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Response of dissolved and particulate organic carbon and nitrogen in runoff to monsoon storm events in two watersheds of different tree species composition

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Abstract. Heavy storm events may increase the amount of organic matter in runoff from forested watersheds as well as the relation of dissolved to particulate organic matter. Little is known about the behaviour of dissolved and particulate organic N and its relations to C. This study evaluated the effects of monsoon storm events on the runoff fluxes and on the quality of dissolved (< 0.45 µm) and particulate (0.7 µm to 1 mm) organic carbon and nitrogen (DOC, DON, POC, PON) in a mixed coniferous/deciduous (mixed watershed) and a deciduous forested watershed (deciduous watershed) in South Korea. During storm events, DOC concentrations in runoff increased with discharge, while DON concentrations were stable. DOC, DON and NO_3-N fluxes in runoff increased linearly with discharge, whereas nonlinear responses of POC and PON fluxes were observed. The cumulative C and N fluxes in runoff were in the order; DOC > POC and NO_3-N > DON > PON. The cumulative DOC fluxes in runoff during the 2 months study period were much larger at the deciduous watershed (16 kg C ha^{-1}) than at the mixed watershed (7 kg C ha^{-1}), while the cumulative NO_3-N fluxes were higher at the mixed watershed (5.2 kg N ha^{-1}) than at the deciduous watershed (2.9 kg N ha^{-1}). Cumulative fluxes of POC and PON were similar at both watersheds. Quality parameters of organic matter in soils and runoff suggested that the contribution of near surface flow to runoff was larger at the deciduous than at the mixed watershed. Our results demonstrate different responses of dissolved C and N in runoff to storm events as a combined effect of tree species composition and watershed-specific flowpaths.

Keywords. Dissolved organic carbon, Dissolved organic nitrogen, Particulate organic carbon, Particulate organic nitrogen, Monsoon storm, forested watershed

1 Introduction

Forested watersheds play an important role for human wellbeing in that they are often used as source areas for drinking water basins. As much of the dissolved organic matter (DOM) in aquatic systems originates from soil derived organic matter, the export of terrestrial carbon (C) and nitrogen (N) into aquatic environments is a primary link between these systems

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(Bauer and Bianchi, 2011; Bianchi, 2011; Camino-Serrano et al., 2014; Canham et al., 2012). The export of terrestrial C and N occurs in the form of dissolved and particulate organic carbon and nitrogen (DOC, DON, POC, PON). Particulate organic matter can be operationally classified into fine (0.1 to 63 µm) and coarse (63 µm to 2 mm) fractions (Richey, 2005). The export of POC was in some cases the major C export in stream (Dhillon and Inamdar, 2013; Jung et al., 2012; Kim et al., 2010; Lloret et al., 2013). On the contrary, DOC was reported as the dominant organic C form in a temperate headwater catchment (Johnson et al., 2006), a tropical rainforest catchment (Bass et al., 2011) and for several large tropical watersheds such as Amazon, Orinoco, Parana and Mengong (Lloret et al., 2013).

In regions with seasonally large differences in precipitation, most of the annual organic C export from forested watershed to steams is driven by heavy storm events with cyclones and hurricane (Dhillon and Inamdar, 2013; Lloret et al., 2013). Such conditions are pronounced in the Korean peninsula in which the monsoon season (Jeong et al., 2012; Kim et al., 2010), represented 52% and 83% of the annual DOC and POC runoff fluxes. During storm events, a change in hydrological flow paths in watersheds has been often observed from deeper to upper soil layers (Bass et al., 2011; Sanderman et al., 2009; Singh et al., 2014). Surface flow-inducing storm events can alter the fluxes and concentrations of DOC and POC in runoff by shifting preferential flows through macropores, surface runoff and lateral flow (Katsuyama and Ohte, 2002; Kim et al., 2010; McGlynn and McDonnell, 2003).

