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Dynamics of dissolved and particulate organic carbon and nitrogen in forest ecosystems

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List of Abbreviations

BayCEER	Bayreuth Center of Ecology and Environmental Research
CPOC	Coarse particulate organic carbon
CPOM	Coarse particulate organic matter
DM	Dry mass
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DTN	Dissolved total nitrogen
EC	Electrical conductivity
EEM	Excitation-emission matrix
FLF	Fulvic-like fluorescence
FPMM	Fine particulate mineral matter
FPOC	Fine particulate organic carbon
FPOM	Fine particulate organic matter
FPON	Fine particulate organic nitrogen
HIXem	Humification index deduced from fluorescence emission spectra
HLF	Humic-like fluorescence
n.s.	No significant
OM	Organic matter
p	Significance
PLF	Protein-like fluorescence
POC	Particulate organic carbon
POM	Particulate organic matter
PON	Particulate organic nitrogen
r	Correlation coefficient
S.D.	Standard deviation
SOM	Soil organic matter
$SUVA_{280}$	Specific ultraviolet absorbance at 280 nm
TN	Total nitrogen
TOC	Total organic carbon
TON	Total organic nitrogen
TSS	Total suspended solid
UV	Ultraviolet

Summary

Severe precipitation events become more frequent due to global warming. The changes of climate will also affect the vegetation and in many temperature forest regions broadleaf trees will become more dominant as they are expected to better cope the future climate. These changes together can affect to soil C and N dynamics in forests by changing the production and consumption of organic matter and by manipulating the export of C and N to aquatic ecosystems draining forested watersheds.

The general goal of this study was to investigate the effects of heavy precipitation events and tree species on the quantity and quality of dissolved and particulate organic C and N in forested soils and watersheds. In the field study, the effect of precipitation events and tree species on the export of fine particulate and dissolved organic C and N (FPOC, FPON, DOC and DON) from forests to streams was studied in a purely deciduous forested (PD) and a mixed coniferous/deciduous (MCD) forested watershed in South Korea during the 2013 during monsoon season. The concentration of DOC, DON, FPOC and FPON, isotope abundance of ^{13}C and ^{15}N and spectroscopic properties ($SUVA_{280}$, HIXem and fluorescence intensity) were measured in soil solutions and runoff samples.

In the laboratory study with batch and percolation experiments, the depletion and recovery of potential DOC and DON pools were investigated in spruce, larch, beech and deciduous forest floors at 5°C and 15°C.

In the studied forested watersheds, DOC was the dominant form of organic C export during both dry and wet periods. Only following single heavy storm events, FPOC fluxes exceeded those of DOC. NO_3-N was the dominant form of N in runoff. The DOC/DON ratio in runoff varied with increasing discharge while the ratio of FPOC/FPON was independent of discharge. Dissolved and particulate organic matter in runoff originated mostly from forest floor leachates and from upper mineral soil. The quality parameters of DOC indicated also a change of hydrological flow paths from deeper to upper soil during heavy storm events. In the MCD watershed the deeper soil solution contributed mostly to DOC in runoff during both low and high discharge, while in the PD watershed the origin of DOC in runoff was from deeper soil (soil solution) during low discharge and from forest floor during high discharge. During the wet period the total DOC export fluxes were much larger in the PD watershed (16 kg C ha^{-1}) than in the MCD (7 kg C ha^{-1}) watershed, which coincided with larger net DOC release from the deciduous forest floors than from the coniferous. NO_3-N export fluxes in runoff during the

wet period were higher in the MCD watershed (5 kg N ha^{-1}) than in the PD (3 kg N ha^{-1}). The total export fluxes of DON, FPOC and FPON in runoff were similar between two watersheds.

In the two laboratory experiments, DOC and DON pools in forest floors behaved similar in response to depletion and recovery as indicated by the stable DOC/DON ratio over incubation time. The recovery of DOM pools following leaching was rather fast, mostly within 14 days, but depended on biological activity (temperature), extraction volume and tree species. The recovery and production rate of DOM was in the order; high > low temperature, large > small extraction volume/percolation rate, Oi > Oe > Oa layers and also deciduous/broadleaved > coniferous samples. The effect of DOC leaching on soil CO_2 evolution was low in forest floors, indicating the refractory character of the DOC leached.

The findings from both field and laboratory showed that the quantity and quality of dissolved organic C and N were controlled by the biological (microbial activity, tree species), physical (flushing and leaching) and hydrological (precipitation) processes.

In conclusion, this study demonstrated the overwhelming effect of heavy precipitation events on the export of dissolved and particulate organic matter from forested watersheds. Future changes in the precipitation regime and tree species will cause changes in the export of organic C and N from forested watersheds into aquatic ecosystems.

Keywords: Dissolved organic carbon (DOC), Dissolved organic nitrogen (DON), fine particulate organic carbon (FPOC), fine particulate organic nitrogen (FPON), forested watershed, forest floor, heavy precipitation, mineralization, soil respiration

Zusammenfassung

Extreme Niederschlagsereignisse werden in Zukunft in Folge des Klimawandels zunehmen. Das veränderte Klima wird darüber hinaus auch in der temperaten Zone zu einer Zunahme der Fläche an Laubwäldern führen, da diese vermutlich besser an zukünftige Klimabedingungen angepasst sind als Koniferen.

Das generelle Ziel der Arbeit war es die Auswirkungen extremer Niederschlagsereignisse und der Baumart auf den Export von gelöstem organischen Kohlenstoff (DOC) und Stickstoff (DON) sowie von fein-partikulärem Kohlenstoff und Stickstoff (FPOC, FPON) in bewaldeten Einzugsgebieten zu untersuchen. Dazu wurden die Konzentrationen von DOC, DON, FPOC und FPON, die Isotopensignaturen ^{13}C und ^{15}N sowie die spektroskopische Eigenschaften der gelösten organischen Komponenten ($SUVA_{280}$, HIXem und Fluoreszenzintensität) in Bodenlösungen und Abflussproben in einem Laubwald- (PD) und in einem Mischwald- (Laub und Nadelwald, MCD) Einzugsgebiet in Korea während der Monsun-Saison 2013 bestimmt.

In Laborversuchen wurde darüber hinaus in Batch- und Perkolationsexperimenten die Dynamik der Erneuerung der Pools von DOC und DON nach einer massiven Extraktion mit hohen Wassermengen untersucht. Dazu wurden Proben aus Humusauflagen von Buche, Fichte, Lärche und einem Laub-Mischwald verwendet.

In den bewaldeten Einzugsgebieten war DOC die dominante Form des Exports von organischem Kohlenstoff sowohl in der Trockenzeit als auch in der Monsun-Saison. Nur nach extremen Niederschlägen kam es vereinzelt zu einem Überwiegen der Flüsse an FPOC. Die Verhältnisse von DOC/DON im Abfluss variierten mit der Abflusshöhe, während die Verhältnisse von FPOC/FPON konstant blieben. Die gelösten Substanzen im Abfluss stammten zum größten Teil aus der Humusauflage und die partikulären vom oberen Mineralboden. Die Qualitätsparameter von DOC zeigten eine Änderung der hydrologischen Fließwege bei hohen Niederschlägen an, hin zum Oberboden. Im MCD Einzugsgebiet resultierte der DOC im Abfluss dennoch meist aus tieferen Bodenschichten, während tiefere Bodenschichten im PD Einzugsgebiet als Quelle für DOC nur in der Trockenzeit agierten.

In der Monsun-Saison erreichte der DOC Austrag aus dem PD Einzugsgebiet mit 16 kg C ha^{-1} einen deutlich höheren Wert als im MCD Einzugsgebiet (7 kg C ha^{-1}). Die Austräge an NO_3-N in der Monsun-Saison waren mit 5 kg N ha^{-1} im MCD höher als im PD Einzugsgebiet (3 kg N ha^{-1}). Die Austräge von DON, FPOC und FPON waren hingegen in beiden Einzugsgebieten ähnlich.

In den beiden Laborexperimenten verhielten sich DOC und DON identisch in Hinblick auf die Dynamik bei Freisetzung und Erneuerung der Pools. Die Erneuerung der Pools von DOC und DON nach massiver Freisetzung war relativ rasch, innerhalb von < 14 Tagen und hing von der biologischen Aktivität (Temperatur) und der Baumart ab. Die Rate der Erneuerung war in der Reihenfolge hohe Temperatur > geringe Temperatur, hohes Extraktionsvolumen > geringes Extraktionsvolumen, L > Of > Oh Lage und Laubbäume > Nadelbäume.

Die Extraktion von DOC erniedrigte die CO_2 Emission der Bodenproben nicht oder nur gering, was den rekalzitranten Charakter des extrahierten DOC unterstreicht.

Die Ergebnisse der Freiland- und Laborstudien zeigten somit den Einfluss von biologischen (mikrobielle Aktivität und Baumart), physikalischen (Fließwege) und hydrologischen (Niederschlagsereignisse) Prozessen auf die Dynamik von DOC und DON in Böden und in Einzugsgebieten.

Zusammenfassend zeigt diese Arbeit den dominierenden Effekt hoher Niederschlagsereignisse auf den Export von gelösten und partikulären organischen C und N Verbindungen in bewaldeten Einzugsgebieten. Zukünftige Änderungen der Niederschlagsintensitäten und der Baumart werden daher die Exporte von C und N aus bewaldeten Einzugsgebieten in nachgeschaltete aquatische Systeme verändern.

Schlüsselworte: Gelöster organischer Kohlenstoff (DOC), gelöster organsicher Stickstoff (DON), fein-partikulärer organischer Kohlenstoff (FPOC), fein-partikulärer organischer Stickstoff (FPON), bewaldete Wassereinzugsgebiete, Humusauflage, hohe Niederschläge, Mineralisation, Bodenrespiration.

1 INTRODUCTION

1.1 General background

1.1.1 Definition of dissolved and particulate organic matter in solutions

Total organic matter in terrestrial and aquatic solutions is operationally classified by size, like dissolved organic matter (DOM < 0.45 μm) and particulate organic matter (POM > 0.45 μm) (Thurman 1985, Kalbitz et al. 2000, Tank et al. 2010, Bolan et al. 2011). Previous studies have often used a 0.7 μm pore size of glass filter for POM fraction for technical aspects in the analysis (Bauer and Bianchi 2011, Mostofa et al. 2013). POM is again fractionated in fine particulate organic matter (FPOM) from 0.45 μm to 1 mm and coarse particulate organic matter (CPOM) that is larger than 1 mm (Tank et al. 2010).

POM is made up by living organisms and detritus (dead organisms and fragments of cells or organisms), whereas DOM mainly comprises bioactive organic matter (able to promote biochemical reactions), refractory organic matter (resistant to bacterial decomposition) coming from the decay of plant and animal remains in soil as humus that is abundant in forest floors, labile/nutrient (easily decomposable/consumable by organisms) and volatiles (Table 1.1).

Table 1.1.1 Classification of organic matter in soil and aquatic ecosystems by size, type and constituents

Size	Acronym	Type	Constituents
> 1 mm	CPOM	Live	Fauna (earthworms, milli/centipedes)
		Dead	Organic detritus
			Woods and leaves
0.45 μm - 1 mm	FPOM	Non-colloidal/colloidal	Microorganisms (bacteria, fungi, algae, protozoa)
			Zoo/phytoplankton
< 0.45 μm	DOM	Bioactive	Enzymes, vitamins, hormones
		Refractory	Humic/fulvic acids, lignin, melanin, chitin
		Labile/nutrient	Lipids (fats, waxes, resins)
			Carbohydrates (sugars, celluloses, hemicelluloses)
			Proteinaceous (amino acids, proteins, peptides)
		Volatile/phytotoxic	Alcohols
			Hydrocarbons (aldehydes, ketones, phenolic acids, coumarins, glycosides, short-chain alphatic acids)

Source from Wild 1993, Stevenson and Cole 1999, Bertoni 2011

1.1.2 Significance of DOM in terrestrial and aquatic ecosystems

DOM comprises only a small part of soil organic matter (SOM), nevertheless, it influences biogeochemical processes in terrestrial and aquatic ecosystems because of its mobility and activity (Bolan et al. 2011, Kaiser and Kalbitz 2012, Tipping et al. 2012a). DOM production is related to carbon (C) and nitrogen (N) mineralization in forest soils (Michel and Matzner 2002, Smolander and Kitunen 2011) and, moreover, it plays a key role in transport and cycle of C (Bauer and Bianchi 2011, Bianchi 2011, Borken et al. 2011) and N (Dannenmann et al. 2011, Canham et al. 2012, Tipping et al. 2012b). Dissolved organic carbon (DOC) leaching from topsoil adds to the C pool of the soil (Kalbitz and Kaiser 2008) and serves as an e- donor in denitrification, resulting in the emission of greenhouse gases, such as nitrous oxide (N_2O) and nitric oxide (NO), (Korom 1992, Orosz 2006). Similarly, the supply of plant-derived DOM (from crop) to the soil increased soil CO_2 and N_2O emissions (Qiu et al. 2015) as DOM in soil can influence nutrient and energy supply to microorganisms (Fagerberg et al. 2010, Schmidt et al. 2011, Jones and Kielland 2012). DOM mobilization in soils can be controlled by sorption to soil minerals or by (co-)precipitation with reactive mineral phases, such as metal oxides (Al and Fe) and hydroxides (Schwesig et al. 2003, Kalbitz et al. 2005), as reflected by decreasing DOC release in mineral soils (Kaiser and Guggenberger 2000, Kalbitz et al. 2000, Kalbitz and Kaiser 2008, Kindler et al. 2011).

Several studies investigated the metal binding of DOM and the effects on DOM and metal mobility in soils. The mobility of heavy metals (e.g. Al, Fe and Cu cations) decreased at lower DOC concentrations (Strobel et al. 2001, Nierop et al. 2002). Similar to the mobility of heavy metal, the mobility of pesticide increased with increasing DOM concentration and decreasing sorption capacity in soils (Li et al. 2005, Song et al. 2008).

In aquatic ecosystems, DOM influences the nutrient cycle through metabolism (catabolism and anabolism) (Liu and Tay 2000), for example, the uptake of inorganic C by autotrophs (e.g. vascular plants and algae) and the consumption of organic C and the release of inorganic C by heterotrophs (e.g. animals and fungi) (Bianchi 2006, Bianchi and Bauer 2011). DOM and also POM in streams are subjected to a decomposition by biodegradation (Tank et al. 2010, Yoshimura et al. 2010, Jung et al. 2015) and photodegradation (Larson et al. 2007, Koehler et al. 2012, Chen and Jaffé 2014). This process can produce new autochthonous DOM or nutrients in water (Yoshimura et al. 2010, Jung et al. 2015). The mobility and activity of DOM are significant with respect to water quality. As the redox activity of DOM is high, DOM in aquatic

environment can cause a depletion of oxygen and deterioration of water quality (Borch et al. 2009). Furthermore, DOM is related to proliferation (bacterial increase) within the drinking water distribution system. Most effective and cheap way of killing the harmful bacteria, which cause waterborne disease is chlorination treatment in water plants. However, DOM with chlorine can produce disinfection by-products that are recognized to be genotoxic and carcinogenic to human beings (Lee and Hur 2014).

Therefore, the DOM in terrestrial and aquatic ecosystems has been identified as an important part of the natural nutrient cycling, the contaminant mobility and the drinking water quality.

1.1.3 Cycling of DOC and DON in forested watersheds

C cycling and role of DOC in soils

The most important sources of DOM in soils are plant litter (Michalzik and Matzner 1999, Park et al. 2002) and also humus (Park and Matzner 2003). The forest floor has been identified as a primary potential pool for DOM. Potential DOC pools in forest soils are controlled and replenished by C inputs from plant litter, throughfall, root exudates and decaying of fine roots and microbial biomass (Figure 1.1) (Kalbitz et al. 2000, McDowell 2003, Bolan et al. 2011).

The actual DOM in soils is a product of microbial production and consumption of SOM and a result of physical and chemical processes in forest soils (Moore and Dalva 2001, McDowell 2003, Park and Matzner 2003, Bolan et al. 2011). Biodegradation/decomposition is one of the primary formation process for DOM (Kalbitz et al. 2003, Schwesig et al. 2003, Kalbitz and Kaiser 2008, Bolan et al. 2011). However also DOM can act a substrate for soil microorganisms with up to 90% of DOM being degraded (Kalbitz et al. 2003, Kiikkilä et al. 2006; 2011). DOM may add to the SOM pool through sorption (Guggenberger and Kaiser 2003, Kalbitz et al. 2005, Kalbitz and Kaiser 2008, Don and Schulze 2008, Kindler et al. 2011), POM formation (Schwesig et al. 2003, Kalbitz et al. 2005) and humification (Osman 2012).

N cycling and role of DON in soils

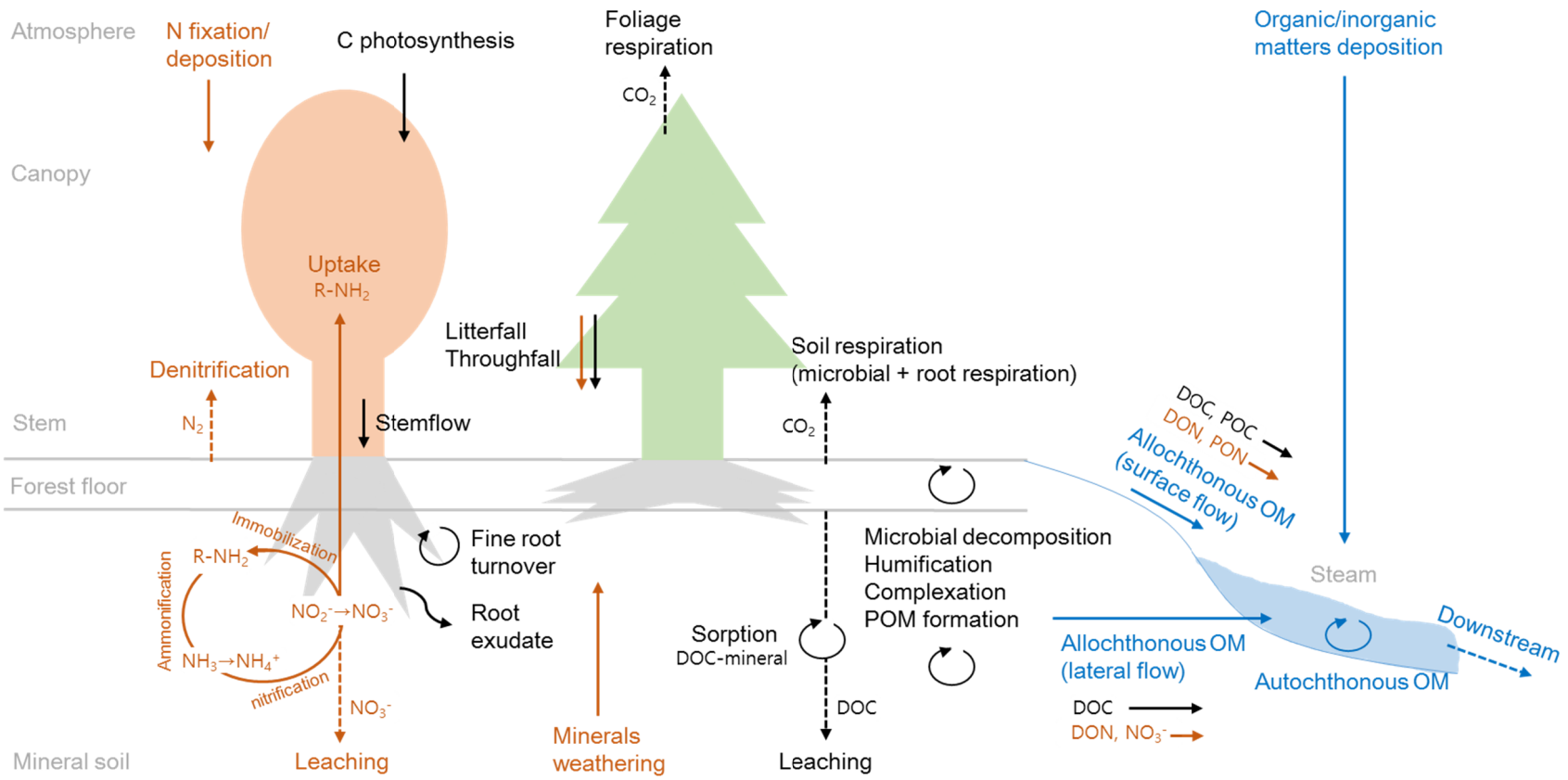
N cycle comprises processes of N_2-fixation, ammonification (N mineralization) and nitrification that increase plant available N, whereas denitrification, immobilization and leaching result in permanent or temporal N loss from the soils (Figure 1.1.1) (Wild 1993, Stevenson and Cole 1999, Johnson et al. 2005). Soil N originates from biological N_2 fixation that refers to the conversion process of atmospheric N_2 to a plant available N form via N_2-

fixing bacteria. But N can also be deposited by rainwater in the form of NH_4^+ or NO_3^-. Ammonification is the process of NH_4^+ formation from organic N ($R\text{-}NH_2$). Nitrification is the oxidation process of ammonium to NO_2^- and finally to NO_3^-. Nitrate can be denitrified to gaseous forms of N (N_2, N_2O, NO) or be assimilated/immobilized by plants and soil organisms (Dannenmann et al. 2011). Beside nitrate, N losses from soils to stream can also occur in the form of dissolved organic nitrogen (DON). Nitrate losses from forest ecosystems are enhanced under conditions of high N deposition (Brookshire et al. 2007). Unlike to nitrate, ammonium reacts with other cations of the exchange complex and it can be fixed by clay minerals (Stevenson and Cole 1999).

OM cycling in runoff from forested watershed

Organic matter (OM) in aquatic ecosystems contains significant components from autochthonous production by algal and vascular plant communities through cellular lysis and physical breakage of cells (Bauer and Bianchi 2011). Considerable amounts of organic matter are transported from soils to streams in the form of DOC POC, DON and PON (Alvarez-Cobelas 2008; 2012) through hydrological flow paths that include surface runoff and groundwater (Frank et al. 2000, Dawson and Smith 2007, Tank et al. 2010, von Schiller et al. 2010, Smith et al. 2013), and erosion under heavy precipitation events (Dawson and Smith 2007, Hilton et al. 2012, Jeong et al. 2012, Smith et al. 2013).

Most of the labile DOC fractions in water originates from autochthonous OM and were degraded initially (Koehler et al. 2012) and also substantial amounts of terrestrially derived OM, like particulate organic carbon (POC) degrade downstream (Jung et al. 2015). Yoshimura et al. (2008) observed 5% of FPOM and 45% of CPOM biodegradation during 80 days. DOM photodegradation by solar radiation in water depends on the wavelength and sunlight penetration (Bertoni 2011, Mostofa et al. 2013). In the forested watershed, DOM photodegradation in the upstream had no effect on the decomposition of the exported DOM from forested watersheds to streams (Larson et al. 2007). Other processes acting on DOC in streams are flocculation or polymerization that removes DOC, particularly the high molecular weight and humic components (Bauer and Bianchi 2011, Bianchi and Bauer 2011).



Source from Stevenson and Cole 1999, Bolan et al. 2011, Borken et al. 2011, Augusto et al. 2014

Figure 1.1.1 Sources (*straight arrow*), losses (*dotted arrow*) and mechanism (*circle arrow*) of carbon (*Black*) and nitrogen (*orange*) in forest soils and organic matter (OM: *blue*) in stream in forested watershed. Organic matter includes DOC, DON, POC and PON

1.2 Carbon and nitrogen export from forested watersheds

Forested watersheds play an important role for human wellbeing in that they are often used as source areas for drinking water basins. Streams from forested watershed often have a good water quality of low pollutant concentrations like N or pesticides. For drinking water quality and aquatic life, the concentrations of DOM in streams are of relevance as DOM needs to be removed (Oulehle and Hruska 2009, Delpla et al. 2014). Furthermore, the concentrations of DOM in steams increased in the last decades in Europe and elsewhere. The reason for the increase was a topic for several publications (Clark et al. 2010, Sucker and Krause 2010, Halliday et al. 2012, Pärn and Mander. 2012). DOM plays an important role in terrestrial and aquatic ecosystems (Thurman 1985). DOM in soil can influence many processes such as C and N mineralization in forest soil (Michel and Matzner 2002, Smolander and Kitunen 2011), nutrient and energy supply to microorganisms (Fagerberg et al. 2010), metals binding and contaminant mobility (Strobel et al. 2001, Nierop et al. 2002, Li et al. 2005, Song et al. 2008), and transport and cycle of C (Bauer and Bianchi 2011, Bianchi 2011, Borken et al. 2011) and N (Canham et al. 2012). In aquatic systems, DOM influences the nutrient cycle, the light penetration and is subjected to decomposition by bio- (Tank et al. 2010, Jung et al. 2015) and photodegradation (Larson et al. 2007, Koehler et al. 2012, Chen and Jaffé 2014).

The export of organic C and N from terrestrial to aquatic systems can occur in the form of DOC and DON, but also in the form of POC and PON of different size as FPOM and CPOM. As much of the DOM in aquatic systems originates from soil derived OM, the export of terrestrial C and N into aquatic environments is a primary link between these systems (Battin et al. 2008, Bauer and Bianchi 2011, Bianchi 2011, Canham et al. 2012, Camino-Serrano et al. 2014). In forest soils, the forest floor has been identified as a primary source for DOM because the highest concentrations of DOC and DON are consistently found in forest floor leachates (Michalzik et al. 2001, Inamdar et al. 2011, Camino-Serrano et al. 2014, Wu et al. 2014). At the terrestrial and aquatic interface, soil derived DOM is transferred to the stream by different hydrologic flow paths, like surface flow and groundwater discharge (Frank et al. 2000, Dawson and Smith 2007, Tank et al. 2010). POM is also transported to the stream from vegetation, from litterfall, from soils by surface flow and by wind (Benfield 1997, Abelho 2001, Smith et al. 2013).

The transfer of DOC and POC from the terrestrial to the aquatic part of watersheds is strongly dependent on the flow paths, with high exports under high flow conditions and surface near

flow. Hence, the precipitation dynamic plays an important role, especially heavy precipitation episodes need to be considered. As an example, 52% and 83% of the annual DOC and POC exported from forested watersheds to stream was driven by heavy storm events, like summer monsoon (Kim et al. 2010, Lloret et al. 2013). The importance of heavy storm events for POC export has also been underlined in other studies (Johnson et al. 2006, Kim et al. 2010, Hilton et al. 2012, Jung et al. 2012, Smith et al. 2013) and POC export was in some cases the major C export with stream water (Kim et al. 2010, Lloret et al. 2013, Dhillon and Inamdar 2013).

Few studies have compared the contribution of fine vs. coarse POC export. Johnson et al. (2006) reported that FPOC export was greater than CPOC from forested headwater catchment, representing 37% and 4% of the total annual organic C export, respectively, whereas Vidal-Abarca et al (2001) suggested that CPOC was major component (57%) of total POC export and measured the greatest export in a saline and semiarid stream during storm events. On the contrary, in other watersheds, DOC was the dominant export of organic C with 60 - 70% contribution to the total annual organic C export in a temperate headwater catchment (Johnson et al. 2006) and in a tropical rainforest catchment (Bass et al. 2011). In addition, Lloret et al. (2013) assembled annual C export studies in large tropical and small mountainous watersheds and concluded that DOC is the major part of the total organic C export in large watersheds such as Amazon, Orinoco, Parana and Mengong.

Previous studies have shown a strong relationship between the DOC and POC export and the discharge in forested watershed. DOC export increased often linearly with increasing discharge whereas POC export responded exponentially to discharge in forested watersheds (Kim et al. 2010, Dhillon and Inamdar 2013). This implied that DOC export only increase with discharge if large potential DOC pools are available in the watershed. Otherwise large water volume would cause the dilution in DOM and POM concentrations in streams (Tipping et al. 1999, Bass et al. 2011). Especially during heavy storm events, the change in hydrological flow paths was observed from deeper to upper soil (e.g. forest floor) in watersheds (Sanderman et al. 2009, Bass et al. 2011, Singh et al. 2014), but the flow paths also depended on antecedent soil moisture conditions (Bernal et al. 2002, Kim et al. 2010). Hence, surface flow-inducing storm events can alter the flux and concentration of DOC and POC by shifting preferential flow through macropores, surface runoff and lateral flows (Katsuyama and Ohte 2002, McGlynn and McDonnell 2003, Kim et al. 2010). The exponential response of POC export to discharge often has a threshold for the initiation of erosion (Thurman 1985, Dawson and Smith 2007, Jeong et al. 2012). Soil erosion induced by strong storm events acts efficiently on soils that

lack vegetation cover (Dawson and Smith 2007, Stallard 2011, Janeau et al. 2014) and on steep hillslopes (Hilton et al. 2012, Jung et al. 2012). Smith et al. (2013) proposed that significant amounts of POC from biomass are transferred from the hillslope by strong precipitation events while fossil POC from sedimentary bedrock dominates in POC export as soon as the rain stopped.

Little data are available on the relative partitioning of DON and PON export and it remains open, if organic N in runoff from forested watersheds behaves similar to C. Alvarez-Cobelas et al. (2008) reported that annual export flux of DON was weakly related to that of PON in catchments (r^2= 0.40, n=43). Several studies have found that DON fluxes correlated highly with DOC fluxes in throughfall, forest floor and mineral soil (Solinger et al. 2001, Michalzik et al. 2001, Wu et al. 2010) and in stream water (von Schiller et al. 2015). However, Singh et al. (2015) showed mostly weak relationships between DOC and DON concentration for five streams at the base flow and at the storm flow. DON export differed from DOC in response to watershed cover (Clark et al. 2004), to C/N ratio of organic and mineral soil (Aitkenhead-Peterson et al. 2005) and to precipitation amounts (Inamdar et al. 2008).

In many forest ecosystems, DON was considered the major form of N in forest floor percolates (Schmidt et al. 2010, Jones and Kielland 2012) and in stream water from forested watershed (Frank et al. 2000, Kaushal and Lewis 2003, Pellerin et al. 2006, Alvarez-Cobelas et al. 2008, Yates and Johnes 2013). Export of inorganic N (NO_3^-, NH_4^+) also adds to N loss from terrestrial systems. Some studies have found that NO_3-N was the predominant form of annual N flux in forest soils (Solinger et al. 2001) and in streams (Bernal et al. 2005, Inamdar and Mitchell 2007, Sebestyen et al. 2008). The concentrations of organic and inorganic N in surface water in watersheds change with N inputs (Pellerin et al. 2006, Canham et al. 2012, Mast et al. 2014). High input of atmospheric N and fertilizer resulted in the leaching of significant amount of NO_3-N (Alvarez-Cobelas et al. 2008), while DON appeared to be the dominant form N export in pristine forested watershed (Frank et al. 2000) and with low rate of N deposition (Kaushal and Lewis 2003). A greater influence of storm events on NO_3-N export was observed than on DON exports in forested watershed (Bernal et al. 2005, Inamdar and Mitchell 2007, Vegas-Vilarrúbia et al. 2012).

As mentioned earlier, the exports of terrestrial C and N into aquatic environments are not only related to precipitation intensity and antecedent soil moisture conditions, but also to watershed characteristics such as soil type, slope, size, forest type and vegetation (Clark et al. 2004, Alvarez-Cobelas et al. 2008; 2012, Fujii et al 2009, Borken et al. 2011, Camino-Serrano

et al. 2014, Singh et al. 2015). Different tree species might affect the fluxes of DOC, DON, POC and PON in runoff. This may result from different litter and humus quality, which influence the composition and reactivity of DOM in soil solutions and runoff. DOM from coniferous litters generally comprises more refractory (e.g. hydrophobic acid, lignin) and aromatic compounds, relatively larger proportion of high molecular weight compound (100 kDa > 1kDa) and is more acidic than DOM from broadleaved litter, whereas DOM from broadleaved litters contain more labile compounds (e.g. hydrophilic neutrals, bases, sugar, amino acids) and a larger proportion of relatively low molecular weight substances (1 kDa > 100 kDa) (Kaiser et al. 2001b, Don and Kalbitz 2005, Hansson et al. 2011, Kiikkilä et al. 2013). Previous studies have been often reported larger concentrations and fluxes of DOC and DON in forest floor leachates of coniferous than of deciduous forests (Kalbitz et al. 2004, Fröberg et al. 2011, Hansson et al. 2011). In addition, broadleaved forests (n = 111) exhibited 23% lower DOC concentration than coniferous forests (n = 219) in the surface layer, while mean DOC concentration did not differ in the deeper mineral soil between coniferous and broadleaved forests (Camino-Serrano et al. 2014). Also, higher forest floor C stocks were mostly found in coniferous tree species (*Larix, Pinus, Picea*) in temperate and boreal regions (Vesterdal et al. 2013). However, different results on tree species effects were published. Higher DOC and DON concentration and higher C and N mineralization rates in forest floor were found under oak and beech compared to Norway spruce and Douglas-fir (Trum et al. 2011) and under silver birch compared to Norway spruce and Scots pine (Smolander and Kitunen 2011). No systematic difference was found between coniferous and hardwood site in concentration and flux of DOC and DON in 42 case studies (Michalzik et al. 2001) and also between coniferous and broadleaved forest floor leachates in DOC concentrations that were in the order; pine > oak > spruce > beech (Broken et al. 2011).

Substantial DOC amounts from forest floor are transferred to the mineral soil (Neff and Asner 2001, Michalzik et al. 2001; 2003, Park and Matzner 2003, Fröberg et al. 2007, Kalbitz and Kaiser 2008, Tipping et al. 2012a). Sanderman and Amundson (2009) found that DOC release from organic layer contributed 22% of the annual C inputs at 40 cm depth in coniferous forest soil. Borken et al. (2011) reported that an average of 87% and 95% of DOC from the organic layers were retained in 20–30cm depth of the mineral soils and in the underlying subsoils, respectively because of the strong retention. However, DOC concentration of soil solution decreases with depth, hence soil solution from deeper mineral soil contains relatively small amount of DOC (Neff and Asner 2001, Fujii et al. 2009, Sanderman et al. 2009, Inamdar et al.

2012, Camino-Serrano et al. 2014) because of mineralization (Tipping et al. 2012a), sorption to soil minerals or formation of POM (Neff and Asner 2001, Schwesig et al. 2003). Michalzik et al. (2003) concluded that the supply DOC from forest floor to mineral soil depends on the continual metabolic production of easily leached humic substances, in contrast, DOC concentration and flux in mineral soil are controlled by sorption processes, involving relatively large leachable OM pools. DOM mobilization with water fluxes appear to have a non-negligible effect on soil C distribution in forest soil (Tipping et al. 1999, Kalbitz et al. 2000, Park and Matzner 2003, Gielen et al. 2011).

Likewise DOC and DON in forest floor, previous studies have shown inconclusive results about concentration and fluxes of DOC and DON in mineral soils for broadleaved vs. coniferous forests. For example, DOC concentrations and fluxes in the mineral soil were found relatively higher under coniferous than deciduous or broadleaved forest stand, but did not differ in deeper soil under 60 cm (Schwesig et al. 2003, Kalbitz et al. 2004, Camino-Serrano et al. 2014). In summary, the effects of tree species on the export of DOC, DON, POC and PON from forested watershed warrants future investigations as a clear picture cannot be derived from the published data.

As a result of global warming, heavy precipitation events have occurred more common in recent decades, often associated with hurricanes, typhoons, or cyclones, and have become stronger and more frequent (IPCC 2013, Melillo et al. 2014). Furthermore, several studies have predicted that the dominant tree type becomes gradually deciduous and/or broadleaved tree by global warming (Fisichelli et al. 2014, Ma et al. 2014, McIntyrea et al. 2015). In view of future forest management, predicting the tendency of organic C and N exports from forest to aquatic ecosystems is important with regard to decision supporting and risk evaluation.

The Soyang basin area is located in the upstream region of the Han River, which is the main source of drinking water for about 23 million citizens in South Korea. DOM and POM from forested watersheds in Soyang basin gather in the Han River. Thus, the quantity and the quality of DOM and POM in Soyang basin likely affect the properties of drinking water in the Han River.

