

# Organic carbon fluxes in a boreal catchment – spatial variability of bioavailability and importance of the riparian zone

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## ABSTRACT

Organic carbon as an important water quality factor was investigated in 13 riparian zones (RZs) and 14 stream sites in the 67 km<sup>2</sup> boreal Krycklan catchment in Northern Sweden during 2008 to 2009. For comparisons of up- and downslope locations, also three sites with different distances to the stream were analysed. The RZs are characterized by various hydro-morphological soils while stream sites differed in land use type. The study aimed at clarifying connections between riparian and stream water focussing on spatial variability of the bioavailability of total organic carbon (TOC) in RZs and streams. Objectives were to test whether the hydrochemical signal of stream TOC character is created in the RZ or in upslope locations, and analyse the spatial and temporal variability of TOC in soil and stream water as well as at up- and downstream locations all over the catchment area. Investigations were based on TOC concentration and exports as well as the biologically-relevant indices absorbance ratio  $A_{254}/A_{365}$  and specific ultraviolet absorbance (SUVA<sub>254</sub>) index. In direct comparison, riparian soils and (first-order) streams agreed better in biological indices than TOC exports with the latter varying more than related  $A_{254}/A_{365}$  and SUVA<sub>254</sub>. The ranges of organic carbon concentrations were quite similar in streams and riparian soils. The biological indices were mainly consistent. High  $A_{254}/A_{365}$  and low SUVA<sub>254</sub> values both indicated good bacterial growth and bioavailability of TOC. Volume-weighted biological indices matched well comparing RZs and streams -independently of soil type classification or related land use type-, indicating exports of similar carbon character with almost the same aromaticity and expected bioavailability from both locations. This again emphasizes the hypothesis of RZs as playing a key role in determining the chemical status of streams. At the whole-catchment-scale, up- and downstream locations showed similar decreasing TOC export tendencies in downstream direction with higher temporal and spatial variability in RZs and the same carbon bioavailability by volume-weighted  $A_{254}/A_{365}$ . The volume-weighted SUVA, however, did not give such a clear picture. In conclusion, biological indices were useful in characterizing and assessing bioavailability of organic carbon between different locations; but research questions remained.

# 1 INTRODUCTION

Awareness grows regarding water as an essential element on Earth in terms of life cycles and special ecosystems which, however, is increasingly threatened and therefore needs to be protected in a sustainable way in landscape scale (Buffam et al., 2007). Aquatic ecosystems are highly connected to and influenced by the surrounding areas. In Northern Sweden this refers mainly to boreal ecosystems and landscapes playing a key role for the streams and lakes in a catchment (Laudon et al., 2004a).

Water coming from a catchment area takes many dissolved substances, i.e. former solid chemical compounds solved in water in this case, with it on its way to surface water bodies, including large amounts of organic carbon coming from the soil. As main sources of this dissolved organic carbon (DOC) the organic top soil layers of the riparian zones (Findlay et al., 2001; Bishop et al., 2004) and organic podzol soils of conifer forests can be stated (Kortelainen and Saukkonen, 1998; Mattsson et al., 2003) together with wetland ecosystems in general (Creed et al., 2003). Boreal forests and mires store about 50% of the total soil organic carbon worldwide (Schlesinger, 1997). Changes in land use, pollution events as well as climate change can influence the amount of DOC in water bodies with high further impacts on water chemistry and living organisms in surface waters (Schindler, 1997). Moreover, few studies (e.g. Ågren et al., 2007; Buffam et al., 2007) in boreal ecosystems showed that small catchment basins strongly modify the chemical properties, and especially total organic carbon (TOC), of bigger streams of meso-scale catchments.

Generally, TOC can be split into dissolved organic carbon (DOC) and particulate organic carbon (POC) where DOC contains all particles smaller than 0.45  $\mu\text{m}$  (Stumm and Morgan, 1996). Several regional studies for Swedish streams and lakes showed that the fraction of POC is negligible compared to DOC which dominates with ~95% (Ivarsson and Jansson, 1995; Laudon and Bishop, 1999, Köhler et al., 2002a; Ågren et al., 2008b). Thus, TOC is a good proxy for the concentration of DOC in these surface waters (Laudon et al., 2004a, Löfgren et al., 2010) and used as main term in this study.

### **1.1     *The riparian zone***

Within the last few meters of land close to a stream or lake, the riparian zone (RZ) is located as an interface between the terrestrial and aquatic ecosystems. Hence, the RZ has a main function in terms of hydrochemistry within a catchment particularly regarding processes in short-term perspective (Fiebig et al., 1990; Hill, 2000; Buffam et al., 2001) and carbon export from terrestrial to aquatic systems (Bishop et al., 1990; Hinton et al., 1997). Even though RZs are found on less than 5% of the total catchment area in Northern Sweden, they still count for the major part of TOC which gets exported to boreal streams. While water passes from upslope areas through the soil profile of the RZ, it gets in contact with chemical characteristics of the soil at the scale of hours to days (Bishop et al., 2004) which can change the amount and composition of dissolved substances in the water. Hence, organic carbon quantity increases significantly compared to upslope concentrations (Bishop et al., 1990; Laudon et al., 2007; Köhler et al., 2009). This is even more pronounced in terms of high flow (Bishop and Pettersson, 1996) because superficial soil layers contain higher organic carbon concentrations (Bishop et al., 2004). Thereby, rising groundwater levels allow the connection and activation of upper organic carbon-rich soil horizons to the water flow (Bishop et al., 2004; Petrone et al., 2007).

Transport of carbon is not only discussed as carbon dioxide or methane emissions being released from (wetland) ecosystems into the air (e.g. Moore and Knowles, 1989; Granberg et al., 2001; Heikkinen et al., 2002), also the export of organic carbon from boreal ecosystems to streams and its impact to catchments was investigated by many scientists (e.g. Moore et al., 1998; Pastor et al., 2003; Laudon et al., 2004a; Ågren et al., 2007), highlighting the important position of TOC in carbon budgets (Cole et al., 2007). This organic carbon is considered to play a key role in many biological and geochemical processes in surface waters in the boreal zones (Laudon et al., 2004a).

### **1.2     *Forested and wetland-dominated catchments***

In the last years, more attention was spent on boreal forest ecosystems which often show higher TOC concentrations in their surface waters compared to temperate forests (Laudon et al., 2011). This in turn illustrates

a more important role of these regions in global carbon cycling context. Certainly, the TOC concentrations in boreal streams vary in space and time (Köhler et al., 2008), also dependent on hydrological and soil characteristics and the local vegetation of the surrounding ecosystems (Tranvik and Jansson, 2002).

Boreal landscapes in Northern Sweden consist mainly of two different types: forests and wetlands, with the latter covering almost one quarter of the area (Laudon et al., 2004a). Arable land represents a small proportion here.. TOC character and concentration may spatially change depending on the percentage coverage of forests and wetlands in the area (Ågren et al., 2008b). Thereby, the spatial variability of TOC concentrations was found to be higher at base flow (and highest in headstreams draining wetlands) and low for larger stream size further downstream (Laudon et al., 2011). Generally, carbon concentration during high flow is related to the extent of a catchment and its properties (Laudon et al., 2011). This catchment area also shows a negative correlation to annual TOC export when computed for total drainage area and not for single subcatchments (Ågren et al., 2007). In addition, several other factors influence the annual export of organic carbon into water bodies. TOC export varies with flow or discharge (Ågren et al., 2007) and is strongly positively correlated with wetland coverage within a certain area, both seasonally and annually (Ågren et al., 2007; Buffam et al., 2007, Ågren et al., 2008a). Hence, TOC export rates are larger from wetland-mires than from forests (e.g. Raymond and Hopkinson, 2003, Ågren et al., 2007). Thus, wetlands are considered to be the major reservoir of TOC being leached into streams and lakes in boreal ecosystems (Dillon and Molot, 1997; Hope et al., 1997).

Besides, TOC concentrations as well as exports decrease from highest values near headwater locations to sites further downstream with higher stream order (Mattsson et al., 2003; Temnerud and Bishop, 2005). Reasons for this observed spatial pattern can be changes in flow pathways that the water takes through the soil towards streams as well as changes in soil composition: For instance, larger shares of postglacial sediments at lower downstream catchment parts are able to better adsorb organic material and therewith, the export of TOC from sediment-rich sites may be reduced (Kalbitz et al., 2000). Small headwaters form the main source of



TOC export per unit area and therefore influence the export of organic material disproportionately strongly (Ågren et al., 2007).

The chemical composition in a stream is in short-term controlled by the RZ in an inter-annual scale (Seiberg et al., 2009). Within one year, the carbon export varies but is estimated to be more constant in wetlands (Laudon et al., 2004a). Thereby, TOC concentration is mainly dependent on precipitation events during the snow-free season (May to November; Köhler et al., 2008). Apart from that, carbon concentration and export to streams are enhanced for forested zones compared to wetland-mires during wet years (Köhler et al., 2008).

However, the carbon export rate is found to be relatively stable during the snow melting period (spring flood) in April and May with linearly correlated TOC export with water quantity (being present as snow during winter, turning into water through melting) in both forested and wetland-dominated catchments (Hagedorn et al., 2000; Köhler et al., 2008). During high flow, the importance of forests rises as they form the major source of TOC being exported within a catchment (Schiff et al., 1998; Kendall et al., 1999; Laudon et al., 2004a; Laudon et al., 2011). In this period, organic carbon coming from a forested site increases in concentration, while it demonstrates an opposite trend when leached from a peat-forming wetland i.e. a mire (Köhler et al., 2008). Explanations may be, firstly, larger dilution effects for TOC coming from wetlands (Schiff et al., 1998) and secondly, additionally activated soil layers closer to the surface in the RZ of forested ecosystems which are rich in organic substances (Kendall et al., 1999; Bishop et al., 2004). Within forested catchments, riparian peatlands were identified as main source of TOC exports by some studies (e.g. Bishop et al., 1993; Creed et al., 2003). Complementary to this, in the situation of low flow -as for instance in winter months- organic carbon concentrations are higher in streams draining wetlands than in those originating in forested areas (Buffam et al., 2007; Ågren et al., 2008b). Laudon et al. (2011) summarizes the origin of organic carbon as predominantly wetlands at low flow conditions and forest areas during high flow times.

Furthermore, exports of organic carbon vary with specific tree vegetation during the snow-melting period and snow-free season: Norway spruce generally produces higher amounts of litter than pine trees, resulting in

increased leaching of organic substances into the soil as well as larger TOC exports (Strobel et al., 2001).

In general, flow pathways differ between forested and wetland sites during the snow-melting period with high flow conditions. In forests, water mainly infiltrates into the soil and passes through the top soil (subsurface flow path) with only 10-30% of 'new' or 'event' water (Laudon et al., 2007) flowing into a stream or lake (Fig. 1.a). This includes the possibility of activation of more organic-rich soil layers closer to the surface and export of new TOC from the site (Bishop et al., 2004). In contrast, water coming from wetlands shows a larger share of overland flow due to a continuously frozen soil layer close to the surface, resulting in >50 % of 'new' or 'event' water totally (Laudon et al., 2007, Fig. 1.b).

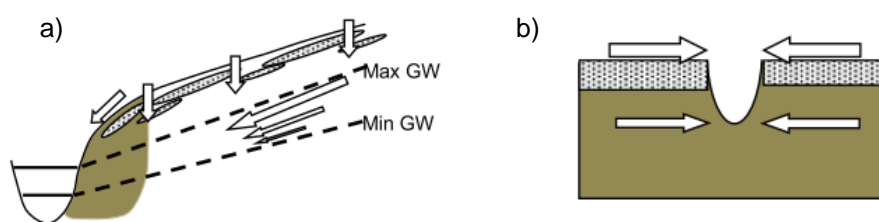


Figure 1: Flow pathways of water flowing from an upslope area towards a stream for **a)** a forested catchment with mainly subsurface flow (coloured part illustrates riparian zone; GW = groundwater level) and **b)** a wetland-dominated catchment with higher proportion of overland flow (shaded part shows frozen soil surface layer); taken from Laudon et al., 2011.

### 1.3 Interactions of soil and water

In boreal landscapes, different factors influence the chemical status of stream water: catchment properties, size of the stream, flow and season (Ågren et al., 2007; Buffam et al., 2007). Thereby, TOC is found to play a key role with regard to water quality in the streams (Shafer et al., 1997; Hruška et al., 2003). Due to the fact that the chemical properties of various TOC sources within a catchment area may differ, information can be gained by water chemistry analysis about which soils (and therewith specific areas) of a catchment are connected to a stream for different hydrological events (Hood et al., 2006).

Amongst others, two hydrological parameters related to TOC concentration determine water quality: temperature and pH value. Rising temperatures are correlated with increasing organic carbon production (Christ and David,

1996b) which is even more pronounced during wet years (Köhler et al., 2008). Regarding the second factor, the concentration of TOC markedly influences the pH values in soils (Hruška et al., 2003) and boreal surface waters (Köhler et al., 2002b); the latter is especially noticeable during high runoff periods (Laudon and Bishop, 2002). The strong association of organic carbon with organic acid concentrations and therefore with low pH values may cause acidic conditions in wetlands of boreal catchment areas (Urban et al., 1989). In addition, organic carbon has an effect on export of other elements like metals (Bishop et al., 1995) through binding and transporting these substances which can also impacts the water quality. An example for this may be the reduced toxicity of aluminium bound to organic carbon (Cory et al., 2006).

Several studies demonstrated that TOC concentrations are increasing with rising water levels in the RZ for streams draining forests (Findlay et al., 2001; Bishop et al., 2004; Ågren et al., 2008b; Köhler et al., 2008). In riparian soils, carbon amounts in the soil water depend on the soil layers that got activated by the water flow taking different pathways through the soil (Bishop et al., 2004; Lyon et al., 2011). Thereby, high groundwater tables in the soil result in larger TOC concentrations due to increased surface-near organic matter production found in the riparian soils (Grabs et al., 2010; Lyon et al., 2011) which is enhanced by raised soil wetness and temperature (Christ and David, 1996a, 1996b; Köhler et al., 2008). Especially moraine soils are able to build up thick peat layers (Ågren et al., 2007) -mainly at wet and humid locations- that lead to large carbon export from these sites particularly from the upper soil horizons. This was further confirmed when looking closer at the soil profile: TOC concentration decreases with increasing soil depth (Bishop et al., 2004; Seibert et al., 2009; Lyon et al., 2011). Moreover, a higher proportion of aliphatic substances is analysed for water-soluble organic carbon when located closer towards the soil surface in forest ecosystems (Van Miegroet et al., 2005). In climatic terms, the groundwater level in the RZ may increase in cold, i.e. low evapotranspiration, or wet conditions into top soil layers which are rich in organic substances and thus connected to the downslope water flow (Köhler et al., 2008), exporting carbon into surface waters. This is not expected to happen in case of higher evapotranspiration than precipitation, resulting in low groundwater levels in the soil, including also the RZ (Köhler et al., 2008).

In contrast to wetter conditions, dry soils with low groundwater tables are characterized by faster metabolism of organic matter into CO<sub>2</sub> and a basically thinner organic layer in well-aerated soil conditions (Grabs et al., 2010), resulting in less TOC quantity. Possible reasons are potentially smaller microorganism numbers (indicated by lower bacterial growth efficiency) together with reduced carbon availability (Marschner and Kalbitz, 2003) and lower degradation rates of organic matter. This leads to higher amounts of heavy and aromatic organic carbon compounds remaining in the soil while smaller (aliphatic) compounds may have reacted and expired in form of CO<sub>2</sub>.

One important concept for the RZ describes the complex interactions between soils and surface waters: the 'double paradox' of runoff generation by Kirchner (2003). This concept indicates a rapid response to extreme events, for instance heavy rainfall, to be noticed at the discharge area as large amounts of 'old' or 'pre-event' water with varying chemical properties investigated via isotope measurements. Bishop et al. (2004) confirmed this double paradox concept for the boreal areas of Northern Sweden by explaining the first paradox (rapid mobilization of pre-event water) with the transmissivity feedback mechanism (Bishop et al., 1990). According to this mechanism, rising groundwater levels lead to lateral soil layers of high hydraulic conductivity close to the surface of a soil profile getting activated, which in turn supports large volumes of water flowing off an area (Bishop et al., 2004). A juxtaposition of lateral flows in the vertical soil profile of a RZ is used to validate the second paradox (chemical variability of pre-event water). In practical terms, the double paradox can be used to identify human impacts on water quality and quantity regarding generated runoff, including hydrological and biogeochemical processes (Bishop et al., 2004).

This influence on hydrochemistry with focus on organic carbon is described in more detail by Seibert et al. (2009) using the Riparian Profile Flow-Concentration Integration Model (RIM) to demonstrate the interplay of integrated flow and concentration (varying with soil depth) and the varying chemistry of stream water (Bishop et al., 2004).

#### **1.4 Bioavailability of organic carbon**

TOC exported from the landscape represents an important source for microorganisms (Jansson et al., 2000), especially in terms of biological growth (Jansson et al., 2007). Depending on the source and on previous microbial degradation of the carbon compounds (Buffam et al., 2001; Kalbitz et al., 2003) as well as the type of exported carbon the bioavailability in a water body differs. This is also confirmed for higher-order streams draining forests by Berggren et al. (2007). Thereby, the quality of organic carbon influences bacterial growth efficiency, i.e. bacterial production per unit of assimilated carbon (Del Giorgio and Cole, 1998), which is also related to nutrient availability (nitrogen, phosphorus; Del Giorgio and Cole, 1998). Berggren et al. (2007) showed more pronounced nutrient limitation for bacterial production in case of streams coming from forested areas compared to wetland-mires. In the Västrabäcken catchment in Northern Sweden, limitation in nutrients comes along with excessive carbon availability (Berggren et al., 2010).

When organic carbon is consumed by bacteria, the majority gets lost through respiration and is not converted into growth (Del Giorgio and Cole, 1998). Apart from that, photodegradation of TOC may take place (Bertilsson and Tranvik, 2000). Bacterial production through consumption of organic carbon in the aquatic systems plays an important role in terms of microbial food chains (Azam et al., 1983; Jansson et al., 2007), directly influencing the function of food webs in the water by a positive correlation of production of bacteria and phytoplankton (Cole et al., 1988; Berggren et al., 2010).

TOC from forest soils seems to encourage microorganisms more than carbon exported from mires due to its specific properties (Berggren et al., 2007; Ågren et al., 2008a), resulting in higher bacterial production and growth efficiency in streams (Berggren et al., 2007). One reason may be aromatic compounds: carbon exported from forests showed less aromatic structures than organic carbon coming from mires (Kalbitz et al., 2003) which goes along with higher potential uptake by microorganisms for forest-derived carbon (Köhler et al., 2002a).

Within the different types of organic carbon, low-molecular weight (LMW) TOC fractions contribute more to bacteria growth than complex organic molecule (Tranvik and Jørgensen, 1995); Berggren et al. (2010) also

confirmed this fact for streams in boreal landscapes like in Northern Sweden. This LMW TOC may originally be released by mycorrhizal fungi and plant roots or leached from dead roots or litter as LMW organic acids (Van Hees et al., 2006). For microorganisms in boreal aquatic systems, the LMW DOM coming from terrestrial sources is directly available and forms an important source for bacterial production (Berggren et al., 2010). In this context, temporal variation was noticed: the spring flood period is the main event of large export of highly bioavailable TOC from forested sites (Ågren et al., 2008a) -due to higher organic carbon quantities coming from forest areas- which may fully count for all bacterial production (Berggren et al., 2010). Thereby, the carbon input to streams and lakes seems to be larger than biological exhaustion rates (Ågren et al., 2008a).

To further characterize the composition of organic carbon with regard to bioavailability, two indices were investigated in this study: absorbance ratio  $A_{254}/A_{365}$  and  $SUVA_{254}$  index. The absorbance ratio correlates the measured absorbance at two wavelengths (254 and 365 nm) with each other; the outcome provides information about the molecular weight of TOC since both parameters are negatively correlated (De Haan, 1993; Dahlén et al., 1996). Moreover, the ratio  $A_{254}/A_{365}$  shows a positive correlation with bacterial production as a study from Northern Sweden indicated (Berggren et al., 2007). The specific ultraviolet absorbance ( $SUVA_{254}$ ) of carbon is calculated by dividing the absorbance at 254 nm by the measured TOC concentration (Ågren et al., 2008a). This factor is positively correlated with the fraction of aromatics in TOC (Weishaar et al., 2003; Fu et al., 2006): the larger the  $SUVA$  value, the higher the aromaticity of organic carbon. According to Perdue (1998), these large aromatic compounds result in lower bioavailability of TOC compared to carbon with higher aliphatic fractions.

