Master Eaux, Sols et Environnements

RAPPORT DE STAGE

# Annual dissolved organic carbon dynamics in a boreal landscape

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# Presentation of the laboratory

My master's thesis completed within the University of Helsinki in the department of agriculture and forestry, was carried out in one of the fourth SMEAR (Stations for Measuring the forest Ecosystem-Atmosphere Relationships) research stations all based in Finland: SMEAR I in Värriö; **SMEAR II in Hyytiälä**; Urban-SMEAR III in Kumpula, Helsinki and SMEAR IV in Kuopio.

These measurement stations regroup scientists with multidisciplinary skills (physics, chemistry, meteorology and biology) who conduct research programs in various fields. A common goal based on climate change as well as overall pollution effect on ecosystem have led scientists to work all together.

SMEAR II station particularly, is a continuous monitoring station and includes a 124m tower for atmospheric measurements, a 18m tower for irradiation measurements, another tower for tree physiology measurements and a 35m tower for aerosol measurements. From 50 to 100 people work in this station on various interests *(Source: SMEAR)*.

***SMEAR station in Hyytiälä***
***(source: SMEAR station)***

# Introduction

Boreal ecosystem is known as one of the largest biomes on Earth, making up around 22% of the global forested area. In Finland especially, first forested European country, ¾ of the land area is covered by managed forests, mainly with coniferous species of pines and spruces (Metla, 2012). Terrestrial forest ecosystem in these regions account for up to 40% of the world carbon storage, with 25% in peatlands accounting for $3.10^6$ ha in Finland, 10% of the land area (IPCC, 2010). A part of terrestrial Carbon storage is stocked within the vegetation and soil, especially in the organic layer where 80% of the terrestrial organic carbon is stored. It has been shown that a large proportion of it is transferred to inland waters, about 80% of dissolved organic compounds found into water ecosystems is from allochthonous source (Regnier et *al.,* 2013).

Even though the area covered by freshwater ecosystems is comparatively small to the terrestrial area at a global scale, Finland accounts more than 10% of lakes and streams over the country. Several studies reveal the importance of inland waters, not just as a simple neutral "pipe" that leads carbon from land source to ocean, but as a fully-fledged member of the terrestrial carbon cycle (Cole et *al.,* 2007, Köhler et *al.,* 2002, Oquist et *al.,* 2002). In fact, several processes have been attributed to explain that between 30 and 80% of organic carbon entered is lost in the lake (Algesten et *al.,* 2003). For instance, Cole and *al.,* in 2007 reveal that among the 1.9Pg $C.yr^{-1}$ transferred through the streams ecosystem under temperate climate, 39% is released as carbon dioxide in the atmosphere via mineralization process and 12% is buried into lake sediments, while the rest is export to ocean. In aquatic boreal zone, about half of the organic carbon entering into water system has been seen to be outgassed to the atmosphere under $CO_2$ form (Algesten et *al.,* 2003). Other studies tend to display different export values, and it is therefore essential to understand organic carbon dynamics and parameters influencing them. Hence several factors have been identified and may explain the dynamics of organic carbon exports from land such as soil type (Clarke et *al.,* 2007, Aitkenhead et *al.,* 1998), geology and hydrology (Dinsmore et *al.,* 2013, Clark et *al.,* 2007, Mulholland et *al.,* 1997), those latter constitute catchment characteristics. Vegetation (Ågren et *al.,* 2007), altitude (Ågren et *al.,* 2010), solar radiation (Köhler et *al.,* 2002) and acid deposition (Hudson et *al.,* 2003) are considered for their part as regional factors.

Besides numerous factors, organic carbon concentration varies during the year (seasonality) and is closely tied to annual hydrologic events and discharge. Snowmelt during springtime is the major hydrological event of the whole year and can account for 37 to 45% of the annual carbon loss through runoff (Dyson et *al.,* 2010) and studies have shown that most of the annual export of Dissolved Organic Carbon (DOC) occurs at times of high-, short-rainfall intensity (Clark et *al.,* 2007, Ågren et *al.,* 2010). In the same way, organic carbon loss increases rapidly with higher water residence time in the lake (Algesten et *al.,* 2003).

Knowing the DOC dynamics in a catchment is crucial to figure out the impacts that those concentrations have on the ecology of aquatic systems at local scale. Organic carbon is a source of nutrients and energy for microbial production, and is responsible of release of $CO_2$ in the atmosphere by mineralization process, making the lake a net source of carbon dioxide (Wallin et *al.,* 2012, Huotari et *al.,* 2011, Rasilo et *al.,* 2011). But it can also attenuates ultraviolet radiation through the water and therefore ensures the protection of microorganisms (Morris et *al.,* 1995), affecting water transparency at the same time and causing depression of primary productivity (Köhler et *al.,* 2002).

As a result, variation of DOC fluxes may have major impacts on physical, chemical and biological processes of the lake. Recent studies conjecture and predict possible effects of climate change on DOC patterns in high latitude catchments, and their consequences at local scale (biota community) as well as global scale (Dinsmore et *al.,* 2013, Clark et *al.,* 2007). A larger number of papers have led scientists to agree on a consortium that precipitation and temperatures may increase across the globe with climate change, thereby rising dissolved organic matter (DOM) decomposition and DOC export from terrestrial ecosystems to the atmosphere.

Even though a large number of studies have been conducted on organic carbon dynamics, it reveals that the main parameters responsible of the variations are still debated, and the relationships between them remain unclear.

I carried out a study in the aim to assess temporal variation on DOC fluxes in the way to create a DOC pattern across the year, but also understand how a combination of different parameters that vary spatially and temporally may affect organic carbon cycle in a boreal catchment. This work is also the opportunity to better understand the key role of inland waters in the organic carbon cycle.

# 1 Overview

DOC constitutes the major fraction (90-95%) of the total organic carbon (Algesten, et *al.,* 2003) the remaining 5-10% forms the particular organic carbon. Commonly, these molecules (100-100,000 Da) are defined as the retained organic fraction after water filtration at 0.22 to 0.45$\mu$m. While only 20% of the DOC represents low molecular weight compounds such as carbohydrates and amino acids, most of it (8O%) is composed of high molecular weight complex compounds, the *humic substances*. Even though the structure is still largely unknown (Leenheer and Croué, 2003, Kalbitz et *al.,* 1999).

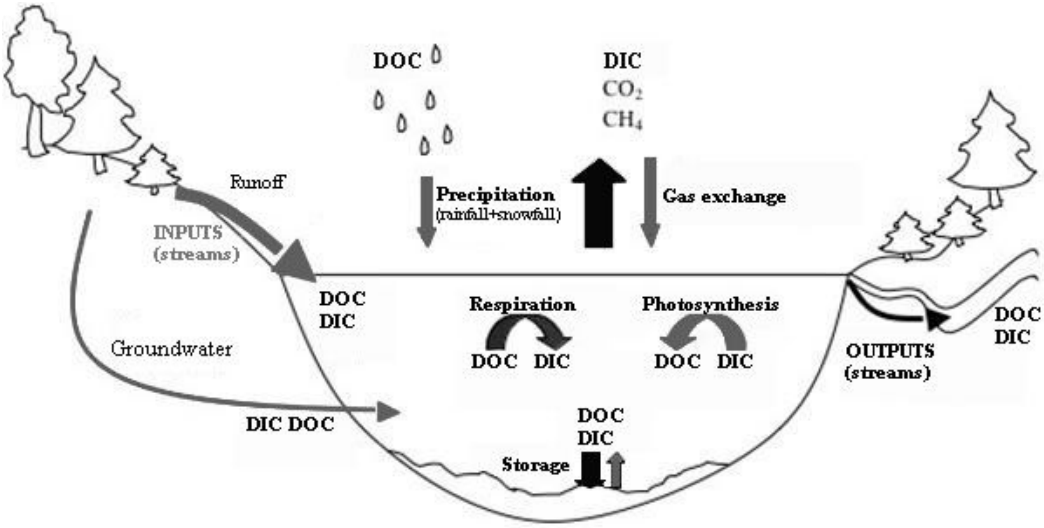


**Figure 1: Organic carbon cycle around lake system between terrestrial and aquatic ecosystems (DOC=Dissolved Organic Carbon, DIC=Dissolved Inorgnic Carbon), grey and black arrows are identified as DOC production and breakdown respectively)**
***Source: inspired of "Eastmain1-role of boreal lakes in the carbon cycle", 2012 document***

## 1.1 Sources of DOC

### 1.1.1 Allochthonous DOC versus autochthonous DOC

Two major sources of DOC are generally assumed in lakes. *Autochthonous DOC* is produced within the aquatic ecosystem itself, from the activity and the development of phototrophic organisms (macrophytes, phytoplankton and benthic algae) but it also results of degradation by bacteria. This labile colorless DOC is composed of carbohydrates and amino acids and is thus supposed to be more easily degraded by heterotrophic organisms.

*Allochthonous DOC* is generated through the degradation of soil organic matter or *SOM* (plants, roots, etc) and anthropic compounds then released to be transported in aquatic ecosystems. Extensively processed within the soil, this darker DOC is a combination of high-weight molecular compounds. For this reason, it has long been suggested that terrestrial DOC is recalcitrant to bacterial breakdown (Qualls et *al.,* 1992) resulting in a slow decomposition and assumed by several authors, such as Vähätalo and Wetzel in 2004 to largely influence inlands water composition. In consequence, allochthonous DOC has been assumed by numerous authors to constitute the main input of organic carbon in inland waters.

This slow degradation is one of the reasons for which several authors infer terrestrial organic carbon to influence mainly the composition of inland waters (Vähätalo and Wetzel, 2004). Another cause could be that soils, especially at Northern latitudes, have the largest carbon reservoirs on Earth (Aitkenhead et *al.,* 1998, Moore et *al.*, 2003). Moreover, high flow events are known to increase DOC concentrations in streams, which underpin the fact that allochthonous DOC is likely to influence inland waters. Quality and molecular DOC analyses underline this idea revealing lignin presence, a characteristic component of vascular plant

(Leenheer and Croué, 2003). Other noteworthy arguments such as $^{13}$C isotopic composition highlights as well the key role of terrestrial carbon (Raymond and Bauer, 2001).

### 1.1.2 Production and control of DOC stock

Given the key role that allochthonous organic matter plays in shaping lake metabolism, it is therefore fundamental to identify and further to better understand the mechanisms in the landscape that influence the delivery of organic carbon into aquatic systems.

