedimentation is a major sink of NOM in lakes and impacts the calibration of  $k_0$ , it is a sensitive parameter. The settling velocity however, do not influence the seasonal fluctuations (as  $k_0$  do) but the overall decline of TOC over the year.

For the modelling of photooxidation's influence on Colour, three parameters were calibrated:  $k_{photo}$  the maximum relative photooxidation rate,  $I_{min}$ , the minimum PAR light necessary to achieve photooxidation, and  $I_{1/2}$ , the PAR light necessary for the photooxidation rate to be half of its maximum. In addition,  $I_{surface}$  (radiation reaching the water surface) were set to 51  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$  based on the annual average maximum radiation at Ekoln and  $\eta$  (light extinction factor) were set to 0.25 based on the calibration done by Lindqvist (2019). The three parameters,  $k_{photo}$ ,  $I_{min}$  and  $I_{1/2}$  take part in defining at what rate the maximum photooxidation rate decrease with depth, i.e. access to light. This was investigated by visually plotting the parameters using the Monod equation (equation 9) and in practice by analysing what relations between the three gave good results at all depths.

For the calibration of Colour, values for  $k_{photo}$  were tested in the interval 0.01-0.015  $\text{d}^{-1}$ , and values of  $I_0$  and  $I_{1/2}$  in the intervals of 0-5 and 3.5-10  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$  respectively. When plotting the parameters using the Monod relation, it could be concluded that the most sensitive parameter were

$k_{photo}$  considering how it influences the concentrations at all depths (figure 18a, Appendix section 8.4).  $I_{min}$  and  $I_{1/2}$  can be judged to have an equal effect on the calibration, but they influence the simulated concentrations at different depth. A higher value of  $I_{min}$  (e.g. 1 or 2 instead of 0) creates a slightly better fit at the surface, yet a much worse fit at depth 15 and 30 meters (figure 18b, Appendix section 8.4). Changes in  $I_{1/2}$  have a noticeable effect at the surface (lower value of 3 causes more oxidation, value of 5 causes less oxidation), yet a negligible effect at depth 15 and 30 meters. The effect of the parameters  $k_{photo}$ ,  $I_{min}$  and  $I_{1/2}$  can be seen in Appendix section 8.4 in figure 18.

A parameter that has not been of great focus in this study is the value of dispersion for both Colour, TOC and PFAS. Default values for the horizontal and vertical dispersion are 1, but for vertical dispersion value of 0.01 was used for this study. The value of 1 was tested, and it could be concluded that the change did not have an impact on the major fluctuation, only on the small scale variations.

The calibrated parameters, with final values, for the modelling of TOC and Colour are presented in table 8. A performance validation was done according to section 3.4.1 *Performance validation* and gave the following results for TOC: RMSE = 1.86 TOC mg/l and NSE = 0.644, and for Colour: RMSE = 7.99 Pt mg/l and NSE = 0.937. It should be reminded that this study has a main focus of capturing physical processes influencing TOC and Colour. It was not possible to validate the model for a different time period using different data than that used for the calibration. As mentioned in section 3.4 *Validation*, RMSE and NSE values for this study should only be seen as supportive information, considering the few observed measurements that they are based on. This implies that the analysis of the calibration is mainly qualitative and based on visual interpretation of the simulated seasonal variations of the variables.

**Table 8:** Calibrated values for the parameters for decay and sedimentation for TOC, and photooxidation for Colour. Parameters that were calibrated are marked with an '\*'. For photooxidation  $I_{surface}$  was defined by calculations using radiation data, and  $\eta$  was already defined for Ekoln by Lindqvist (2019).

TOC	<b>Decay</b>	
	* $k_0$	0.001 d <sup>-1</sup>
	* $\theta$	1.07
Colour	<b>Sedimentation</b>	
	* $v_{sm}$	0.001 md <sup>-1</sup>
	<b>Photooxidation</b>	
	* $k_{photo}$	0.0125 d <sup>-1</sup>
	* $I_{min}$	0 $\mu$ mol photons m <sup>-2</sup> s <sup>-1</sup>
* $I_{1/2}$	4 $\mu$ mol photons m <sup>-2</sup> s <sup>-1</sup>	
	$I_{surface}$	51 $\mu$ mol photons m <sup>-2</sup> d <sup>-1</sup>
	$\eta$	0.25

The values of  $\theta$  used by Hanson et al. (2011) and Hanson et al. (2014) for northern lakes (1.073 and 1.07 respectively, corresponding to Q10 value of 2) were considered representative for Ekoln and were used as a starting point in the calibration. It should be noted that in the study by Hararuk et al. (2018) they estimate a value for Q10 of 1.45 (approximately a  $\theta$  of 1.038) which they discuss is much

lower than the commonly assumed value of a Q10 of 2 for biological decay. Hanson et al. (2011) and Hanson et al. (2014) estimated  $k_0$  to be  $0.001 \text{ d}^{-1}$ , while Hararuk et al. (2018) report a higher decay rate of  $0.007 \text{ d}^{-1}$ . It should be noted that variations in decay rates can vary between studies depending on what processes are assumed to be negligible, i.e. how many processes are to be represented in the decay rate.

When comparing simulations using  $\theta$  values of 1.06, 1.07 and 1.08 it can be concluded that water temperatures during the winter are too low to be influenced by degradation despite changes in  $\theta$ . A higher value of  $\theta$  than that seen in literature (1.07), did cause a slightly better estimate for depth 15 and 30 meters during the winter, but is not judged to be realistic regarding the estimation of the long term seasonal fluctuations. This dilemma exists for  $k_0$  as well, and the error is most likely caused by the simplification of not including autochthonous TOC input in the model, which causes the model to underestimate the concentrations during the summer months. Calibrating the parameters further for the model would not lead to an improvement of capturing the actual physical processes. First when autochthonous TOC is implemented in the model, will it be relevant to test more precise values of  $k_0$  and  $\theta$ . As it is now, the calibration of TOC show that values for  $k_0$  and  $\theta$  found in literature, also captures the major fluctuations of TOC in Ekoln.

The inclusion of sedimentation in this case induced a decrease in the reference decay rate ( $k_0$ ). While decay varies over the year (due to temperature dependency), the sedimentation is relatively constant over the year. This implies that the sedimentation process could have been excluded which would have resulted in an overall higher decay rate to achieve almost the same fit. This was noted in the process of calibration when changes in  $vsm$  had a very similar effect as an equal change in  $k_0$ .

Very little literature were found regarding  $I_{min}$  and  $I_{1/2}$ , and the calibration were therefore mostly based on the default values of the DHI ECO Lab template for Algae and Sediment DHI (2017a) ( $5 \mu\text{mol photons m}^{-2}\text{s}^{-1}$  for both parameters). Considering how the parameters relate (see equation 9), it is not likely that  $I_{min}$  and  $I_{1/2}$  are the same value, but rather that  $I_{min}$  is smaller than  $I_{1/2}$ . Regarding the photooxidation rate,  $k_{photo}$ , a reasonable interval of  $0.006\text{-}0.013 \text{ d}^{-1}$  was calculated based on results from Amon & Benner (1996), which is to be compared to the default value of  $0.02 \text{ d}^{-1}$  in the ECO Lab template by DHI (2017a).

### 4.2.3 Impact of decay, sedimentation and photooxidation

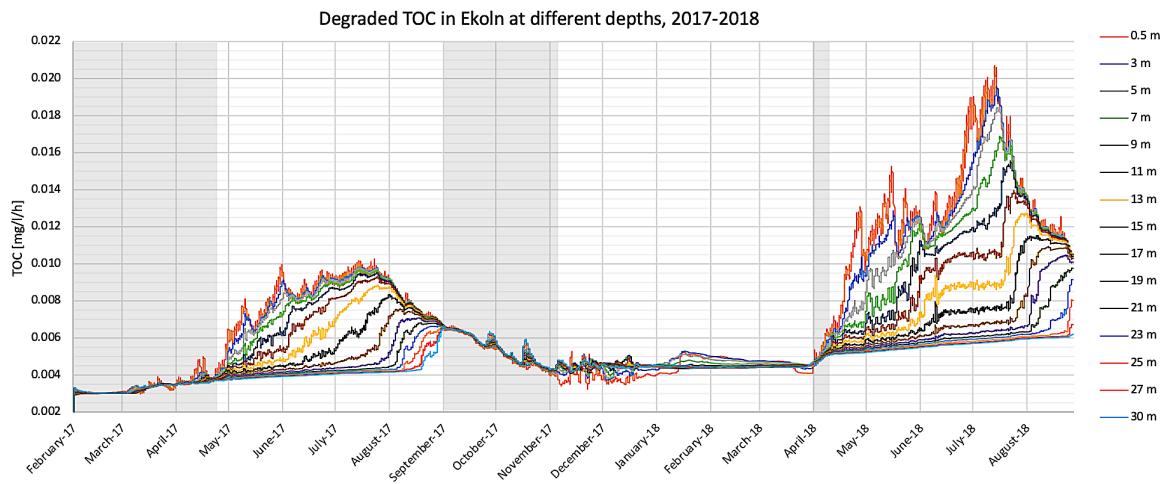
By comparing the simulated concentrations in figure 7a, 7b with simulations done without any processes influencing TOC and Colour in the lake, it could be concluded how much TOC or Colour was degraded due to the processes added in the model. For TOC this comparison showed that approximately 7.2 % of the TOC amount in Ekoln was degraded/removed due to decay and sedimentation. Of this difference (7.2 %), approximately 84 % was due to decay, and 16 % due to sedimentation. Doing the same comparison for Colour showed that approximately 30 % of the Colour in Ekoln were degraded due to photooxidation. The simulations without any processes activated in the model are presented in Appendix section 8.3, for Colour in figure 16 figure and for TOC in 17. For TOC it is notable that the simulation without any processes actually fits the observed data better until March 2018, while for the second summer in 2018 the simulation in figure 7a (including decay and sedimentation) fits the observations better.

What cannot be easily interpreted in figure 7 is the amount of degraded TOC or Colour due to one specific process in the vertical water profile over the seasons. This is presented in figure 9, where the amount of degraded (or sedimentated) TOC and Colour is plotted over the time period. Considering the temperature dependency of the processes of decay, it is expected that the maximum decay happens during summer and that very little decay occur during winter. This pattern can be observed in figure 9a showing the amount TOC degraded at each depth due to decay. In this figure the mixing events can also be distinguished, causing the degradation to be the same in the entire profile. This is to be expected considering that decay is dependent on temperature and therefore should follow the same patterns as the temperature variations in the vertical profile.

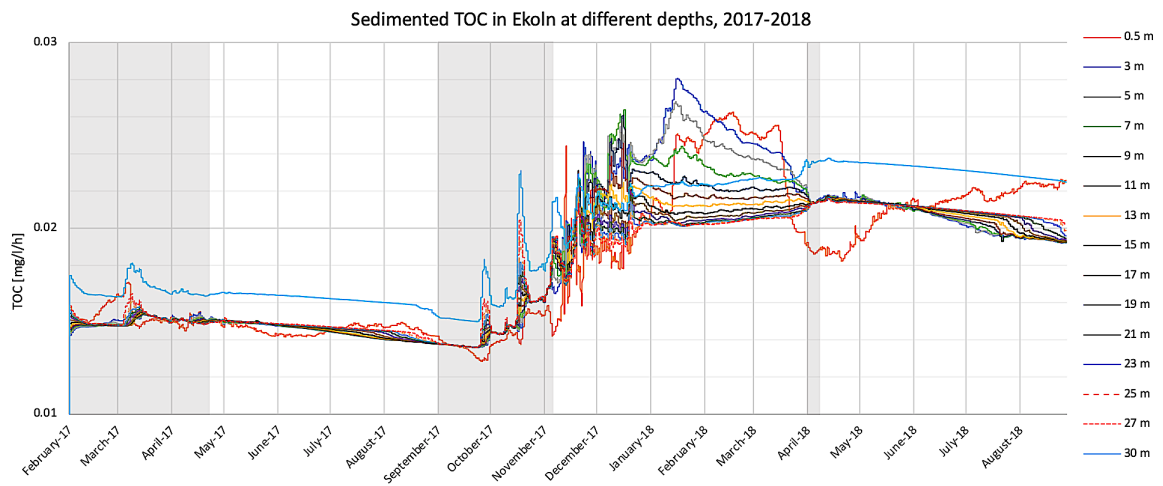
Sedimentation is expected to be the highest during winter and summer stagnation, and minimal during mixing events (Stabel 1987). This typical pattern can not be observed in figure 9b showing the amount of TOC sedimentated at each depth. There are changes in the patterns that match with the events of mixing in September to November in 2017, and in April 2018, but these changes do not particularly distinguish themselves from the rest of the year. The biggest difference in the amount of sedimented TOC, can be seen between the surface and depth 30 meters.