DON was the major form of N in runoff from pristine forested watersheds (Alvarez-Cobelas et al., 2008; Frank et al., 2000; Kaushal and Lewis, 2003; Pellerin et al., 2006; Yates and Johnes, 2013). Only few data are available on the partitioning of DON and PON fluxes in runoff from forested watersheds (Inamdar et al., 2015). The question remains open, if organic N in runoff – either dissolved or particulate – from forested watersheds behaves similar to organic C or not. Some studies reported that concentrations of DON and DOC correlated strongly (von Schiller et al., 2015), but also their weak relationships were found (Singh et al., 2015).

Tree species might influence the export of dissolved organic matter from forested watersheds. DOM from coniferous litter generally comprises more refractory (e.g. hydrophobic acid, lignin) and aromatic compounds, and a relatively larger proportion of high molecular weight compounds than DOM from deciduous litter. It is also more acidic than DOM from deciduous litter (Don and Kalbitz, 2005; Hansson et al., 2011; Kiikkilä et al., 2013). Moreover, higher DOC and DON concentrations were found in oak, beech and silver birch forest floors compared to Norway spruce, Douglas-fir and Scots pine (Smolander and Kitunen, 2011; Trum et al., 2011).

As a result of global warming, heavy storm events have occurred more frequently and became stronger in recent decades (IPCC, 2013). Furthermore, forest management, namely the selection of tree species, might influence the export of organic matter from forested watersheds. The influence of both drivers should be known in order to better understand the link between terrestrial and aquatic ecosystems and to support an efficient downstream water quality management. The goal of this study was thus to investigate the influence of tree species and heavy storm events on the fluxes of dissolved and particulate forms of C and N from a mixed coniferous/deciduous and a deciduous forested watershed. To do so, a measuring campaign was conducted in South Korea during the 2013 monsoon season.

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2 Materials and methods

2.1 Study area and site

The Lake Soyang basin area (Figure 1) is located in the upstream region of the Han River, which is the main source of drinking water for about 23 million citizens of South Korea (Lee et al., 2013; Park et al., 2010). Annual air temperature ranges from 10 to 15°C with -6°C in January and 26°C in August. Annual precipitation ranges from 1200 to 1500 mm and the summer monsoon usually accounts for 50 to 60% of the annual precipitation (Korean meteorological administration). Korean mountainous forests are mostly composed of broadleaved forests representing 47% of the total forested area (coniferous forest 38%, mixed forest 12%) and most of the broadleaved forests of South Korea are distributed within the Gangwon province (Korea forest research institute, 2013).

The mixed coniferous/deciduous forested watershed (mixed watershed) (Figure 1) is located in Seohwa, the Gangwon province (Lat. 38.206828 N, Long. 128.185719 W, 368 to 682 m above sea level). The area of the mixed watershed (Table 1) is 15.6 ha with 6.1 ha of coniferous forest (39%) and 9.5 ha of deciduous forest (61%). Two research plots as one in the coniferous part (MC plot) and the other one in the deciduous part (MD plot) were established. The slope of the mixed watershed as obtained from a digital elevation model ranges from 4.0 to 41° with an average of 28°. The lower part of the mixed watershed is dominated by coniferous species, including *Larix kaempferi* (Lamb.) Carr. (Japanese larch) and *Pinus densiflora* Siebold & Zucc. (Japanese red pine). The upper part of the mixed watershed is dominated by deciduous species, such as *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).

The deciduous forested watershed (deciduous watershed) (Figure 1) is located in Haean, the Gangwon province (Lat. 38.251532, N 128.11991 Long. W, 586 to 1005 m above sea level). The area of the deciduous watershed (Table 1) is 39 ha and is covered by various deciduous species. A research plot as deciduous plot (DD plot) was established in this watershed. The slope of the deciduous watershed ranges from 4 to 53° with an average of 24°. The dominant tree species are *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). The distance between the two watersheds is ca. 6 km.

2.2 Experimental design

2.2.1 Water sampling

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

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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.

Before storm events in June 2013, 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 in July 2013, throughfall, forest floor leachate and soil solution were collected after each storm event, and runoff samples were collected every 1 or 2 h in the weir at the two watersheds using automatic collectors (6712 Portable Sampler, Teledyne Isco Inc., Lincoln, NE, USA). Discharge at the outlet of the watersheds was measured by a v-notch weir. During routine runoff sampling, water quality parameters including water temperature, pH and electrical conductivity were measured in situ. Water samples were cooled at 4°C and then were filtered (see 2.4) within 2 days after sampling. Filtered solution samples were frozen for 1 month until further analysis of water quality and quantity.