Korean mountainous forests are mostly covered by broadleaved forests, 47% of total forests (coniferous forest 38%, mixed forest 12%) (Korea forest research institute 2013). Most of the broadleaved forests in South Korea distributes in Gangwon-do with high diversity of tree species. Especially, the area of broadleaved forests in Gangwon-do increases from 32% in 1995 to 55% in 2013 (Korea forest research institute 2013). The 82% of artificial forest in South

Korea are represented by coniferous trees because of economic reasons. The economically important tree species in South Korea are *Pinus densiflora, Larix leptolepis* and *Pinus koraiensis* (Korea forest service 2004). The area of coniferous forests in South Korea decreases by disease and pest and by global warming (Korea forest service 2004). The global temperature combined land and ocean surface increased 0.78°C from the average of the 1850-1900 period to the 2003-2012 period (IPCC 2013), while the average annual temperature of Korea increases much faster (1.7°C) from 1912 to 2008 (Korea meteorological administration). Also, the mean annual precipitation increased visually 220 mm from the decade average of 1910s to 2000s (Korea meteorological administration). The changing climate suggests that forest management considers other than coniferous species and also calls for research on the effects of tree species on water quality.

1.3 Dynamics of dissolved organic carbon and nitrogen in forest floors

In forest soils, the forest floor has been identified as a primary source for DOM. The highest concentrations and fluxes of DOM were found in forest floor leachates (Michalzik et al. 2001, Inamdar et al. 2011, Camino-Serrano et al. 2014, Wu et al. 2014) leading to substantial C inputs into the underlying mineral soil (Borken et al. 2011).

The release of DOM from SOM is a rather complicated process as it is driven by biological, physicochemical and hydrological processes. Decomposition of litter, microbial activity, C/N ratio (Michel and Matzner 2002) and root exudates (Giesler et al. 2007) are prominent examples for biological controls, whereas pH and ionic strength determine the surface charge and solubility of organic substances (Naidu et al. 1994, Clark et al. 2005, Deb and Shukla 2011, Moldan et al. 2012). As a result of this complicated situation, the DOM dynamics in soils are either neglected in soil C models or the modelling is still hampered by conceptual deficits and lack of empirical data describing the pool of leachable DOM and its dynamics in terms of depletion and recovery (Michalzik et al. 2003, Braakhekke et al. 2011, Tipping et al. 2012a, Augusto et al. 2014). The release of DOM from forest floors is seen as a result of the mobilization of a potential pool of DOM (Park and Matzner 2003), the latter being build up by decomposition processes of SOM. The potential pool of DOM might be exhausted or replenished according to the environmental and site conditions. Several factors have been shown to influence the release (and likely the recovery) of DOM pools in forest floors, but

there is still a lack of knowledge on the size of the pool, the time scales and the conditions related to its depletion and recovery.

The release of DOM from forest floors depends on the activity of soil microorganisms as decomposition of SOM is a major process of DOM formation (Kalbitz et al. 2000, Michel and Matzner 2002). The mineralization of C and N correlated significantly with DOC and also DON release from forest floors, indicating strong interactions between SOM mineralization and DOM release from forest floors (Gödde et al. 1996, Moore et al. 2008, Smolander and Kitunen 2011, Sanderman and Kramer 2013).

The quality of SOM influences the DOM release. High quality of SOM (fresh leaves > decomposed leaves > humus) favour mineralization rates of C (Kanerva and Smolander 2007, Trum et al. 2011, Sanderman and Kramer 2013) and also higher net release of DOM (Kalbitz et al. 2003, Trum et al. 2011). The substrate quality can control the release of DOC from the forest floor through its biodegradation, representing large DOC production and CO_2 production from Oi horizon compared to Oa in forest scale (Trum et al. 2011, Sanderman and Kramer 2013). Plant-derived carbohydrates seem easily degradable while lignin-derived C substrates (aromatic compounds) likely are the most stable and contribute more strongly to the DOM release from forest floors (McDowell 2003, Michel et al. 2006, Kalbitz and Kaiser 2008, Moore et al. 2008). For examples, the microbial activity (soil respiration) and DOM production in forest floor Oa layers decreased significantly with increasing N content and decreasing C/N ratio (Gödde et al. 1996, Michel and Matzner 2002, Michel et al. 2006) suggesting that higher N deposition leads to increase accumulation of C and N in forest floors (Michel and Matzner 2002) and/or to inhibition of lignolytic enzyme-activity (Pregitzer et al. 2004, Michel et al. 2006). However, in other studies no significant relationship between DOC production and N content was found (Evans et al. 2008, Borken et al. 2011).

Tree species will have an effect on DOM dynamics in forest floors as the quality of SOM under different tree species differs in lignin content, microbial activity and C/N ratio. As mentioned earlier, higher concentration and fluxes of DOM were found in coniferous than in deciduous forest floor (Kalbitz et al. 2004, Fröberg et al. 2011, Hansson et al. 2011, Camino-Serrano et al. 2014). However, opposite results on tree species effects were also published (Trum et al. 2011, Smolander and Kitunen 2011). Also, the quality of DOM differs between

coniferous and deciduous tree species as indicated by the microbial use of DOM. Higher degradability was observed for DOM from deciduous SOM than for DOM from coniferous (Trum et al. 2011, Kiikkilä et al. 2011; 2012). Higher rates of soil respiration (soil CO_2 evolution) or decomposition was found for deciduous SOM than for coniferous (Wang et al. 2006, Buzek et al. 2009, Smolander and Kitunen 2011, Augusto et al. 2014). In case of fresh litter contradicting observations were reported with higher mineralization or degradability of DOM from coniferous than DOM from deciduous litter (Kalbitz et al. 2003, Don and Kalbitz 2005, Kiikkilä et al. 2013). Some studies have reported no difference of soil respiration between deciduous and coniferous SOM (Vesterdal et al. 2012, Wunderlich et al. 2012). Up to now, the effect of tree species on the mineralization or degradability in DOM or SOM from forest has still been controversial.

Temperature is a driver for DOM leaching from forest floors via the effect on the microbial processes (Fröberg et al. 2006). Many studies have reported the positive relationship between soil CO_2 evolution and soil temperature (Christ and David 1996, Janssens and Pilegarrd 2003, Jonard et al. 2007, Kao and Chang 2009, Vesterdal et al. 2012, Wunderlich et al. 2012, Jiang et al. 2013). A stronger temperature-dependence of C mineralization was observed at low temperature and for stabile substrates than at higher temperature and for labile substrates (Gödde et al. 1996, Karhu et al. 2010, Hamdi et al. 2013, Kirschbaum 2000; 2013). Also, a decrease in the temperature dependence of decomposition was observed when comparing long-term (annually or centennially) incubations with short-term incubations (Marschner and Bredow 2002, Karhu et al. 2010, Kirschbaum 2010). Some studies have investigated the temperature dependence of DOM release from forest floors (Christ and David 1996, Gödde et al. 1996, Moore et al. 2008, Borken et al. 2011). Only a few studies have reported Q_{10} values for DOC release from forest floors. Like with C mineralization, the Q_{10} for DOC release increased at lower a temperature (Gödde et al. 1996, Moore et al. 2008, Gauthier et al. 2010). According to Moore et al. (2008), Q_{10} values for cumulative DOC production of organic layer from forests (n = 16) were in the range of 1.0-2.9, 1.1-6.8 and 0.6-2.3 at 3-10 °C, 3-22 °C and 10-22 °C, respectively.

Dynamics of precipitation and water fluxes are key drivers for DOM fluxes in terrestrial ecosystems (Tipping et al. 1999, Kalbitz et al. 2000, Park and Matzner 2003, Gielen et al. 2011). Field studies have shown a strong, linear and positive relation between the fluxes of DOM from

forest floors and the water fluxes (Michalzik et al. 2001, Neff and Asner 2001, Schmidt et al. 2010, Borken et al. 2011, Wu et al. 2014). Frequent leaching increased the DOM release from forest floors in laboratory experiments (Gödde et al. 1996, Judd and Kling 2002). By definition, the fluxes of DOM from forest floor increase with the precipitation and the amount of water percolating the forest floors (Kaiser et al. 2001a), which indicates that the forest floors act as a buffer in respect to the water fluxes and that the pool of potential DOM is not easily exhausted (Kalbitz et al. 2004). As a consequence, this would imply that the recovery rate of DOM is rather large. The recovery rate or the production rate of DOM in forest floors has not been studied so far. However this would be a premise when modelling the release of DOM from forest floors in a dynamic and precipitation driven manner. If the recovery of the potential pools to original values is similar for DOC and DON is another open question. Different source pools of DOC and DON might exist in soils with different turnover rates (C rich litter/humus vs. N rich microbial biomass) might induce differences in response. The response of DOC and DON fluxes to changes in environmental conditions in fact often differed (Park and Matzner 2003, Kalbitz et al. 2007, Buzek et al. 2009, Inamdar et al. 2012). Oppositely, some studies have found that concentrations and fluxes of DOC are strongly related to those of DON in forest floor leachates (Michalzik et al. 2001, Jones and Kielland 2012).

Extreme precipitation events, which occur for example in a monsoon climate, accelerate the DOM release from soils. Hence, in this study, the effect of large water fluxes on the release of DOM from forest floors and the subsequent recovery of DOM pools is investigated in detail by measuring DOM fluxes from forest floors in the field and by sequential extraction of forest floor samples in the laboratory.

1.4 Goals and Hypotheses

In the field study, the effect of precipitation intensity and of tree species on the export of fine particulate (0.7µm-1 mm) and dissolved (< 0.45 µm) organic C and N from forest to the stream was investigated in a purely deciduous forested watershed and in a mixed coniferous/deciduous watershed in South Korea. The following hypotheses were tested,

1) The ratios of DOC/DON and FPOC/FPON are independent of discharge.

2) FPON is the dominant form of N export in runoff.

3) DOM and FPOM in runoff originate mostly from forest floor leachates.

4) The export fluxes of DOC, DON, FPOC and FPON from a mixed coniferous/deciduous forested watershed differ from that of a purely deciduous watershed.

In the laboratory experiments, the release of DOC and DON from forest floors and the recovery of pools were investigated in incubation experiments using soil samples from coniferous and deciduous forests. The following hypotheses were tested,

5) The depletion and the recovery of the DOC and DON pools behave similar.

6) The recovery rate of the DOM pools depends on tree species, microbial activity and temperature.

7) As DOM from forest floors is already a product of decomposition and mainly composed of rather stabile substances, the leaching of even large amounts of DOC does not influence the CO_2 evolution in the forest floor.

2 MATERIALS AND METHODS

2.1 Site description

2.1.1 Research site in Korea

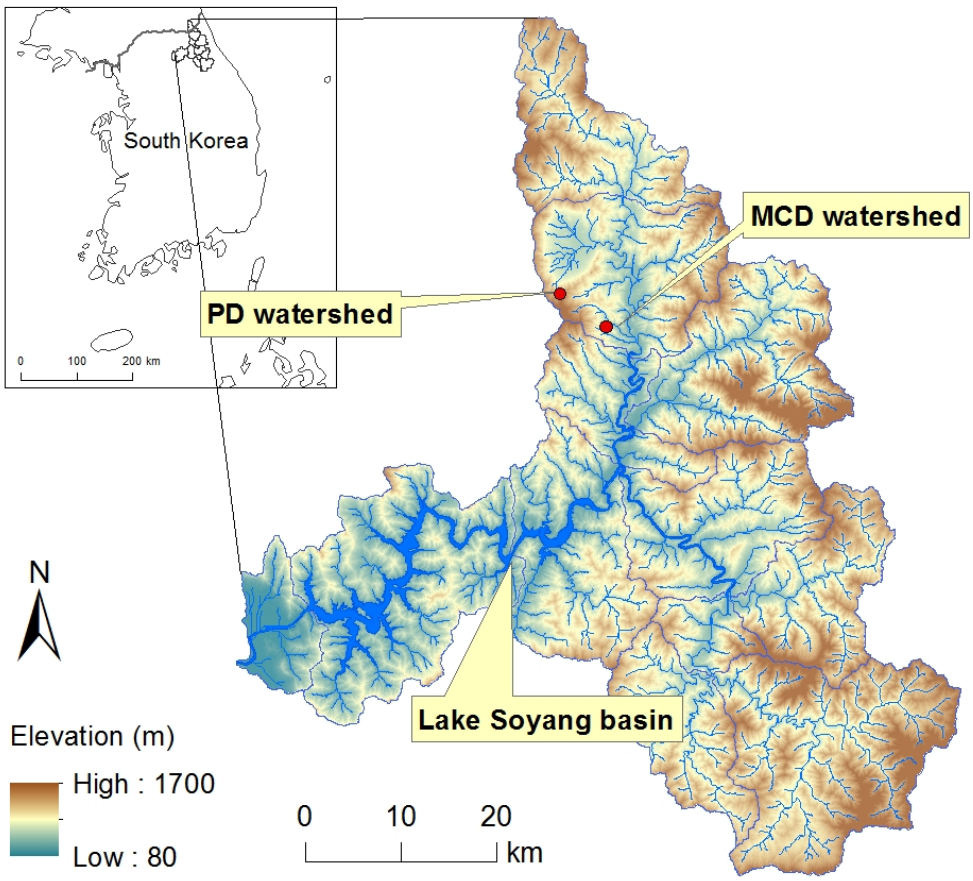
In South Korea, about 70% of Korea peninsula is mountainous with granite and granite-gneissic bedrock (Korean ministry for food agriculture, forestry and fisheries). South Korean forests are made up of natural forests (85%) and artificial forests (15%) (Korea forest research institute 2013). The dominant tree type in the natural forests is broadleaved tree (54%) with coniferous 31% and mixed tree 14%, whereas the abundant tree type in artificial forests is coniferous trees (82%) in South Korea (Korea forest research institute 2013) , which have been mostly re-established after the Korean War from 1950 to 1953 (Korea forest service 2004). The average altitude is 433 m (68% of below 500 m) above sea level. The mean annual air temperature is from 10 to 15ºC with -6ºC in January and 26ºC in August.

The study was carried out in two sub-watersheds of the Soyang basin in Gangwon-do, South Korea, which is dominated by forested mountainous land (85%). The first watershed is the mixed coniferous/deciduous forested watershed (MCD watershed) in Seohwa (Lat. 38.206828 N, Long. 128.185719 W, 368-682 m above sea level). The second is the purely deciduous forested watershed (PD watershed) in Haean (Lat. 38.251532, N 128.11991 Long. W, 586-1005 m above sea level). The distance between the two sub watersheds is ca. 6 km. Annual precipitation is from 1200 to 1500 mm and the summer monsoon accounts for about 50-60% of the annual rainfall in South Korea. Data and samples were collected in June and July 2013 during the monsoon season. The summer monsoon precipitation for 2013 in Gangwon-do (781 mm) was 102% of the common year value. In 2013, the total precipitation in Seohwa and Haean was recorded 86 mm and 70 mm in June, and 683 mm and 636 mm in July, respectively. The total precipitation in July 2013 accounted around half of the annual rainfall, 1312 mm in Seohwa and 1330 mm in Haean in 2013 (Korea meteorological administration).

There are three research plots in this study. The two plots as coniferous (MC) and deciduous (MD) are in the MCD watershed and another deciduous plot (PD) is located in the PD watershed. In the MCD watershed, the lower part of watershed is dominated by coniferous stands, including *Larix kaempferi* (Lamb.) Carr. (Japanese larch) and *Pinus densiflora* Siebold & Zucc. (Japanese red pine). Its upper part is dominated by deciduous stand, such as a mix of *Juglans mandshurica* Maxim. (Manchurian walnut), *Acer pictum* subsp. *mono* (Maxim.)

H.Ohashi (Mono maple), *Quercus dentata* Thunb. (Daimyo oak), *Tilia amurensis* Kom. (Lime tree) and *Ulmus davidiana* var. japonica (Rehder) Nakai (Japanese elm). In the MCD watershed of 15.6 ha in total 6.1 ha (39%) are represented by coniferous stands and 9.5 ha (61%) by deciduous stands. The slope of the mixed watershed as obtained from a digital elevation model ranges from 4.0 to 41° with an average of 28°.

In case of PD watershed, the tree species are dominated by *Juglans mandshurica* Maxim. (Manchurian walnut), *Acer pictum* subsp. *mono* (Maxim.) Ohashi (Mono maple), *Quercus dentata* (Daimyo oak), *Quercus mongolica* (Mongolian oak) and *Fraxinus rhynchophylla* (Korean/Chinese ash) comprising 58% of the entire basin area 39 ha. The slope of the deciduous watershed ranges from 4 to 53° with an average of 24°. In three plots, the characteristics of O-layer consist of moder-like O-layer, containing distinct Oi layer and less distinct Oe/Oa layers in both forested watersheds and the mineral soil up to 50 cm depth is loam texture. Typical soils in the forested mountain slopes are acid Cambisols according to the FAO World Reference Base for Soil Resources (Jeong et al. 2012).



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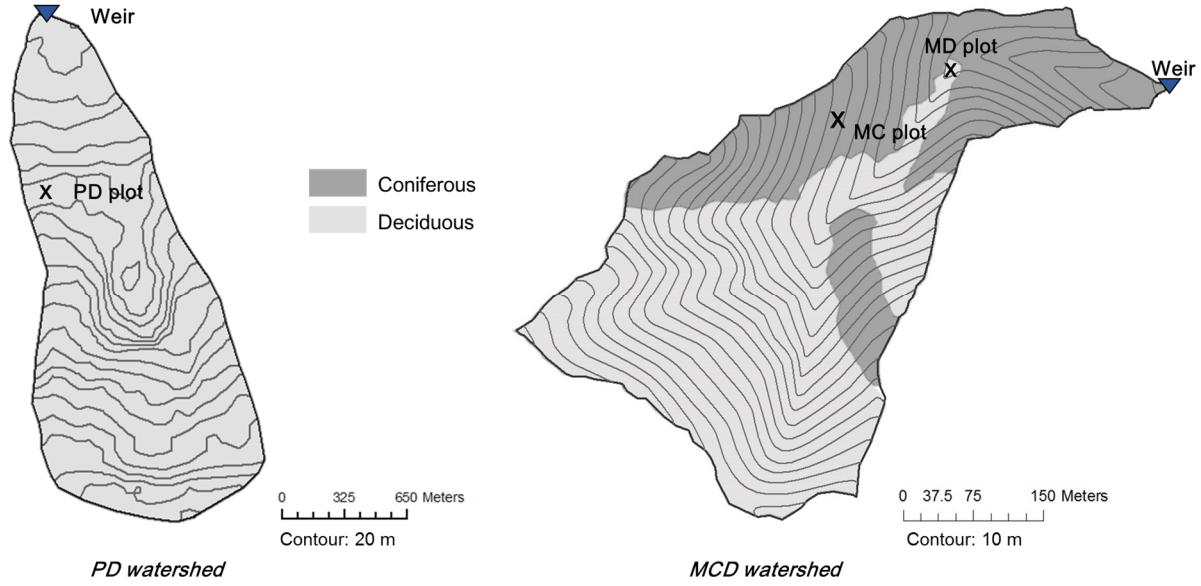


Modified the map of Lake Soyang basin from Jung et al. (2015)

Figure 2.1.1 Location of the research sites in Lake Soyang basin, South Korea.

2.1.2 Research sites in Germany

For the laboratory experiments, soil samples were additionally taken under Norway spruce and European beech forests in Germany. Mean annual precipitation and air temperature is 750 mm and 7.5°C at the beech and 1160 mm and 5.3°C at the spruce site (Gerstberger et al. 2004).

The Coulissenhieb site is located in Fichtelgebirge, Bayern, Germany (Lat. 58°08′N, Long. 11°52′E) and is dominated by Norway spruce (*Picea abies* (L.) Karst.). The soils are Dystric Cambisols (FAO World Reference Base for Soil Resources) derived from weathered granitic bedrock with a sandy-loamy texture. The forest floor is of moder type, comprises distinct Oi, Oe and Oa layers and has a thickness from 8 to 12 cm.

The Steinkreuz site is placed in Steigerwald National Park, Bayern, Germany (Lat. 49°52′N, Long. 10°27′E), dominated by European beech (*Fagus sylvatica* L.). Soils are classified as Dystric and Gleyic Cambisols (FAO classification) developed from underlying Triassic sandstones and have a sandy-loamy texture. The forest floor has a mean thickness of 4 cm and is classified as a moder type containing distinct Oi and Oe layers and a thin and fragmentary Oa layer.

2.2 Field study

2.2.1 Instrumentation and water sampling in stream and forest

In the Korean watersheds, bulk precipitation samplers (n=2) were installed at each watershed in an open area located ~100 m from the plots. Throughfall collectors (n=5) were equipped with filters to prevent large particles from entering. Forest floor leachate was collected beneath the organic layer along the slope side using zero tension lysimeters (n=5) of 185 cm^2 made of acrylic material. Soil solution was collected at a depth of ~50 cm with suction lysimeters (n=5) made of ceramic cups. The suction of suction lysimeters was maintained through manual pumping with syringe after taking samples.

Water samples were sampled during summer in June and July 2013. During the dry-period in June, water samples of throughfall, forest floor leachate and soil solution were collected at about weekly intervals, and runoff samples were collected 3 times per week. During storm events, runoff samples were collected every 1 or 2 h in the weir at the two watersheds using an autosampler (6712 Portable Sampler, Teledyne Isco Inc., Lincoln, NE, USA). During routine runoff sampling, water quality parameters were measured in situ, including water temperature, pH and electrical conductivity. Water samples were refrigerated at 4°C after sampling and were stored after filtration with a pre-rinsed 0.45 µm cellulose-acetate membrane filter (Whatman) in the freezer until further analysis of water quality and quantity.

Discharge data were provided by Jean-Lionel Payeur-Poirier, Department of Hydrology, University of Bayreuth. In brief, discharge at the outlet of the watersheds was measured using leveloggers (Model 3001 Levelogger® Edge, Solinst) by a v-notch weir. Barometric pressure was measured using barologgers (Model 3001 Barologger® Edge, Solinst) and was used to compensate levelogger data at each watershed.

2.2.2 Soil characteristics

The total stock of the Oi and Oe+Oa layers was collected by hand in a 20 cm x 20 cm frame with 10 replicates in each plot. Mineral soil samples were collected from 3 pits in each plot in 10 cm depth intervals up to 50 cm. Soil samples were air-dried and crushed to pass through a 2 mm sieve, and then analyzed by the following methods.

Soil pH was measured using a soil to solution (0.01 M $CaCl_2$) ratio of 1:2.5 after shaking for 2 hours. Total C and N contents were analyzed using an elemental analyzer (vario MAX CN,

Elemental, Germany). Soil texture was determined by sedimentation. The clay, silt and sand are defined as < 0.002 mm, 0.002 to 0.05 mm and 0.05 to 2 mm, respectively.

2.3 Laboratory study

Forest floor samples were taken from spruce, beech, larch and mixed deciduous (oak, birch, maple) forest sites. Samples of the Oi, Oe and Oa layers in the spruce and Oi and Oe+Oa layers in the beech forest floor were sampled in August 2014, Bayern, Germany. In October 2014 samples were taken from Oi and Oe+Oa layers in the larch from the MC plot (in the MCD watershed) and in the deciduous forest floor from the PD plot (in the PD watershed), Gangwon-do, South Korea. Macrofauna and other coarse material (twigs, root and gravel) were removed and the soil samples were mixed to ensure homogeneous conditions by hands. The litter samples (Oi layer) were chopped into 1 cm^2 pieces before the experiments. Artificial throughfall was simulated according to the average throughfall chemistry of the coniferous forest in Bavaria Germany with a pH of about 4.0 and an electrical conductivity of 50.0 µS/cm with the following composition: 1.5 µmol L^{-1} $MnCl_2$, 13 µmol L^{-1} $MgCl_2$, 1.5 µmol L^{-1} K_3PO_4, 0.2 µmol L^{-1} $FeSO_4$, 10.0 µmol L^{-1} $Al(NO_3)_3 \cdot H_2O$, 99.1 µmol L^{-1} $CaSO_4$, 87.1 µmol L^{-1} NH_4NO_3, 20.0 µmol L^{-1} K_2SO_4 and 7.0 µmol L^{-1} Na_2SO_4. Dry weight of soil samples after the extraction experiment were measured after oven-drying at 60°C for 48 hours. The extracted solutions were analyzed for pH and electrical conductivity and then filtered through a pre-rinsed 0.45 µm cellulose-acetate membrane filter (Whatman) and stored at 3°C until further analysis. The filtered solutions were analyzed for the DOC and DON concentration and the specific UV absorbance at 280 nm ($SUVA_{280}$).

The soil samples were subjected to exhaustive water extractions combined with measurements of soil respiration. In the batch experiments, the recovery of depleted DOM pools was investigated by allowing different time spans or recovery (before the next extraction) at different temperatures. In the percolation experiments, the production rate of DOM was investigated by permanent extraction.

2.3.1 Batch experiment

The experimental procedure is illustrated in Figure 2.3.1. Forest floor samples were placed in 1 L glass jars in 3 replicates and stored initially in temperature controlled dark chambers of either 5°C or 15°C for 1 week for pre-incubation. After that, an initial extractions of soil

samples were conducted in an equilibrium extraction with artificial throughfall at a small (1:5) and large (1:20) ratio of wet soil to solution (10 g : 50 ml and 10 g : 200 ml). DOM was extracted from the soil sample at an equilibration time of 2 hours without shaking to avoid colloid formation. The soil samples in the glass jars were kept in Nylon meshes to avoid losses of SOM particles during the extraction process and also an air-mesh was placed under the soil-bags to avoid anaerobic conditions of the samples at the bottom of the glass jars. After extraction of DOM, the soil samples were brought to field capacity. To measure the recovery of the pools, samples were incubated in glass jars after the initial extraction for 1, 3, 7 and 14 days at 5°C and 15°C, and then subsequently extracted again at the initial soil solution ratios. Control samples were established without any DOM extraction.

The initial CO_2 release from soil samples was measured at 20 ± 2 hours later after the initial extraction, and then soil CO_2 release were again measured after each incubation days. One sample from the 3 replicates was measured for DOC and DON concentration. UV absorbance at 280 nm was used to calculate DOC concentration for other samples with a linear regression between DOC concentration and UV absorbance at 280 nm (spruce samples: $r^2 = 0.97$, larch samples: $r^2 = 0.98$, beech samples: $r^2 = 0.90$, mixed deciduous samples: $r^2 = 0.99$).

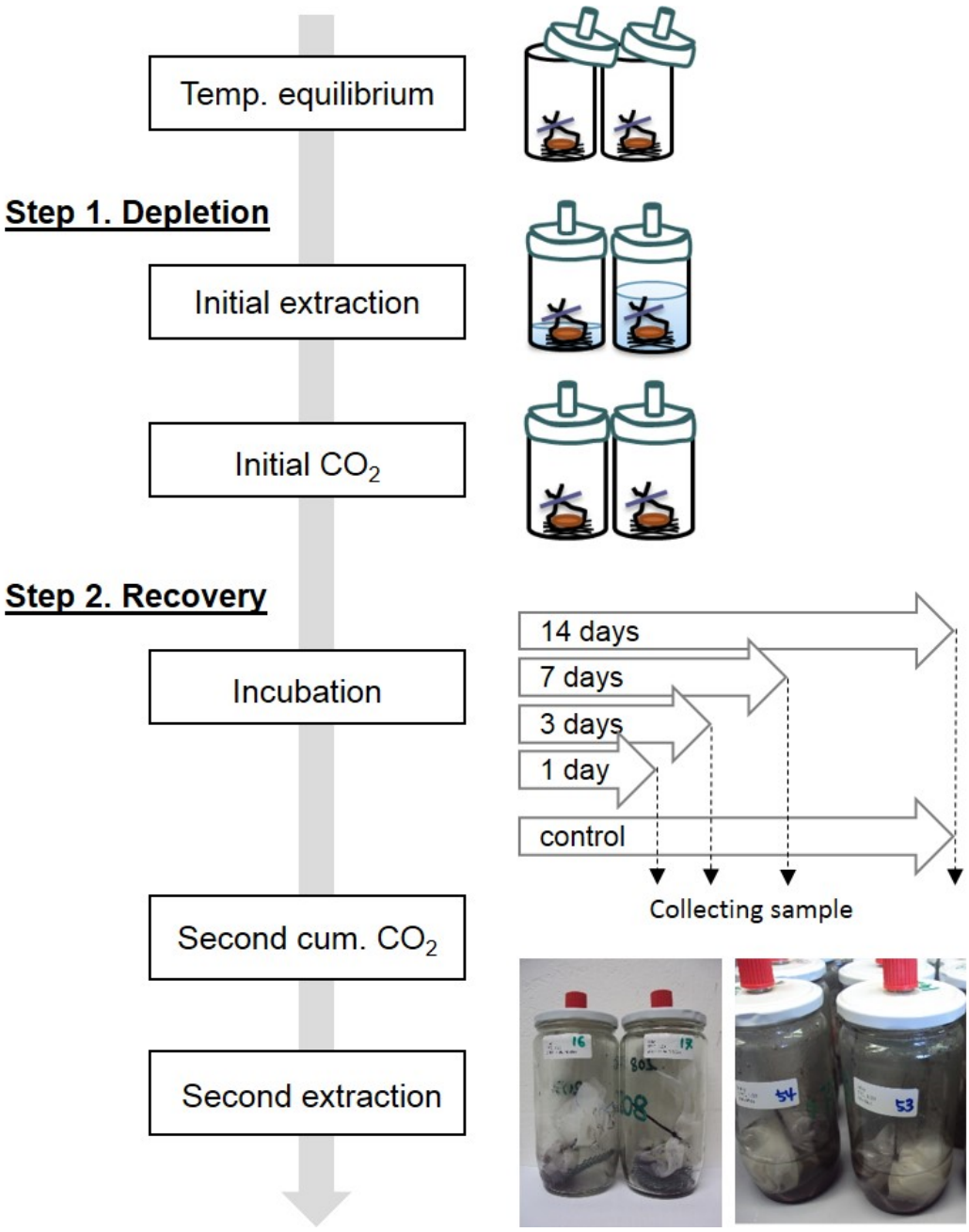


Figure 2.3.1 Flow diagram of the batch experiment. The first step is the depletion of the DOM pool and the second step is the recovery of the DOM pool. The second extraction was done with initially extracted samples, not with the controls

2.3.2 Percolation experiment

The experimental setup for the percolation experiments is illustrated in Figure 2.3.2 and Figure 2.3.3. Forest floor samples were filled in syringe columns (diameter: 2.9 cm, volume: 50 ml) in 3 replicates. The amount of wet soil in the columns was 4 g for Oi layers and 7 g for Oe+Oa and Oa layer samples. After drying the wet soils, the weight of dry mass ranged from 2 to 3 g. All of the samples in the columns were brought to field capacity prior to irrigation by adding 3.5 ml of artificial throughfall. To prevent the losses of large particles during the percolation, pre-washed glass fiber filters were placed on the top and bottom of packed soil samples in the columns. To avoid drying of the soil by evaporation, the syringe columns were sealed with a rubber stopper. The soils were incubated at constant temperatures of either 5°C or 15°C in dark chambers. The soil samples were percolated continuously in columns with low (3 ml d^{-1} = 7 mm d^{-1}) or high (15 ml d^{-1} = 36 mm d^{-1}) percolation rate with artificial throughfall for 25 days. Peristaltic pumps were used for the percolation. The percolated solutions from the soil columns were collected by free drainage and were collected with the intervals of 5 days (5, 10, 15, 20 and 25 days). After 25 days of the percolation experiment, the total amount of the percolated solution was about ca. 75 ml with the low percolation rate and ca. 375 ml with the high percolation rate. Control samples were established without any percolation experiment.

After the percolation process at 5, 10, 15, 20 and 25 days, the soil columns were placed in the airtight glass-jars, and the soil CO_2 evolution was measured for 10 hours. For DOC and DON concentration, 3 replicates from day 5 and 25 and one sample from day 10, 15 and 20 were measured. UV absorbance at 280 nm was used to calculate DOC concentrations for other samples with a linear regression between DOC concentration and UV absorbance at 280 nm (for r^2 see 2.3.1).

Figure 2.3.2 Setup of the percolation experiment with pumps, thin tubes, rubber stoppers, syringe columns, solution bottles

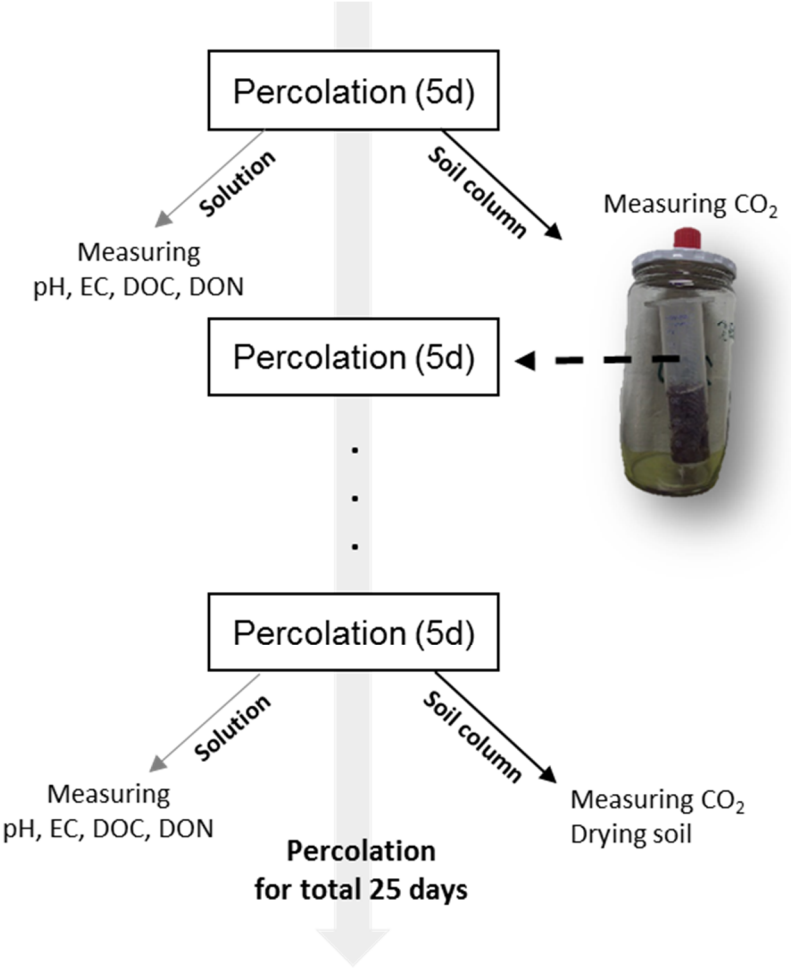


Figure 2.3.3 Diagram of the percolation experiment. After percolating the soil samples for a 5 days period, the percolated solutions were analyzed for pH, EC (electrical conductivity), DOC and DON. Furthermore soil CO_2 evolution was measured.

In the batch experiment, the depletion and recovery of DOM pools were described with by the decrease in DOM release after the initial extraction and the following increase in DOM release by the following extractions. In the percolation experiment, DOM release after the permanent extraction reached the steady-state. The production rate of DOM was ideally calculated as the remaining release rate of DOM at the steady-state (Figure 2.3.4).