### **1.5 Objectives**

This study concerns spatial variability of organic carbon and its bioavailability in riparian soil and stream water from a two-year investigation in the boreal Krycklan catchment in Northern Sweden. Thereby, the report aims at testing the following hypotheses:

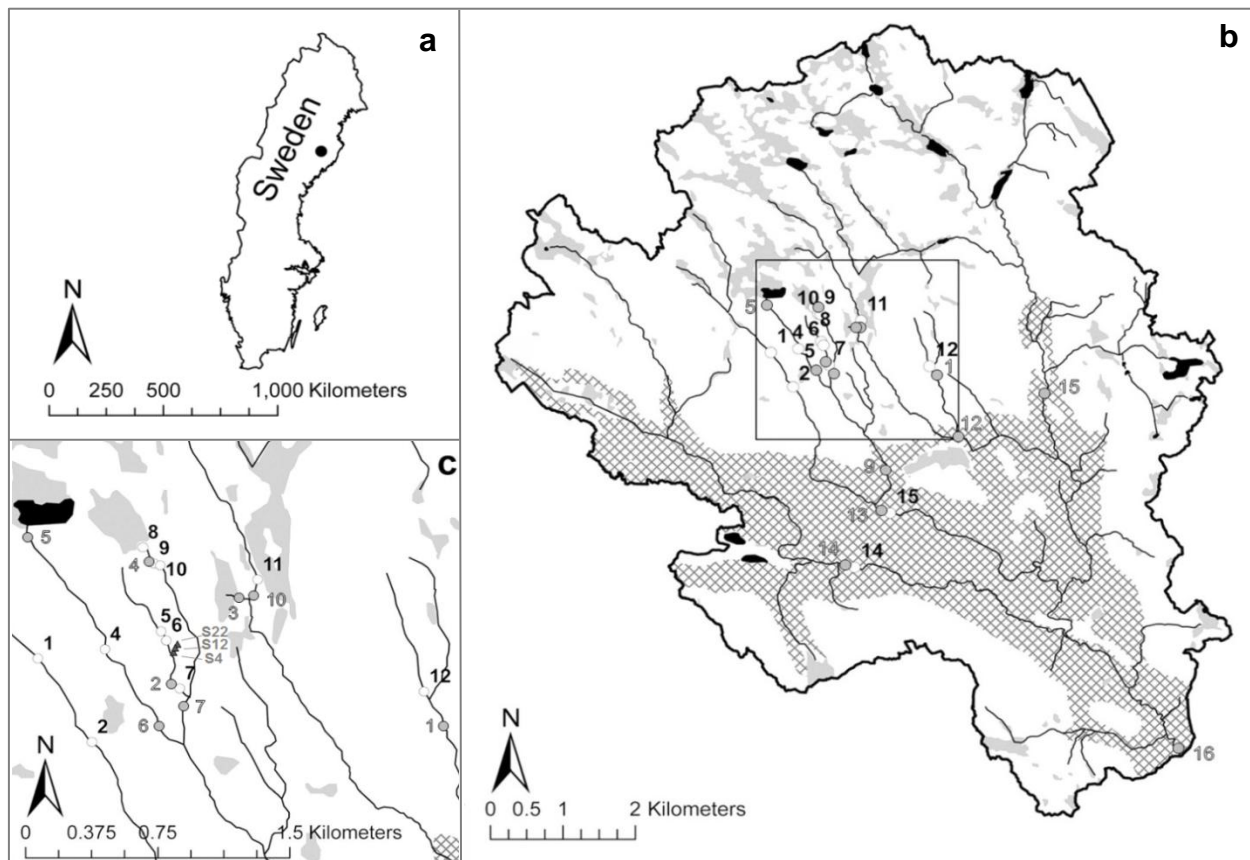
- Regarding riparian soils, the objective is to investigate distinctions of TOC quality within the soils of RZs which vary in hydromorphological soil parameters, for instance, less bioavailable carbon in sediment soils. Since RZs have been hypothesized to control the water chemistry in streams, this should also be shown for organic carbon character to test whether the chemical signal is created in the RZs (and not at upslope locations) and influence the hydrochemical situation in the streams.
- For streams, TOC character with regard to varying land use in forest- and wetland-dominated subcatchments shall be examined to identify differences in bioavailability.
- In the end, interactions between RZ and stream water are analyzed from a hydrobiochemical point of view by comparing export fluxes and bioavailability for a few special cases from riparian soils with (mainly first-order) streams as well as up- and downstream locations all over the Krycklan catchment.

In order to formulate statements about the bioavailability of organic carbon, calculated exports of total organic carbon in riparian soils and streams as well as the (volume-weighted) quotients of absorbance ratio  $A_{254}/A_{365}$  and  $SUVA_{254}$  index were used.

## 2 MATERIAL & METHODS

### 2.1 Study site description

This study was based in the Krycklan catchment in Northern Sweden, which is located near Vindeln (64°14' N, 19°46' E), approximately 50 km northwest of Umeå (Grabs et al., 2010; see Fig. 2). The catchment consists of a total drainage area of about 67 km<sup>2</sup> and stretches out from 130 to 369 m above sea level (Cory et al., 2006). Scientific observations in this forested region started already in 1923 with the implementation of the Svartberget research area (Wallin et al., 2010). Within the last decades, many studies were carried out focusing on biogeochemical aspects and hydrological variability in RZs and their function within catchments. Since October 2007, the Riparian Observatory in the Krycklan Catchment (ROK) supports the work and cooperation between researchers within the field of boreal hydrology in this mesoscale catchment that is stated to be representative for a typical boreal forested area (Grabs et al., 2010).



**Figure 2:** Location of the Krycklan catchment in Northern Sweden (a), including the locations of 13 Riparian Observatories (white circles, black numbers) as well as the 14 monitored streams (grey circles, grey numbers) (b) and detailed including the S-transect sites (dark grey triangles, grey S-numbers) (c); changed after Lyon et al., 2011. - Note that R3, R13, C8 and C11 do not exist in this study.



The main soil types in the catchment are glacial tills and peat (Ågren et al., 2008a), underlain by gneissic bedrock. Especially in the upper moraine parts of the area at higher elevations, organic-rich peatland as well as small lakes and wetlands have developed (Grabs et al., 2010); here also many headstreams are found. At lower elevations, the catchment is dominated by sediment deposits where some streams of higher order are situated in the landscape (Buffam et al., 2007; Grabs et al., 2010). Further uphill and therewith at greater distance from surface waters, well-drained podzol is present in the area (Grabs et al., 2010).

The catchment is mainly forested (88 % coverage; Grabs et al., 2010) with domination of Scots pine [*Pinus sylvestris* (L.)] in upper locations and Norway spruce [*Picea abies* (L.)] as well as deciduous tree species like *Alnus* spp. or *Betula* spp. in lower areas with higher moisture content (Ågren et al., 2007; Grabs et al., 2010). In the more acidic and oligotrophic wetlands including mires (covering 8 %; Buffam et al., 2007), different *Sphagnum* (L.) moss species can be found (Ågren et al., 2008a). About 3 % of the catchment area is in agricultural use and the remaining 1 % covered with lakes. Since 1923 the forested catchment is monitored by researchers while forestry practices were still carried out on a low level (Grabs et al., 2010).

The climate of the Krycklan area is mainly characterized by long winters and short summers (Lyon et al., 2011) with lowest precipitation rates in spring time (Vedin et al., 1995). The annual mean values are approximately 1.7 °C as temperature and 612 mm as precipitation (Laudon et al., 2011); half of this is falling in form of snow (Haei et al., 2010). The snow cover occurs from October to May for 171 days per year on average (Ottosson-Löfvenius et al., 2003). Hence, the two months of snow melting (April and May) are considered to comprise the hydrological main event (Buffam et al., 2007), causing high flow from a catchment area. This represents about 40 to 60 % of the runoff of one year (Laudon et al., 2011) and thus, transports high amounts of organic matter (Berggren et al., 2010). Köhler et al. (2008) suggest about 50% of the precipitation leaves the catchment as discharge to surface waters, while the second half is evapotranspired.

## 2.2 Presentation of monitored riparian and streams sites

In this study, mainly two data sets from the Krycklan catchment area were used: samples from riparian zone as well as directly from stream sites.

### *Riparian zone*

13 riparian sites within the ROK (R1-15, note that R3 and R13 do not exist in this study; see Table 1) were conducted in riparian soils with differences in some hydromorphological parameters like the content of organic substances. All sampling sites were assigned to one of four different groups in terms of soil characteristics and groundwater table positions: dry, humid, wet moraine and sediment sites (see Table 1). Within the moraine soils, this distribution refers to median groundwater levels which are located at  $\leq -0.45$  m for dry,  $> -0.45$  to  $\leq -0.15$  m for humid and  $> -0.15$  m for wet moraine soils compared to the soil surface (Grabs et al., 2010).

**Table 1:** Characteristics and classification of the 13 monitored riparian zone sites of this study, after Grabs et al., 2010.

Site	Corresponding catchment	Soil characteristics	Soil classification
R1	Fulbäcken	mineral till	moraine, dry
R2	Fulbäcken	organic till	moraine, wet
R4	Stortjärnsbäcken	mineral till	moraine, dry
R5	Västrabäcken	organic till	moraine, humid
R6	Västrabäcken	organic till	moraine, humid
R7	Västrabäcken	organic till	moraine, humid
R8	Kallkällsmyren	organic till	moraine, wet
R9	Kallkällsbäcken	mineral till	moraine, dry
R10	Kallkällsbäcken	organic till	moraine, humid
R11	Stormyrbäcken	mineral-organic sediment, sandy	Sediment
R12	Renberget	mineral till	moraine, dry
R14	Åhedbäcken	mineral sediment, silty	Sediment
R15	Långbäcken	mineral sediment, silty	Sediment

In advance, landscape analysis was performed to determine the properties of different possible locations within the RZ by using a regional map (scale 1:100 000, Geological Survey of Sweden, Uppsala, Sweden) in combination with a terrain analysis. This was supported by the light detection and ranging (LIDAR) technique with a resolution of 1 m, followed by field excursions to better differentiate between varying moisture content and soil types (Grabs et al., 2010). The resulting terrain-specific digital elevation model (DEM) with a 5 m resolution based on the LIDAR data and with stream network data included was then evaluated with help of the software SAGA GIS (Böhner et al., 2008; Conrad, 2007), containing information about the slope, contributing upslope areas as well as the topographic

wetness index (Beven and Kirkby, 1979) to describe the position of the groundwater table. More details are described in the manuscript of Grabs et al. (2010).

Additionally to the 13 ROK sites, another three sampling sites (S4, S12 and S22) of the so-called S-transect located in the Västrabäcken subcatchment were included in the analysis (see Fig. 2.c). These sites distinguished in their distance to the stream (4, 12 and 22 m, with S4 being situated in the RZ) as well as soil characteristics and therewith contributed to the hydrochemical conditions in the streams to different degrees. This data was mainly used for comparisons of up- and downslope locations with the aim to further test whether RZs influence the stream situation with regard to carbon quality (Creed et al., 2003; Hruška et al., 2009; Seibert et al., 2009, Borken et al., 2011).

#### *Stream sites*

Besides the monitored RZ and S-transect sites, this study also includes 14 stream sites corresponding to 14 (partly) nested subcatchments (C1-16, note that C8 and C11 do not exist in this study; Table 2) in the same catchment. Therefore, data collection took place from January 2008 to December 2009 with temporal variation between every two days during the spring flood period to monthly samplings during winter months with low flow situation. These monitored stream sites cover a range of first to fourth order and mainly two different land use types: forests and wetlands (proportions see Table 2). For reason of characterization, each corresponding catchment is assigned to 'forest' (< 2% wetland coverage), 'mixed' (2-30 % wetland coverage) and 'wetland' (> 30 % wetland coverage; measured in percentage of wetland of total subcatchment area; division adopted from Buffam et al., 2007). Two sites (C1, C2) are related to 'forest' and three sites (C3-C5) are drained by a wetland-dominated area; for all other sites the corresponding subcatchment is categorized as 'mixed' (Table 2).

In order to delineate the subcatchments for the streams sites and their characteristics like land use or catchment area, a 50 m-grid DEM and topographical digital map (scale 1: 50 000, Lantmäteriet, Gävle, Sweden) was used in the programme ArcGIS 8.0, combined with field monitoring to further determine the catchment boundaries for all subcatchments smaller than 2 km<sup>2</sup> (Buffam et al., 2007).

**Table 2:** (Sub)Catchment description and characterization of the 14 monitored stream sites C1 to C16 (without C8 and C11) of this study; data mainly based on Buffam et al., 2007.

Site	Associated catchment	Stream order	Land use type <sup>a</sup>	Area [km <sup>2</sup> ]	Forest [%] <sup>b</sup>	Wetland [%] <sup>b</sup>	Lake [%] <sup>b</sup>	Arable [%] <sup>b</sup>
C1	Risbäcken	2 <sup>c</sup>	forested	0.66	98.7	1.3	0	0
C2	Västrabäcken	1	forested	0.13	100.0	0	0	0
C3	Lillmyrbäcken	1	wetland	0.03	24.0	76.0	0	0
C4	Kallkälsmyren	1	wetland	0.19	59.6	40.4	0	0
C5 <sup>d</sup>	Stortjärnen Outlet	1	wetland	0.85	59.0	36.3	4.7	0
C6	Stortjärnbäcken	1	mixed	1.30	72.8	24.1	3.1	0
C7 <sup>e</sup>	Kallkälsmbäcken	2	mixed	0.50	85.1	14.9	0	0
C9	Nyängesbäcken	2	mixed	3.10	84.9	13.8	1.3	0
C10	Stormyrbäcken	3	mixed	2.90	74.2	25.8	0	0
C12	Nymyrbäcken	3	mixed	5.40	84.1	15.5	0	0.3
C13	Långbäcken	3	mixed	7.20	89.1	9.9	0.6	0.4
C14	Åhedbäcken	3	mixed	14.0	90.4	5.1	0.6	3.9
C15	Övre Krycklan	4	mixed	20.0	83.2	14.0	1.7	1.0
C16 <sup>f</sup>	Krycklan Outlet	4	mixed	67.0	88.0	8.3	0.7	3.0

<sup>a</sup> land use type based on wetland percentage of total subcatchment area; <2% wetland coverage = forested, 2-30% wetland coverage = mixed, >30% wetland coverage = wetland; after Buffam et al., 2007.

<sup>b</sup> percentage of total subcatchment area

<sup>c</sup> after Wallin et al., 2010

<sup>d</sup> outlet to a humic headwater lake

<sup>e</sup> representative discharge measurement for the whole catchment

<sup>f</sup> outlet of the total Krycklan catchment area, including all subcatchments

### 2.3 Discharge measurements

In 2008, the total discharge of 348 mm/y was slightly lower than in 2009 with 374 mm/y. Runoff measurements were conducted at the outlet of the stream site C7 with help of a 90 V notch in a heated dam house. The resulting specific discharge serves as estimation for calculations of all other sites for both, riparian soils and streams, assuming that this small 0.5 km<sup>2</sup> Nyänget catchment (= Svartberget catchment of stream site C7; see Table 2; Wallin et al., 2010) is representative for the whole Krycklan catchment area (Ågren et al., 2007; Laudon et al., 2007; Björkvald et al., 2008). Thereby, Laudon et al. (2004b) quantified the uncertainties in discharge measurement at site C7 to be +/- 5%.

### 2.4 Soil water measurements and calculations in the RZ

#### Soil water measurements

A pair of porous lysimeters (K100 ceramic suction cups - UMS©, with 1±0.1 µm pores; see Grabs et al., 2010) was installed at all RZ sites within one to two meters distance from a stream at five different depths (15, 30, 45, 60 and 75 cm below the soil surface). The installation of the measuring instruments occurred in upslope direction of the soil investigation pit

(approximately 1 m wide and deep) on the way the water takes down to the stream. Due to the lysimeter pore size, all particles  $>1\ \mu\text{m}$  diameter are filtered out in the riparian soil water (POC was found to be negligible; Laudon and Bishop, 1999; Ågren et al., 2008b). At each of these depths and all 13 riparian locations, manual soil water extraction took place to examine TOC concentration and the whole absorbance spectrum at nine occasions (also called campaigns): once a month in May, June, July, August, September and October 2008 (six in total) as well as in June, August and September 2009 (three times; see Grabs et al., 2010).

Before the actual soil sampling, about 50 ml of water was extracted to be abolished as a flushing procedure for all lysimeters (Grabs et al., 2010). Adjacent soil water was then collected in pre-evacuated and acid-cleaned Duran glass bottles (with 3.5 bars of pressure; Milli-Q® rinsed Duran vessels; see Grabs et al., 2010) within 24 to 48 hours at each lysimeter. The sampling occurred by suction with about 1 bar (100 kPa) of pressure (Lyon et al., 2011). All taken soil-water samples were stored under cool and dark conditions and usually frozen within one day to allow subsequent analyses. Measurements of total organic carbon were carried out by using a Shimadzu TOC-5000 analyser (Grabs et al., 2010). For the collection of groundwater data, pre-perforated PVC pipes were set up in the middle of each pit to serve as groundwater wells in between the lysimeter installations and the stream. The water level was monitored automatically on an hourly basis with help of water logging devices (Trutrack® capacitance rods; see Grabs et al., 2010).

Regarding the further calculations, average values per depth layer were determined from both TOC values of one pair of lysimeters if both lysimeters provide useable data (otherwise only one value was used for calculation). In consequence, one TOC value for each depth of every sampling location (13 sites) at all occasions (9 campaigns in total: 6 in 2008, 3 in 2009) should be obtained.

The absorbance spectrum was measured continuously from 190 nm to 510 nm (ultraviolet to visible light) using 1 cm quartz cuvettes in a Hewlett Packard 8452A diode array spectrophotometer (Ågren et al., 2008b); this procedure took place within 24 hours after sampling of the riparian soil water. Thereby, all cuvettes were cleaned every time before using and deionized water served as blank. Analyses were repeated for each soil

water sampling (each lysimeter of every depth of all sites). The absorbance  $A_\lambda$  [ $\text{m}^{-1}$ ] per length at a certain wavelength  $\lambda$  was calculated via  $A_\lambda = \frac{a_\lambda}{d}$  with  $a_\lambda$  being the unit less absorbance at a wavelength and  $d$  as pathlength [ $\text{m}$ ] (Ågren et al., 2008b). This parameter  $A_\lambda$  (in this study for  $\lambda = 254$  and  $365$  nm) is needed for further calculations to determine the absorbance ratio  $A_{254}/A_{365}$  as well as the specific ultraviolet absorbance ( $\text{SUVA}_{254}$ ) index at a wavelength of  $254$  nm by dividing by the TOC concentration:

$$\text{SUVA}_{254} = \frac{A_{254}}{\text{TOC}} \left[ \frac{\text{m}^{-1}}{\text{mg} \cdot \text{C} \cdot \text{L}^{-1}} \right].$$

#### *Export fluxes calculations*

Daily lateral fluxes of TOC from the 13 riparian observatories were estimated using the RIM approach (Seibert et al., 2009). For each of the nine campaigns, measured concentrations at each site were linearly interpolated to obtain continuous concentration profiles (in  $\text{mg/l}$ ). The continuous profiles were integrated with the water flux curve (dimensionless). The water flux curve for each site was estimated from the relationship between measured groundwater levels and specific discharge (Grabs et al., 2010). The integration was done only in the saturated part of the profile, i.e., below the measured groundwater table. Thus, daily flow-weighted concentrations were obtained. Flow-weighted concentrations (in  $\text{mg/l}$ ) were subsequently multiplied by the specific discharge in  $\text{mm/day}$  to obtain fluxes in  $\text{mg/m}^2/\text{day}$ . Daily concentrations and daily groundwater levels were necessary to calculate annual exports. Thereby, daily concentrations were easily estimated by linear interpolations between measured concentrations at each campaign for each depth and site. Daily groundwater levels were back calculated from the equation (Grabs et al., 2010) which established the relationship between observed values and specific discharge. Not all groundwater levels were measured in the two-year period of our study, therefore we decided to have a homogeneous group of data with only modelled values. Annual exports (in  $\text{kg/ha/y}$ ) were then easily calculated by summing up daily estimations.

Values of  $A_{254}/A_{365}$  and  $\text{SUVA}_{254}$  were treated analogously as TOC values to estimate fluxes. In those cases, a volume-weighted mean absorbance ratio and SUVA are obtained, rather than a traditional export. The volume-weighted means were given arbitrary units of  $\text{Abs/ha/y}$  and  $\text{SUVA/ha/y}$

since the objective was to compare relative values rather than analysing absolute numbers (Ledesma et al., 2012).

For the RZ and stream comparisons, analyses were based mean values of TOC exports and the related biological indices for the two corresponding months in 2008 and 2009 to determine similarities between riparian soil and stream water measurements and up- and downstream locations. For this reason, also averaged discharge was used for the two sampled years.