Meteorological data at the study area were used from the weather station of the Korean meteorological administration.

2.2.2 Soil sampling

The total stock of the Oi and Oe+Oa layers was collected at each plot in a 20 × 20 cm frame for 10 replicates. Mineral soil samples were collected from 3 pits at each plot in 10 cm depth layers down to 50 cm depth. In case of the DD plot, the sampling of mineral soil was not possible more than 40 cm depth due to massive rock. Before the analyses, soil samples were air-dried and crushed to pass through a 2 mm sieve. Soil pH was measured from a solution of 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.

2.3 Calculation

2.3.1 Fluxes of C and N in runoff

Before storm events in June 2013, the fluxes of DOC were calculated on a weekly basis by multiplying the DOC weekly mean concentration in runoff by the weekly mean discharge. The concentrations of DON, NO_3-N, POC and PON in runoff were partly below the detection limit. Thus, the detected minimum concentrations were applied to the calculation of their export fluxes as 0.03 mg DON L^{-1}, 0.5 mg NO_3-N L^{-1}, 0.003 mg POC L^{-1}, 0.0003 mg PON L^{-1}. During the period of storm events in July 2013, the fluxes of DOC, DON, NO_3-N, POC and PON in runoff were computed at 1 or 2 h intervals by multiplying the measured concentrations with corresponding discharge. The storm events during monsoon season were identified from the start to the end of precipitation with more than a day interval between each storm event.

2.3.2 Statistic for origin of DOM and POM

The normality of data was tested with the Shapiro-Wilk Test. When the normality was passed as the *p* value less than 0.05, the Holm-Sidak Test was used for both pairwise comparisons and comparisons versus a control group. When the normality

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test failed, the Dunn's Test was used for all pairwise comparisons and comparisons against a control group with rank-based-ANOVA.

2.4 Chemical analyses

After filtration through a pre-rinsed cellulose acetate membrane filter (0.45 µm, Whatman), the concentrations of DOC and dissolved total nitrogen (DTN) in water samples were measured by a total organic carbon analyzer (Shimadzu V-series, TOC-CPH). DON concentration was calculated as the difference between total nitrogen and mineral-N (NO_3^- + NH_4^+). Nitrate and ammonium concentrations were measured by flow injection (MLE Dresden, FIA-LAB).

In this study, the POC and PON fraction is defined as the size class 0.7 µm to 1 mm. Samples were filtered through a 1 mm mesh to remove larger particulate materials and then finally filtered through a pre-rinsed 0.7 µm pore size glass filter (GF/F, Whatman). Before using the glass filters, the filters were pre-combusted at 450°C to remove any organic material. The residues of particulate material on the GF/F filters were analysed for POC and PON after drying at 65°C using an elemental analyser (Carlo Erba1108, Milano, Italy) coupled to a ConFlo III interface and an isotope ratio mass spectrometer (Finnigan MAT, Bremen, Germany).

The absorption spectra of DOM were obtained at wavelengths from 200 to 600 nm using a UV-visible spectrophotometer (HACH, DR5000). Specific ultraviolet absorbance ($SUVA_{280}$) values were determined by UV absorbance at 280 nm divided by the DOC concentrations and multiplied by 100.

For fluorescence excitation-emission matrices, fluorescence intensities were recorded with a luminescence spectrometer (LS-50B, Perkin-Elmer) following the method of Baker (2001), Chen et al. (2007), and Hur and Cho (2012). Excitation and emission slits were both adjusted to 10 nm. DOM samples were diluted under the ultraviolet absorbance of 0.1 at 280 nm to avoid inner-filter correction, and then were adjusted to pH 3.0 for the fluorescence measurements. The fluorescence intensities of all samples were normalized to units of quinine sulfate equivalents. The humification index (HIXem) was calculated by dividing the emission intensity from 435 to 480 nm region by intensity from 300 to 345 nm (Zsolnay et al., 1999). Fluorescence characteristics of water samples were interpreted as fulvic-like fluorescence (FLF), humic-like fluorescence (HLF) and protein-like fluorescence (PLF) (Fellman et al., 2010; Singh et al., 2014).