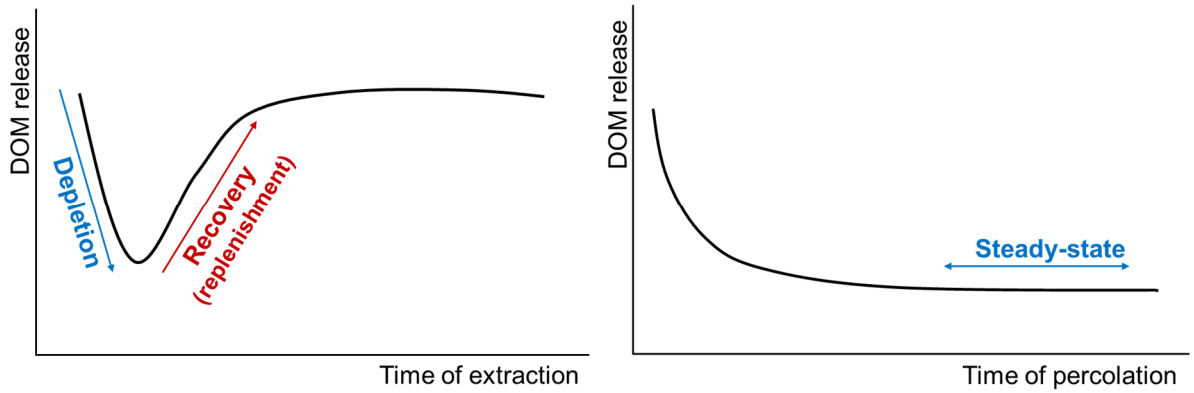


Figure 2.3.4 Ideal results of the depletion and recovery of DOM pools in the batch experiment (*left*) and the steady state of DOM production rate in the percolation experiment (*right*)

2.4 Analytical methods

Dissolved and fine particulate organic matter

For DOC and DON analysis, samples were filtered through a pre-rinsed cellulose acetate membrane filter (0.45 µm, Whatman). For the field study, the concentration of DOC and dissolved total nitrogen (DTN) of water samples were measured by a total organic carbon analyzer (Shimadzu V-series, TOC-CPH). External DOC and DTN standards were prepared using potassium hydrogen phthalate and potassium nitrate, respectively. The relative precision of the DOC analyses was less than 3%, as determined by repeated measurements. For the laboratory study, DOC concentration was measured using a total N/C analyzer (Analytik Jena, multi N/C 2100). DON was calculated as the difference between total nitrogen and mineral-N (NO_3^- + NH_4^+). Nitrate and ammonium concentrations were measured by flow injection analysis (MLE Dresden, FIA-LAB). The detection limit of TN, NO_3^- and NH_4^+ are 0.1 mg N L^{-1}, 0.01 mg N L^{-1} and 0.02 mg N L^{-1}, respectively.

For fine particulate organic carbon (FPOC) and nitrogen (FPON) analysis, samples were filtered through a 1 mm mesh filter to remove larger particulate materials and then finally filtered through a pre-rinsed 0.7 µm pore size of glass filter (GF/F, Whatman). The GF/F filters were combusted at 450°C to remove organic materials in the filters. The concentrations of total suspended solid (TSS) were measured by weight difference of GF/F filters before and after filtration of the water samples. The filters were dried at 105°C and re-weighed for calculating TSS. The small amounts of particle materials on GF/F filters were analyzed for FPOC and FPON using an elemental analyzer/continuous flow isotope ratio mass spectrometer. Fine

particulate mineral matter (FPMM) was calculated by difference between TSS and FPOC.

UV-visible spectroscopy

Absorption spectra of DOM were obtained by scanning the absorbance at the wavelengths from 200 nm to 600 nm using a UV-visible spectrophotometer (HACH, DR5000) at a scanning rate of 15 nm s^{-1}. Specific ultraviolet absorbance (SUVA) is commonly used as the index of aromatic compound. $SUVA_{280}$ values of the samples were determined by the UV absorbance at 280 nm divided by the DOC concentrations and multiplied by 100.

Fluorescence spectroscopy

Fluorescence spectroscopy methods have been proposed to determine the extent of humification of DOM by quantifying the shift of the emission spectra toward longer wavelength. Fluorescence excitation–emission matrices (EEM) were recorded with a luminescence spectrometer (LS-50B, Perkin-Elmer). Excitation and emission slits were both adjusted to 10 nm. The excitation wavelengths (Ex) ranged from 250 to 600 nm and emission wavelengths (Em) ranged from 280 to 550 at 5 mm intervals using 1 cm quartz cell. DOM samples were diluted under the ultraviolet absorbance 0.1 at 280 nm to avoid inner-filter correction and adjusted pH 3.0 for the fluorescence measurements (Baker 2001). To limit second-order Raleigh scattering, a 290 nm cutoff filter was used for all samples (Chen et al. 2003). The fluorescence response to a blank solution (distilled-deionized water) was subtracted from the spectrum of each sample. Finally, fluorescence intensities of all samples were normalized to units of quinine sulfate equivalents (QSEs) based on fluorescence measured from a series of diluted quinine sulfate dehydrate solutions in 0.05 M sulfuric acid at the excitation/emission wavelengths of 350/450 nm (Chen et al. 2007). Relative precisions of < 2% will be routinely obtained based on replicated fluorescence measurements.

The humification index (HIX) was calculated by dividing the emission intensity from 435 to 480 nm region by intensity from 300 to 345 nm (Zsolnay et al. 1999).

For this study, fluorescence characteristics of water samples were identified with three distinct fluorescence regions, such as fulvic-like fluorescence (FLF), humic-like fluorescence (HLF) and protein-like fluorescence (PLF). FLF was comprised of two components, C1 at Ex = 300 nm, Em = 400 nm and C6 at Ex = 350 nm, Em = 426 nm. HLF consisted of C2, C3, C4 and C5 components corresponding to Ex = 340 nm, Em = 454 nm; Ex = 270/370 nm, Em = 484 nm; Ex = 280/410 nm, Em = 522 nm and Ex = 270/380 nm, Em = 462 nm, respectively.

PLF components were identified with three components, C7 (Ex = 280 nm, Em = 326 nm), C8 (Ex = 240 nm, Em = 338 nm) and C9 (Ex = 250 nm, Em = 450 nm). Total nine components were used to calculate %FLF, %HLF and %PLF (Fellman et al. 2010, Singh et al. 2014).

^{13}C and ^{15}N isotope abundance

For measuring the ^{13}C and ^{15}N isotope abundance, water samples, were filtered through a pre-rinsed cellulose acetate membrane filter (0.45 µm, Whatman), and then freeze-dried. Laboratory standard gases were calibrated with respect to international standards by using the reference substances ANU sucrose and NBS 19 for the C isotopes (standards from the International Atomic Energy Agency, Vienna, Austria). Reproducibility and accuracy of the isotope abundance measurements was controlled by measures of an in-house acetanilide standard (Gebauer and Schulze, 1991). At least 6 test substances with varying sample weights were routinely analyzed within each batch of 50 samples. Maximum variation within and between batches is always below 0.1‰ for δ^{13}C and δ^{15}N.

Flux calculation

The total DOC and DON flux of throughfall, forest floor leachates and soil solution in the three plots (Table 3.1.6) were calculated only during the wet period because the calculation of the water fluxes during the dry period might be not realistic. The water volume of throughfall was measured after each storm event, respectively. The water flux for forest floor leachates was calculated as 90% of throughfall and the water flux for soil solution were computed as 90% of the water flux with forest floor percolates. The net release of forest floor was obtained by subtracting the throughfall fluxes from forest floor leachates fluxes.

The total export fluxes of DOC, DON, NO_3-N, FPOC and FPON in runoff (Table 3.1.4) were calculated separately during the dry period and during the wet period. During the dry period, the total export flux of DOC was calculated as weekly export flux of DOC by multiplying the mean DOC concentration per week by the weekly discharge. The concentrations of DON, NO_3-N, FPOC and FPON were partly under the detection limited. Thus, the detected minimum concentrations were applied to the calculation of their export flux. During the wet period, the total export fluxes of DOC, DON, NO_3-N, FPOC and FPON in runoff were computed at 2 hour intervals by multiplying measured concentration by the corresponding discharge.

CO_2 evolution

To measure CO_2 evolution from soil samples during the laboratory experiments, samples were placed in an airtight glass jar with a silicon septa on the top of lid. CO_2 concentrations were measured as CH_4 by a gas chromatograph equipped with a flame ionization detector. Gas samples (10 µl) were taken by hand from the headspace of the airtight jars and then injected. The soil respiration rates were calculated from the linear increase in CO_2 in the glass jars head space. CO_2 standards with the concentrations 380 ppm, 600 ppm, 1000 ppm, 3000 ppm and 10000 ppm were used for calibration. The mean precision of CO_2 measurement ranges from 4% (10000 ppm) to 8% (380 ppm).

3 RESULTS

3.1 Field study

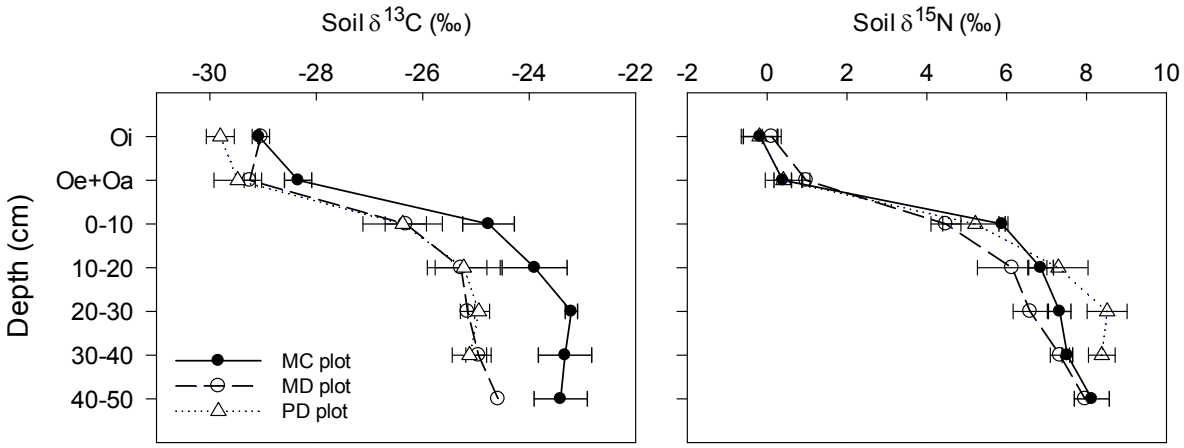
3.1.1 Soil properties and hydrological dynamics

Properties of forest floor and mineral soils

The depth of O-layer in the MC plot was thinner than in the MD and the PD plot (Table 3.1.1). The volume of the rock fraction (> 2mm) at the MD plot in 20 to 50 cm depth was larger than at the MD and the PD plot. The bulk density generally increased with depth, but was generally rather low indicating no compaction of the soil and a high water conductivity. Both, Oi and Oe+Oa layers in the MC plot (pH 4.3) were more acidic than in the MD (pH 5.4) and the PD (pH 4.9) plot, while the pH of the mineral soil was similar in the three plots (pH 4.1 to 4.7). The C content of O-layers in all plots was in the range of 45 - 48% in Oi and 34 - 38% in Oe+Oa layer. The contents of C and N (%) of the mineral soil were smaller in the MC plot than in the MD and the PD plot, especially the N % of the mineral soil in the MC plot was consistently low in the range from 0.2 to 0.27%. The C/N ratio in all plots decreased from the O-layer to the mineral soil. The C/N ratio of mineral soil was slightly higher in the MC plot than in the MD and the PD plot because of the low contents of N % in the MC plot. The total C and N stock of the O-layer in the PD plot was less than in the MC and the MD plot. On the contrary, the total C and N stocks of the mineral soil was smaller in the MC plot than in the MD and the PD plot.

The soil $\delta^{13}C$ and soil $\delta^{15}N$ values significantly increased with soil depth (Figure 3.1.1). The signatures in the O-layers differed significantly from those in the mineral soil. In the O-layers, the $\delta^{13}C$ ranged from -28 to -30‰ but from -23 to -27‰ in the mineral soil. The $\delta^{13}C$ of soil organic matter in the MC plot was slightly higher than in the MD and the PD plot. The soil $\delta^{15}N$ was not different between the plots, but was much lower in the O-layers (0 to 1 ‰) than in the mineral soil (4 to 8 ‰).

Soil texture had a mean composition of 44%, 38% and 18% in the MC plot, 40%, 38 % and 22% in the MD plot, and 49%, 29% and 22% in the PD plot for sand, silt and clay, respectively. The sampling of mineral soil at the PD plot to a depth of 40 to 50 cm was not possible due to the massive rocks.



Error bars represent one standard deviation (n=3)

Figure 3.1.1 Soil profiles of ^{13}C (*left*) and ^{15}N (*right*) isotope abundance in mixed coniferous (MC), mixed deciduous (MD) and purely deciduous (PD) plot

Hydrological characteristics

The hydrological characteristics of storm events during the summer monsoon in the MCD and the PD watershed in July 2013 are summarized in Table 3.1.2. The base flow in June ranged from 0.017 to 0.098 mm h^{-1} with an average 0.032 mm h^{-1} in the MCD watershed and from 0.040 to 0.106 mm h^{-1} with an average 0.061 mm h^{-1} in the PD watershed. During the monsoon in July, similar hydrological characteristics of storm events were observed in both watersheds, such as the start of storm events, total precipitation amounts and precipitation intensity. The strongest storm events were recorded more than 100 mm precipitation. The highest precipitation intensity coincided to the largest discharge in both watersheds. The discharge before start of a storm event increased gradually from 0.03 to 2.06 mm h^{-1} in the MCD watershed and also from 0.1 to 1.3 mm h^{-1} in the PD watershed.

Table 3.1.1 Properties of forest floor and mineral soils in three research plots

Plot	Soil layer	Depth (cm)	Rock fraction Vol. (%)	Bulk Density (g cm^{-3})	pH($CaCl_2$)	C (%)	N (%)	C/N ratio	C stock (kg m^{-2})	N stock (g m^{-2})	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Texture (%) Sand	Silt	Clay
MC[a]	Oi	+2.7 - +1.5			4.39	47.85	1.66	28.74	0.31 ± 0.12	14 ± 5	-29.1 ± 0.0	-0.2 ± 0.4			
	Oe+Oa	+1.5 - 0			4.23	38.40	1.93	19.89	0.54 ± 0.32	30 ± 18	-28.3 ± 0.3	0.4 ± 0.2			
									∑0.85	∑44					
	Mineral soil	0 - 10	25.3 ± 15.5	0.90 ± 0.05	4.46	3.26	0.27	12.13	2.51 ± 0.15	207 ± 13	-24.8 ± 0.5	5.9 ± 0.1	43.1	37.0	19.9
	Mineral soil	10 - 20	19.3 ± 3.8	1.00 ± 0.06	4.48	2.57	0.20	12.92	2.38 ± 0.49	184 ± 38	-23.9 ± 0.6	6.9 ± 0.3	42.9	39.4	17.6
	Mineral soil	20 - 30	16.5 ± 8.5	1.12 ± 0.09	4.49	2.75	0.22	12.69	2.56 ± 0.26	202 ± 20	-23.2 ± 0.1	7.3 ± 0.3	43.3	39.1	17.6
	Mineral soil	30 - 40	29.7 ± 17.1	1.22 ± 0.01	4.47	2.59	0.20	12.65	2.42 ± 0.23	191 ± 18	-23.3 ± 0.5	7.5 ± 0.1	46.9	35.4	17.8
	Mineral soil	40 - 50	18.4 ± 7.4	1.02 ± 0.11	4.42	2.35	0.20	11.74	1.96 ± 0.16	167 ± 13	-23.4 ± 0.5	8.1 ± 0.4	45.0	36.8	18.2
									∑11.8	∑951					
MD[b]	Oi	+5.5 - +3			5.47	47.91	1.66	28.88	0.16 ± 0.70	7 ± 3	-29.0 ± 0.2	0.1 ± 0.2			
	Oe+Oa	+3 - 0			5.37	34.23	1.60	21.36	0.54 ± 0.43	33 ± 27	-29.3 ± 0.1	1.0 ± 0.1			
									∑0.70	∑40					
	Mineral soil	0 - 10	19.6 ± 1.3	0.78 ± 0.02	4.65	5.92	0.49	12.15	3.70 ± 0.09	304 ± 8	-26.3 ± 0.4	4.5 ± 0.4	41.4	39.6	19.0
	Mineral soil	10 - 20	22.3 ± 3.0	0.94 ± 0.06	4.62	3.47	0.29	11.83	2.54 ± 0.27	215 ± 22	-25.3 ± 0.5	6.1 ± 0.9	39.8	37.0	23.2
	Mineral soil	20 - 30	32.4 ± 9.2	1.38 ± 0.06	4.56	3.08	0.25	12.30	2.86 ± 0.34	232 ± 28	-25.2 ± 0.1	6.6 ± 0.4	38.8	38.3	22.9
	Mineral soil	30 - 40	45.6 ± 26.2	1.24 ± 0.11	4.52	2.77	0.24	11.45	1.99 ± 0.76	173 ± 66	-25.0 ± 0.2	7.3 ± 0.2	34.1	41.6	24.3
	Mineral soil	40 - 50	40.0	1.30	4.40	2.26	0.21	10.76	1.77	164	-24.6	8.0	44.8	33.0	22.2
									∑12.9	∑1088					
PD[c]	Oi	+4.3 - +2			4.94	45.50	2.12	21.49	0.10 ± 0.06	5 ± 3	-29.8 ± 0.3	-0.2 ± 0.5			
	Oe+Oa	+2 - 0			4.92	35.42	1.82	19.44	0.38 ± 0.13	23 ± 8	-29.5 ± 0.4	0.4 ± 0.5			
									∑0.48	∑28					
	Mineral soil	0 - 10	11.8 ± 7.3	0.90 ± 0.05	4.56	4.82	0.43	11.27	3.83 ± 0.49	340 ± 44	-26.4 ± 0.7	5.2 ± 0.8	50.8	29.6	19.6
	Mineral soil	10 - 20	14.8 ± 3.3	1.10 ± 0.21	4.11	3.06	0.30	10.28	2.86 ± 0.46	278 ± 45	-25.2 ± 0.7	7.3 ± 0.7	48.9	29.7	21.5
	Mineral soil	20 - 30	10.2 ± 9.6	1.07 ± 0.05	4.04	2.63	0.27	9.61	3.02 ± 1.01	315 ± 105	-24.9 ± 0.2	8.5 ± 0.5	49.4	29.8	20.8
	Mineral soil	30 - 40	13.5 ± 10.0	1.02 ± 0.18	4.15	2.33	0.22	10.52	2.49 ± 0.93	236 ± 88	-25.1 ± 0.3	8.4 ± 0.3	48.0	27.4	24.6
	Mineral soil	40 - 50	Basement rock						∑12.2	∑1169					

Numbers are means with on standard deviation (n=3)

[a] Coniferous plot in mixed coniferous/deciduous forested watershed in Seohwa

[b] Deciduous plot in mixed coniferous/deciduous forested watershed in Seohwa

[c] Deciduous plot in purely deciduous forested watershed in Haean

Table 3.1.2 Hydrological characteristics and maximum concentration of DOC, DON, FPOC and FPON for sampled storm events in mixed coniferous/deciduous forested watershed (MCD) and purely deciduous forested watershed (PD) during wet period

Watershed	Start time		Duration	No. of samples	Total precipitation	max. intensity	avg. intensity	max. discharge	Discharge before start of a storm event	max. DOC	max. DON	max. FPOC	max. FPON
			(h)		(mm)	(mm h^{-1})	(mm h^{-1})	(mm h^{-1})	(mm h^{-1})	(mg C L^{-1})	(mg N L^{-1})	(mg C L^{-1})	(mg N L^{-1})
MCD	2013. July. 02	9:00	15	16	40.0	8.5	2.7	0.17	0.03	3.7	0.1	0.04	0.002
	2013. July. 08	3:00	24	15	56.5	10.0	2.4	0.55	0.04	3.7	0.4	0.06	0.004
	2013. July. 11	9:00	12	12	44.5	10.0	3.7	1.47	0.52	2.1	0.2	0.03	0.003
	2013. July. 14	2:00	11	12	117.0	34.0	10.6	8.89	1.21	2.4	0.2	10.7	0.730
	2013. July. 14	23:00	20	14	55.5	7.0	2.8	1.90	2.06	1.5	0.05	0.01	0.001
PD	2013. July. 08	3:00	32	21	117.5	20.0	3.6	3.16	0.10	6.9	0.6	8.6	0.58
	2013. July. 11	9:00	15	20	43.5	8.0	2.9	3.07	0.58	5.0	0.2	0.3	0.02
	2013. July. 14	2:00	10	12	95.0	32.0	9.5	7.39	1.07	5.1	0.2	3.2	0.21
	2013. July. 15	0:00	20	11	53.5	7.0	2.7	2.32	1.30	3.6	0.2	0.3	0.02
	2013. July. 18	14:00	9	10	58.0	20.5	6.4	6.61	0.32	5.2	0.2	1.1	0.08

3.1.2 Concentrations in runoff

Concentration of DOC, DON, FPOC and FPON in runoff in response to discharge

The concentrations of DOC, DON, FPOC and FPON in runoff in June and July 2013 in relation to discharge are presented in Figure 3.1.2. During the dry period with discharge < 0.5 mm h^{-1} in June 2013, the runoff DOC concentration ranged from 0.7 to 1.4 mg C L^{-1} with an average of 0.97 ± 0.17 mg C L^{-1} in the MCD watershed and from 1.2 to 2.4 mg C L^{-1} with an average of 1.44 ± 0.40 mg C L^{-1} in the PD watershed (Figure 3.1.2 and Table 3.1.5). During the monsoon storm events in July, the DOC concentration in response to discharge increased in the PD watershed, but remained relatively stable in the MCD watershed (Figure 3.1.2). The mean runoff DOC concentration during the wet period increased slightly from 1.0 to 1.8 mg C L^{-1} in the MCD and largely from 1.4 to 3.5 mg C L^{-1} in the PD watershed compared to the dry period, respectively (Table 3.1.5). The maximum concentration of DOC was instantaneous 3.7 mg C L^{-1} in the MCD watershed and 6.9 mg C L^{-1} in the PD watershed (Table 3.1.2). The maximum concentrations of DOC and DON in runoff were found in the initial storm event during monsoon, and then the maximum values decreased generally in subsequent storm events.

The runoff DON concentrations in June was not quantifiable due to the high mineral-N (NO_3^- + NH_4^+) background. Low DON concentrations < 0.05 mg N L^{-1} were not included in this study because of analytical uncertainties. During the wet period in July 2013, the DON concentrations in runoff from both watersheds were independent of discharge.

During the dry period in June 2013, the runoff FPOC and FPON concentrations were below detection limited. Under heavy storm events, the concentrations of FPOC and FPON in runoff varied considerably (Figure 3.1.2). The concentrations of FPOC and FPON in runoff increased with discharge in the MCD watershed while no general response was observed in the PD watershed. However in single events, a response of concentrations to discharge was found as well. For example, the FPOC concentration in runoff sharply increased from 0.4 to 2.8 mg C L^{-1} at 1 mm h^{-1}, from 1.7 to 8.7 mg C L^{-1} at 3 mm h^{-1} in the PD watershed and 1 to 10.7 mg C L^{-1} at 9 mm h^{-1} discharge in the MCD watershed. The maximum concentration of FPOC and FPON was 10.7 mg C L^{-1} and 0.7 mg N L^{-1} in the MCD watershed and 8.6 mg C L^{-1} and 0.6 N L^{-1} in the PD watershed (Table 3.1.2). Moreover, the maximum concentration of FPOC and FPON in runoff were not only related to the initial storm event in the PD watershed, but corresponded to the maximum precipitation intensity in the MCD watershed.

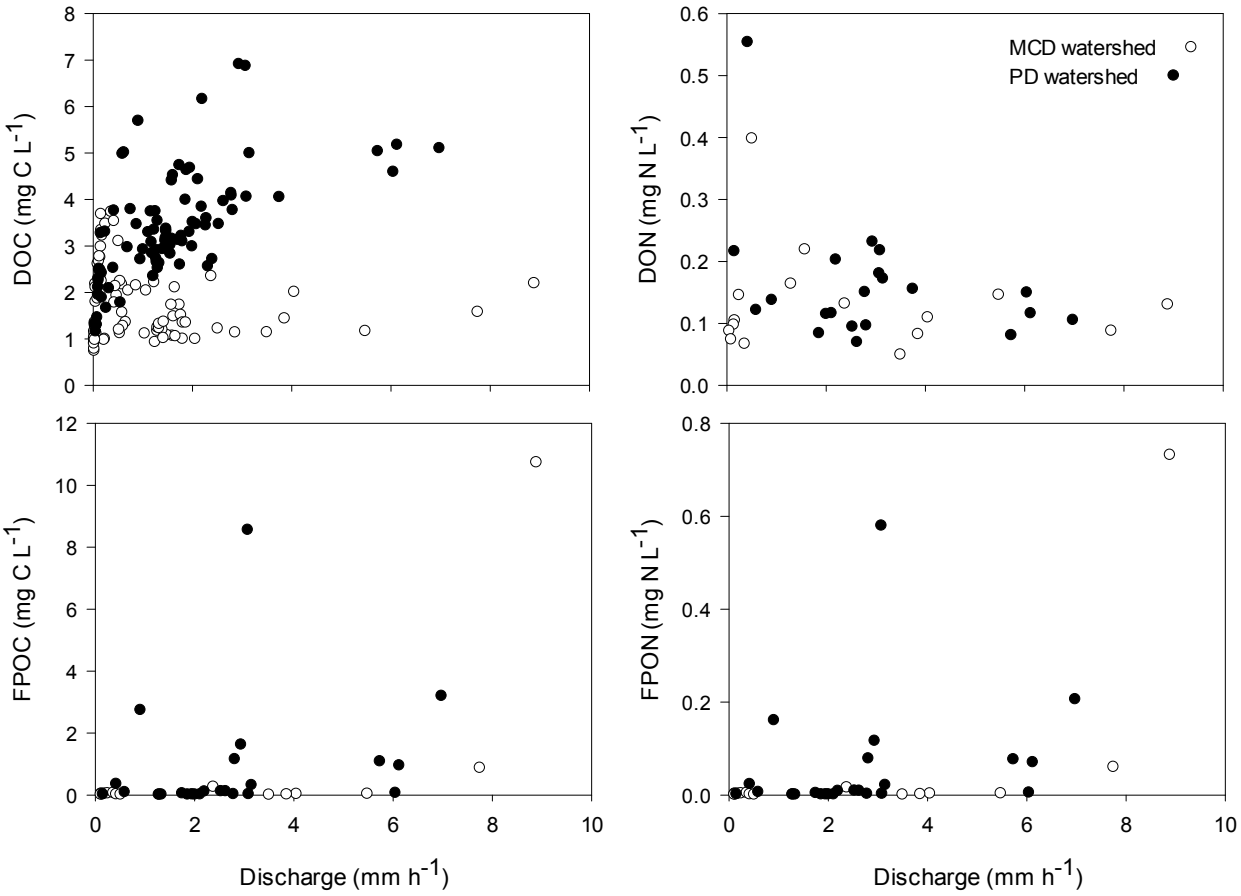


Figure 3.1.2 Relationship between the discharge and the concentration of dissolved organic carbon (DOC) and nitrogen (DON) and fine particulate organic carbon (FPOC) and nitrogen (FPON) in runoff from mixed coniferous/deciduous forested watershed (MCD) and purely deciduous forested watershed (PD)

The correlation between the concentrations of DOC and DON in runoff was not observed, while the concentration of FPOC correlated significantly with FPON in runoff from the MCD (r = 0.99***) and the PD (r = 0.99***) watershed (Table 3.1.3). The different correlations were found in the two watersheds. The relations of DOC concentration with FPOC (r = 0.60**) and FPON (r = 0.60**) were only observed in the PD watershed. The concentration of DON in runoff was independent of DOC, FPOC and FPON in runoff from both watersheds.

Table 3.1.3 Correlation coefficients matrix (Pearson's) of DOC, DON, FPOC and FPON concentrations (mg L^{-1}) in runoff from MCD and PD watershed.

	DOC	DON	FPOC
MCD watershed			
DON	0.01		
FPOC	-0.10	0.03	
FPON	-0.10	0.03	0.99***
n	20	15	17
PD watershed			
DON	0.16		
FPOC	0.60**	-0.04	
FPON	0.60**	-0.04	0.99***
n	24	23	24

**$p < 0.01$, ***$p < 0.001$

Hysteretic relationships between discharge and DOC concentration

The runoff DOC concentrations in response to discharge had a clockwise hysteretic loop (Figure 3.1.3) with higher concentrations on the rising than on the falling limb. The maximum DOC concentration was measured shortly before peak flow. DOC concentration increased rapidly from 1 to 3.7 mg C L^{-1} in the MCD watershed and from 2 to 7 mg C L^{-1} in the PD watershed. A hysteretic loop was not observed for DON, FPOC and FPON concentration (data not shown).

Relationships between discharge and fine particles

The concentration of TSS, FPOC and FPMM increased with increasing discharge in a stepwise relation (Figure 3.1.4). The concentration of TSS in runoff from the PD watershed responded with larger temporal variability to discharge than from the MCD watershed. TSS in runoff was mostly composed of mineral matter. At the strongest storm events with more than 100 mm precipitation, FPOC and FPMM represented 6% (8.6 mg L^{-1}) and 94% (80 mg L^{-1}) of TSS in the MCD watershed and 11% (10.7 mg L^{-1}) and 89% (168 mg L^{-1}) of TSS in the PD watershed, respectively.

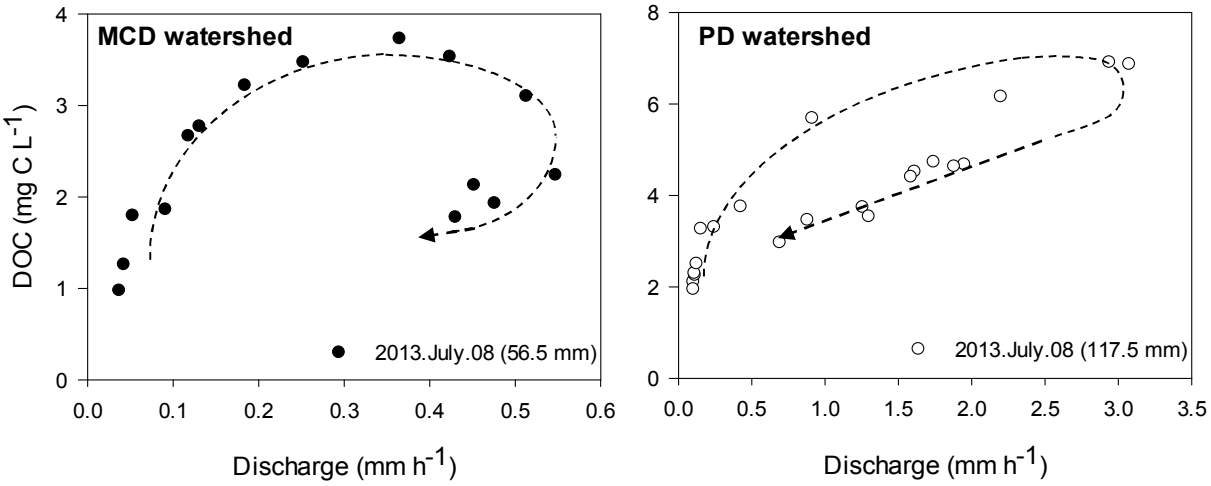


Figure 3.1.3 Hysteretic relationships between discharge and concentration of dissolved organic carbon (DOC) in runoff from MCD (*left*) and PD (*right*) watershed

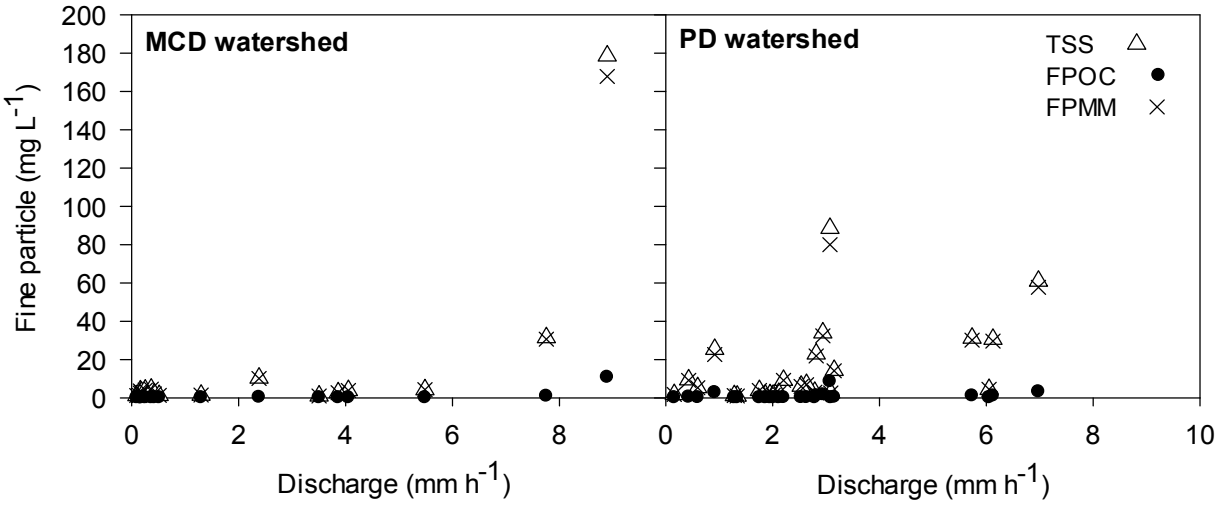


Figure 3.1.4 Relationship between discharge and concentration of total suspend solid (TSS), fine particulate organic carbon (FPOC) and fine particulate mineral matter (FPMM) in runoff from MCD (*left*) and PD (*right*) watershed during heavy storm events

3.1.3 Export fluxes

Export of DOC, DON, FPOC and FPON in response to discharge

The DOC and DON export fluxes with runoff was positively and linearly correlated to the discharge in both watersheds (Figure 3.1.5). The DOC export fluxes from the PD watershed were 2-3 times larger than that from the MCD watershed, whereas the DON export was not significantly different between both watersheds. The FPOC and FPON fluxes in both watersheds increased during heavy storm or high-intensity discharge events. Discharge over a certain threshold induced the sharp response of the FPOC and FPON export fluxes. For example, the fluxes of FPOC and FPON reached 950 g C ha^{-1} h^{-1} and 67 g N ha^{-1} h^{-1} at discharge > 9 mm h^{-1} in the MCD watershed and 260 g C ha^{-1} h^{-1} and 20 g N ha^{-1} h^{-1} at discharge > 3 mm h^{-1} in the PD watershed. Before reaching the discharge threshold, the FPOC export fluxes was much lower than DOC. At peak flow, however, the FPOC export fluxes in the MCD watershed exceeded 5 times those of DOC. The same trend was found for the relation of FPON and DON export fluxes. The pattern of FPOC export fluxes coincided with those of FPON, while a relation of DOC and DON export fluxes was not observed.

The fluxes of organic C and N in runoff were in the order; DOC > FPOC and DON > FPON during the dry period and during smaller storm events, whereas during heavy storm events, FPOC and FPON export fluxes was far ahead of DOC and DON. FPOC and FPON export fluxes from the PD watershed was generally higher than those from the MCD watershed, while the DON export was not different between the two watersheds.

Export of N in response to discharge

The export fluxes of NO_3-N responded stronger to discharge than those of DON and FPON (Figure 3.1.6). The export fluxes of NO_3-N and DON were significantly correlated to discharge, while the relationship between FPON export fluxes and discharge was not significant. The N forms in runoff were in the order; NO_3-N > DON > FPON during smaller storm events, whereas FPON export fluxes exceeded DON during heavy storm events. At heavy storm events the order of N forms was, NO_3-N > FPON > DON. The export fluxes of DON and FPON were only slightly different between the watersheds, while the export fluxes of NO_3-N from the MCD watershed were 2 times higher than from the PD watershed.