#### *Size of the soil organic pool*

Despite the poverty of literature regarding the role of the size of organic carbon pool on stream water DOC concentrations, DOC reveals to be positively correlated to soil organic matter concentration in the catchment (Kalbitz et *al.,* 1999, Lambert, 2013, Ågren et *al.,* 2007). The resulting, northern regions are especially concerned since their soils constitute a large stock of organic carbon. Whereas boreal vegetation contains only 88Pg of C, forests soils may have a pool of about 471Pg C (Lal, 2005). The high content of carbon in these regions is mainly due to climate, vegetation and geology parameters. The accumulation of organic carbon is indeed greater in environments subject to low temperature, mid precipitation and low evaporation as well as poor nutrient bedrock that provide good conditions to allow carbon accumulation. Aitkenhead et *al.,* in 2000 conducted a study on the riverine DOC dynamics from terrestrial ecosystems to oceans within various biomes and revealed more substantial DOC export in boreal (64kg.ha$^{-1}$.yr$^{-1}$) than in temperate (43kg.ha$^{-1}$.yr$^{-1}$) ecosystems, but those results highly depend on vegetation. This is particularly stressed in wetlands where high water table prevents a good oxygenation of soils. Land use may then be considered (wetlands proportion) as a determining factor to predict DOC concentrations in soils as well as climate and flow path in the soil profile (Aikenhead et *al.,* 1998).

#### *Variation of soil DOC content*

Despite the importance of quantity of Soil Organic Matter (SOM) content, its quality contributes largely to DOC productivity. The main reason for this variability might be the SOM C/N ratio. A low ratio would be assigned to a low production of DOC, conversely a wide ratio would stand for higher DOC concentrations. Therefore, deciduous forests show more significant DOC production than coniferous stands (Kalbitz et *al.,* 1999). In addition, the degradation process that undergoes SOM within the soil profile is another crucial piece of organic carbon cycle. The community of living organisms in soils is very variable and shows different capacity to degrade SOM (Christ and David, 1996, Andersson et *al.,* 2000). Poor conditions in boreal landscapes such as low temperature, low alkalinity (pH<5) as well as high humidity rate are likely to influence the decay of SOM by impacting microbial activity in high latitude soils.

Numbers of studies have demonstrated the role of temperature in SOM degradation. Thereby, the majority of authors agrees to say that an increase of temperature as for aim to enhance DOC production (Karhu et *al.,* 2009, Christ and David 1996, Kalbitz et *al.,* 1999, Xu and Saiers 2010). In fact, a rise of temperature is known to have direct effects on microbial activity (Andersson et *al.,* 2000, Gaultier et *al.,* 2009, Christ and David, 1996), while Xu and Saiers (2010) highlight the major impact on abiotic processes (desorption, diffusional mass transfer and DOC solubility). This trend of DOC increase with highest temperature is rather found in laboratory studies, whereas natural conditions reveal the complexity of interactions between several factors (hydrological conditions, litter quality…) that control DOC mobile production (Andersson et *al.,* 2000, Kalbitz et *al.,* 1999). In the case of boreal climates, low temperature and frozen soil decrease microbial activity to its minimum, Andrews et *al* (2000) goes further by suggesting a lack of diversity of microorganisms at low temperature. Regardless, Xu and Saiers in 2010, underplayed the importance of temperature in microbial activity and encompassed the idea that even though poor conditions in spodosol are supposed to deplete microbial activity, it still persists at temperatures close to 0°C.

Then, owing to the fact that organic matter is negatively charged, its solubility is thus naturally influenced by pH (Kalbitz et *al.,* 1999). A decrease of pH tends to diminish DOC solubility as a result of increasing positive charges on the hydroxides that can adsorb OM on their surfaces. This way a raise of pH causes indirectly a highest amount of negative charges on humus colloids and thus the solubility of DOC is greater (Andersson et *al.,* 2000). Nevertheless, contradictory experimental results can be found for mineral horizons of podzol that show an increase of DOC mobilization after pH rise. This result might be attributed to an enhancement of metal-organic complexes solubilization (Kalbitz et *al.,* 1999).

Although temperature and pH parameters are important in DOC regulation, soil moisture is crucial for life. Several studies have indicated increasing DOC mobilization with increasing soil moisture, as a result of large rainfall events (Kalbitz et *al.,* 1999, Xu and Saiers, 2010). Further, recent results have shown that the most important increase of DOC concentration, at the beginning of large rainfall events, occurs just after dry periods at the end of summer (Kalbitz et *al.,* 1999, Lambert, 2013). In fact, in keeping with our previous assessment, higher temperatures at the end of summer are likely to enhance SOM degradation and then rehydration may improve conditions of DOC production. At the opposite, soil saturation condition that causes anaerobic conditions may also enhance the release of DOC in soil water. These results do not have to be seen as opposite to drought condition since mechanisms involved are different, but are still able to release DOC in soil solution.

## 1.2 DOC export from terrestrial to aquatic ecosystems

Transfer of dissolved organic carbon implies the latter to be mobile into the soil. Generally, this fraction is located into macro and mesopores and will be then transported through the soil to the river. Multiples factors are then likely to impact the pathway of C delivery.

### 1.2.1 Flow path

Carbon and hydrological cycles are closely related to each other. Of the numerous studies to explain DOC export to streams, most have been carried out on the *flow path of water* and its strong link to seasonal variations across the year (Ågren et *al.,* 2008, Clark et *al.,* 2007, Ågren et *al.,* 2007, Laudon et *al.,* 2004, Kalbitz et *al.,* 2000). A widespread observation shows that as a result of high rainfall or snowmelt events, discharge and DOC concentrations are positively correlated and particularly high during the early stages of snowmelt or rainfall events (Hope et *al.,* 1994, Laudon et *al.,* 2004). However, a large discrepancy amongst studies suggests that this model might be too simple and corrections have to be made by considering other interactions.

Despite the fact that DOC concentration in lake and rivers is influenced by the size of SOM pool within the soil profile, its transfer to water ecosystems shows often an overall depletion. In fact, it has been observed that water DOC load occurs in superficial horizons of the soil, where organic carbon stock is located, and then undergoes depletion as it passes through the soil profile. Several mechanisms that play a role in this decrease have been identified. Though this DOC decrease is mostly driven by adsorption onto minerals (clay, oxides/hydroxides), mineralization into carbon dioxide represents another significant factor despite all (Hope et *al.,* 1994, Xu and Saiers, 2010). In order to prevent DOC removal, the good connection between pore is then essential. This feature called “hydraulic conductivity” depicts the pathway of water through the soil, and is highly dependent on soil properties (structure, texture..) and flow dynamics. Hence the necessity to understand the flow pathway into the soil, in order to predict DOC concentration in the lake water. In this sense, authors as Laudon et *al.,* in 2004 and Kendall et *al.,* in 1999 attempted to follow the path of water during rainfall and snowmelt events based on isotopic approaches. By definition the flow will be more concentrated in DOC if it occurs in the shallower organic horizons and then directly transferred to streams. The opposite will be also true in the case of water goes vertically through the deepest horizons in the soil leading to lower DOC concentrations.

### 1.2.2 Linking to soil type & hydrology

The two most important soils in boreal regions, peat and organo-mineral soils are extremely different whether based on their profile or their behavior towards hydrological events. Contrary to peat soils that are composed of several layers of more or less decomposed organic carbon, the organo-mineral soils (mostly podzols) are only constituted of a relatively thin horizon of organic matter on the top of several underlying mineral horizons. Interactions between soil features and hydrological events will lead to variation in DOC export. Thus, three hydrological patterns can be differentiated across a year in a boreal landscape: (1) snow cover season, (2) snowmelt season and (3) snow-free season (Ågren et *al.,* 2007). (1) The snow-covered season implies a low water stream level that comes mainly from groundwater. Consequently, only the deepest parts of the soil profiles are drained by the water table. In that condition, while the water leaving the organo-mineral soils is relatively poor in DOC since those lowest horizons are mainly composed of mineral horizons, the water draining organic soils is richer in DOC. (2) The snowmelt season as the most important hydrological event in boreal regions (for instance Ågren et *al.,* 2010, Laudon et *al.,* 2004) results in the elevation of groundwater level in soils. The upper horizons, with high organic matter content in mineral soils, release water relatively more concentrated in DOC. On the contrary, peat soils are mainly waterlogged across the year (high DOC content), therefore an input of poor DOC water content by groundwater or snowmelt contributes to a dilution of drainage water. Organic-mineral soils provide a high export of DOC in the catchment during snowmelt season. (3) The snow-free season is mostly characterized by base flow punctuated by several high discharge events due to rainstorms. Higher temperature and oxic conditions emphasize DOC production by microorganisms. Hence, higher DOC exports in the catchment during high flow events. This way, discharge and DOC concentration are positively correlated in podzol, and negative in mineral soils.

### 1.2.3 Linking to catchment slope

While hydrology and soil type features are often taking into account in DOC balance, catchment physiography is mostly unconsidered. Indeed slope catchment is unequivocally linked to DOC export. Ferland et *al.,* in 2012 briefly suggested that flat catchments have generally a higher C delivery to streams. This observation can be explained by a greater contact of the top-horizons (C pool) with water as well as a higher organic carbon storage (wetlands). However, these findings are not consistent with our previous hypothesis. In fact, in flat catchments, water goes vertically through the soil that as for effect to emphasize retention processes (adsorption and mineralization). While, in soils located on slopes, transfers occur mostly laterally, that prevents therefore these removal processes. Nonetheless, Ferland observation can be true in saturation condition and when water passes through macropores without being slowed down, which is the case in wetland catchments already waterlogged and likely located in flat topography.

*N.B.: Although autochthounous primary production can supply lake ecosystem, in boreal region terrestrial DOC inputs are considered as more substantial in driving lake metabolism. For this reason, the purpose of this study is not to investigate further on this path.*

## 1.3 DOC cycling in aquatic systems

Once inputs identified, organic carbon cycle implies to consider net losses as well: the aquatic mediated return to the atmosphere, a long term C storage in sediments and transport toward other streams.

### 1.3.1 Internal organic carbon cycling in aquatic systems

Although a general model of thermal cycle highly correlated to seasons in lakes has been admitted, it is nonetheless very variable since the latter is driven by a suite of factors such as lake morphometry, and meteorological conditions (King et *al.,* 1997). Thermal stratification only occurs during winter and summer seasons and its dynamics changes mainly upon lakes depth and morphology. Indeed, this water movement is highly variable and may not occur in shallow lake. In winter, the lake is usually covered by several centimeters of ice and snow that prevents water movement. During snowmelt in spring, water is getting cooler, which leads to a vertical mixing. Summer period is stressed by higher temperatures in the epilimnion compared to hypolimnion layer, the lake is stratified again. As autumn comes, the colder superficial layers drop to the bottom of lake whilst the deep layer less dense goes to the upper part. This seasonal dynamic system is essential to renew oxygen in bottom waters and bring nutrients to the upper parts. Consequently thermal structure variation across the year plays an important role in lake productivity and nutrient cycling.