After filtration (0.45 µm, Whatman) and freeze-drying of water samples, ^{13}C and ^{15}N isotope abundances of DOC and DTN were measured using an elemental analyzer (Carlo Erba1108, Milano, Italy) coupled to a ConFlo III interface and an isotope ratio mass spectrometer (Finnigan MAT, Bremen, Germany).

3 Results

3.1 Soil and hydrological characteristics

The structures of the organic layers at the MC, MD and DD plots are similar, representing a moder-like organic layer, with distinct Oi-layers and less distinct Oe and Oa-layers, but the depth of O-layer in the MC plot (ca. 3 cm) was thinner than in the MD and DD plot (ca. 5 cm). The typical soils of the forested mountain slopes are Dystric Cambisols (FAO, 2014). Soil texture at all plots ranged from 40-44%, 30-38% and 18-22% for sand, silt and clay, respectively. The C content of the organic layers at all plots ranged from 45 to 48% in the Oi and from 34 to 38% in the Oe+Oa layers. The C/N ratio at all plots decreased from the organic layer (20-29) to the mineral soil (10-12) down to 40-50 cm depth. The soil $\delta^{13}C$ and soil $\delta^{15}N$ values significantly increased with soil depth from -29 to -24‰ and from 0 to 8‰, respectively.

The average discharge was much less before storm events in June 2013, 0.03 mm h^{-1} at the mixed watershed and 0.06 mm h^{-1} at the deciduous watershed (data not shown) compared to during storm events in July 2013. During storm events, the hydrological characteristics were similar at both watersheds (Table 2). In the study period, the highest precipitation coincided with the maximum precipitation intensity, the highest precipitation intensity and the maximum discharge at the mixed watershed and at the deciduous watershed on July 14th, 2013.

3.2 Concentrations of carbon and nitrogen in runoff during storm events

The increase of the DOC concentrations in runoff with discharge was steeper at the deciduous watershed (e.g. 1.9 to 6.9 mg C L^{-1} on July 8th, 2013) than at the mixed watershed (e.g. 1.0 to 3.7 mg C L^{-1} on July 8th, 2013) (Figure 2a). In contrast, the DON concentrations in runoff from both watersheds were independent of discharge (Figure 2b). The highest concentrations of DOC and DON in runoff were observed during the earlier storm events (Table 2). The NH_4-N concentrations were at any time negligible (< 0.05 mg N L^{-1}).

During storm events, the concentrations of POC and PON in runoff increased steeply and instantly after a threshold on July 8th and July 14th, 2013 (Figure 2d, 2e). For example, at the mixed watershed, an increase of POC was observed up to 10.7 mg C L^{-1} at the largest discharge of 9 mm h^{-1} (Figure 2d, Table 2). At the deciduous watershed, the POC concentration in runoff increased to 8.6 mg C L^{-1} at the first large storm event with 3 mm h^{-1} discharge. The following more intense storms did result in lower POC concentrations. The pattern of POC concentration coincided with those of PON (r=0.99).

The runoff DOC concentrations in response to discharge had a clockwise hysteretic loop with higher concentrations on the rising than on the falling limb (Figure 2a). No hysteretic loops were observed for DON, POC and PON (Figure 2b, 2d, 2e).

The DOC/DON ratio in runoff ranged from 5 to 60 (Figure 2c). DON concentrations lower than 0.05 mg N L^{-1} were not considered for calculation of DOC/DON ratios. In response to increased discharge, the DOC/DON ratio were stable at the mixed watershed, while there was a tendency for increasing DOC/DON ratios with discharge at the deciduous watershed. On the contrary, there was no response of the POC/PON ratio to discharge. Unlike to DOC/DON ratio, the POC/PON ratio ranged narrowly from 10 to 20 at both watersheds (Figure 2f) with an average of 12 at the mixed and 13 at the deciduous watershed.