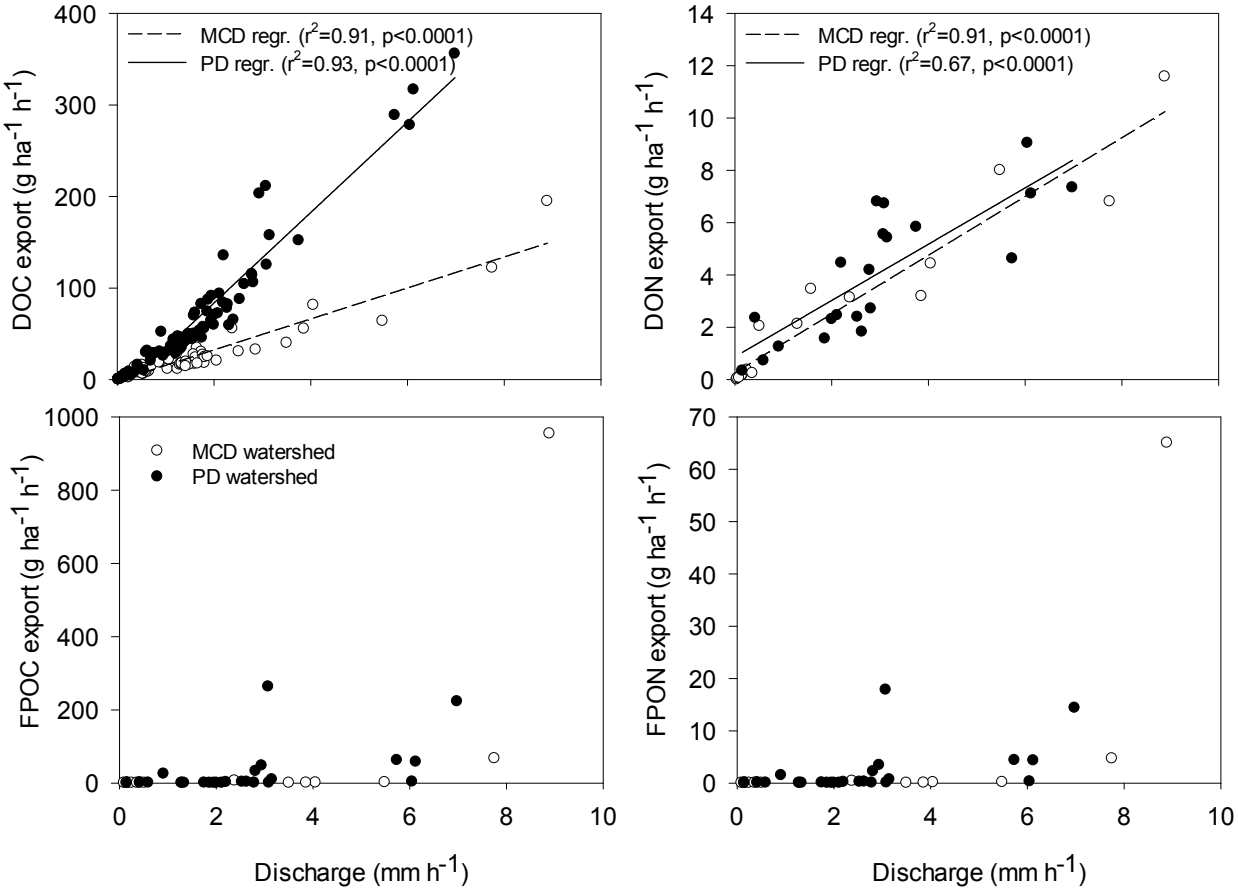


Figure 3.1.5 Relationship between discharge and fluxes of dissolved organic carbon (DOC) and nitrogen (DON) and fine particulate organic carbon (FPOC) and nitrogen (FPON) in runoff from mixed coniferous/deciduous forested watershed (MCD) and purely deciduous forested watershed (PD)

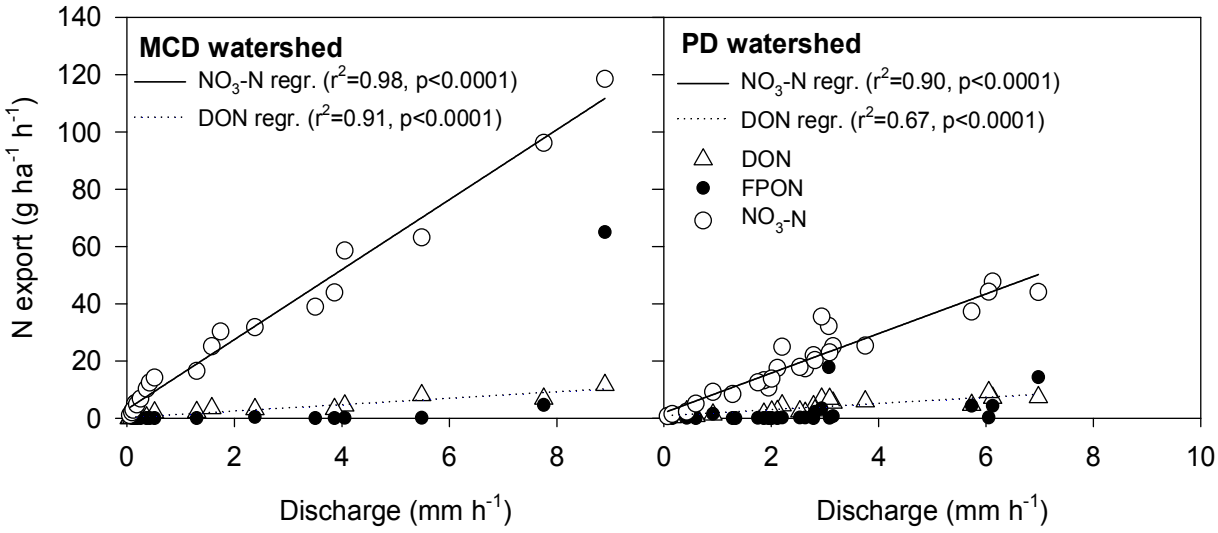


Figure 3.1.6 Relationship between discharge and nitrogen (N) fluxes with dissolved organic nitrogen (DON), fine particulate organic nitrogen (FPON) and nitrate (NO_3-N) in runoff from MCD (*left*) and PD (*right*) watershed during heavy storm events

Cumulative export fluxes of C and N

The cumulative export fluxes of DOC, DON, NO_3-N, FPOC and FPON in runoff from June to July 2013 are summarized in Table 3.1.4. Both the MCD and the PD watersheds received similar amounts of precipitation. The DOC export fluxes in the monsoon season in July was more than 20 times of the DOC export fluxes in June, while the total precipitation in July was only 6-7 times the amount of June. FPOC and FPON were almost not exported from both watersheds during the dry period, with less than 0.01 kg ha^{-1}. However, similar to DOC and DON, the total export fluxes of FPOC, FPON and also NO_3-N increased extremely in both watersheds during the wet period. The total export fluxes of DOC and DON were larger in the PD than in the MCD watershed, whereas those of NO_3-N, FPOC and FPON were smaller in the PD than in the MCD watershed during the wet period. The export fluxes of total organic C (DOC+FPOC) and total organic N (DON+FPON) were higher in the PD (17.6 kg C ha^{-1} and 0.6 kg N ha^{-1}) than in the MCD watershed (9.0 kg C ha^{-1} and 0.4 kg N ha^{-1}) during the wet period. The C and N exports with runoff from both watersheds were in the order; DOC > FPOC and NO_3-N > DON > FPON. The DOC export fluxes contributed 75% and 92% of the total C export in the MCD and the PD watershed, respectively. NO_3-N export fluxes represented 93% and 82% of the total N export in the MCD and the PD watershed respectively. The export fluxes

of NH_4-N in runoff were negligible even under the heavy storm due to low concentrations of 0.05 mg N L^{-1}.

Table 3.1.4 Total precipitation, total discharge and total fluxes of DOC, DON, NO_3-N, FPOC and FPON in runoff during dry (June 2013) and wet (July 2013) period

Watershed	Period	Total precipitation	Total discharge	DOC export	DON export	NO_3-N export	FPOC export	FPON export
		(mm)	(mm)	(kg C ha^{-1})	(kg N ha^{-1})	(kg N ha^{-1})	(kg C ha^{-1})	(kg N ha^{-1})
MCD	Dry[a]	86.0	21.8	0.22	0.02	0.43	0.001	0.0001
	Wet[b]	508.0	380.7	6.74	0.26	5.20	2.22	0.15
PD	Dry[a]	70.5	52.4	0.85	0.1	0.52	0.01	0.001
	Wet[b]	498.0	439.5	16.13	0.52	2.87	1.46	0.11

[a] From 01 June 2013 to 30 June 2013

[b] From 01 July 2013 to 20 July 2013

3.1.4 Properties of DOM and POM in runoff as influenced by discharge

DOC/DON and POC/PON ratio

The DOC/DON and the FPOC/FPON ratios were calculated with runoff samples sampled under heavy storm events (Figure 3.1.7). DON concentrations < 0.1 mg N L^{-1} were not considered for ratio calculations. The DOC/DON ratios in runoff had a wide range from 5 to 50, while the FPOC/FPON ratios had a relatively narrow range from 10 to 20. In response to discharge, the runoff DOC/DON ratios tended to be stable in the MCD watershed and to increase in the PD watershed. There was no response of the FPOC/FPON ratios to discharge with average ratios of 12 in the MCD and 13 in the PD watershed.

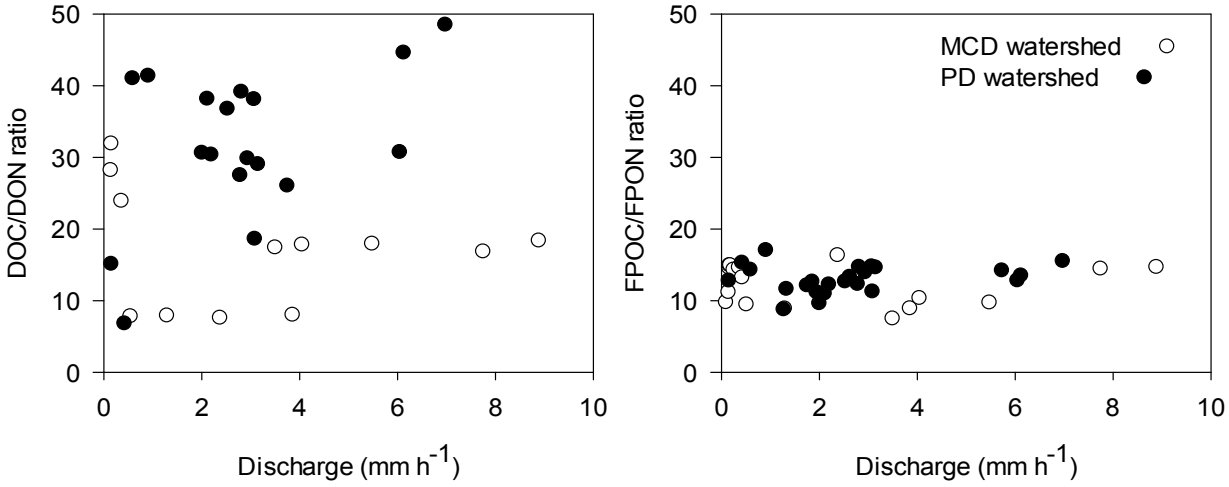


Figure 3.1.7 Relationship between discharge and ratio of dissolved organic carbon to nitrogen (DOC/DON) and of fine particulate organic carbon to nitrogen (FPOC/FPON) in runoff from MCD and PD watershed during heavy storm events (DON concentrations of < 0.1 mg N L^{-1} were not considered for ratio calculations)

^{13}C and ^{15}N isotope abundance in runoff

The $\delta^{13}C_{DOC}$ and $\delta^{15}N_{DTN}$ from the MCD watershed were relatively constant with discharge at about -22‰ and -1‰, while those signature decreased from -26‰ to -28‰ and from -2‰ to -1‰ in the PD watershed with increasing discharge. The $\delta^{13}C_{DOC}$ was lower by 2-4‰ in runoff from the PD watershed than from the MCD watershed. On the contrary, the $\delta^{15}N_{DTN}$ in both watersheds became more similar (ca. 0 ‰) with increasing discharge. The $\delta^{13}C_{FPOC}$ increased similarly in both watersheds from -27.5‰ to -26.5‰ with increasing discharge. The correlation of $\delta^{13}C_{FPOC}$ and discharge was significant in the MCD watershed ($r^2 = 0.60$, $p<0.0005$), but was not significant in the PD watershed. In contrast, the $\delta^{15}N_{FPON}$ was independently from discharge in both watersheds in the range of 0‰ to 4‰.

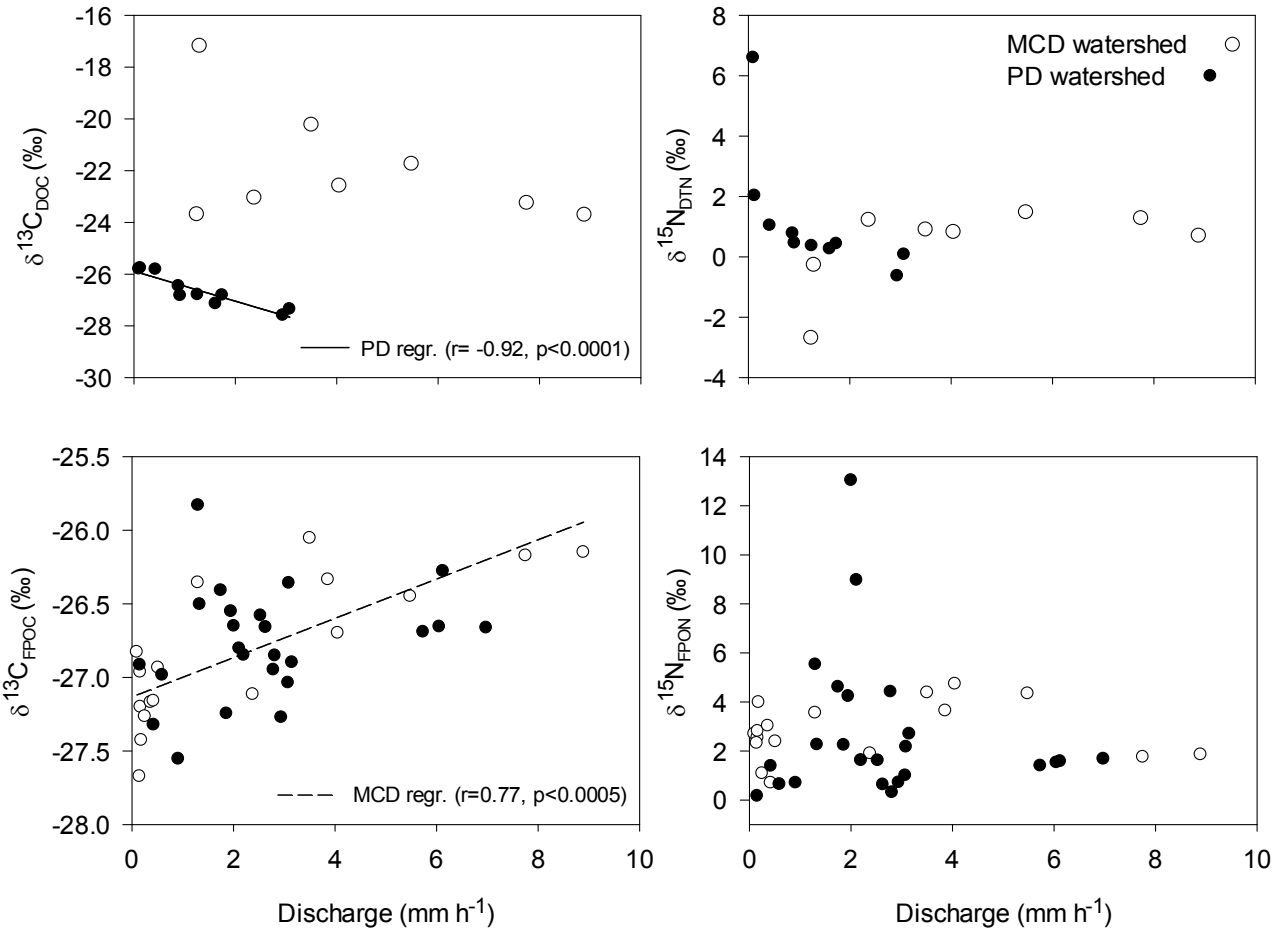


Figure 3.1.8 Relationship between discharge and isotope abundance of $^{13}C_{DOC}$, $^{13}C_{FPOC}$, $^{15}N_{DTN}$ and $^{15}N_{FPON}$ in runoff from MCD and PD watershed during heavy storm events

DOM quality in response to discharge

Changes of runoff DOM quality were observed with increasing discharge in the MCD and the PD watershed (Figure 3.1.9). The values of $SUVA_{280}$ distributed widely from 1.0 to 3.0 L mg C^{-1} m^{-1} in both watersheds, but at relatively high discharge, ranged narrowly from 1.5 to 2.0 L mg C^{-1} m^{-1} in the MCD watershed but remained stable ca. 2.5 L mg C^{-1} m^{-1} in the PD watershed. The values of HIXem increased with discharge in the PD watershed, but were stable around 4 in the MCD watershed. The ratios of PLF/HLF and PLF/FLF decreased with increasing discharge in the PD watershed, but not in the MCD watershed. The dominant fluorescence characteristic of DOM in runoff was HLF compared to FLF and PLF with the mean proportion as 65%, 23% and 13% in the MCD and as 68%, 24% and 7% in the PD watershed, respectively.

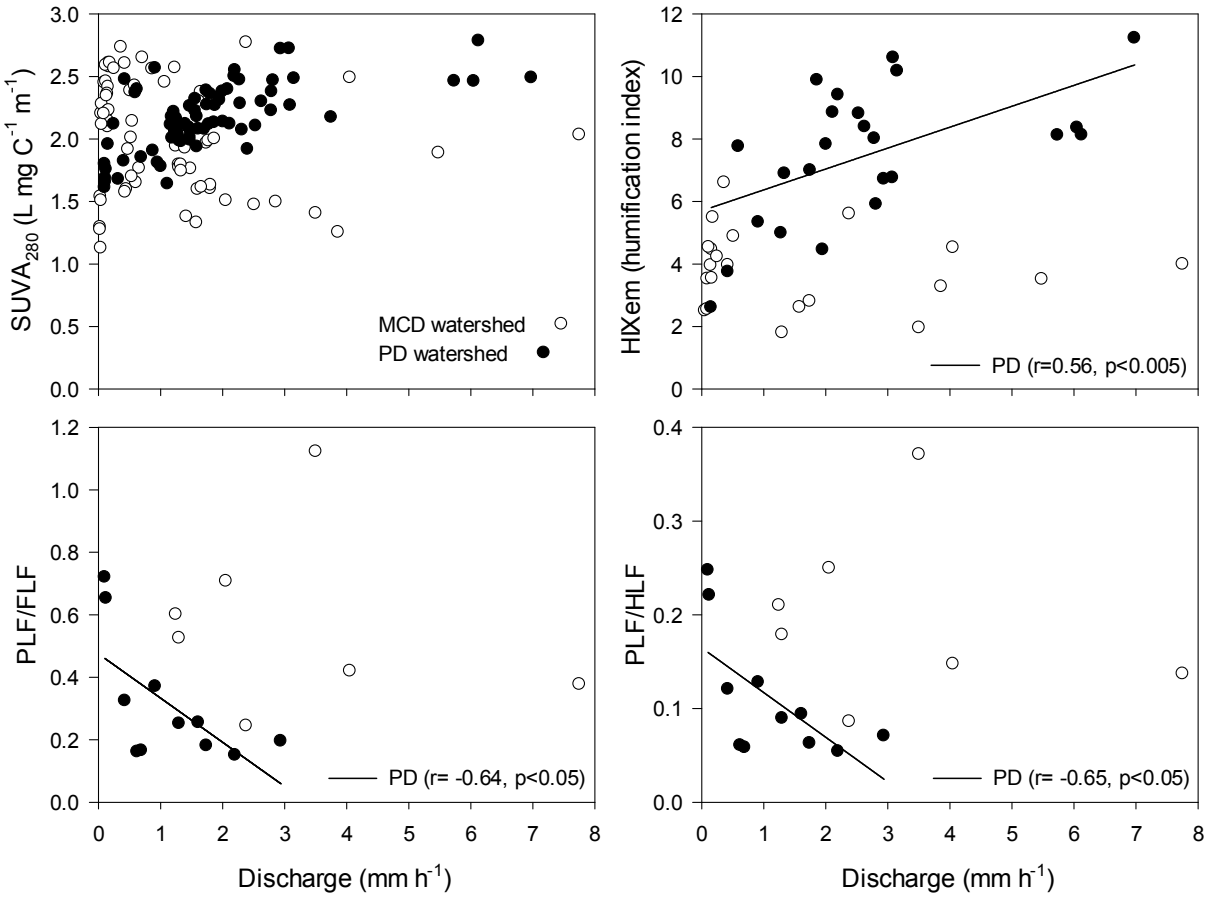


Figure 3.1.9 Relationship between discharge and specific ultraviolet absorbance ($SUVA_{280}$), humification index (HIXem), protein-like fluorescence/humic-like fluorescence (PLF/HLF) and protein-like fluorescence/fulvic-like fluorescence (PLF/FLF) in runoff during heavy storm events

3.1.5 Quantity and quality of throughfall, forest floor leachates and soil solution

Chemistry of throughfall, forest floor leachates and soil solution

The mean DOC and DON concentrations increased from throughfall to forest floor leachates and then declined in soil solution and runoff (Table 3.1.5). The concentrations of DOC and DON were highest in forest floor leachates and lowest in runoff. The concentrations of DOC and DON in solutions during the dry period were much higher than those during the wet period in all three plots. The mean DOC concentration of throughfall was larger in the MC plot than in the MD and PD plot, while the mean DOC concentrations of forest floor leachates and soil solution were higher in the MD than the PD and the MC plot during both dry and wet periods.

DON concentration of throughfall in the MC plot was lower during the dry period, whereas it was higher during the wet period than in the MD and PD plot. DON concentration in forest floor leachates was higher in the MD plot both during the dry and the wet period. DON concentrations of soil solution in all plots were small and similar. The DOC/DON ratio of solutions increased in the wet period. The highest DOC/DON ratios were generally found in forest floor leachates.

The values of $SUVA_{280}$ and HIXem were highest in forest floor leachates (Table 3.1.5). The values of $SUVA_{280}$ were stable or decrease from the dry to the wet period. HIXem increased in the wet period in forest floor leachates and soil solution. The dominant fluorescence component of DOM was HLF in all solutions and the highest HLF were observed in forest floor leachates.

The electrical conductivity (EC) of throughfall, forest floor leachates and soil solutions was higher during the dry than during the wet period (Table 3.1.5). The highest EC was found in forest floor leachate. The pH of throughfall, forest floor leachates and soil solutions in the MC plot was more acid than that in the MD and the PD plot.

Table 3.1.5 Solution chemistry of throughfall, forest floor leachates, soil solution in MC, MD and PD plot and runoff from MCD and PD forested watershed during dry (June 2013) and wet (July 2013) period

Plot		DOC (mg C L^{-1})		DON (mg N L^{-1})		DOC/DON		$SUVA_{280}$[a] (L mg C^{-1} m^{-1})		HIXem[b]		PLF/FLF[c]		PLF/HLF[d]		EC[ef]		pH[f]	
		mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)	mean	S.D. (n)
Dry period																			
MC	Throughfall	32	38.4 (16)	0.59	0.4 (10)	12.1	10.3 (10)	2.2	0.8 (16)	3.8	0.5 (6)					32.2	13.8 (16)	5.0	0.5 (16)
	Forest floor leachates	32.1	13.0 (11)	1.6	1.2 (9)	19.5	12.3 (8)	2.7	2.1 (11)	4.6	0.9 (9)					38.7	10.3 (12)	5.4	0.4 (12)
	Soil solution	2.4	0.9 (14)	0.86	0.5 (12)	6.4	8.6 (12)	1.4	0.2 (14)	2.1	0.4 (9)					26.2	2.4 (12)	5.7	0.6 (15)
	Runoff	1.0	0.2 (10)	<0.1		9.7	1.7 (10)	1.0	0.3 (10)	1.8	0.7 (5)					60.0	5.8 (10)	6.7	0.2 (10)
MD	Throughfall	11.7	11.3 (16)	0.95	0.3 (10)	14.3	11.2 (10)	1.9	0.6 (16)	2.6	0.6 (10)					34.2	31.9 (16)	6.5	0.5 (16)
	Forest floor leachates	43.3	32.4 (15)	2.68	1.2 (9)	29.6	46.2 (9)	5.2	3.4 (15)	6.8	1.3 (11)					71.7	29.8 (16)	5.9	0.2 (16)
	Soil solution	14.1	3.4 (3)	0.9	0.2 (3)	15.9	2.2 (3)	2.0	0.3 (3)	3.9	2.4 (2)					68.9	21.3 (3)	6.5	0.1 (3)
PD	Throughfall	4.6	1.4 (15)	1.3	1.1 (10)	5.4	3.3 (10)	1.9	0.5 (15)	1.3	0.7 (10)					26.2	9.7 (15)	6.4	0.6 (15)
	Forest floor leachates	22.4	8.4 (11)	1.6	0.8 (5)	22.6	18.4 (5)	7.7	2.8 (11)	7.2	1.7 (10)					61.4	22.2 (13)	6.2	0.4 (14)
	Soil solution	3.2	1.7 (18)	0.78	0.6 (13)	5.9	5.4 (13)	1.6	0.6 (18)	3.3	1.4 (9)					20.1	3.7 (18)	6.1	0.5 (21)
	Runoff	1.4	0.4 (8)	<0.15		9.6	2.7 (8)	2.0	0.2 (8)	3.1	1.0 (5)					29.8	2.1 (9)	6.4	0.2 (9)
Wet period																			
MC	Throughfall	8.8	6.1 (17)	0.32	0.2 (9)	26.1	10.8 (9)	2.1	0.5 (17)	2.8	1.1 (9)	1.57	0.17 (2)	0.39	0.01 (2)	15.9	11.3 (17)	4.7	0.4 (17)
	Forest floor leachates	16.3	9.0 (12)	0.5	0.3 (8)	37.2	19 (8)	4.0	1.1 (12)	8.7	1.1 (8)	0.5	0.22 (2)	0.15	0.06 (2)	21.2	12.3 (12)	5.2	0.2 (12)
	Soil solution	1.5	0.3 (12)	0.12	0.1 (6)	15.6	8.7 (6)	1.7	0.2 (12)	2.2	0.3 (6)	1.05	0.46 (2)	0.34	0.13 (2)	21.5	10.0 (15)	5.7	0.2 (15)
	Runoff	1.8	0.8 (75)	0.11	0.1 (21)	20.5	12.0 (16)	2.0	0.5 (75)	3.9	1.2 (22)	0.57	0.29 (7)	0.2	0.09 (7)	40.5	18.4 (75)	6.8	0.1 (75)
MD	Throughfall	3.2	2.6 (17)	0.2	0.1 (9)	14.1	8.3 (9)	2.0	0.4 (17)	1.5	0.8 (9)	1.99	0.98 (2)	0.59	0.21 (2)	10.3	6.3 (17)	6.1	0.2 (17)
	Forest floor leachates	24.8	11.7 (15)	0.84	0.3 (8)	32.5	7.4 (8)	4.8	2.0 (15)	10.6	1.7 (9)	0.44	0.15 (2)	0.14	0.04 (2)	35.8	16.3 (15)	5.9	0.1 (15)
	Soil solution	7.3	4.0 (14)	0.26	0.1 (7)	29.7	19.9 (7)	2.4	0.5 (14)	7.3	1.7 (8)	0.17	0.01 (2)	0.06	0.00 (2)	26	10.0 (14)	5.8	0.2 (14)
PD	Throughfall	2.1	1.8 (23)	0.13	0.1 (6)	13.9	4.2 (6)	1.0	0.6 (23)	0.7	0.4 (10)	1.38	0.59 (2)	0.56	0.17 (2)	9.0	6.3 (23)	5.8	0.4 (23)
	Forest floor leachates	10.9	4.3 (22)	0.5	0.4 (10)	23.7	9.4 (10)	3.7	1.1 (22)	10.8	2.3 (10)	0.18	0.02 (3)	0.06	0.01 (3)	22.6	10.3 (22)	6.2	0.3 (22)
	Soil solution	3.1	1.8 (22)	0.18	0.1 (7)	15.2	4.5 (7)	1.4	0.6 (22)	4.5	2.6 (9)	0.33	0.21 (2)	0.12	0.06 (2)	14.9	3.0 (23)	6.0	0.3 (24)
	Runoff	3.5	1.1 (79)	0.17	0.2 (24)	33.9	14.3 (22)	2.2	0.3 (79)	7.5	2.2 (24)	0.31	0.20 (11)	0.11	0.07 (11)	25.3	5.1 (80)	6.5	0.3 (80)

[a] Specific ultraviolet absorbance at 280 nm

[b] Humification index at the emission mode

[c] %protein like fluorescence/%humic like fluorescence

[d] %protein like fluorescence/%fulvic like fluorescence

[e] Electrical conductivity (µs cm^{-1})

[f] In situ measurement

n: number of samples

Fluxes of DOC and DON with throughfall, forest floor leachates and soil solution

The five storm events with comparable precipitation time and amount were used to calculate the total DOC and DON fluxes with throughfall, forest floor leachates and soil solution (Table 3.1.6). The water flux with throughfall in the MC and MD plots was about 50-70 mm less than in the PD plot. The highest flux of total DOC and DON was found in forest floor leachates. Comparing the plots, higher DOC and DON fluxes with throughfall were found in the MC plot than in the MD and the PD plot. Higher DOC fluxes with forest floor leachates and soil solution were observed in the MD plot than in the other plots. DON fluxes with forest floor leachates were higher in the MD and the PD plot than in the MC plot, while DON fluxes with soil solution was not significantly different among the plots. Hence, the largest net release from forest floor for DOC and DON was also found in the MD and the PD plot.

Table 3.1.6 Total DOC and DON fluxes with throughfall, forest floor leachates, soil solution and net release from the forest floor in MC, MD and PD plot during the wet period (July 2013, with five storm events)

	MC plot			MD plot			PD plot		
	water flux (mm)	DOC (kg ha^{-1})	DON (kg ha^{-1})	water flux (mm)	DOC (kg ha^{-1})	DON (kg ha^{-1})	water flux (mm)	DOC (kg ha^{-1})	DON (kg ha^{-1})
Throughfall	337	25.2	1.0	323	7.3	0.7	391	9.4	0.6
Forest floor leachates	303	47.5	1.5	291	62.1	2.5	352	39.7	2.6
net release of forest floor		22.3	0.5		54.8	1.8		30.3	2.1
Soil solution	273	4.3	0.4	262	18.0	0.8	317	10.2	0.5

Effect of precipitation on DOC concentrations and fluxes

The DOC concentrations of throughfall, forest floor leachates and soil solution in the MC and the MD plot had a larger variation (with maximum up to 100 mg C L^{-1}) during the dry period than during the wet period (Figure 3.1.10). In contrast the variation was less in the PD plot during the dry period. The DOC concentrations in soil solutions were independent from throughfall amount in all plots during both dry and wet periods. During the wet period, a decrease of DOC concentration in throughfall and forest floor leachates was finally found to values less than 10 mg C L^{-1} in the MC and to less than 20 mg C L^{-1} the MD plot by sequent

storm events, whereas the DOC concentration was relatively stable (< 20 mg C L^{-1}) with increasing throughfall in the PD plot.

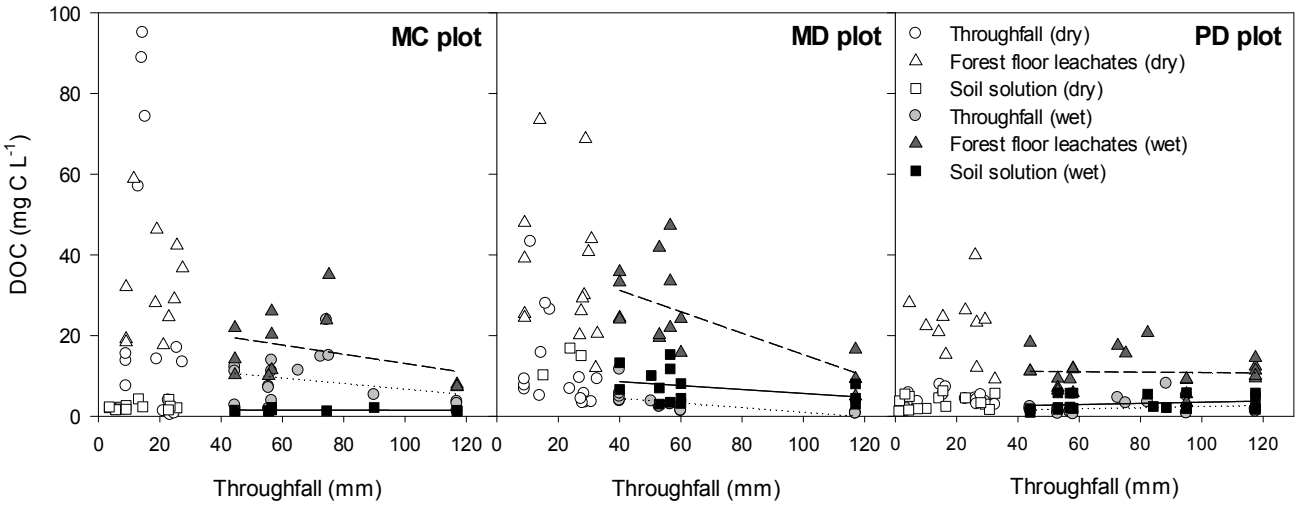
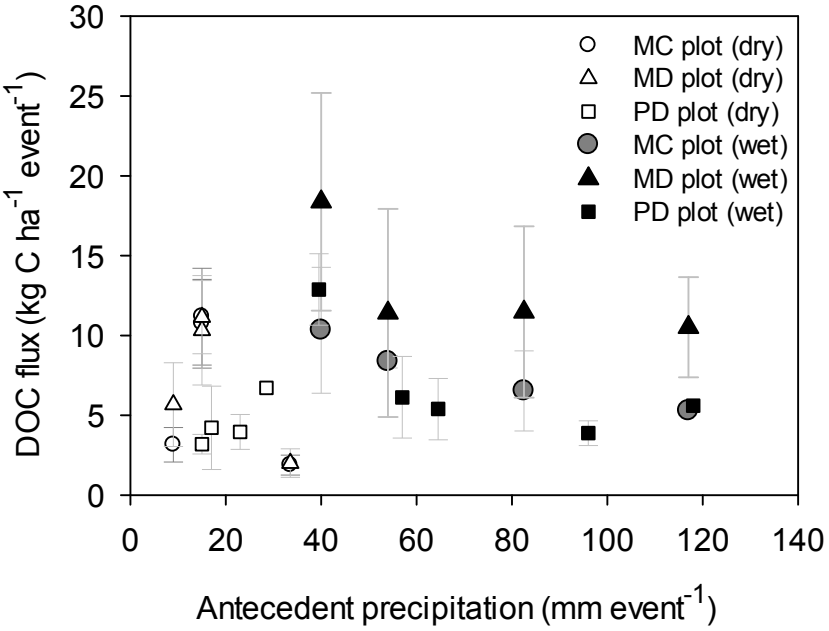


Figure 3.1.10 Relationship between the throughfall amount and the DOC concentration in throughfall, forest floor leachates, soil solution during the dry and wet period in MC, MD and PD plot

A relationship between the amount of antecedent precipitation and DOC fluxes of forest floor leachates was not observed during the dry period. In contrast, a negative relationship was found during the wet period (Figure 3.1.11). During the wet period, the DOC fluxes of forest floor at a specific date were higher after small antecedent precipitation and the fluxes decreased with increasing antecedent precipitation. The decrease in DOC fluxes from forest floors in response to antecedent precipitation from the MC plot (-5 kg C ha^{-1} $event^{-1}$) was smaller than from the MD (-8 kg C ha^{-1} $event^{-1}$) and PD (-7.5 kg C ha^{-1} $event^{-1}$) plot.