In figure 9c the amount of Colour degraded due to photooxidation is presented. This figure shows that the process of photooxidation occurred in the entire lake, not only at the surface. From literature it can be concluded that most of the photooxidation occurs in the upper layer of epilimnion, with the depth dependent on the turbidity of the lake. Haverstock et al. (2012) estimates that approximately 95 % of DOC is degraded within 50 cm from the surface. This behaviour can not be seen in figure 9c although very little is photodegraded below a depth of 23 meters.

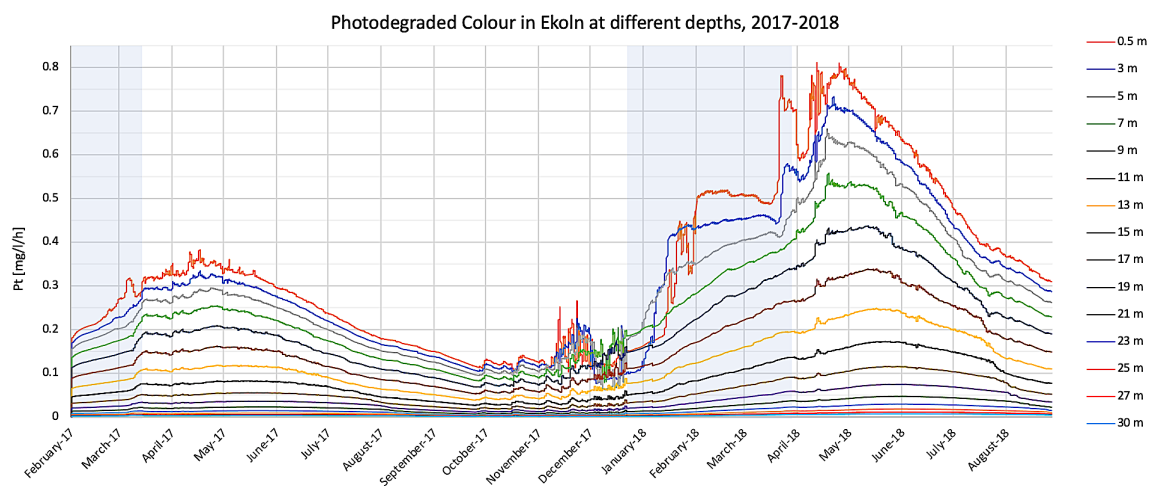
A factor included in the processes of photooxidation is that it is reduced by 90 % when the lake is covered in ice, marked as blue areas in figure 9c. During the melting in April 2018 a sudden increase can actually be observed in photodegraded Colour, which could be caused by the elimination of the ice coverage. The peak in photodegraded Colour in the beginning of April in 2018 (when the lake is still covered in ice) can be related to the extreme peak flow in the rivers (figure 8) occurring at the same time.



(a) Amount of TOC degraded due to decay at different depths.



(b) Amount of TOC degraded due to sedimentation at different depths.



(c) Amount of Colour degraded due to photooxidation at different depths.

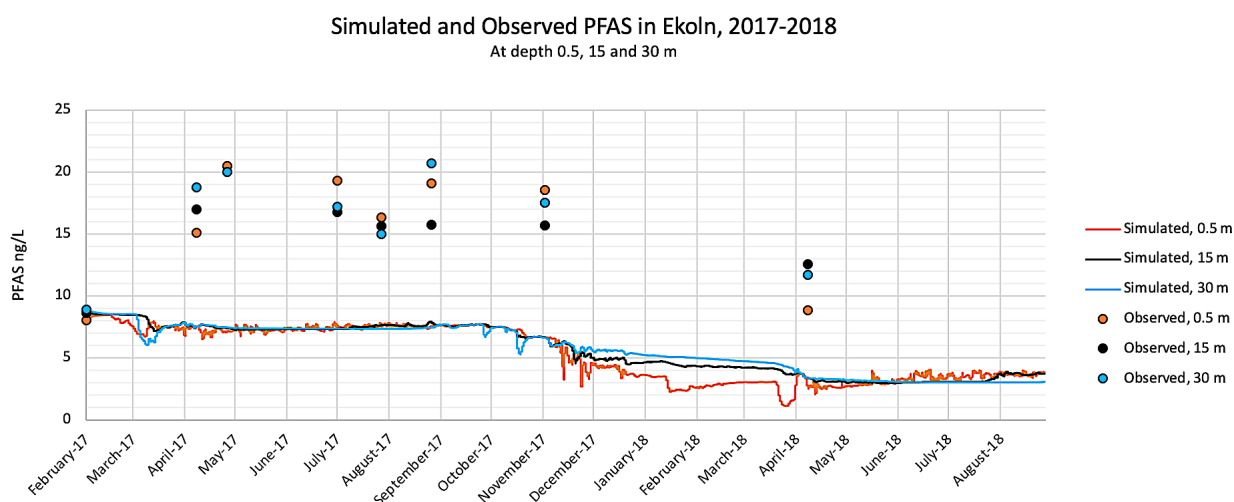
**Figure 9:** The three graphs show the how much TOC or Colour is degraded due decay, sedimentation and photooxidation. The vertical lines mark the 20<sup>th</sup> for every month and the grey areas mark mixing events (figure 9a and 9b), and the blue area marks when the lake is covered in ice (figure 9c).

### 4.3 Modelling PFAS

Two simulations were made for the purpose of getting an idea of the PFAS situation in Ekoln, using the limited data that existed for this project. No degradation process was included for the modelling of PFAS. The two simulations were:

1. Assuming that PFAS enters Ekoln only with discharges from Kungsängsverket
2. Assuming that PFAS enters Ekoln with discharges from Kungsängsverket and with precipitation

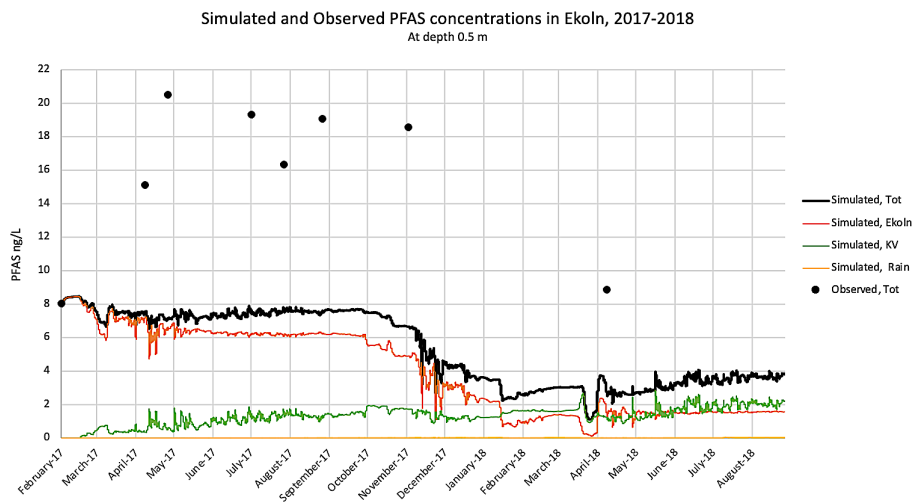
In this study 12 different PFAS were measured which were presented in section 3.1.2 *ECO Lab module*. From simulation 1, using only Kungsängsverket as a source of PFAS to Ekoln, it could be concluded that the simulated concentrations were much lower than those observed. The average PFAS concentration over all depths was 6 ng/l while the average of the observed concentrations was 16 ng/l. As anticipated, the addition of PFAS in precipitation (simulation 2) turned out to have a negligible effect on the total PFAS concentration in the lake. The average concentration of PFAS from precipitation in Ekoln was 0.016 ng/l. In figure 10 the results from simulation 2 are presented, which includes both precipitation and Kungsängsverket as sources of PFAS. The same graph produced from simulation 1 (no precipitation included) is very similar to figure 10 due to the negligible effect of the PFAS added from precipitation. What can be observed in figure 10 is that the measured concentrations in April 2018 are much lower than those measured the same time in 2017. This can be correlated to extreme flow events in 2018 (figure 8) causing a dilution of PFAS in 2018 (figure 10).



**Figure 10:** The graph shows the simulated and observed concentration of PFAS for the period 2017-02-20 to 2018-09-15 at Vreta Udd. In this simulation the only sources of PFAS comes from Kungsängsverket and precipitation. The red, black and blue lines (simulated) and dots (observed) represent values at depths 0.5, 15 and 30 meters respectively. The vertical lines mark the 20<sup>th</sup> for every month.

In figure 11 the concentration of PFAS are shown specifically for depth 0.5 m. In this graph PFAS concentrations are separated depending on the origin, to differentiate the distribution of PFAS from different sources. The different origins are: Ekoln (originating from the initial concentration in the

lake), Kungsängsverket (KV) and precipitation. The concentrations for depth 15 and 30 m show a very similar distribution between the different sources as for 0.5 m, and can be seen in Appendix section 8.5 in figure 19b and 19c. When comparing the simulated average total concentration of PFAS with the observed, it can be concluded that the simulation only accounts for approximately 40 % of the observed concentrations. When analysing the impact of KV, PFAS originating from KV stands for approximately 7 % of the observed concentrations in the lake. The average PFAS concentration from precipitation is 0.016 ng/l which is why the yellow line, representing PFAS from precipitation, is close to zero in figure 11. The concentrations observed can be compared to the guideline value of 90 ng/l PFAS in drinking water (Livsmedelsverket 2021). As previously mentioned these guidelines were investigated this fall, and will most likely be set to lower values based on new research regarding health effects of PFAS (Livsmedelsverket 2020).



**Figure 11:** PFAS concentrations separated in terms of origin at depth 0.5 meters. KV stands for Kungsängsverket and the black lines and dots mark the simulated versus observed total concentrations of PFAS. The vertical lines mark the 20<sup>th</sup> for every month

## 5 Discussion

*The results from modelling time variations of NOM are discussed based on a scientific validation procedure. The discussion regarding the results from modelling PFAS are focused on presenting suggestions of improvements for future studies of PFAS.*

### 5.1 Modelling time variations of NOM

The main objective of this project was to calibrate the model for degradation of NOM, using two measures: TOC and Colour. Based on the results presented in section [4.2 Modelling time variations of NOM](#) it can be concluded that it has been possible to reproduce time variations of NOM. This was done using the equations presented in section [3.2 Constructing within-lake processes for NOM](#) and by calibrating the equation parameters based on previous studies and theory. Two major factors that are judged to have had the greatest impact on the simulations of TOC and Colour are the simplification of not including autochthonous NOM in the simulation of TOC, and the simplification of only including photooxidation as a process affecting Colour. These factors, together with uncertainties and potentials of the model, are discussed in the following sections. Focus lies in discussing both strengths, weaknesses, risks and potentials with the model in accordance to the suggested process of validation of hydrological models presented by Biondi et al. ([2012](#)) (see section [3.4 Validation](#)).