## **2.5 Stream water measurements and calculations**

### *Stream water measurements*

Measurements of TOC concentration and absorbance data took place at least once a month with higher frequencies of up to once a week during the main hydrological events, especially during the snow-melting period. Stream water samplings were taken using acid-washed 250 ml high-density polyethylene bottles after they were rinsed several times with stream water (Ågren et al, 2007). Further on, analyses of the water samples were carried out in the laboratory for different parameters, including organic carbon concentration and absorbance at different wavelengths.

The applied methods to determine these factors changed during the two years of data collection. Starting in 2008, total organic carbon was measured via 'Hach-lange IL 550' with NIDIR (non-dispersive infra-red detector) technique to detect CO<sub>2</sub> concentrations after combustion at 800 °C. From February 2009 on, another method was implemented: NPOC (non purable organic carbon) using 'Shimadzu TOC-VcpH + TNM1', which automatically includes a degassing process of CO<sub>2</sub> by addition of HCl 2M as acidic component. Afterwards, all values were checked for differences via regression analyses; this statistical check confirmed no significant difference between the results from both applied methods.

Absorbance of the water samples was also determined via two different techniques. First, the 'HP8452A' photospectrometer described above was used with blanks and standards checked in intervals until September 2009, then starting in April 2009, additionally an UV spectrophotometer 'Varian Cary 50 Conc' with an included autosampler unit with 1 cm cuvette and position-fixed blanks and standards came into play. Also in this regard,

statistical analysis did not show significant differences between the outcomes of both measuring instruments.

#### *Export fluxes calculations*

Annual loads (in kg/ha/y) of TOC were calculated by first linear interpolations between observed concentrations to complete daily series and then summing daily products of concentrations and flows (Grimvall, 2004; Ledesma et al., 2012). Flows at each site were obtained from specific runoff measured at site C7. Flow-weighted means of absorbance ratio and SUVA were estimated analogously as TOC and given the same arbitrary units as in the case of riparian sites.

## **2.6 Statistical analyses**

For further data processing, mainly the programmes Microsoft Excel (2010 Microsoft Cooperation) and JMP® 9.0.0 (2010 SAS Institute Inc., Cary, NC, USA) were used for handling the data, creating graphs and computing (statistical) analyses. Missing values (RZ sites: TOC concentration at the first campaign and absorbance measurements at the last campaign; stream sites: few single values for TOC concentration and absorbance during the whole experimental period) were predicted using the 'Fit Least Squares Predicted Values' function of JMP® based on available values of either TOC concentration and absorbance at 254 nm, respectively. In both data sets, riparian zone and stream sites, the worst outliers (obvious measuring errors, e.g. stream TOC concentration in January 2009 at C3 and  $A_{254}$  and  $A_{365}$  on 3<sup>rd</sup> November 2009 for all sites apart from C1 and C2) and negative values (literally not possible for concentration and absorbance measurements) were discarded (in total about 3% of all values).

Statistically, main application was the function 'Fit Y by X' for using One-way Analysis of Variances (ANOVA) to test for differences among various sites, depths and land use types in the data sets, with parameters like  $A_{254}/A_{365}$  or  $SUVA_{254}$  as independent variables and a probability of  $\leq 0.02$  for F. In case of significant differences, pairs of mean values were compared with each other via the 'Student's t' operation to detect significantly different factors. Thereby, the statistical level was  $\alpha \leq 0.05$  for Student's t.



### 3 RESULTS

#### 3.1 Riparian zone

##### 3.1.1 TOC concentration and biological indices

###### TOC concentration

Basic TOC concentration and absorbance at 254 nm showed a correlation of  $R^2=0.73$  ( $p<0.0001$ ,  $n=694$ ) in linear regression in RZs which allowed for predicting missing values in the data set, resulting in a good correlation of  $R^2=0.80$  ( $p<0.0001$ ,  $n=938$  including predicted values).

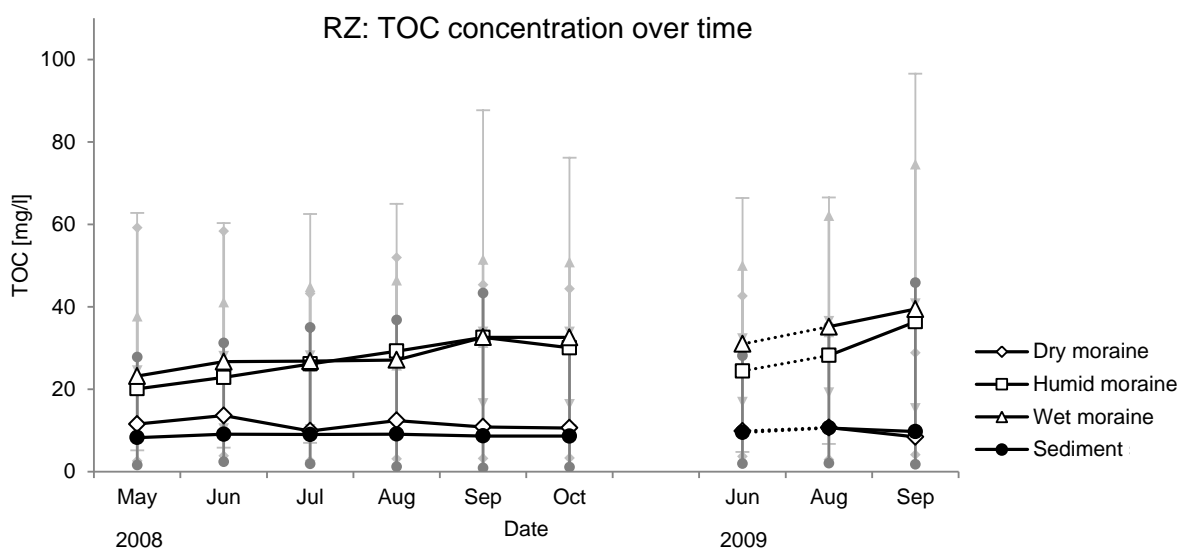
**Table 3:** Medium observed groundwater table position and average values of TOC concentration, TOC export, ratio  $A_{254}/A_{365}$  and its volume-weighted ratio as well as the SUVA index at 254 nm plus volume-weighted SUVA of TOC export for each of the 13 riparian zone sites (R1-R15, without R3 and R13), sorted group-wise, as average of 2008 to 2009.

	Site	Median observed groundwater table position [cm]*	TOC concentra- tion [mg/l]	TOC export [kg/ha/y]	Ratio $A_{254}/A_{365}$	$A_{254}/A_{365}$ of TOC export [Abs/ha/y]	SUVA <sub>254</sub> [m]	SUVA <sub>254</sub> of TOC export [SUVA /ha/y]
dry	R1	-54	10.3	34.4	3.7	13.3	4.4	16.2
	R4	-62	4.8	19.7	4.0	10.5	4.3	12.2
	R9	-47	21.2	71.4	4.1	12.5	5.1	19.2
	R12	-60	7.2	20.8	4.1	13.0	4.7	12.3
moraines humid	R5	-15	19.3	87.0	4.1	14.1	4.9	15.5
	R6	-19	40.4	176.3	3.8	13.8	4.6	18.0
	R7	-28	36.1	155.2	4.5	15.7	5.4	16.1
	R10	-24	16.5	66.4	3.9	14.0	5.1	16.6
wet	R2	-8	34.8	205.8	4.1	14.7	4.4	16.9
	R8	-3	35.8	146.7	4.4	14.4	6.1	15.4
sediment	R11	-3	12.1	99.9	3.2	12.7	5.2	32.5
	R14	-2	2.8	11.5	2.7	9.7	5.9	15.7
	R15	-51	14.7	40.6	3.3	12.3	5.8	27.8

\*data taken from Grabs et al., 2010

Comparing the absorbance data for the two wavelengths 254 and 365 nm, linear regression of both parameters confirmed a strong correlation for RZ sites (with  $R^2=0.94$ ,  $p<0.0001$ ,  $n=834$  without predicted values;  $R^2=0.95$ ,  $p<0.0001$ ,  $n=938$  including predicted values). At stream sites,  $A_{254}$  and  $A_{365}$  were almost identical with good correlations of  $R^2=0.98$  with ( $p<0.0001$ ,  $n=725$ ) and without outliers and negative values ( $p<0.0001$ ,  $n=719$ ).

Generally, TOC concentration ranged from 3 to 40 mg/l (Table 3) with regard to all 13 riparian sites and varied over time with a relatively stable development within one year (Fig. 3). Thereby, a slight increase of organic carbon concentration became visible towards the end of both sampled years for humid and wet horizons (September and October 2008, September 2009) while dry moraine and sediment sites rather showed stable TOC concentrations in autumn. However, due to the fact that only nine samplings were done within the two-year period, trends should rather be handled with care.



**Figure 3:** Change of TOC concentration in mg/l over time in 2008 to 2009, divided according to the four soil characteristics groups within the riparian zone; grey error bars show spatial variability (minimum and maximum).

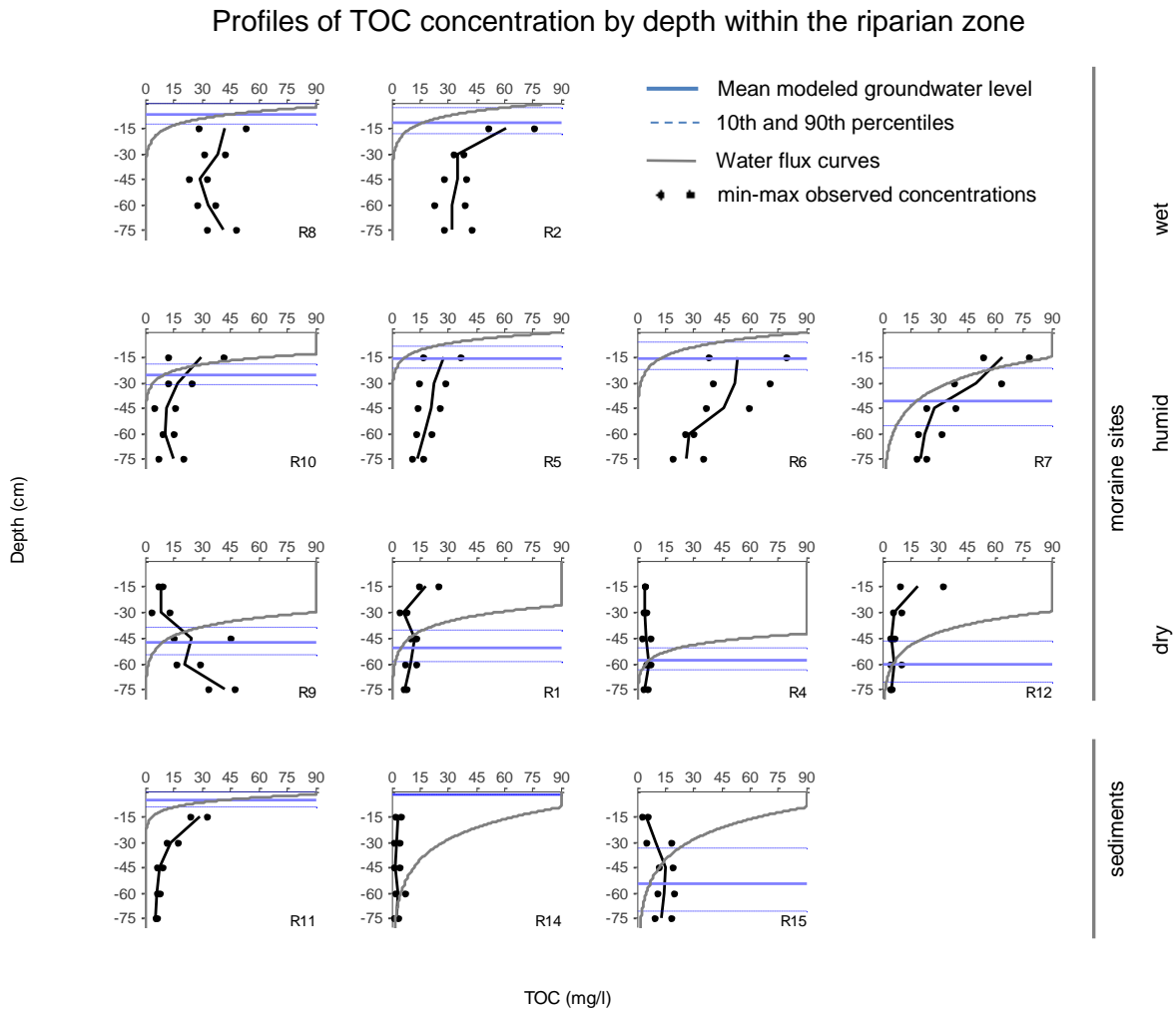
Statistically, dry moraine and sediment sites did not distinguished from each other with TOC concentration means of 11.0 mg/l and 9.2 mg/l, respectively, but presented significantly lower TOC concentration than humid and wet moraine sites which differed significantly ( $R^2=0.34$ ,  $p<0.0001$ ,  $n=938$ ; Table 4).

**Table 4:** TOC concentration and export, the absorbance ratio  $A_{254}/A_{365}$  and  $SUVA_{254}$  index per group classified by soil characteristics within the RZ, mean values of 2008 to 2009.

Group	TOC concentrations* [mg/l]	TOC export* [kg/ha/y]	Ratio $A_{254}/A_{365}$ *	$SUVA_{254}$ * [L/mg/m]
Dry moraine	11.0 <sup>c</sup>	36.6 <sup>c</sup>	4.1 <sup>b</sup>	4.1 <sup>c</sup>
Humid moraine	27.8 <sup>b</sup>	121.2 <sup>ab</sup>	4.1 <sup>b</sup>	4.8 <sup>b</sup>
Wet moraine	30.8 <sup>a</sup>	176.2 <sup>a</sup>	4.4 <sup>a</sup>	4.5 <sup>bc</sup>
Sediment	9.2 <sup>c</sup>	50.7 <sup>bc</sup>	3.1 <sup>c</sup>	7.2 <sup>a</sup>

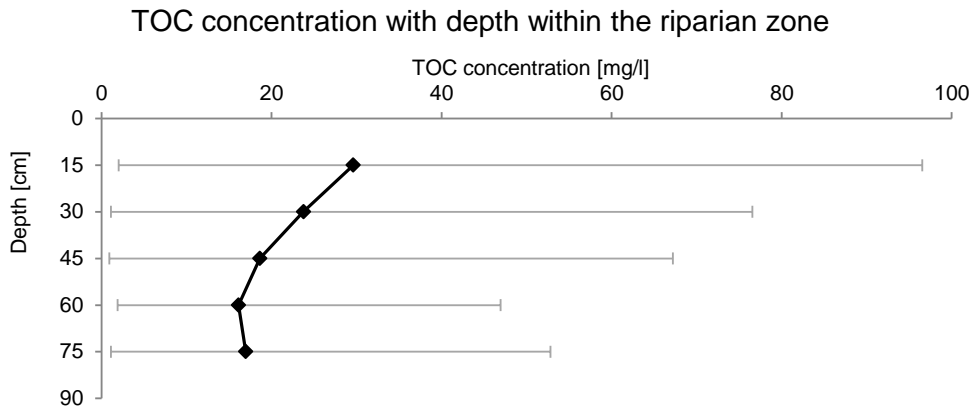
\*Significant differences given by letters: different letters show significant differences between groups with  $\alpha=0.05$  as statistical level.

TOC concentration profiles (Fig. 4) also confirmed that wet horizons contained more TOC than dry sites (Table 3 and 4); only exception was R9 with relatively higher concentrations at deeper soil layers. Humid horizons were more similar to wet moraine sites with higher TOC concentrations decreasing with increasing depth. Sediment sites presented rather stable but lower carbon concentrations with large spatial variation in the upper soil layer at R11 and R15. Site R14 contained least TOC and showed similar concentrations like dry moraine site R4 even though R14 was very wet with a medium groundwater level at -2 cm below the soil surface (R4: -62 cm; see Table 3). More information about organic carbon at these sites can be found in Grabs et al. (2010) as well as in Lyon et al. (2011).



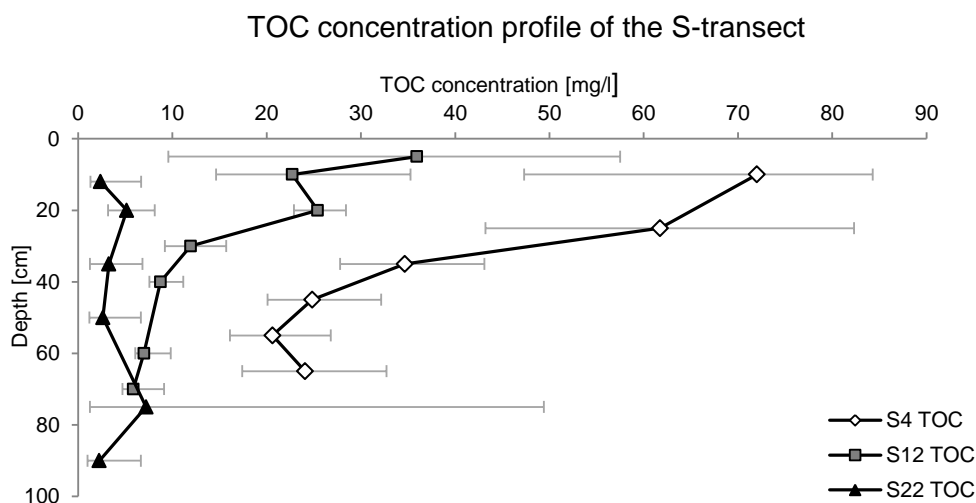
**Figure 4:** Vertical profiles of TOC concentration in mg/l by depth in cm from all monitored sites of the riparian zone (R1-R15, without R3 + R13) including spatial variation (black dots), ordered by soil characteristics; data from 2008 to 2009. Horizontal blue lines represent median modelled groundwater table positions with 10<sup>th</sup> and 90<sup>th</sup> percentiles marked as dashed blue lines. Grey curves illustrate the water flux curve; after Grabs et al., 2010.

Organic carbon concentrations changed with depth showing a decreasing trend towards deeper soil layers (Fig. 5). Here, significantly highest TOC values closest to the soil surface came along with highest spatial variability; lowest concentrations were found at 60 cm depth together with smallest spatial variability.



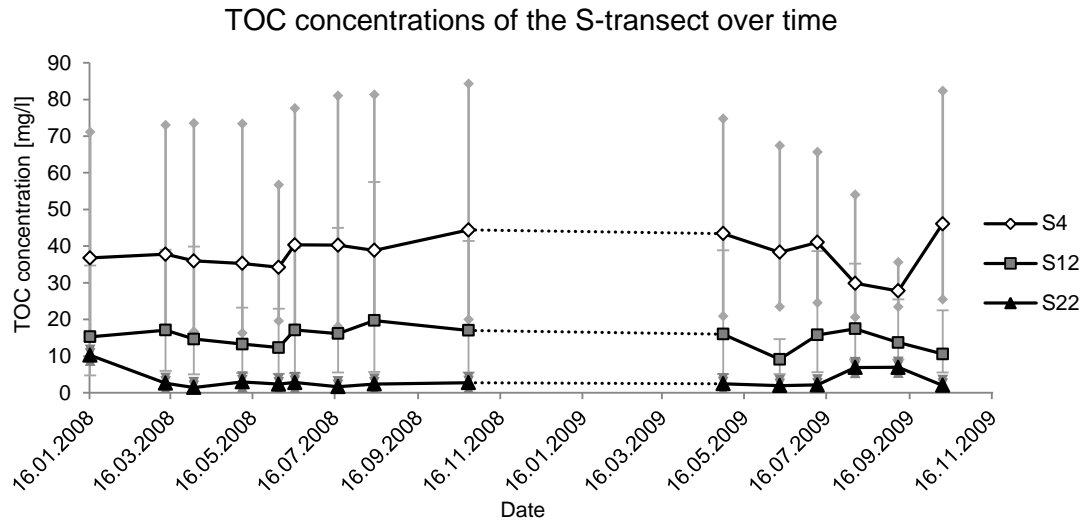
**Figure 5:** Concentration of total organic carbon in mg/l with depth in cm for the riparian zone sites, mean for 2008 to 2009; the grey error bars show spatial variability (minimum and maximum).

The S-transect sites as a particular example of humid horizons drew a similar picture of decreasing concentrations of organic carbon with increasing soil depth for the sites located closer to the stream (S4, S12; Fig. 6). S22 showed a different trend of almost stable TOC concentrations with depth (means ranging from 2.4 to 5.2 mg/l) with exception of the 75 cm layer with highest concentration (7.2 mg/l) and largest temporal variability.



**Figure 6:** Vertical soil profile of total organic carbon concentrations in mg/l per depth in cm for the three monitored sites S4, S12 and S22 of the S-transect assigned to humid moraine soils in 2008 to 2009; the grey error bars show temporal variability (minimum and maximum).