### *DOC degradation in lakes*

There is now increasing evidence that most of lakes in boreal regions act as net sources of carbon dioxide to the atmosphere (Marchand et *al.,* 2009, Lapierre et *al.,* 2013, Dinsmore et *al.,* 2013). These emissions of $CO_{2,}$ that constitute feedback control, are fuelled and driven by both terrestrially and autochthonous DOC. According to Algesten et *al.,* (2003), between 30 and 80% of the DOC that gets into the lake is lost in it. Amongst these losses, removal processes of DOC from water are due to microbial mineralization, or photolytic process. Depending on the water residence time (WRT) these mechanisms will be more or less efficient. While microbial degradation results in mineralization into carbon dioxide of DOC compounds, photo-oxidation of organic material produces low weight molecular compounds but also mineralizes it into atmospheric gas ($CO_2$, CO).

Respiration process is suggested to account for most of the fluxes that occur in water column, especially in deeper lakes (Ferland et *al.,* 2012, Köhler et *al.,* 2002), Köhler et *al.,* in 2002, suggested that respiration allocates 4,2 to 5,8% of the breakdown of initial TOC concentration. Assuming that terrestrial DOC is recalcitrant to biological degradation, few authors assigned its degradation then as mostly photochemical (Köhler et *al.,* 2002). However, recent studies provided contrary assumptions that the part of biologically degradable DOC remained steady (Algesten et *al.,* 2003, Lapierre et *al.,* 2013).

Differences in DOC degradation values upon studies may result of variations in DOC loading and quality in lakes ecosystems that is likely to be due to the different organic carbon sources or modification along the transfer between soils and water ecosystems (Marchand et *al.,* 2009).

### *DOC burial in lake sediments*

Compared to other processes within the carbon cycle, flocculation of dissolved organic carbon in the sediments has not been as much investigated. The majority of the studies were conducted at regional scales (Ferland et *al.,* 2012) whereas only a minority (Kortelainen et *al.,* 2004) was performed at larger scale (Finland). Despite, this lack of reliable results, authors agree on the fact that smaller lakes have greater long-term permanent carbon burial rates than the largest one. Based on Algesten study, DOC burial is diminished as the surface of the lake increases 5.7, 4.4, 2.3 and 1 g $C.m^{-2}.yr^{-1}$ for <$1km^2$, 1-10, 10-100 and >$10km^2$ respectively. Water residence time has been shown to be closely related to DOC degradation in aquatic systems. A negative correlation has been found between water residence time and DOC concentrations. In fact, the emission rate of $CO_2$ from lakes is up to tenfold more important than stream ecosystems. Although carbon storage rate in lakes is highly variable across the studies, likely due to spatial variations, Ferland et *al.,* in 2012 assessed the areal carbon stock of 23 kg $C.m^{-2}$ in lake sediments. Lake shape and size are the two only factors known to influence greatly this rate, but a lot of uncertainties remain in this domain and need to be better understood.

**Literature overview has provided information about the role and the importance of inland waters as a conduit of organic carbon to the atmosphere. Nonetheless, there still exist multiple discrepancies across the studies. This is mostly due to their interactions in real conditions that cannot be explained by taking them independently.**

## 1.4 Objectives and hypotheses

The overall aim of this study is using data collected at 3 different locations to depict, analyze and therefore understand organic carbon dynamics in a southern boreal catchment in focusing on the role of inland waters. To do so we first feature the seasonal hydrological pattern across our 4 years dataset, they are crucial to identify whether a consistent relationship might exist between them. Likewise, DOC concentrations and fluxes variations are investigated across the season and throughout the year. A comparison of the outlet stream of Kuivajärvi with another outlet from a lake called Vakea-Kotinen lake situated at c.a. 100km at the South-East of Finland will be done.

All along the study we attempt to assess DOC export and transport within the water ecosystems in our catchment. Three hypotheses have to be defined:

(1) Positive correlation between DOC and discharge
(2) DOC dynamics are mostly driven by discharge within the catchment
(3) $[DOC]_{inlet} = [DOC]_{outlet}$ ?

# 2 Material and methods

## 2.1 Study site

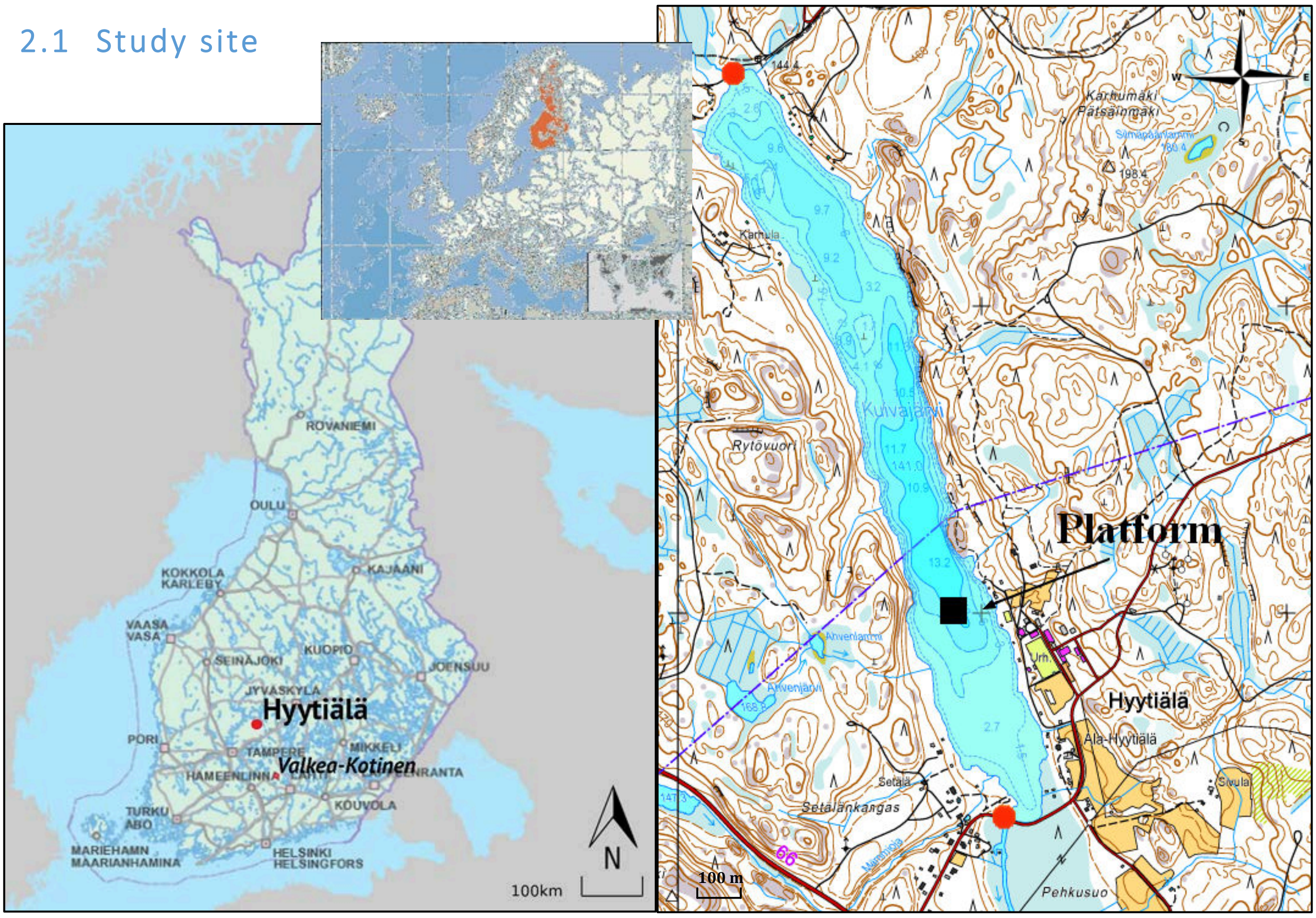


Figure 2: The Kuivajärvi catchment location including the lake, and both inlet and outlet streams at Hyytiälä research station. The map on the right shows red dots identified as the sampling locations at the mouth of the lake, whereas the solid black box within the lake represents the platform location, where the samples are collected at the epi- and the hypolimnion.
Source: National Land survey, *www.paikkatietoikkuna.fi*

This study is performed around the lake Kuivajärvi (Fig.2) and its streams: Saarijärvenpuro (inlet) and Huikonjoki (outlet) that are located in central Finland (N61°50.743', E24°17.134').

The lake Kuivajärvi is situated at ca. 600 m of the Station for Measuring Forest Ecosystem – Atmosphere Relation (SMEAR II) providing necessary wherewithal to set up a thorough study nearby. The mean annual temperature and precipitation calculated over 30 years are 3.5°C and 711mm respectively. With an area of 63.8 ha in surface, the lake measures ca. 2.6 km in length and its maximum depth is ca. 13m (unpublished Miettinen et *al.*, unpublished). The vicinity of lake Kuivajärvi is mostly flat but the elevation of the site can vary up to 40m. Besides its black and dark color the lake belongs to mesotrophic state: its productivity rate reaches 13.4mg.L$^{-1}$ of DOC in average for the 2010-2013 period. The inlet at the North of Kuivajärvi, called Saarijärvenpuro is situated downstream of the lake Saarijärvi and has a length of ca. 250m. The latter drains mostly wetlands (haplic podzols) and histosols (Dinsmore et *al.*, 2013) above managed forests. So far, the

outlet stream called Huikonjoki has never been the subject of any study, some parameters such as the soil type of the riparian zone remains thereby unknown.
The approximate size of the catchment is 1200 ha and consists mostly of managed pine forests, although some peatlands and agricultural lands are also present as well as haplic podzol covering the igneous and metamorphic bedrock.

## 2.2 Sampling and measurements

Samplings started in 2010 and ended up in 2013. Yet some gaps in our results will be pointed out due to several reasons (material issues for instance).

### 2.2.1 Precipitation & discharge measurements

Precipitation was monitored from 2010 until 2013 on a half hourly interval basis by the SMEAR-II station. Tretyakov rain gauge with windshield was used to collect precipitation at 20m above the canopy. The water was then stocked into aluminum covered bottles. At wintertime, 7 snow collectors devices (20cm diameter) were required to stock snowfall. The meltwater was then weighted in order to obtain the snow water content (Finnish Meteorological Institute).