3.3 Fluxes of carbon and nitrogen

The fluxes of DOC, DON and NO_3-N in runoff were linearly correlated to discharge at both watersheds (Figure 3). The fluxes of DOC and NO_3-N increased with a much steeper slope at the deciduous and at the mixed watershed, respectively.

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Only when discharge exceeded a certain discharge threshold, POC and PON fluxes increased in a non-linear response. Before reaching the discharge threshold, the POC fluxes were much lower than the DOC fluxes. At a single peak flow event on July 14th 2013, the POC fluxes at the mixed watershed were 5 times greater than the DOC fluxes. The same trend was found for PON and DON fluxes. At the deciduous watershed, only one event caused slightly larger POC than DOC fluxes during the study period.

The cumulative C and N fluxes from both watersheds were in the order; DOC > POC and NO_3-N > DON > PON (Table 3). The DOC fluxes as the dominant C flux form contributed 75% and 92% of the total organic C flux at the mixed and the deciduous watersheds, respectively. The cumulative fluxes of DOC and DON were higher at the deciduous watershed (16 kg C ha^{-1} and 0.5 kg N ha^{-1}) than at the mixed watershed (6.7 kg C ha^{-1} and 0.26 kg N ha^{-1}). The cumulative fluxes of POC and PON were small at both watersheds with only minor differences. Before storm events in June 2013, POC and PON were almost not exported at both watersheds. However, the cumulative fluxes of POC and PON increased extremely during heavy storm events in July 2013. NO_3-N fluxes as the dominant N flux form represented 93% and 82% of the total N flux at the mixed and the deciduous watershed, respectively. The cumulative fluxes of NO_3-N was about twice as high (5.2 N ha^{-1} yr^{-1}) at the mixed watershed than at the deciduous watershed (2.9 N ha^{-1} yr^{-1}).

3.4 Chemical properties of DOM and POM in runoff

The chemical properties of DOM changed with increased discharge at the deciduous watershed, while no significant changes were observed at the mixed watershed (Figure 4). At the deciduous watershed, $SUVA_{280}$ and HIXem increased with increased discharge, while PLF/FLF, PLF/HLF, $\delta^{13}C_{DOC}$ and $\delta^{15}N_{DTN}$ decreased.

At the mixed watershed, the ranges of the DOC/DON ratio, $SUVA_{280}$ and HIXem in runoff were similar to those in throughfall and soil solution, while PLF/FLF in runoff corresponded more to those in forest floor percolates (Figure 5). In contrast at the deciduous watershed, these parameters were all closely related to the quality of forest floor leachates as being likely a mixture of forest floor leachates and soil solution. Comparing between plots, the distributions of the DOM quality parameters at the MC and MD plot were similar in throughfall and forest floor leachates, but they were different in soil solution. These parameters at the MD and DD plot were similarly distributed in throughfall, forest floor leachates and soil solutions.

The range of the POC/PON ratio in runoff was similar to that of the POC/PON ratio of upper and deeper mineral soil layers at both watersheds (Figure 6). The same holds for the $\delta^{13}C_{POC}$ values. The $\delta^{15}N_{PON}$ in runoff had a huge variation, with averages being larger than those of the forest floor, but less than those of the mineral soil.

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4 Discussion

4.1 Different response of DOC to increased discharge at the mixed and the deciduous watershed

Simultaneous analyses of C and N concentrations and isotopic ratios in both DOM and POM allowed us to characterize watershed-specific biogeochemical responses to four heavy rainfall events of the monsoon season at both watersheds. The four events represented a substantial proportion of the annual precipitation in the region. While the number of events was rather low, consistent patterns emerged from this rare opportunity to examine concurrent changes in elemental composition and isotopic ratios during intense rainfall events. The increase of DOC concentrations and fluxes in runoff induced by heavy storm events and increasing discharge is consistent with the findings of previous studies (Dhillon and Inamdar, 2013; Jeong et al., 2012; Johnson et al., 2006; Lloret et al., 2013). In our study, the response to discharge and the cumulative fluxes of DOC in runoff were much larger at the deciduous than at the mixed watershed. Only few studies compared different tree species effects on DOC exports (mixed coniferous and deciduous vs. deciduous). Similar to our results larger annual DOC fluxes at a deciduous forested catchment than at a mixed catchment were reported (Amiotte-Suchet et al., 2007).