#### 5.1.1 Simplification of not including autochthonous input of NOM

The assumption of autochthonous NOM being negligible is believed to be the biggest source of error in the calibration of TOC. For the modelling of the major fluctuations of NOM it is a reasonable simplification to assume that the allochthonous part of NOM is dominating, and for the case of Ekoln no data at this point exists to estimate the autochthonous fraction of NOM. This simplification was also made in Hanson et al. ([2014](#)) for their lake modelling study of DOC. They concluded that the increases in observed concentrations of DOC during the summer (that can be observed for TOC in this study) was due to the increase of primary production. Although the primary production stands for a smaller amount of NOM input to Ekoln it is still something that can be observed in the results. Mainly because the effect of the autochthonous input of approximately 5% (based on results from another humic Swedish lake investigated by Jonsson et al. ([2001](#))) is not spread out evenly through the year but occurs during a few month. The fact that Ekoln has very high concentrations of both Nitrogen, Phosphorus and Silicate creates a good foundation for a high primary production by phytoplankton during summer (Wallman, Wallin, & Tjällén [2010](#)). The study by Wallman, Wallin, & Tjällén ([ibid.](#)) showed on the other hand that Ekoln, despite the high values of nutrients compared to other basins in Mälaren, had some of the lowest concentrations of chlorophyll. These results are contradicting and underscore the value of further investigations of autochthonous input in Ekoln. The results presented by Wallman, Wallin, & Tjällén ([ibid.](#)) show however that the peak in chlorophyll occur in May for Ekoln, which correlates with the peak in measured TOC concentrations observed in the results from this study. It was noted that the simulation of TOC without any degradation process affecting TOC (figure [17a](#), Appendix), show a much better fit for the concentrations in the summer of 2017. This implies that the amount of TOC that is mineralized in the model during the summer of 2017 (figure [7a](#)), roughly could be estimated to be the amount of autochthonous TOC produced in the lake.



It can also be observed that simulated concentrations of TOC match observed measurements much better for the second summer in 2018 which is an effect of the extreme flow events in the winter and spring of 2018, causing high inflows allochthonous TOC. As discussed in Sobek et al. (2006) high concentrations of humic substances block sunlight necessary for primary production, which impedes the production of autochthonous TOC even more. This implies that the autochthonous input most likely was smaller during 2018 than in 2017.

The simplification may also have an effect on how much of TOC is degraded in this simulation. Results showed that TOC concentrations only decreased with 7 % due to decay and sedimentation, which is much lower than the number of 40-60 % (degraded and sedimented) presented by Hanson et al. (2011) for lakes with WRT of 1-6 years, and approximately 60 % (degraded and sedimented) presented by Sobek et al. (2006) for a lake with a WRT of 0.6 years. If autochthonous NOM would be included in future studies, this would most likely result in a higher a decay rate and/or settling velocity which would increase the amount of TOC degraded/sedimented in Ekoln.

Of the TOC loss of 7 %, decay represents approximately 80 % and sedimentation 20 %. This relation can be compared to results from Sobek et al. (ibid.) showing that sedimentation stands for approximately 40 % of the loss, and for Jonsson et al. (2001) were sedimentation stands for approximately 60 % of the loss (both in comparison with what was respired). This implies that it could be of relevance to test higher values for the settling velocity when autochthonous input of TOC has been estimated in the model. The settling velocity in this study is calculated using a theoretical settling velocity, this method is also suggested to be investigated further considering that little literature were found regarding settling velocities for organic matter. If data over the relation between POC and DOC in Ekoln would exist, this would help greatly in estimating the settling velocity. The processes chosen to influence TOC are still judged to present a good enough representation of the major fluctuations of TOC concentrations in Ekoln, considering the simplifications made.

The increase of TOC during the summer can not be observed in neither simulated nor observed concentrations of Colour, nor can it be connected to an increase in discharge from the rivers. This further indicates that the increase of TOC during the summer is of autochthonous origin (less coloured) and is not loaded into the lake from the rivers. The simplification is therefore judged to only represent a minor source of error for the simulation of Colour, considering that Colour dominates by organic matter with allochthonous origin (more coloured than autochthonous NOM).

### 5.1.2 Effects of choosing photooxidation as only process affecting Colour

The calibration of Colour show that photooxidation is a very important process influencing the degradation of NOM. Photooxidation, as the only process affecting Colour, managed very well to simulate time variations of Colour in Ekoln. The results showed that 30 % of the Colour were degraded due to photooxidation which can be compared to the number of 10 % presented by Jonsson et al. (ibid.). Their study were investigating organic carbon (OC), and it could therefore be expected that the fraction of photooxidated OC should be higher for a study analysing a fraction of OC specially influenced by photooxidation. The results from this study confirms, together with other studies (Hanson et al. 2011; Hararuk et al. 2018; Jonsson et al. 2001) that photooxidation is an important process to include

when analysing mineralization of organic matter. And as results from Hararuk et al. (2018) also show, is that photooxidation is a particularly important process for organic matter in northern lakes, where access to light can be high, despite low water temperatures.

A discovered consequence of the calibration of photooxidation was that the process of photooxidation occurred in the entire lake, although with a declining effect with depth, which is misleading considering that photooxidation in reality is restricted to the upper layer of epilimnion (Amon & Benner 1996; Haverstock et al. 2012). The results, seen in figure 9c, indicates that the calibration of photooxidation in this study most likely compensates for a process/processes reducing the amount of Colour further down in the vertical profile. It could be concluded that an increase of  $I_{min}$  from 0 to 1 resulted in a much better fit at the surface, but an overall worse fit (overestimation of the concentration) for the two other depths. This alteration also reduced the impact of photooxidation to the upper 16 meters which could be considered to be more realistic. This discovery implies that the calibration of especially  $I_0$  and  $I_{1/2}$  are strongly impacted of the assumption of only including photooxidation as a process affecting Colour. The reduction in concentration at lower depths are most likely represented by a combination of processes such as biological mineralization, sedimentation or coagulation with Iron (which creates colloids that settles (Köhler & Lavonen 2015)). Considering the lack of literature for  $I_0$  and  $I_{1/2}$  it would be of the greatest interest to investigate these parameters further. By for example limiting photooxidation to the surface and investigate how this affects the values of  $I_0$  and  $I_{1/2}$ , and what processes should be included to achieve this.

For Colour it was also assumed that during periods of ice coverage, only 90 % of the radiation should reach the water. Considering that the fit is good during the periods of ice coverage, it could be assumed that the settings for ice are good. It could still be of interest to test the effect of assuming that the radiation reaching the water during these periods is negligible, as assumed by Haverstock et al. (2012) in their study. This could cause a decrease of the concentrations during these periods which could cause a better fit for the surface.

### 5.1.3 Uncertainties in input and output data

The simulations of the temperature profiles (figure 13a and 13b in Appendix) showed that the model did not manage to time the mixing event in September for both 2017 and 2018. Modelling the temperature profile correctly will have a great effect on how water from inflows distributes between epilimnion and hypolimnion in the lake, which in turn will affect how organic matter is distributed in the profile. Hararuk et al. (2018) conclude several factors that influence the performance of models simulating DOC and mention physical processes to be of great importance. Especially density-dependence, are mentioned as one of the major processes influencing the performance of models simulating DOC (ibid.). The temperature deviation seen in September, could cause an error in the estimation in TOC and Colour during this period. Considering that the water temperature profiles match observed concentrations very well for the rest of the year, this should not be a major cause of error for the simulation overall, but still a factor to consider. Lindqvist (2019) discusses the uncertainties that the wind data causes. Considering that no new wind data measured closer to Ekoln was available for this project, this is still a source of uncertainty and most likely the reason behind the deviation in the water temperature profiles.

The mesh that is used in the model was discussed in section [3.1.1 Hydrodynamic module](#). The mesh used for this study was originally developed to best capture temperature profiles, which gave it less resolution horizontally. This is not optimal for simulating substance transport. Another mesh was tested, originally developed by Tyréns AB ([2018](#)) (with higher resolution) this resulted in a very high computation time. Considering the aim with this project and time restrictions, it could be argued that this is not necessary for calibrating the model for time variations of NOM. This is however an important factor to consider for future studies of for example PFAS or other contaminants, where a more precise distribution of the substances can be vital.

As also mentioned in [3.1.1 Hydrodynamic Module](#) the data for ice is collected from Skarven, a much smaller basin south of Ekoln. This could cause an underestimation of the periods when Ekoln is covered in ice, which would have an effect on photooxidation. This is an important uncertainty to consider, because the periods when the lake is covered with ice, coincides with when the access to light increases. This implies that ice will have a great effect in reducing the photooxidation during the end of this period. As discussed in Hararuk et al. ([2018](#)) these are periods when water temperatures are low and little bacterial decay occur, which makes photooxidation to an important process during these periods.

#### 5.1.4 Potential developments and applications

One improvement that would have the greatest effect is to include autochthonous NOM. This would be most relevant for the modelling of TOC, and less relevant for Colour. This would create a much better estimate of TOC during the summer and cause a better calibration for the parameters for decay and sedimentation. Based on previous studies (Jonsson et al. [2001](#); Sobek et al. [2006](#)) of Swedish humic lakes it could be possible to make a rough estimation of the production of NOM during summer in Ekoln, which could improve the calibration a lot. Regarding Colour the first step would be to add an additional process (e.g. sedimentation), this would make it possible to limit photooxidation to the surface and therefore get more realistic values for  $I_0$  and  $I_{1/2}$ . For Colour it would also be interesting to evaluate the possibility of no radiation reaching the water during periods of ice coverage, instead of a reduction of 90 % as in this study.

Another factor that could be considered to improve the model is to include more variables other than TOC and Colour. By including for example a recalcitrant and a labile load of TOC, it would be of interest to add Colour and TOC into the same simulation were degraded Colour would create labile TOC. This alteration is already implemented regarding DOC in the template made by DHI for Algae and Sediment (DHI [2017a](#)). This kind of adjustment would create a more realistic simulation of NOM in Ekoln, which could give a better picture of the whole lake carbon budget.

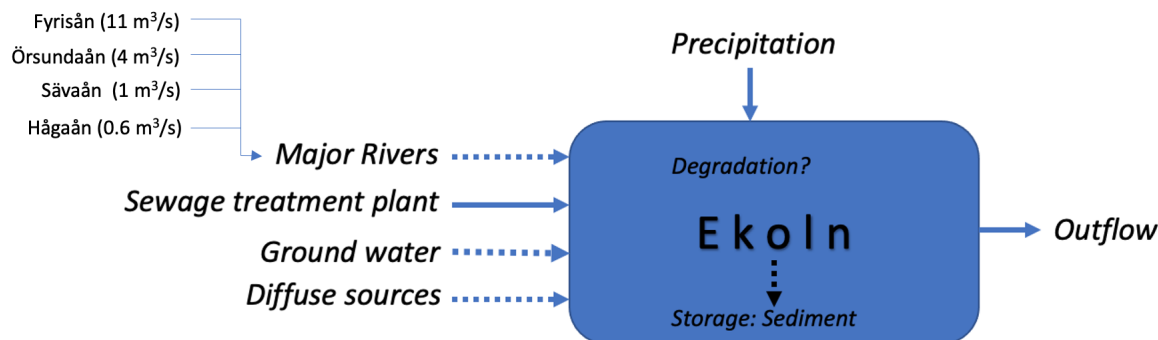
Considering that water from Ekoln is used for drinking water, a major application for the model is connected to monitor water quality. If the model continues to be developed, the results presented in this study can be used to predict water quality hazards connected to climate change and extreme events. This study can also provide a better insight of the carbon budget in Ekoln, which would add to the knowledge of carbon budgets and fluxes in Mälaren and in lakes in general. Considering the amount of processes that organic matter is involved in this would lead to increased knowledge of transportation and storage of for example nutrients and inorganic and organic contaminants.