Discharge parameter was performed at the mouth of the inlet (side of an access road) and the outlet (under a small bridge), the locations are visible in figure 2. The measurements were realized ($m^3.s^{-1}$) with a FlowTracker device as the volume of water flowing through the river per unit of time. The stream cross section was divided into subsections of 20cm each. From there, the area was calculated with water level information measured with an automatic Barologger device every 30min, and width measurement by using a FlowTracker device. The latter provided discharge measurements based on acoustic information, allowing to generate a discharge curve, or hydrograph (discharge versus time). For both inlet and outlet the procedure was the same and performed every 30 minutes, except at some periods mostly due to several material issues (30/01 until 29/03/10, 10/02 until 04/04/11 and 15/08 until 05/09/13).
*N.B.: Discharge data from Valkea-Kotinen outlet stream were obtained continuously from 2010 until 2013*

### 2.2.2 DOC measurements

The measurements were carried out for 4 years, from 2010 until 2013. From May 2010 until the end of 2013, the samples were taken weekly during the open water period, and once a fortnight during ice-cover period. Samplings were performed on a platform in the middle of the lake (Fig.2 and Annex 2) at 2 depths: (1) 5cm underwater at the top of the water column and (2) above 12cm at the bottom of lake ensuring that sediment was not disturb. In the case of streams, the sampling locations were the same as for discharge measurements.

Water samples were filtered through a 0.45$\mu$m cellulose filter on the same day and then frozen at -18°C prior to any measurement during 1 year. A second filtration was realized, after the samples were thawed, at 0.45$\mu$m in order to get rid of the remaining particulate organic matter (POC). DOC concentrations were then measured by using a Total Organic Carbon Analyzer (TOC-$V_{CPH}$, Shimadzu®). Three calibration standards were added as well: Total Carbon, Inorganic Carbon and Total Nitrogen calibration standards at 100, 10 and 10$mg.L^{-1}$ respectively. The dosage was determined by combustion catalytic oxidation. By this method, the liquid samples are heated at 680°C and burnt in presence of oxygen. As a result, carbon dioxide is generated by oxidation. DOC concentration is then deduced by subtracting total carbon concentrations and inorganic carbon concentrations.

### 2.2.3 Other parameters

Three parameters have been recorded for 4 years, with nonetheless some interruptions in measurements depending on the considered parameter.

*Air temperature (°C)* was measured every half an hour from 2010 until 2013 yet with a gap in the database of several months (from 01/08/11 until 31/12/11). The measurements were performed at 16m of height.

*Gross Primary Production (µmol.m$^{-2}$.s$^{-1}$).* This term refers to the notion of primary production, and is described as the amount of energy generated by primary producers in a given time. It was obtained indirectly via net production in a catchment with the relation Net primary production = Gross Primary Production – Respiration, and was conducted every 30 min from 2010 until 2012 (gap from 01/08/11 until 31/12/11).

*Evapotranspiration* is known as the sum of transpiration of the canopy and the evaporation from the surfaces. Those latter depend on temperature, solar radiation, soil moisture and vapour pressure deficit. In this study, we used eddy covariance method as a direct measurement to assess evapotranspiration from the ecosystem. Following which we measured wind fluctuation (sonic anemometer) and water vapour density (hygrometer). The eddy covariance fluxes were computed from measured covariance between wind velocity and vapour density in order to obtain a 30min interval basis database recorded from 2010 until 2012.

*Flux calculations* Concentrations of DOC (mg.L$^{-1}$) were multiplied by the discharge (L.s$^{-1}$) of the streams to assess the load (mg.s$^{-1}$) on a daily basis. Load was then divided by catchment area (ha) to obtain finally fluxes in kg.ha$^{-1}$.yr$^{-1}$.

*Water residence time* (yr) was computed as the mean annual discharge divided by the volume of the lake (m$^{3}$).

# 3 Results

## 3.1 Hydrology and climate

The yearly precipitation and temperature over the study period (2010-2013) were 720mm and 4.2°C in average (Annex 1). A variation occurs across the years, 2010 was the driest with only 600mm of rain recorded as well as the warmest with a mean annual temperature of 2.8°C. At the opposite 2012 turned out to be the wettest, with an annual precipitation average of 906mm, whereas the amount of rainfall in 2011 and 2013 ranged between 752 and 621mm respectively. Likewise, years differed considerably in discharge ranges. In 2010 and 2013, the discharge was at its lowest with values barely higher than 0.10m$^{3}$.s$^{-1}$ in the inlet, and 0.20 m$^{3}$.s$^{-1}$ in the outlet. On the contrary, 2012 had the greatest discharge over the 4 years study within the inlet (0.17m$^{3}$.s$^{-1}$) and the outlet (0.44m$^{3}$.s$^{-1}$) brooks. The outlet stream discharge is across the year between 1 and 3.3 times above the discharge of the inlet stream.

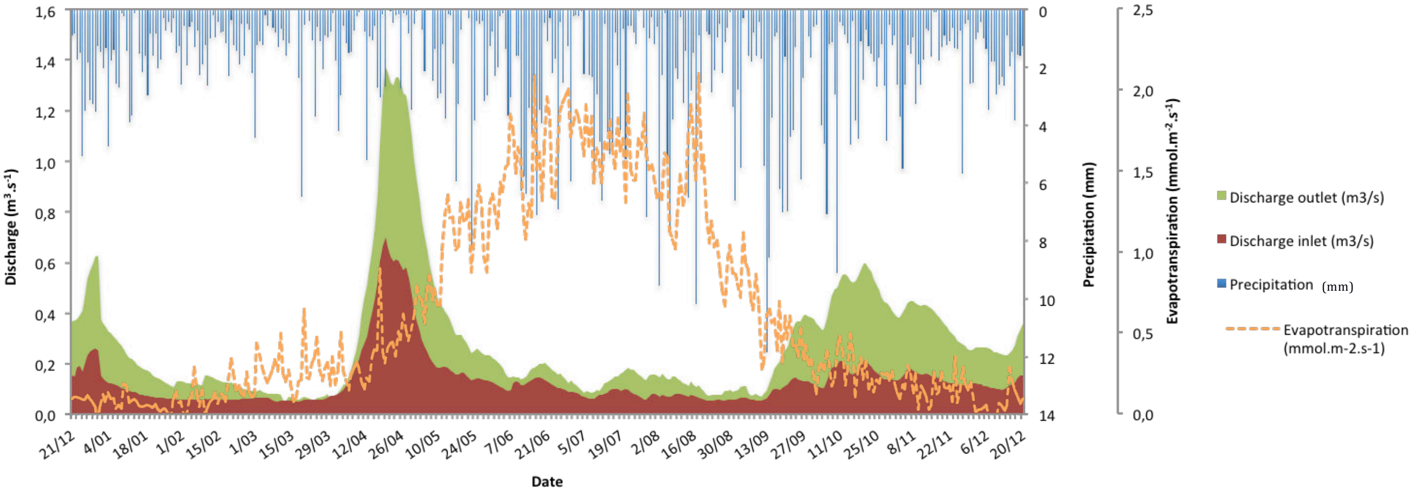


**Figure 3: Hydrograph from inlet and outlet streams and daily evapotranspiration (dashed line) average rate for 4 years (2010-2013) in the Kuivajärvi catchment**

The mean annual hydrograph of 4 consecutive years is given in figure 1 as well as the dispersion/deviation across the years (Fig. 3). The highest precipitation values were recorded in Autumn, (387.02mm in September), whereas the minimum occurred at wintertime (137.75mm in February). These high rainfall events do not fit with high flow events, since two main peaks of discharge are identified in April and October (1.37 and 0.63m$^{3}$.s$^{-1}$). Although, there is no obvious relationship between streams discharge and precipitation across the year (R<0, P=0.00 and $\varrho_{\text{inlet}}=0.17$, $\varrho_{\text{outlet}}=0.01$), to attempt to establish connections between these two parameters, we consider seasonal patterns.

- *Wintertime* is characterized by negative temperature values and can even reach -13°C on 23rd December. From February more than 50% of precipitation fell as snow. Consequently, the discharge within the streams is quite steady and reaches the base flow, the values ranged from 0.09 to 0.06 $m^3.s^{-1}$ in the inlet, and from 0.22 to $0.07m^3.s^{-1}$ in the outlet. Despite rather strong correlation coefficients ($\varrho_{\text{inlet\&outlet}}=0.37$), probably due to the consideration of the early winter period without snow cover, figures 3-4 provide evidences that discharge responses to precipitation events are inexistent.

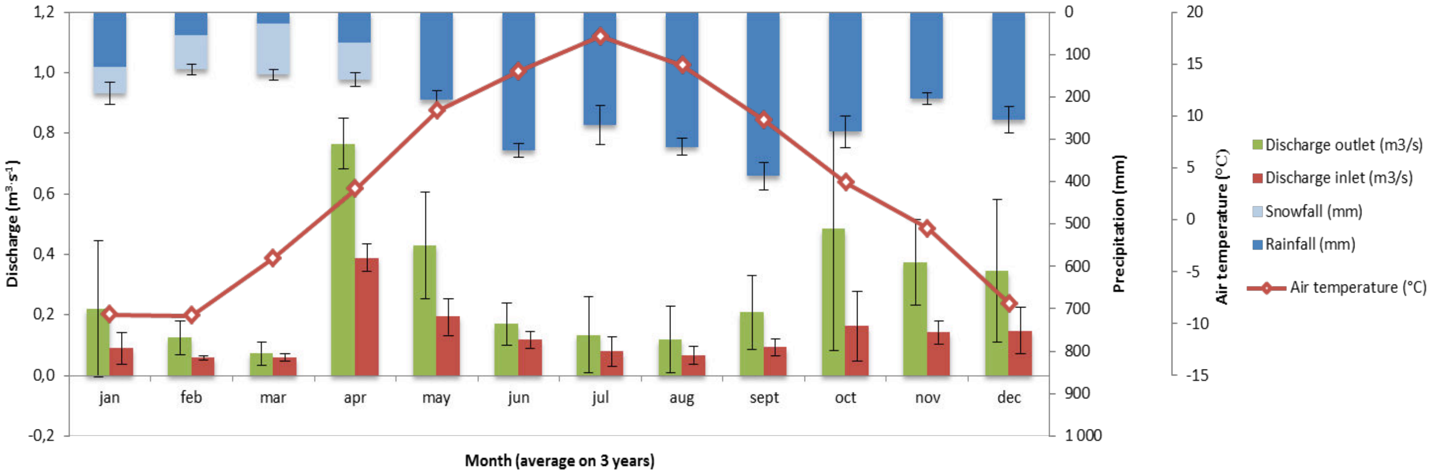


**Figure 4: Time series of the inlet and outlet brooks (monthly average) discharge assessed from 2010 until 2013 in the Kuivajärvi catchment.**

