Soil Solution DOC Dynamics
During Winter in Boreal Hillslopes

Paulina Bastviken

When plants and animals die they are decomposed into microscopic particles of organic carbon. In the ground, these carbon particles are dissolved in the soil water and eventually transported to the stream channel with the flow of the groundwater. Today the quantities of dissolved organic carbon (DOC) have been observed to increase in many lakes and streams around the world, which constitute a threat against the water quality and ecologic environment of these surface waters. The amount of organic carbon that is dissolved and transported in the soil water is mainly controlled by processes related to temperature and hydrology, two factors which vary seasonally. Because of difficulties to sample soil water at temperatures below 0°C studies of DOC transport between soil and water during the winter season are limited. This study therefore conducted a winter sampling of soil water, with the focus on DOC. Samples were collected in March 2014 at sites along three hillslopes, orthogonal to two streams, in a typical Swedish boreal forest northwest of Umeå. The soil water was extracted with the help of suction lysimeters installed at different depths in the soil, and heating equipment powered by batteries. The collected samples were analyzed for DOC concentration and absorbance after which the results were grouped together with results from previous sampling campaigns, conducted in the summer and autumn of 2013. Parallel to this, data representing a longer time series (2009 to 2012) at another hillslope was processed. During the summer and autumn an increase in DOC concentration was observed. The increase was assumed to be caused by high production and effective degradation of organic matter in the soil during this warm period. Generally, a decrease in the DOC concentration then followed during the winter season. One possible reason for this decrease could be that the bacterial degradation in the soil continued, during the winter, and transformed the dissolved carbon into CO_2 and CH_4. Another possibility is that the DOC was flushed into the streams by autumn rain events. The study also found differences concerning the DOC concentration and character in the soil water, as well as the seasonal variation of these parameters, with soil depth and distance from the stream along the hillslope profile. These differences could be correlated to the organic content of the soil, from which the soil water had been extracted.

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Supervisors: José Ledesma and Kevin Bishop

Sammanfattning

När växter och djur dör bryts de ner till mikroskopiska organiska kolpartiklar. I jorden löser sig dessa kolpartiklar i markvattnet och förs så småningom ut i bäckfåran med grundvattenströmningen. Idag har mängden upplöst organiskt kol (DOC) observerats öka i många sjöar och vattendrag runt om i världen, vilket utgör ett hot mot den vattenkvalitén och den ekologiska miljön i dessa ytvatten. Hur mycket organiskt kol som löser sig och transporteras i markvattnet kontrolleras i huvudsak av processer relaterade till temperatur och hydrologi, två faktorer som varierar med årstiderna. På grund av svårigheter att provta markvatten vid temperaturer under 0°C är kolflödet mellan mark och vatten under vintersäsongen endast undersökt i begränsad utsträckning. För att råda bot på detta gjordes i denna studie en vinterprovtagning av markvatten, med avseende på DOC. Prov samlades in i mars månad 2014 från provpunker längs tre backprofiler, ortogonala till två bäckar, i en typisk svensk barrskog nordväst om Umeå. Markvattnet extraherades med hjälp av suglysimetrar, installerade på olika djup i marken, och batteridriven värmeutrustning. I de insamlade proverna analyserades koncentrationen och karaktären av DOC varefter resultatet sammanfördes med analysresultat från tidigare provtagningar, utförda sommaren och hösten 2013. Parallellt bearbetades även data, insamlat under en längre tidsperiod (2009 till 2012), från en annan backprofil. Under sommar- och höstsäsongen observerades en koncentrationsökning av DOC i markvattnet. Ökningen antogs bero på hög produktion och effektiv nedbrytning av organiskt material i marken under denna varma period. Under vinterhalvåret följde sedan, generellt sett, en minskning i koncentrationen av DOC. En möjlig anledning till minskningen skulle kunna vara att den bakteriella nedbrytningen i marken fortsatte under vinternsäsongen och omvandlar det upplösta kolet till CO_2 och CH_4. En annan möjlighet är att kolpartiklarna spolades ut i vattendragen av regnskurar under hösten. I studien observerades även skillnader gällande koncentration och karaktär av DOC i markvattnet, samt den säsongsmässiga variationen av dessa parametrar, med markdjupet och avståndet från bäckfåran längs backprofilen. Dessa skillnader kunde kopplas till mängden organiskt material i jorden, varifrån markvattnet provtagits.

Abstract

When plants and animals die they are decomposed into microscopic particles of organic carbon. In the ground, these carbon particles are dissolved in the soil water and eventually transported to the stream channel with the flow of the groundwater. Today the quantities of dissolved organic carbon (DOC) have been observed to increase in many lakes and streams around the world, which constitute a threat against the water quality and ecologic environment of these surface waters. The amount of organic carbon that is dissolved and transported in the soil water is mainly controlled by processes related to temperature and hydrology, two factors which vary seasonally. Because of difficulties to sample soil water at temperatures below 0°C studies of DOC transport between soil and water during the winter season are limited. This study therefore conducted a winter sampling of soil water, with the focus on DOC. Samples were collected in March 2014 at sites along three hillslopes, orthogonal to two streams, in a typical Swedish boreal forest northwest of Umeå. The soil water was extracted with the help of suction lysimeters installed at different depths in the soil, and heating equipment powered by batteries. The collected

samples were analyzed for DOC concentration and absorbance after which the results were grouped together with results from previous sampling campaigns, conducted in the summer and autumn of 2013. Parallel to this, data representing a longer time series (2009 to 2012) at another hillslope was processed. During the summer and autumn an increase in DOC concentration was observed. The increase was assumed to be caused by high production and effective degradation of organic matter in the soil during this warm period. Generally, a decrease in the DOC concentration then followed during the winter season. One possible reason for this decrease could be that the bacterial degradation in the soil continued, during the winter, and transformed the dissolved carbon into CO_2 and CH_4. Another possibility is that the DOC was flushed into the streams by autumn rain events. The study also found differences concerning the DOC concentration and character in the soil water, as well as the seasonal variation of these parameters, with soil depth and distance from the stream along the hillslope profile. These differences could be correlated to the organic content of the soil, from which the soil water had been extracted.

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1. Introduction

Water of good quality is a resource of indisputable importance. In human society, water is needed both in everyday life, for drinking, growing food, maintaining hygiene etc., and in the form of a chemical substance in many various industrial processes. The state of the water is also greatly important from the ecological perspective, since it plays a key role in maintaining an environment in good condition.

Today, one of the threats against good water quality in the northern hemisphere is leaching of large, and increasing, quantities of organic carbon into surface waters (Evans et. al., 2005). High concentrations of dissolved organic carbon (DOC) in streams and lakes have many environmental impacts. Altered light climate (Jones et. al., 1992), microorganism growth (Jones et. al, 1992; Löfgren et. al., 2003) and mobilization of toxic substances (Bergkvist et. al., 1989) are examples of such impacts, which all may disturb the balance in the aquatic ecosystem. In addition, as a consequence of these disturbances, DOC may become the source of drinking water contamination (Löfgren et. al., 2003; Lavonen et. al., 2013).

These problems have led to increasing efforts to gain more knowledge of DOC origin and transport (Haei et. al., 2010). Research in this field has revealed the soil immediately adjacent to the water, only a few meters wide from the shoreline, as one key morphological factor controlling the DOC export to surface waters (Bishop et. al., 2004). This near-stream soil is referred to as the riparian zone. High organic content deep down into the soil profile, in combination with the hydrological mechanisms in this region, located at the base of the slope, make the riparian zone contribute with substantial amounts of the total DOC ending up in the stream (Dosskey & Bertsch, 1994; Hinton et. al., 1998).

Besides the hydrological control of DOC release, temperature is an important factor, governing primary production and degradation of organic matter (Hope et. al., 1994). Consequently, the DOC concentration in soil water and streams varies seasonally as product of these two controlling factors. Many studies have examined the seasonality (Eckhardt & Moore, 1990; Köhler et. al., 2008; Haei et. al., 2010; Ågren et. al., 2012) but it is still unclear how the winter affects DOC transport in high latitude boreal landscape with long duration of snow cover, (Ågren et. al., 2012). One reason for the lack in temporal coverage during the winter season is that snow cover and soil frost complicate sampling of soil water. Challenging these difficulties, this study aimed at investigating the effect of winter conditions on soil water DOC dynamics.

To address this aim, sampling was conducted at different locations in a boreal catchment during a winter campaign and analyzed together with previously collected data. The concentration and character of the DOC were examined.

2. Background

DOC in soil water and the factors controlling DOC export to streams including hydrology and various soil characteristics of the boreal catchment are the main focus of this study. This section therefore contains background information concerning origin, chemical properties and environmental impacts of DOC, followed by a description of the riparian zone influence on DOC transport. In the end of the section the parameter absorbance, used for estimating DOC character, is also introduced.

2.1. DOC

Since water is a common compound on earth, living organisms need to be hydrophobic to not to get dissolved by the environment surrounding them. When these organisms eventually die and, through the oxidizing work of bacteria and fungi, become decomposed organic matter the solubility in water increases (Kleber & Johnson, 2010). This increase in solubility is due to the gain of oxygen-containing functional groups, like -OH and -COOH, which by their polar character can interact with the polar water molecules. The process by which the organic matter becomes soluble is highly dependent on the structure of the carbon compounds and the pH of the surroundings (Kleber & Johnson, 2010). Other processes that result in carbon in solution, besides microbial degradation, are root exudation and chemical leakage from plant litter (Kalbitz et. al., 2000).

DOC is defined as the amount of carbon that remains in a water sample after letting the water pass through a filter of size 0,45 micrometer (Ledesma, 2012). Total organic carbon (TOC), on the other hand, also includes the carbon particles trapped in the filter. Usually, in boreal catchments the particle fraction is so small, in comparison to the dissolved fraction, that one can consider DOC and TOC to be equal (Laudon et. al., 2004; Ågren et. al., 2007). This generalization is used in this study, after verification in the laboratory analysis (data not shown), and DOC is chosen as main term.

High concentration of DOC in surface waters can have many environmental impacts. For example, large quantities of DOC cause the color of the water in streams and lakes to turn into a nuance of yellow to brown (Löfgren et. al., 2003), a phenomena called *brownification*. This color can disturb food web interactions by changing the light climate in the water environment, which affects organisms depending on photosynthesis (Jones et. al., 1992), and by being a substrate for bacteria and fungi (Jones et. al., 1992; Löfgren et. al., 2003). In other words, DOC can cause microorganism growth which in its turn can put the aquatic ecosystem out of balance. A secondary consequent of this, problematic for human society, is that increased amounts of microorganisms in surface water increase the amount of microorganisms in the drinking water supply. This contamination may give the water an unwanted taste and odor or in the worst case become the source of disease (Löfgren et. al., 2003; Lavonen et. al., 2013).

DOC can also cause chemical disturbances in the water environment. Even though not toxic in itself, DOC can easily form complexes with heavy metals (Bergkvist et. al., 1989) and organic pollutants (Dawson et. al., 2009), a chemical reaction which mobilizes these toxic substances in the water. In addition, the -COOH-groups of the DOC can release protons and thereby contribute to acidification (Eshleman & Hemond, 1985).

DOC compounds can have many various chemical structures which give the carbon molecules different properties. This is referred to as the DOC character or quality. Degradation rate and bacterial growth are for example affected by the character of the DOC, since the chemical structure of the carbon compounds regulates the bioavailability (Ågren et. al., 2008). Smaller (low-weight) and less complex (aliphatic) DOC molecules are easier for bacteria to consume in comparison to larger (high-weight) and more complex (aromatic) molecules (Ågren et. al., 2008). Vegetation type and level of soil saturation are major controls of DOC character, which can be used to investigate DOC origin (Ågren et. al., 2008). How the character is used when examining DOC is further explained in the absorbance section (2.3).