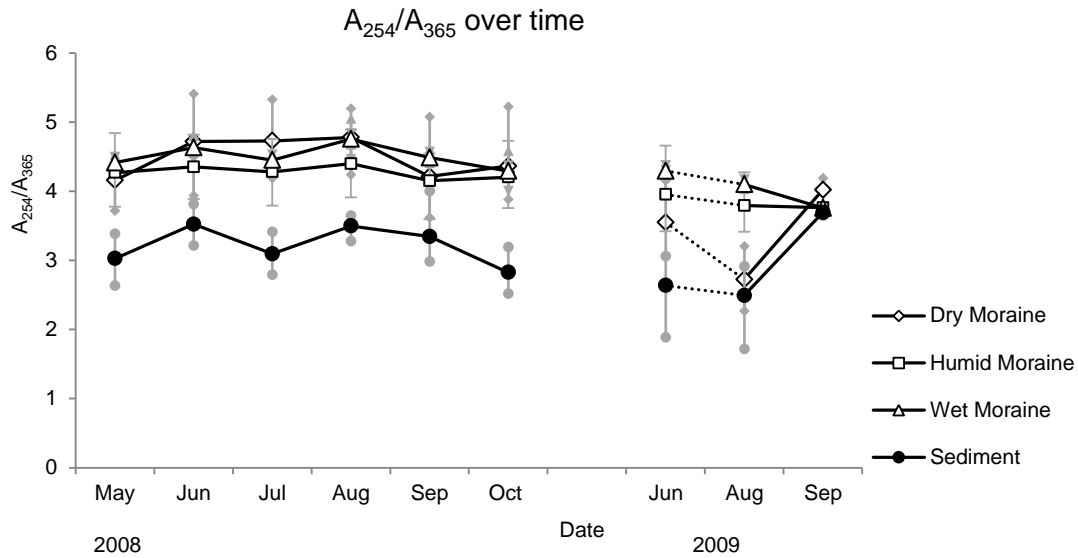
TOC concentrations of S-transect sites varied a little over time but constantly differed significantly between the three monitored sites in their means (Fig. 7). S4 as riparian soil site showed highest values for TOC concentration (mean 38.9 mg/l), medium values were measured at S12 (15.1 mg/l) and lowest concentrations for S22 (3.6 mg/l;  $R^2=0.52$ ,  $p<0.0001$ ,  $n=263$ ) which is located in greatest distance to the water body.



**Figure 7:** TOC concentrations in mg/l as mean of the soil profiles over all depths varying over time for 2008 to 2009 for three sites of humid moraine (S4, S12 and S22 with 4, 12 and 22 m of distance); grey error bars represent spatial variability (minimum and maximum).

#### $A_{254}/A_{365}$

In terms of absorbance ratio, a clear difference became obvious between higher values for moraine sites compared to lower ones for sediment sites (see Fig. 8). One-way ANOVA and Student's *t* showed significant differences between wet moraine (mean 4.4), humid/dry moraine and sediment sites (mean 3.2;  $R^2=0.16$ ,  $p<0.0001$ ,  $n=938$ ; see Table 4). The calculated absorbance ratio of humid (mean 4.14) and dry (4.08) moraine sites did not differ significantly according to Student's *t* with  $\alpha=0.05$ . Comparing all four groups with each other, differences in variation could be noticed:  $A_{254}/A_{365}$  varied much more within dry moraine and sediment sites than within the other two moraine soil groups. At the last sampling date of the second year (2009), the variability of absorbance ratio values of the four groups was reduced basically due to prediction of missing values for this campaign.

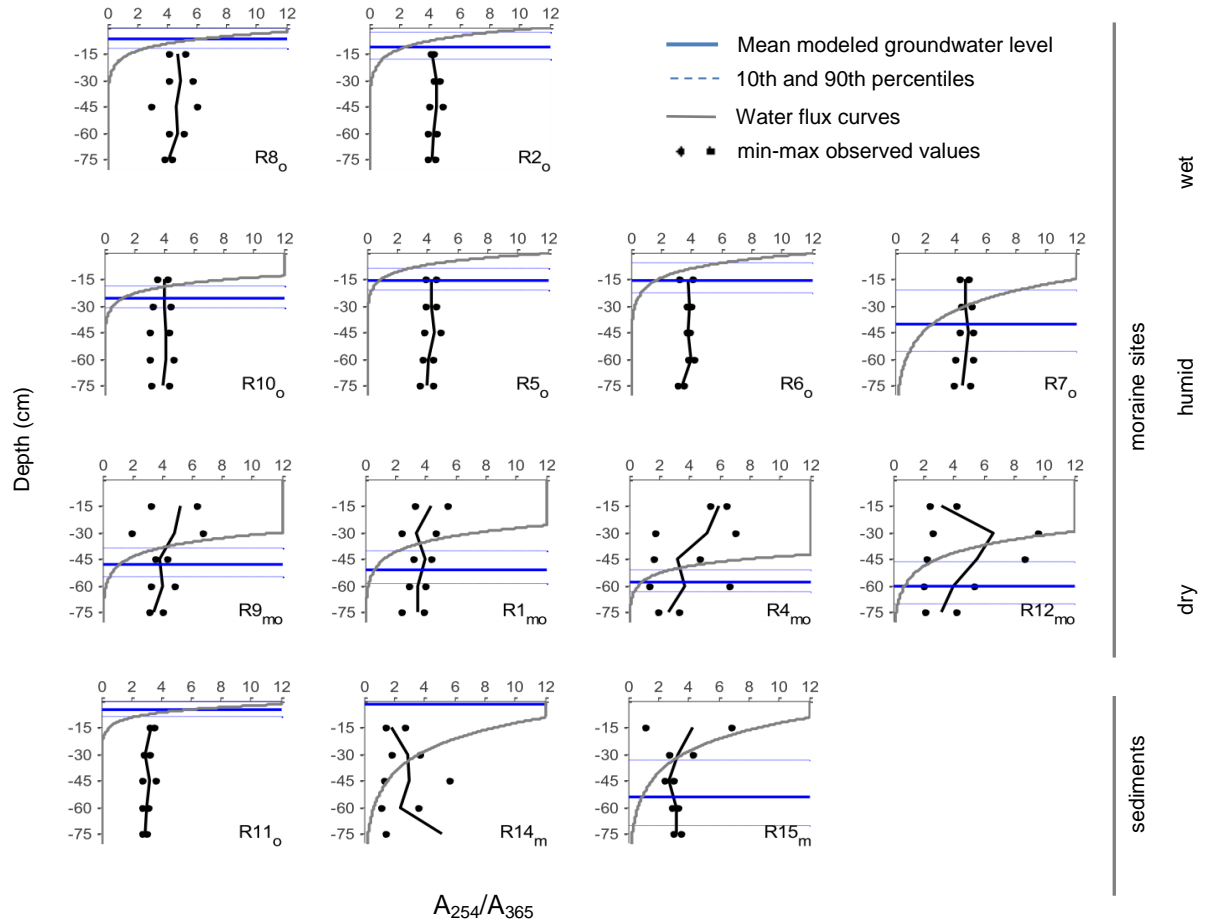


**Figure 8:** Distribution of the absorbance ratio  $A_{254}/A_{365}$  over time for 2008 to 2009 for four different soil character groups within the investigated riparian zone sites; grey error bars represent spatial variability (minimum and maximum).

Analysing the whole data set, absorbance ratio also varied with depth with highest values for the 30 cm soil layer (mean 4.1) and lowest for a depth of 60 cm (3.9) and 75 (3.7) which all differed significantly from each other ( $R^2=0.02$ ,  $p=0.0004$ ,  $n=938$ ). The 15 cm (3.95) and 45 cm (4.01) soil layer could not be distinguished statistically from the 30 and 60 cm layers. However, the total spatial variability of mean values was lower for  $A_{254}/A_{365}$  than for e.g. total organic carbon concentrations.

A more detailed look at the depth distribution of  $A_{254}/A_{365}$  values within sampling locations illustrated a relatively high spatial stability of the absorbance ratio (Fig. 9). This counted mainly for wet and humid moraine sites as well as for R11 and R15 within the sediment soils. However, dry moraine sites as well as R14 within the sediment sites were more spatially variable in the soil profile than wet and humid horizons. Broadly, dry moraine sites showed a decreasing trend of  $A_{254}/A_{365}$  with increasing depth, while site R14 presented an opposite behaviour with higher ratio values towards deeper soil layers. Wet and humid moraine sites and site R11 had temporally stable  $A_{254}/A_{365}$  values as it is shown in Fig. 9 being minimum and maximum observed ratios similar. The rest of the sites showed considerably larger temporal variability, especially in those layers above the median groundwater level.

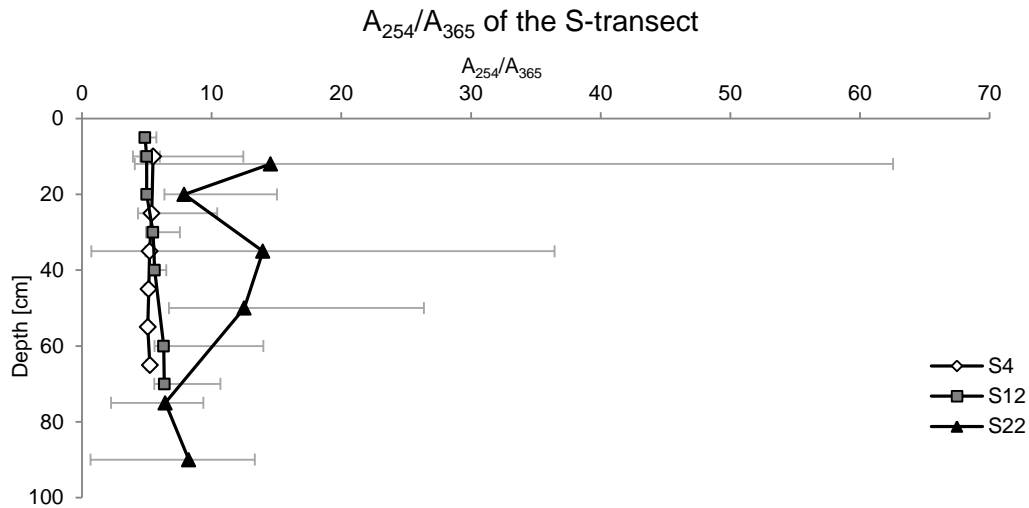
### Profiles of $A_{254}/A_{365}$ by depth within the riparian zone



**Figure 9:** Vertical soil profiles of the absorbance ratio  $A_{254}/A_{365}$  values by depth in cm for the single monitored sites of the riparian zone including temporal variation (black dots), ordered by soil characteristics; data for 2008 to 2009. Horizontal blue lines represent median modelled groundwater table positions with 10<sup>th</sup> and 90<sup>th</sup> percentiles marked as dashed blue lines. Grey curves illustrate the water flux curve; after Grabs et al., 2010.

Similar to the uniform depth distribution of humid moraine sites, the S-transect also showed spatially very stable absorbance ratios with depth for sites at closer distance to the water body (S4, S12; Fig. 10). For S12, a slight tendency towards higher ratio values with increasing depth was visible. In contrast to that, high spatial variation was found for the upslope site (S22) without any clear trend:  $A_{254}/A_{365}$  was lowest at 75 cm (6.4) and 20 (7.9) cm and highest at 12 cm (14.5) and 35 (14.0) cm soil layer. Additionally, also the temporal variability was much higher for S22 than for the other two locations where the distribution over time was more stable. This higher temporal variability at S22 as a dry site (deep groundwater flow) is in agreement with illustrated larger temporal variation at dry moraine

sites (Fig. 9) compared to humid horizons (like S4 is assigned to). Statistically, site S22 differed significantly with very high values (mean 10.7) from S4 and S12 within the S-transect which did not show large differences (S4: 5.3 and S12: 5.6;  $R^2=0.21$ ,  $p<0.0001$ ,  $n=258$ ).

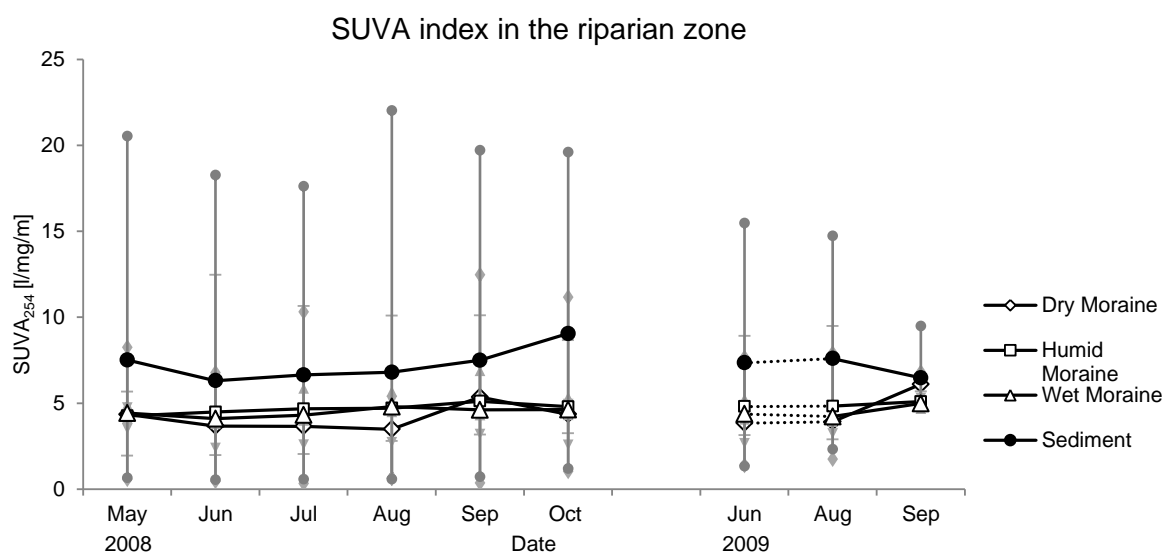


**Figure 10:** Depth distribution of absorbance ratio  $A_{254}/A_{365}$  values for the monitored sites of the S-transect within humid moraine soils in 2008 to 2009; grey error bars show temporal variability (minimum and maximum).

#### *SUVA<sub>254</sub> index*

A noticeable division between moraine sites with generally lower and quite similar SUVA indices and sediment sites with higher values per depth turned out. Thereby, sediment sites (mean 7.2 l/mg/m) distinguished significantly from humid moraine (mean 4.8 l/mg/m) and dry moraine sites (mean 4.1 l/mg/m;  $R^2=0.15$ ,  $p<0.0001$ ,  $n=938$ ; see Table 4). Only wet moraine sites did not differ significantly from the other two moraine sites with an intermediate mean of 4.5 l/mg/m. Rather similar to absorbance ratio,  $SUVA_{254}$  values varied spatially with highest range for sediment compared to moraine sites (Fig. 11). The spatial variability between the two years of data sampling was slightly reduced in 2009 compared to the first year 2008. For the last campaign in September 2009, a shift of the regular pattern of higher SUVA values for sediments than for moraine locations towards more similar indices for all four groups was observed, coming along with noticeably lower spatial variability.



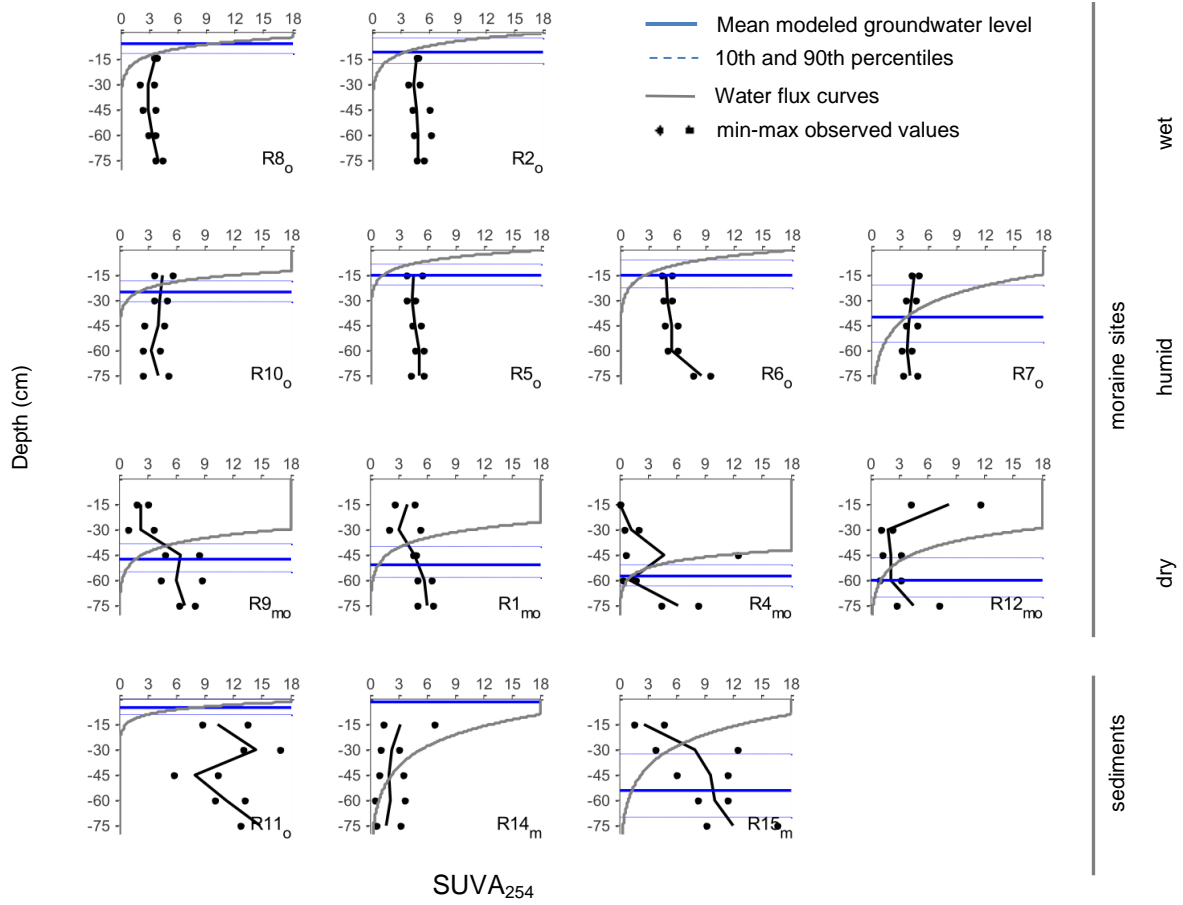


**Figure 11:** Development of  $SUVA_{254}$  indices over time for the four groups (dry, humid, wet moraine sites, sediment sites) of the monitored riparian zone sites in 2008 and 2009; grey error bars show spatial variability (minimum and maximum).

Regarding the depth distribution, the total data set did not show any definable pattern for  $SUVA_{254}$  values except for the deepest soil layer of 75 cm which presented a slightly larger SUVA index compared to all other sampled depths. With a mean of 6.3 l/mg/m, this deepest level differed significantly from all other tested soil layers ranging from 4.6 l/mg/m at 45 cm to 5.0 l/mg/m at 15 cm depth ( $R^2=0.04$ ,  $p<0.0001$ ,  $n=938$ ).

Similar to the absorbance ratio,  $SUVA_{254}$  indices also gave a relatively uniform picture with regard to spatial distribution within the single sites (Fig. 12). This was especially true for wet and humid moraines sites: while these locations were considerably stable in their  $SUVA_{254}$ , dry moraine and sediment sites varied more spatially and temporally. Coming along with the spatial stability, humid (apart from R10) and wet moraine soils also did not show large temporal variability. Sites R4, R9 and R12 (dry moraines) as well as R11 and R15 (sediments) altered conspicuously with depth, with R4, R9 and R15 (plus R1 and R6) rather describing an increasing tendency of SUVA values with increasing depth while the indices of R11 and R12 did not present any specific pattern. In general, dry moraine sites showed lowest  $SUVA_{254}$  indices for 30 cm and highest for the 75 cm depth layer; sediment sites had the smallest SUVA index at 15 and 45 cm depth and also the highest  $SUVA_{254}$  value at the deepest sampled layer.