- In boreal landscapes, *Spring* season is especially stressed by a major snowmelt event that occurs in mid-April. The plot (b) in figure 5 depicts the snowmelt event day by day, and its consequences on streams discharge variations. When temperatures reach the 0°C threshold, discharge starts to increase abruptly, fuelled by snowmelt. Laudon et *al.*, 2007 and more recently Dinsmore et *al.*, 2013 denoted this period as the *rising limb*. In the following fortnight approximately discharge rises of 0.62 and 1.30 $m^3.s^{-1}$ in the inlet and outlet respectively. Discharge reaches a peak on the 20th of April (inlet=0.71 $m^3.s^{-1}$, outlet=$1.37m^3.s^{-1}$), this period is called *peak flood* (Fig. 5, Spring plot). The *falling limb* witnesses then a significant downtrend, until attains, 0.17 and $0.31m^3.s^{-1}$ the 19th of May in the inlet and outlet. Spring snowmelt is the main hydrological event in boreal landscapes and accounts for 38 to 42% of annual discharge in Huikonjoki and Saarijärvenpuro brooks. Negative Spearman correlation values ($\varrho_{\text{inlet}}=0.06$, $\varrho_{\text{outlet}}=-0.10$) sustain the idea that discharge and precipitation parameters are independent from each other.
- Although *Summer* season is dominated by high amounts of rainfall (1/3 of annual precipitation), the temperature is also greater (15.2°C in average). As a result, the evapotranspiration reached its maximum rates (c.a. $1.5mmol.m^{-2}.s^{-1}$). These results are consistent with an overall decrease of discharge values, which attain base flow state one more time. Yet considering a smaller time scale (Fig. 5) hydrographs indicate a good respond ($\varrho_{\text{inlet}}=0.06$, $\varrho_{\text{outlet}}=0.10$) of streams to rainfall event. Though the poor frequency of our samplings (daily scale) prevents accurate assessments of time lag, figure 5 displays flow response peaks from 1 to 2 days after storm event.
- *Autumn* season is stressed by a similar response pattern following precipitation events as in Summer time ($\varrho_{\text{inlet}}=0.08$, $\varrho_{\text{outlet}}=0.08$), even though discharge values are far greater owing to lower temperatures (-0.7°C in average). Besides, standard deviation (Fig. 4) displays a wide range of discharge dispersion values across the years ($\sigma_{\text{inlet}}\pm0.12$, $\sigma_{\text{ioutlet}}\pm0.40$ in October).

Although there is no clear and tangible statistical evidence of their relationship, it appeared to be a link between discharge and precipitation.

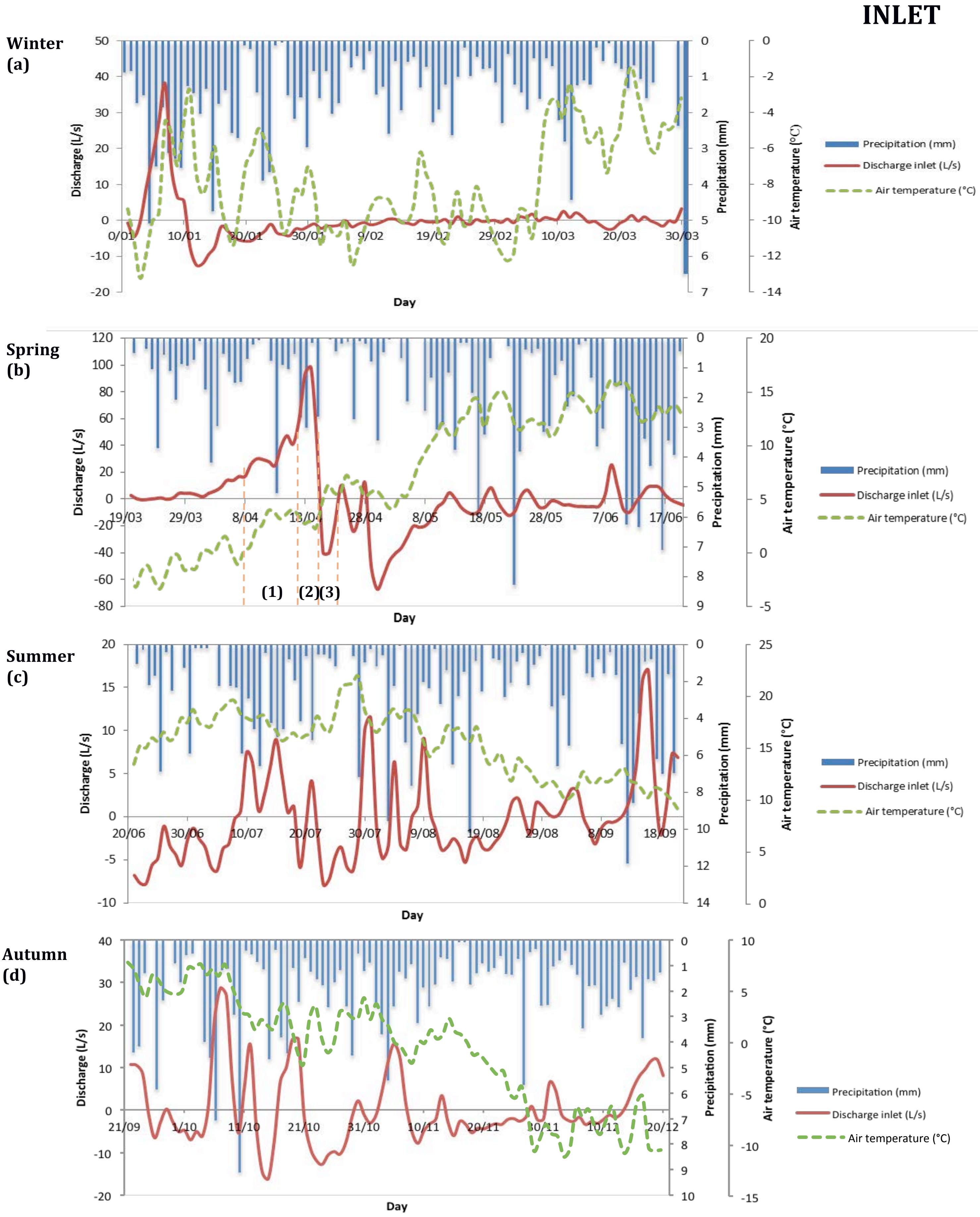


Figure 5: Seasonal variations of precipitation, discharge (discharge from one day subtracted by the discharge of the previous day) and air temperatures (dashed line) of the inlet stream. Only the inlet is represented due to similar pattern with the outlet. Numbers are identified as: (1) rising limb, (2) peak flood, (3) falling limb.

## 3.2 DOC concentrations variations

Although a difference in concentrations of DOC would be expected between lotic and lentic ecosystems, there is no clear distinction between them two. The concentrations ranged from 8.48 to 19.76 mg/L in streams and between 11.44 and 16.47mg/L in the lake regardless of depth (Fig. 6). Brooks water appeared to be slightly more sensitive to DOC concentration variations than lake water (CV=0.17 and CV=0.10 respectively) throughout the year, as we can see in spring, when DOC concentrations markedly rise in streams compared to the lake where the water remains quite steady.

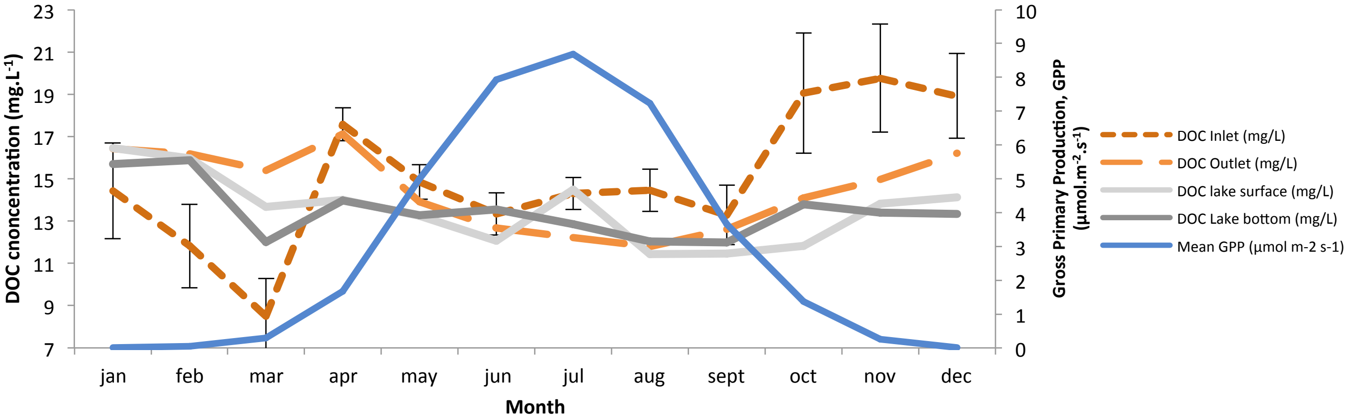


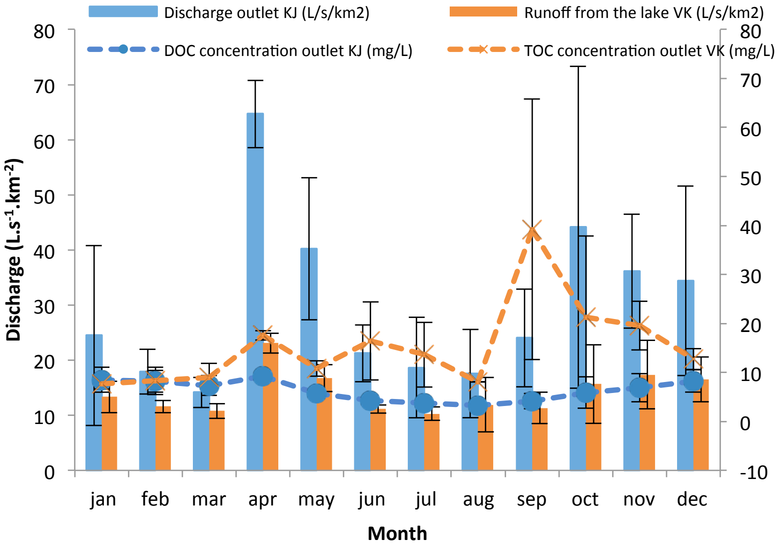
**Figure 6: Seasonal variations in DOC concentrations (mg/L) at different locations: in the lake water (epi- and hypolimnion), in the inlet and outlet streams. The average gross primary production is also visible.**

DOC concentrations are the highest in 2012 and the lowest in 2013, with values of 15.93mg/L and 13.12mg/L respectively, then 2010 and 2011 were equivalent with 13.99mg/L. Based on figure 6, similarly to hydrological parameters, DOC concentrations underwent also seasonal changes. DOC concentration pattern at wintertime is stressed by a steady state (c.a. 16mg/L) followed by an overall depletion from February until March. The major decrease reaches 8.48mg/L within the inlet, whereas the lake bottom, lake surface and outlet slightly drop to 12.02, 13.68 and 15.4mg/L respectively. Although DOC concentrations are substantially higher across the year in the inlet than in the outlet (at the maximum 1.2 times higher), snow-cover season is stressed by lower values within the inlet stream (Fig.6). Moreover, there is no clear evidence of water column stratification in this lake, even though winter season shows a relative stability of the water column, the concentrations indicate a gradual enrichment. At spring season, despite the inlet undergoes high variations in DOC concentrations by peaking at 17.58mg/L, lake and streams are subjected to a slight increase of 1.34mg/L in average. Regardless of the lentic ecosystem, DOC concentrations rise in both inlet and outlet during the rising period and drop before discharge is back to normal condition. The overall concentrations remain relatively low in summer and the values do not exceed 15mg/L. The epilimnion layer within Kuivajärvi lake is characterized by a rise in July, concomitantly with a higher rate (8.68$\mu$mol.m$^{-2}$.s$^{-1}$) of Gross Primary Production. DOC concentrations increase in autumn, particularly in November with values as 19.76 within the inlet.