One process that reduces the export of DOC to surface waters is dissolved organic matter (DOM) sorption, a process of adsorption of DOM to the surfaces of mineral particles (Dahm, 1981). Especially, aluminum- and iron oxides (Dahm, 1981; Kaiser & Guggenberger, 2000) in clay minerals tend to effectively remove the DOC from solution. In this process the functional groups of the DOC form complexes with the metals through ligand exchange (Gu et. al. 1995; Kaiser & Guggenberger, 2000), a reaction which place and hold the DOC in solid phase. DOC can be chemically removed from soil solution by mineralization (Glazel et. al., 2004). During this process the DOC is decomposed by microorganisms and transformed into inorganic compounds, such as CO_2 and CH_4. The third process, by which the concentration of DOC in the soil water is reduced, is lateral flushing through the aquatic conduit (Dyson et. al., 2011). This last process will be further explained in the next section, Riparian zone.

2.2. Riparian zone

When precipitation lands on the ground surface in a catchment, it infiltrates the soil and percolates down to the groundwater table. After reaching this level, the water flow downslope according to the pressure gradient, until eventually reaching the stream channel. During this part of the hydrological cycle, the water is constantly affected by the chemical characteristics of the soil it is travelling through (Bishop et al., 2004). The quantity and composition of dissolved substances in the soil solution therefore change along the way.

Postglacial processes have developed a soil cover in boreal catchments of Sweden which can be classified according to the slope (Bishop et al., 2004). Upslope soils, covering the mayor part of the catchment, consist of podzols while more organic and saturated soils are found, just adjacent to the stream, in the so called riparian zone (Bishop et al. 2004).

In the riparian zone, organic carbon is accumulated all through the soil profile due to the level of saturation and the slow degradation rates (Haei, 2010). This large amount of organic carbon, in combination with the fact that all precipitation falling within the watershed needs to pass through this narrow body of soil before entering the stream, make the riparian zone a local hotspot for DOC export to surface waters (Dosskey & Bertsch, 1994). In addition to the soil characteristics of the riparian zone, a hydrological factor, referred to as the transmissivity feedback mechanism (Rodhe, 1989; Bishop et. al. 2004), has a central role in the DOC release. This mechanism occurs due to the increase in conductivity upward in the vertical soil profile. During rain fall events or snow melt, the groundwater table rises in the soil profile and enters soil layers both richer in organic matter and more hydraulically conductive (Fig. 1). The high flow of water through this conductive and organic layer flushes the DOC from the soil water, increasing the export of carbon to the stream (Bishop et. al., 2004).
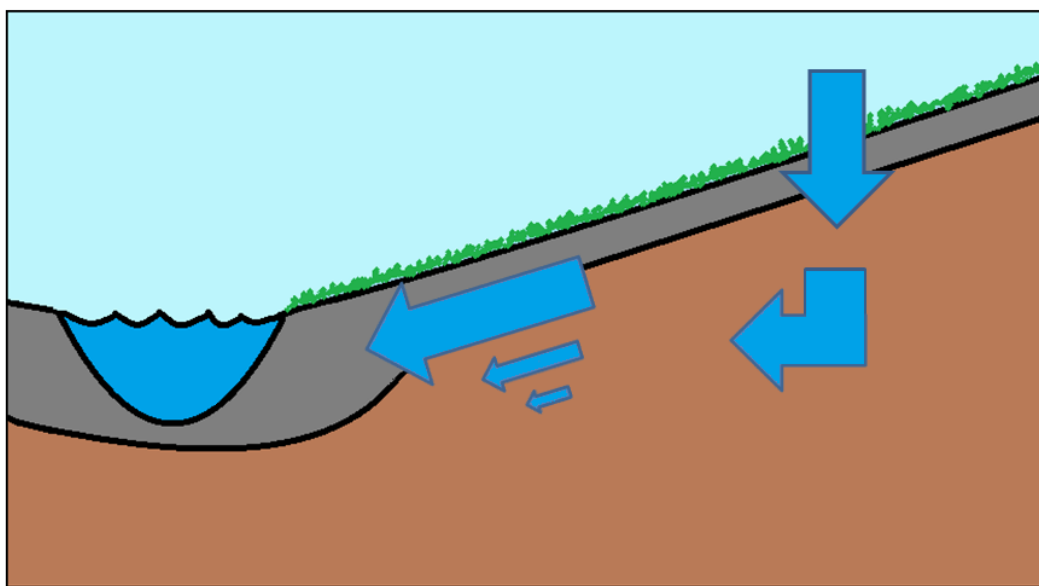
Figure 1.Schematic illustration of the riparian zone, modified after Winterdahl et. al. (2011). The grey color display soil rich in organic matter and blue arrows display the infiltration and lateral flow through the soil. Increasing size of arrows indicates higher conductivity.

2.3. Absorbance

One way of characterizing DOC is to measure its spectroscopic properties (Chin et. al., 1994). By investigating how a water sample absorbs different wavelengths, information concerning the size and structure of the carbon compounds within the sample can be gained. This information can then be used to derive the mobility (Chin et. al., 1994; Löfgren et. al., 2003) and bioavailability of the carbon molecules (Perdue, 1998; Löfgren et. al., 2003), determine the tendency for the carbon to react with pollutants (Chin et. al., 1994; Löfgren et. al., 2003) or trace the environment which the carbon originates from (Ågren et. al., 2008).

The general principle of the method is that radiation of a known wavelength and intensity is sent through one side of a cuvette containing the sample and that the remaining intensity is measured on the opposite side. In mathematical terms, absorbance (A) is the transmitted intensity (I_1) divided by the incident intensity (I_0) of a wavelength, presented in the form of a logarithm ($A = \log(I_1/I_0)$) (Fuwa & Vallee, 1963). The unit of absorbance is cm^{-1}, which refers to the thickness of the sample cuvette, through which the radiation is sent.

Regarding characterization of DOC, two particular wavelengths (254 nm and 365 nm) have been empirically proven to be useful as a ratio (A_{254}/A_{365}), to investigate the relative amount of low-weight and high-weight carbon compounds (Ågren et. al., 2008; Maehder, 2012). A high value of the ratio A_{254}/A_{365} corresponds to a high content of aliphatic compounds in the DOC, which are compounds more mobile and available for microorganisms (Ågren et. al., 2008). If to consider origin, a high A_{254}/A_{365} corresponds to DOC likely to have been derived from forest areas, where the soils are of mineral character. In opposite, a low A_{254}/A_{365} indicates a high content of high-weight carbon compounds, with low mobility and bioavailability, usually derived from organic soils in wetlands (Ågren et. al., 2008). How the molecule character of the DOC affects the binding capacity between the DOC and toxic

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substances is more complex. This depends, among other things, on the pH of the surroundings and on the type of contaminant (Kordel et. al., 1997).

Together with the absorbance ratio a useful spectrometic parameter, describing the character of the DOC, is Specific Ultraviolet Absorbance (SUVA) (Weishaar et. al., 2003). The SUVA is defined as the absorbance of ultra violet radiation at a given wavelength after the absorbance has been normalized for DOC concentration. If the wavelength of 254 nm is used, the SUVA will correlate positively to a high fraction of aromatic carbon (Weishaar et. al., 2003).

3. Objectives and hypotheses

The project objectives were to investigate seasonal variability of DOC concentration and character in the soil water of a boreal catchment, and to examine how the seasonal trend may vary vertically in the soil or between different locations relative to the stream channel. Within the seasonality, the study especially aimed at investigating the variability during winter conditions.

The differences between locations and horizons, regarding percentage of organic matter and the level of saturation, were hypothesized to affect the DOC concentration and character of the soil water. Organic horizons were, in comparison to mineral horizons, expected to contain soil water with high concentration of DOC (Michalzik & Matzner, 1999; Kalbitz et. al., 2000, Ågren et. al., 2008, Grabs et. al., 2012), characterized by high-weight (Gu et. al., 1995; Ågren et. al., 2008) and complex molecules (McKnight et. al., 1992; Ågren et. al., 2008)

In addition, the DOC concentrations were thought to be more variable in organic horizons, than in mineral horizons, as DOC was expected to be adsorbed to the surface of mineral particles (Dahm, 1981; McDowell, 1985; Hope et. al., 1994).

A third hypothesis was that the seasonal variation of DOC concentration would follow a cyclic pattern governed by lateral flow rates and primary production. The DOC concentration in the soil water was expected to increases during the summer season to reach its maximum value in the autumn (Köhler et. al., 2008), as a consequence of high temperatures generating vegetation growth and intensive bacterial activity (Christ & David, 1996). During the winter, the DOC concentration was then thought to remain high, because of low lateral flow rates deep down in the soil profile, until decreasing rapidly in the spring due to snow melt flushing (Ågren et. al., 2007; Buffram et. al., 2007; Köhler et. al., 2009).

4. Material and methods

4.1. General overview

During a winter field campaign in 2014, soil water samples were collected at three riparian and four upslope monitoring sites, together forming three lines orthogonal to stream water channels (transects), in a boreal catchment. At each site the samples were collected along a depth profile with the use of previously installed suction lysimeters. Heating boxes were placed above the ground where the lysimeters are placed in order to decrease the risk of water freezing during the sampling procedure. After collection, the soil water samples were weighed and frozen before being further analyzed in the water laboratory at SLU Umeå.

To be able to investigate seasonality, data from previous campaigns, in the summer and autumn of 2013, were considered together with the data collected in the present study. A longer time series and a broader spatial coverage were obtained by using data from three other monitoring sites, one riparian and two upslope (from now on called the S-transect). The data available from the S-transect had been collected regularly, from the spring 2009 to the end of the autumn 2012. Under the following headings, the study site and the sampling method are described in more detail.

4.2. Study area

The winter campaign in March 2014 was conducted in the 68 km^2 boreal Krycklan catchment (Figure 2), located approximately 50 km northwest of Umeå, in the north of Sweden (Ledesma et. al., 2013).

The bedrock of the area consists of Svecofennian gneissic rock, to the greatest extent of sedimentary origin (Ågren et. al., 2007). Overlaying the bedrock glacial till and glacio-fluvial deposits form a sediment cover, up to tens of meters thick (Ledesma et. al., 2013). The soil profiles in the upslope regions display well-developed iron podzols, while more organic soils are found in the riparian zones (Ledesma et. al., 2013). In general, the topography forms a gentle slope toward the southeast with the elevation ranging between 372 and 126 m a.m.s.l (Ledesma et. al., 2013).

The catchment are mainly covered by forest (88%), with some elements of wetland (8%), agricultural landscape (3%) and lakes (1%) (Grabs et. al., 2012). In the forest the tree volume consists of Scots pine, Norway spruce and Deciduas forest, dominated by Birch (Ledesma et. at, 2013).

Climatic data (1981-2010) display an annual mean daily temperature of 1,8 °C and an annual mean precipitation of 640 mm (Ledesma et. al., 2013). Half of the precipitation falls as snow and the duration of the snow cover is from October to May, on average 168 days per year (Laudon et. al., 2011). Mean annual runoff and evapotranspiration is 321 mm/year and 319 mm/year, respectively (1981-2009) (Ledesma et. al., 2013).