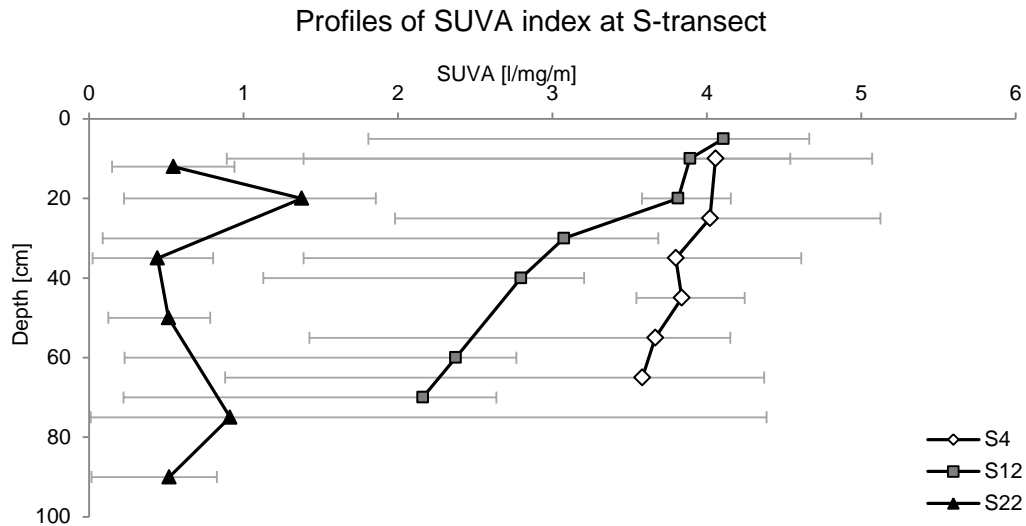
### Profiles of SUVA<sub>254</sub> by depth within the riparian zone



**Figure 12:** Vertical soil profiles of SUVA<sub>254</sub> index in l/mg/m by depth for the single monitored riparian zone sites (R1+R15, without R3 and R13) including temporal variation (black dots), ordered by soil characteristics; data for 2008 to 2009. Horizontal blue lines represent median modelled groundwater table positions with 10<sup>th</sup> and 90<sup>th</sup> percentiles marked as dashed blue lines. Grey curves illustrate the water flux curve; after Grabs et al., 2010.

For the S-transect, the distribution of SUVA<sub>254</sub> with depth demonstrated a slightly decreasing tendency of the indices with increasing depth (Fig. 13); this applied especially for S4 and S12. Even though S4 is part of the humid moraine riparian soils, this pattern did not totally approve the stable distribution of SUVA with depth as presented in Fig. 12. S22 as location furthest away from the stream did not state any particular tendency but highest SUVA values at 20 cm (1.4 l/mg/m) and 75 cm (0.9 l/mg/m) depth and the lowest index for the 35 cm (0.4 l/mg/m) level (Fig. 13). Thereby, S22 illustrated higher spatial variability in its measured data than the two other sites closer to the stream. However, the opposite was observed for temporal variability which was highest for the downslope locations S12 and especially S4. Statistically, the three sites differed significantly in their

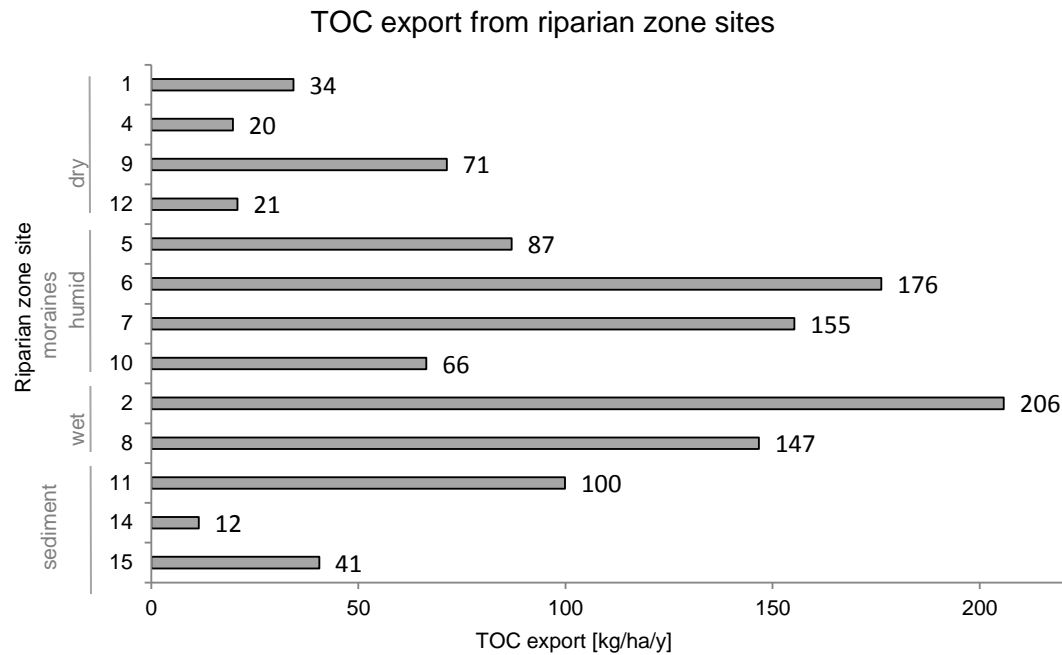
SUVA<sub>254</sub> means, with the largest SUVA index for S4 (3.8 l/mg/m), followed by S12 (3.1 l/mg/m) and very low values at S22 (0.7 l/mg/m;  $R^2 = 0.73$ ,  $p < 0.0001$ ,  $n = 259$ ).



**Figure 13:** Vertical soil profile of SUVA<sub>254</sub> indices in l/mg/m with depth in cm for the three sites of the S-transect (S4, S12, S22) within the ROK assigned to the humid moraine sites in 2008-2009; temporal variability is given by grey error bars (minimum and maximum).

### 3.1.2 Export fluxes in the RZ

TOC exports in the RZs ranged from 11.5 to 205.8 kg/ha/y with lowest values for sediment site R14 and dry sites R4 and R12 and highest exports from R2, R6 and R7 (wet and humid horizons; see Fig. 14 and Table 3). Statistical analysis stated significant differences between the four soil characteristics groups ( $p = 0.012$ ) with highest TOC exports from wet horizons and lowest values at dry moraine sites (see Table 4). Humid moraine and sediment soils showed intermediate carbon exports that were not significantly different from the other means according to Student's *t*.



**Figure 14:** Calculated export of total organic carbon in kg/ha/y from all monitored sites of the riparian zone (R1-R15, without R3 + R13) as an average value of 2008 and 2009, sorted group-wise.

The volume-weighted mean ratios  $A_{254}/A_{365}$  of the exported TOC were more equally distributed than the carbon exports, ranging from 9.7 to 15.7 Abs/ha/y (see Table 3) with lowest values for the sediment site R14 and dry moraine site R4 and highest ones measured at humid horizon R7 and wet moraine site R2. Here, R4 and R14 deviated clearly from the other sites which was also visible in statistical terms: Separating the sites into the four groups by soil characteristics, wet (14.6 Abs/ha/y) and humid (14.4 Abs/ha/y) moraine sites differed significantly from dry moraine (12.3 Abs/ha/y) and sediment (11.6 Abs/ha/y) when comparing the volume-weighted mean values per site ( $R^2=0.002$ ,  $p<0.0001$ ,  $n=9503$ ). Thereby, no significant difference was found between wet and humid horizons as well as dry moraine and sediment sites, respectively.

In comparison, volume-weighted mean  $SUVA_{254}$  values of exported organic carbon varied more with values from 12.2 to 32.5  $SUVA/ha/y$  (Table 3) with dry moraine sites (R4, R12) showing lowest and sediment sites (R11, R15) highest values. In statistical terms, sediment sites demonstrated significantly higher volume-weighted  $SUVA$  means of TOC export (25.3  $SUVA/ha/y$ ) than all moraine sites. Humid (16.5  $SUVA/ha/y$ ), wet (16.1  $SUVA/ha/y$ ) and dry (14.9  $SUVA/ha/y$ ) horizons did not differ statistically from each other ( $R^2=0.01$ ,  $p<0.0001$ ,  $n=9503$ ).

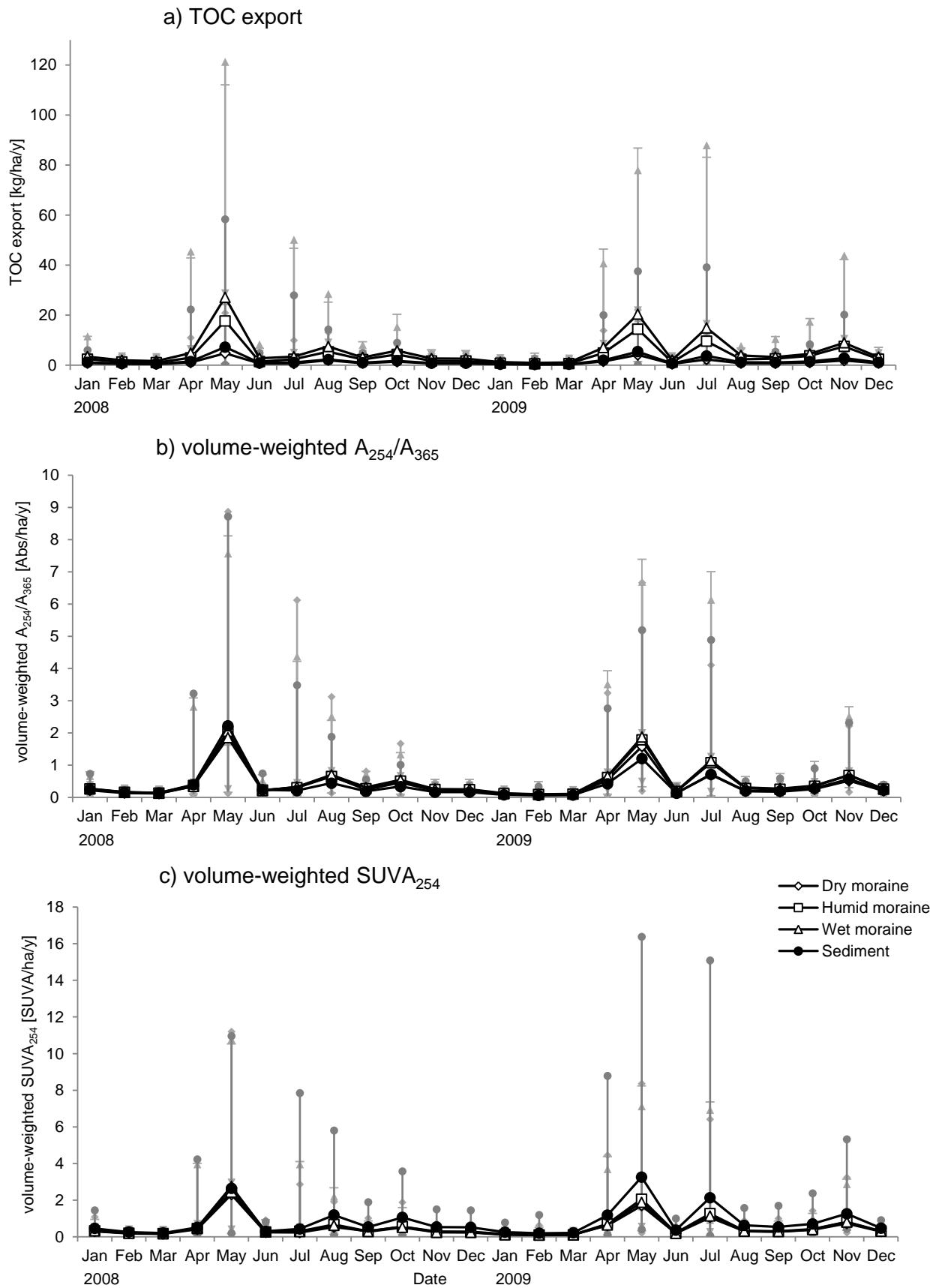


Figure 15: Export of organic carbon in kg/ha/y (a) as well as volume-weighted mean  $A_{254}/A_{365}$  in Abs/ha/y (b) and volume-weighted mean  $SUVA_{254}$  in SUVA/ha/y (c) of the exported TOC over time from 2008 to 2009 with monthly average values; error bars represent spatial variability (minimum and maximum).

Analysing the three parameters related to export fluxes over time, similar patterns became visible (Fig. 15). Within the two-year sampling, TOC exports and the related  $A_{254}/A_{365}$  and SUVA indices of the carbon fluxes showed a relatively stable distribution with some increases during the regular spring flood in May 2008 and 2009 as well as in July and November 2009. Smaller raises in fluxes were found e.g. in August and October 2008.

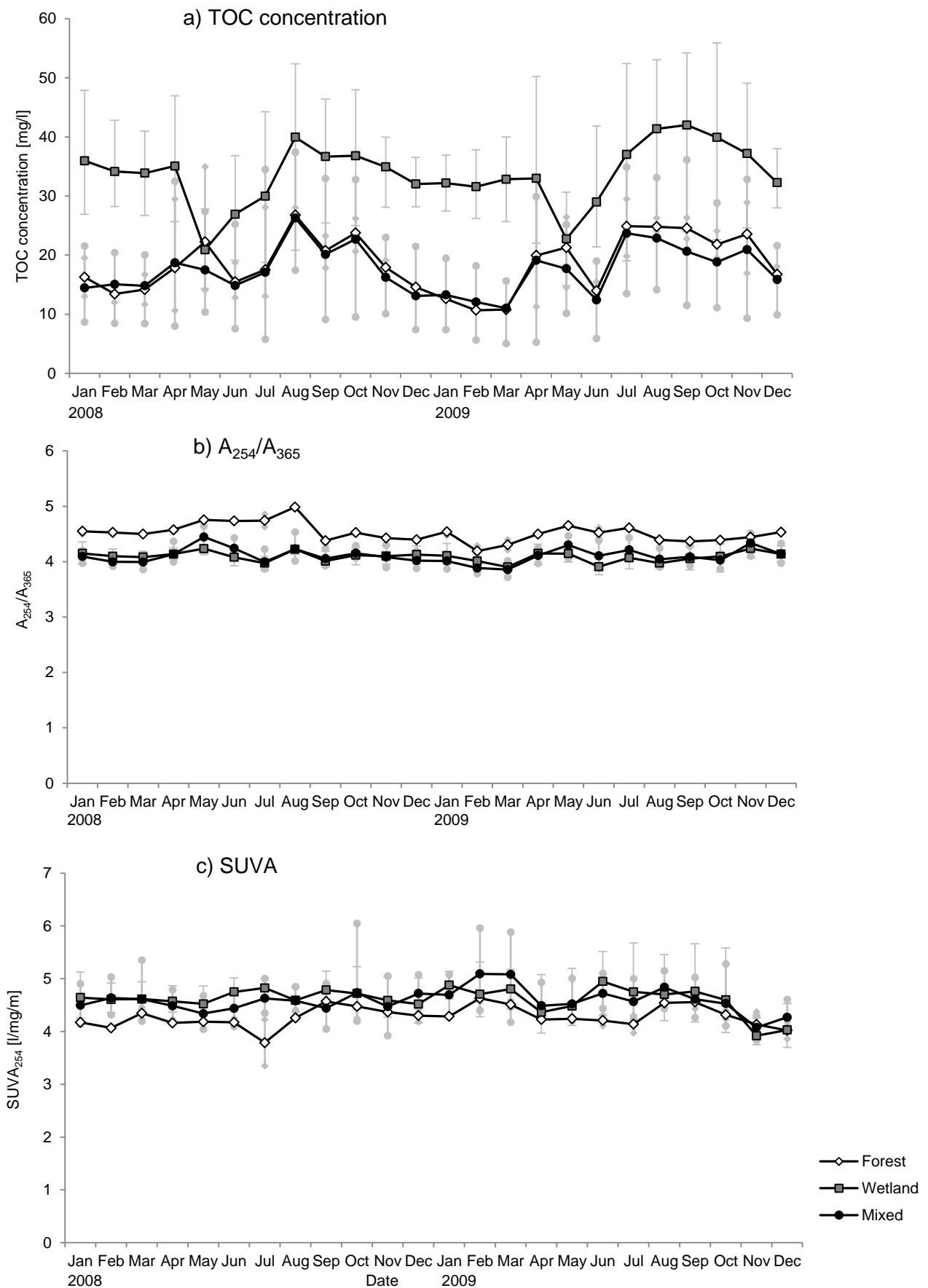
Sediment sites exported lower organic carbon than moraine sites (Fig. 15.a) but showed highest volume-weighted SUVA indices for these carbon fluxes (Fig. 15.c), as was significantly stated also by statistical analysis. Regarding volume-weighted  $A_{254}/A_{365}$  (Fig. 15.b), all groups seemed to react relatively similar but sediment and dry moraine sites presented lower values than wet and humid horizons as also confirmed statistically. The peaking months had in common that the spatial variability of the measured data increased markedly. This was found especially for humid and wet moraine sites in case of TOC export and in 2009 also for volume-weighted means of absorbance ratio of these export fluxes. Volume-weighted SUVA of the TOC export spatially varied most for sediment, in spring 2008 the spatial variation was comparable for all groups.

## 3.2 Streams

### 3.2.1 TOC concentration and biological indices

For more detailed investigation, the monitored stream sites were classified into three groups regarding land use type: forest (C1+C2), wetland (C3-C5) and mixed (C6-C16, note that C8 and C11 do not exist in this study), using percentage of wetland coverage of the total (sub-)catchment as decisive factor. For almost all investigated parameters significant differences were found in terms of land use groups.

Concentration of total organic carbon was highest for wetland sites (32.2 mg/l), followed by forest-draining (19.8 mg/l) and mixed subcatchments (18.3 mg/l) which did not distinguish significantly from each other ( $R^2=0.37$ ,  $p<0.0001$ ,  $n=719$ ; see also Fig. 16.a). Generally, regarding correlation of basic factors, stream sites presented a better correlation of the investigated TOC concentration with  $A_{254}$  than RZ sites (with  $R^2=0.85$ ,  $p<0.0001$ ,  $n=724$  in terms of raw data;  $R^2=0.92$ ,  $p<0.0001$ ,  $n=719$  with few excluded outliers excluded).



**Figure 16:** Distribution of TOC concentration in mg/l (a), absorbance ratio  $A_{254}/A_{365}$  (unitless, b) and SUVA<sub>254</sub> index in l/mg/m (c) over time with respect to the three land use categories (forest-draining, wetland-draining and mixed) for all monitored stream sites; based on monthly mean values for 2008 to 2009; error bars represent variability (minimum and maximum).

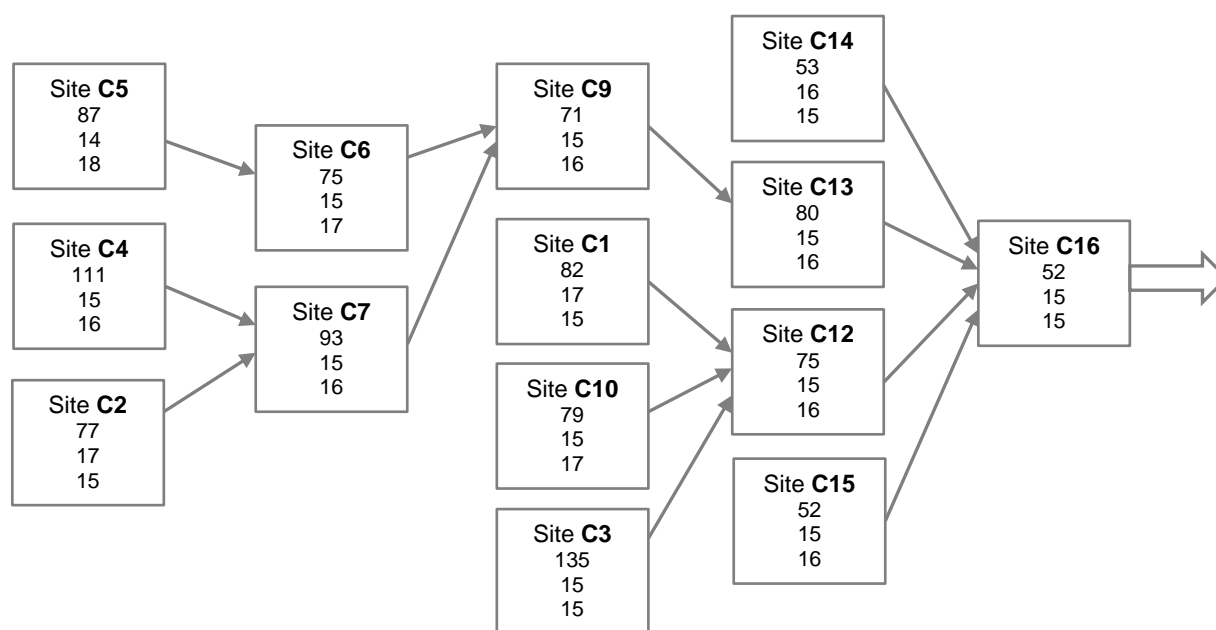
The absorbance ratio was relatively stable over time within the stream sites with only small temporal variations within the two sampled years 2008 and 2009. Even though  $A_{254}/A_{365}$  values did not differ much, statistically, significant distinctions were found between all three land use types. Thereby, forested-draining streams (mean 4.6) showed highest ratios, followed by mixed (4.2) and wetland-dominated (4.1) subcatchments ( $R^2=0.34$ ,  $p<0.0001$ ,  $n=711$ ; Fig. 16.b). With respect to SUVA indices, the opposite pattern became apparent: forested sites presented the lowest mean of 4.3 l/mg/m and therewith distinguished from the other two land use types in a significant way (4.55 and 4.60 l/mg/m for mixed and wetland-dominated sites;  $R^2=0.07$ ,  $p<0.0001$ ,  $n=711$ ). Despite significant differences and similar to  $A_{254}/A_{365}$ , the latter average values for sites related to wetland and mixed land use were quite close to each other in numbers. In general, also  $SUVA_{254}$  values were temporarily relatively stable in the investigated three land use categories (Fig. 16.c). Only a small decrease of the forest-related curve in July 2008 was noticeable as well as a slight increase of SUVA values in February and March 2009 in all three curves.