## 3.3 DOC-discharge relationship comparison between Valkea-Kotinen and Kuivajärvi outlets

Comparisons were made between Kuivajärvi and Valkea-Kotinen boreal catchments in Southern Finland (Annex 1, Fig. 2). Same method was used to assess DOC and discharge values, except that discharge measurements were conducted on a V-notch weir. Although the streams involved are both outlet brooks from a lake, it emerges that the Valkea-Kotinen catchment is constituted by a smaller and shallower lake (30ha, 6.5m) than Kuivajärvi (64ha, 14m). Furthermore, Valkea-Kotinen (VK) lake is also a wind exposed place whereas Kuivajärvi (KJ) is at the opposite, quite protected from the wind. Discharge values in VK outlet ranged from 1.59 to 15.98 L.s$^{-1}$.km$^{-2}$ and from 3.33 to 39.64 L.s$^{-1}$.km$^{-2}$ in KJ outlet.

Assuming that total organic carbon (TOC) is composed of 95% of DOC (Köhler et *al.*, 2002, Haei et *al.*, 2010, Algesten et *al.*, 2003, Laudon et *al.*, 2003), it is therefore consistent to compare DOC and TOC concentrations of the catchments. Organic carbon concentrations in VK outlet were in overall 1.5 times higher than KJ outlet. Despite a relative similar trend between discharges of both outlets, DOC concentrations patterns reveal to be different. DOC concentrations rose during snowmelt (April) in both catchments, in VK outlet stream they also tended to build up during Summer (June), while we previously saw that they decreased in KJ outlet at this very period. Concentrations were significantly greater in VK outlet in September (41.56 mg/L) compared to KJ inlet at the same period (12.60 mg/L). In fact, the peak unfolds one month later in KJ catchment. A general strong increase of DOC concentrations appears in VK outlet during September (41.56 mg/L), whereas a slighter peak happens later in October in KJ lake.



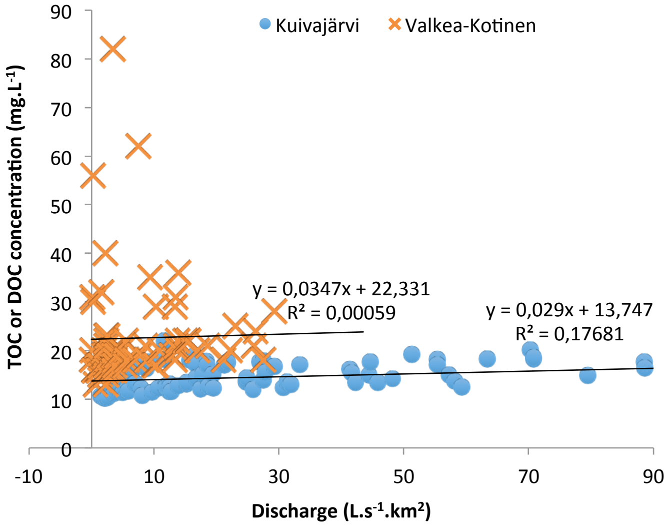


Figure 7: Comparisons of average DOC concentrations ($mg.L^{-1}$) and discharge ($L.s^{-1}.km^{-2}$) in Kuivajärvi and Valkea-Kotinen catchments.

Figure 8: Relationship between Kuivajärvi and Valkea-Kotinen outlet streams discharge and DOC concentrations

According to the linear regression (Fig. 8) Kuivajärvi outlet indicates although weak, a stronger positive correlation (P=0.07, R=0.400) between concentrations of organic carbon and discharge than VK (P=0.00, R=0.060). Punctual low discharge rates appear to show really high DOC concentrations in VK outlet (Fig. 7). Based on Kuivajärvi precipitation data, the catchments were subjected to a long dry period from 22/09/10 until 23/10/10. A storm event occurred then on the 24th when the daily rainfall reached 5.30mm. Consecutively to this substantial rainfall event, DOC concentrations peaked, as a result, to 56mg/L (not shown in this study).

## 3.4 DOC fluxes variations

Fluxes ($kg.ha^{-1}.yr^{-1}$) within streams were calculated using discharge data (L/s), DOC concentrations (mg/L) and catchment area (ha). In our study, DOC export values ranged between 32.07 $kg.ha^{-1}.yr^{-1}$ in summer and 273.04 $kg.ha^{-1}.yr^{-1}$ in spring within the inlet and the outlet respectively. DOC fluxes within the brooks display in average: 48% of annual export at spring season, 27% in autumn (discharge constituted mainly by storm events) against only 10% in summer (Fig. 9).

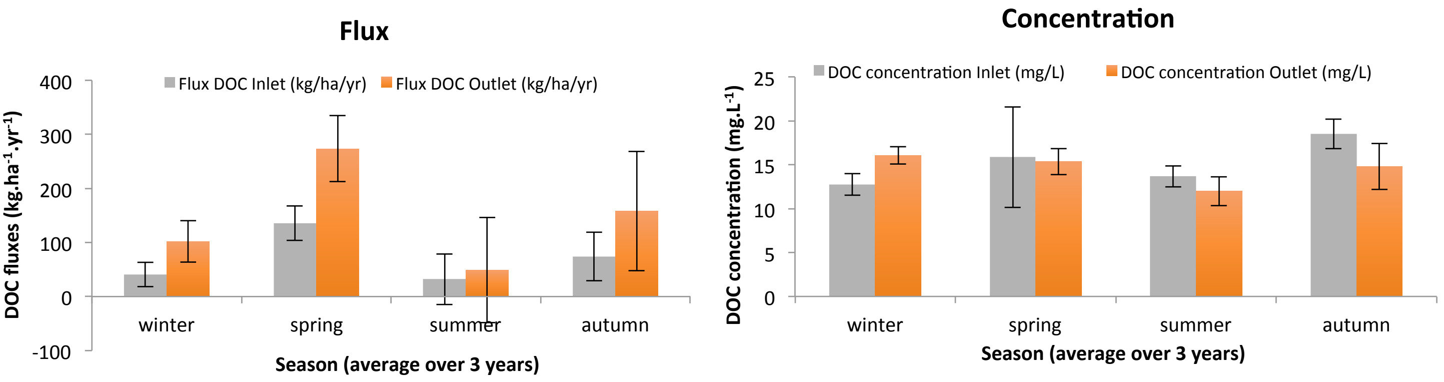


Figure 9: Seasonal average variations of fluxes in $kg.ha^{-1}.yr^{-1}$ (left) and concentrations in $mg.L^{-1}$ (right) of DOC in inlet and outlet streams

In the line with previous observations, DOC concentrations tend to be lower within the outlet stream, which can be related to a higher DOC export. However, one discrepancy in winter appears to show higher organic carbon concentrations in outlet stream without showing any substantial impact on DOC fluxes. Plotting the percent of total DOC export against the flow duration provides a way of assessing the relative impact of different flow sectors on DOC export (Fig.10). It displays that around 56% of DOC fluxes occur in the highest 10% of discharge in both input and output streams.

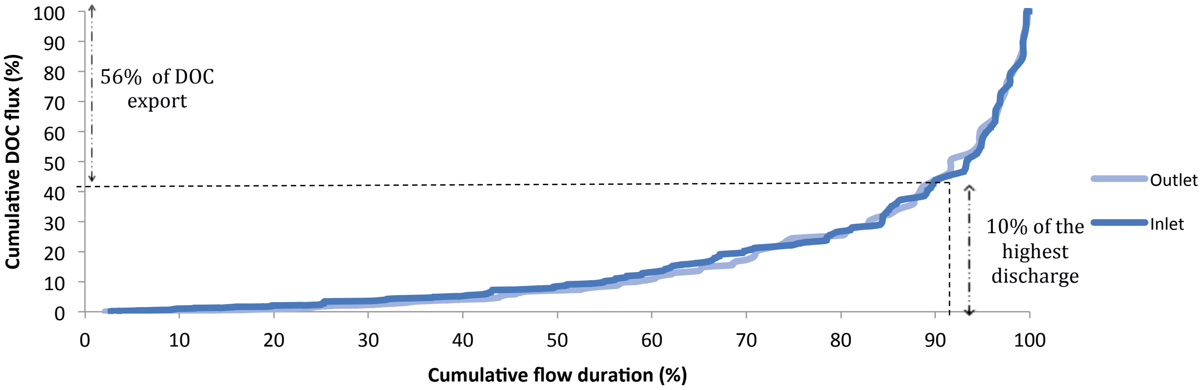


Figure 10: Relationship between flow duration and DOC export from 2010 until 2013 in inlet and outlet streams (after Hinton et *al.*,1997 and Clark et *al.*,2007)