Forestry and alternated drainage paths are activities which have affected the area, but the anthropological impacts on the catchment are considered to be rather low (Ledesma et al., 2013). Today, less than 1% of the catchment is harvested yearly and the central part is left with no management (Ledesma et al., 2013). The Krycklan catchment is a part of the Svartberget field research infrastructure which is in the regime of Swedish University of Agricultural Science (SLU) (Laudon, 2012). The catchment has been the object of several hundred scientific publications (Laudon, 2012) since it became an area of research in 1923 (Ledesma, 2012)

One of the present monitoring systems, installed in 2007, is the Riparian Observatory of Krycklan (ROK) (Grabs et. al., 2012). The observatory consists of 13 instrumented sites riparian soil profiles (sites), spatially spread over the catchment in sedimentary and till deposits (Grabs et. al., 2012). The equipment installed at the sites will be further describes under the section Sampling procedure (4.3).

The seven sites, sampled June to March (2013-2014), are together forming three transects, orthogonal to three different streams located in the middle of the Krycklan catchment (figures 2 and 3). At each transect one riparian site from the ROK are located at the base of the slope, approximately 1-2 m from the stream. Further from the stream one or two upslope sites make the transects complete. The upslope sites, installed in 2012, were sampled for the first time in June 2013.

For practical reasons these transects will in the following text be referred to as the ROK-transects. Separately the names of the transects will also include the numbers of the riparian sites, as in the example of the ROK2-transect which include the riparian site number 2 (R2) and the upslope sites number 34 and 35 (U34 and U35). Details about the ROK-transects are presented in table 1 and the observation equipment, installed at all the sites, will be described under the heading sampling procedure.

The S-transect was established in 1992 (Seibert et. al., 2009) and consists of three observation sites along a line following the direction of the lateral groundwater flow, adjacent to the same stream as the ROK5-transect. The sites, in the transect, have been sampled monthly since 1996 (Seibert et. al., 2009). The dataset used in this study was sampled once a month to every second month, from April 2009 to December 2012. The details of the observation sites along the S-transect are presented in table 2.

Table 1. Description of ROK-transects.

Transect	Site	Distance from stream [m]	Profile depth [cm]	Mean groundwater level [cm]	Soil Description	Vegetation
ROK2	R2	1-2	75	4	Peat	-
ROK2	U34	26-27	75	0	Peat to 0-20 cm depth, uneven thickness, then Gley soil	Birch
ROK2	U35	53-54	75	>47*	Gley podzol	Pine
ROK5	R5	1-2	75	11	Peat	-
ROK5	U36	24-25	90	>37*	Podzol	Pine
ROK10	R10	1-2	75	16	Peat	-
ROK10	U37	16-17	75	>14*	Podzol	Spruce

*The groundwater level was below recognizable depth during several campaigns. At these occasions the maximum measurable depth are used.

Table 2. Description of the S-transect, reconstructed after information in Nyberg et. al. (2001) Stählin et. al. (2001) and Seibert et. al. (2009).

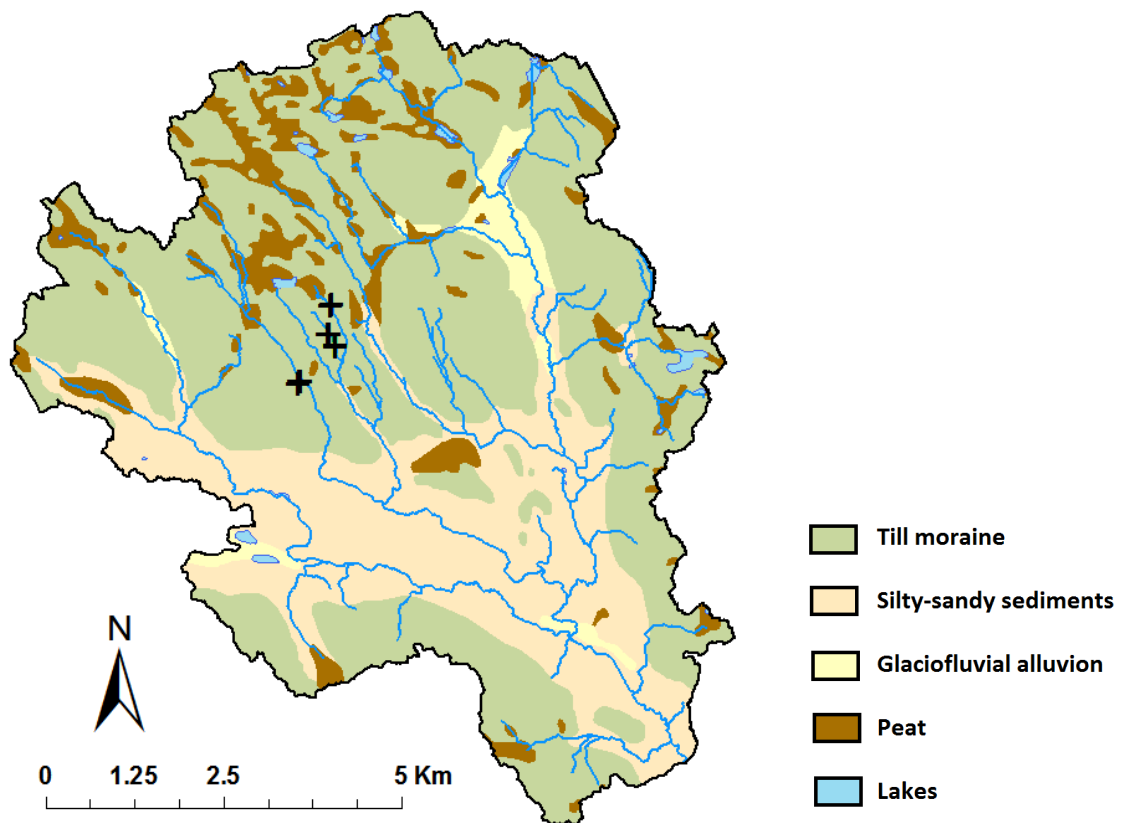| Transect	Site	Distance from stream [m]	Profile depth [cm]	Groundwater level [cm]	Soil Description	Vegetation
S	S4	4	65	30-40	Peat to 30 cm depth, organic-rich mineral soil to 60 cm depth, then mineral soil	-
S	S12	12	70	30-40	Peat to 20 cm depth, organic-rich mineral soil to 50 cm depth, then mineral soil	Spruce
S	S22	22	90	55	Podzol	Pine

Figure 2. Krycklan catchment with sampling sites positions. Map: José Ledesma (2014).
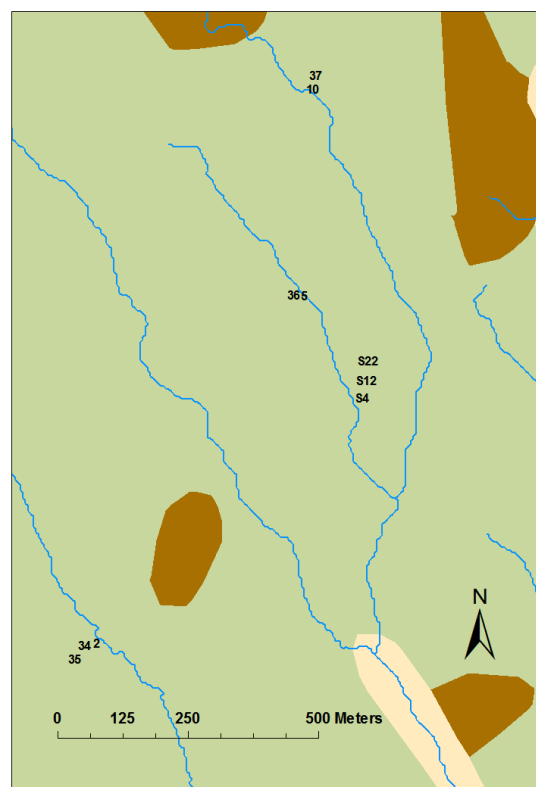

Figure 3. Sampling sites positions in close-up view. Map: José Ledesma (2014).

4.3 Sampling procedure

The soil water samples were collected using suction cup lysimeters. A suction lysimeter is a small ceramic cylinder which, similar to the soil texture, has a porous structure able to accommodate soil water. The lysimeters are buried at different depths in the soil, and connected to thin tubes which can transport soil water to the surface. During sampling, sterile needles are attached to the end of the tubes, at the surface, and extraction of water is then enabled by inserting these needles into the rubber caps of previously vacuumed sampling bottles.

The lysimeter setup in the ROK-transects consists of a depth profile with a pair of suction lysimeters installed 15, 30, 45, 60 and 75 cm below the ground surface. An extra pair of lysimeters is installed, at 90 cm depth, at U36. In order to monitor the position of the groundwater table in the vicinity of the lysimeters, all observation sites are also equipped with a perforated PVC tube hosting an automatic water logging device (Ledesma, 2012). Figure 4 displays the sampling equipment at an observation site in a cross section.
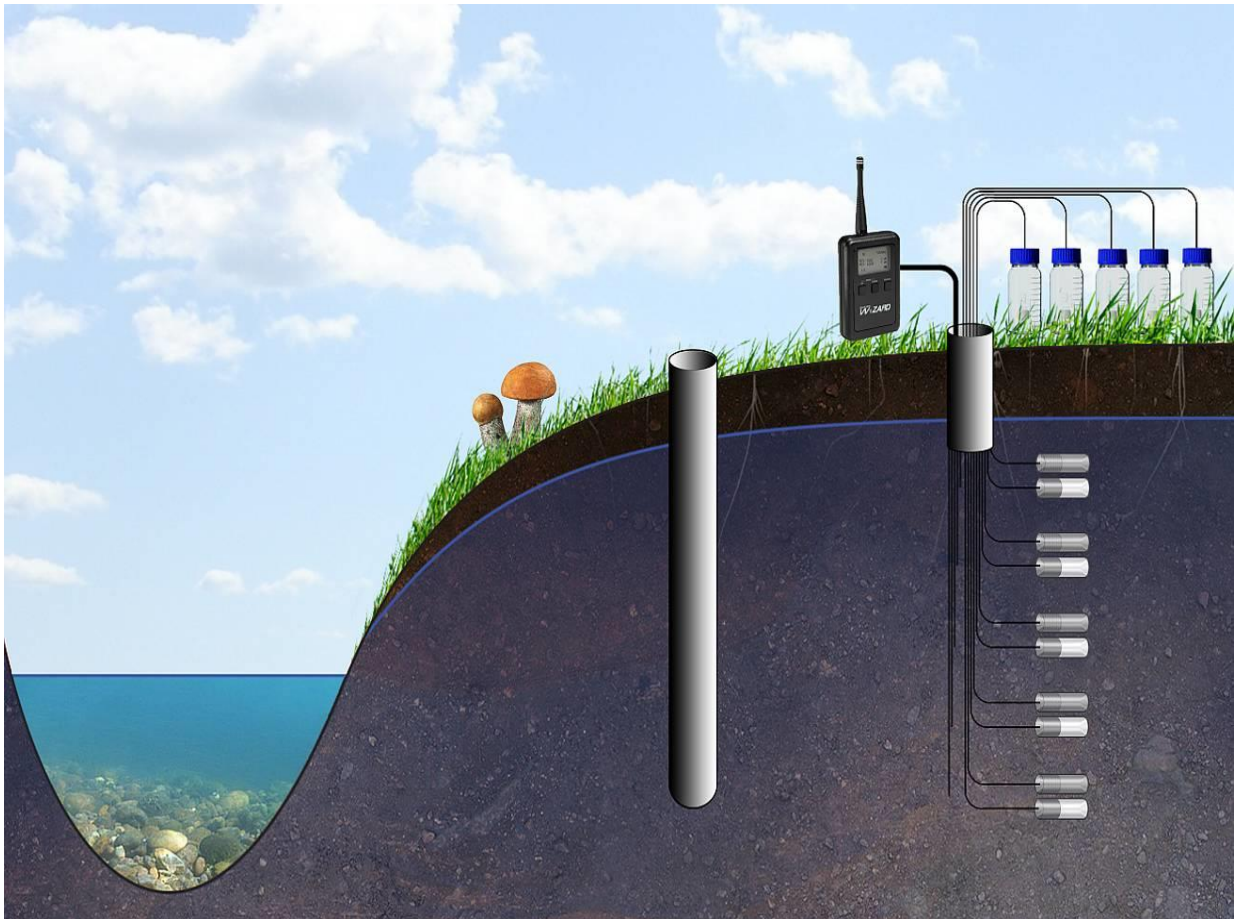

Figure 4. Illustration of lysimeter setup. (Grabs et. al., 2012).