### 3.2.2 *Export fluxes in the streams*

Regarding the monitored stream sites, TOC export varied from 52 to 135 kg/ha/y (see Fig. 17; Table 5), showing decreasing values with increasing stream order. When comparing annual averages, first-order streams (sites C2-C6) showed significantly highest exports of organic carbon (mean 97.2 kg/ha/y) whereas the lowest amount of exported TOC was measured in forth-order streams (sites C15 and C16: mean 51.9 kg/ha/y;  $R^2=0.46$ ,  $p=0.0018$ ,  $n=28$ ). Second- and third-order streams did not significantly differ from each other (81.9 and 71.8 kg/ha/y on average, respectively). In terms of stream order, volume-weighted means of absorbance ratio and  $SUVA_{254}$  of exported TOC did not show any significant differences (with  $p=0.4667$  for volume-weighted  $A_{254}/A_{365}$  and  $p=0.5338$  for volume-weighted  $SUVA_{254}$ ).



### Export flow scheme for the sampled stream sites



**Figure 17:** Flow scheme of three calculated export values as an average of 2008 to 2009 of the nested (sub)catchments of the monitored stream sites C1-C16 (without C8 and C11; average values from 2008-2009) - first value: specific TOC export in kg/ha/y, second value: volume-weighted  $A_{254}/A_{365}$  of exported organic carbon in Abs/ha/y, third value: volume-weighted  $SUVA_{254}$  of TOC exports in SUVA/ha/y; diagram changed after Ågren et al., 2007.

Dividing the whole data set into the three land use categories, wetland-draining streams showed significantly higher TOC exports (111.4 kg/ha/y) than forest-dominated streams and mixed subcatchments (79.3 and 70.0 kg/ha/y, respectively;  $R^2=0.53$ ,  $p<0.0001$ ,  $n=28$ ).

Volume-weighted  $A_{254}/A_{365}$  of carbon exports were relatively stable when comparing all stream locations, values ranged from 14.2 to 16.8 Abs/ha/y (Table 5) with lowest values for sites C5 and C6 as a wetland-draining and a mixed site and highest volume-weighted absorbance from C1 and C2 which both drain forested areas. All these listed streams were categorized as first- and second-order streams. Statistically, a similar picture was confirmed: forest-draining streams exported significantly highest values (mean 16.7 Abs/ha/y) while streams coming from mixed subcatchments and wetlands could not be differentiated significantly (15.2 and 14.9 Abs/ha/y, respectively;  $R^2=0.74$ ,  $p=0.0006$ ,  $n=14$ ).

**Table 5:** Average values per site of TOC concentration, TOC export, absorbance ratio  $A_{254}/A_{365}$ , the related volume-weighted mean of TOC export as well as the SUVA index at 254 nm and its volume-weighted mean of exported organic carbon for each of the 14 stream sites; sorting after increasing (sub)catchment size within the three land use types; all values represent averages for 2008 to 2009.

Site	Land use type <sup>a</sup>	(Sub)catchment size [km <sup>2</sup> ] <sup>b</sup>	TOC concentration [mg/l]	TOC export [kg/ha/y]	Ratio $A_{254}/A_{365}$	$A_{254}/A_{365}$ of TOC export [Abs/ha/y]	SUVA <sub>254</sub> [m]	SUVA <sub>254</sub> of TOC export [SUVA /ha/y]
C2	forested	0.13	19.0	76.7	4.5	16.6	4.3	15.3
C1	forested	0.66	20.6	82.0	4.6	16.8	4.2	15.1
C3	wetland	0.03	40.1	135.5	4.2	15.4	4.2	15.1
C4	wetland	0.19	33.8	111.3	4.1	15.1	4.4	15.5
C5	wetland	0.85	24.5	87.4	4.0	14.2	5.1	17.8
C7	mixed	0.50	25.0	93.1	4.1	16.0	4.6	15.9
C6	mixed	1.30	20.0	75.2	4.0	14.7	4.9	17.4
C10	mixed	2.90	21.2	78.5	4.1	15.0	4.7	16.5
C9	mixed	3.10	18.3	70.7	4.2	15.4	4.5	16.0
C12	mixed	5.40	19.8	75.5	4.1	15.1	4.5	15.8
C13	mixed	7.20	20.9	80.2	4.2	15.2	4.7	16.4
C14	mixed	14.0	13.6	52.9	4.3	15.9	4.3	15.4
C15	mixed	20.0	13.2	52.0	4.2	15.2	4.5	15.7
C16	mixed	67.0	12.4	51.7	4.2	15.2	4.3	15.1

<sup>a</sup> land use type based on wetland percentage of total subcatchment area; <2% wetland coverage = forested, 2-30% wetland coverage = mixed, >30% wetland coverage = wetland; after Buffam et al., 2007.

<sup>b</sup>after Buffam et al., 2007.

Also carbon export-related volume-weighted SUVA<sub>254</sub> indices were quite equally distributed with two sites being a little conspicuous: C5 and C6 showed highest export values with 17.8 and 17.4 SUVA/ha/y, respectively, while all other sampling locations varied between 15.1 and 16.5 SUVA/ha/y (Table 5). However, one-way ANOVA and Student's t showed no significant difference between all three land use types but -contrary to the volume-weighted absorbance ratio distribution- forests presented lowest values with 15.2 SUVA/ha/y on average, mixed sites already showed 16.0 SUVA/ha/y and wetland-draining streams had highest volume-weighted SUVA of TOC exports with 16.2 SUVA/ha/y ( $R^2=0.15$ ,  $p=0.4097$ ,  $n=14$ ).

### 3.3 Comparison of fluxes from riparian zones and streams

Within all 13 investigated riparian zone and 14 stream sites, five pairs of one sampling location each of RZ and stream site were compared (see

Table 6) with regard to exports of total organic carbon as well as the volume-weighted means of absorbance ratio and SUVA index of this exported TOC. Reasons for the choices were two main factors. First, it had to be a first-order stream; otherwise raised export measurements or other influences from upstream locations would potentially distort the whole picture. Secondly, the sampled riparian site should be located in the same subcatchment of the monitored stream site to ensure a correct direct comparison.

Table 6: Comparison of five pairs of each one riparian zone site and one stream location including stream order and soil characters; note that stream site C2 is used three times to be compared with different riparian soil sites within the same subcatchment Västtrabäcken.

Pair	Stream sites	Stream order	RZ sites	Soil character
C2 / R5	C2	1	R5	humid moraine
C2 / R6	C2	1	R6	humid moraine
C2 / R7	C2	1	R7	humid moraine
C4 / R8	C4	1	R8	wet moraine
C6 / R4	C6	1	R4	dry moraine

#### *Total organic carbon*

One-way ANOVA and Student's t stated no significant difference of TOC export between RZs and streams when comparing single annual values for 2008 and 2009 ( $R^2=0.02$ ,  $p=0.6095$ ,  $n=16$ ), even though the overall mean values per location differed with 117.0 kg/ha/y for export from riparian soils and 87.7 kg/ha/y for TOC measured in the streams.

Table 7: Comparison of exported TOC and volume-weighted absorbance ratio  $A_{254}/A_{365}$  and  $SUVA_{254}$  index of the export fluxes of selected sites of sampled streams and riparian zone; all values represent averages for 2008 to 2009.

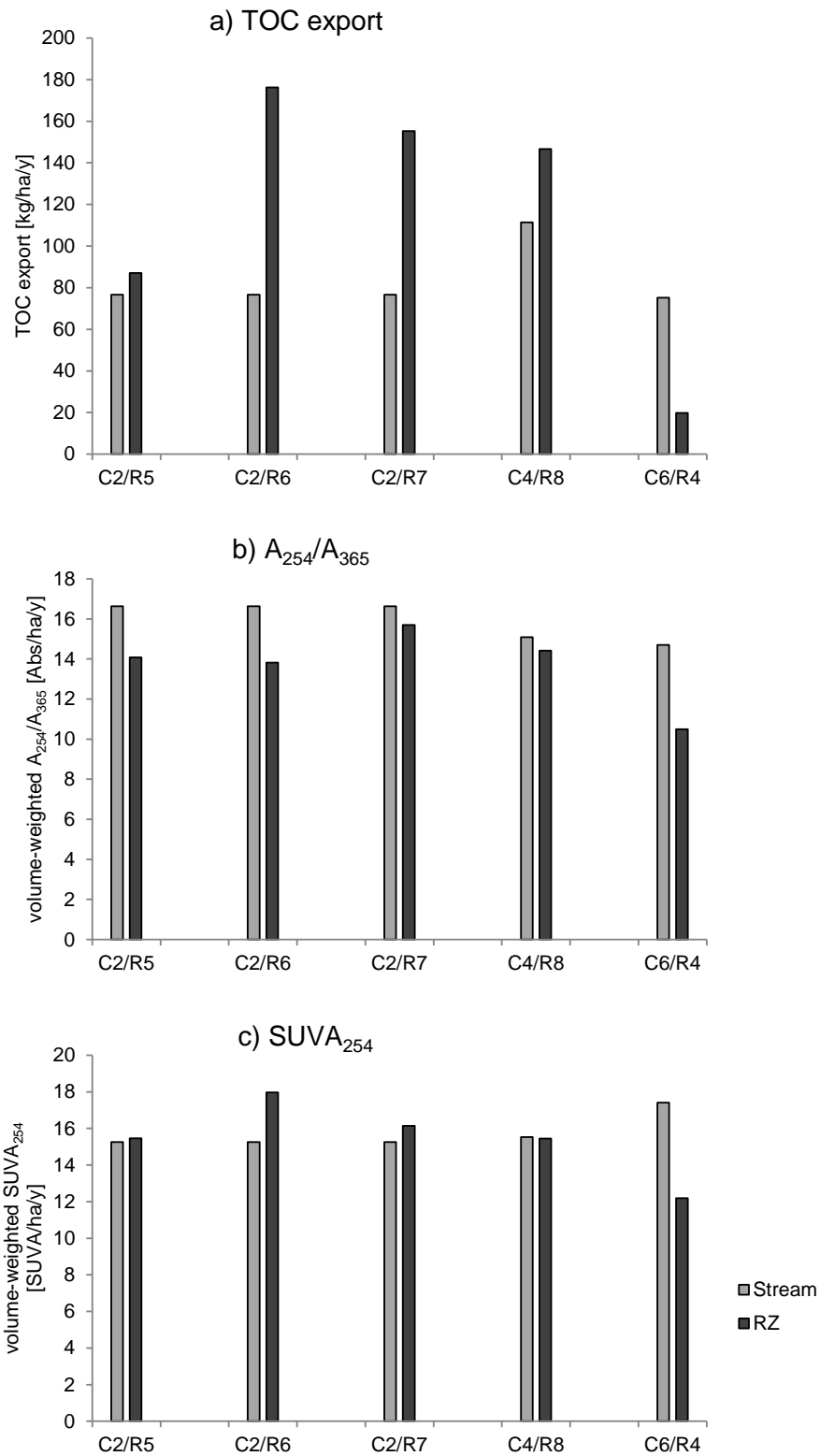
Pair	TOC [kg/ha/y]		$A_{254}/A_{365}$ [Abs/ha/y]		SUVA [SUVA/ha/y]	
	Stream	RZ	Stream	RZ	Stream	RZ
C2/R5	76.7	87.0	16.6	14.1	15.3	15.5
C2/R6	76.7	176.3	16.6	13.8	15.3	18.0
C2/R7	76.7	155.2	16.6	15.7	15.3	16.1
C4/R8	111.3	146.7	15.1	14.4	15.5	15.4
C6/R4	75.2	19.7	14.7	10.5	17.4	12.2

Comparing TOC of streams and RZs, the amounts of exported carbon differed for most pairs (Fig. 18.a); only for C2/R5 with one of the humid

moraine sites, the expectation 'what comes out of the soil should be found in the stream' seemed to be true. However, for the other two humid moraine sites (R6, R7), the TOC exports were much higher in the RZ than investigated at the forest-draining stream site C2. The pair C4/R8 as a wetland-dominated example showed little less TOC in the RZ as the humid moraine sites and considerably more TOC than the other two stream locations. Nevertheless, the TOC export from the riparian soil at R8 is approximately 35 kg/ha/y larger than the quantity measured in the stream (compare with Table 7). The fifth pair demonstrated the opposite trend: the TOC amount of the dry moraine soil site R4 is about 55 kg/ha/y lower than the export from the mixed stream site C6. Generally, riparian soil TOC varied more in their exports looking at these sites while stream sites showed higher stability in their exported amounts of organic carbon.

#### $A_{254}/A_{365}$

In terms of the absorbance ratio, the volume-weighted  $A_{254}/A_{365}$  values of exported TOC did not differ much with representative first-order stream sites constantly illustrating slightly higher absorbance values than measured at the related riparian soils located in the same subcatchment for all five pairs. Almost similar values were found especially for two cases, namely C2/R7 as forest-related/humid moraine example and C4/R8 as wetland sample (Fig. 18.b). In comparison, stream monitoring showed less variation in the volume-weighted  $A_{254}/A_{365}$  values of carbon exports within the compared sites than found in the RZs. Still carbon exports were almost similar with regard to volume-weighted  $A_{254}/A_{365}$ . This was also approved statistically by RZ and stream sites not differing significantly from each other when comparing the means of 2008 and 2009: volume-weighted  $A_{254}/A_{365}$  of exported TOC with 13.7 Abs/ha/kg as average value for riparian soils was a little lower than 15.5 Abs/ha/kg measured in streams ( $R^2=0.22$ ,  $p=0.0642$ ,  $n=16$ ).



**Figure 18:** Comparison of selected stream sites (C2, C4, C6) and riparian zone sites (R4-R8) in terms of TOC export in kg/ha/y (**a**) as well as volume-weighted means of absorbance ratio  $A_{254}/A_{365}$  in Abs/ha/y (**b**) and  $SUVA_{254}$  index in SUVA/ha/y (**c**) of exported TOC; all data represent average for 2008 to 2009.

### *SUVA<sub>254</sub> index*

All volume-weighted SUVA means of TOC exports related to forest-draining stream site C2 showed lower values in the stream than for the representative RZ sites (Fig. 18.c). The opposite pattern was true for the last case C6/R4 with much higher within-stream volume-weighted SUVA indices than for riparian soils. Still, values varied more for riparian soils than for measurements in the stream water of the same subcatchment, similarly to TOC export and volume-weighted absorbance ratio comparisons. Statistically, carbon export-related volume-weighted SUVA indices did not differ significantly between the two sampling locations: one-way ANOVA and Student's *t* calculated means of 15.4 and 16.1 SUVA/ha/y for riparian zone and stream sites, respectively ( $R^2=0.02$ ,  $p=0.5776$ ,  $n=16$ ). Thereby, the wetland-draining pair for C4 (15.5 SUVA/ha/y) and R8 (15.4 SUVA/ha/y) and also C2 (15.3 SUVA/ha/y) and R5 (15.5 SUVA/ha/y; see Table 7) fitted very well with almost the same export values. C6/R4 differed most by more than 5 units (C6: 17.4 SUVA/ha/y, R4: 12.2 SUVA/ha/y; Table 7). Nevertheless, volume-weighted mean SUVA indices of carbon export fluxes were relatively similar, like also shown for  $A_{254}/A_{365}$  fluxes and further supported by statistical calculations.

### *Whole catchment perspective*

For reason of comparisons of RZ and stream sites and identification of tendencies in the whole catchment area, stream locations were divided into upstream (e.g. C1-C10 with lower stream order of 1-2; note that C8 does not exist in this study) and downstream sites (C12-C16 with the latter being the outlet of the whole Krycklan catchment area, generally higher stream order of 3-4; see Table 2). This procedure was more difficult for riparian soils since the numerical system of stream order was not applicable here. Therefore, R14 and R15 were set as representative downstream sites due to their location clearly southeast in the Krycklan catchment whereas all other RZ sites were grouped as rather upstream locations (compare Fig. 2).

Analysing TOC export fluxes and volume-weighted means of absorbance ratio and SUVA indices for all RZ and stream sites (see Table 3 and 5), similar patterns were found. Export fluxes of organic carbon decreased with water flow direction towards downstream locations both in riparian soils and streams when comparing up- and downstream sites (up- and downstream

averages in RZ 98.5 and 26.0 kg/ha/y, in streams 91.0 and 62.5 kg/ha/y, respectively). This decreasing tendency was better noticeable along the gradient with water flow direction for streams though, since TOC exports varied a lot within the riparian sites, especially in the upstream sites. An analogous pattern was also visible between representative RZ and stream sites for volume-weighted  $A_{254}/A_{365}$  of the carbon fluxes which remained almost the same all over the catchment up- and downstream (up- and downstream averages in RZ 13.5 and 11.0 Abs/ha/y, in streams 15.4 and 15.5 Abs/ha/y, respectively). In terms of volume-weighted SUVA indices of the exported TOC, the comparison did not match that well: while  $SUVA_{254}$  stayed at a similar level within all stream sites (up- and downstream averages 16.1 and 15.7 SUVA/ha/y), the values rather increased from upstream to downstream locations in riparian soils (17.4 and 21.8 SUVA/ha/y, respectively). However, variation in values was generally higher within RZ than within streams; this was also true for SUVA which made a comparison of up- and downstream location more difficult.

## 4 DISCUSSION

### 4.1 *Riparian Zone*

#### 4.1.1 *TOC concentration and biological indices*

##### *TOC concentration*

TOC concentration in the RZs varied between 3 and 40 mg/l (average values per site; see Table 4); this range is smaller than the one of organic carbon exports of 12 to 206 kg/ha/y but comparable with the one of TOC concentrations measured in the streams of 12 to 40 mg/l. This agrees with the creation of chemical signals of the stream in the riparian area (Creed et al., 2003; Seibert et al., 2009). Organic carbon concentrations and exports including depth distribution are discussed in details in Grabs et al. (2010) and Lyon et al. (2011).

Regarding the S-transect, decreasing TOC concentrations towards deeper soil layers found at S4 (and S12) were further confirmed by several studies (Bishop et al., 2004; Seibert et al., 2009; Lyon et al., 2011). However, with larger distance to the stream (S22), the depth distribution was more stable without a definable trend. Highest TOC at the riparian site S4 is in accordance with Cory et al. (2007) who explained increased organic carbon levels at sites next to the stream (S12 and even more pronounced for S4) compared to upslope locations with enhanced flow pathways closer to the soil surface. Also Bishop et al. (2004) presented that water at upslope sites like S22 mainly flows through deeper carbon-poor soil layers while the flow path at riparian sites is more superficial, leaching larger TOC quantities from the soils. This got further confirmed by Laudon et al. (2011) illustrating altering soil types with distance to the stream in the Västströmen catchment: S4 consists of organic soils rich in TOC whereas S22 is dominated by podzol with mainly mineral soils and only an organic top-layer of 10-15 cm. However, only the carbon-poor mineral part and not the organic layer are hydrologically connected. Also Hinton et al. (1998) and Cory et al., (2007) attested the reduced importance of upslope water flow paths for organic carbon compared to RZs. Upslope concentration in Cory et al. (2007) was lower than 5 mg/l which fits well to 4 mg/l showed here for S22; however, riparian TOC concentration of 16 mg/l in their study was less than half of the concentration of 39 mg/l in S4. The result of S4 consisting



of more than twice the carbon concentrations of S12 is complicated to explain with the analysed data of this study. Conceivable explanations can be stronger sorption processes and stabilization of carbon (Kalbitz et al., 2000) at S12 due to the mineral component of the organic-rich mineral soil profile (Laudon et al., 2011), enhancing the already lower TOC concentrations compared to S4 or rather deeper water flow path through the (mineral) soil. According to Cory et al. (2007), superficial water flow paths are higher and more pronounced at 4 m compared to 12 m distance to the stream, leading to larger organic carbon measured at RZ site S4.

Additionally, several authors (e.g. Creed et al., 2003; Seibert et al., 2009; Borken et al., 2011) stated that it is the riparian soil that affects hydrochemical changes in the streams and not locations upslope. This also fits to the observation of similar ranges of TOC concentration in RZs and streams in this study and further justifies the assumption of riparian sites being treated as representative for the RZs in comparison with stream sites.

#### *Biological indices*

It is conspicuous that absorbance ratio and SUVA indices were consistent while also behaving approximately opposite in numbers: high  $A_{254}/A_{365}$  values coincide with low SUVA indices and the other way around (also stated by e.g. Ågren et al., 2008b). This can be explained by high absorbance ratio and low SUVA both highlighting good bioavailability and bacterial growth of the investigated TOC compounds.