## 5.2 Modelling PFAS

The second objective for this project was to evaluate the potential for modelling PFAS in Ekoln. The goal was to investigate what requirements are necessary for a successful modelling of PFAS in Ekoln.

Figure 12 presents a conceptual picture of the inflows and outflows of PFAS to Ekoln. The dotted lines represent sources that are not yet accounted for in the model. The results from this study showed that the contribution from precipitation is negligible (0.016 ng/l) and that the sewage treatment plant Kungsängsverket (KV) only represent 7 % of the observed concentrations in Ekoln. Overall it can be concluded that the simulated total concentration of PFAS only accounts for approximately 40 % of the observed total concentrations.

The average concentration of PFAS in the discharge from KV is 83 ng/l. This is to be compared to the average concentrations of PFAS in Fyrisån of 18 ng/l, based on four measurements done in Fyrisån in 2015 (Gago-Ferrero et al. 2017). The reason why these measurements have not been used in this study is because no observed measurements of PFAS exists in Ekoln for 2015. The difference between KV and Fyrisån is that the average discharge from KV 0.6 m<sup>3</sup>/s based on data from 2017-2018, while the average discharge from Fyrisån during the same period is 11 m<sup>3</sup>/s. Applying the average PFAS concentration from 2015 for Fyrisån this implies that Fyrisån contributes with an amount of 198 µg PFAS/s, while KV only contributes with 50 µg/s. Considering that KV lies upstream in Fyrisån, the concentration from KV is already accounted for in the concentrations of PFAS in Fyrisån (which were measured downstream KV), still the numbers give an indication of the importance of including major rivers like Fyrisån in the simulation. In the simulations done now PFAS from KV are diluted by the water from Fyrisån. This implies that Fyrisån most likely is a major source of PFAS to Ekoln.



**Figure 12:** Conceptual picture of the inflows and outflows of PFAS in Ekoln. The dotted lines mark those sources that are not accounted for in the simulation of PFAS in this study.

Other rivers that could be of importance are Örsundaån, Sävaån and Hågaån . Considering the average discharge based on the period 2017-2018, presented in brackets in figure 12, Örsundaån could be considered to be of extra interest. It is however, of great interest to monitor PFAS concentrations in all rivers inlets, considered that sources of PFAS may exist that is not known. Another potential source for PFAS to Ekoln is the groundwater entering Ekoln mainly from the Uppsala esker, considering that the flow from the esker is estimated to 0.05 m<sup>3</sup>/s it is assumed to have a negligible effect on the total concentration of PFAS in Ekoln. The flow from the four major river inlets to Ekoln are estimated to

account for 95 % of the inflow to Ekoln, the rest is diffuse sources. The contribution of PFAS from diffuse sources will only be relevant if PFAS sources are found that are not connected to any of the rivers.

As showed in figure 12, PFAS could be stored in Ekoln due to sedimentation. Studies show that the storage of PFAS in sediment could be of relevance (Kong et al. 2018; Sánchez-Soberón et al. 2020). Kong et al. (2018) conclude from their results that the water was not a big sink of PFOS and PFOA, considered that they were either transported to the sediments or the outflow. The sediments also seem to be relevant considering the results of Kong et al. (ibid.) showing that the highest degradation of PFOA occurred in the soil and sediment. Their results also showed that the degradation of PFOS was negligible both in air, water, soil and sediment. Considering results from Kong et al. (ibid.) and Sánchez-Soberón et al. (2020) it would be reasonable to assume that degradation of PFAS in Ekoln is negligible. A potential degradation of PFAS should still be taken into account when analysing PFAS in Ekoln in futures studies. A factor also worth mentioning is the part organic matter plays in the transportation and distribution of PFAS, this was concluded by Kong et al. (2018) to be something that should be investigated further based on their results. For the two simulations of PFAS done in this study nothing was done regarding PFAS chemical properties influencing its behaviour in Ekoln. The same settings for dispersion (scaled eddy viscosity formulation) were used for PFAS as for TOC and Colour, this is a parameter that should be investigated further considering its effect on PFAS distribution on a smaller scale.

A constant wish is always to have more and better data, which is of course seldom fulfilled in reality. This is on the other hand where modelling could contribute with information regarding PFAS in and around Ekoln. By getting access to data from just one source, e.g. Fyrisån, this could be enough to conclude if the rest of the sources' contribution of PFAS can be assumed to be negligible or if there is a major input of PFAS still missing. Considering the attention PFAS has received the past years, and the new regulations that have arrived from EU just this year, this further emphasises the importance of continuing mapping and modelling PFAS. This type of studies could contribute to important information of how PFAS is distributed in lakes, and how we can reduce the threat from PFAS in our drinking water.

Considering the conclusions made in this study of PFAS a few factors regarding how the model can be developed to better model PFAS in Ekoln can be summarised as followed:

- More data is required from other sources (rivers, groundwater, diffuse sources). Monitoring PFAS continuously in some of the major inlets is judged to be of particular interest (Fyrisån and Örsundaån).
- To include Fyrisån as a source is considered to be vital for future modelling studies of PFAS in Ekoln
- Investigate processes influencing PFAS in Ekoln. The most relevant being sedimentation, but it would also be of value to investigate degradation, although it is expected to be very small.
- Investigate settings regarding PFAS chemical properties, such as absorption to organic matter and dispersion.

## 6 Conclusions

The main focus of this project was to further develop the model for lake Ekoln to include transportation of NOM and PFAS. The first objective of this project, and main focus, was to calibrate the model for time variations of NOM in Ekoln in terms of TOC and Colour. This was done using processes of decay and sedimentation for TOC, and photooxidation for Colour. For the modelling of these two variables it was assumed that the autochthonous fraction of TOC and Colour were negligible and that the chosen processes of decay, sedimentation and photooxidation, should be able to capture the major seasonal variations.

The calibration of TOC using decay and sedimentation resulted in a reference decay constant at 20°C,  $k_0$ , of 0.001 d<sup>-1</sup>, Arrhenius temperature coefficient (reference temperature 20°C),  $\theta$ , of 1.07 and settling velocity,  $v_{sm}$ , of 0.001 md<sup>-1</sup>. The calibration of Colour using photooxidation as only process resulted in a maximum photooxidation rate,  $k_{photo}$ , of 0.0125 d<sup>-1</sup>, minimum PAR light necessary for photooxidation to occur,  $I_{min}$ , of 0  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$  and PAR light halfsaturation,  $I_{1/2}$ , of 4  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$ . For photooxidation a light extinction factor for Ekoln was defined as 0.25, and a mean annual maximum of daily radiation,  $I_{surface}$ , was set to 51  $\mu\text{mol photons m}^{-2}\text{s}^{-1}$  based on radiation data for Ekoln. Conclusions from the two calibrations of TOC and Colour are:

- The assumption of autochthonous input were judged to be the biggest source of error in the calibration of TOC. This caused an underestimation of the concentrations of TOC during summer, which influenced how accurate the calibration of parameters for decay and sedimentation could be performed.
- Decay and sedimentation can be concluded to capture the major seasonal variations of TOC, but this will be much improved if future model studies of Ekoln were to include an estimate of the autochthonous input of TOC during summer.
- The assumption of autochthonous input can be concluded to have a minor influence on the calibration of the model for Colour. This confirms that Colour primarily is a measurement of allochthonous organic matter.
- It can be concluded that photooxidation captures the seasonal variations of Colour in Ekoln very well, which confirms the importance of photooxidation as a degradation process of NOM. To create a more realistic simulation of where photooxidation occur in the water profile, it is suggested that other processes such as mineralization, sedimentation or coagulation with Iron should be included in future studies of Colour.

If the model continues to be developed, the results presented in this study can be used to predict water quality hazards connected to climate change and extreme events and lead to increased knowledge of transportation and storage of nutrients, inorganic and organic contaminants and carbon budgets in lakes.

In the simulations done only the sewage treatment plant Kungsängsverket and precipitation were included, this due to limited data from other sources.

The second objective of this project was to investigate what is required to successfully model PFAS in Ekoln. Due to limited data, the simulations only used the sewage plant Kungsängsverket and

precipitation as PFAS sources. The simulations showed that the simulated total concentrations of PFAS in Ekoln, only accounts for 40 % of the observed concentrations measured in Ekoln and that PFAS from precipitation is negligible. The results indicated that more measurements of PFAS around and in Ekoln are necessary for future studies of PFAS in Ekoln. For future studies it is judged to be vital to include Fyrisån as a PFAS source, and to look into within-lake processes that influences PFAS distribution.

## 7 References

### Published

- Ahrens, Lutz & Mirco Bundschuh (2014). Fate and effects of poly- and perfluoroalkyl substances in the aquatic environment: A review. *Environmental Toxicology and Chemistry* 33.9. \_eprint: <https://setac.onlinelibrary.wiley.com/doi/pdf/10.1002/etc.2663>, pp. 1921–1929. URL: <https://setac.onlinelibrary.wiley.com/doi/abs/10.1002/etc.2663> (visited on 09/10/2020).
- Ahrens, Lutz et al. (Aug. 11, 2014). *Screening of perfluoroalkyl substances and organic flame retardants in Swedish rivers*. NV-06565-13. Uppsala: Institution för vatten och miljö, Sveriges Lantbruksuniversitet (SLU), p. 38.
- Ahrens, Lutz et al. (June 2015). Stockholm Arlanda Airport as a source of per- and polyfluoroalkyl substances to water, sediment and fish. *Chemosphere* 129, pp. 33–38.
- Amon, R. M. W. & R. Benner (May 1, 1996). Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system. *Geochimica et Cosmochimica Acta* 60.10, pp. 1783–1792. URL: <http://www.sciencedirect.com/science/article/pii/S0016703796000555> (visited on 10/08/2020).
- Armitage, James et al. (Nov. 1, 2006). Modeling Global-Scale Fate and Transport of Perfluorooctanoate Emitted from Direct Sources. *Environmental Science & Technology* 40.22. Publisher: American Chemical Society, pp. 6969–6975. URL: <https://doi.org/10.1021/es0614870> (visited on 09/10/2020).
- Biondi, Daniela et al. (Jan. 1, 2012). Validation of hydrological models: Conceptual basis, methodological approaches and a proposal for a code of practice. *Physics and Chemistry of the Earth, Parts A/B/C*. Estimating and representing uncertainty in applied hydrology, hydraulics and water quality studies 42-44, pp. 70–76. URL: <http://www.sciencedirect.com/science/article/pii/S1474706511001537> (visited on 11/16/2020).
- Catalán, Núria et al. (May 2016). Organic carbon decomposition rates controlled by water retention time across inland waters. *Nature Geoscience*.
- DHI (2017a). *DHI 3 Algae and Sediment Model - MIKE ECO Lab Template, Scientific Description*. Photooxidation, page 58, Monod, page 96.
- (2017b). *Heavy Metal - MIKE ECO Lab Template, Scientific Description*.
- (2017c). *MIKE ECO Lab - Numerical Lab for Ecological and Egent Based Modelling, User Guide*.
- (2017d). *Water Quality - MIKE ECO Lab WQ Templates - Scientific Description*.
- Evans, C.D., Donald Monteith, & D.M. Cooper (Dec. 2005). Long-term increase in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental pollution* 137. URL: <https://reader.elsevier.com/reader/sd/pii/S0269749105000540?token=E37B9F6E68A41C7B95D46787C642C41D4B9B68D94C629CB768885DADC07F2E0DECBE42D758F6312> (visited on 09/01/2020).
- Fredricsson, Malin et al. (Dec. 2018). *Nationell luftövervakning - Sakrapport med data från övervakning inom Programområde Luft t.o.m. 2017*. C 360. IVL Svenska Miljöinstitutet, Naturvårdsverket.
- Gago-Ferrero, Pablo et al. (Dec. 1, 2017). Impact of on-site, small and large scale wastewater treatment facilities on levels and fate of pharmaceuticals, personal care products, artificial sweeteners, pesticides, and perfluoroalkyl substances in recipient waters. *Science of The Total Environment*