To increase the probability of extracting water from the suction lysimeters in potentially freezing condition during the campaign in March 2014, heating boxes were installed at all the sites before sampling (fig. 5). The heating equipment consisted of a car battery which, through a transformer and a thermostat, was connected to a heating cable. The heating box also contained an inner box of isolating styrofoam,

with space for the sampling bottles. When installing a box, the heating cable was inserted as far down as possible down the pipe where the lysimeters tubes come to the surface, which in most cases was approximately one to two decimeters. The effect and importance of the heating box was difficult to evaluate as generally the batteries stopped functioning during the time of sampling, or did not function at all. Luckily, mild temperatures contributed to enough water being sampled at all sites except R2 and U34.

Figure 5. Heatingbox. Photo: Paulina Bastviken (2014).

The soil water samples were collected in acid-washed highly-density polyethylene bottles (250 mL) (Ledesma, 2012). Prior to the sampling, the bottles were vacuumed in the laboratory at SLU Umeå (fig. 6). This was done so that the pressure difference between the bottles and the lysimeters could drive the water up the lysimeter tubes. In order to extract the water left in the lysimeter tubes since the previous sampling campaign, smaller rinsing bottles (50 mL) were connected to the lysimeters before the sampling bottles.
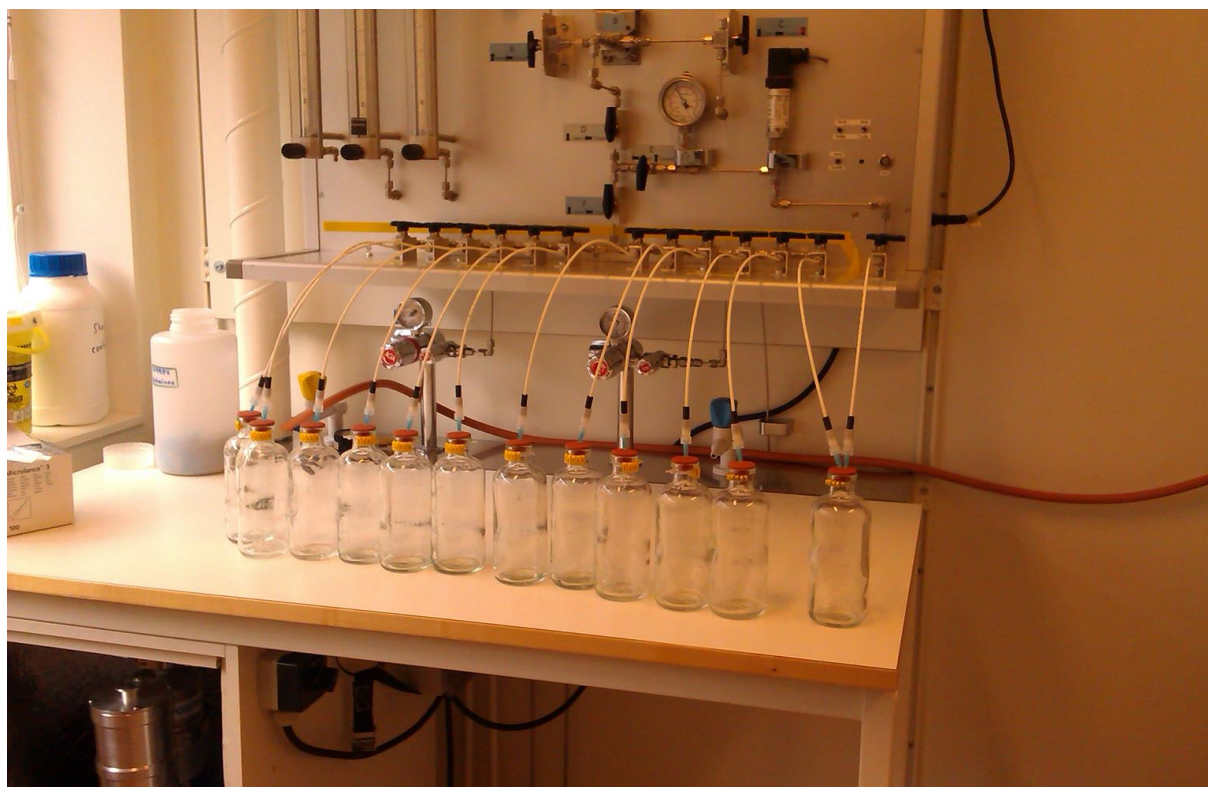

Figure 6. Sampling bottles being vacuumed. Photo: Paulina Bastviken (2014).

When sampling at all sites had been completed, rinsing bottles and soil water samples were transported to the laboratory at SLU Umeå where they were weighted. After checked for possible remaining vacuum, the rinsing bottles were poured away while the soil water samples were placed in a cooling room. Approximately 2-4 days after collection the water samples were subsampled and analyzed for TOC concentration, pH and absorbance, at SLU Umeå. During the data processing, worth mentioning is that a quality check was done on the A_{254}/A_{365} data, removing all extreme values likely to be misleading. These extreme values are the result of absorbance ratios derived from samples with very low DOC concentration, where the potential errors in the absorbance measurements are larger than the actual values of absorbance.

Except for the heating box, the data from all previous campaigns, at the ROK-transects and the S-transect, had been collected according to the same procedure as the sampling in March 2014.

5. Results

In this section, the result of the study will be presented and described. The DOC concentration and DOC character will be addressed under separate headings. Graphs containing the same type of data are plotted in the same scale to make them easy to compare.

5.1. DOC concentration

5.1.1. ROK-transects

During summer and autumn 2013 (June to October) all riparian sites in the ROK-transects displayed an increase in soil water DOC concentration. Also site U35 exhibited this tendency, but with a temporary decrease in the DOC concentration during August and September. At the remaining upslope observational sites the DOC concentration remained relatively stable throughout the summer and autumn. In the following winter (October to March) the DOC concentration decreased at site R5 and R10, as well as at site U35. The concentration, at site U37, remained stable, while the samples at site U36 revealed a small increase in DOC concentration during the season. At site R2 and U34, soil frost prevented collection of samples during the winter campaign. A persistent tendency, throughout the sampling period and at all sites, is that the changes in DOC concentrations seem to become less evident deeper down in the soil profile. Figure 7 illustrates the seasonality of the DOC concentration at all ROK-transects.

To investigate general relationships, the organic content of the soil at all lysimeter depths were plotted against the corresponding annual mean DOC concentration (fig. 8). This revealed that higher DOC concentrations are found in horizons containing more organic material. In figure 9, the mean annual DOC concentrations are visualized along the depth profile at each site.