Within the RZ, the absorbance ratios of moraine sites were significantly higher than the ones of sediment samples which indicates lower molecular weight of TOC (Lindell et al., 1995; Dahlén et al., 1996; Obernosterer and Herndl, 2000) and enhanced bacterial growth efficiency (Berggren et al., 2007; Berggren et al., 2009) for moraine locations. This, in turn, means less bacterial production resulting in higher molecular weight of carbon compounds at sediment sites. Here, lower absorbance ratio values may also be caused by generally smaller hydraulic conductivity including increases transit times in sediments than in till or peat soils (Laudon et al., 2007) plus the fact that most small organic carbon compounds are potentially degraded already during a longer reaction time in sediment soils (Lee and Henrichs, 1993) so that only higher molecular weight fractions are left, especially visible in case of R14.

At the same time, moraine sites were relatively similar in their lower SUVA values compared to sediment sites, showing lower fraction of aromatic structures in TOC (Weishaar et al., 2003; Fu et al., 2006) and higher bioavailability (Perdue, 1998). Within the moraine samples, wet moraine soils with shallowest mean groundwater levels of <15 cm below the surface showed significantly largest  $A_{254}/A_{365}$  values. This implies lower molecular carbon weight than measured at humid and dry sites probably because of higher bacterial growth efficiency, followed by enhanced biological degradation processes. Greater organic matter production induced by higher water levels (Grabs et al., 2010; Lyon et al., 2011) may also come into play.

Regarding  $SUVA_{254}$ , sediment sites presented highest indices in riparian soil water, being related to increased aromaticity. Furthermore, this organic carbon is less bioavailable according to the negative correlation of aromaticity and bioavailability found by Perdue (1998). That is explicable by long reaction times in sediment soils (Lee and Henrichs, 1993) and therewith, enhanced potential (bio-)degradation especially of the smaller and easily available organic molecules in addition to comparatively low TOC concentrations (Buffam et al., 2008) and export fluxes in sediment soils poor in organic substances (Blomberg, 2009). Moreover, increased sorption to mineral surfaces like of sediment soils as a successful stabilization mechanism (Sollins et al., 1996; Kaiser and Guggenberger, 2000; Kalbitz et al., 2000) may account for reduced bioavailability, further supported by the assumption of lower degradability of adsorbed organic compounds (Marschner and Kalbitz, 2003). The shifts of the observed pattern of absorbance and SUVA ratio values at the last campaign (Fig. 8 and 11) are possibly due to the data handling and analysis. Since measured absorbance values in the riparian soil samples were not reliable for the last sampling in September 2009, all  $A_{254}$  and  $A_{365}$  values were predicted from existing TOC concentrations. These predictions which were used to calculate both biological indices for this last campaign seem to have influenced the spatial variability and observed tendencies in earlier samplings to a large extent.

In terms of depth distribution, the basic slight tendency of decreasing absorbance ratio values with increasing depth as found for dry moraine examples is also stated by Ågren et al. (2008b) and indicates heavier

carbon molecules with lower bacterial growth at deeper soil layers. Largest absorbance ratios at the 30 cm soil layer may be in accordance with generally higher hydraulic conductivity towards the surface (Rodhe, 1987; Schiff et al., 1998; Bishop et al., 2004). Thereby, the profiles of  $A_{254}/A_{365}$  are characterized by a high stability, in some cases especially at wet and humid moraine soils organic carbon character does not obviously seem to change with depth as shown by almost vertical profile lines (see Fig. 9). For SUVA, a clear pattern in depth distribution is missing but organic carbon from the deepest soil layer is expected to be less bioavailable while more aromatic, indicated by a slightly larger SUVA index (6.3 l/mg/m). This counts especially for dry moraine examples (R4, R9) and hence, shows the opposite behaviour to decreasing  $A_{254}/A_{365}$  values with depth for dry horizons as well as for one sediment site (R14). Possible explanations applying for less bioavailable carbon at deeper dry sites could be lower hydraulic conductivity with depth (Rodhe, 1987) plus limited activity and decomposition processes of microorganisms due to dry conditions (Marschner and Kalbitz, 2003). Furthermore, generally lower TOC concentrations at these sites in combination with decreasing TOC concentrations at deeper soils (Seibert et al., 2009; Lyon et al., 2011) can be mentioned. However, wet and partly also humid moraine soils present very stable profiles with low temporal variability (see Fig. 12) where almost vertical lines state only minimum changes in carbon characteristics. While wet horizons generally do not alter considerably regarding both parameters,  $A_{254}/A_{365}$  and SUVA, dry soils vary more in biological indices and therewith in carbon quality aspects. Also the temporal variability is markedly higher for dry horizons, easily relatable to larger groundwater level changes depending on special hydrological events (note that modelled groundwater table position changes using 10<sup>th</sup> and 90<sup>th</sup> percentiles represent also more variation for dry sites compared to wet sites in the two parameters, absorbance ratio and SUVA, Fig. 9 and 12).

Physical reasons for lower  $A_{254}/A_{365}$  values with depth at two sampling sites R11 and R15 can be smaller hydraulic conductivity at sediment sites (Laudon et al., 2007) as well as generally decreasing conductivity with depth, leading to less bioavailable carbon fractions from these locations. R14, however, showed a high absorbance ratio for the lowest depth at 75 cm, illustrating low molecular weight of TOC and larger bioactivity. This is in contrast to the SUVA index at sediment locations which was higher at the

deepest layer compared to the layers above, indicating less bioavailable organic carbon with higher fraction of aromatic structures. Also Van Miegroet et al. (2005) and Ågren et al. (2008b) described increasing SUVA indices towards deeper layers for forest riparian soils and higher stability with depth for forest soils (Van Miegroet et al., 2005). However, in the study of Ågren et al. (2008b) SUVA values were a little lower with 3.7 to 4.5 l/mg/m for wetland and forest riparian soils. Against it, Sanderman et al. (2009) found decreasing aromaticity coming along with reduction in SUVA with increasing depth in the soils which again would mean higher bioavailability as also stated by larger  $A_{254}/A_{365}$  for deep sediment soil layers.

However, humid and especially wet moraine RZ sites are almost invariably formed of organic soils and not faced with great water table changes, so they represent quite stable environmental conditions. This results in a relatively uniform depth distribution of absorbance ratio and SUVA compared to dry moraine and sediment sites. More shallow and constant groundwater levels (<15 cm under the surface) over time at wet moraine soils also means a stable hydraulic conductivity at top soil layers and less varying biological soil processes which basically accounts for relatively well bioavailable TOC, indicated by a rather low  $SUVA_{254}$  index. Insignificantly higher SUVA values at humid compared to wet locations indicate higher aromaticity together with reduced bioavailability for TOC coming from these humid moraine soils.

Results from the S-transect (S4, S12) as additional example for humid horizons including the stream-distance parameter also agree with the findings of stable absorbance ratios at humid moraine sites. But SUVA shows an opposite trend to depth distribution at dry sites and decreased with depth, meaning less aromatic but therefore more bioavailable carbon fractions at deeper soil layers. This applies to the riparian site S4 and even more to S12. S22, however, presented significantly lower SUVA indices than the other two S-transect sites with a more diverse distribution without any specific tendency with depth, resulting in organic carbon being highly aliphatic but surprisingly easily available for organisms. The higher SUVA index at 30 cm depth may be due to larger hydraulic conductivity of this particular soil layer.  $A_{254}/A_{365}$  demonstrated almost twice as high ratio values at S22 than for S4 and S12, including also a spatially more dynamic

depth distribution which indicates lower molecular weight of carbon compounds and much larger bacterial growth efficiency with clearly higher bacterial productivity further away from the stream. Additional to this enhanced spatial variability, the increased temporal variability at S22 as a dry site (due to deep groundwater flow paths; Bishop et al., 2004) matches with illustrated larger temporal variation in vertical soil profiles at dry moraine sites compared to humid horizons (like S4 is characterized; Fig. 9). Still, a slight tendency of higher absorbance ratio values towards the surface can be noticed that was also stated for the same site in an earlier study by Ågren et al. (2008b), coming along with even more bacterial growth at near-surface locations. However, the remarkable high bioavailability of organic carbon further away from the stream may not influence riparian and stream TOC discussed in this study to a large extent because these soils are hydrologically not connected to the sites of interest (Bishop et al., 2004).

Summing up, spatial distribution was less stable in case of TOC concentrations than in terms of the biological indices. Thereby, the spatial stability of  $A_{254}/A_{365}$  within the single sites is comparable to the one of  $SUVA_{254}$ . It implies that TOC quality is not influenced or deformed in very large scale with depth or when comparing various RZ locations: similar organic carbon character is found within the whole Krycklan catchment, independently of different soil types or hydromorphological conditions. Similar for all three investigated parameters, variability within the data was larger for sediment and dry moraine sites than for the other two groups of moraine riparian soils. Possible explanations for more wide-spread values that are these locations consist of different soil types with mineral, semi-organic and organic soils whereas humid and wet moraine sites are dominated by organic soils and higher water tables that lead to less variability in organic carbon concentrations and biological indices.

#### *4.1.2 Export fluxes in the RZ*

Comparing the TOC export values from the riparian soil samples of 12 to 206 kg/ha/y with the variation within the stream, the RZ shows a range of carbon export that is more than twice as large as the one of the streams (52 to 135 kg/ha/y). A similar relation of difference was found for TOC

concentration minima and maxima of the RZ and in streams in the same catchment (Buffam et al., 2007; Grabs et al., 2010).

Smallest export fluxes from sediment sites may result from generally low TOC concentrations whereas for dry moraine sites, the fluxes are explainable by reduced expected water flow through the riparian soil due to low groundwater tables (>45 cm underneath the soil surface on average) and therewith missing connection of soil layers closer to the surface. Hydraulic conductivity decreases with increasing depth (Rodhe, 1987) and, thus, influences the water flow through the riparian soil and the exported TOC amounts (Hinton et al., 1998; Schiff et al., 1998; Nyberg et al., 2001; Laudon et al., 2004b). When the water level raises (for instance, during heavy rainfall or episodic flood events in spring), the superficial soil layers get activated and connected due to changes towards higher water flow pathways (e.g. Cory et al., 2007; Petrone et al., 2007). Subsequently, higher amounts of organic carbon are exported from the RZ into the streams (Bishop et al., 2004; Köhler et al., 2009). This applies also to wetter riparian superficial soil layers with largest hydraulic conductivities (Rodhe, 1987; Schiff et al., 1998), resulting in organic carbon being connected to the water flow paths. Thereby, export of organic carbon is directly depending on TOC concentration in the RZ and water flow paths through the soil (Hinton et al., 1998). Thus, highest export fluxes from wet (even significantly) and humid moraine sites which show highest TOC concentration are not surprising. Moreover, these findings also agree with experiments in other catchment areas (Fiebig et al., 1990; Hinton et al., 1998).

Analysing the development of TOC exports over the two-year study period, all temporal variation within a year shown as peak values (see Fig. 15) can directly be related to discharge increases, further demonstrated by e.g. Hagedorn et al. (2000) and Ågren et al. (2007) who described a positive correlation between TOC and discharge. Discharge peaks are caused by special hydrological events like the ice melting and resulting flood period in spring as well as heavy rain in July and November of the second investigation year. To a lesser extent, precipitation events may also be responsible for increased TOC export and related changes in the biological indices in August and October 2008. Larger spatial variability in TOC at those peak events does not agree with observed decreasing spatial

variability with discharge increases (Buffam et al., 2007); however, several studies (e.g. Ågren et al, 2007; Buffam et al., 2007; Köhler et al., 2008) also confirmed enhanced organic carbon export during spring flood periods. The observation of sediment soils presenting highest volume-weighted SUVA of the export fluxes and low volume-weighted absorbance ratio values matches well with the described conspicuous consistent pattern of both biological indices.

The picture presented by volume-weighted mean  $A_{254}/A_{365}$  of carbon exports shows statistically higher values for wet and humid moraine sites compared to as well as dry moraine and sediment locations with slightly higher temporal variation in the latter two groups for dry (R4, R9, R12) and sediment soils (R14, R15; see Fig. 9). Organic carbon of humid and wet horizons is therewith expected to be better available for organisms with enhanced bacterial growth conditions than in case of the other two groups. Thereby, the depth distribution is relatively stable for both biological indices (Fig. 9, 12), especially for wet and humid moraine sites which present a very constant pattern. However, more uncertainties in volume-weighted SUVA values exist also mainly for dry horizons (especially R4, R12) and sediments (R11, 15) as illustrated by larger temporal variation (Fig. 12). Lower temporal variability at humid and wet moraine riparian sites may be due to well-connected soils to the water flow as described above and therewith, contribute permanently high amounts of bioavailable organic carbon to the water bodies than drier locations or sediment sites (particularly R15). The latter two groups may potentially rather be subject of groundwater level changes and internal differences between the air-filled and water-filled soil pores.

Nevertheless, the constant depth distribution and similarities for humid and wet moraine sites between the sites of volume-weighted  $A_{254}/A_{365}$  and SUVA values of TOC export fluxes indicate consistent carbon character coming from all these riparian sites. At the same time, this means that TOC is similarly bioavailable for organisms and supports bacterial growth in the same way independently from its origin in the RZ regarding humid and wet horizons. Dry moraine and sediment locations export TOC with lower bioavailability as shown by lower volume-weighted absorbance ratios, and for sediments, further confirmed by significantly highest volume-weighted

SUVA indices, additionally illustrating highly aromatic carbon fractions in the exported TOC compared to moraine sites.

## **4.2 Streams**

### *4.2.1 TOC concentration and biological indices in streams*

TOC concentrations range from 12 to 40 mg/l in streams (see Table 5) which is about the same order as the measurements of riparian soils stated above. This range corresponds approximately with literature TOC concentration values within the Krycklan catchment (4 to 41 mg/l by Buffam et al., 2007 and Wallin et al., 2010 in two different studies) and another catchment in Northern Sweden (River Öre basin, 4 to 66 mg/l; Temnerud et al., 2007). Also Cory et al. (2007) stated comparative carbon concentration of RZs and streams. The result of highest organic carbon concentrations measured in wetland-dominated streams was also confirmed by other studies (e.g. Hope et al., 1994; Mulholland, 2003; Ågren et al., 2008b).

Forest-related streams (C1, C2) showed higher absorbance ratios than wetland-dominated sites (e.g. C4, C5) which is also found by Berggren et al. (2010) who compared biochemical parameters of forest streams, mire and lake outlets. In this study, however, the differences between the land use groups in this study are not as pronounced as stated by Berggren et al. (2010). Larger  $A_{254}/A_{365}$  values in forest-draining streams indicate lower molecular weight of TOC and higher expected biological growth compared with the other two investigated land use types. Also Berggren et al. (2007) and Ågren et al. (2008a) agreed on forest derived organic carbon increasing bacterial production and growth efficiency in streams more than carbon coming from mires. Van Hees et al. (2006) suggest that those LMW fractions of organic carbon character are produced by mycorrhizal fungi or roots or leached out from litter or dead plant material which happens at larger scale in forest ecosystems than in oligotrophic mires or wetlands due to faster degradation of organic compounds (Ågren et al., 2008a). According to Berggren et al. (2010), terrestrial LMW organic matter is directly available for microorganisms in streams and of high importance for bacterial production. The fact that streams related to mixed land use show intermediate -even though significantly different-  $A_{254}/A_{365}$  values compared to wetland- and forest-draining stream sites is in accordance with the



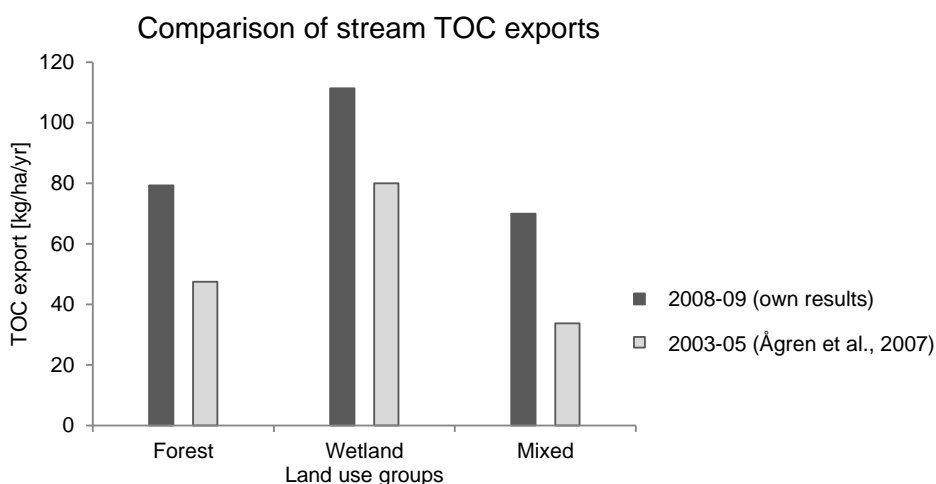
medium percentage of wetland coverage in the classification system with a division in the three land use types after Buffam et al. (2007).

Stream  $SUVA_{254}$  indices behaved consistent to  $A_{254}/A_{365}$ : forest-draining sites showed lowest SUVA values, implying also high bioavailability and rather lower aromaticity of TOC. The connection is further confirmed by relatively high degradation of organic matter of forest litter being inversely correlated to aromaticity (Kalbitz et al., 2003). This enables microorganisms to better uptake carbon coming from forest sites (Köhler et al., 2002a). These results also match with findings of Ågren et al. (2008b) who described larger SUVA values with increasing wetland coverage. However, in their study, the difference between landscape types was less pronounced for  $SUVA_{254}$  indices than for e.g. the absorbance ratio which cannot be confirmed here. Also other studies (Tipping et al., 1999; Hagedorn et al., 2000; Kalbitz et al., 2003) stated differences between streams draining catchments of different vegetation which is consistent to this report's results: carbon-rich stream water from peatland or wetland sites was found to have larger hydrophobicity and aromaticity of organic carbon (=larger SUVA value) than forest-draining stream water which at the same time indicates lower bioavailability (Perdue, 1998). This is reflected e.g. in highest SUVA values of TOC export from C5 and C6 as one wetland-draining and one mixed land use related stream site comparing all stream sites (see Table 5). Ågren et al. (2008a) illustrates lower organic matter production and smaller degradation rates in (oligotrophic) mires than in forests which may be one explanation for less bioavailable TOC in mixed and wetland-related water bodies.

In addition to statistically similar SUVA indices for mixed and wetland-draining sites, mixed land use were also more similar to wetland-dominated stream sites than to forest-related sites for  $A_{254}/A_{365}$  even though significant differences occur for this ratio. Generalized, absorbance ratio and SUVA both indicate organic carbon of lower molecular weight and enhanced biological productivity and bioavailability when being leached from forested subcatchments than compared to wetland-dominated areas.

#### 4.2.2 Export fluxes in the stream

Regarding export fluxes in streams, TOC values varied between 52 and 135 kg/ha/y which is slightly higher in numbers than usual TOC export ranges of 10 to 100 kg/ha/y in temperate and boreal rivers (Hope et al., 1994; Mulholland, 2003; Ågren et al., 2007). Further Scandinavian studies confirm similar results with lower variation of annual average TOC exports between 36 to 76 kg/ha/y (Northern Sweden, Laudon et al., 2004) or 26 to 71 kg/ha/y (Finland, Kortelainen et al., 1997). Most export fluxes are within the expected TOC range given in literature but two wetland-draining sites differ from this range: C3 with 135 kg/ha/y and C4 with 111 kg/ha/y (see Table 5, Fig. 16). However, also earlier studies concerning organic carbon in the same catchment presented highest areal specific exports from these two locations compared to all other sampling sites of each study: Ågren et al. (2007) measured 99 and 88 kg/ha/y for site C3 and C4 as mean TOC exports for 2003 to 2005; also Wallin et al. (2010) described highest values of dissolved inorganic carbon export measured at these wetland-related sites (15 and 14 kg/ha/y, respectively).



**Figure 19:** Comparison of averaged stream TOC exports in kg/ha/y (2008-2009) with literature values (2003-2005, from Ågren et al., 2007) divided into land use groups including data from all 14 monitored stream sites C1-C16 (note that C8 and C11 do not exist in this study).