- 601-602, pp. 1289–1297. URL: <http://www.sciencedirect.com/science/article/pii/S0048969717313669> (visited on 11/11/2020).
- Guo, Rui et al. (Mar. 13, 2020). Occurrence, partition and environmental risk assessment of per- and polyfluoroalkyl substances in water and sediment from the Baiyangdian Lake, China. *Scientific Reports* 10.1. Number: 1 Publisher: Nature Publishing Group, p. 4691. URL: <https://www.nature.com/articles/s41598-020-61651-6> (visited on 09/11/2020).
- Hanson, Paul C. et al. (July 14, 2011). Fate of Allochthonous Dissolved Organic Carbon in Lakes: A Quantitative Approach. *PLoS ONE* 6.7. Ed. by Terence Evens, e21884. URL: <https://dx.plos.org/10.1371/journal.pone.0021884> (visited on 08/28/2020).
- Hanson, Paul C. et al. (2014). Quantifying lake allochthonous organic carbon budgets using a simple equilibrium model. *Limnology and Oceanography* 59.1. \_eprint: <https://aslopubs.onlinelibrary.wiley.com/doi/pdf/10.4319/lo.2014.59.1.0167> (visited on 09/06/2020).
- Hararuk, Oleksandra et al. (2018). Model-Data Fusion to Test Hypothesized Drivers of Lake Carbon Cycling Reveals Importance of Physical Controls. *Journal of Geophysical Research: Biogeosciences* 123.3. \_eprint: <https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1002/2017JG004084>, pp. 1130–1142. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1002/2017JG004084> (visited on 09/03/2020).
- Haverstock, Sarah et al. (Aug. 1, 2012). Modeling the photo-oxidation of dissolved organic matter by ultraviolet radiation in freshwater lakes: Implications for mercury bioavailability. *Chemosphere* 88.10, pp. 1220–1226. URL: <http://www.sciencedirect.com/science/article/pii/S0045653512004419> (visited on 10/08/2020).
- Houser, Jeffrey N. et al. (June 1, 2003). The dual influences of dissolved organic carbon on hypolimnetic metabolism: organic substrate and photosynthetic reduction. *Biogeochemistry* 64.2, pp. 247–269. URL: <https://doi.org/10.1023/A:1024933931691> (visited on 09/22/2020).
- Johansson, Linda (2003). *Utvärdering av långsiktiga trender i Mälaren - En studie av råvattenkvalitet vid Lovö vattverket 1935-2002*. 23-2003. Uppsala: Institutionen för Markvetenskap, Sveriges Lantbruksuniversitet.
- Jonsson, Anders et al. (2001). Whole-lake mineralization of allochthonous and autochthonous organic carbon in a large humic lake (örträsket, N. Sweden). *Limnology and Oceanography* 46.7. \_eprint: <https://aslopubs.onlinelibrary.wiley.com/doi/pdf/10.4319/lo.2001.46.7.1691>, pp. 1691–1700. URL: <https://aslopubs.onlinelibrary.wiley.com/doi/abs/10.4319/lo.2001.46.7.1691> (visited on 09/03/2020).
- Koehler, Birgit et al. (2012). Reactivity continuum of dissolved organic carbon decomposition in lake water. *Journal of Geophysical Research* VOL. 117 (G01024).
- Köhler, Stephan & Elin Lavonen (2015). *Löst Organiskt kol i dricksvatten - En syntes av erfarenheter av GenoMembranprojektet*. 2015-13. Svenskt Vatten Utveckling, p. 56.
- Köhler, Stephan et al. (Oct. 1, 2002). Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden. *Aquat. Sci* 64.
- Köhler, Stephan et al. (Aug. 15, 2013). In-Lake Processes Offset Increased Terrestrial Inputs of Dissolved Organic Carbon and Color to Lakes. *PLoS ONE* 8.8. Ed. by Caroline P. Slomp, e70598. URL: <https://dx.plos.org/10.1371/journal.pone.0070598> (visited on 08/28/2020).
- Kong, Xiangzhen et al. (June 1, 2018). Multimedia fate modeling of perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS) in the shallow lake Chaohu, China. *Environmental Pol-*

- lution 237, pp. 339–347. URL: <http://www.sciencedirect.com/science/article/pii/S0269749117338666> (visited on 09/11/2020).
- Lambert, Thibault & Marie-Elodie Perga (Oct. 2019). Non-conservative patterns of dissolved organic matter degradation when and where lake water mixes. *Aquatic Sciences* 81.4, p. 64. URL: <http://link.springer.com/10.1007/s00027-019-0662-z> (visited on 08/27/2020).
- Leenheer, Jerry A. & Jean-Philippe Croué (Jan. 1, 2003). *Characterizing Dissolved Aquatic Organic Matter*. Environmental Science & Technology.
- Lindqvist, Sandra (June 2019). *Vilken effekt har framtida klimat på strömningsmönster i Ekoln - en modelleringsstudie baserad på MIKE 3FM*. Examensarbete. Uppsala: Uppsala Universitet och Sveriges Lantbruksuniversitet.
- Löfgren, Stefan, Martin Forsius, & Tom Andersen (2003). *Vattens färg - klimatbetingad ökning av vattens färg och humushalt i nordiska sjöar och vattendrag*. Nordic - Council of Ministers, p. 12. URL: [http://info1.ma.slu.se/IMA/Publikationer/brochure/Vattens\\_farg.pdf](http://info1.ma.slu.se/IMA/Publikationer/brochure/Vattens_farg.pdf).
- Löfgren, Stefan & Lars Lundin (2003). Mer humus i svenska vatten. *FAKTA skog* 15, p. 4.
- MIKE powered by DHI (n.d.[a]). *MIKE 21 & MIKE 3 Flow Model FM - Hydrodynamic Module, Short Description*. DHI. URL: [file:///Users/fridaekman/Downloads/MIKE213\\_FM\\_HD\\_Short\\_Description.pdf](file:///Users/fridaekman/Downloads/MIKE213_FM_HD_Short_Description.pdf) (visited on 08/25/2020).
- (n.d.[b]). *MIKE 21 & MIKE 3 Flow Model FM - MIKE ECO Lab Module, Short description*. DHI. URL: [file:///Users/fridaekman/Downloads/MIKE213\\_FM\\_EL\\_Short\\_Description.pdf](file:///Users/fridaekman/Downloads/MIKE213_FM_EL_Short_Description.pdf) (visited on 08/25/2020).
- Monod, Jacques (Oct. 1, 1949). The growth of bacterial cultures. *Annual Review of Microbiology* 3.1. Publisher: Annual Reviews, pp. 371–394. URL: <https://www.annualreviews.org/doi/10.1146/annurev.mi.03.100149.002103> (visited on 10/15/2020).
- Monteith, Donald et al. (Nov. 22, 2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450.7169, pp. 537–540.
- Myszograj, Sylwia (Jan. 1, 2018). Reaction rate coefficient  $k_{20}$  and temperature coefficient in organic waste thermal disintegration. *ITM Web of Conferences* 23, p. 00026.
- Persson, Irina et al. (2012). Kväveavskiljningens effekt på Ekoln. 2012, p. 68.
- Rosenqvist, Lars et al. (Oct. 2017). *Spridning av högfluorerade ämnen i mark från Stockholm Arlanda Airport*. B 2289. IVL Svenska Miljöinstitutet, p. 121.
- Sánchez-Soberón, Francisco et al. (Aug. 1, 2020). Multi-box mass balance model of PFOA and PFOS in different regions of San Francisco Bay. *Chemosphere* 252, p. 126454. URL: <http://www.sciencedirect.com/science/article/pii/S0045653520306470> (visited on 09/11/2020).
- Sepp, Margot et al. (Jan. 1, 2018). Do organic matter metrics included in lake surveillance monitoring in Europe provide a broad picture of brownification and enrichment with oxygen consuming substances? *Science of The Total Environment* 610-611, pp. 1288–1297. URL: <http://www.sciencedirect.com/science/article/pii/S0048969717321770> (visited on 09/17/2020).
- Sierra, Carlos A. (2012). Temperature sensitivity of organic matter decomposition in the Arrhenius equation: some theoretical considerations. *Biogeochemistry* 108.1. Publisher: Springer, pp. 1–15. URL: <https://www.jstor.org/stable/41410578> (visited on 10/16/2020).
- SLU (Sept. 22, 2020). *Stephan Köhler, Professor at the Department of Aquatic Sciences and Assessment; Section for Geochemistry and Hydrology*. E-mail.
- Sobek, Sebastian et al. (Dec. 2006). A Carbon Budget of a Small Humic Lake: An Example of the Importance of Lakes for Organic Matter Cycling in Boreal Catchments. *AMBIO: A Journal of the Human Environment* 35.8. Publisher: Royal Swedish Academy of Sciences, pp. 469–475. URL:

[https://bioone.org/journals/ambio-a-journal-of-the-human-environment/volume-35/issue-8/0044-7447\(2006\)35\[469:ACBOAS\]2.0.CO;2/A-Carbon-Budget-of-a-Small-Humic-Lake--An/10.1579/0044-7447\(2006\)35\[469:ACBOAS\]2.0.CO;2.full](https://bioone.org/journals/ambio-a-journal-of-the-human-environment/volume-35/issue-8/0044-7447(2006)35[469:ACBOAS]2.0.CO;2/A-Carbon-Budget-of-a-Small-Humic-Lake--An/10.1579/0044-7447(2006)35[469:ACBOAS]2.0.CO;2.full) (visited on 10/14/2020).

Söderholm, Gunnar & Maria Svanholm (Sept. 2018). *Högfluorerade ämnen (PFAS) i Mälarens vattenpelare*. Miljöförvaltningen.

Sonesten, Lars et al. (2013). *Mälaren tillståndsutvecklingen 1965-2011*. OCLC: 941120745. Uppsala: Sveriges lantbruksuniversitet, Institutionen för vatten och miljö, Sveriges lantbruksuniversitet. URL: <http://urn.kb.se/resolve?urn=urn:nbn:se:slu:epsilon-e-2142> (visited on 08/20/2020).

Stabel, Hans-Henning (Oct. 1, 1987). Settling velocity and residence time of particles in Lake Constance. *Swiss journal of hydrology* 49.3, pp. 284–293. URL: <https://doi.org/10.1007/BF02538289> (visited on 10/08/2020).

Su, Chao et al. (Dec. 1, 2018). Multimedia fate and transport simulation of perfluorooctanoic acid/perfluorooctanoate in an urbanizing area. *Science of The Total Environment* 643, pp. 90–97. URL: <http://www.sciencedirect.com/science/article/pii/S0048969718322320> (visited on 09/11/2020).

Swedish Environmental Protection Agency (2016). *Högfluorerade ämnen (PFAS) och bekämpningsmedel - en sammantagen bild av förekomsten i miljön*. 6709. OCLC: 1001584711. Stockholm: Naturvårdsverket.

— (Jan. 2019). *Vägledning om att riskbedöma och åtgärda PFAS-föroreningar inom förorenade områden*. 6871. Naturvårdsverket, Statens Geotekniska Institut, p. 48.

Tyréns AB (2018). *Spridningsmodell för Ekoln - steg 1*. 1.1.

Uppsala Universitet (Sept. 21, 2020). *Hans Bergström, Professor emeritus at Department of Earth Sciences, Program for Air, Water and Landscape Sciences; Meteorology*. E-mail.