The relationship between the DOC concentration and the organic content of the soil was further investigated by classifying all lysimeter horizons into three categories according to the percentage of carbon (organic, organo-mineral and mineral), and then by examining the seasonality of the DOC concentration for each category separately (fig. 10). The DOC concentration in the mineral horizons was stable at 5 mg/L throughout the sampling period. This was also the case for the organo-mineral horizons during summer and autumn. During the winter season, the DOC concentrations in the organo-mineral horizons then increased, but it should be noted that this increase only was based on one single sample. In the organic horizons, an increase in soil water DOC concentration occurred during summer and autumn, followed by a decrease during winter.
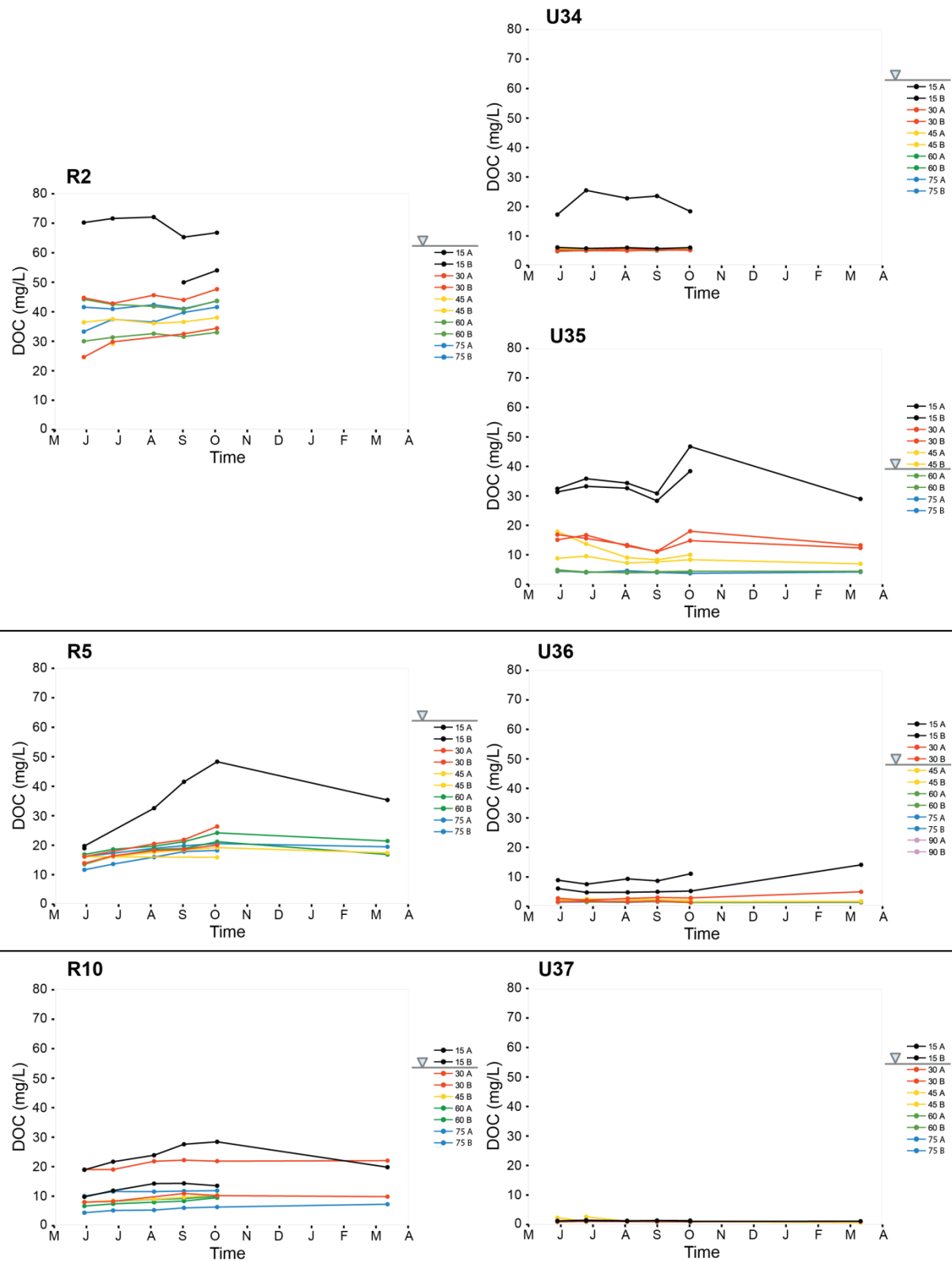
Figure 7. Seasonal variability (June 2013 to March 2014) of soil water DOC concentration at all sites in the ROK-transects. The colors illustrate the depth of the lysimeter position which is written in centimeters in the legend. The black line and the blue triangle display the average groundwater table during the period of sampling, relative to the lysimeters.
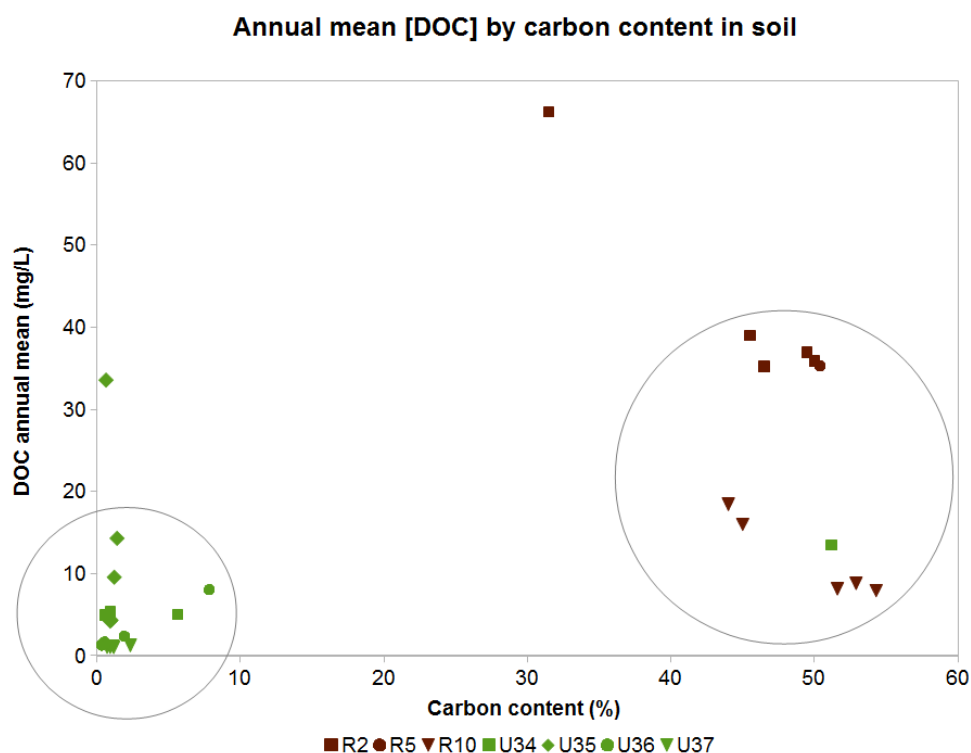
Figure 8. Annual mean DOC concentration plotted against carbon content of the soil, in the horizons of the lysimeter positions. The legend indicates which ROK-sites the lysimeters belong to (brown color for lysimeters in the riparian zone, green color for lysimeters upslope and different shapes on the symbols for different sites).
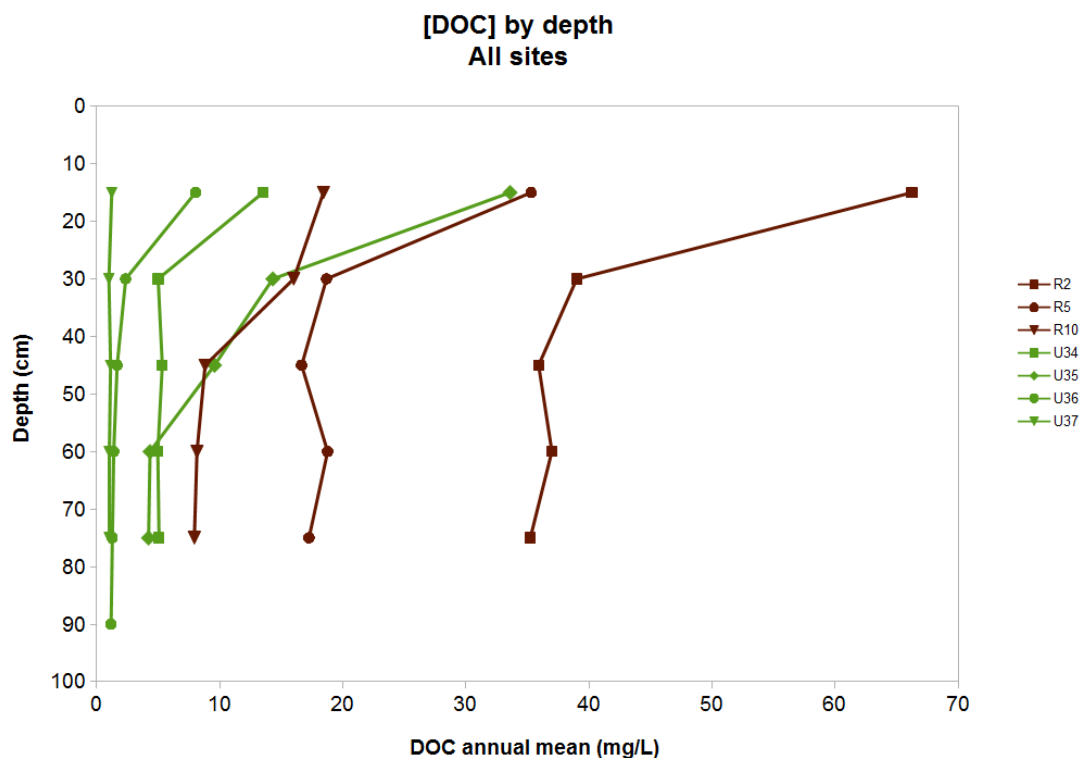

Figure 9. Annual mean DOC concentration plotted against depth at each ROK-site (the lysimeters are illustrated with the same symbols as in figure 8).

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[DOC] in organic horizons

[DOC] in organo-mineral horizons
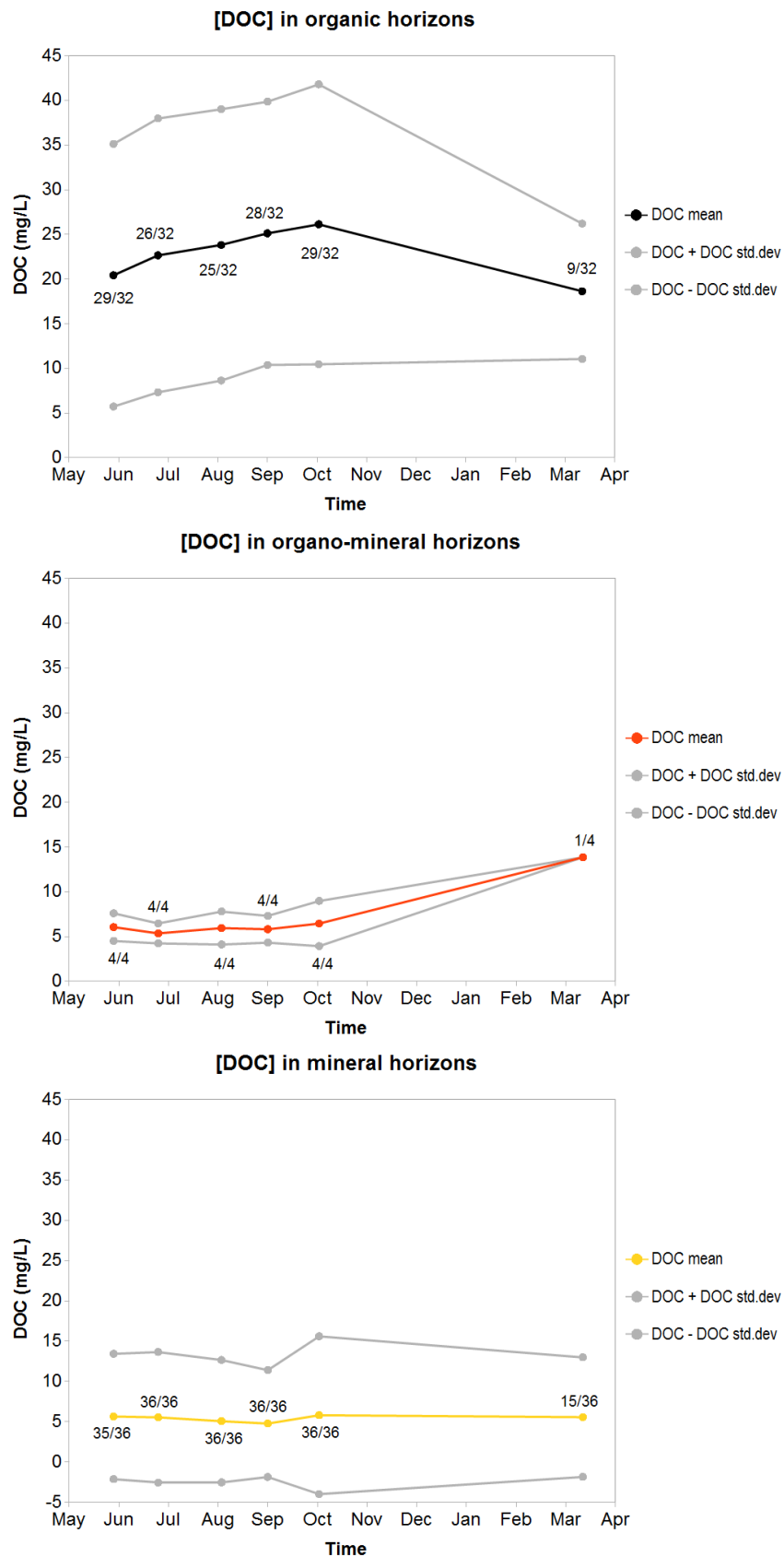

[DOC] in mineral horizons

Figure 10. DOC concentration in horizons classified as organic (>15% C), organo-mineral (3-15% C) and mineral (<3% C). Numbers beside campaigns indicate how many samples that were successfully extracted out of the total amount of available lysimeters in each category.

5.1.2. S-transect

In the graphs of figure 11 and 12, based on samples from the S-transect, the data cover three years (April 2009 to December 2012) of DOC concentration variability. To make the winter trends in these figures clear, the winter seasons according to the climatic definition (first of December to last of February), were marked with a grey background.

At site S4 (fig. 11) the DOC concentrations varied between 20 to 90 mg/L during the sampling period and, similar to the riparian sites sampled at the ROK-transects, lower and less varied concentrations can be correlated with increasing depth. A cyclic pattern is also visible at S4. The seasonal cycle displays an increase in DOC concentration, from approximately may to November, followed decrease, ending in may the year after.

The winter trends in 2009 and 2010 look similar taking into account the difference in sampling frequency during September to March. This would suggest a slow decrease in DOC concentration during these two winters, followed by a more rapid decrease in the beginning of the spring. The rapid decrease in spring, which ends with local minimum values of DOC concentration, is recurrent during the period and correlates well with data of discharge (fig. 11b).