# 4 Discussion

We performed in this study a traditional black box approach as described in Gergel et *al.,* in 1998 in which we consider the whole catchment inputs and outputs of the lake. The tributaries of Kuivajärvi lake have average annual DOC exports and discharge rates of 8.7 g C m$^{-2}$.yr$^{-1}$ and 349.0 mm.yr$^{-1}$ respectively for the inlet and from 17.4 g C m$^{-2}$.yr$^{-1}$ and 784.4 mm yr$^{-1}$ in the outlet respectively. Whereas Agren et *al.*, in 2007 conducted a study in Sweden on 13 forested and wetland catchments and found DOC fluxes ranged between 1.4 and 9.9 g C m$^{-2}$.yr$^{-1}$ and discharge values from 271 to 326 mm.yr$^{-1}$. Our DOC fluxes results are therefore 1.5 to 3.0 fold more important than Agren results, these higher values might be the result of higher streams discharge in our work. However, Valkea-Kotinen catchment characterized by lower discharge rates, showed higher annual DOC concentrations in the outlet (22.5 mg.L$^{-1}$) compared to Kuivajärvi. Another hypothesis would suggest to consider the catchment and lake areas (Annex 1), they are in average 18 to 40 fold respectively higher than Kuivajärvi catchment. Multiple studies, as Agren et *al.,* 2007, Gergel et *al.,* 1999 showed the negative relationship between the size of the catchment area and the DOC concentrations in the streams that could explain the higher DOC concentrations in the Valkea-Kotinen catchment. This is nonetheless a contradictory result with the idea that DOC would be attended to decline with longer water residence times as a result of low discharge values in Valkea-Kotinen lake. However, studies (Miettinen et *al.,* unpublished, Peltoma and Ojala, 2011 for instance) explained that Valkea-Kotinen lake is wind-sheltered on the contrary of Kuivajärvi lake exposed to the wind. This results to a higher DOC production by photosynthetic organisms in Valkea-Kotinen lake system and as a consequence higher DOC concentrations. Kortelainen et *al.,* in 1997 reported a range from 2.6 to 8.8 g.m$^{-2}$.yr$^{-1}$ in Finland, which is therefore more similar to what we saw.

Moreover, our results show more substantial DOC export within the outlet. That indication would suggest that Kuivajärvi lake is a net source of DOC (autoDOC production), However, our data do not provide annual DOC emission from the lake itself, Indeed, this relative higher organic carbon export from the outlet can be conjectured as an input of DOC brought by numerous small streams joining the lake and/or by the major importance of wetlands in term of soil Carbon storage that would explain the greater export in the outlet.

On the contrary of what we expected, DOC concentrations in streams are akin to what we saw in the lake. DOC would have been expected to be quite stable seasonally, compared to fluxes of DOC in streams. In fact, water residence time is crucial in determining DOC fluxes, owing to the rate of DOC degradation. The water spends in average 267 days in the lake Kuivajärvi before flowing out, resulting in higher rates of degradation (heterotrophic organisms, photolysis). But our observations do not give any evidence of a greater degradation in lentic than lotic ecosystems, since DOC concentrations are roughly similar. Even though we only know the role of rivers as a collector and driver of DOC from land to lakes, streams participate nonetheless to DOC export to the atmosphere and several processes such as sorption onto streambed occurred as well as DOC production.

## 4.1 Snow free season

This period stressed by the absence of snow/ice is the longest and lasts c.a. 5-6months and shows only 10 to 27% of annual export in the summer and autumn seasons respectively. Our results display different patterns between summer and autumn seasons.

Summer season is featured by a poor relationship between discharge and precipitation (r=0.063 and 0.103 inlet and outlet, P=0): with discharge rates at their lowest (15% and 11% of the annual discharge of inlet and outlet respectively) whereas the precipitation amount is substantial (34% of annual precipitation). Hence, most of the stream discharge is likely to be sustained by the groundwater table. In fact, though these results appear as contradictory the high temperatures displayed in summer favour the increase of evapotranspiration rates and therefore counteract incoming water to penetrate the soil/generate a flow. Furthermore, regardless of spatial variations within the catchment, DOC concentrations remain at a steady state at summer period and only 10±2% of DOC export occurs in streams at this time. While DOC concentration is stable in streams and the bottom layer of the lake, the epilimnion indicates a sudden increase of DOC concentrations at mid-Summer (July) in the same time that GPP peaked. The increase of photosynthesis activity and therefore of DOC concentrations within the epilimnion layer at summertime occur as a result of high temperatures and solar radiation rates. In terrestrial area for the same reason, the primary production rises then at this time promoting allochthonous DOC production within the superficial layers of the soil subjected to temperature and solar radiation variation. Thus, both sources of DOC increase. However, the autochthonous organic carbon compounds are extremely labile and although our results do not provide strong evidence about their breakdown, a previous study conducted in the same lake (Miettinen et *al.,* unpublished) showed a rise of $CO_2$ emissions at this period. In fact, this DOC is easily degraded by heterotrophic organisms and photodegradation (<1% Hudson et *al.,* 2003), it is thereby mineralized into $CO_2$ gas, and appear therefore on the plot as a drop of organic carbon concentrations. Despite a relative constancy, a small but notable decrease of DOC concentration occurs also in the bottom of the lake, related to the summer stratification within the water column impeding water connection between epi and hypolimnion. Miettinen et *al.,* (unpublished) provides the evidence showing that the absence of mixing column water tends to generate hypoxia near the bottom sediment and therefore favor anaerobic DOC degradation processes.

As the autumn season comes, DOC concentrations increase as well as DOC fluxes that represent 27% of annual export in both inlet and outlet streams regardless the spatial variations, this is consistent with both temperature (16°C to 0°C in average in summer and autumn respectively) and evapotranspiration rates (1.4 and 0.2 mmol $m^{-2}s^{-1}$ in average in summer and autumn respectively) that decrease after the summer. Hydrographs indicated as a consequence good relative responses of stream discharge following precipitation events (ϱ=0.08, P=0.00). These observations are in line with several papers that displayed high DOC export in autumn (Pumpanen et *al.,*2013, Mullolhand and Hill, 1997, Olsson et *al.,* 2009, Hudson et *al.,* 2003, Laudon et *al.,* 2003). We can suppose that the elevation of soil moisture has for effect to restore a proper flow path within the soil profile and as a consequence to flush-out DOC pool, previously stored during summer, from land to water ecosystems. Freeman et *al.,* 2002 went further suggesting that significant temperatures are likely to increase DOC stocked within soil profile during the previous dry season, and then be mobilized and flushed down to aquatic systems as a result of substantial storm events in Autumn. It is emphasized in peatlands where the superficial layer is air-exposed and SOM is oxidized to produce DOC.

This is consistent with Valkea-Kotinen outliers identified at low discharge and high DOC concentrations in scatter-plots (Fig.7 and 8). Those values are likely to occur after a long dry period, when DOC is mobilized with substantial precipitation.

Although the ratio organic/organomineral soils is unknown in our study and owing to the fact that DOC concentrations are higher in the inlet compared to the outlet, the analogy with other catchments submitted in multiple studies roughly assesses that outlet stream would be more concentrated in wetlands than the inlet brook. DOC export from land to water ecosystems depends mostly on hydrological pathway, therefore organic and organo-mineral soils (both constituting the Kuivajärvi catchment) appear to vary by their different properties, and profiles. Indeed, histosols are composed of one thick organic layer (c.a. 0.5-1m) and a very poor mineral content, whereas spodosols are constituted by a thin organic layer (c.a. 5-10cm), in which DOC is usually well-drained facilitating water percolation throughout the soil. However, DOC compounds may be as a result adsorbed onto mineral surfaces, precipitated in B horizons or simply utilized by plants as they are transported through the soil by water, and therefore limit DOC export to aquatic systems. These processes are rather small in peatlands where the poor mineral content does not impede, or only at a small proportion, DOC movement. Our supposition is in agreement with several studies that suggest a substantial export of organic compounds in organic soil types compared to spodosols (Hinton et *al.,* 1997, Pumpanen et *al.,* 2013, Laudon et *al.,* 2004).

## 4.2 Snow cover season

In consequence of low temperatures (<0°C) the lake is mostly frozen at this period and the majority of precipitation falls as snow. However, due to more powerful hydrodynamics, streams are still in activity, even though the discharge is at base flow and mostly fed by groundwater. The poor correlation coefficients ($\varrho$=0.370 in average in both streams) stress the idea that the impact of precipitation on discharge is rather without any effect. Ice cover on the lacustrine ecosystem blocks inputs into the lake, there is therefore no supply of oxygen, light and DOC implying low and stable DOC level at first (Jan-Feb). In a second time, DOC concentrations start to drop from February, of 1.23 fold on average. Several reasons can explain this: (1) decrease of oxygen leads to decrease in decomposition and/or (2) other anaerobic processes that degrade also DOC into water column. This supposition is consistent with Miettinen (unpublished) study that exhibits a $CO_2$ and $CH_4$ increase generated by the latter processes into the lake column in winter.

Snow-cover season is associated with highest concentrations in the outlet, whereas during the rest of the year, organic carbon concentrations remain higher in the inlet stream. The first possible explanation to this observation is given by the hypothesis that stream DOC concentrations is negatively correlated to slope. Indeed, topography, hydrology and soil type also play a role on DOC concentrations. Thus wetlands are more likely located in low relief areas with rather small hydrological conductivity and discharge rates. In our outlet stream it would result to a greater contact between soil water and organic-rich soils enabling DOC concentrations increase as well as DOC fluxes in water stream (Agren et *al*., 2010, Ferland et *al*., 2012). This remark implies to consider the outlet as a stream draining riparian zone mainly composed of wetlands. A second possible explanation that stressed our suppositions is related to snow/ice cover layer. In fact, as I mentioned above, stream water mostly fed by groundwater in winter remains as a result at base-flow condition, and the water circulation is rather low within the soil profile. The snow cover and the frozen soil prevent water to percolate in upper horizons and therefore stream water mainly drains the deepest layers within the soil profile. The resulting, the deepest horizons of the histosols, highly concentrated in organic carbon, are the source of DOC drained/brought in the outlet stream. Inversely, in inlet stream surrounded mostly by forest stands, where spodosols make up the majority, the deepest horizons are very poor in organic-carbon and are assumed to be the origin of a DOC-poor water source for the inland ecosystems. However, the soils in Hyytiälä stations are never totally frozen during the winter, due to the efficient insulation of snow cover.

Although streams show low relative DOC fluxes, it is still important to consider them since they account for up to 15% of annual DOC export and their role is more substantial in the autumn and in the spring than in the summer. This is especially true within the outlet stream (18%) showing more substantial fluxes than the inlet (14%). This indication is in line with our findings implying that DOC production and DOC transport from land to water systems still exist in the nearshore area in particular, where soils are always in contact with water. Wetlands are thereby a crucial factor of DOC concentration in winter season.