Uppsala Vatten och Avfall AB (Sept. 29, 2020a). *Jonas Helander-Claesson, process engineer*. E-mail.

— (Sept. 29, 2020b). *Sofie Boman, environmental controller*. E-mail.

Von Einem, Jessica & Wilhelm Granéli (2009). *Effects of fetch and dissolved organic carbon on epilimnion depth and light climate in small forest lakes in southern Sweden*. American Society of Limnology and Oceanography, Inc.

Wallman, Karin, Mats Wallin, & Christer Tjällén (Dec. 2010). *Synoptisk undersökning av Mälarens vattenkemi 2010-08-23 samt en jämförelse mellan åren 2008-2010*. 2010:06. Uppsala: Institutionen för vatten och miljö, SLU & Mälarens vattenvårdsförbund.

Wetzel, Robert G. (2001). *Limnology: Lake and River Ecosystems*. Third edition. Elsevier. 198 pp.

## Online

EFSA (Sept. 17, 2020). *PFAS in food: EFSA assesses risks and sets tolerable intake*. European Food Safety Authority. Section: News. URL: <https://www.efsa.europa.eu/en/news/pfas-food-efsa-assesses-risks-and-sets-tolerable-intake> (visited on 12/11/2020).

Kemikalieinspektionen (Aug. 25, 2020). *Högfluorerade ämnen – PFAS*. KEMI, kemikalieinspektionen. URL: <https://www.kemi.se/kemiska-amnen-och-material/hogfluorerade-amnen-pfas> (visited on 08/26/2020).

- Livsmedelsverket (Sept. 17, 2020). *Efsa fstställer bedömning av PFAS-ämnena*. URL: <https://www.livsmedelsverket.se/om-oss/press/nyheter/pressmeddelanden/efsa-faststaller-bedomning-av-pfas-amnen> (visited on 12/10/2020).
- (Jan. 19, 2021). *Riskhantering PFAS i dricksvatten och egenfångad fisk*. URL: <https://www.livsmedelsverket.se/produktion-handel--kontroll/dricksvattenproduktion/riskhantering-pfas-i-dricksvatten-egenfangad-fisk> (visited on 01/26/2021).
- Mälarens Vattenvårdsförbund (2020a). *Dricksvatten*. URL: <http://www.malaren.org/malaren/nyttjande-och-paverkan/dricksvatten/> (visited on 05/10/2020).
- (2020b). *Mälarens uppdelning i bassänger*. URL: <http://www.malaren.org/malaren/malaren-och-dess-naromrade/malarens-uppdelning-i-bassanger/> (visited on 05/07/2020).
- Norrvatten (Oct. 25, 2019). *Internationellt utbyte om naturligt organiskt material*. URL: </om-norrvatten/nyheter/nyhetsarkiv/nyheter-2019/internationellt-utbyte-om-naturligt-organiskt-material/> (visited on 08/27/2020).
- SLU (n.d.). *Miljödata MVM - En webbtjänst med mark-, vatten- och miljödata*. SLU - Miljödata MVM. URL: <https://miljodata.slu.se/MVM/Search> (visited on 09/28/2020).
- SMHI (n.d.[a]). *Januari 2018 - Höga flöden och vattenstånd*. URL: <https://www.smhi.se/klimat/klimatet-da-och-nu/manadens-vader-och-vatten-sverige/laget-i-sveriges-sjoar-och-vattendrag/januari-2018-hoga-floden-och-vattenstand-1.129021> (visited on 12/09/2020).
- (n.d.[b]). *Ladda ner meteorologiska observationer*. URL: <https://www.smhi.se/data/meteorologi/ladda-ner-meteorologiska-observationer/#param=totalCloudCover,stations=all,stationid=97530> (visited on 09/21/2020).
- (n.d.[c]). *Ladda ner meteorologiska observationer*. URL: <https://www.smhi.se/data/meteorologi/ladda-ner-meteorologiska-observationer/#param=precipitation24HourSum,stations=all> (visited on 11/30/2020).
- (n.d.[d]). *Mälaren - Vattennivå*. URL: [http://www.airviro.smhi.se/cgi-bin/malaren/apub.stncolmap2.cgi?page=ShowMapG&areaid=MA&gsize=450x370&stnshow=true&stngroup=0xffffffff&backgroundimg=images/blank.gif&mappostop=0&mapposleft=0&infocgi=apub.infostn2.cgi&macropath=stn&infoframe=\\_blank&rsrc=Monitoring.6.MainPage&lefthtmlpage=&apptag=colorstn&nrdec=1&subs=TEMP&year=now](http://www.airviro.smhi.se/cgi-bin/malaren/apub.stncolmap2.cgi?page=ShowMapG&areaid=MA&gsize=450x370&stnshow=true&stngroup=0xffffffff&backgroundimg=images/blank.gif&mappostop=0&mapposleft=0&infocgi=apub.infostn2.cgi&macropath=stn&infoframe=_blank&rsrc=Monitoring.6.MainPage&lefthtmlpage=&apptag=colorstn&nrdec=1&subs=TEMP&year=now) (visited on 09/21/2020).
- (n.d.[e]). *Modelldata per område - Vattenwebb*. SMHI. URL: <https://vattenwebb.smhi.se/modelarea/> (visited on 09/30/2020).
- SMHI, Naturvårdsverket, & Strålsäkerhetsmyndigheten (n.d.). *STRÅNG - a mesoscale model for solar radiation*. Strång, SMHI. URL: <http://strang.smhi.se/> (visited on 10/21/2020).
- Swedish Environmental Protection Agency (Jan. 22, 2020). *Högfluorerade ämnen i miljön*. Naturvårdsverket. URL: <https://www.naturvardsverket.se/Sa-mar-miljon/Manniska/Miljogifter/Organiska-miljogifter/Perfluorerade-amnen/> (visited on 08/20/2020).
- Uppsala vatten och Avfall (n.d.). *Perfluorerade ämnen i några dricksvattenbrunnar*. Uppsala Vatten. URL: <https://www.uppsalavatten.se/hushall/vatten-och-avlopp/dricksvatten/perfluorerade-amnen-i-nagra-dricksvattenbrunnar/> (visited on 08/26/2020).
- VISS (2019). *Mälaren-Ekolen*. VISS, Vatteninformationssystem Sverige. URL: <http://viss.lansstyrelsen.se> (visited on 08/18/2020).

## Unpublished

SLU (Sept. 22, 2020). *Stephan Köhler, Professor at the Department of Aquatic Sciences and Assessment; Section for Geochemistry and Hydrology*. E-mail.

Uppsala Universitet (Sept. 21, 2020). *Hans Bergström, Professor emeritus at Department of Earth Sciences, Program for Air, Water and Landscape Sciences; Meteorology*. E-mail.

Uppsala Vatten och Avfall AB (Sept. 29, 2020a). *Jonas Helander-Claesson, process engineer*. E-mail.  
— (Sept. 29, 2020b). *Sofie Boman, environmental controller*. E-mail.

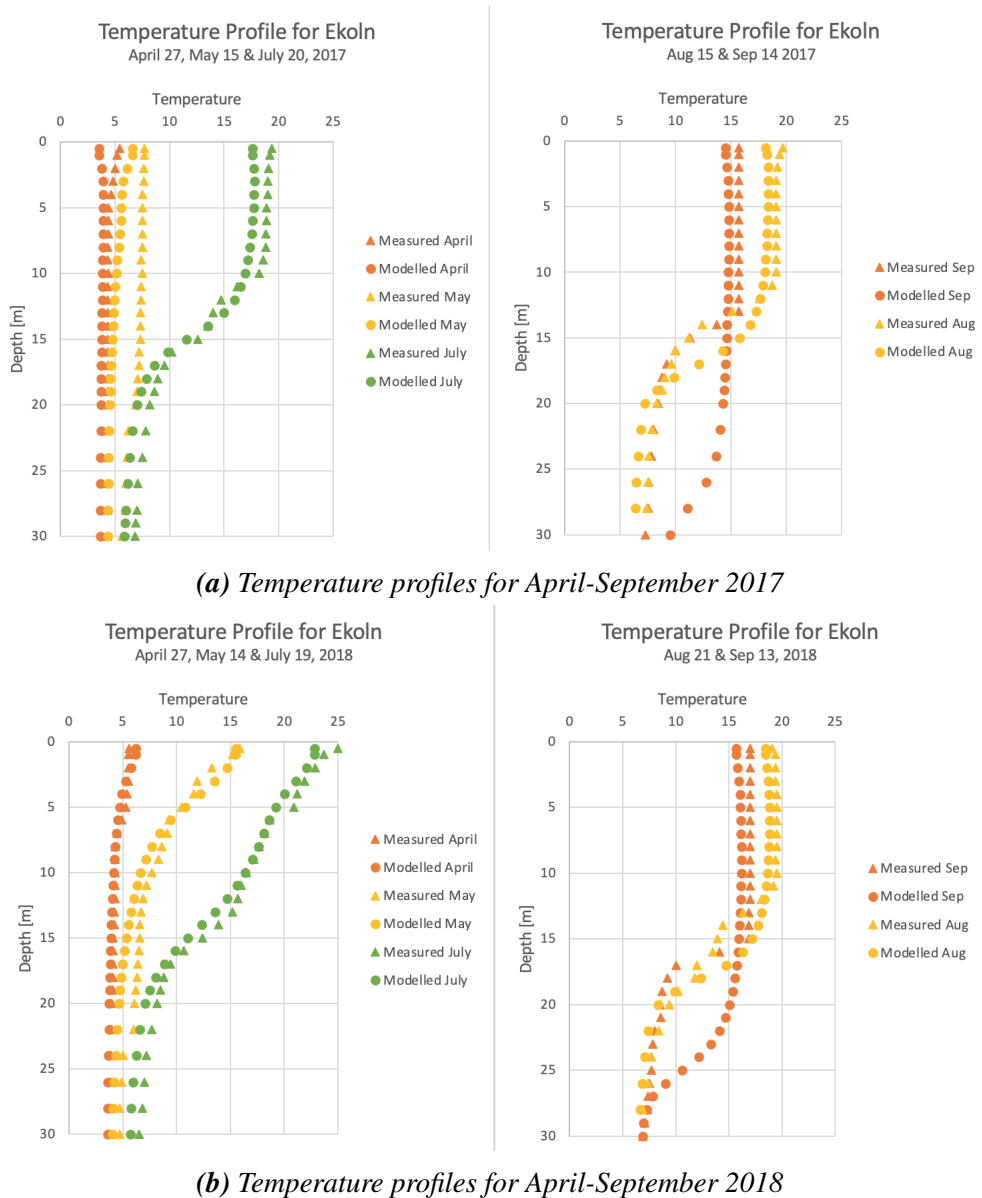
## Maps

*Ekoln* (2020). In collab. with Google Maps. URL: <https://www.google.com/maps/place/Ekoln/@59.722507,17.4640346,11z/data=!4m5!3m4!1s0x465fb667668cf995:0xcee64239c7b3101b!8m2!3d59.7322!4d17.6102901> (visited on 12/03/2020).