Along the depth profile at site S4 the pattern of variation changes. The lysimeters at 10 and 25 cm depth display quick drops in DOC concentration during summer, a drop which is displayed earlier further down in the profile in 2009 and 2011 while not displayed at all in these deeper horizons in 2010. After plotting the DOC concentrations against precipitation data these drops seemed to be correspond to great rainfall events (fig. 11a).

In the end of the winter between 2011 and 2012 a break in the cyclic trend at S4 is displayed. The DOC concentrations in the lower horizons start to increase at the same time as a rapid decrease occurred in the horizons from the top two lysimeters. Meteorological records from the period show a temperature drop, down to -30°C, at point of time for this break in the seasonal trend (fig. 11c).

At the upslope site S12 (fig. 12) the soil water contained less DOC, with concentrations ranging from 5 to 40 mg/L. The concentrations seem more stable throughout the period than at S4, but very few samples had been collected from the top three lysimeters at S12. The lack of data could hide eventual variation in the shallower horizons. The frequently mentioned tendency, of DOC concentration decreasing with depth, is visible at site S12 and the lysimeter at 20 cm depth display the same respond to precipitation events, as the shallower lysimeters at site S4.

The samples from the upslope site S22 displayed low DOC concentrations from 1 to 5 mg/L independent on depth and with no visible seasonality (fig. 12).
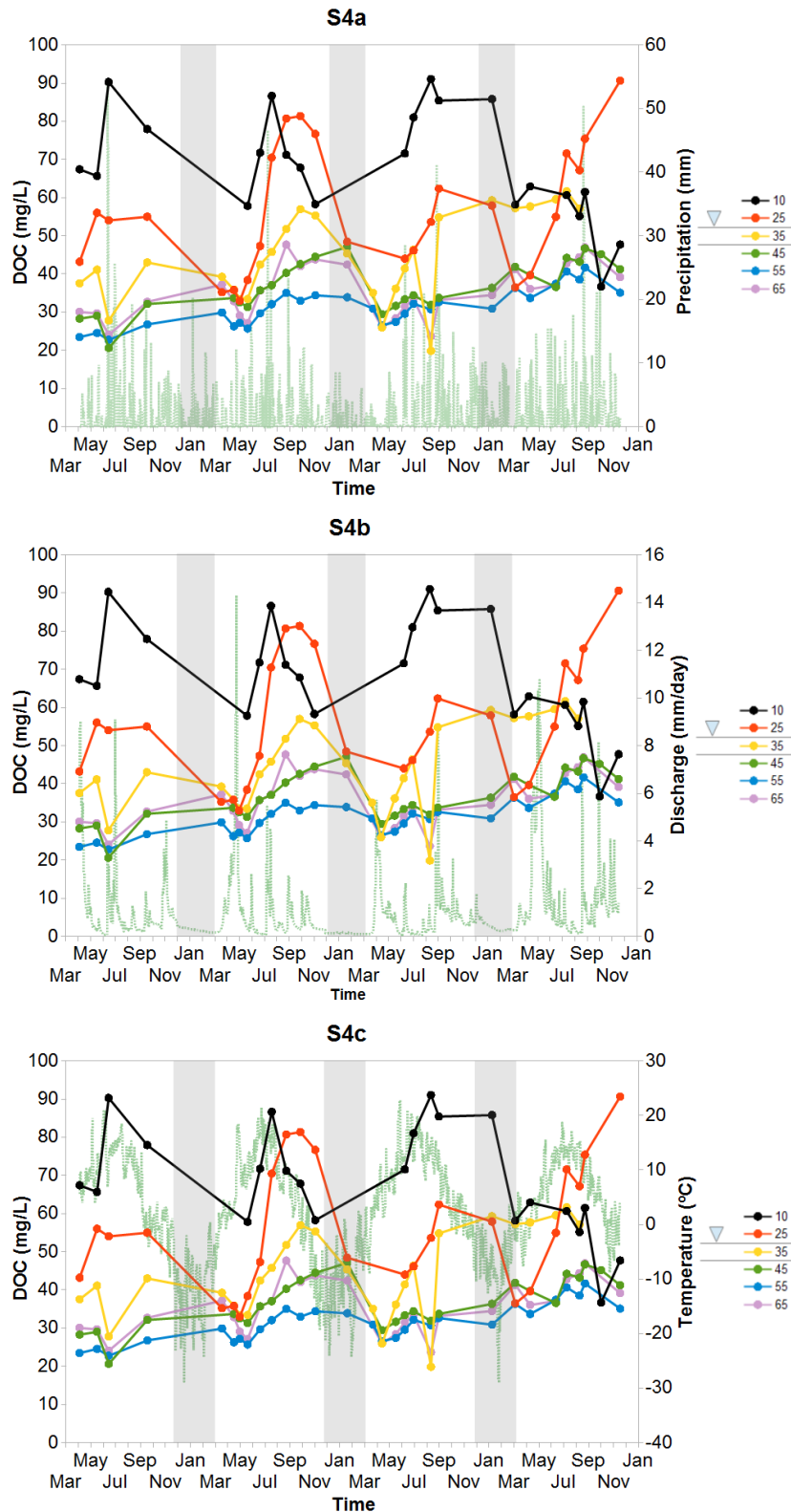
Figure 11. Seasonal variability (April 2009 to December 2012) of soil water DOC concentration at the riparian site S4 in the S-transect, including precipitation (a), discharge (b) and temperature (c) (all with a green, dotted line). As in figure 6, the colors illustrate the depth of the lysimeter position. The lysimeter depth in centimeter and the relative position of the groundwater table is displayed in the legend. The winter seasons are marked with grey areas.
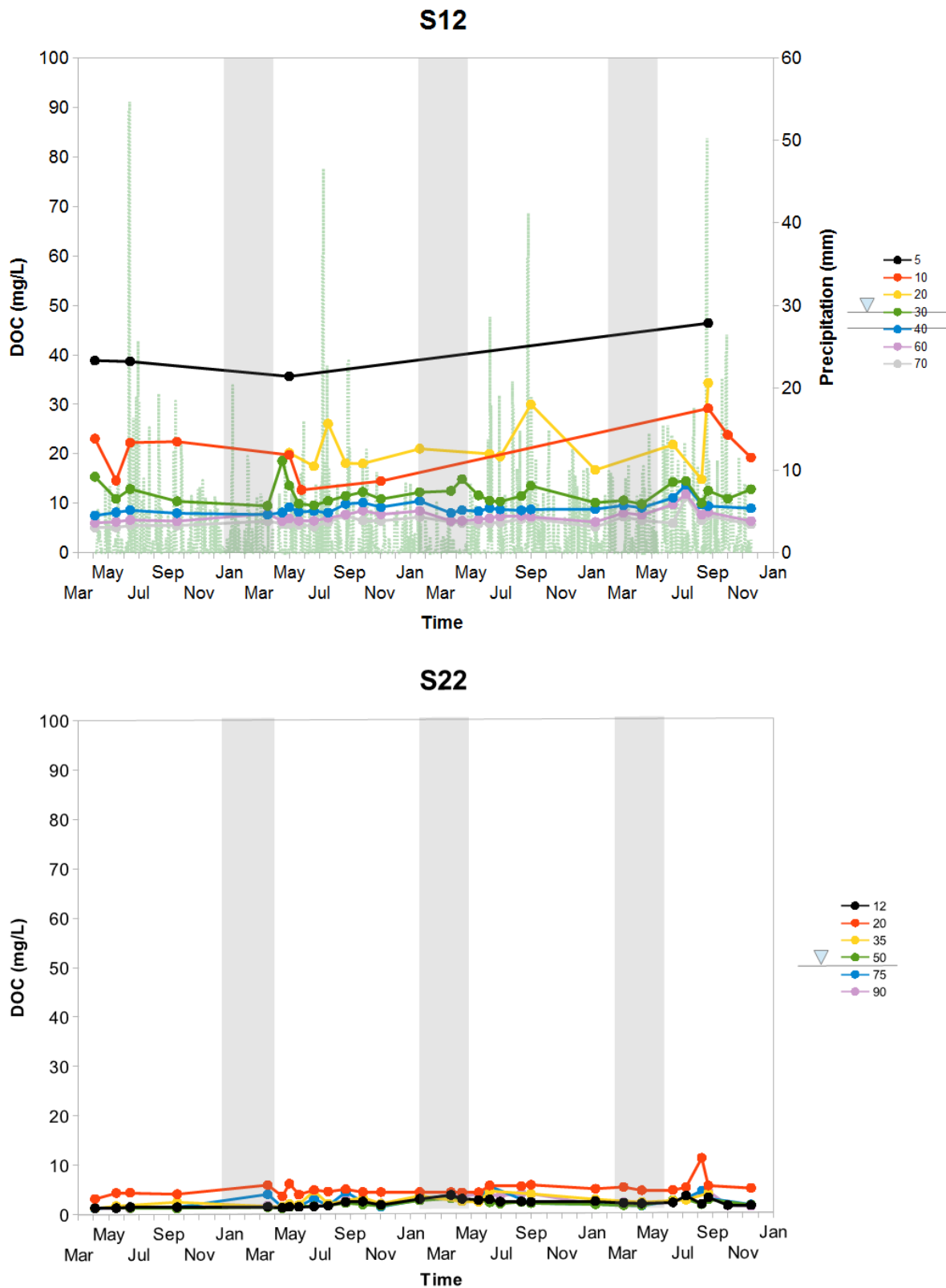
Figure 12. Seasonal variability (April 2009 to December 2012) of soil water DOC concentration at the sites upslope, S12 and S22, in the S-transect. Precipitation data (green dotted line) is included in the graph displaying DOC concentrations at site S12. The winter seasons are marked with a grey area, otherwise the symbols are the same as in figure 7.

5.2. DOC character

5.2.1. ROK-transects

At all riparian sites, both the A_{254}/A_{365} and the $SUVA_{254}$ stayed relatively stable throughout the whole sampling period, with values between 3 and 6 in general. The DOC in the soil water samples collected at 15 cm depth in the riparian profiles (the horizon richest in organic matter) display a vague tendency to coincide with the lowest A_{254}/A_{365} and highest $SUVA_{254}$. As an exception, the $SUVA_{254}$ at site R5 exhibits the reverse of this tendency, correlating positively with increasing depth.