The different response of DOM quality parameters in runoff to discharge between the two watersheds, such as the large response of runoff DOC concentration to discharge (Figure 2a) and the significant change in runoff DOC quality parameters (Figure 4) at the deciduous watershed, are likely due to shifting of hydrological flow paths at the deciduous watershed. Also, the distribution of DOC quality parameters in runoff between forest floor leachates and soil solution at the deciduous watershed (Figure 5) indicated that a larger proportion of the DOC in runoff results from forest floor leachates at the deciduous while this proportion was less at the mixed watershed. Previous studies have reported that positive relationships between discharge and DOM concentrations in runoff point to changing hydrologic flow paths from deeper soil to upper soil layers and forest floors at high discharge (Aitkenhead-Peterson et al., 2005; Bass et al., 2011; Sanderman et al., 2009). As the similar watershed characteristics (slope and soil textures) and the precipitation regime at both watersheds, the differences between the watersheds are likely due to the tree species effects on the infiltration of precipitation water into the soil and on the mobilization of DOM. The tree species effect became obvious although the proportion of coniferous tree species was only 39% of the watershed area. Several processes might be involved to explain the tree species effect: i) In the deciduous litter layer the leaves are overlapping and are partly impermeable which may cause more surface near flow than in coniferous litter layers with large pore spaces in between needles. In general, ii) the relatively higher level of hydrophobicity of coniferous forest floors compared to deciduous forest floors (Butzen et al., 2014) can result in less DOC release from coniferous forest floors. Moreover, iii) the mobilization of DOC in soils depends on throughfall chemistry (Kalbitz et al., 2000). Throughfall at the MC plot was more acidic (pH 4.7±0.4) and had a higher ionic strength (15.9±11.3 µS cm^{-1}) than at the DD plot (pH 6.1±0.2, 10.3±6.3 µS cm^{-1}) and the MD plot (pH 5.8±0.4, 9.0±6.3 µS cm^{-1}). Acidity and ionic strength are negatively related to DOC release from soils (Clark et al., 2011; Michalzik et al., 2001; Moldan et al., 2012). Lastly, iv) in stream generation of DOC from litter might be involved (Johnson et al., 2006) if more leaf than needle litter enters the stream.

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4.2 Organic and inorganic nitrogen in runoff

The patterns of DOC/DON ratios in response to discharge were also different at the two watersheds (Figure 2c). Large DOC/DON ratios at high discharge at the deciduous watershed resulted from the positive response of DOC concentration and the independent response of DON concentration to discharge. No significant changes in DOC/DON ratios at the coniferous watershed were due to the relatively small increase in DOC concentration and the stable DON concentration. The changing response of the DOC/DON ratio at the deciduous watershed again points to a larger proportion of near surface flow to runoff at high discharge because the DOC/DON ratio of the forest floor leachates was larger than those of the soil solution.

At both watersheds, NO_3-N was the dominant form of total N flux in runoff (Table 3). Several studies have reported that DON accounted for the dominant fraction of N in undisturbed forested watersheds (Alvarez-Cobelas et al., 2008; Frank et al., 2000; Kaushal and Lewis, 2003; Pellerin et al., 2006). Substantial fluxes of NO_3-N and the dominance of NO_3-N over DON in runoff are likely due to a certain degree of N-saturation (N supply > N demand) of these forested watersheds (Aber et al., 1998; Compton et al., 2003). Hence, the finding of the dominant NO_3-N of total N flux implies that the N deposition in the area seems quite high (estimated between 24-51 kg N ha^{-1} yr^{-1} , Berger et al., 2013). In July 2013, the cumulative N flux in throughfall was however similar at the both watersheds (data not shown). Hence, the differences in N deposition between the two watersheds unlikely explain higher NO_3-N fluxes in runoff at the mixed than at the deciduous watershed (Table 3). The C/N ratio of the forest floor was found to be a good indicator of NO_3-N release with increasing fluxes at low C/N ratios (Borken and Matzner, 2004; MacDonald et al., 2002). However, the C/N ratio of the organic layer at the mixed watershed (20-28) was higher than at the deciduous watershed (19-21), which does not agree with the findings of MacDonald et al. (2002). Overall, it seems that a larger N uptake by the deciduous trees at the deciduous watershed could explain the differences in NO_3-N fluxes.