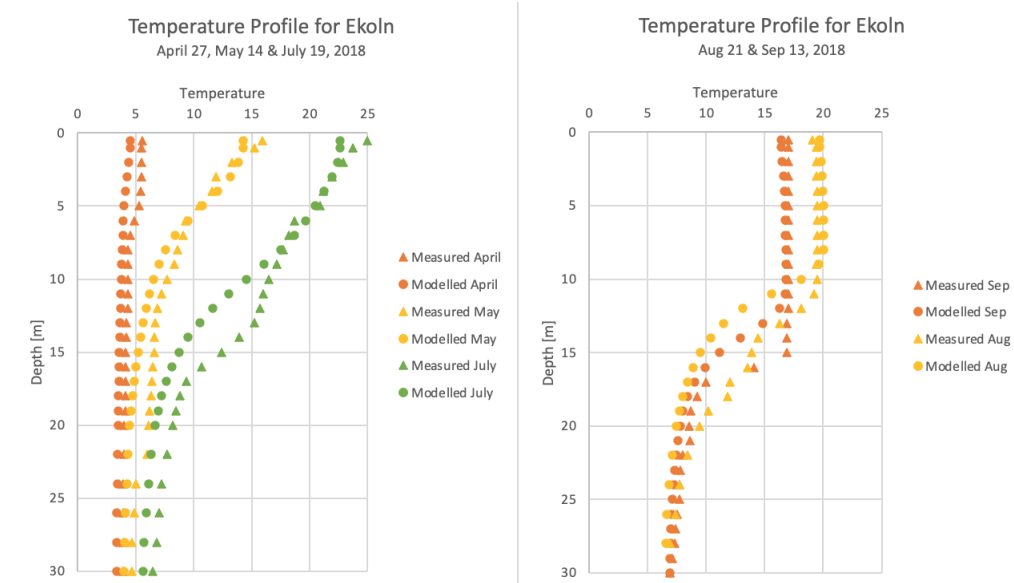
# 8 Appendix

## 8.1 Temperature profiles

In figure 13 are the simulated temperature profiles for the period February 2017 - September 2018. In figure 13a and 13b are the temperature profiles for 2017 and 2018 respectively. The temperature profiles are plotted together with measured temperatures in Ekoln at Vreta Udd. In figure 14 are the results from the calibration done by Lindqvist (2019) for the period February to September 2018, which was the period for which the hydrodynamics were calibrated for.



**Figure 13:** Temperature profiles for the period simulated in this project: February 2017 - September 2018. The circles represent simulated values, and the triangles observed values, both measured at Vreta Udd in Ekoln.



**Figure 14:** Temperature profiles from Lindqvist (2019) calibration of the model for the year 2018.

## 8.2 Simulated temperatures at different depths.

In figure 15 the variation in Ekoln's temperature profile is showed using simulated temperatures at 15 different depths.

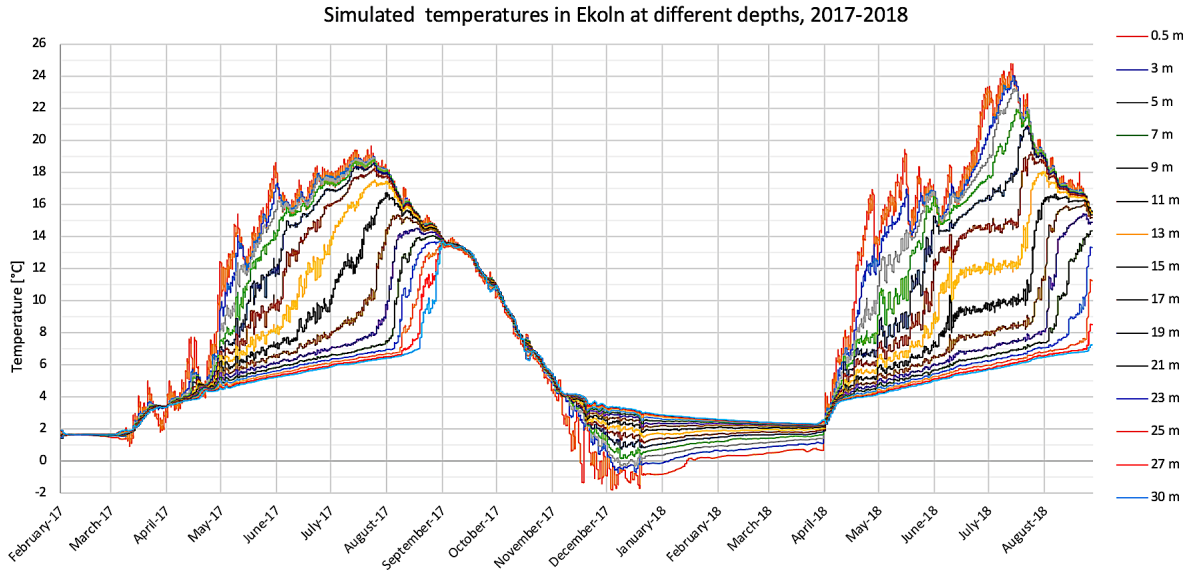


Figure 15: Simulated temperatures for 15 depths from 0.5 m - 30 m in Ekoln

## 8.3 Simulations without any processes impacting TOC and Colour

Figure 16 and 17a show simulation results Colour and TOC when no processes impact them. In figure 17 are also figure 17b and 17c that show the effect of how decay and sedimentation separately impact TOC.

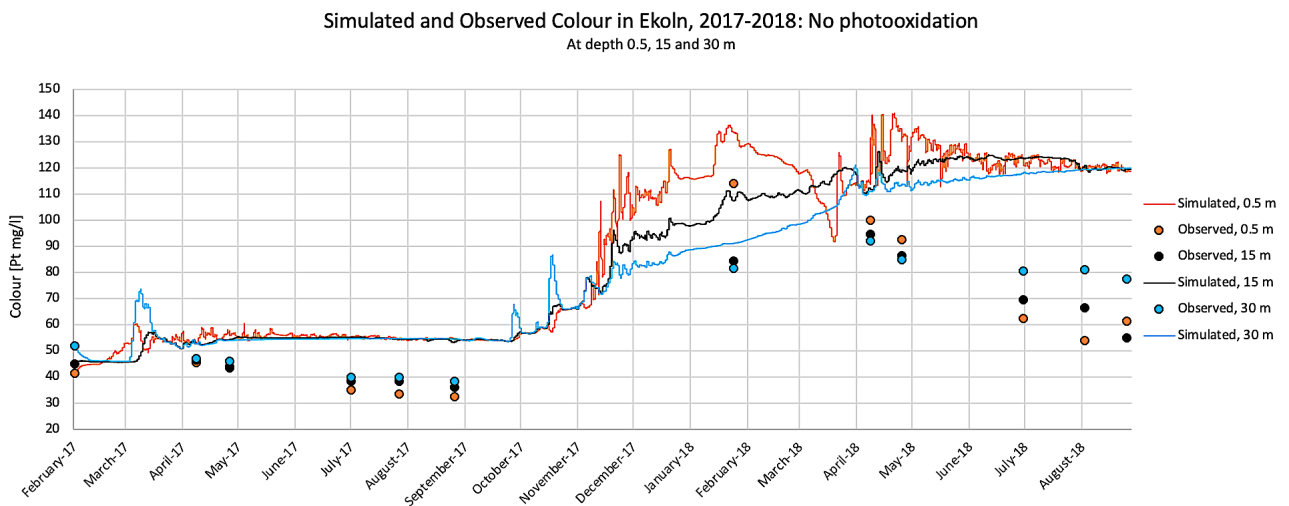
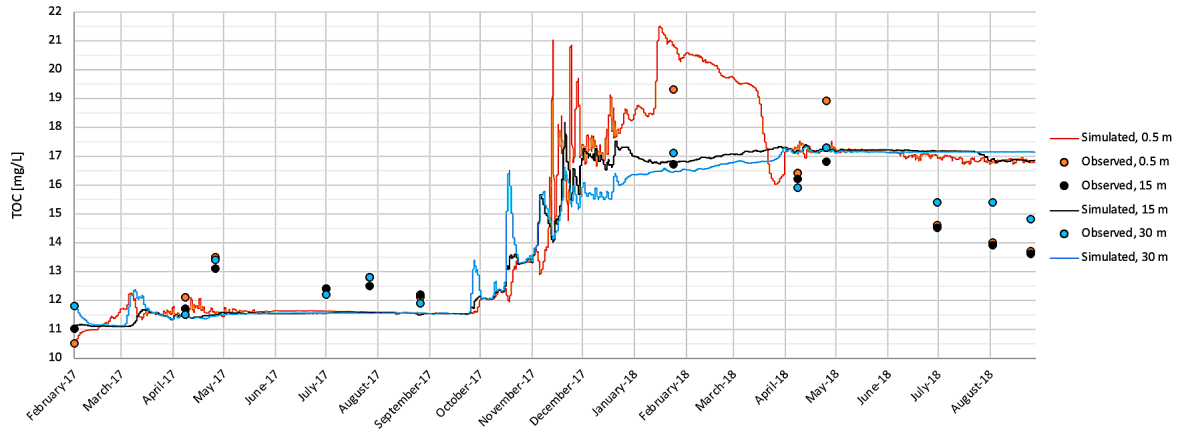


Figure 16: The graph show the simulation of Colour when photooxidation is not impacting Colour, i.e. no photooxidation is occurring.

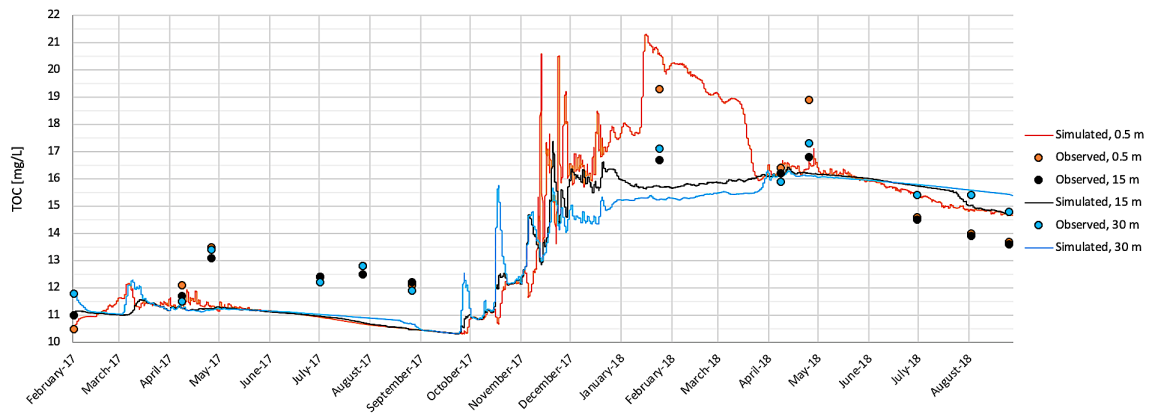


Simulated and Observed TOC in Ekoln, 2017-2018: No decay or sedimentation  
At depth 0.5, 15 and 30 m



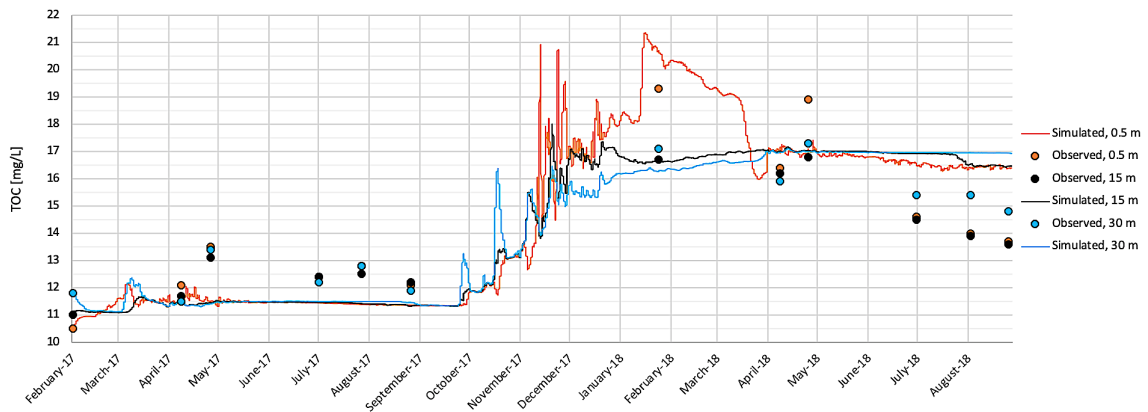
(a) Simulated and observed concentrations of TOC without decay nor sedimentation.