The absorbance ratios were generally more varied in the samples from the upslope sites, than in the samples from the riparian sites. A clear depth-dependent trend is seen in both the A_{254}/A_{365} and the $SUVA_{254}$ of site U35, where the shallower, more organic horizons correlate with values indicating higher molecular weight and higher aromaticity. The A_{254}/A_{365} at site U35 also became more varied with depth, a trend which as well can be seen at site U34 and U36 where one of the lysimeters at 15 cm depth extracted water with more seasonally stable absorbance ratio than other lysimeters. In figure 13 and 14 the results from the character analysis, absorbance and SUVA, for all ROK-transects are illustrated.
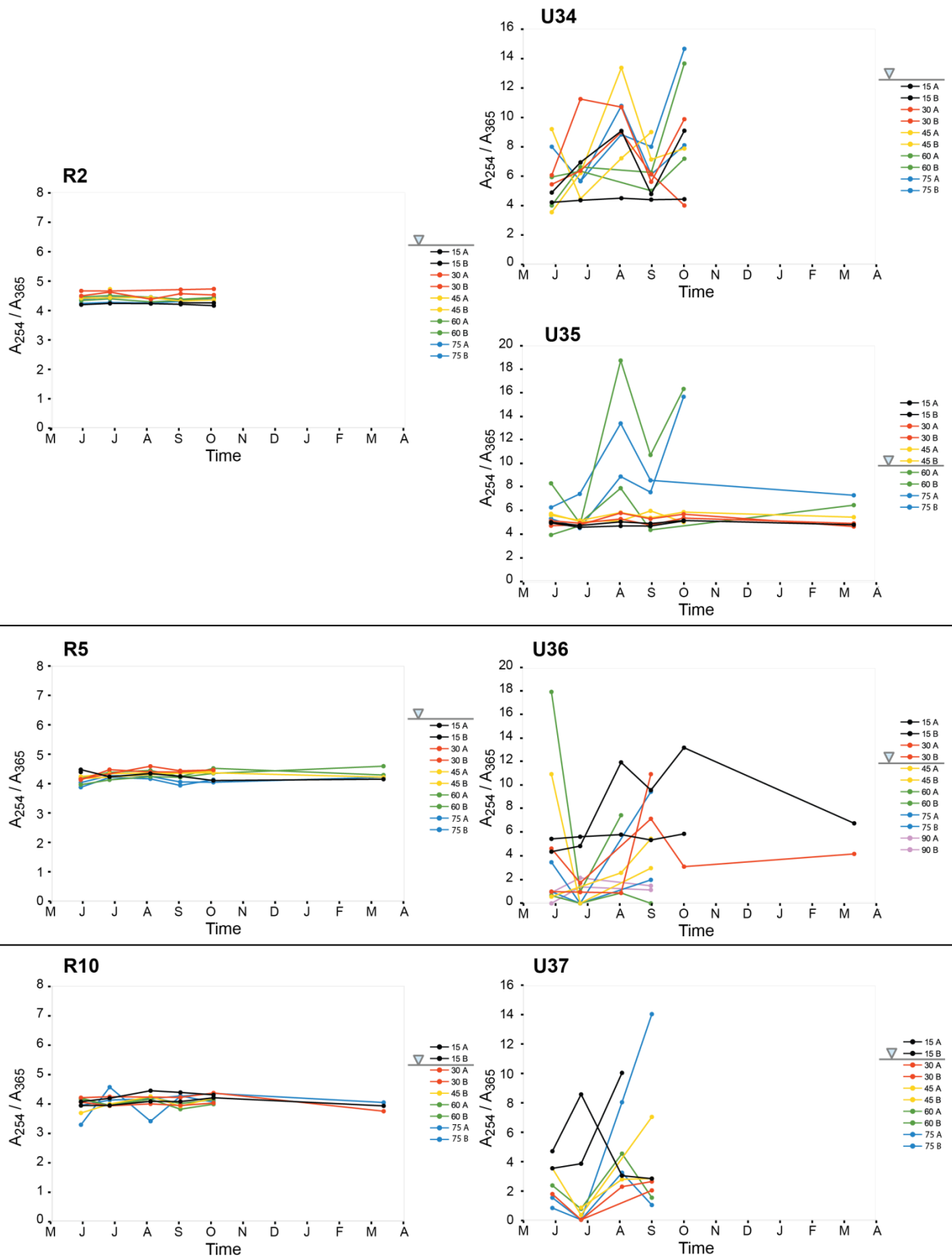
Figure 13. Seasonal variability (June 2013 to March 2014) of A_{254}/A_{365} at all sites in the ROK-transects. Illustration symbols are the same as in figure 7.
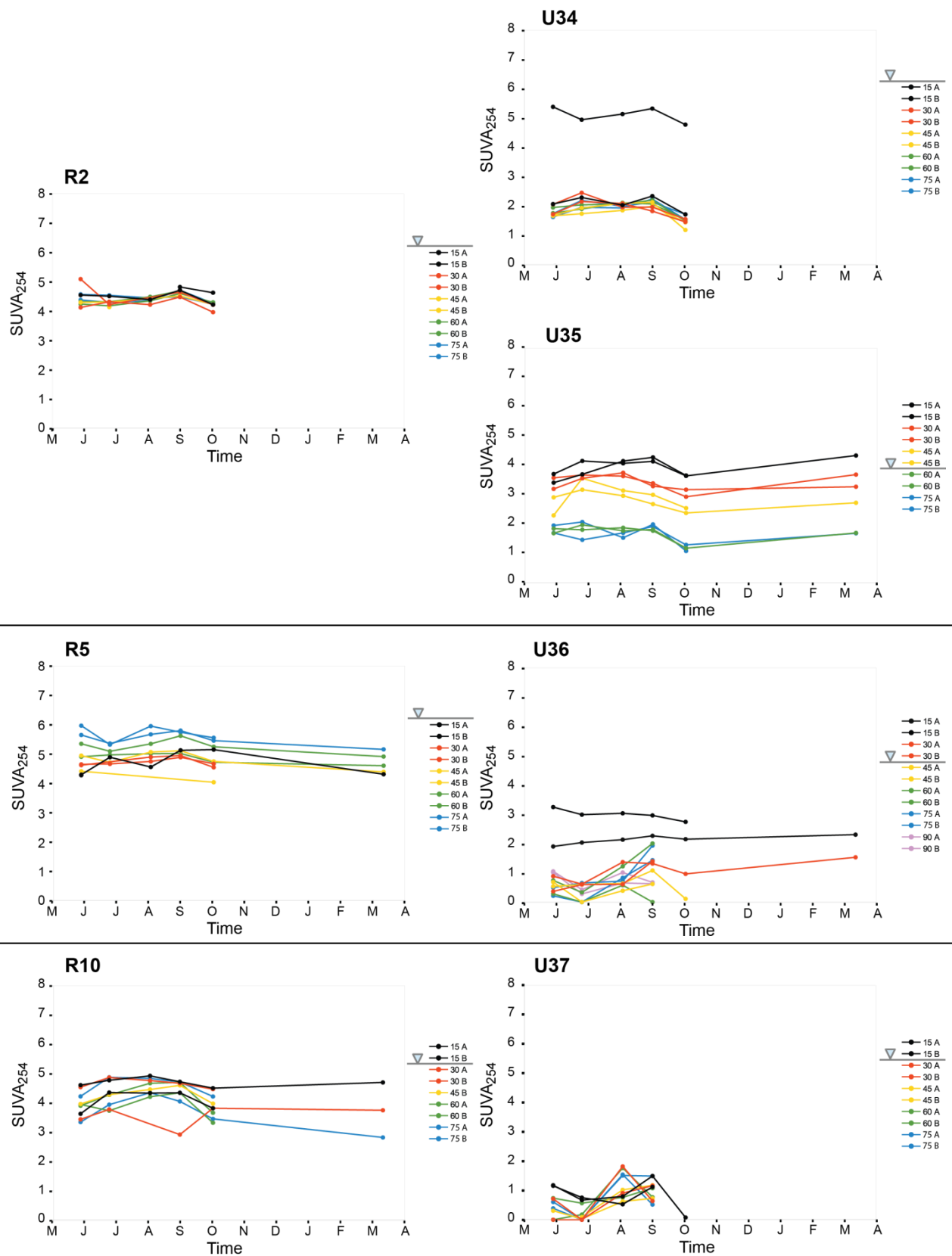
Figure 14. Seasonal variability (June 2013 to March 2014) of SUVA$_{254}$ at all sites in the ROK-transects. Illustration symbols are the same as in figure 7.

5.2.2. S-transect

The absorbance ratio from the sites in the S-transect followed the same pattern as the absorbance ratio from the ROK-transects. S4, the riparian site, (fig. 15) displays ratios temporally stable around 5 with small variations along the depth profile. Going upslope to S12 (fig. 16), a depth trend is visible with shallower horizons correlating to lower absorbance ratio. The ratio range at S12 is approximately 4-7 and more variability seems to be present in comparison to S4. Differences with depth are hard to distinguish since the shallower lysimeters, 5, 10 and 20 cm depth, were sampled much less frequently than the deeper lysimeters. At the upslope site S22 (fig. 16) the variability in time and along the depth profile is high, with absorbance ratios shifting from around 0 to 15.
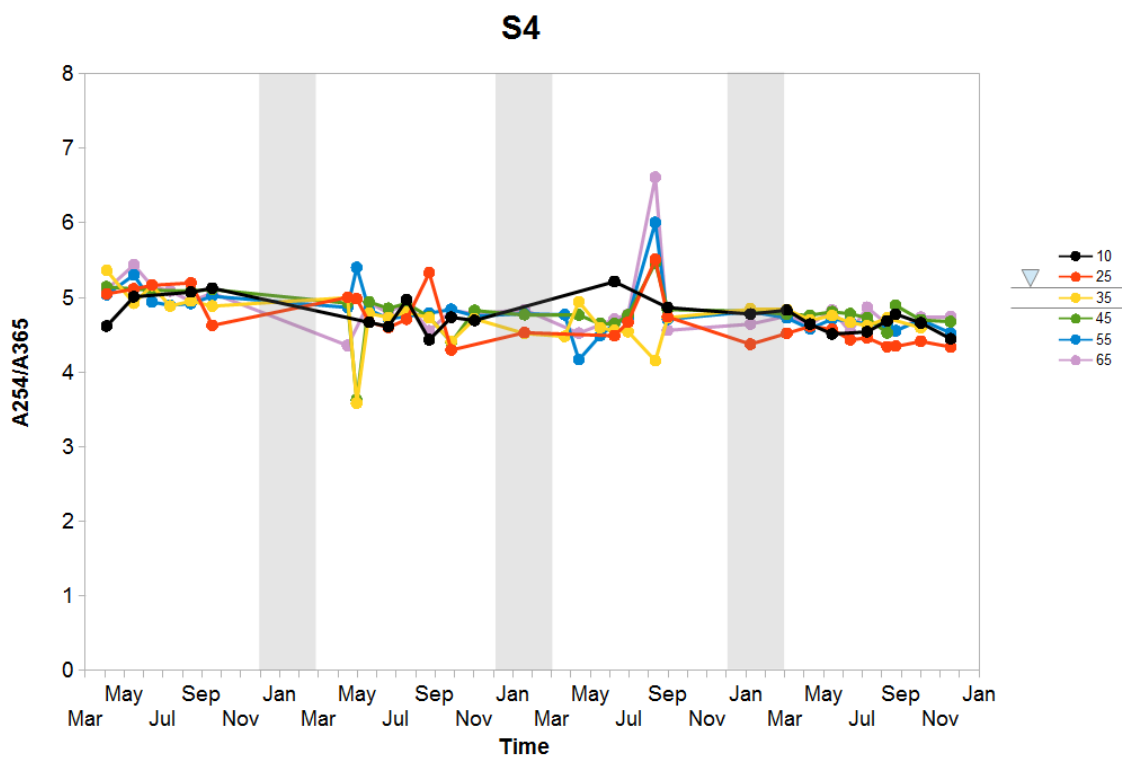