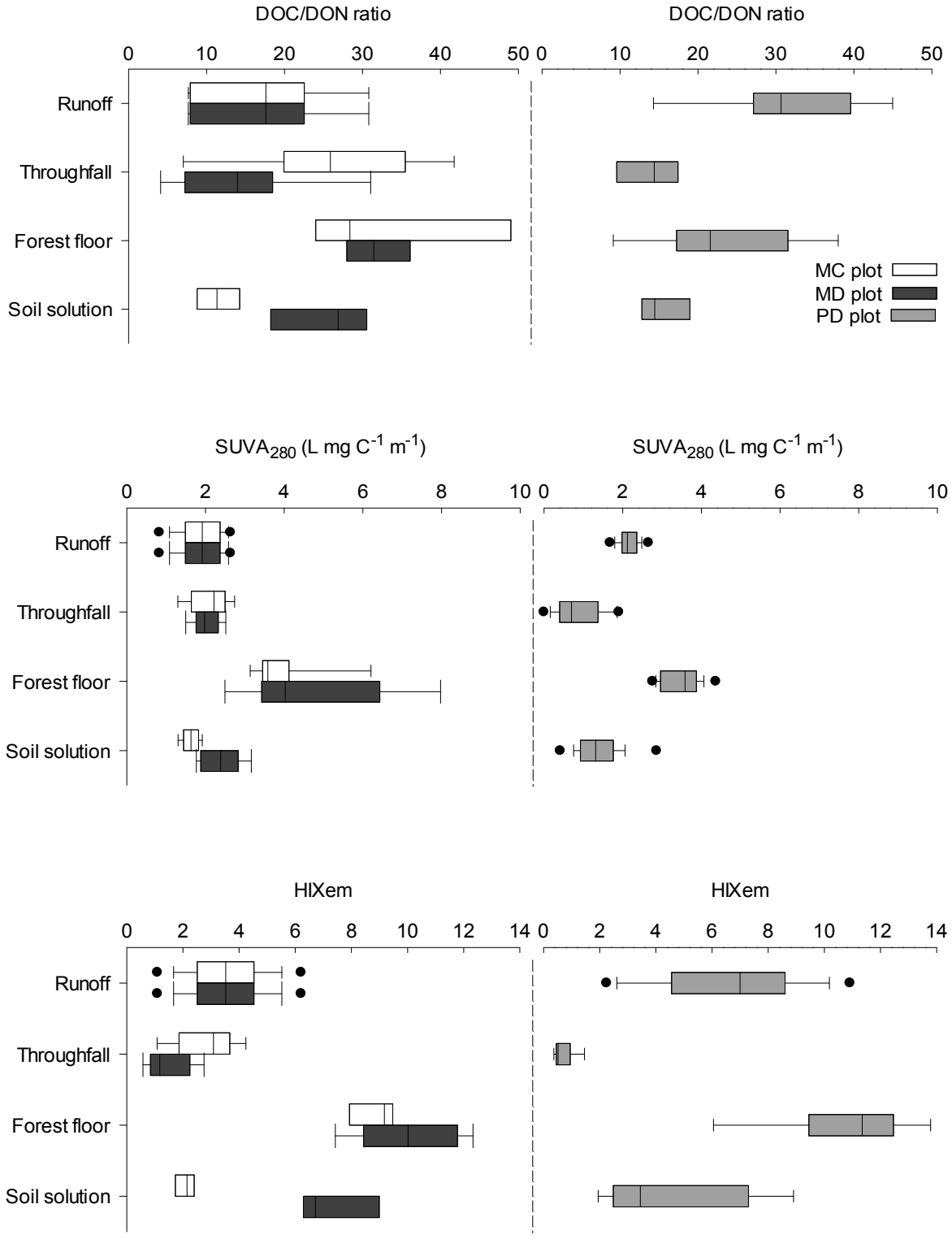
Error bars represent one standard deviation (n=3)

Figure 3.1.11 Relationship between the amount of antecedent precipitation and actual DOC fluxes with leachates from forest floor of MC, MD and PD plot during dry and wet period

3.1.6 Origin of DOM and POM in runoff

In the runoff from the MCD watershed, the range of DOC/DON and $SUVA_{280}$ was similar to the range of soil solution and the range of $\delta^{13}C_{DOC}$ of deeper soil (Figure 3.1.12). Also, the range of POM quality parameters of runoff was similar to the range of particulate C/N of upper/deeper soil (Figure 3.1.13). HIXem, $\delta^{13}C_{FPOC}$ and $\delta^{15}N_{FPON}$ of runoff were weakly related to those of mineral soil. Unlikely, the range of PLF/FLF, PLF/HLF and $\delta^{15}N_{DTN}$ of runoff was not related to that of soil solution.

In contrast, in the PD watershed, the DOM quality parameters DOC/DON, PLF/FLF, PLF/HLF and $\delta^{15}N_{DTN}$ of runoff were similar to those of forest floor percolates (Figure 3.1.12). The range of $SUVA_{280}$, HIXem and $\delta^{15}N_{FPON}$ of runoff was weakly related to forest floor percolates. However, the range of $\delta^{13}C_{DOC}$ of runoff was not related to that of forest floor percolates. The range of particulate C/N and $\delta^{13}C_{FPOC}$ of runoff distributed similarly to that of the upper soil in the PD plot (Figure 3.1.13).


DOC/DON ratio
0 10 20 30 40 50
Runoff
Throughfall
Forest floor
Soil solution
MC plot
MD plot
PD plot
SUVA280 (L mg C-1 m-1)
0 2 4 6 8 10
HIXem
0 2 4 6 8 10 12 14

(continue)

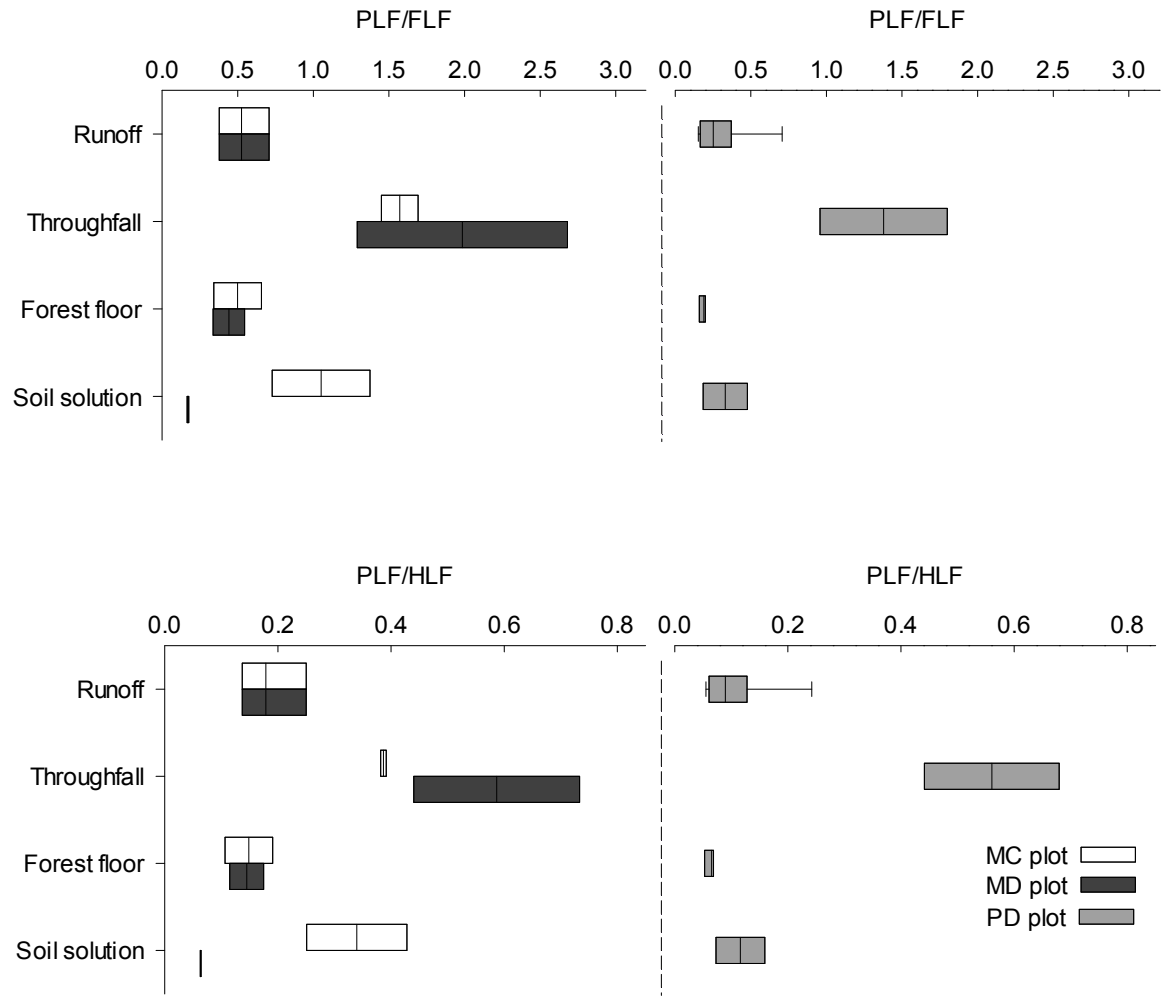


Figure 3.1.12 DOC/DON ratio, $SUVA_{280}$, HIXem, PLF/FLF, PLF/HLF of runoff from MCD (*left column*) and PD (*right column*) watershed and of throughfall, forest floor and soil solution from MC, MD and PD plot during the wet period

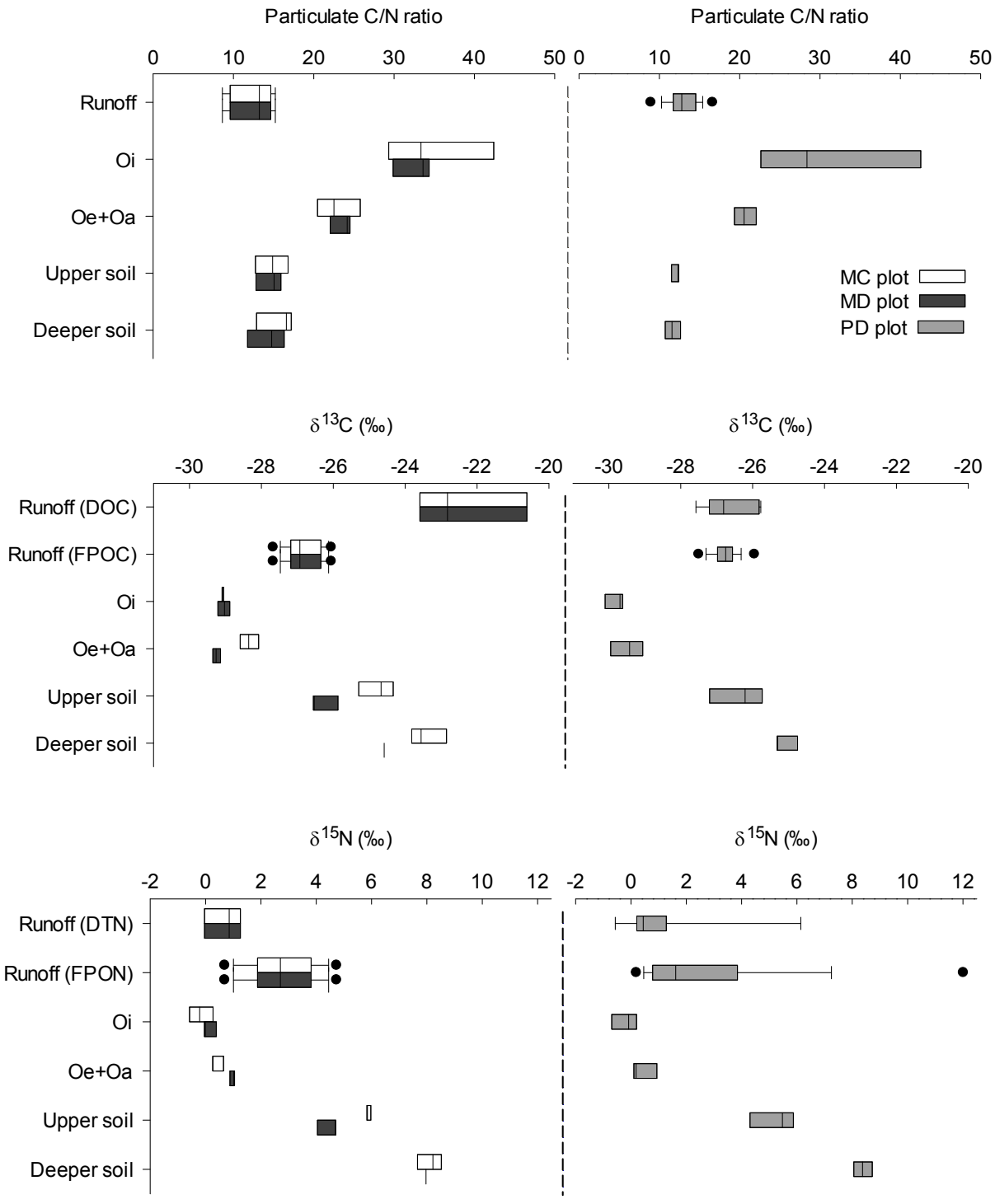


Figure 3.1.13 Particulate C/N ratio, $\delta^{13}C$, $\delta^{15}N$ of runoff from MCD (*left column*) and PD (*right column*) watershed, and of Oi, Oe+Oa, upper soil (0-10 cm depth) and deeper soil (40-50 cm depth in MC and MD plot, 30-40 cm depth in PD plot) from MC, MD and PD plot

3.2 Laboratory study

3.2.1 Forest floor properties

The depth of the O-layers in the spruce site was thicker than in the larch, beech, deciduous site (Table 3.2.1). The pH of the O-layers decreased from the Oi to the Oa layer. The O-layers under the spruce (pH 3.0) and larch (pH 4.3) stands were more acidic than under the beech (pH 4.6) and deciduous (pH 4.9) stands. The C contents of the O-layers in all sites were higher in the Oi (45-48%) than the Oe and Oa layer (21-42%). The contents of N of the O-layers were slightly larger in the deciduous (1.8-2.1%) than in other sites (1.0-1.9%). The C/N ratio of the O-layers decreased from the Oi layer to the Oa layer. The C/N ratio of the O-layers was lower in the deciduous (19-21) than other sites (19-29) because of the high contents of N % in the deciduous site. The total C and N stock of the O-layers was highest under spruce stands and was lowest under deciduous stands as following order; spruce > beech > larch > deciduous stands. The deciduous stand comprises mixed species (see chapter 2.3).

Table 3.2.1 Properties of forest floor at the different sites

	Layer	Thickness (cm)	pH ($CaCl_2$)	C (%)	N (%)	C/N	C stock (kg m^{-2})	N stock (g m^{-2})
Spruce	Oi	2.1[a]	3.6[b]	45.8[a]	1.7[a]	27[a]	0.74[a]	27[†]
	Oe	2.2[a]	2.9[b]	42.1[a]	1.8[a]	22[a]	1.20[a]	55[†]
	Oa	4.2[a]	2.6[b]	21.2[a]	1.1[a]	19[a]	1.42[a]	75[†]
							∑3.36	∑157
Larch	Oi	1.2	4.4	47.9	1.7	28	0.31	14[††]
	Oe+Oa	1.5	4.2	38.4	1.9	20	0.54	30[††]
							∑0.85	∑44
Beech	Oi	1.0[b]	4.7[b]	47.2	1.7	28	0.20[b]	7[†]
	Oe+Oa	2.0[b]	4.5	26.2	1.0	26	2.49[bc]	95[†]
							∑2.69	∑102
Deciduous	Oi	2.3	4.9	45.5	2.1	22	0.10	5[††]
	Oe+Oa	2.0	4.9	35.4	1.8	20	0.38	23[††]
							∑0.48	∑28

[a] Data from Schulze et al. (2009)

[b] Data from Gerstberger et al. (2004)

[c] Data from Schütt et al. (2014a)

[†] Calculated data with C/N ratio and C stock from [abc] references

[††] Own data

3.2.2 Batch experiment

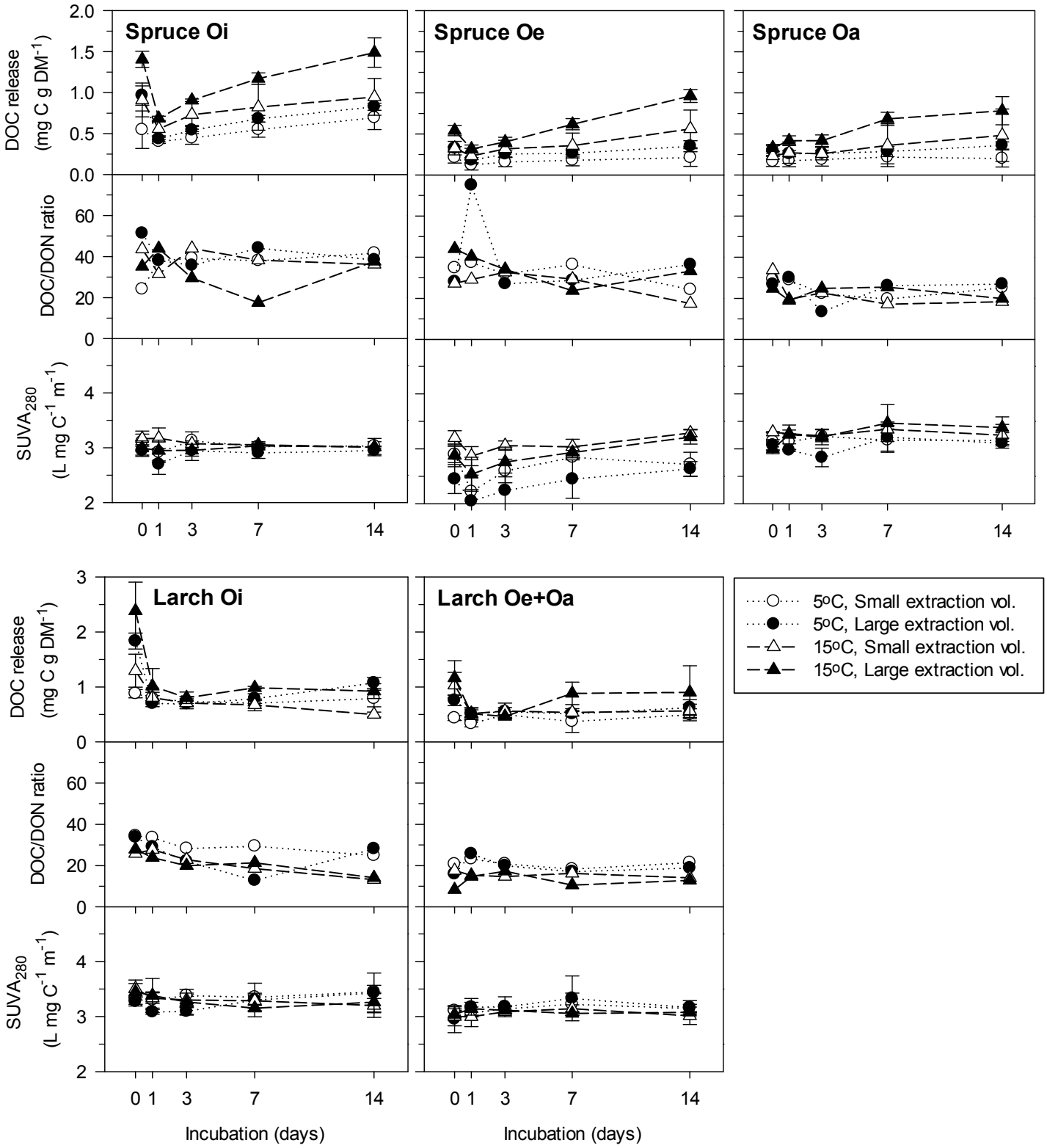
DOC and DON extraction

The DOC release in the O-layers was higher at 15ºC than at 5ºC. Furthermore the larger extraction volume (200 ml) released more DOC than the small extraction volume (50 ml) (Figure 3.2.1). The initial extraction of DOC was in the order; Oi > Oe > Oa layers and deciduous > beech ≥ larch > spruce O-layer. The averages of the DOC release at the initial extraction were (in mg C gDM^{-1}) 2.6 and 0.8 for Oi and Oe+Oa of deciduous, 1.4 and 1.0 for Oi and Oe+Oa of beech, 1.6 and 0.9 for Oi and Oe+Oa of larch, and 0.93, 0.34 and 0.26 for Oi, Oe and Oa of spruce samples, respectively. The DOC pool in the O-layers of spruce and beech site was depleted after the initial extraction and then recovered within the 14 days of the batch incubation. However, a depletion of the DOC pool after the initial extraction was not observed in spruce Oa layers. In contrast to the O-layers of spruce and beech, some DOC pools in the O-layers of larch and deciduous site did not recover after the initial depletion.

In all solutions from the batch experiment (Figure 3.2.1), the DOC/DON ratios were rather stable with an average of 38, 29 and 24 for Oi, Oe and Oa of spruce, 25 and 18 for Oi and Oe+Oa of larch, 41 and 25 for Oi and Oe+Oa of in beech, and 33 and 25 (10-50) for Oi and Oe+Oa of deciduous solutions, respectively. The highest DOC/DON ratios were found in Oi layers.

$SUVA_{280}$ values (in L mg C^{-1} m^{-1}) were also rather stable throughout the experiment (Figure 3.2.1) with an average of 3.0, 2.8 and 3.2 for Oi, Oe and Oa of spruce, 3.3 and 3.1 for Oi and Oe+Oa of larch, 3.4 and 3.7 for Oi and Oe+Oa of beech, and 4.1 and 3.1 for Oi and Oe+Oa of deciduous solutions, respectively. $SUVA_{280}$ values were slightly higher in beech and deciduous than spruce and larch solutions.

The extracted solutions were more acidic in spruce than in deciduous samples. The pH values of the extracted solutions were stable throughout the extraction time with an average of 4.4, 3.9 and 3.6 for Oi, Oe and Oa of spruce, 5.2 and 4.7 for Oi and Oe+Oa of larch, 4.8 and 4.7 for Oi and Oe+Oa of beech, and 6.4 and 5.6 for Oi and Oe+Oa of deciduous solutions (data not shown).


Spruce Oi
Spruce Oe
Spruce Oa
Larch Oi
Larch Oe+Oa
DOC release (mg C g DM-1)
DOC/DON ratio
SUVA280 (L mg C-1 m-1)
Incubation (days)
5oC, Small extraction vol.
5oC, Large extraction vol.
15oC, Small extraction vol.
15oC, Large extraction vol.

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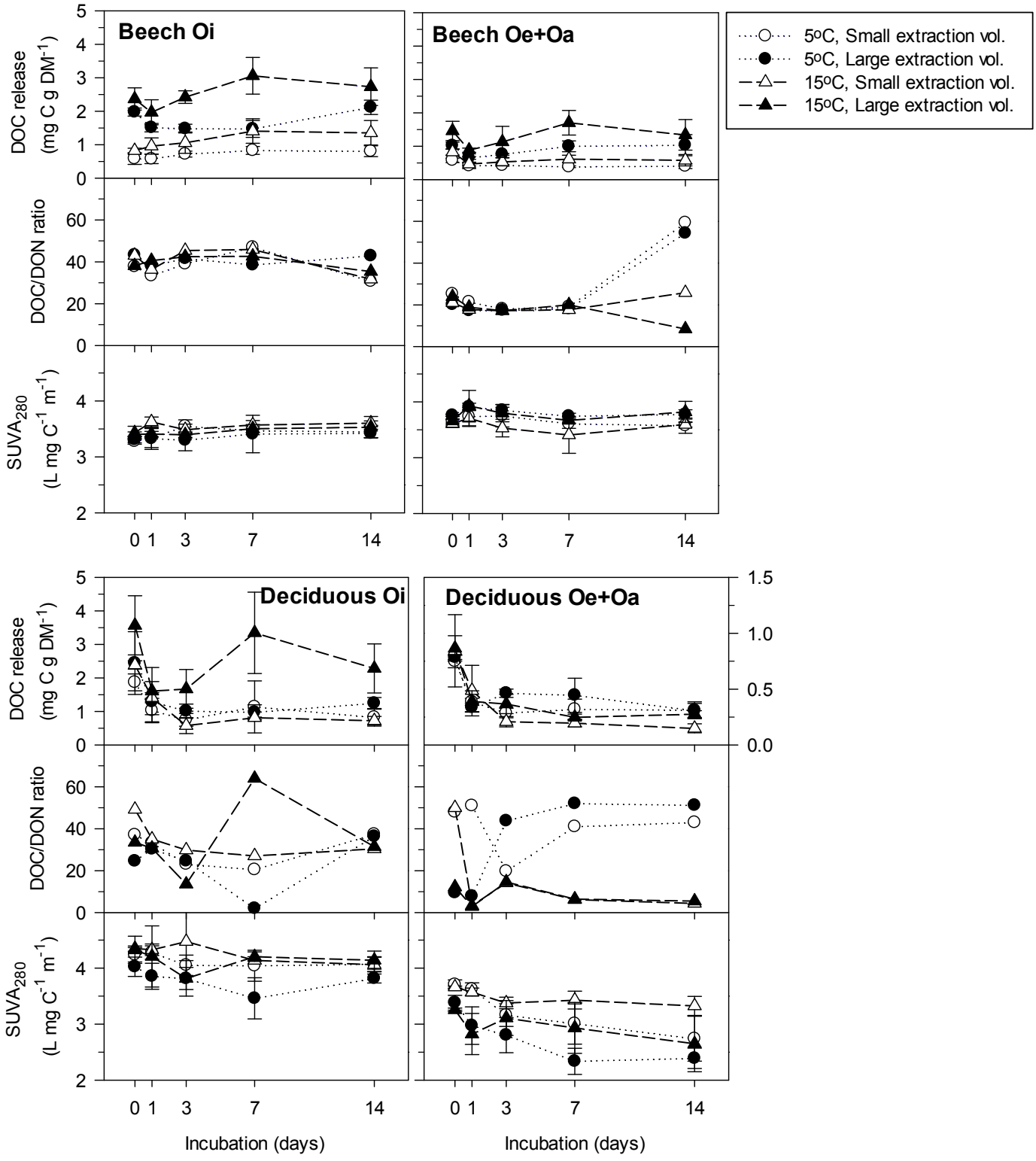


Error bars represent one standard deviation (n=3)

Figure 3.2.1 DOC release, DOC/DON ratio and $SUVA_{280}$ value of the extracted solutions from spruce, larch, beech and deciduous organic layers during 14 days of batch incubation

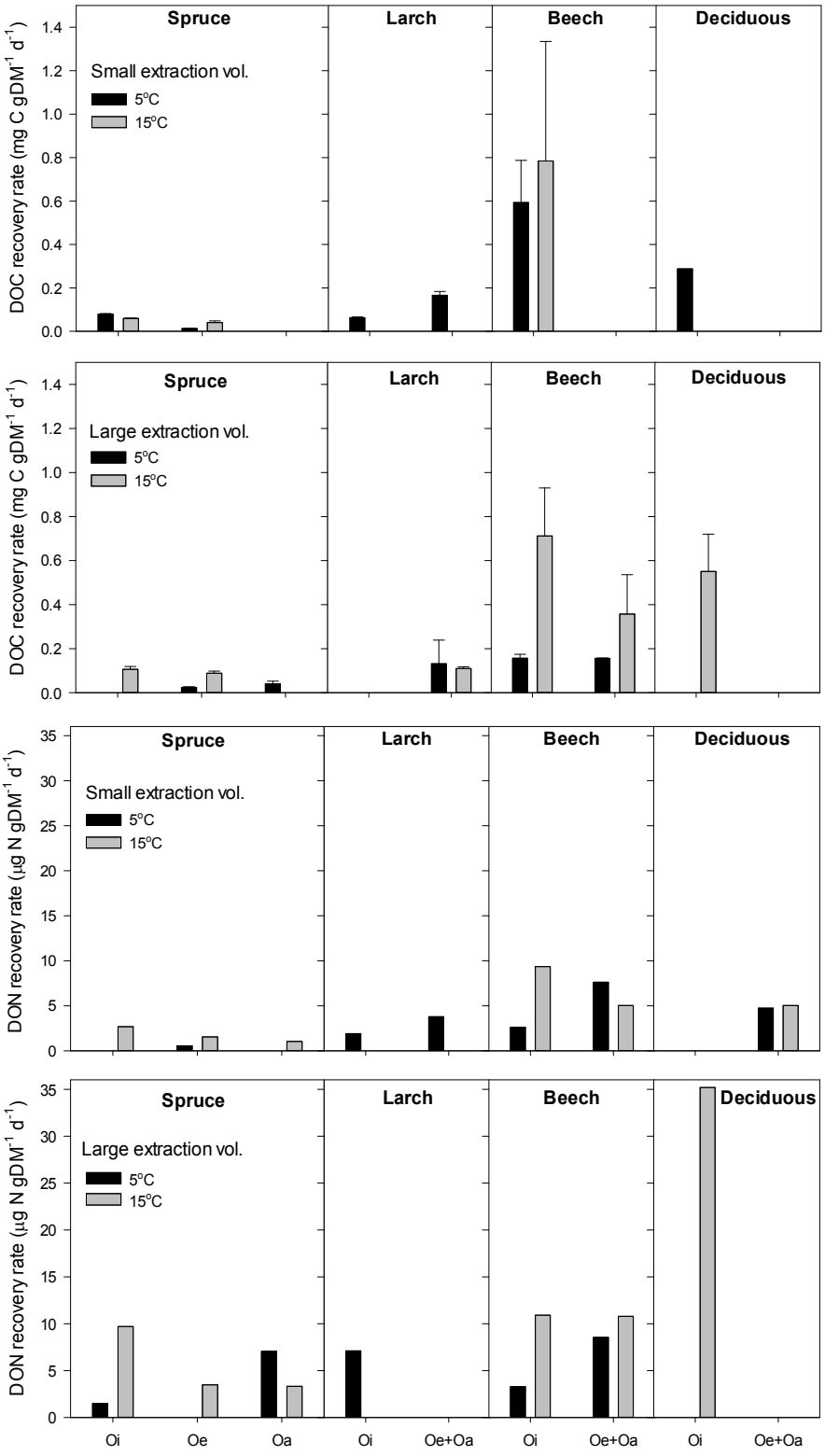
Recovery rate of DOC and DON

The recovery rates of DOC and DON the O-layers were calculated by the amount of DOC recovered to the initial DOC level divided by the days until DOC recovered (Figure 3.2.2).

The highest recovery rate of DOC and DON in the O-layers was found at 15ºC and in beech Oi and mixed deciduous Oi layers. A positive effect of the large extraction volume on the recovery rate of DOC and DON was found for some samples at 15ºC. The average recovery rates of DOC for all treatments ranged (in mg C gDM^{-1} d^{-1}) from 0.02-0.1 in spruce, 0.06-0.15 in larch, 0.16-0.75 in beech and 0.29-0.55 in deciduous samples, respectively. The average recovery rates of DON for all treatments ranged (in µg N gDM^{-1} d^{-1}) from 1-7 in spruce, 4-5 in larch, 3-10 in beech and 5-35 in deciduous samples, respectively.

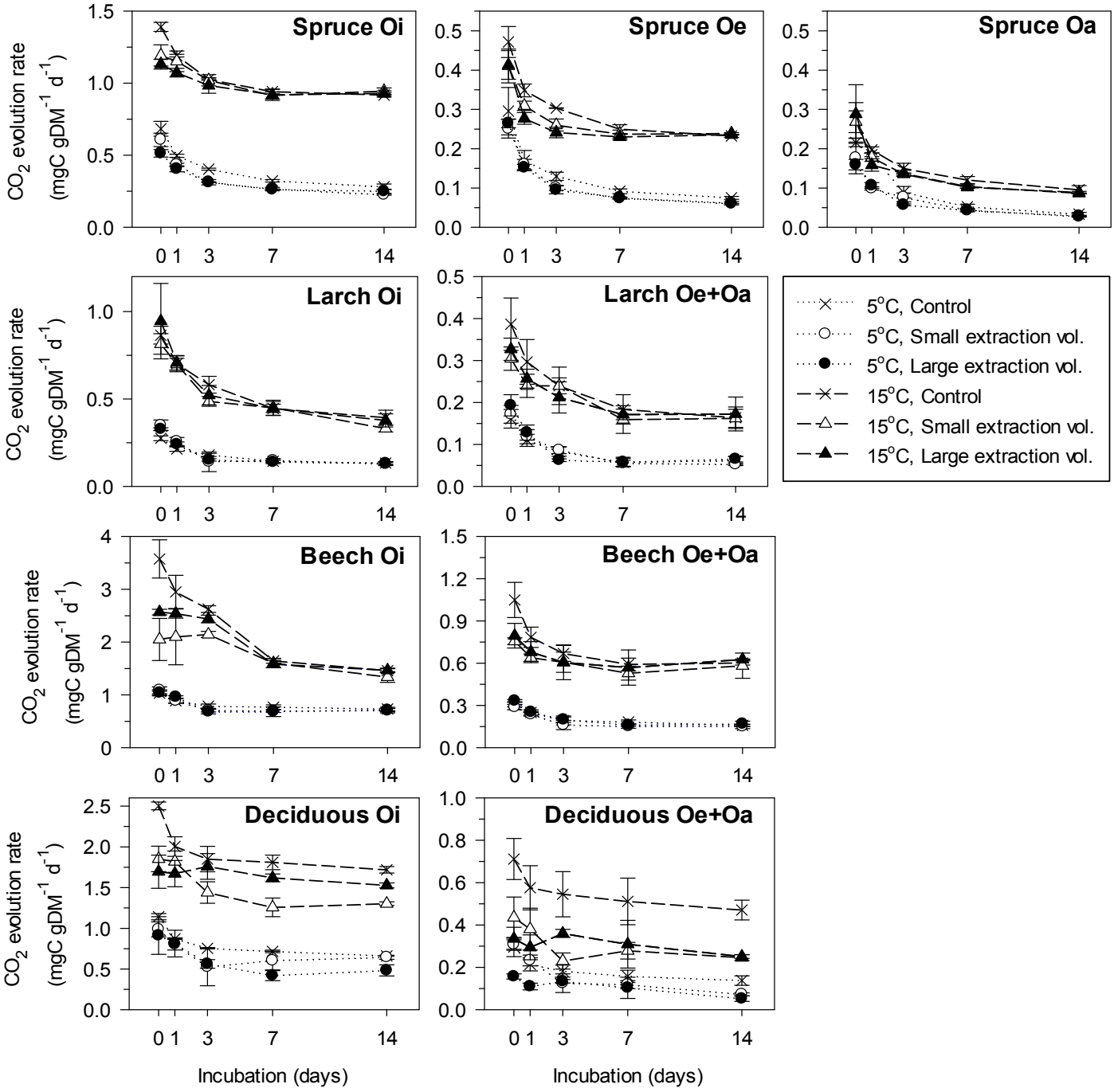
CO_2 evolution

The CO_2 evolution from all samples was highest after the initial extraction (0 day of incubation), and then decreased asymptotically with time and reached stable rates mostly after 7 days of batch incubation (Figure 3.2.3). The CO_2 evolution was clearly larger at 15ºC than at 5ºC and generally larger in control samples without DOC extraction than in samples with extraction. The CO_2 evolution became similar between samples with different extraction volume during the 14 days of batch incubation. The initial CO_2 evolution rate by the substrates was in the order; Oi > Oe > Oa layer and beech > deciduous > spruce > larch samples. The ranges of initial CO_2 evolution rate were (in mg C gDM^{-1} d^{-1}) 0.5-1.2, 0.3-0.4 and 0.2-0.3 for Oi, Oe and Oa of spruce, 0.3-1.0 and 0.2 - 0.3 for Oi and Oe+Oa of larch, 1.1-2.6 and 0.3-0.8 for Oi and Oe+Oa of beech and 0.9-1.9 and 0.2-0.4 for Oi and Oe+Oa of deciduous samples, respectively.



Error bars represent one standard deviation (n=3) for DOC data

Figure 3.2.2 DOC and DON recovery rate of spruce, larch, beech and mixed deciduous organic layers (No recovery was found for missing bars)



Error bars represent one standard deviation (n=3)

Figure 3.2.3 CO_2 evolution rate from soil samples of spruce, larch, beech and mixed deciduous forest floor with extraction (small; 50 ml and large; 200 ml) and without extraction (control)

Q_{10} values for initial C fluxes

With both small and large extraction volumes, Q_{10} values for the initial CO_2 evolution rate were mostly greater for Oi (1.7-2.9) than for Oe and Oa (1.4-2.6) layers (Table 3.2.2). However, Q_{10} values for the initial CO_2 evolution rate were not influenced by the extraction volumes and tree species.

Q_{10} values for initial DOC and DON release ranged from 1.0 to 2.4 and from 0.9 to 2.9, respectively. Higher Q_{10} values for initial DOC and DON release were found generally with small (0.9-2.9) extraction volume than large (0.9-2.0) and also for spruce and larch (0.9-2.9) compared to beech and deciduous samples (0.9-1.5). However, the differences in Q_{10} between the different O-layers for initial DOC and DON release were not consistent.