## 4.3 Snowmelt season

Once the temperature exceeds the threshold of 0°C, snow starts to melt and an increase in discharge occurs consecutively to this event. Snowmelt is the major hydrological event in boreal landscapes since it accounts for 38 to 42% of annual discharge in Huikonjoki and Saarijärvenpuro streams respectively. Our results displayed at this period, a marked increase of annual DOC concentration and export, in fact 48% of annual DOC export occurs at spring period, although it lasts only 1-2 months. The figure 10 provided the evidence that 60% of DOC was exported during the 10% of highest flow in the streams, and as a result mostly happened during spring season.

Although it is now accepted that wetlands are a major source of DOC during the all year and realized higher exports, discrepancies remain amongst studies concerning the positive or negative relationship between DOC and discharge during snowmelt season. The flushing-effect due to spring snowmelt has been reported to cause the dilution of DOC concentrations in some streams and lake (e.g. Agren et *al.,* 2010, Clark et *al.,* 2007, Hudson et *al.,* 2003). Other authors have found on the contrary an overall increase of DOC concentrations with discharge (e.g. Hope et *al.,* 1994). A general idea connected to the distinction of soil type as in open-water period between organo-mineral soils and wetlands has been suggested since then (Agren et *al.,* 2010, 2008 for instance). **(1)** Indeed, in organo-mineral soils (forested areas), spring snowmelt that provides a significant discharge level, is associated with a rising water table and a shift in the main runoff pathway from the low mineral layers where DOC is adsorbed to the upper organic layer where DOC is mainly produced. On consequence, as Laudon et *al.,* 2004 suggested water runs off by lateral flow without undergoing any degradation/storage process within the soil profile, this observation is underpinned by the finding that water from snowmelt does not impact soil horizons deeper than 90cm, likely due to lower hydraulic conductivity in deeper horizons, limiting as a result the adsorption and degradation processes (all the flow occurs in the upper parts of the soil). Higher discharge level is also likely to connect and activate DOC pools, previously blocked into the soil during base-flow. Furthermore, using isotopic and hydrometric measurements conducted on forested and peatland catchments, Laudon et *al.,* in 2007 pointed out the importance of flow pathway within the soil and further explain the dilution effect. In forested catchments, the event water from snowmelt infiltrates the soil and tends to push the pre-event water (old water previously stored before precipitation event) out ending up in streams. **(2)** On the contrary, although histosols are an important source of DOC and provide high amounts of DOC during baseflow, spring flood might be the cause of a dilution of DOC. Laudon et *al.,* in 2007 showed that streams draining wetland catchments display a low contribution of prevent water during spring season suggesting therefore that snowmelt water, poor in DOC, is likely to directly feed aquatic ecosystems without percolating within the soil profile. This hortonian flood that runs off at the soils surface is explained firstly by the low hydraulic conductivity of soils horizons, and secondly by the fact that those soils are already saturated before the spring. Laudon et *al.,* in 2004 provided more information by bringing out that during the early part of the snowmelt period, infiltration/flow is limited in depth by frozen layer and suggested that snowmelt does not affect soil horizons deeper than 90cm, argue in favour of overland poor-DOC flow at the soil subsurface when the soil is saturated.

According to the findings described above, the outlet stream drains mostly organic soils, compared to the inlet riparian zone constituted mostly by an organo-mineral land that may constitute the largest contributor of DOC at springtime. The positive correlation between discharge and DOC concentrations found in Kuivajärvi catchment means that in overall, it is mostly composed of organo-mineral soils However, this positive relationship is rather poor and can be interpreted with 3 aspects: (1) the catchment is composed of both wetlands and forested catchment. Forested areas remain the major DOC contribution to stream water even though wetlands would constitute a non negligent coverage proportion, (2) a part of the amount of DOC is previously flushed-out with previous autumn precipitations events, (3) DOC stock still partly frozen and as a consequence non-mobilizable. Moreover, our results at spring period stress our previous hypotheses suggesting that the inlet (located in a slope/hill) is mainly composed of organo-mineral soils and as a consequence DOC concentrations markedly increase as discharge rise. Whereas, at the exception of winter period, the outlet stream shows relative low DOC across the year, but more important DOC fluxes all along the year, stressing that outlet might mainly be surrounded by organic soils (histosols).

## 4.4 Uncertainties

This study is a preliminary investigation of the dissolved organic carbon cycle in a boreal catchment, and as a consequence does not involve detailed analyses in overall. Strong uncertainties have first notably been reported by Clark et *al.,* 2007 concerning low frequency monitoring of DOC and discharge measurements. Fortnightly to weekly monitoring appeared to miss an important degree of variance in DOC concentrations especially during storm events, at spring and summer time, when numbers of consecutive high and low flow conditions occur, for instance. Furthermore, snow cover season is a period of low sampling frequency for DOC as well as discharge parameters, we therefore chose most of the time to realize the average of our 4 years results in the way to attenuate annual variations, gaps in the data and attempt to create a general pattern of Kuivajärvi lake across the year. The catchment is therefore considered as a whole without taking details/heterogeneity into account, neither of annual variation.

Except export and transport of DOC in aquatic systems we did not have access to other components of DOC cycle, such as its degradation (photolysis and degradation by microorganisms) and its flocculation processes. Miettinen et *al.,* (unpublished) and other studies conducted nearby provided nonetheless some clues we used by measuring $CO_2$ and $CH_4$ within the water column and by using Eddy covariance method. Furthermore, although we know DOC concentrations in the water, our measurements did not separate terrestrial and aquatic organic carbon, we therefore advanced the hypothesis that allochthonous organic compounds are the main sources of DOC in boreal aquatic ecosystems. This information is crucial to predict terrestrial income in aquatic ecosystems and to assess the role and the efficiency of DOC breakdown processes (photolytic, degradation by microorganisms). Thereby, this limitation prevents to estimate the support and the role of terrestrial ecosystem in DOC supply in aquatic ecosystems. Wetland proportions are a major factor determining DOC variations in numbers of studies, it is however difficult to assess its role in our catchment since the distribution of vegetation and land cover remained unknown to our knowledge. We had to rely on assumptions of several studies utilizing IHS method about what occurs within the horizons of the soil. As we saw above, the flow path and DOC storage are widely variable related to soil type, and therefore important in determining DOC export. Numbers of studies and especially Miettinen et *al.,* (unpublished) conducted on the same catchment, brought nonetheless information and answers about what occurs in the catchment.

# CONCLUSION

Although predicting episodic export of DOC from the terrestrial landscape is hard due to the lack of data, we tried nonetheless through this study to depict and understand organic carbon dynamics. DOC concentrations in Kuivajärvi catchment vary according to several factors such as: catchment characteristics (slope, vegetation, land cover, hydrology …) and climate (precipitation, temperature …). Our findings suggested that DOC export reacts differently throughout the year, and especially across the seasons. Indeed, spring snowmelt that represents the major annual hydrologic event in boreal countries accounts for the half of annual DOC fluxes, whereas summer and winter seasons realize only 25% of these exports. The hydrology, in agreement with the first hypothesis made at the beginning, is one of the most important factor underlying DOC variations, a positive relationship between discharge and DOC concentrations has been identified despite its low correlation. Discrepancies across studies, especially at Spring time were explained by catchment characteristic variations, dominated by soil and vegetation types. Indeed, forested catchments have been seen to control DOC export during this time inversely to the rest of the year, when wetlands explain the majority of the variation.

Furthermore, the highest fluxes of organic carbon in the outlet compared to the inlet is not fully explained here, but it highlights nonetheless the role of inland waters not as “neutral pipes”, which only brings water from terrestrial to ocean ecosystems, but as a component in Carbon cycle. Therefore, on the contrary to the initial hypothesis, there is still a fraction of organic carbon entering within water that is not took into account in this study and need to be further explored.

Although DOC concentrations in aquatic ecosystems have been rather successfully depicted across the year from simple landscape and regional characteristics, high monitoring frequency study would allow to detail all hydrological and DOC changes during the year and thereby to complete and adjust our study. Moreover, a long-term time series would give an assessment of DOC change across the year. This raises the necessity to create a program including hydrological (path in the soil, groundwater participation, water cycle…), DOC high frequency monitoring, vegetation and soil types repartition would give the possibility to create a model attempting to fit and predict with fidelity organic carbon cycle in all boreal catchments at first and then extend to a larger scale.

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# Annexes

### Annex 1: Characteristics of Kuivajärvi and Valkea-Kotinen catchment

| | Characteristics of Kuivajärvi catchment | Characteristics of Valkea-Kotinen catchment |
|---|---|---|
| **Coordinates** | 61° 50'N, 24° 17'E | 61° 14'N, 25° 04'E |
| **Max. elevation (m)** | 40 m | 156 m |
| **Min. elevation (m)** | | |
| **Climate zone** | Southern boreal | Southern boreal |
| **Annual mean temperature (°C)** | 3.5°C | 3.1°C |
| **Annual mean precipitation (mm)** | 711 mm | 618 mm |
| **Catchment area (ha)** | 1 219 ha | 30 ha |
| **Vegetation** | Managed pine forests (*Pinus sylvetris*) | *Pinus sylvestris, Picea abies* |
| **Pedology** | Riparian haplic podzols, histosols around the streams | Drained peatlands, mires |
| **Geology** | Igneous and metamorphic rocks | Granodiorite and veined gneiss |
| **Lake area (ha)** | 63.8 ha | 3.6 ha |
| **Volume lake (m3)** | 3 109 062 $m^3$ | 77 000 $m^3$ |
| **Max. depth (m)** | 14m | 6.5m |
| **Trophic type** | mesotrophic | mesotrophic |
| **Mean pH** | | 5.3 |
| **Water Residence Time (day)** | 267 days | |

## Annex 2: Platform on the lake Kuivajärvi (see Fig.2)

# Summary

This preliminary study, conducted in southern Finland, monitored dissolved organic concentrations (DOC) over 4 years, to observe temporal and spatial variations within a boreal drainage lake catchment. The mean annual export ranged between 8.7 g C $m^{-2}.yr^{-1}$ and 17.4 g C $m^{-2}.yr^{-1}$ in the inlet and the outlet respectively. Despite the extensive research on this subject, a lot is still unknown about what influence mostly organic carbon concentrations in inland waters. It reveals that DOC variations are driven by parameters differing with the season considered, and the location. Spring snowmelt, the most important hydrological event in northern latitudes, accounts for 38 to 42% of the annual discharge in Huikonjoki and Saarijärvenpuro respectively and is linked to a significant DOC export (48%). Whereas, summertime and snow cover period exports, at base flow condition, realize only a part of 25%. Our results suggested that DOC concentrations and export are mainly driven by hydrology, implying a positive correlation between discharge and DOC. Differences across studies were explained by wetland coverage, and particularly by the different flowpath in spodosols and histosols.

Keywords: DOC, lake, boreal, cycle, hydrology