Figure 15. Seasonal variability (April 2009 to December 2012) of A_{254}/A_{365} at the riparian site, S4, in the S-transect. The colors illustrate the depth of the lysimeter position. The lysimeter depth in centimeter and the relative position of the groundwater table is displayed in the legend. The winter seasons are marked with grey areas.
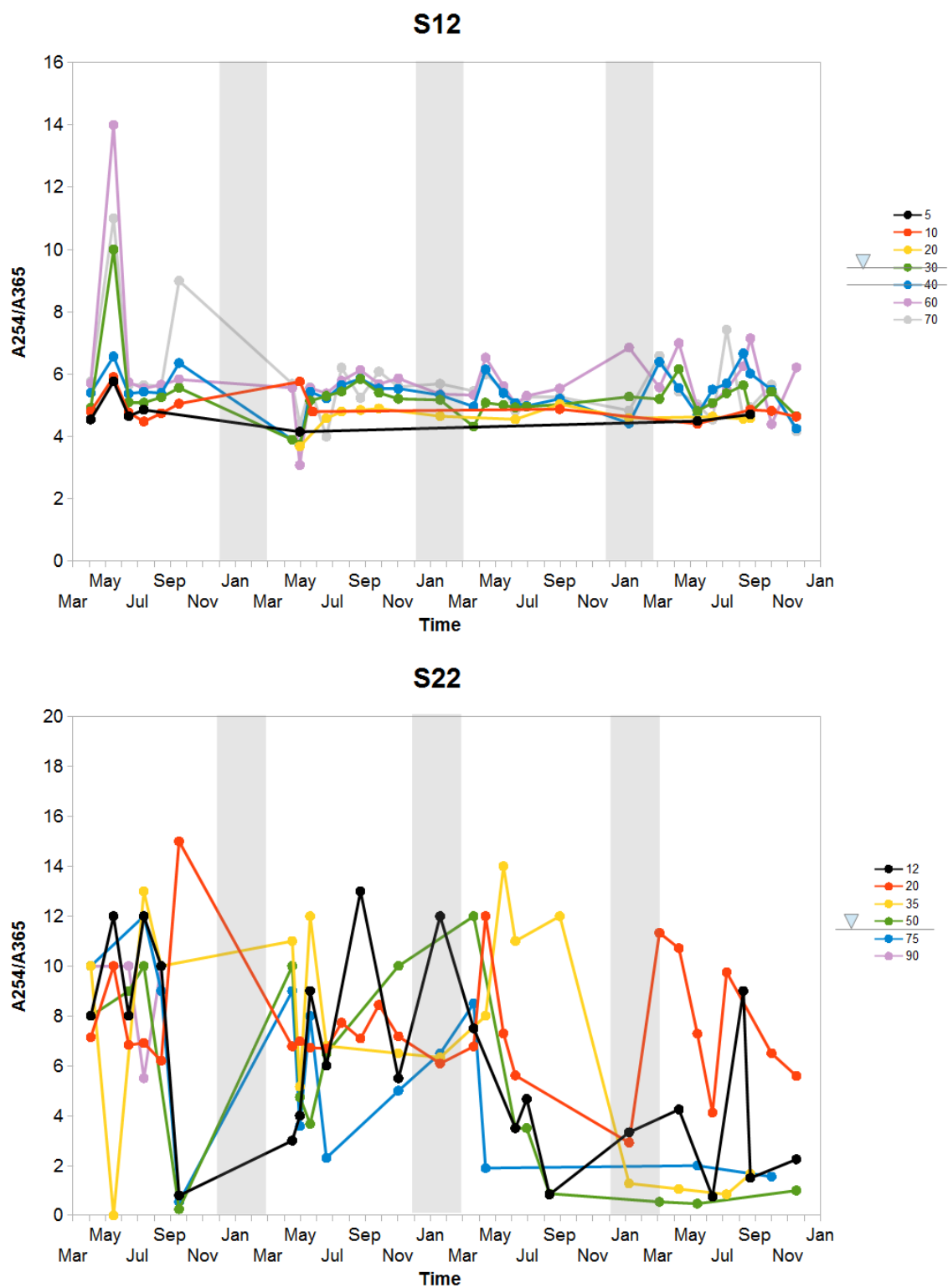
Figure 16. Seasonal variability (April 2009 to December 2012) of A_{254}/A_{365} at the upslope sites, S12 and S22, in the S-transect. The symbol system is the same as in figure 15.

6. Discussion

Following the same structure as the presentation of the result, the DOC concentrations and character will be discussed separately.

6.1. DOC concentration

6.1.1. General trends

The result did reflect the fact that organic soil is a source material for DOC (Kleber & Johnson, 2010) by displaying a clear correlation between the DOC concentration in the soil water and the carbon content of the soil. Organic horizons did, in general, accommodate soil water with higher DOC concentration in comparison to more mineral horizons. As a consequence the riparian sites, with high content of organic matter all through the soil profile, displayed higher levels of DOC in the soil water than the upslope mineral sites. An exception from this tendency was site U35. At this site samples revealed a low carbon content in the soil while the collected soil water, contained high levels of DOC. Explanations for this are not obvious. One hypothesis is that spatial variation in vegetation (on the ground surface or in the form of roots) provided carbon easily dissolved at this site. Local variation in pH, promoting the dissolving processes (Kleber & Johnson, 2010), could also perhaps have led or contributed to this result. The dataset available for this study was not sufficient to better understand the relatively high DOC concentration at U35.

Another difference, between organic and mineral soils, was the level of variability in the DOC concentration. The DOC concentration in the water from mineral horizons displayed more stability. Together with the concentration of DOC being low in these horizons, this supports the theory of DOM sorption in mineral soils removing carbon from solution (Dahm, 1981; Kaiser & Guggenberger, 2000).

6.1.2. ROK-transects

The seasonal trend during summer and autumn (2013), at all the riparian sites in all the ROK- transects, was that the concentration of DOC increased in the soil water. This followed the hypothesis that primary production and high bacterial activity are the factors controlling the level of soil water DOC during high temperature seasons (Christ & David, 1996).

During the following winter, the main trend (displayed at site R5, R10 and U35) was that the concentration of soil water DOC decreased. The reason for this decrease could be low DOC input in combination with continued DOC consumption by bacteria. If this is the case, the DOC in the soil under the snow cover is mineralized into CO_2 or CH_4 (Glazel et. al., 2004) that either stays in the solution or escape to the atmosphere. Another possibility is that the DOC was flushed in late autumn rain events (Dyson et. al., 2011), which the long period with no data during the winter season would hide. To be able to rule out one or the other of the suggested processes more frequent sampling would have been required. Analysis of CO_2 in the samples would also provide helpful information.

Showing an opposite trend during the winter season, the lysimeter at 15 cm depth at site U36 is displaying an increase in DOC concentration. Similar to site U35, this result could reflect the influence of spatial variation, regarding vegetation and pH, on DOC concentration. It should also be mentioned that it is this measurement which

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causes the DOC increase during winter in the organo-mineral horizons of the ROK-transects (fig. 10), as this was the only sample extracted from this category during the winter campaign.

Site U37 displayed no change in DOC concentration by season or by depth. The high mineral content in the soil is probably making the DOM sorption the dominant factor controlling DOC concentration at this site.

The results from the ROK-transects reflect how DOC concentrations in the horizons of boreal hillslope profiles change during a warm winter condition. Likely is that the trend would be different during other temperature conditions (Haei et. al., 2010), with for example more or less extensive soil frost (Ågren et. al, 2012). In addition to climatic setting, global warming is therefore an important factor to consider in the quest for understanding the present and future winter seasonal dynamics of soil water DOC in different geographical regimes.

6.1.3. S-transect

Site S4 at the S-transect displayed a general cyclic pattern consistent with the hypothesis of DOC fluctuations during summer, autumn and spring. The changes in DOC concentration in combination with the precipitation and discharge data suggest effects of lateral flushing and dilution (Rodhe et. al., 1989; Bishop et. al., 2004; Dyson et. al., 2011), both related to snow melt and summer/autumn rain events. The difference in the response along depth profile is likely an effect of the position of the groundwater level and the amount of infiltrating water.

During the winter seasons 2009 and 2010 the general decrease in DOC at S4 could, similar to the riparian zones at the ROK-transects, be related to DOC mineralization and flushing events. The fluctuation observed in the winter 2011, when the shallower lysimeter horizons display a rapid decrease in DOC concentration at the same time as the lower horizon accumulate DOC in the soil water, is possibly related to another process. In the study conducted by Ågren et. al. (2012), DOC freeze out due to soil frost is described as a process increasing DOC concentrations in the deeper parts of the soil profile. The ice developing from the top of the soil profile transport the DOC downward, as the organized structure in the ice crystals are unwilling to accommodate these organic molecules. This process may explain the fluctuations in the winter 2011 at site S4, since the variation in the DOC concentration is accompanied by a significant temperature decrease and potentially a significant soil frost. Unfortunately no data of soil frost depth was available for the sites and time of this study.

According to the data available at the upslope sites S12 and S22 the DOM sorption seemed to be dominating over the seasonal trends due to the mineral composition of the soil. Low frequency in successful extraction of samples from the shallower horizons at site S12 is though possibly hiding larger variability.

6.2. DOC character

6.2.1. ROK-transects and the S-transect

A clear trend of low absorbance ratio and high SUVA was observed in the organic horizons of all transects while the opposite was observed for the mineral horizons. This was an expected result which indicated higher content of high-weight and

aromatic molecules in the soil solution of more organic soil (Weishaar et. al., 2003; Ågren et. al., 2008).

That no change in absorbance was displayed, along with decreases in DOC concentration possibly related to bacterial mineralization, suggests that different fractions may be limited and that there is organisms present in the soil specialized in consuming the carbon of the available character.

The high variability in the DOC character in soil horizons with high mineral content could be an indication of the high temporal and spatial variability of the organic carbon in these soil bodies. On the contrary, the peat at the riparian sites forms a more stable source of organic carbon molecules. It is though important to take into account that the accuracy of absorbance depends on the concentration of DOC. The measurement errors, in the data from the upslope sites, are probably enhancing the variability to a great extent due to the low DOC concentration at these locations (especially site U36 and U37).

A chemical process affecting the A254/A365 and the SUVA254, suggested by Maloney et. al. (2005) and Köhler et. al. (2013), is mobilization of aluminum and iron. This could also have an influence on the data, increasing the absorbance in the soil water samples.

7. Conclusion

The organic content of the soil was reflected in the DOC concentration and character of the soil water. Soil water from horizons with high percentage of organic matter contained higher concentrations of DOC, with a higher fraction of high-weight and complex molecules (Weishaar et. al., 2003; Ågren et. al., 2008), compared to soil horizons with low organic content. The concentrations of DOC were also observed to be more varied in the soil water from organic horizons than in the soil water from mineral horizons.

Regarding the variability of the DOC character, the absorbance analysis revealed higher variability in the mineral horizons than in the organic horizons. Since the potential error in the absorbance measurement increases with lower DOC concentration, the true variability of the DOC character was though probably lower than shown in the figures of this study.

At the riparian sites, the DOC concentration seasonality was dominated by an increase in the summer/autumn and a decrease in the spring, likely being the result of increased primary production in combination with bacterial activity (Christ & David, 1996) and lateral flushing during snow melt (Ågren et. al., 2007; Buffram et. al., 2007; Köhler et. al., 2009). Rain fall events during summer and autumn were effecting the DOC concentrations intra-seasonally, by diluting and flushing the DOC in the soil horizons (Rodhe, 1989; Bishop et. al. 2004; Dyson et. al., 2011). The main seasonal trend during winter was that the DOC levels had decreased. The reasons for this decrease were in this study thought to be bacterial mineralization (Glazel et. al., 2004) or late autumn rain events. Fluctuations in the DOC concentration, likely to be related to DOC freeze out (Ågren et. al., 2012), were also observed. The sites upslope and the mineral horizons remained relatively stable throughout all seasons, supporting theories of DOM sorption (Dahm, 1981; McDowell, 1985; Hope et. al., 1994) as a strong control of DOC concentration.

8. Acknowledgement

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