Table 3.2.2 Q_{10} values for initial CO_2 evolution rate, initial release rate of DOC and DON with small (50 ml) and large (200 ml) extraction volume in the batch experiment

Tree species	layer	Small extraction vol.			Large extraction vol.		
		Initial CO_2	Initial DOC	Initial DON	Initial CO_2	Initial DOC	Initial DON
Spruce	Oi	2.0	1.8	0.9	2.2	1.4	2.0
	Oe	1.6	1.6	1.8	1.6	1.7	1.1
	Oa	1.5	1.6	2.9	1.8	1.0	1.4
Larch	Oi	2.3	1.5	1.8	2.9	1.3	1.3
	Oe+Oa	1.8	2.4	1.7	1.7	1.5	1.3
Beech	Oi	1.7	1.4	1.1	2.5	1.2	1.5
	Oe+Oa	2.6	1.4	1.5	2.4	1.4	1.0
Deciduous	Oi	1.9	1.3	0.9	1.9	1.5	1.3
	Oe+Oa	1.4	1.1	1.1	2.1	1.1	0.9

Relationships between recovery rate of DOC and DON and CO_2 evolution rate

The initial CO_2 evolution rate correlated positively and significantly with the recovery rate of DOC ($r = 0.78^{***}$) and the DOC/DON ratio ($r = 0.60^{***}$), while the relationship between the initial CO_2 evolution rate and the recovery rate of DON was relatively weak ($r = 0.51^{*}$) (Table 3.2.3 and Figure 3.2.4). The recovery rate of DOC was weakly correlated to that of DON ($r = 0.47^{*}$) and also to the DOC/DON ratio ($r = 0.42^{*}$). However, the recovery rate of DON was not related to DOC/DON ratio. Significant correlation of the initial CO_2 evolution

and the recovery rate of DOC and DON were found with $SUVA_{280}$ and also weakly with pH, but no significant relationship was observed to conductivity.

Influence of DOC extraction on soil respiration

CO_2 evolution was generally larger in the O-layer samples without extraction (control) than in those with extraction (Figure 3.2.5). The difference in CO_2 evolution between the different extraction volumes (small and large) was relatively small, although the amount of DOM extracted was in a similar order of magnitude than the CO_2 evolution. Only significant regressions were shown in Figure 3.2.5. Some significant decrease of the CO_2 evolution after the initial DOC extraction was observed in spruce, beech, deciduous samples mostly at 15°C compared to at 5°C, while no significant relationship between the extracted DOC and the CO_2 evolution was found in larch samples. The decrease of CO_2 evolution caused by the DOC extraction (control-extracted samples) was larger in deciduous (14-53%) and beech (6-43%) with the range from 0.3 to 2 mg C gDM^{-1} d^{-1} than in spruce (2-27%) and larch (6-21%) samples with the range from 0.1 to 0.3 mg C gDM^{-1} d^{-1}, data that were positive value of control-extracted samples were only present. Similar to the decreased CO_2 evolution, DOC release was higher in deciduous and beech (0.7-3.5 mg C gDM^{-1}) than in spruce and larch samples (0.4-2 mg C gDM^{-1}).

Table 3.2.3 Correlation coefficients matrix (Pearson's) of the initial CO_2 evolution rate, the recovery rate (Rrec.) of DOC and DON and solution variables (DOC/DON ratio, $SUVA_{280}$, pH and electrical conductivity) for 9 forest floors in the batch experiment

	Initial CO_2	Rrec. DOC	Rrec. DON	n
Rrec. DOC	0.78***			23
Rrec. DON	0.51*	0.47		23
DOC/DON	0.60***	0.42*	0.09	36
$SUVA_{280}$	0.52**	0.58**	0.68***	36
pH	0.34*	0.44*	0.52*	36
EC	0.10	0.18	0.12	36

*p<0.05, **p<0.01, ***p<0.001

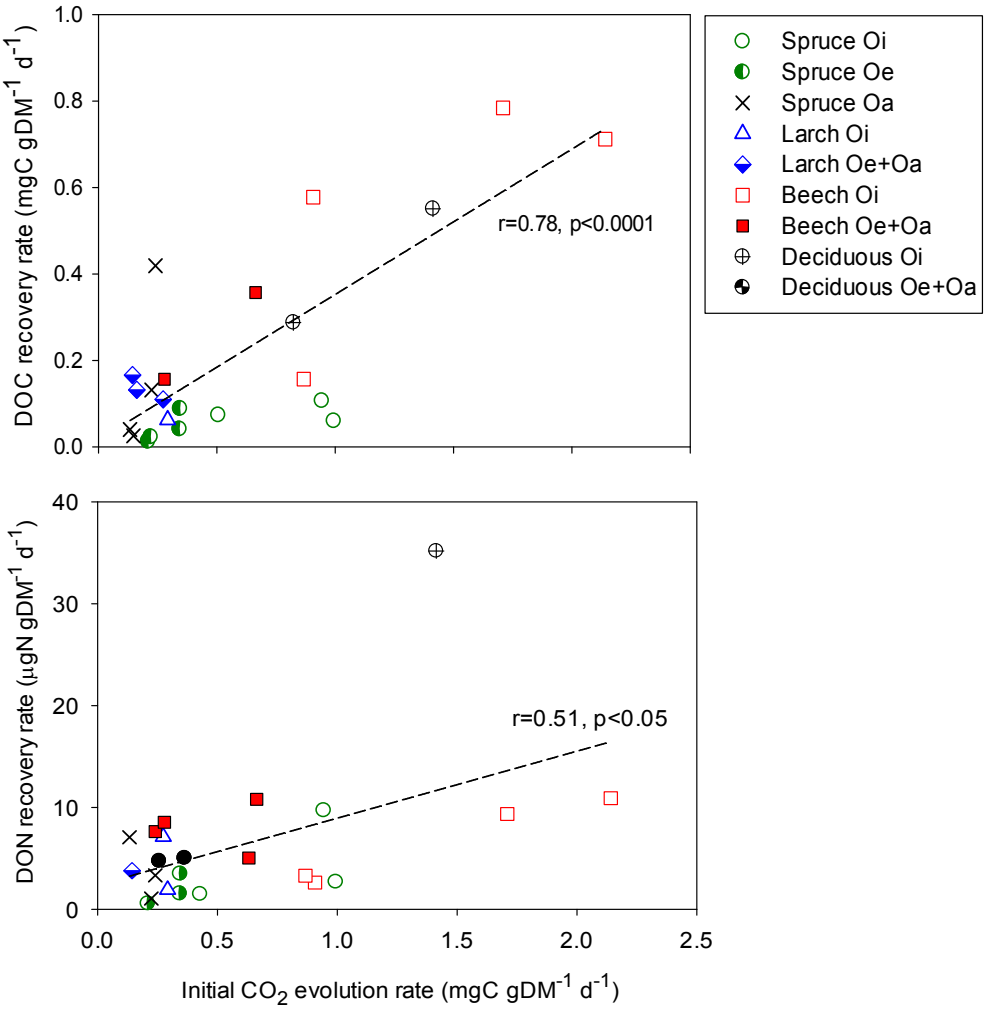
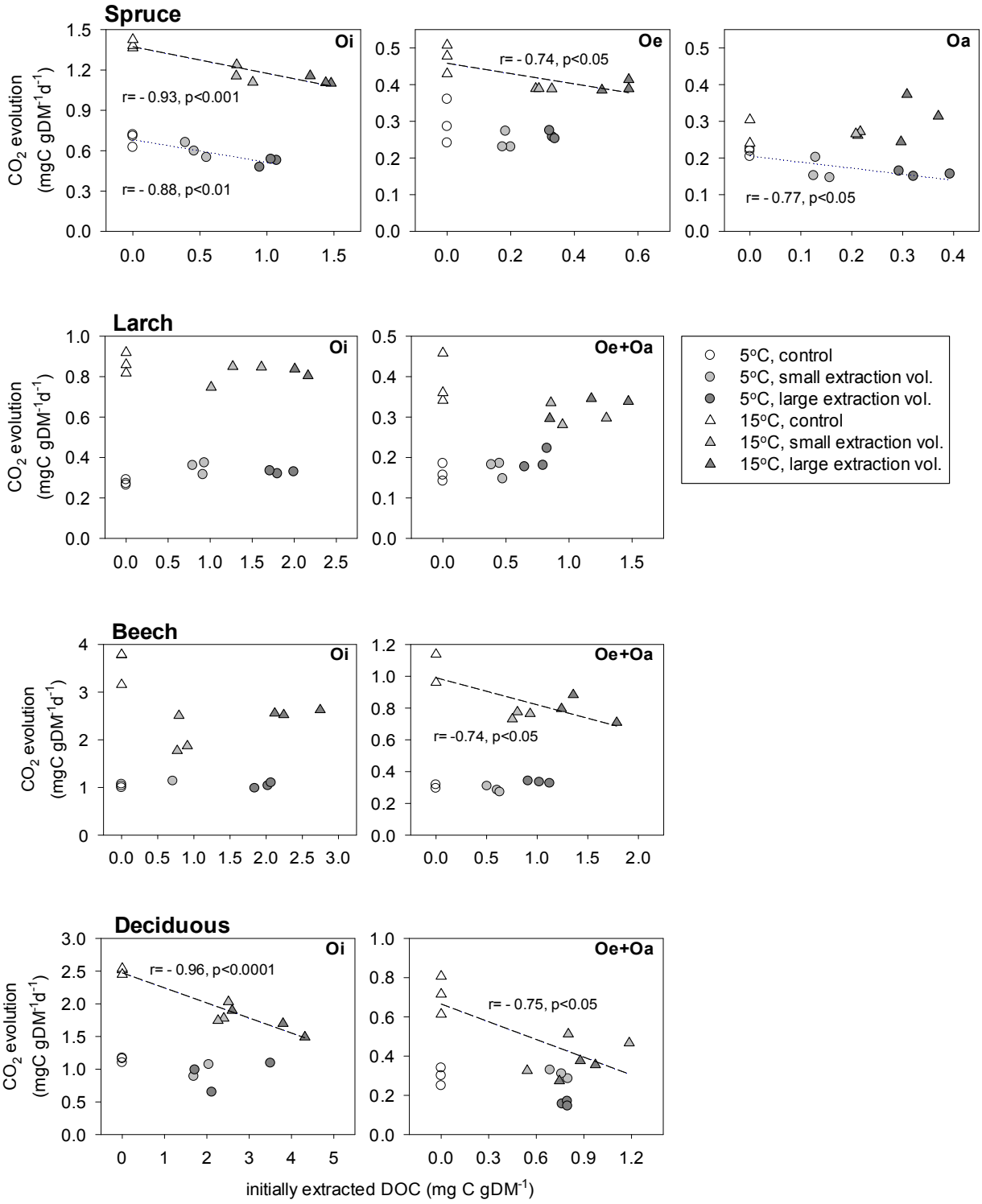


Figure 3.2.4 Relationship between the initial CO_2 evolution rate and the DOC and DON recovery rate at different temperatures (5ºC and 15ºC) and extraction volumes (50 ml and 200 ml). Non-recovered samples are not included



Significant regressions were only shown

Figure 3.2.5 Relationship between the initially extracted DOC and the CO_2 evolution after initial DOC extraction from organic layers in the batch experiment

3.2.3 Percolation experiment

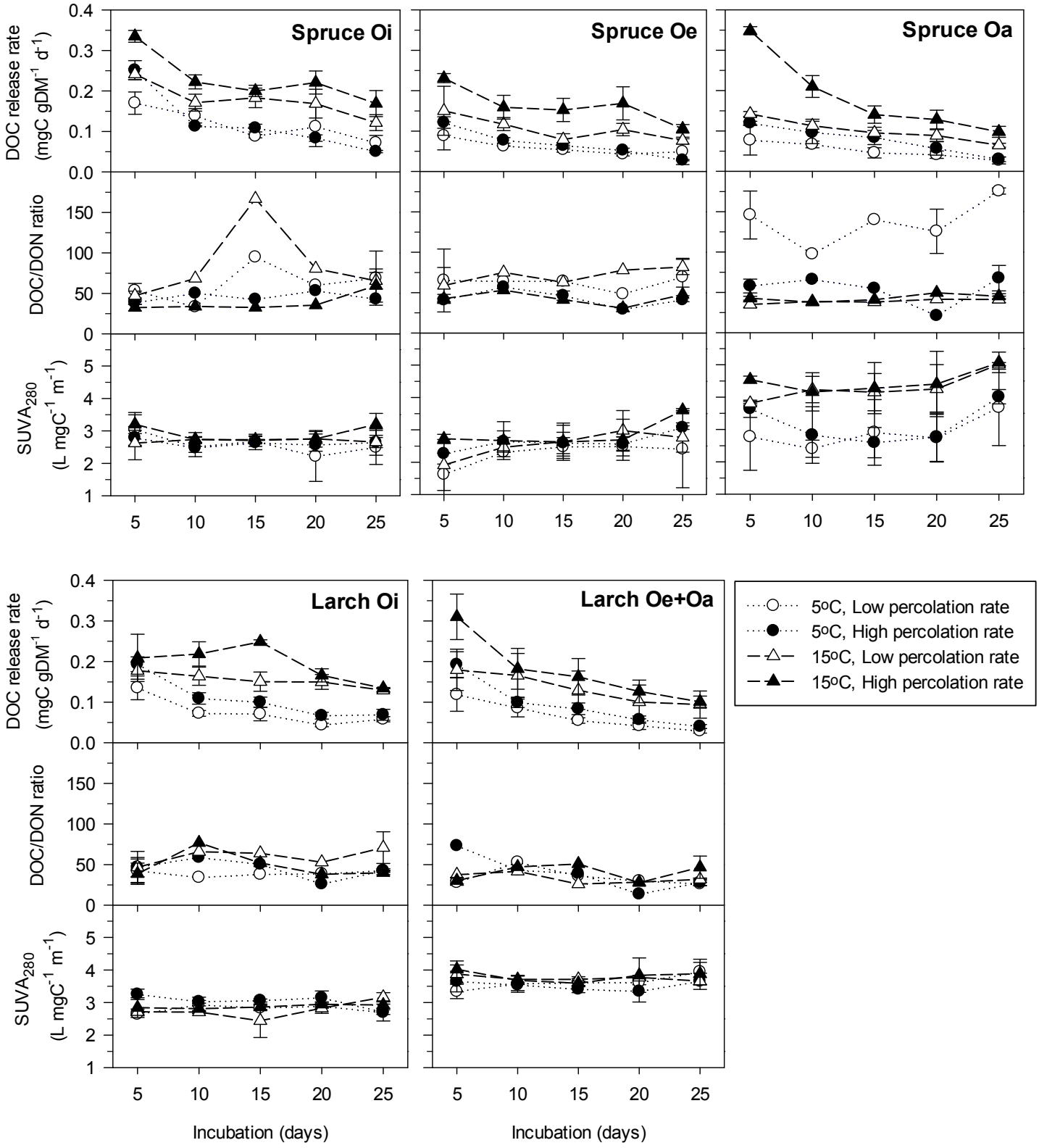
DOC and DON extraction

Similar to the DOC release in the batch experiment, in the percolation experiment, the DOC release rate was found higher at 15°C than at 5°C and higher at 15 ml d^{-1} percolation rate than at 3 ml d^{-1} (Figure 3.2.6). The initial DOC release rate in the O-layers after 5 days of percolation was in the order; Oe+Oa ≥ Oi samples from spruce and larch, while the order was Oi > Oe+Oa in beech and deciduous samples. Furthermore, the release was in the order; deciduous ≥ beech > spruce > larch O-layer. The averages of the initial DOC release were (in mg C gDM^{-1} d^{-1}) 1.2 and 0.1 for Oi and Oe+Oa of deciduous, 0.8 and 0.5 for Oi and Oe+Oa of beech, 0.25, 0.15 and 0.17 for Oi, Oe and Oa of spruce and 0.18 and 0.20 for Oi and Oe+Oa of larch samples, respectively. After the 20 days of percolation incubation, the DOC release in the O-layers reached almost stable values and became similar between samples of different treatments. The DOC release rate at the steady-state decreased sharply to 81% and 69% of the initial DOC release after 5 days in beech and deciduous, while the decline was relatively small (46% and 53% of the initial DOC release rate) in spruce and larch samples, respectively.

Similar to the results of the batch experiment, DOC/DON ratios and $SUVA_{280}$ values in the percolated solutions were almost stable during the 25 days of percolation incubation. DOC/DON ratios were on average 53, 57 and 65 for Oi, Oe and Oa of spruce, 49 and 38 for Oi and Oe+Oa of larch, 24 and 22 for Oi and Oe+Oa of in beech, and 124 and 40 for Oi and Oe+Oa of deciduous solutions, respectively (Figure 3.2.6).

$SUVA_{280}$ values of DOM (in L mg C^{-1} m^{-1}) were stable during the percolation with an average of 2.7, 2.7 and 3.8 for Oi, Oe and Oa of spruce, 2.9 and 3.7 for Oi and Oe+Oa of larch, 3.5 and 3.9 for Oi and Oe+Oa of beech, and 2.8 and 3.2 for Oi and Oe+Oa of deciduous solutions, respectively. $SUVA_{280}$ values were higher in percolates from Oa or Oe+Oa than from Oi samples in all percolated samples and were greatest in beech samples (Figure 3.2.6).

Also stable pH values of the extracted solutions were observed with an average of 4.5, 3.6 and 3.4 for Oi, Oe and Oa of spruce, 5.9 and 5.3 for Oi and Oe+Oa of larch, 6.4 and 4.8 for Oi and Oe+Oa of beech, and 6.6 and 7.4 for Oi and Oe+Oa of deciduous solutions (data not shown).


Spruce Oi
Spruce Oe
Spruce Oa
Larch Oi
Larch Oe+Oa
DOC release rate (mgC gDM-1 d-1)
DOC/DON ratio
SUVA280 (L mgC-1 m-1)
Incubation (days)
5oC, Low percolation rate
5oC, High percolation rate
15oC, Low percolation rate
15oC, High percolation rate

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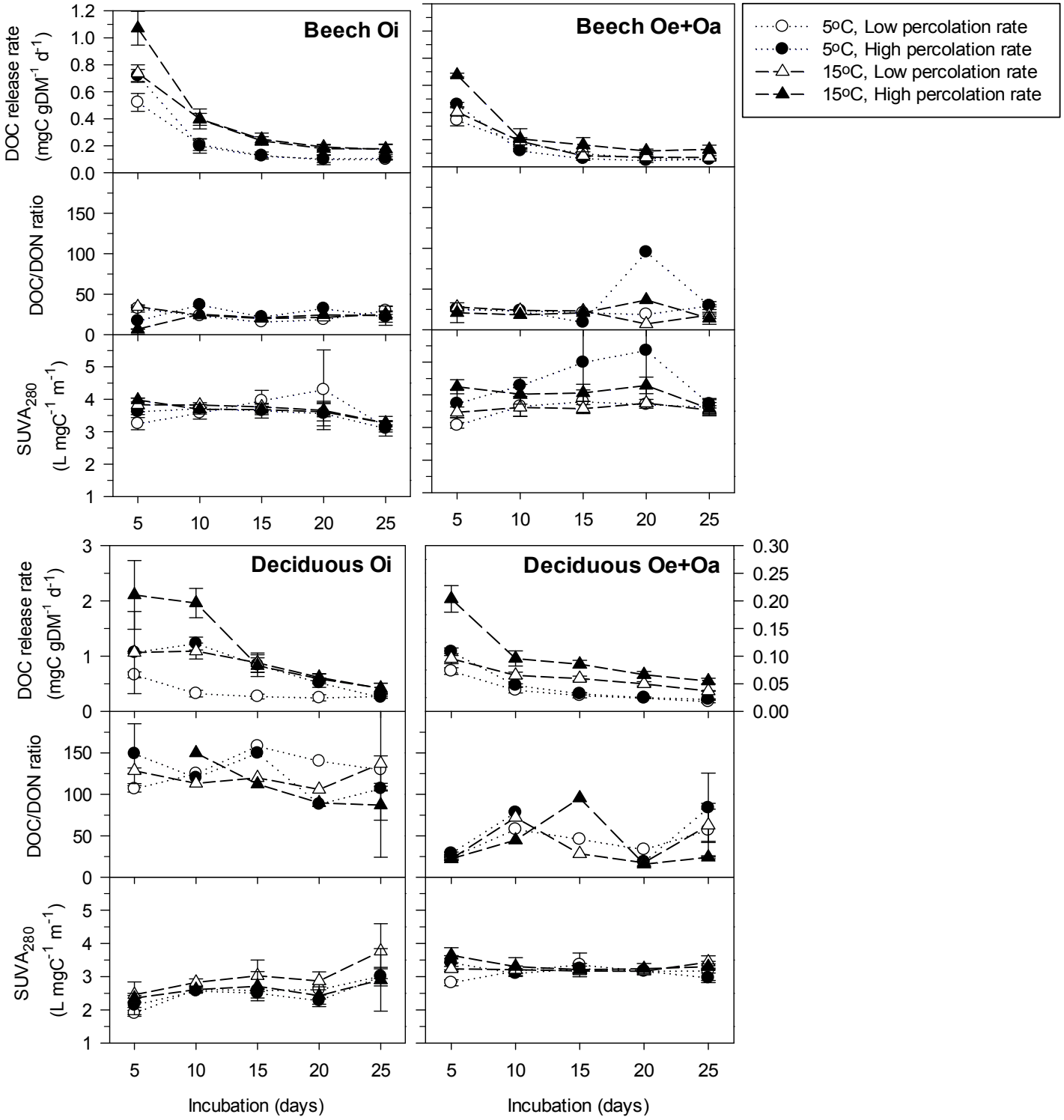


Error bars represent one standard deviation (n=3)

Figure 3.2.6 DOC release rate, DOC/DON ratio and $SUVA_{280}$ value of the percolated solutions from spruce, larch, beech and deciduous organic layers during 25 days of percolation

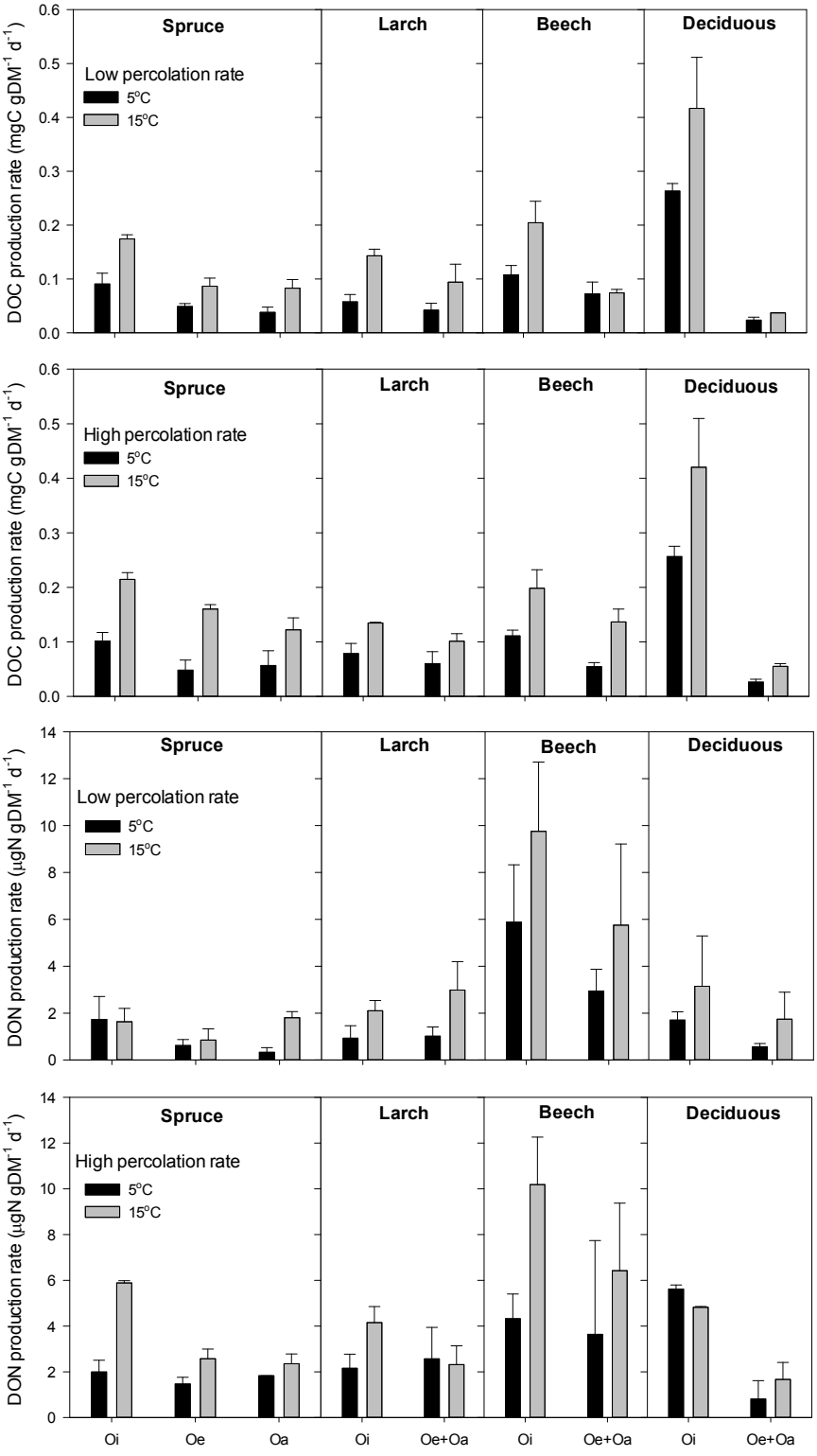
Production rate of DOC and DON

The production rate of DOC and DON was determined as the remaining release rate of DOC at 20 days of percolation incubation (steady-state assumption) (Figure 3.2.6).

The production rate of DOC and DON was generally larger at 15ºC than at 5ºC, increased positively with percolation rate and was in the order; Oi > Oe ≥ Oa samples (Figure 3.2.7). The production rate of DOC was in the order; deciduous > beech ≥ spruce > larch samples, while the production rate of DON was in the order; beech > deciduous ≥ spruce ≥ larch samples. An average of the production recovery rates of DOC for all treatments ranged (in mg C gDM^{-1} d^{-1}) from 0.05-0.2 in spruce, 0.05-0.1 in larch, 0.06-0.2 in beech and 0.03-0.4 in deciduous samples, respectively. An average of the production rates of DON for all treatments ranged (in µg N gDM^{-1} d^{-1}) from 1-4 in spruce, 1.5-3 in larch, 3-10 in beech and 0.6-4 in deciduous samples, respectively.

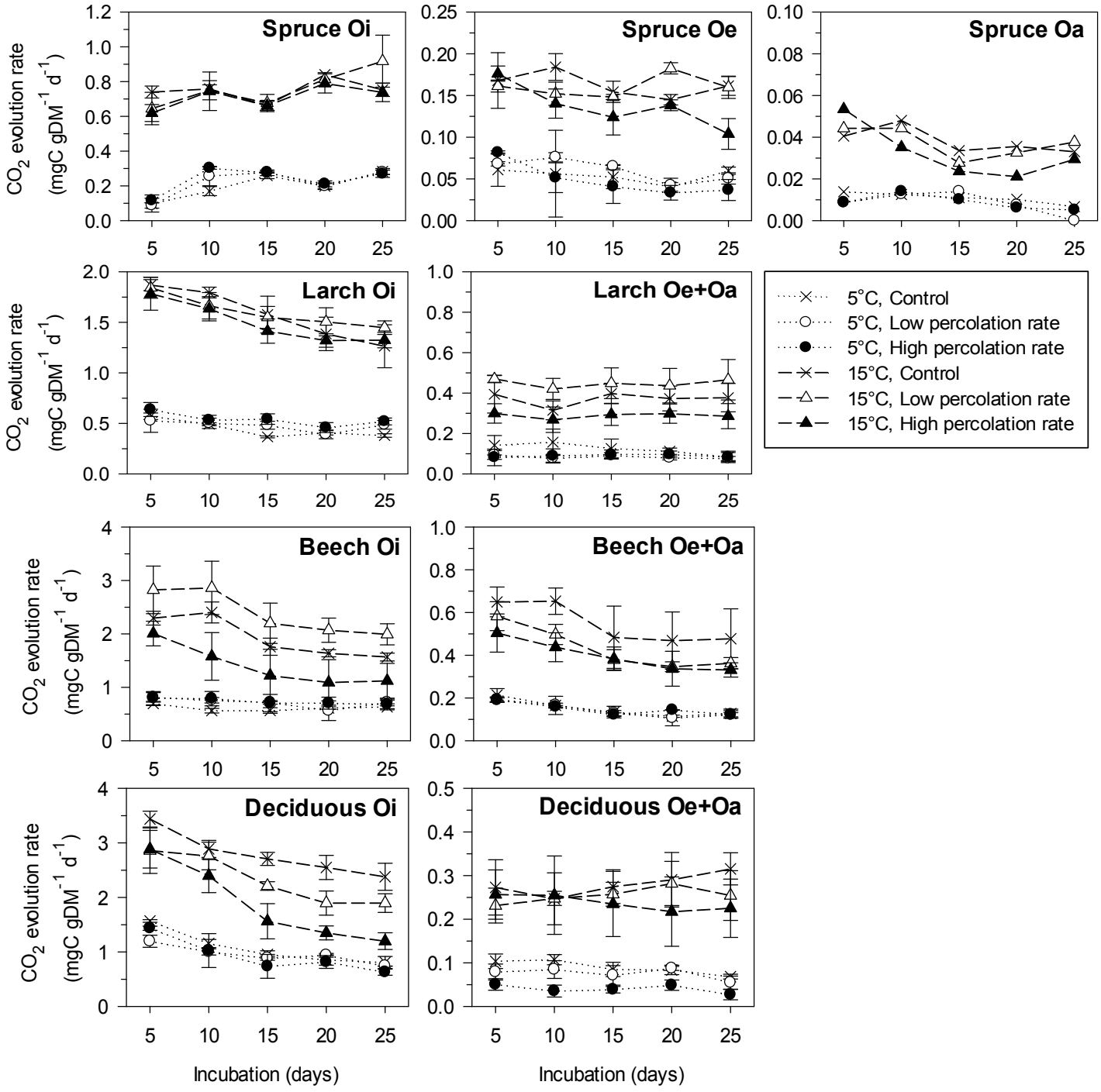
CO_2 evolution

The CO_2 evolution was clearly larger at 15ºC than at 5ºC and generally larger in controls and small percolation rate than for the large percolation rate (Figure 3.2.8). The CO_2 evolution rate decreased overall during the 25 days of percolation incubation. The CO_2 evolution rate at the end of the percolation incubation (steady-state of DOM release) was in the order; Oi > Oe > Oa layers and deciduous > beech > larch > spruce samples. The average of CO_2 production for the different treatments ranged (in mg C gDM^{-1} d^{-1}) 0.3-0.8, 0.05-0.2 and 0.01 - 0.03 for Oi, Oe and Oa of spruce, 0.5-1.5 and from 0.1-0.5 for Oi and Oe+Oa of larch, 0.7-2.1 and 0.1-0.4 for Oi and Oe+Oa of beech and 0.7-2.0 and 0.04-0.3 for Oi and Oe+Oa of deciduous samples, respectively.



Error bars represent standard deviation (n=3)

Figure 3.2.7 DOC and DON production rate of spruce, larch, beech and deciduous organic layers



Error bars represent one standard deviation (n=3)

Figure 3.2.8 CO_2 evolution from samples of spruce, larch, beech and deciduous forest floor as dependent on temperature and percolation rate (small; 3ml d^{-1} and large; 15 ml d^{-1}) and without percolation (control)

Q_{10} values

Q_{10} values for the CO_2 production at steady state were larger in Oe and Oa (2.6-5.9) than in Oi samples (1.6-3.3) for both high and low percolation rates (Table 3.2.4). Q_{10} values for CO_2 production were slightly higher for low than for high percolation rate, but the values were not different for tree species.

The Q_{10} values for production of DOC and DON were similar ranging from 1.0 to 3.3 and from 0.9 to 3.1 respectively (except one outlier of 5.9). No effects of percolation rate and tree species on Q_{10} values for the production rate of DOC and DON were found. Also, the different O-layers did not influence the Q_{10} values for the production of DOC and DON.

The range of Q_{10} values for the production of DOC and DON was more narrow than for CO_2 production and below the 1:1 line batch experiment (Figure 3.2.9).

Table 3.2.4 Q_{10} values for production rate of CO_2, DOC and DON with low (3 ml d^{-1}) and high (15 ml d^{-1}) percolation rate in the percolation experiment

Tree species	Layer	Low percolation rate			High percolation rate		
		Rpro. CO_2	Rpro. DOC	Rpro. DON	Rpro. CO_2	Rpro. DOC	Rpro. DON
Spruce	Oi	3.2	1.9	0.9	2.9	2.1	3.0
	Oe	3.3	1.8	1.4	3.6	3.3	1.8
	Oa	4.6	2.2	5.5	3.4	2.2	1.3
Larch	Oi	3.3	2.5	2.3	2.7	1.7	1.9
	Oe+Oa	5.5	2.2	2.9	3.2	1.7	0.9
Beech	Oi	3.1	1.9	1.7	1.6	1.8	2.4
	Oe+Oa	2.8	1.0	2.0	2.6	2.5	1.8
Deciduous	Oi	2.3	1.6	1.8	1.9	1.6	1.0
	Oe+Oa	3.7	1.6	3.1	5.9	2.1	3.1

Production rate (Rpro.): the mean value of CO_2 evolution rate, DOC and DON release rate at steady-state

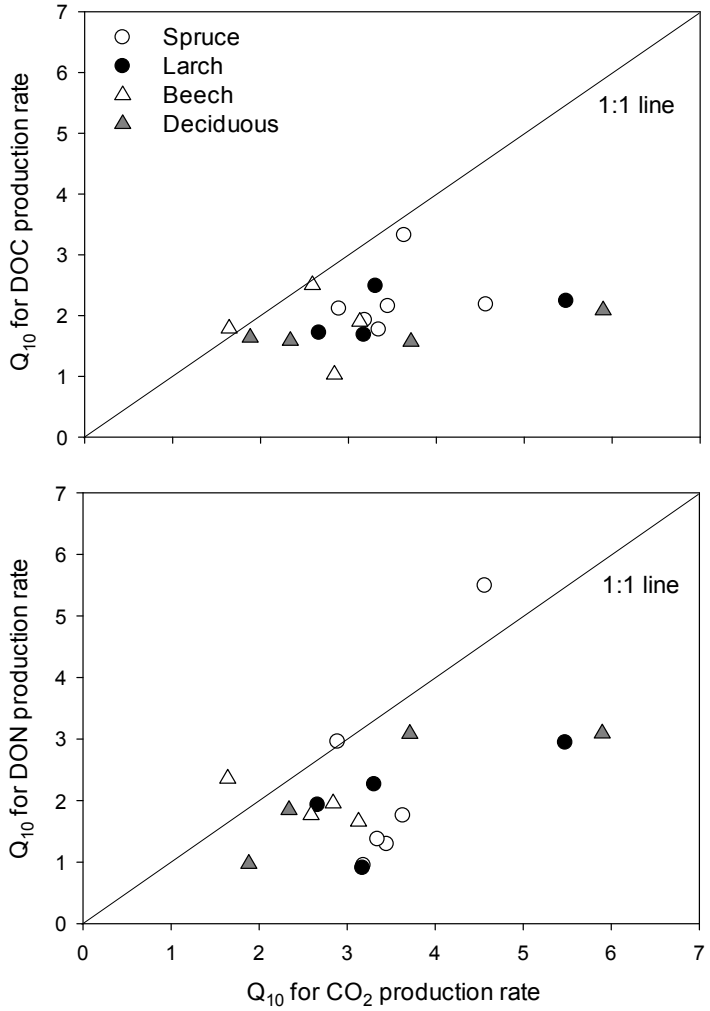


Figure 3.2.9 Relationship between Q_{10} for the CO_2 production and Q_{10} for the DOC (*top*) and DON (*bottom*) production in the percolation experiment

Relationships between production rate of DOC and DON and CO_2 evolution

The CO_2 production was positively and significantly correlated to the production rate of DOC (r = 0.76***) and DON (r = 0.59***) (Table 3.2.5 and Figure 3.2.10). Similar to the correlation results in the batch experiment, the production rate of DOC correlated weakly with that of DON and with the DOC/DON ratio (r = 0.56***) and also the production rate of DON was not related to DOC/DON ratio. Differently to the correlations in the batch experiment, the production rate of CO_2, DOC and DON was not related to $SUVA_{280}$ value, and the production rate of CO_2 and DOC was weakly related to pH and electrical conductivity.