Simulated and Observed TOC in Ekoln, 2017-2018: Only decay  
At depth 0.5, 15 and 30 m



(b) Simulated and observed concentrations of TOC when only decay impacts TOC.

Simulated and Observed TOC in Ekoln, 2017-2018: Only sedimentation  
At depth 0.5, 15 and 30 m



(c) Simulated and observed concentrations of TOC when only sedimentation impacts TOC.

**Figure 17:** The graphs show the simulated concentration of TOC when there are no processes impacting TOC and show the separated impact from decay and sedimentation on TOC.

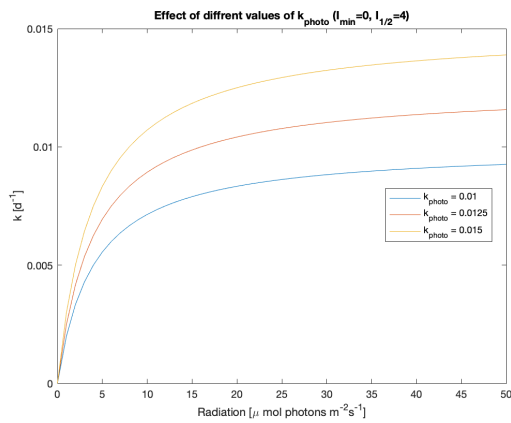
## 8.4 Sensitivity analysis

In table 9 scaled decay rates,  $k$ , are presented, using different values for  $\theta$  and water temperature.  $k$  is calculated using:  $k = k_0 \cdot \theta^{T-20}$ , where  $k_0 = 0.001 \text{ d}^{-1}$  for a reference temperature  $20^\circ\text{C}$ .

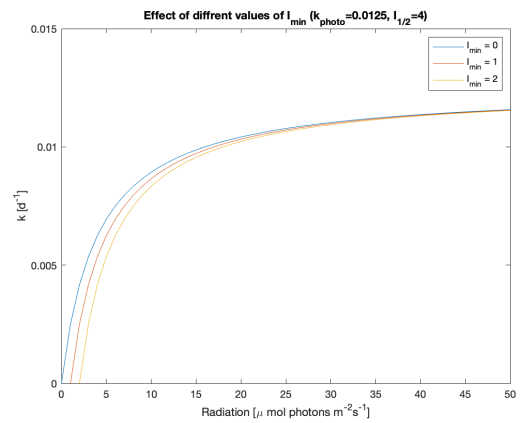
**Table 9:** The table presents calculated scaled decay rates,  $k$ , based on the reference decay rate,  $k_0 = 0.001 \text{ d}^{-1}$ , and reference temperature  $20 \text{ C}^\circ$ .

$\theta$	Water temperature [ $^\circ\text{C}$ ]									
	0	2	4	6	8	10	12	14	16	18
<b>1.01</b>	0.00082	0.00084	0.00085	0.00087	0.00089	0.0009	0.00092	0.00094	0.00096	0.00098
<b>1.03</b>	0.00055	0.00059	0.00062	0.00066	0.00070	0.00074	0.00079	0.00084	0.00089	0.00094
<b>1.05</b>	0.00038	0.00041	0.00046	0.00051	0.00056	0.00061	0.00068	0.00075	0.00082	0.00091
<b>1.07</b>	0.00026	0.00030	0.00034	0.00039	0.00044	0.00051	0.00058	0.00067	0.00076	0.00087
<b>1.09</b>	0.00018	0.00021	0.00025	0.00030	0.00036	0.00042	0.00050	0.00060	0.00071	0.00084
<b>1.11</b>	0.00012	0.00015	0.00019	0.00023	0.00029	0.00035	0.00043	0.00053	0.00066	0.00081

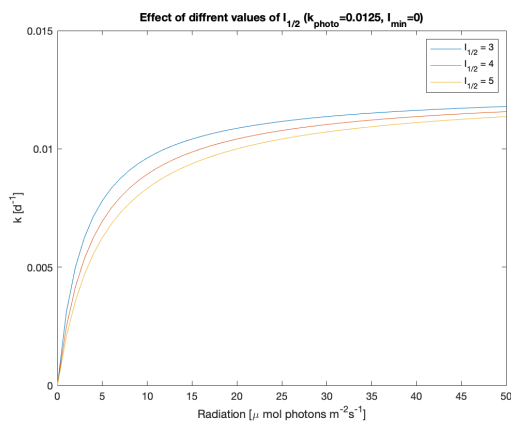
In figure 18 the effect of changes in the parameters of photooxidation can be observed for the scaling of the photooxidation rate ( $k$ ). The values of  $k_{photo} = 0.0125$ ,  $I_{min} = 0 \text{ } \mu\text{mol photons m}^{-2}\text{s}^{-1}$ ,  $I_{half} = 4 \text{ } \mu\text{mol photons m}^{-2}\text{s}^{-1}$  are the original set of values used for the calibration, which is represented by the red line in figure 18a and 18c, and the blue line in figure 18b. The radiation shown on the x-axis represent the radiation reaching the water at a certain depth and can therefore be interpreted as 50 being at the surface, and 0 being at depth 15-30 meters. These can be compared to figure 18d showing how radiation declines with depth in the water profile. The yellow line marks a value  $I_{surface}$  of  $51 \text{ } \mu\text{mol photons m}^{-2}\text{s}^{-1}$  which is used in the model.



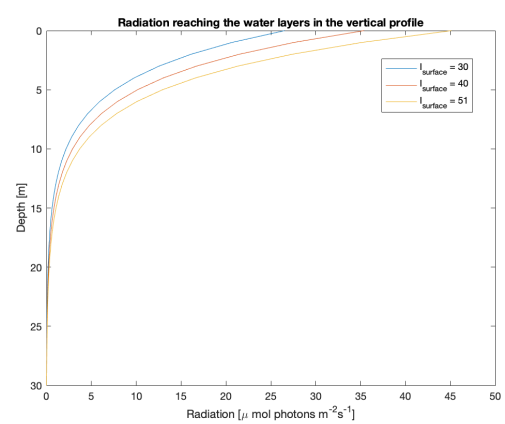
(a)



(b)



(c)

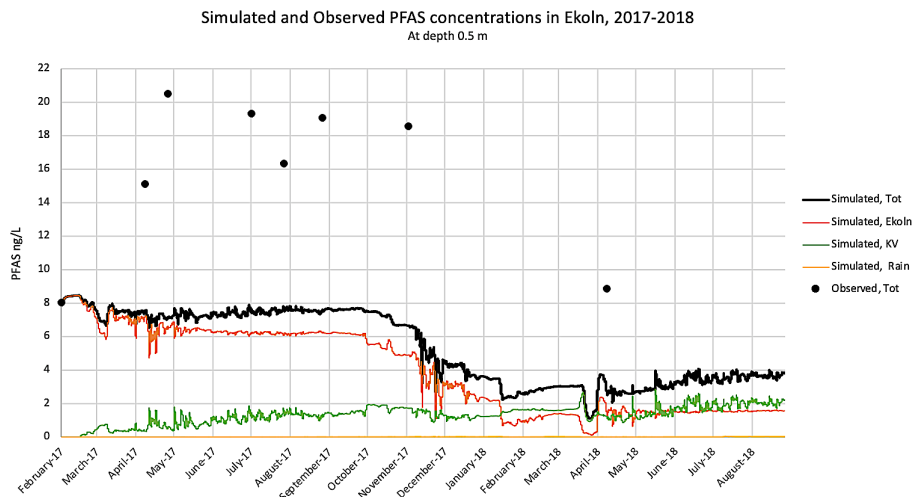


(d)

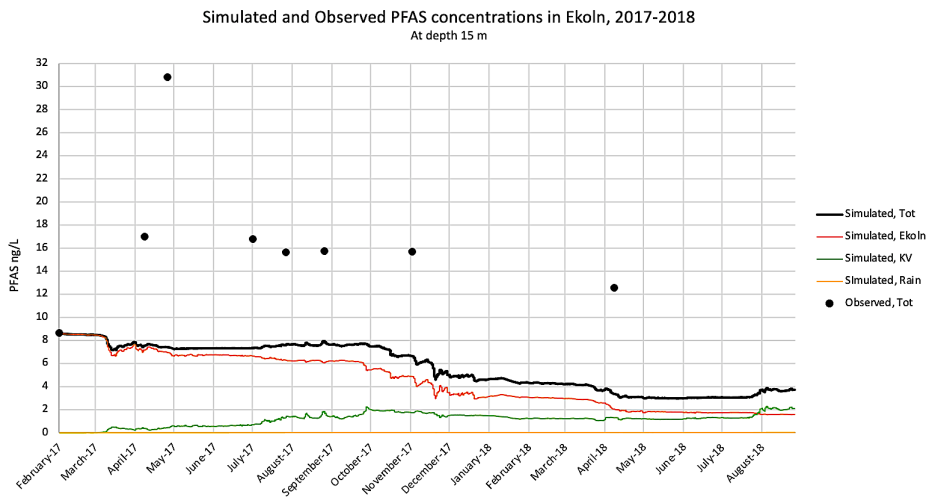
**Figure 18:** Figures a-c show the effect the  $k_{photo}$ ,  $I_{min}$  and  $I_{half}$  respectively. Figure d, show how the radiation declines with depth in the water profile.

## 8.5 PFAS simulations

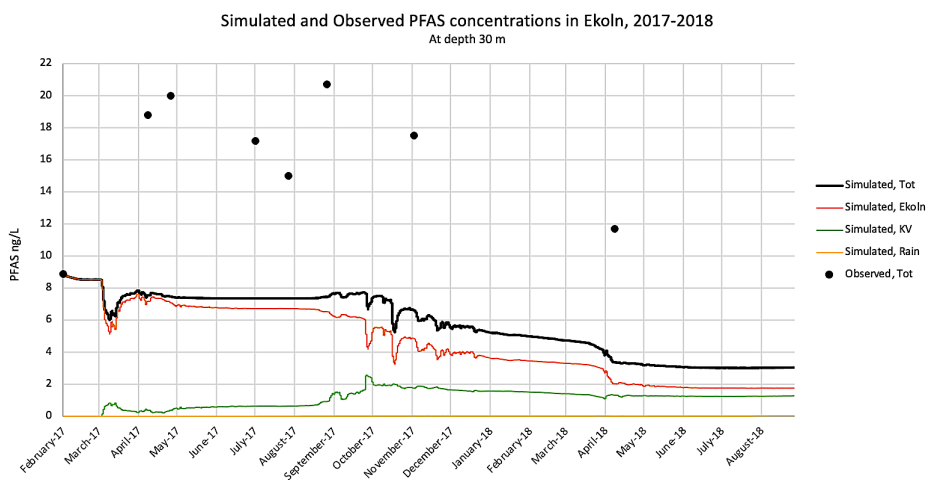
In figure [19a](#), [19b](#) and [19c](#) the PFAS concentrations with different origins together with the total concentration are presented at depths 5 m, 15 m and 30 m. The different origins are: Ekoln (originating from the initial concentrations in Ekoln at the start of the simulation), Kungsängsverket (KV) and precipitation. The average PFAS concentration from precipitation from the the three depths is 0.016 ng/l which is why the yellow line, representing PFAS from precipitation, is close to zero.



(a) PFAS concentrations separated in terms of origin at depth 0.5 meters.



(b) PFAS concentrations separated in terms of origin at depth 15 meters.



(c) PFAS concentrations separated in terms of origin at depth 30 meters.

**Figure 19:** PFAS concentrations separated in terms of origin (Ekoln, Kungsängsverket and precipitation) at depth 0.5, 15 and 30 meters. KV stands for Kungsängsverket and the black lines and dots mark the simulated and observed total concentrations of PFAS.