In comparison, exports for 2008 to 2009 were higher than during the sample period of 2003 to 2005 (Ågren et al., 2007; see Fig. 19) which is founded by a direct relation to discharge (e.g. Kortelainen et al., 1997; Urban et al., 1989; Hagedorn et al., 2000; Mulholland, 2003; Temnerud and Bishop, 2005; Ågren et al., 2007) as well as differences and uncertainties within the two sample years. Higher water flow within a catchment leads to

increased exports (Ågren et al., 2007). Runoff of 269 mm/y as mean for 2003-2005 (Ågren et al., 2007) was considerably lower than 361 mm/y for 2008-2009. Together with larger TOC quantities being leached out of wetlands compared to forested or mixed sites (Creed et al., 2003; Mulholland, 2003; Raymond and Hopkinson, 2003; Ågren et al., 2008a), the obviously increased TOC exports for sites C3 and C4 in the presented data set should be reasonable. Wetlands exporting significantly higher TOC amounts than the two other land use types were further supported by Ågren et al. (2007) stating that wetland coverage is the strongest correlated factor to TOC export. Buffam et al. (2007) confirmed the same for base flow while the correlation is less pronounced during snow-melting in the Krycklan area. A negative correlation between forest coverage and area-specific export of TOC also matches with these findings (Ågren et al., 2008a).

Compared to fluxes in RZs, volume-weighted  $A_{254}/A_{365}$  of the carbon exports in the streams were even more stable with a range from 14.2 to 16.8 Abs/ha/y (RZ: 9.7 to 15.7 Abs/ha/y); the same counts for volume-weighted SUVA of TOC exports which varied between 15.1 and 17.8 SUVA/ha/y (RZ: 12.2 to 32.5 SUVA/ha/y). Thus, the quality of organic carbon is expected to be relatively constant in the streams -independently from land use type- while the quantity may vary much more (TOC export fluxes show higher temporal variability). This almost contrasts the statement from above about significant differences between forest-draining and wetland-related streams of absorbance ratio and SUVA index. Here, for the volume-weighted biological indices, carbon character does not distinguish much between the two main land use types, forests and wetlands.

Even though the characteristics of carbon export fluxes are quite stable, few investigated sites strike the eye. So do stream locations C5 and C6 as one wetland-draining and one mixed site present lowest volume-weighted absorbance ratio of TOC exports and at the same time highest volume-weighted SUVA indices. This means export of low bioavailable but high-molecular weighted carbon structures with large aromaticity. Against it, forest-related locations (C1 and C2) rather export highly bioavailable LMW organic carbon with low fraction of aromatic structures as indicated by significantly largest volume-weighted  $A_{254}/A_{365}$  and comparatively low volume-weighted SUVA of carbon being exported. Similar observations are

also found by Ågren et al. (2008a) and Berggren et al. (2010) concerning the large share of LMW fractions in forest, as described by absorbance ratio and SUVA without taking the flow factor into account. Furthermore, Kalbitz et al. (2003) and Ågren et al. (2008b) stated positively correlated SUVA values with wetland area. Also Köhler et al. (2002a) presented potentially larger bacterial uptake of carbon from forested areas.

Nevertheless, the overall relatively stable volume-weighted  $A_{254}/A_{365}$  and SUVA indices of the exported carbon fluxes are remarkable, indicating the same quality of exported carbon with regards to similar bioavailability of TOC. This further agrees with study results of Fellman et al. (2008) stating no big difference between forest and peatland areas in the view of the biodegradable part of TOC. At the same time, statistical analyses did not detect significant differences for mixed and wetland-draining subcatchments at least in case of volume-weighted SUVA and for  $A_{254}/A_{365}$ . Lacking of specific literature especially regarding absorbance ratio and SUVA in relation to carbon export fluxes impede further comparisons.

#### **4.3 Comparison of fluxes from riparian zones and streams**

Several authors (Bishop et al., 1993; Hinton et al., 1998; Creed et al., 2003; Seiberg et al., 2009) found that the RZ influences the chemical dynamics of the stream to a much larger extend than upslope areas. This counts especially for TOC playing a key role for stream water quality (Shafer et al., 1997; Hruška et al., 2003). The same is also shown in this study by matching TOC concentrations as well as absorbance ratio and SUVA indices of S-transect site S4 to all riparian sites compared to S22 and, in addition, by similar ranges of TOC concentration in the RZs and streams. The difference of upslope and riparian sites supports the idea of a chemical signal of a stream created in the RZ and not at upslope areas. Assuming this also being true for export fluxes of TOC and its accompanying volume-weighted  $A_{254}/A_{365}$  and  $SUVA_{254}$  indices, comparisons of quantities leached out from riparian soils and those being measured in the streams are generally feasible.

### *Total organic carbon*

Comparisons of particular locations belonging to subcatchments related to first-order streams and surrounding riparian soils representing such a subcatchment with each other result in the expectation of similar TOC quantities in the RZs and in the streams only being true for one case: C2 (forest) and R5 (humid moraine). The other two humid moraine sites R6 and R7 export relatively very high TOC amounts and exceed the in-stream values approximately twice. The fact that these sites even overrun the wet moraine example R8 in TOC exports is surprising but on average with taking R5 into account, humid horizons still export less carbon compounds than wetlands. However, R6 and R7 already presented comparatively highest TOC concentrations (see Table 3), even more than both wet moraine sites. Statistics result in larger (but not significantly) TOC export from wet compared to humid moraine sites only because the other two humid soil sites (R5, R10) consisted of relatively small carbon concentrations.

Already one difference is given by the groundwater level height: Sites with groundwater levels close to the soil surface (<15 cm below the surface like wet moraine sites) often show large TOC amounts (Seibert et al., 2009; Lyon et al., 2011) that can easily be exported by water flowing through permanently connected carbon-rich soil layers (Bishop et al., 2004) at a more constant level. Hence, it is not surprising that R8 exports more TOC than the related stream site C4. For wet sites like R8 dilution can occur through surface runoff, particularly in times of saturated or partly frozen soils (see also Fig. 1; Laudon et al., 2007). Even though wetlands form a major TOC source in boreal catchments (Dillon and Molot, 1997; Hope et al., 1997. Laudon et al., 2004) and C4 consists of significantly highest TOC within the streams, also dilution effects in the stream need to be taken into account that are especially noticed in wetland streams (Schiff et al., 1998; Buffam et al., 2007).

Humid moraine soils, in contrast, demonstrate little lower groundwater levels (between 45 and 15 cm below the soil surface) so that the surface-near soil layers as largest TOC sources (Bishop et al., 2004; Sanderman et al., 2009) only get hydrologically connected in times of enhanced discharge from upslope areas at or after precipitation events. This may lead to enormous TOC quantities being leached from humid soils after these water

level rises so that over time, higher variation in the organic carbon exports are noticed (Grabs et al., 2010). However, one needs to keep in mind that uncertainties remain in the calculations and measurements, including groundwater monitoring, for all sites, leading to handling some results with care. The classification on the basis of groundwater table positions is an artificial system with certain thresholds at 15 and 45 cm soil depth that determine if a site is ranked as wet, humid or dry moraine site. The groundwater level of site R5 (-15 cm, see Table 3), for instance, may include few measurement mistakes and resulting uncertainties which may also be due to e.g. the simplicity of the RIM modelling approach. This could have resulted in a potential assignment of this site to the wet moraine horizons instead of the actual suggested humid moraine classification. That is one possible reason why differences in carbon export especially between R5 and R6 which are located closely to each other exist, even though both sites consist of only organic soils in the decisive upper layers and show similar water levels (-15 and -19 cm, respectively, see Table 3). Additionally, a remaining problem of linking a riparian site to a stream as being representative for a whole subcatchment occurs since still some flow paths connections between RZ and stream are unknown and the chemical status of stream water is influenced by both, terrestrial (mainly in RZs) and in-stream processes (Löfgren et al., 2011). Missing information about water flow from riparian sites into streams could have led to further uncertainties. However, for a preferably exact comparison in a best possible way it is important that both sampling locations to compare are situated in the same subcatchment since (sub-)catchments were defined by the presumed water flow in the catchment basin and therewith, direct influences of the chemical status can be assumed.

Generally, more organic carbon is exported from the RZs than measured in the streams for most compared pairs; this does not work in long-term view having in mind that the chosen riparian sites are assumed to be representative for the whole RZ. Possible explanations for this result can be within-stream processes (Löfgren et al., 2011), measured particle size differences or spatial variation of TOC export within the RZ along the stream. The fact that RZs vary along streams can be emphasized e.g. by groundwater level differences coming along with wetness which plays an important role regarding the carbon concentration (Köhler et al., 2009, Lyon et al., 2011), and therefore, regarding TOC. In this context, exported carbon

quantities are often higher in riparian soils than in streamwater. TOC in a stream can get oxidized by photo-degradation (e.g. Bertilsson and Tranvik, 2000; Köhler et al., 2002a) and microorganisms in the water (Jansson et al., 2000) or may sink down as riverine sediment in case of bigger particles; all processes result in decrease of TOC in the stream water (Laudon et al., 2004). In terms of particle sizes, differences exist for riparian soil and stream water although the same compounds of TOC are measured in both locations. This is due to the fact that POC as part of the total organic carbon spectrum consists of larger non-dissolved particles which are mainly retained in the soils and not leached out into the stream water. Hence, these potentially heavier non-dissolvable fractions of organic carbon still form part in the measurements of riparian soils but (usually) not in streams, leading to comparatively smaller export measurements at stream sites. Organic carbon was almost only found in form of DOC in boreal waters and environment (Ivarsson and Jansson, 1994; Gadmar et al., 2002) where POC quantities can be treated as negligible (Laudon and Bishop, 1999; Ågren et al., 2008b). Therewith, potential differences between exports of riparian soil and stream water with higher values for RZs can occur.

Organic carbon coming from R4 and mixed-stream site C6 shows the opposite situation with riparian soil exporting less than the TOC amount measured in the stream. One possible reason can be the water level dependence of riparian soils in terms of organic carbon build-up being larger, the higher the groundwater level is (Lyon et al., 2011). As a dry moraine site, R4 presents a low average groundwater table at  $\leq 0.45$  m depth; in doing so, rather small rates of TOC production can be expected (Grabs et al., 2010). Additionally, carbon is less available for microorganisms when soils get dry (Marscher and Kalbitz, 2003). Moreover, near-surface soil layers being rich of organic material usually demonstrate increasing hydraulic conductivities when hydrologically connected to the water flow path (Schiff et al., 1998; Bishop et al., 2004). However, this can only happen in case of large precipitation events due to low basic groundwater table in dry soils (R4: deepest groundwater level position at -62 cm, Table 3). Hence, R4 is the riparian site with lowest TOC concentration and export values (see Table 4). Based on the distance of approximately 500 m in between the location of R4 and C6, one could discuss to what extent R4 can be treated as a completely representative location for all riparian sites, especially since some links between riparian

soil water and stream water are not completely known yet (Löfgren et al., 2011). In case of an assumed reduced distance between both compared sites, the difference between TOC exports could possibly be smaller. In this particular example, a mixture of organic carbon qualities and quantities from different RZ locations upstream are likely to be measured in the stream, resulting in potentially higher TOC export measurements in the stream and less similar to the RZ values.

Concerning the higher variation in TOC exports in RZs compared to rather constant export measurements in stream water, internal and external impacts can be named (Marschner and Kalbitz, 2003). Riparian sites are more diverse in their soil characteristics (e.g. mineral, semi- and organic soils with different properties) and depending on water level changes. Since hydromorphological conditions including wetness (Köhler et al., 2009) are very important in terms of organic carbon content, this larger temporal and spatial variability is also reflected in RZ export fluxes. The variation does not occur at stream sites to the same extent and is more pronounced in RZs. However, also in-stream TOC concentrations and exports get affected by changes in discharge, resulting in e.g. possible dilution effects (Buffam et al., 2007), but rather in short-term scale.

### *Biological indices*

Analysing both data sets with regard to volume-weighted  $A_{254}/A_{365}$  as well as SUVA indices of the TOC export fluxes, values of stream and riparian soil measurements are within the same range with only minor differences, indicating generally similar carbon quality of the exported organic carbon in the whole catchment area with almost the same expected bacterial growth capacities as well as molecular weight and aromaticity. In detail, streams most often presented slightly higher values for volume-weighted absorbance ratio and SUVA than RZ sites which may primarily be based on uncertain values used in further calculations. Compared to TOC exports, the stream-RZ differences are smaller in this comparison, also attesting rather similar biological indices.

Ågren et al. (2008b) described a connection between RZs and the adjacent streams when concluding that increasing groundwater tables in riparian soils lead to rising absorbance ratios in stream water (due to higher



$A_{254}/A_{365}$  in organic carbon closer to the surface). The same is found when comparing the single pairs of all five specially analysed cases with each other: volume-weighted  $A_{254}/A_{365}$  of the carbon fluxes in the streams are little higher than in riparian soils. Thereby, export fluxes tend to vary more in RZ sites for all three components (TOC and volume-weighted absorbance ratio and SUVA of the TOC export), possibly explicable by the dependence of leaching or export processes on groundwater level changes in the riparian soil whereas water flow is more constant in streams. However, statistically, no significant difference was found between volume-weighted absorbance ratio and SUVA of carbon exports in RZs and stream measurements. Hence, the remaining distinctions are very small and possibly due to uncertainties of values or simply natural variability. Generally, literature values and statements are complicated to include in this part of the discussion since comparisons of the volume-weighted biological indices within and between RZ and streams in this way are done for the first time.

Regarding more detailed comparison, averaged carbon exports from humid moraine soils (R5-R7) and forest-draining streams (C2) with slightly higher bioavailability and enhanced bacterial growth -as indicated by volume-weighted SUVA and absorbance ratio of TOC exports in comparison with other pairs, especially C6/R4- can be explained by the fact that these sites consist of almost only organic soils. Together with relatively high groundwater tables giving reason for larger TOC concentrations (Lyon et al., 2011), this means that potentially more degradable organic compounds are leached out which additionally comes along with faster degradation of organic matter in forests (Ågren et al., 2008a). Moreover, expected lower metabolization of carbon into  $\text{CO}_2$  as described for dry sites (Grabs et al., 2010) accordingly implies more exported and measured bioavailable organic matter at humid riparian soils.

For the case of wet moraine site R8 and wetland-draining stream C4, volume-weighted  $\text{SUVA}_{254}$  of carbon exports coincide very well, showing almost the same value for both locations; a rather similar picture is presented by volume-weighted  $A_{254}/A_{365}$ , too. Both indicate intermediate bioavailable exported TOC with a rather balanced relation of low and high molecular weight fractions and medium aromaticity compared to the other pairs in this direct comparison. This may be explained by an interaction of

relatively thick organic layers in the wet soils (Grabs et al., 2010) but rather low actual organic matter production with reduced degradation at wet horizons compared to forest-related sites (Ågren et al., 2008a).

For the pair C6/R4, stream site draining mixed landscape as well as the dry moraine example present lowest volume-weighted absorbance ratio, meaning higher weighted TOC molecules and less bacterial production from these areas. Again, volume-weighted SUVA indices contrast the pattern of volume-weighted  $A_{254}/A_{365}$  at least regarding C6 with highest SUVA. Hence, this site rather exports carbon of high aromatic and less bioavailable character. However, R4 does not fit perfectly into this pattern with a lower volume-weighted SUVA index. In detail, slightly larger volume-weighted  $SUVA_{254}$  for C6 compared to R4 can be explained by in-stream processes like heavier molecules sinking down on the ground of the water body or the fact that POC is found at riparian sites but not exported to streams in the same amount as already discussed in the particle size section of TOC. Therewith, this special example does not confirm the overall picture of similar characteristics of TOC coming from riparian soils compared to organic carbon found in stream water as well as all other pairs do. However, statistically, no significant differences occur between the discussed RZ and stream sites. Thus, this comparison again matches with the overall picture of similar biological indices indicating almost the same carbon qualities in the catchment with only minor distinctions of the exported organic carbon.

#### *Whole catchment perspective*

In terms of stream order and a comparison of up- and downstream locations, the clear decreasing tendency of exported TOC quantities with increasing stream order from headwaters to downstream locations is also stated by earlier studies (e.g. Mattsson et al., 2003; Laudon et al., 2004; Ågren et al., 2007; Wallin et al., 2010) for both, measurements in riparian soil and stream water. Possible explanations are biochemical processes in the stream, runoff-generation or landscape element influences like from mires or peatlands and forests as well as groundwater inflow from organic-poor riparian zones further downstream (Hope et al., 1994; Temnerud, 2005; Temnerud and Bishop, 2005; Ågren et al., 2007; Buffam et al., 2007). Thereby, a higher proportion of sediment soils with low organic carbon

concentrations further downstream at RZ sites related to higher-order streams (mainly R14, R15) may cause lower TOC export from the riparian soils (Ågren et al., 2007; Buffam et al., 2008). As described above, silty sediments are able to adsorb high amounts of organic substances due to larger specific surface area and thus, the (carbon) concentration can be further reduced (Kalbitz et al., 2000). This can result in smaller export fluxes of organic carbon -amongst others- in streams, especially located downstream in the catchment like, for instance, sites C14-C16.

The comparison of volume-weighted  $A_{254}/A_{365}$  in riparian soil and stream water confirms no distinct tendencies between up- and downstream locations which indicates rather similar organic carbon character coming from all investigated sites with almost the same good bacterial growth conditions all over the Krycklan catchment. For volume-weighted SUVA indices of the exported TOC, the picture is not as clear due to higher temporal and spatial variability in the RZs while stream sites up- and downstream export similar organic carbon regarding aromaticity and bioavailability. However, the general range of volume-weighted SUVA is rather narrow, and together with earlier stated group-wise investigation and statistics for this index, the same finding of relatively similar carbon character from the whole catchment can be supported.

## 5 CONCLUSION

For riparian soils and stream sites of the Krycklan catchment, relations were investigated by the use of TOC concentration, absorbance ratio and SUVA index as well as their export-related values. Thereby, a conspicuous relation is confirmed: high  $A_{254}/A_{365}$  values coincide with low  $SUVA_{254}$  indices -both illustrating good bacterial growth and bioavailability of organic carbon- and vice versa. Analyses of all three parameters at upslope and riparian sites confirm the expected creation of hydrochemical signals of stream water in the RZ and not at upslope areas. For this reason, direct comparisons of organic carbon leached out from riparian soils and those measured in the streams are reasonable. In this study, first-order streams and riparian sites close-by differed more with regard to TOC quantities than quality. Volume-weighted  $A_{254}/A_{365}$  and  $SUVA_{254}$  of the carbon export fluxes matched very well, especially for wet-moraine riparian and wetland-dominated stream site. Thereby, this comparison agreed in highly bioavailable TOC exports with low molecular weight and small proportion of aromatic structures relative to the other investigated pairs.

Generally, export fluxes varied more in RZs for TOC export as well as volume-weighted absorbance ratio and SUVA than in streams. This may be explicable by the dependence of export processes on groundwater level changes in the riparian soil in contrast to more constant water flow in streams. Further possible explanations for slight discrepancies regarding comparison between stream and RZ sites may be unequally measured particle sizes at both locations (rather large POC fractions were additionally measured at riparian soils but retained in the RZ and not leached into streams) or in-stream processes as well as generally assumed (partly relatively large) uncertainties in measurements or the relative simplicity of the RIM model.

For riparian soils, factors like soil characteristics (organic, semi-organic or mineral soil) as well as wetness (indicated by groundwater table position) strongly influence TOC quantity and also quality in a reduced extent. Thereby, decreased bacterial production result in less bioavailable carbon of higher molecular weight as well as smaller TOC amount at sediment and dry moraine sites whereas organic carbon was larger in quantity and bioavailability when being leached from soils with constantly high water

level (wet and humid moraine sites). TOC from sediment also differs in aromaticity by showing larger aromatic compounds than moraine sites, coming along with reduced bioavailability, as indicated by higher SUVA indices

Ranges of TOC concentrations were almost similar in streams and riparian soils. Thereby, mixed landscapes and wetlands did not differ statistically in  $SUVA_{254}$  values and only showed small differences regarding  $A_{254}/A_{365}$ , referred to generally similar carbon qualities from these locations. Closer examination found organic carbon from forest-dominated streams being characterized by little lower molecular weight and reduced aromaticity, coming along with slightly enhanced biological growth and bioavailability compared to wetland- and mixed land use related streams. In general, volume-weighted mean biological indices of these TOC exports were more stable in stream measurements than carbon exports themselves. A comparison of up- and downstream sites for riparian soils and stream sites showed TOC reductions towards downstream locations which were more variable -temporally and spatially- in the RZs. Furthermore, the site- and pairwise comparison approved that organic carbon quality all over the Krycklan catchment is similar, rather independently from group classification according to soil characterization or related land use type. At the same time, this indicates the same bioavailability and support of bacterial growths as well as similar aromaticity of TOC from RZ and streams. This again emphasizes the basic idea of RZs playing an important role in determine the hydrochemical conditions in streams.

In the end, the use of biological indices simplifies the characterization of organic matter and allows the assessment of its bioavailability for (micro-) organisms in the surrounding environment, even though the type of organic carbon is not directly determined. Further research may be needed to finally answer remaining questions with regard to differences between TOC exports measured in riparian soil and streams and variation in absorbance ratio and SUVA between both locations and analyses in smaller temporal scales. Additionally, missing links between water flow paths from RZ into streams are to be clarified.

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