Table 3.2.5 Correlation coefficients matrix (Pearson's) of production rates (Rpro. for CO_2, DOC and DON) and solution variables (DOC/DON ratio, $SUVA_{280}$, pH and electrical conductivity) in the percolation experiment

	Rpro. CO_2	Rpro. DOC	Rpro. DON	n
Rpro. DOC	0.76***			36
Rpro. DON	0.59***	0.48**		36
DOC/DON	0.28	0.56***	-0.25	36
$SUVA_{280}$	-0.18	-0.23	0.22	36
pH	0.45**	0.26	0.24	36
EC	0.42**	0.43**	0.11	36

*p<0.05, **p<0.01, ***p<0.001

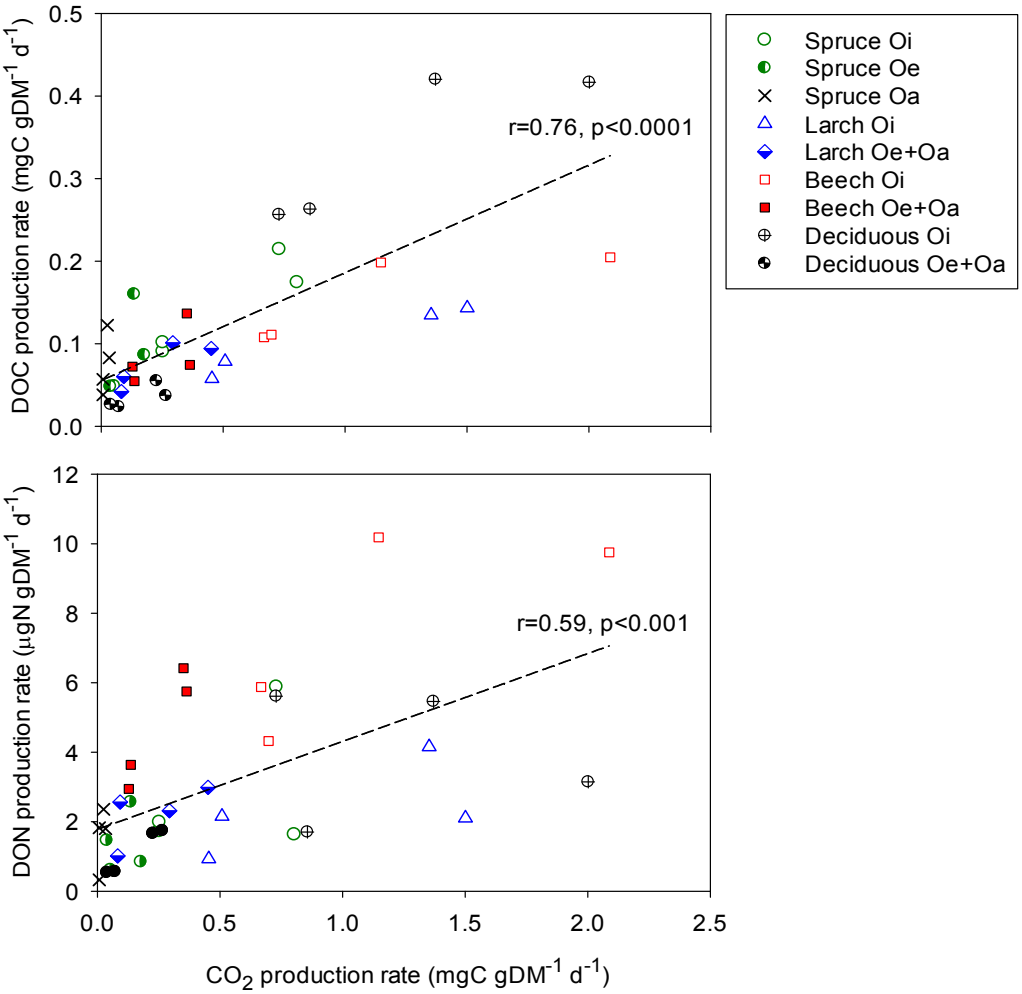
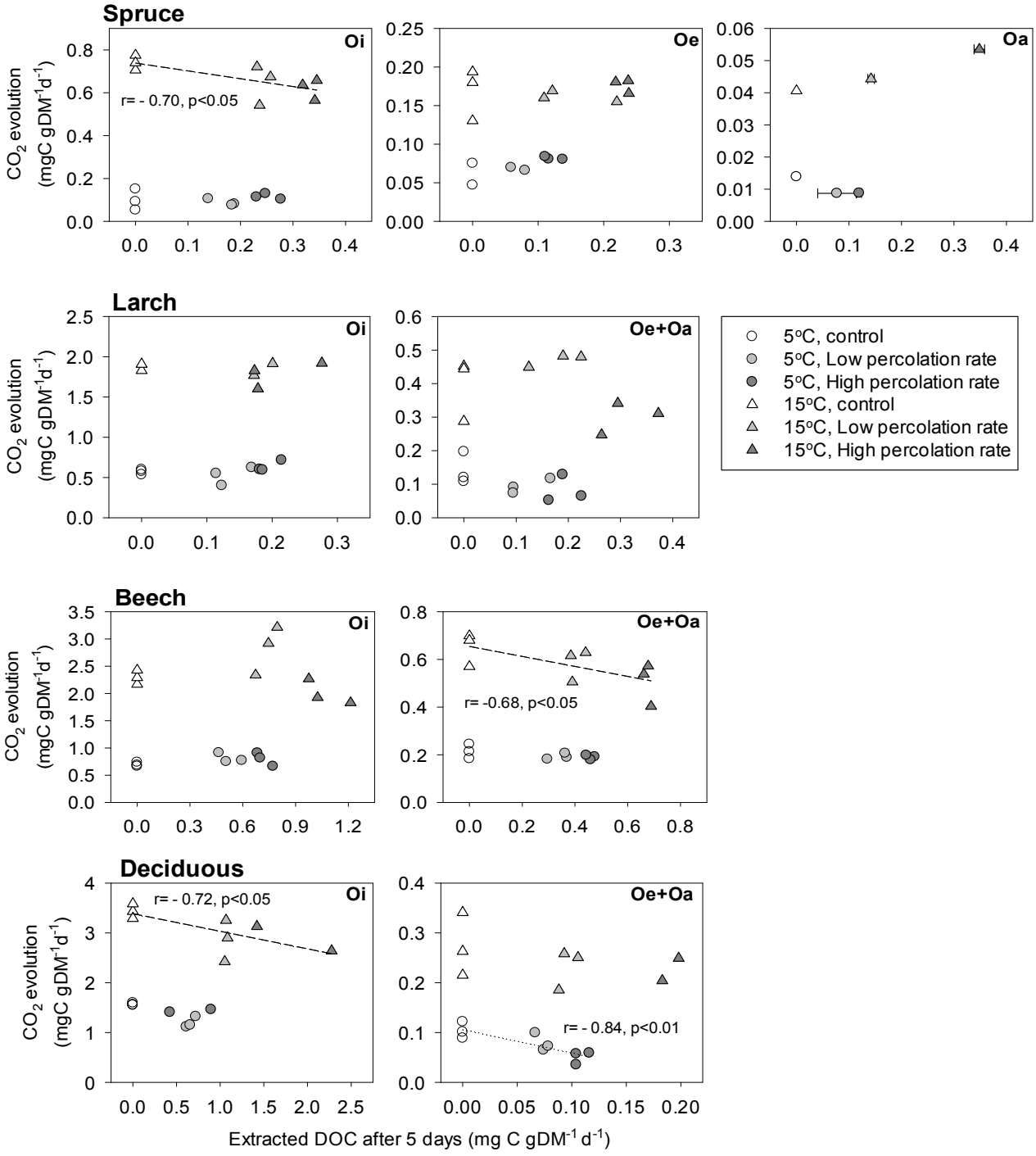


Figure 3.2.10 Relationship between the CO_2 production rate and the DOC (*top*) and DON (*bottom*) production rate in the percolation experiment (all values included from different temperatures and percolation rates)

Influence of DOC extraction on soil respiration

Similar to the result of the batch experiment, CO_2 evolution was generally larger in the O-layer samples without percolation (control) than in those with the percolation experiment (Figure 3.2.11). The difference in the CO_2 evolution between the different percolation rates (low and high) was small compared to the difference in the extracted DOC. Significant regressions were only shown in Figure 3.2.11. Similar to the result of the batch experiment, a decrease of CO_2 evolution after the 5 days of extraction was observed in few samples (spruce Oi, beech Oe+Oa, deciduous Oi and deciduous Oe+Oa) mostly at 15ºC, whereas no significant relationship between the CO_2 evolution and the extracted DOC were observed in larch samples. The decrease of CO_2 evolution caused by percolation (control-percolated samples) was larger in deciduous (0.02-0.6 mg C gDM^{-1} d^{-1}) and beech (0.02-0.3 mg C gDM^{-1} d^{-1}) than in spruce (0.01-0.1mg C gDM^{-1} d^{-1}) samples, but in any case the amount of extracted DOC was much larger than the decrease in CO2 evolution. The amount of extracted DOC was higher in deciduous and beech (0.1-1 mg C gDM^{-1} d^{-1}) than in spruce and larch samples (0.1-0.35 mg C gDM^{-1} d^{-1}).



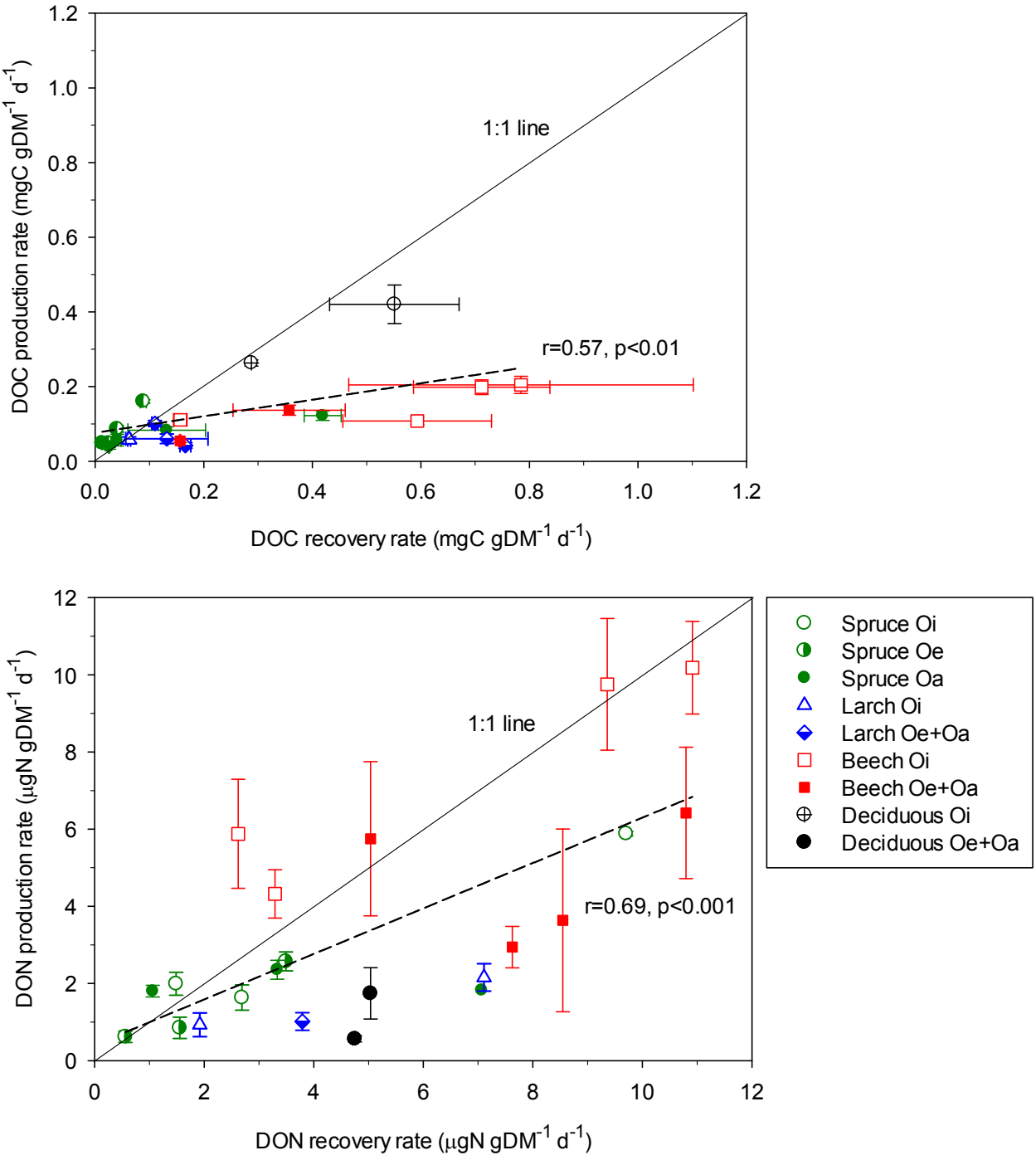
Significant regressions were only shown

Figure 3.2.11 Relationship between the extracted DOC and the CO_2 evolution after 5 days of percolation

3.2.4 DOC and DON recovery in batch vs. percolation experiment

The relationships between the DOC recovery rate derived from the batch experiment and the production rate derived from the percolation experiment were significant for both DOC ($r = 0.57$, $p < 0.01$) and DON ($r = 0.69$, $p < 0.001$) (Figure 3.2.12). However, the DOC recovery rate in the batch experiment was larger than the DOC production in the percolation experiment, which was also observed for DON in most samples. In both extraction experiments, higher recovery and production rate of DOC and DON were found for beech and deciduous than for spruce and larch samples. In case of some beech samples the recovery and production rate of DON distributed around the 1:1 line.

If both experiments are considered together, the rate of DOC recovery and production correlated strongly with the CO_2 evolution rate ($r = 0.70$, $p < 0.0001$) (Figure 3.2.13). Between tree species, the rate of DOC recovery and production increased stronger with the CO_2 evolution in deciduous (beech + deciduous) samples ($r = 0.76$, $p < 0.0001$), while it was almost independent of the CO_2 evolution rate for coniferous (spruce + larch) samples ($r = 0.22$, $p = 0.2$). Similar to DOC, a stronger relationship of the CO_2 evolution to DON recovery and production rate was observed in deciduous ($r = 0.50$, $p < 0.01$) than in coniferous ($r = 0.31$, $p = 0.08$) samples. However, if all data are taken together, the relationship of the CO_2 evolution to DON recovery and production ($r = 0.46$, $p < 0.001$) was weaker than for DOC ($r = 0.70$, $p < 0.0001$).



Error bars represent one or two standard deviation (n=3)

Figure 3.2.12 Relationship between the DOC and DON recovery rate derived from the batch experiment and the production rate derived from the percolation experiment

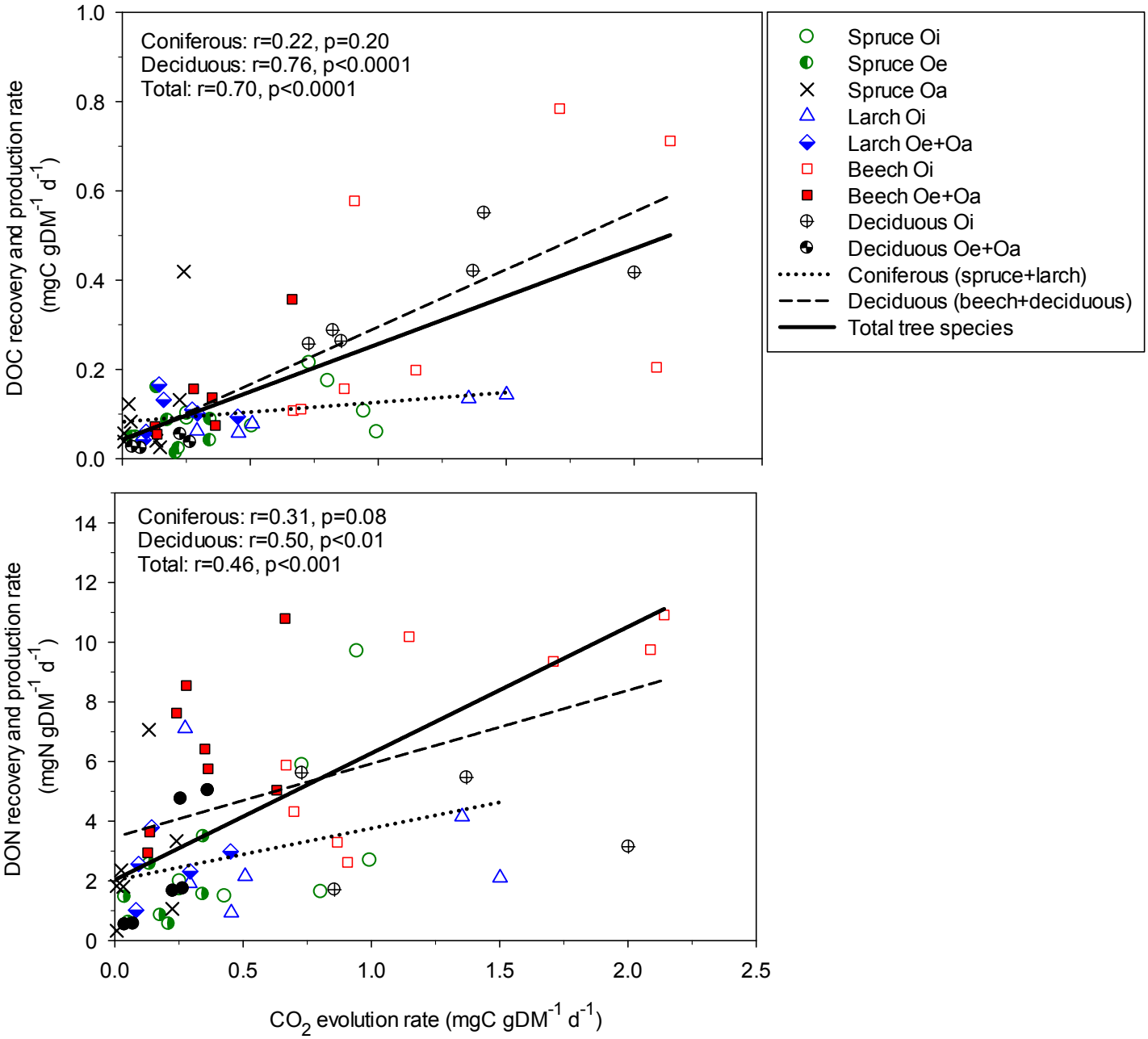


Figure 3.2.13 Relationship between the CO_2 evolution rate (or the CO_2 production rate) and the recovery and production rate in DOC (*top*) and DON (*bottom*) by tree species in the batch and percolation experiment experiment

3.2.5 DOC and DON recovery in laboratory vs. field scale

Extrapolating recovery and production rates to field scale

Extrapolation of the recovery and production rates of DOC and DON in the O-layers to the field scale was done by the C and N stocks of the O-layers from Table 3.2.1 (Table 3.2.6). The extrapolated DOC and DON production rates were higher in Oa than in Oi and Oe layers and also larger in spruce than in beech, following the order spruce > beech > larch > deciduous organic layers. The sum of the extrapolated DOC and DON production rate in the O-layer were only presented for the percolation experiment because some samples in the batch experiment did not show recovery.

Table 3.2.6 Extrapolated DOC and DON production rates (kg ha^{-1} d^{-1}) in the organic layers

		Batch experiment				Percolation experiment			
		kg DOC ha^{-1} d^{-1}		kg DON ha^{-1} d^{-1}		kg DOC ha^{-1} d^{-1}		kg DON ha^{-1} d^{-1}	
		5°C	15°C	5°C	15°C	5°C	15°C	5°C	15°C
Spruce	Oi	1.2	1.3	0.02	0.10	1.6	3.1	0.03	0.06
	Oe	0.5	1.8	0.02	0.09	1.4	3.4	0.03	0.05
	Oa	2.2	18.4	0.48	0.14	3.3	6.7	0.07	0.14
							∑13.2		**∑0.25**
Larch	Oi	0.4		0.04		0.5	0.9	0.01	0.03
	Oe+Oa	2.1	1.5	0.06		0.7	1.4	0.03	0.04
							∑2.3		**∑0.07**
Beech	Oi	1.6	3.2	0.01	0.04	0.5	0.8	0.02	0.04
	Oe+Oa	14.8	33.9	0.76	0.76	5.7	10.5	0.31	0.58
							∑11.3		**∑0.62**
Deciduous	Oi	0.6	1.2		0.08	0.6	0.9	0.01	0.01
	Oe+Oa			0.06	0.06	0.3	0.5	0.01	0.02
							∑1.4		**∑0.03**

Comparison of DOC release from forest floors between field and laboratory scale

Total throughfall amount during summer monsoon in July 2013 was comparable between two forested watersheds, representing 391 mm in the coniferous (larch) forest, Seohwa, South Korea and 449 mm in the deciduous forest, Haean, South Korea (this field study) (Table 3.2.7). Recovery time at the field scale was defined as the period before starting a specific storm event after the previous storm event. The recovery time was similar for both forest floors since the precipitation events occurred at the same time. Net release of forest floor was calculated each storm events by subtracting DOC fluxes from forest floor to throughfall in the coniferous and the deciduous forest. Lab. DOC production (kg DOC ha^{-1}) was calculated the initial DOC release rate or the production rate by multiplying by the recovery time at the field site.

The net release of forest floor decreased from the early to the later storm events from 0.13 to 0.03 kg DOC ha^{-1} mm^{-1} for coniferous forest floor and from 0.10 to 0.06 kg DOC ha^{-1} mm^{-1} for deciduous forest floor (Table 3.2.7) indicating a depletion of the DOC pools. In the coniferous forest floor, the net DOC release was at all dates smaller than the calculated DOC production from laboratory data. In contrast, the net release was larger than the production for the deciduous forest floor at the later rain events. Total net DOC release from the forest floor was less compared to the extrapolated laboratory DOC production in the coniferous forest, while it was similar in the deciduous forest. Between tree species, net DOC release was higher in the deciduous ($\sum$32 kg DOC ha^{-1}) than in the coniferous forest ($\sum$22 kg DOC ha^{-1}), whereas the extrapolated DOC production was smaller in deciduous ($\sum$32 kg DOC ha^{-1}) than in coniferous forest ($\sum$40 kg DOC ha^{-1}).

Table 3.2.7 Throughfall, recovery time, net DOC release from forest floor in coniferous forest (at MC plot in MCD watershed) and deciduous forest (at PD plot in PD watershed) in relation to the extrapolated DOC production in percolation experiment

Start rain		Coniferous forest					Deciduous forest				
		Throughfall	Recovery time before the event*	net release from forest floor at the event		Lab. production	Throughfall	Recovery time before the event*	net release from forest floor at the event		Lab. production
		(mm)	(day)	(kg DOC ha^{-1})	(kg DOC $ha^{-1}mm^{-1}$)	(kg DOC ha^{-1})	(mm)	(day)	(kg DOC ha^{-1})	(kg DOC $ha^{-1}mm^{-1}$)	(kg DOC ha^{-1})
2013.July.2	9:00	75	2	9.4	0.13	11.4 [a]	81	2	8.5	0.10	13.6 [a]
2013.July.8	3:00	54	6	4.0	0.07	13.9 [b]	118	6	10.3	0.09	8.8 [b]
2013.July.11	9:00	46	3	2.6	0.06	6.9 [b]	45	3	4.7	0.10	4.4 [b]
2013.July.12	5:00	55			0.00		57	1.5	1.4	0.02	2.2 [b]
2013.July.14	2:00	117	2.5†	4.8	0.04	5.8 [b]	95	1	3.7	0.04	1.5 [b]
2013.July.15	0:00	44	1	1.5	0.03	2.3 [b]	53	1	3	0.06	1.5 [b]
		∑391		∑22		∑40	∑449		∑32		∑32

[a] Calculated with the initial DOC release rate, 5.7 kg ha^{-1} d^{-1} in larch and 6.8 kg ha^{-1} d^{-1} in deciduous organic layer

[b] Calculated with the production rate at steady-state, 2.3 kg ha^{-1} d^{-1} in larch and 1.5 kg ha^{-1} d^{-1} in deciduous organic layer

* Recovery time was the period before staring the storm event after the previous storm event

† The sampling period of rain events between 2013.July.11th and 2013.July.14th

4 DISCUSSION

4.1 Field study

4.1.1 General pattern of DOM and FPOM in runoff in response to discharge

Dominant forms of organic C and N

During the dry period, DOC and DON were the dominant forms of organic C and N in runoff from both watersheds, while FPOC and FPON fluxes were negligible (Table 3.1.4). The dominance of DOC for organic C in runoff at base flow was also found in other studies with also negligible fluxes of POC (Johnson et al. 2006, Jeong et al. 2012, Lloret et al. 2013, Dhillon and Inamdar 2013).

During the wet period, substantial fluxes of all compounds DOC, DON, FPOC and FPON in runoff were observed (Table 3.1.4). The increase of DOC, DON, FPOC and FPON fluxes in runoff by heavy storm events is consistent with previous studies. More than 50% of annual organic C (DOC + POC) from forested watershed was exported by heavy storm events during the wet period, that last only a short time (Johnson et al. 2006, Kim et al. 2010, Jeong et al. 2012, Dhillon and Inamdar 2013, Lloret et al. 2013). The fluxes of POC (FPOC + CPOC < 2 mm) also increased substantially from base flow to storm flow and the POC fluxes under heavy storm events contributed most to the annual POC fluxes with runoff (Jeong et al. 2012, Dhillon and Inamdar 2013, Lloret et al. 2013).

In this study, DOC was the dominant form of organic C export during dry and wet periods in both watersheds (Table 3.1.4). Several studies have compared the annual fluxes of DOC and POC (FPOC + CPOC < 2 mm) in runoff from forested watersheds (Table 4.1.1). DOC represented 60% to 90% of the annual total organic C fluxes (Boeglin et al. 2005, Johnson et al. 2006, Bass et al. 2011, Jeong et al. 2012), and here data confirm these findings. Most findings on higher annual fluxes of DOC export than POC export were observed in non-mountainous forested watersheds, whereas higher annual fluxes of POC export than DOC export were often observed in mountainous forested watersheds (Table 4.1.1), which does not correspond to the findings of this study. Previous studies have also reported that most of the exported POC in stream from mountainous catchment was observed as old C from sedimentary

bedrock (POC_{fossil}) rather than from recently fixed C (Kao and Liu 1997, Hilton et al. 2012, Smith et al. 2013).

The different findings about the dominant form of organic C in stream from forested watershed seem to be caused by topography of forested watershed. Likely steep slopes induce high fluxes of POC (Hilton et al. 2012, Jung et al. 2012, Janeau et al. 2014) and also DOC (Dick et al. 2014) under severe storm events. Steeper slope was measured in the MCD watershed than in the PD watershed. Under the monsoon, consistently, total fluxes of runoff FPOC were higher in the MCD watershed than in the PD watershed (Table 3.1.4). High POC export has been often related to soil erosion (Dawson and Smith 2007, Hilton et al. 2012, Jeong et al. 2012, Smith et al. 2013). Deforestation on steep slopes in vulnerable areas cause soil erosion with also large C losses (Jung et al. 2012, Janeau et al. 2014).

Flushing effect

The highest concentrations of DOC and DON in runoff were observed in the initial phase of a specific storm event, even at low discharge, while the highest concentrations of FPOC and FPON in runoff were related to the exceedance of a discharge threshold (Table 3.1.2). Similar flushing effects of DOC have been observed in other forested watersheds. For example, the initial flushing by early storm events increased DOC in the stream by about 200% (Hood et al. 2006) or 350% (Frank et al. 2000) compared to base flow. A flushing effect after a dry period was observed for DOC and also for POC (Bass et al. 2011). However, DON was not flushed as efficiently as DOC (Inamdar et al. 2008).

Previous studies have also stated the flushing effect for DOC with hysteretic loops. The clockwise hysteretic loop observed in this study (Figure 3.1.3) was due to increasing DOC concentrations on the rising limb as a result of hydrological flushing of potential DOC pools in topsoil and then decreasing DOC concentrations on the falling limb as a result of depletion of easily mobilized DOC from surficial C pools (Hood et al. 2006, Butturini et al. 2008, Raymond and Saiers 2010, Jeong et al. 2012, Bartsch et al. 2013, Yang et al. 2015). In contrast, the counter-clockwise hysteretic loops with a peak of DOC on the falling limb in runoff were also reported (Inamdar et al. 2008, Strohmeier et al. 2013, Lambert et al. 2014). Hysteretic loops tended to be more frequent with strong precipitation intensity and in initial storm events of monsoon seasons (Jeong et al. 2012).

Table 4.1.1 Export fluxes and concentrations of dissolved and particulate organic carbon (DOC and POC) from non-mountainous and mountainous forested watersheds

Location	Climate	Forest type	Precipitation	DOC		POC		Reference
			(mm yr^{-1})	(kg C ha^{-1} yr^{-1})	(mg C L^{-1})	(kg C ha^{-1} yr^{-1})	(mg C L^{-1})	
non-mountainous								
Mengong, South Cameroon	humid tropical	semi-deciduous	1500-2000	57	14.4	5.8		Boeglin et al. (2005)
Juruena, Brazil	temperate	rainforest (palm)	2379	31.5		17.6		Johnson et al. (2006)
mid-Atlantic Piedmont, USA	humid continental	deciduous	1462	17.5		37.7		Inamdar et al. (2011), Dhillon and Inamdar (2013)
Thompson Creek, Australia	tropical	tropical (mesophyll vine)	4518-7600	23.4[a]	0.9-5.3	8.2[b]	0.1- 3.6	Bass et al. (2011)
mountainous								
Lanyang Hsi, Taiwan	humid subtropical	mixed coniferous-hardwood	3000	41 ± 7	0.5-8	217 ± 47		Kao and Liu (1997)
Capesterre, Guadeloupe Island	humid tropical	tropical rainforest	2000-4300	74	0.5-4.7	183	0.4- 75	Lloret et al. (2013)
Gwangneung, South Korea	temperate	deciduous	1332	40		50		Kim et al. (2010)
Haean, South Korea	temperate	deciduous	1068	6.7	1-4	4.3	< 40	Jeong et al. (2012)

[a] Calculated data with 1.95 kg DOC ha^{-1} $month^{-1}$

[b] Calculated data with 0.68 kg POC ha^{-1} $month^{-1}$

Patterns of DOC, DON, FPOC and FPON

Different patterns of DOM and POM fluxes were observed in the present study (Figure 3.1.5). The DOC and DON fluxes in runoff increased linearly with increasing discharge, whereas the FPOC and FPON export fluxes in runoff responded sharply to discharge exceeding a certain threshold and then reached or even exceeded those of DOC and DON. Before reaching the discharge threshold, the FPOC and FPON fluxes were much lower than the DOC and DON fluxes. Similar dynamic patterns of FPOC and FPON fluxes were observed by Jung et al. (2012).

The DON concentrations in runoff from both watersheds were independent of discharge at concentrations of about 0.3 mg L^{-1} (Figure 3.1.2). The finding that DON response to discharge differs from DOC is consistent with other studies (Clark et al. 2004, Inamdar et al. 2008). During base and storm flow periods, nil or weak relationships between DOC and DON concentration were reported in streams from forested watersheds (Bernal et al. 2005, Singh et al. 2015), whereas similar behaviour of DOC and DON concentrations was observed in streams (Campbell et al. 2000, Goodale et al. 2000, von Schiller et al. 2015). In this study, the correlation between DOC and DON in runoff was surprisingly weak ($r < 0.2$ n.s.). As DON is a component of DOC by definition, this lack of correlation might be due to the very low DON concentrations and the analytical differences in determining DON. DON concentrations were generally less than 0.3 mg L^{-1} and close to detection limit, which causes erratic patterns in the ratios and correlations.

Different response of DOC and POC (FPOC + CPOC < 2 mm) fluxes to discharge was confirmed by several other studies (Kim et al. 2010, Jeong et al. 2012, Dhillon and Inamdar 2013). A linear response of both DOC and FPOC to discharge even under heavy storm events was also reported (Bass et al. 2011). The different response of DOC and FPOC in runoff to discharge indicates different mechanism and sources for DOC and POC. The fluxes of POC from watersheds under heavy storm events have been associated with soil erosion particularly from upper soil layers (Dawson and Smith 2007, Hilton et al. 2011; 2012, Jeong et al. 2012, Jung et al. 2012). Soil erosion occurs efficiently in soils that lack vegetation cover (Dawson and Smith 2007, Stallard 2011). In the watersheds of this study, as a full vegetation cover was given, no surface flow and no surface soil erosion were observed under the monsoon events. The stable C/N ratio of the FPOM (Figure 3.1.7) in runoff of the PD and MCD watershed

corresponded to those of the mineral soil (Table 3.1.1). Hence, the origin of FPOC seems to be the river bench or river bed, eroding at high discharge.

The major form of total fine suspended solids was FPMM (inorganic solids), while FPOC in runoff contributed only 6 to 11% of total fine suspended solids. The finding of small fractions of organic C in suspended solids observed in the PD and MCD watersheds corresponds to Wildhaber et al. (2012) who reported about 5% of organic C in suspended solids in upstream forested watersheds.

NO_3-N as the dominant form of N in runoff

In both watersheds the largest amount of N in runoff was in the form of NO_3-N (Table 3.1.4). The export fluxes of NO_3-N increased strongly with increasing discharge during the wet period (Figure 3.1.6), which was also observed in other studies (Bernal et al. 2005, Inamdar and Mitchell 2007, Vegas-Vilarrúbia et al. 2012). The finding of NO_3-N as the dominant form of N in runoff is similar to findings from others on annual N exports from forested watersheds (Compton et al. 2003, Bernal et al. 2005, Inamdar and Mitchell 2007, Sebestyen et al. 2008). In contrast, some studies have shown that DON took up the dominant fraction of total N export in undisturbed forested watershed (Campbell et al. 2000, Frank et al. 2000, Vanderbilt et al. 2003, Kaushal and Lewis 2003, Pellerin et al. 2006), and even in watersheds with arable farmland, improved grassland and woodland (Yates and Johnes 2013). According to the review by Alvarez-Cobelas et al. (2008) organic N (DON and PON) contributed on average 48% to the total N export comparing N export from catchments (n = 946).

The dominance of NO_3-N over DON in runoff of the PD and the MCD watershed points to a certain degree of N-saturation (N supply > N demand) of these forested watersheds (Aber et al. 1998, Compton et al. 2003), with NO_3-N exports as an indicator of N saturation in ecosystem (Aber et al. 2003). N deposition/input can shift ecosystem from N limitation to saturation (Aber et al. 1998; 2003, Emmett 2007). The N input by deposition in the area is estimated rather high at 24 - 51 kg N ha^{-1} yr^{-1} (Berger et al. 2013), which suggests atmospheric deposition of N as a major driver of NO_3-N in runoff (MacDonald et al. 2002, Sebestyen et al. 2008).

4.1.2 Export fluxes from the mixed coniferous/deciduous and the deciduous forested watershed

DOM

While DOC concentration in runoff increased with increasing discharge in the PD watershed, it was relatively stable during wet period in the MCD watershed (Figure 3.1.2). Furthermore the total DOC export fluxes were much larger in the PD than in the MCD watershed (Table 3.1.4).

Similar results were found by Amiotte-Suchet et al. (2007) with mean annual DOC concentration and fluxes being 2-4 times higher in streams of mixed forested catchment (oak, pine, spruce and douglas-fir) than in those of coniferous (spruce and douglas-fir). Contradicting findings on the role of coniferous vs. deciduous tree species on DOC and DON fluxes and concentrations in soils were published. Often, the concentrations and fluxes of DOC and DON in forest floor leachates were larger in coniferous than deciduous/broadleaved forest (Kalbitz et al. 2004, Fröberg et al. 2011, Hansson et al. 2011, Camino-Serrano et al. 2014), but also opposite results have been published (Trum et al. 2011, Smolander and Kitunen 2011). The fluxes of DON in runoff in this study were generally low, but like with DOC, larger in the PD than in the MCD watershed (Table 3.1.4). This also corresponds to larger net DON release from forest floor in the MD and PD plot (deciduous plots) than in the MC plot (coniferous plot) (Table 3.1.6). What might be the reasons for the differences for the DOC and DON fluxes in the PD and the MCD watershed? As will be shown later, quality parameters of DOC in runoff indicate that much of the DOC in runoff at high discharge originates from the forest floor and DOC seems to be transported to the stream by near surface flow in the upper soil layers. The net release of DOC and DON from the forest floor was found higher in the MD and PD plot (deciduous plots) than in the MC plot (coniferous plot) (Table 3.1.6), indicating that the potential DOC and DON pool in the deciduous is larger than in the coniferous forest floor, despite the larger C stocks in the coniferous forest floor (Table 3.1.1).

The mobilization of DOC and DON in soils depends on substrate quality, environmental conditions and throughfall chemistry (Kalbitz et al 2000). The throughfall and soil solution at the MC plot were more acidic and had a higher salt content than those at the PD and MD plot (Table 3.1.1). Both chemical parameters of the solution are not in favor of DOC release (Michalzik et al 2001, Clark et al. 2011, Moldan et al. 2012) and can explain the differences in the DOC runoff fluxes from both watersheds. The higher DOC amount in forest floor percolates

and runoff from the PD watershed might be also related to the faster decomposition rate of litter resulting in larger production of DOC as compared to the coniferous litter. Lastly, water repellency might be different in coniferous and deciduous forest floors resulting in less DOC release from coniferous forest floors. Butzen et al. (2014) found more hydrophobic properties in coniferous soil than in deciduous soils.

Furthermore, Johnson et al. (2006) also suggested the in-stream generation of DOC from litter, by showing the significant relationship between stream DOC concentration and terrestrial litterfall rate. Yoshimura et al. (2010) investigated the instream DOC release from POM and found DOC release rate significantly different with POM source and size fraction. In the other words, less litter input to the stream in the MCD watershed than in the PD may also cause lower DOC fluxes in the MCD. Unfortunately here I don't have information on the coarse fraction of POM in runoff and cannot test this hypothesis.

As the same factors that influence DOC will influence the release of DON in soils, the above argumentation for DOC might also hold for DON. Similar finding of lower DON leaching in the O-layers under coniferous than in deciduous stands (Table 3.1.6) were reported by Trum et al. (2011). However different findings were reported with higher DON fluxes and N stock in coniferous forest floor and mineral soil than in deciduous forest (Kalbitz et al. 2004, Kiikkilä et al. 2013) or no significant difference between tree species (Michalzik et al. 2001). No relation of DON export and % coniferous area was observed in catchments (Clark et al. 2004), whereas a positive relationships between % broadleaf cover and DON and also NO_3-N concentration was presented by Compton et al. (2003).

FPOM

Responses of FPOC and FPON concentrations in runoff to high discharge were more frequently in the PD watershed than in the MCD watershed (Figure 3.1.2). Above, the conclusion on the source of FPOM was the river bed and benches. Hence, differences in the shape, slope and erodibility of the river bed and benches between the watersheds might explain the differences in response of FPOC and FPON to discharge.

C% of total fine suspended solids was higher in the PD watershed than in the MCD watershed (Figure 3.1.4), however it increased sharply with the response to discharge exceeding a certain threshold in the MCD watershed compared to the PD watershed. As mentioned before in mountainous watersheds, steeper slopes in the MCD watershed would be related to induce soil erosion with large amount C losses.

NO_3-N

The NO_3-N fluxes with runoff during the wet period were about twice as high in the MCD watershed than in the PD watershed (Table 3.1.4). This might be due to differences in N deposition from the atmosphere (MacDonald et al. 2002) or to the ecosystem internal use and fate of N. The total N flux in throughfall during the storm events was found slightly smaller in the MCD watershed (MC plot: 2.4 kg ha^{-1} and MD plot: 1.8 kg ha^{-1}) than in the PD watershed (PD plot: 2.7 kg ha^{-1}) in July 2013 and hence, differences in N deposition cannot explain the differences in NO_3-N losses with runoff. The C/N ratio of the forest floor was also found a good indicator for NO_3-N losses (MacDonald et al 2002) with NO_3-N losses being triggered at low C/N ratios. The C/N ratios of the forest floor in the MCD watershed were slightly higher than in the PD watershed, which does not support the data from MacDonald et al (2002).

Previous studies reported higher NO_3-N leaching in coniferous than in broadleaved stands (Tipping et al. 2012b) or mixed forests (Jost et al. 2011) due to higher atmospheric N deposition. However, no significant impact of tree species on the N output was observed if depositions were similar (MacDonald et al. 2002, Fang et al. 2009, Hansson et al. 2013).

As only a short period of time was measured, the differences between both watersheds in NO_3-N losses need to be considered with caution. Overall it seems that a larger N uptake by the trees of the PD watershed can explain the differences in NO_3-N outputs.

4.1.3 Is DOM in runoff mostly derived from forest floor leachates?

During the dry period, most of the discharge is derived from groundwater that infiltrated the mineral soil, involving the sorption and mineralization of DOM prior to export to stream (Neff and Asner 2001, Dawson and Smith 2007, Tank et al. 2010, Kaiser and Kalbitz 2012, Dick et al. 2014, Singh et al. 2014). Heavy storm events represented the major part of annual DOM export and during these periods the flow path of water differs likely from those in the dry period. Previous studies have observed the change in hydrological flow paths in watersheds from deeper to upper soil under heavy precipitation (Vidon et al. 2008, Sanderman et al. 2009, Bass et al. 2011, Singh et al. 2014). Aitkenhead-Peterson et al. (2005) suggested that changes in DOC/DON ratio in runoff may occur when hydrologic flow paths change to organic layers with different C/N ratio than deeper soil horizons.

The flow paths also depend on antecedent soil moisture conditions (Bernal et al. 2002, Kim et al. 2010). Hence, after a period of drying with soil shrinking storm events can alter the flux

and concentration of DOC and POC by preferential flow through macropores and lateral flows (Katsuyama and Ohte 2002, McGlynn and McDonnell 2003, Kim et al. 2010).

DOM chemistry in runoff changed during storm events within short time. Based on the quality parameters that were investigated in this study, DOC/DON ratio, $\delta^{13}C$ and $\delta^{15}N$ signature and spectroscopic properties, the origin of the DOC at high discharge can be identified.

DOC/DON ratio

The increase of the DOC/DON ratios in runoff from the PD watershed with discharge implies that its origin of DOM was changed from groundwater to surface soil (see depth gradient of soil C/N ratio on table 3.1.1). The increase of runoff DOC/DON ratio in the PD watershed is an indication for a larger contribution of near surface flow to runoff through organic-rich compartments accumulated during the drought period (Bernal et al. 2005). The positive relationship between the discharge and the runoff DOC/DON ratio is similar to findings from others (Sanderman et al. 2009, Bass et al. 2011). They also found that during high flow the origin of DOM was shifted from deeper soil to upper soil by comparing C/N ratios of runoff and soil.

In contrast, the runoff DOC/DON ratio in the MCD watershed was relatively stable (Figure 3.1.7). In case of the MCD watershed the runoff DOC/DON ratio corresponded to soil C/N ratio of mineral soil and Oe+Oa layer (Table 3.1.1) indicating that the origin of DOM in the MCD watershed was more related to deeper soil layers. Stable DOC/DON ratios between base flow and storm flow were reported also in other forested catchments (Campbell et al. 2000, Bernal et al. 2005, Von Schiller et al. 2015) suggesting that the origin of DOM was constantly from the deep soil (Bernal et al. 2005) and/or that DOM was not affected by in-stream microbial processing (nutrient uptake and release) during export (Von Schiller et al. 2010; 2015). Also, the effect of photodegradation on runoff DOM was likely minimal given the dense forest canopy over the stream during the growing season (Singh et al. 2015).

$\delta^{13}C$ signature of DOM

The reason of the use of stable isotopes in natural ecosystems is the fractionation during chemical and biochemical processes. Hence, reaction products tend to become enriched in the

lighter isotope (Bauer and Bianchi 2011). The decline of runoff $\delta^{13}C_{DOC}$ with discharge from the PD watershed (Figure 3.1.8) coincided with decreasing soil $\delta^{13}C_{DOC}$ from deeper to upper soil (Figure 3.1.1). The finding that runoff $\delta^{13}C_{DOC}$ was heavier at low discharge and lighter at high discharge is consistent with other studies (Bass et al. 2011, Lambert et al. 2011, Sebestyen et al. 2008, Sanderman et al. 2009), suggesting the change of DOM origin in runoff from deeper soil to upper soil layers/organic layers at high discharge. High contribution of forest floor to exported POM in forest stream was also found by comparison of $\delta^{13}C$ and $\delta^{15}N$ of soil and suspended solids (Jung et al. 2012). The average concentration of inorganic C [HCO_3^-] in runoff might influence the $\delta^{13}C$ and was calculated for 15-20°C with pH 6.5 for the PD watershed and pH 6.8 for the MCD watershed (Table 3.1.5) using the *Henderson-Hasselbalch equation*,

$$pH = pKa + \log[HCO_3^-]/[H_2CO_3]$$

pKa (6.375) is the dissociation constant.

The concentrations of dissolved CO_2 [HCO_3^-] in runoff were 0.17 mg C L^{-1} in the PD watershed and 0.34 mg C L^{-1} in the MCD watershed. Its concentration can be ignored because the runoff DOC concentration was 10-20 times larger than dissolved CO_2 during heavy storm events.

DOM in upper soil is younger and composed of fresh material compared to DOM in deeper soil that is relatively old and recalcitrant SOM (Sanderman et al. 2009, Bass et al. 2011). These results indicate that runoff DOM generally derived from old SOM from deeper soil layers during dry period, while from younger SOM from upper soil layer during storm events. Hence, from the relatively lighter $\delta^{13}C$ in runoff, the contribution of near surface flow to runoff seems to be less in the MCD watershed than in the PD watershed.

Spectroscopic properties of DOM

$SUVA_{280}$ and HIXem values in runoff increased with increasing discharge in the PD watershed, while in the MCD watershed they were relatively stable (Figure 3.1.9). The patterns of $SUVA_{280}$ and HIXem in runoff in response to discharge corresponded to the increase DOC in runoff from the PD watershed and to the stable DOC in runoff from the MCD watershed (Figure 3.1.2). Previous studies typically published an increase $SUVA_{280}$ and HIXem with increasing discharge due to inputs of surficial C in forested watersheds (Hood et al. 2006,

Vidon et al. 2008, Fellman et al. 2009, Sigh et al. 2015), but contrasting findings have also been reported suggesting a dilution effect at peak flow (Yang et al. 2015).

The increase $SUVA_{280}$ and HIXem values in the PD watershed implied that substantial amounts of aromatic and humic DOC were exported during monsoon. A relatively high HIXem value corresponds to an enrichment of more condensed aromatic structures having electron-withdrawing substituent and/or more conjugation of aliphatic chains (Fuentes et al. 2006). The high $SUVA_{280}$ and HIXem values in forest floor leachates (Table 3.1.5) and the significant increase in aromatic and humic fraction of DOM with discharge suggests that runoff DOM at high flow originated mostly from forest floor. Similar results were found by Inamdar et al. (2011) and Singh et al. (2014). In case of the MCD watershed, the $SUVA_{280}$ and HIXem values were relatively stable and corresponded more to soil solution properties than to forest floor leachates (Table 3.1.5). This again indicates a low contribution of near surface flow in the MCD watershed.

The rations of PLF/FLF and PLF/HLF decreased in runoff from the PD watershed with increasing discharge (Figure 3.1.9). At the high discharge, PLF/FLF and PLF/HLF ratios in runoff corresponded to those in forest floor leachates at the PD watershed (Table 3.1.5). These findings of the increase of HLF and the decrease of PLF with increasing discharge are consistent with other studies in forested watersheds (Hood et al. 2006, Inamdar et al. 2011, Singh et al. 2014; 2015). Previous studies have suggested that the increase in HLF and the decrease in PLF at high flow is due to the contributions from surficial DOM pool during wet period (Inamdar et al. 2011, Singh et al. 2014). It is known that HLF is derived primarily from vascular plant sources, aromatic compounds and likely represent the high-molecular-weight fraction of DOM (Fellman et al. 2010). PLF is mostly composed of carbohydrates and proteins originated from fresh leaf litter in stream water (Wong and Williams 2010), hence is considered more labile fraction of organic matter compared to recalcitrant humic material (Fellman et al. 2010, Yamashita et al. 2011). Previous studies have interpreted PLF as biogeochemical tracer to predict DOM lability and/or biodegradability (Fellman et al. 2009, Singh et al. 2014, Jung et al. 2015). Thereby, the finding of the decrease PLF/HLF in the PD watershed indicates a decrease of labile components and the increase of recalcitrant humic components in the export of DOM by heavy precipitation.

In contrast to the PD watershed, PLF/FLF and PLF/HLF ratios in runoff were independent of discharge from the MCD watershed (Figure 3.1.9) and these ratios varied between those of

forest floor leachates and soil solution (Table 3.1.5). Terajima and Moriizumi (2013) found the stream at the baseflow and the soil solution from coniferous forest contained higher fulvic acid-like material than from deciduous and broadleaved forest. These results indicate that changes in the chemical quality of exported DOM in runoff are different for the PD and the MCD watershed during storm events.

Conclusion on forest floor as a source for DOM in runoff at high discharge

All quality parameters and their dynamics at different discharge indicate that the hydrology of the two watersheds is different. While a larger proportion of near surface flow is proven during high discharge in the PD watershed, runoff in the MCD watershed at high discharge seems more generated by groundwater or by soil solutions from mineral soil. The findings suggest consistently that the forest floor turned out as a main source pool of DOM in the PD watershed, whereas the contribution of DOM from mineral soil was higher in the MCD watershed during storm events.

4.2 Laboratory study

4.2.1 Dynamic of DOM pools in forest floors

Depletion and recovery of DOM pools in forest floors

DOC release decreased after the initial extraction in the batch experiment and after the subsequent percolation in the percolation experiment indicating the depletion of DOM pools in forest floor samples (Figure 3.2.1 and Figure 3.2.6).

After the initial extraction, the O-layer samples were incubated and then DOM was again extracted. After incubation for 7 or 14 days, the extracted DOC reached the initial level of DOC release in several samples, but not in others indicating that the recovery of DOM pools in forest floors depends on leaching conditions and soil properties (Figure 3.2.1). The recovery of DOC pools in forest floors has been poorly studied. Judd and Kling (2002), who reported frequent leaching effects on release of dissolved C, found that DOC was rapidly replenished following leaching

The decline of DOC and DON release by subsequent extraction in the percolation experiment is consistent with previous studies with forest floor samples (Christ and David 1996, Gödde et al. 1996, Moore et al. 2008, Buzek et al. 2009). Buzek et al. (2009) suggested a first-order kinetic of DOC concentration that decreased exponentially with leaching amount.

Batch vs. Percolation experiment

The main difference between the two extraction methods is an equilibrium extraction (for 2 hours) for the batch experiment and a free drainage extraction for the percolation experiment. The two extraction methods resulted in different release and recovery/production of DOM. DOC from the O-layers was released larger by the batch experiment with the range from 1.5 to 3.4 mg C gDM^{-1} at the initial extraction, while the percolation resulted in a range from 0.4 to 1.3 mg C gDM^{-1} d^{-1} after 5 days of percolation (Figure 3.2.1 and Figure 3.2.6).

Larger DOC leaching under the equilibrium could be related to larger contact area between the forest floor sample and the extraction solution, while the released DOM from the percolated soil column originated mainly from the release along the flow paths.

DOC recovery rates derived from the batch experiment were slightly higher (a range from 0.02 to 0.75 mg C gDM^{-1} d^{-1}) than the DOC production rate derived from the percolation

experiment (a range from 0.03 to 0.4 mg C gDM^{-1} d^{-1}). DON recovery rate and production rate were similar in both experiments (range of from 0.6 to 11 μg N gDM^{-1} d^{-1}).

Increasing frequency of leaching could deplete the potential DOM pools (Gödde et al. 1996, Judd and Kling 2002), hence higher DOC release was found at the early stage of leaching than at the later stage (Christ and David 1996, Gödde et al. 1996, Moore et al. 2008, Buzek et al. 2009), corresponding the finding in the percolation experiment (Figure 3.2.6). DOC and DON recovery rates were calculated with the initially and the secondly extracted DOC and DON during 14 days of incubation, whereas DOC and DON production rates were taken as the release at the final steady-state after 20 days of percolation. Because of these methodical differences, the production rate in the percolation experiment could be smaller than the recovery rate in the batch experiment.

Influencing factors on DOC and DON release in forest floors

The extent and rate of the depletion and the recovery of DOM pools in forest floors differed by temperature, extraction solution volume and substrate quality. The recovery and production rate of DOC and DON was in the order; high > low temperature, large > small extraction volume/percolation rate, Oi > Oe > Oa layers and also deciduous/broadleaved > coniferous forest floors (Figure 3.2.2 and Figure 3.2.7).

Similar consistent findings about the controlling factors in DOC and DON release from forest floors were found in previous studies, DOC production was related to 1) temperature (Christ and David 1996, Gödde et al. 1996, Moore et al. 2008, Buzek et al. 2009), 2) substrate properties, such as tree species and quality (Michalzik et al. 2001, Park et al. 2002, Kalbitz et al. 2004; 2007, Buzek et al. 2009, Fröberg et al. 2011, Hansson et al. 2011, Schmidt et al. 2011, Augusto et al. 2014) and 3) hydrological controls, like water flux/precipitation amount (Tipping et al. 1999, Michalzik et al. 2001, Kaiser et al. 2001a, Neff and Asner 2001, Kalbitz et al. 2007, Schmidt et al. 2010, Borken et al. 2011, Wu et al. 2014) and leaching frequency (Gödde et al. 1996, Judd and Kling 2002).

Soil respiration and temperature as drivers for DOC recovery and production

The strong correlations of the initial CO_2 evolution rate with both the recovery rate and the production rate of DOC and of DON (Table 3.2.3 and Table 3.2.5) indicate that DOC and DON production and recovery results from ongoing decomposition of forest floor organic matter.

The finding of the positive relationship between the soil respiration and the DOM production/recovery is consistent with the results of previous studies representing strong interactions between SOM mineralization (CO_2 evolution) and DOM production (Gödde et al. 1996, Moore and Dalva 2001, Neff and Asner 2001, Marschner and Kalbitz 2003, Moore et al. 2008, Cleveland et al. 2010, Smolander and Kitunen 2011, Sanderman and Kramer 2013) suggesting a link between microbial activity and DOM production in soil. According to Michel and Matzner (2002), the activity of soil microorganisms as SOM decomposer is a major process of DOM formation. Temperature has an effect on microbial activity and is one of drivers for the DOM release from forest floors (Christ and David 1996, Fröberg et al. 2006, Moore et al. 2008, Borken et al. 2011). Total C loss (DOC + CO_2) increased also with higher temperature (Gödde et al. 1996, Buzek et al. 2009). Increased temperature caused a large DOC release at the early stage of incubation but had less effect on the final DOC production rate (Christ and David 1996, Gödde et al. 1996, Moore et al. 2008, Buzek et al. 2009), corroborating the findings of this study (Figure 3.2.1 and Figure 3.2.6). In contrast Michalzik et al. (2001), who reviewed 42 case studies in North American and European forest ecosystems, found no correlation between mean annual temperature and DOC concentrations and fluxes in forest floors in the temperature range from 1°C to 16°C probably due to large variation of temporal and spatial scales and water flows among the studies. DOM release from forest floors is controlled mostly by leaching processes at low temperature (during winter and spring), while the DOC pool might be mainly derived from decomposition processes at relatively high temperature (during summer and autumn) (Kaiser et al. 2001b, Schütt et al. 2014b).

The temperature dependence of the DOM production and the CO_2 production was quantified by Q_{10} values. In the percolation experiment, an average Q_{10} for DOC and DON production rate (2.0 and 2.1) was less than for soil respiration (3.3) in the range of 5°C and 15°C (Figure 3.2.9) .

The weaker temperature dependence of DOC production than CO_2 release has been reported by Christ and David (1996), Gödde et al. (1996), Moore and Dalva (2001) and Moore et al. (2008), corresponding to the findings in this study. Moore et al. (2008) reported ratios of CO_2 to DOC production of about 10:1. However, the partitioning of C loss into DOC and CO_2 is dependent on temperature. Gödde et al. (1996) found that the DOC release was the dominant form of C mobilization at low temperature (3°C), while the CO_2 evolution contributed most of the C loss at higher temperature (20°C). Similarly, Moore et al. (2008) observed a ratio of CO_2

to DOC release of about 6 at 3°C and a ratio of 16 at 22°C. According to Buzek et al. (2009), DOC is not primary derived from the labile C pool, which is preferentially consumed by mineralization during the incubation experiment. These results imply that the dominant form of C loss (CO_2 evolution vs. DOC release) depends on temperature in forest floors.

The results of Q_{10} for DOC production and soil respiration in this study correspond roughly to Q_{10} values in previous studies. In the literature, Q_{10} for DOC production ranged from 1.8 to 2.2 at 3-10°C and from 1.0 to 1.2 at 10-20°C, independent of tree species (Table 4.2.1). Q_{10} values for DOC production and CO_2 evolution from forest floors were relatively high at low temperature range indicate that the temperature sensitivity is higher at relatively low temperature range.

In summary, the findings of DOM release related to temperature and soil respiration suggest that the released DOM from forest floors is caused mainly from the biological processes (microbial activity in soil) at relatively high temperature but originates mostly from physical processes (leaching/extraction condition) at low temperature.

Table 4.2.1 Published Q_{10} values for DOC production and CO_2 evolution from coniferous and broadleaved forest floors

Vegetation	Temperature range (°C)	Q_{10} for DOC	Q_{10} for CO_2	Reference
Coniferous				
Spruce	3-10	1.9-2.2	1.5-7.3	Gödde et al. 1996
	10-20	1.0-1.2	1.7	
Spruce	3-28	2.0		Christ and David 1996
Spruce	2-8		3.5	Schütt et al. 2014b
Spruce	8-25		3.0	Karhu et al. 2010
Pine	8-25		3.5	
Hemlock	2-15		3.5	Kao and Chang 2009
Coniferous	3-10	1.8		Moore et al. 2008
	3-22	2.2		
	10-22	1.2		
Spruce	5-15	1.8-3.3	2.9-4.6	This study*
Larch	5-15	1.7-2.5	2.7-5.5	
Broadleaved				
Beech	2-14		4.2	Janssens and Pilegaard 2003
Beech	2-8		4.0	Schütt et al. 2014b
Beech	4-18		1.7	Jonard et al. 2007
Oak	4-18		2.3	
Mixture	4-18		2.0	
Mixed wood	3-10	2.0		Moore et al. 2008
	3-22	2.2		
	10-22	1.1		
Beech	5-15	1.0-2.5	1.6-3.1	This study*
Mixed deciduous	5-15	1.6-2.1	1.9-5.9	

* Data from the percolation experiment in this study

Substrate quality (tree species) as driver of DOC recovery and production

Following the depletion of DOM pools after the initial extraction, the DOM release from forest floors recovered rather fast within 14 days of incubation time (Figure 3.2.1). The recovery and production rate of DOC and DON was in the order; Oi > Oe > Oa layers and deciduous > coniferous O-layer in the batch and percolation experiment (Figure 3.2.2 and Figure 3.2.7). However, in the batch experiment some samples did not recover, especially those from larch and deciduous species. These findings indicate the influence of substrate quality and tree species on the recovery and production rate of DOM from forest floors.

Similar to the findings, several studies have shown that high quality of SOM (like fresh leaves) favours mineralization of C (Kanerva and Smolander 2007, Trum et al. 2011, Sanderman and Kramer 2013), indicating that fresh leaves (Oi) are more important as DOC source than relatively stable substrates like humified forest floor and wood litter (Michalzik and Matzner 1999, Park et al. 2002). However, different findings were also reported from field studies with higher concentrations and fluxes of DOC and DON from Oa than from Oi layers in both coniferous and deciduous forests (Michalzik et al. 2001, Solinger et al. 2001, Fröberg et al. 2003, Kalbitz et al. 2004), suggesting that the humified and older organic pool in the Oa layer contributes substantially to total DOM release from forest floors (Park and Matzner 2003). Moreover, similar contributions of humified layers (Oe+Oa) and fresh litters (Oi) to DOC release were observed (Park et al. 2002, Kalbitz et al. 2007). Discrepancies between laboratory and field studies can be caused by a different thickness of the organic layer in forest soil (Judd and Kling 2002, Borken et al. 2011, Augusto et al. 2014). Oa layer (mor-humus) is normally thick under coniferous stands and can contribute considerably to DOC leaching in spruce forests, whereas leachates from Oe and/or Oi layer (mull- and moder-humus) plays the prominent role in DOC mobilization in deciduous forests (Borken et al. 2011).

Opposite to this study coniferous forest floor produced more DOC than deciduous in a laboratory experiment (Buzek et al. 2009) and at the field scale, concentrations and fluxes of DOC and DON in forest floor leachates under coniferous stand were larger than of deciduous forest (Kalbitz et al. 2004, Fröberg et al. 2011, Borken et al. 2011, Hansson et al. 2011, Camino-Serrano et al. 2014). Inconsistent findings of the effect of tree species on DOM production, concentrations and fluxes cannot be fully explained yet. This study showed the DOM recovery and production rate higher in deciduous forest floors than coniferous. This may result from different SOM properties regarding microbial activity with higher rates in soil respiration and decomposition in deciduous SOM than in coniferous (Wang et al. 2006, Buzek et al. 2009,

Smolander and Kitunen 2011, Augusto et al. 2014). DOM release from forest floors is a product of microbial production and consumption (Moore and Dalva 2001, Park and Matzner 2003), which explains the order of DOM recovery and production with Oi > Oe > Oa layer and deciduous > coniferous forest floor.

Hydrological control (volume/rate of extraction solution) for DOC recovery and production

Large volume/high rates of the extraction solutions resulted in a larger DOM release from forest floor samples (Figure 3.2.1 and Figure 3.2.6) and a faster rate of the DOM recovery/production (Figure 3.2.2 and Figure 3.2.7) than small volume/low rates of extraction.

Previous studies have also shown an increase in the total amount of released DOC with increasing amount of water passing through the soil at the laboratory scale (Gödde et al. 1996, Judd and Kling 2002) and also at the field scale. (Michalzik et al. 2001, Schmidt et al. 2010, Borken et al. 2011, Neff and Asner 2001, Wu et al. 2014). Previous finding of the positive effect of water flux on DOM release from forest floor was interpreted in the way that the pool of potential DOM is not easily exhausted (Kalbitz et al. 2004, Schmidt et al. 2010). However, in this study at the field scale the DOM pool in the forest floor was temporally depleted by heavy storm events (Table 3.2.7). In detail, the net DOC release of forest floor depleted following subsequent storm events and then slightly recovered in both forests, but it did not reach to the initial value of net DOC release during sampling period. The reason for the depletion in this study might be seen in the high precipitation amount during monsoon and also in the thin organic layers at the field sites.

4.2.2 Similar behavior of DOC and DON pools in response to depletion and recovery

DOC and DON in forest floors behaved similar as indicated by the stable DOC/DON ratio throughout the incubation time (Figure 3.2.1 and Figure 3.2.6). DOC recovery and production rate was significantly correlated to DON recovery and production, respectively (Table 3.2.3 and Table 3.2.5). This was not expected, as forest ecosystems, different source pools of DOC and DON in soils such as C rich litter/humus (Sanderman et al. 2009, Inamdar et al. 2012, Camino-Serrano et al. 2014) and N rich microbial biomass might induce different relations between DOC and DON. Yano et al. (2005) suggested that root litter may be most responsible for DON production compared to needle and wood. Similar DOC and DON behaviour in

response to depletion and recovery might be caused by similar sources and by their similar chemical properties. For example, DOC and DON from organic layers are composed mostly of 10-100 kDa size molecules (Kiikkilä et al. 2006).

The finding of similar behaviour of DOC and DON is in accordance with a number of other studies from forest floor leachates (Michalzik et al. 2001, Jones and Kielland 2012), presenting the strong correlation between DOC and DON. However, the overall DOC/DON ratio decreased from 15-25 to 10-16 by sequent leaching of coniferous and deciduous forest floor samples (Buzek et al. 2009). Also, different response of DOC and DON from forest floors was observed with a weak correlation in a forested watershed (Inamdar et al. 2012) and with the changing DOC/DON ratio in a litter manipulation experiment (Park and Matzner 2003, Kalbitz et al. 2007).

Overall there is no obvious rule identified why in some cases there is a good correlation, in others not. Substrate specific factors and environmental conditions seem too variable to deduce a clear picture and this question remains to be resolved by future research.

4.2.3 Effect of DOC leaching on CO_2 evolution

The released DOM from forest floors is already a product of decomposition and mainly composed of relatively refractory component as indicated by high $SUVA_{280}$ values (Figure 3.2.1 and Figure 3.2.6). Hence, it was assumed that DOC leaching from forest floors does not significantly influence soil CO_2 evolution. Corresponding to the expectation, the reduction effect of DOC leaching on soil CO_2 evolution was low in both coniferous and deciduous O-layers because only a few significant and shallow relationship between the extracted DOC and CO_2 evolution was found. This was observed despite the fact that the amount of DOC extracted was much larger than the reduction in CO_2 evolution (Figure 3.2.5 and Figure 3.2.11).

Moore et al. (2008) observed that a smaller proportion of CO_2 was produced at high rates of DOC production, which is inconsistent with the results in this study. Some studies have suggested different controlling processes for soil C mineralization and DOC production because of lacking or weak correlations between CO_2 evolution and DOC production (Gödde et al. 1996, Bengtson and Bengtsson 2007). DOC originates predominantly from the incomplete decomposition of complex C in soils, whereas CO_2 is produced from the consumption of easy degradable young C by microorganisms. Thus labile C contributes only minor to the released DOC (Park et al. 2002, Hagedorn et al. 2004, Buzek et al. 2009), which

is confirmed by the $SUVA_{280}$ data in this study. Mineralization rate constants of DOC from Oi and Oe layers ranged from 0.26-0.27 (labile fraction) to 0.002-0.006 day^{-1} (stabile fraction) (Kalbitz et al. 2003). Relatively much labile DOC was observed from Oi layers compared to Oa, which explains the fact that an effect of DOC release on CO_2 evolution in this study was mostly found in Oi layers. During the experiments of this study, the extraction of DOC was very fast and the mineralization even of the labile fraction was largely prohibited. Overall, the leaching of refractory DOC from forest floors influence has only a small effect on soil CO_2 evolution, as the latter is derived mostly from labile C.

The overall results of laboratory study suggested that DOC release from forest floors is closely related to DON release in response to depletion and recovery. The extent and rate of depletion and recovery DOM pools of forest floors depend on microbial activity, substrate quality and water flux.

4.3 Link between field and laboratory study

Total net DOC release of larch forest floors at the field (∑22 kg DOC ha^{-1}) was smaller than the total production of larch sample at the lab (∑40 kg DOC ha^{-1}) over 15 days, whereas total net DOC release of deciduous forest floors (∑32 kg DOC ha^{-1}) was similar to the total production of deciduous sample (∑32 kg DOC ha^{-1}) (Table 3.2.7). While for the total period, production and release match quite well, the decrease in net DOC release (kg DOC ha^{-1} mm^{-1}) from forest floors in the later precipitation events indicates a depletion of DOM pools at the field sites. In contrast, the rates of DOC production derived from the laboratory experiments indicated that depletion should not occur. Column experiments with forest floors yielded generally higher DOC fluxes than from field measurements (Gödde et al. 1996), indicating an overestimation of the DOC production at the laboratory scale. There are restriction to link the net DOC forest floor release at the field scale and DOC production at the laboratory. The conditions at the laboratory differ from the field conditions in many ways, such as the lack of fresh litter, the lack of preferential flow paths, the constant temperature and water flux with artificial solution with negligible DOC concentration (Moore et al. 2008). As soils have not an infinite capacity to release DOC, the DOM pools are depleted by subsequent leaching without inputs of new potential DOM sources, like fresh leaves and root exudates (Figure 3.2.6). For that reasons, the estimated DOC production rate at the laboratory scale could differ from net DOC release at the field. However, the overall match of the calculated DOC production and the net DOC release observed in the field was quite well with differences of less than 30%. This indicates that the comparing laboratory studies have their value also for the interpretation of field data.

5 CONCLUSIONS

This study underlines the importance of extreme precipitation events for the export of organic C and N from terrestrial to aquatic ecosystems in forested watersheds.

In the field study hypothesis 1-4 were tested.

Hyp. 1) The ratios of DOC/DON and FPOC/FPON are independent of discharge. The first hypothesis was only partly confirmed. DOC/DON ratio in runoff varied widely from 5 to 50 with increasing discharge because of changing flow paths, whereas FPOC/FPON was independent of discharge.

Hyp.2) FPON is the dominant form of N export in runoff. The second hypothesis was not confirmed. NO_3-N as the dominant form of N loss in runoff from forested watersheds points to N-saturation in these forest areas. In case of C export in runoff, DOC was the dominant form of organic C export during both dry and wet periods. Only extreme storm events, FPOC export fluxes exceeded temporally DOC. Mineral soil of the river bed contributed to FPOC and FPON export during heavy storm events.

Hyp.3) DOM and FPOM in runoff originates mostly from forest floor leachates. The third hypothesis was confirmed for the PD watershed. Here, the quality parameters of runoff DOM from the PD watershed indicated a change of hydrological flow paths from mineral soil to forest floor during heavy storm events and the forest floor turned out as a main source of DOM in runoff, while FPOM in runoff originated from the mineral soil close to the river bed. In contrast, the contribution of DOM and FPOM from mineral soils was higher in runoff from the MCD watershed.

Hyp.4) The export fluxes of DOC, DON, FPOC and FPON from a mixed coniferous/deciduous forested watershed differ from that of a purely deciduous watershed. The fourth hypothesis was partly confirmed. During the wet period the total DOC export fluxes were much larger in the PD watershed (16 kg C ha^{-1}) than in the MCD (7 kg C ha^{-1}) because of the larger potential DOM pools in deciduous forest floors. NO_3-N export fluxes in runoff during wet period were higher in the MCD watershed (5 kg N ha^{-1}) than in the PD (3 kg N ha^{-1}) probably because of large N uptake by the deciduous trees in the PD watershed. On the other hand, the total export fluxes of DON, FPOC and FPON in runoff were similar between two watersheds.

In two laboratory studies hypotheses 5- 7 were tested.

H*yp.5) The depletion and the recovery of the DOC and DON pools behave similar.* The fifth hypothesis was confirmed as indicated by the stable DOC/DON ratio and the significant correlation between DOC and DON release over incubation time. This points to similar properties and source pools of DOC and DON.

Hyp.6) The recovery rate of the DOM pools depends on tree species, microbial activity and temperature. The sixth hypothesis was confirmed. The recovery of DOM pools following leaching was rather fast mostly within 14 days, but it depended on biological activity, physical/hydrological effects, substrate quality and tree species. The recovery and production rate of DOM was in the order; high > low temperature, large > small extraction volume/percolation rate, Oi > Oe > Oa layers and also deciduous/broadleaved > coniferous forest floors.

Hyp.7) DOM from forest floors is already a product of decomposition and mainly composed of rather stabile substance. The leaching of even large amounts of DOC does not influence the CO_2 evolution in the forest floor. The seventh hypothesis was confirmed. The released DOM was mainly composed of relatively stable substances as indicated by high and constant $SUVA_{280}$ value. The reduction effect of DOC leaching on soil CO_2 evolution was low in forest floors with only few significant relationships between the extracted DOC and CO_2 evolution.

The overall findings from both field and laboratory studies indicate that the quantity and quality of organic C and N were controlled by the biological, physical and hydrological process and related to their properties of the source pools (substrate quality and tree species).

Future changes in the precipitation regime and tree species will cause changes in the export of organic C and N from forested watersheds into aquatic ecosystems. As global warming induces more severe precipitation events and likely an increase in the area of broadleaved vegetation, the exports of organic C and N to streams will likely increase in the future.

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Appendix

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Declaration / Versicherung und Erklärung

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Hiermit erkläre ich mich damit einverstanden, dass die elektronische Fassung meiner Dissertation unter Wahrung meiner Urheberrechte und des Datenschutzes einer gesonderten Überprüfung hinsichtlich der eigenständigen Anfertigung der Dissertation unterzogen werden kann.

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