4.3 Particulate organic matter in runoff

The cumulative fluxes of POC and PON during the study period were much less than those of the dissolved elements and did not differ significantly between the watersheds. POC and PON fluxes exceed their dissolved fractions only for short time during heavy storm events with more than 100 mm precipitation. The small proportion of particulate fluxes in our study seems to be caused by the relatively moderate precipitation events during the study period. Previous studies in the nearby region considered 100 mm precipitation as a threshold that would induced large POC fluxes (Jeong et al., 2012; Jung et al., 2012). The POC/PON ratios in runoff as well as the $\delta^{13}C_{POC}$ and $\delta^{15}N_{PON}$ were similar to those of the mineral soil and different to those of the forest floor. This indicates that the particulate matter originated from the erosion of mineral soil along the stream benches. Higher annual POC fluxes than DOC fluxes were observed in some mountainous forested watersheds (Kao and Liu, 1997; Kim et al., 2010; Lloret et al., 2013), which does not agree with our finding and some other studies (Dhillon and Inamdar, 2013; Inamdar et al., 2011; Jeong et al., 2012). The differences in findings may be related to the topography of forested watersheds because steeper slopes induce higher fluxes of POC (Hilton et al., 2012; Janeau et al., 2014; Jung et al., 2012).

5 Conclusions

Our study emphasized the role of vegetation cover and site-specific flowpaths for the storm-induced export of C and N in DOM and POM with runoff from forested watersheds. Our results suggest that changes in the precipitation regime, as more severe monsoon storms as predicted in the future, will increase the export of dissolved and particulate organic matter from these watersheds, with the magnitude of storm responses depending on both element/phase and the composition of tree species. The proportion of coniferous tree species at the mixed watershed was sufficient to induce less DOC fluxes and larger NO_3-N fluxes with runoff as compared to the deciduous watershed. Differences in the flow paths between the watersheds are seen as the major trigger for the differences in runoff with a larger proportion of near surface flow at the deciduous watershed. A larger proportion of coniferous forests in the forested watersheds of this region will likely lead to less inputs of organic carbon and larger inputs of inorganic nitrogen to the receiving surface water bodies..

Author contribution

Mi-Hee Lee carried out the experimental work and data evaluation and prepared the manuscript with contribution from all co-authors

Egbert Matzner and Ji-Hyung Park contributed to the design of this study, to data evaluation, interpretation of results and writing of the manuscript

Jean-Lionel Payeur-Poirier supported the field work and provided the discharge data

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References

Aber, J. D., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L. and Fernandez, I.: Nitrogen saturation in temperate forest ecosystems, Bioscience, 48(11), 921–934, 1998.

Aitkenhead-Peterson, J. A., Alexander, J. E. and Clair, T. A.: Dissolved organic carbon and dissolved organic nitrogen export from forested watersheds in Nova Scotia: Identifying controlling factors, Global Biogeochem. Cycles, 19, 1–8, doi:10.1029/2004GB002438, 2005.

Alvarez-Cobelas, M., Angeler, D. G. and Sánchez-Carrillo, S.: Export of nitrogen from catchments: A worldwide analysis, Environ. Pollut., 156(2), 261–269, doi:10.1016/j.envpol.2008.02.016, 2008.

Amiotte-Suchet, P., Linglois, N., Leveque, J. and Andreux, F.: ^{13}C composition of dissolved organic carbon in upland forested catchments of the Morvan Mountains (France): Influence of coniferous and deciduous vegetation, J. Hydrol., 335(3-4), 354–363, doi:10.1016/j.jhydrol.2006.12.002, 2007.

Baker, A.: Fluorescence excitation - Emission matrix characterization of some sewage-impacted rivers, Environ. Sci. Technol., 35(5), 948–953, doi:10.1021/es000177t, 2001.

Bass, A. M., Bird, M. I., Liddell, M. J. and Nelson, P. N.: Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment, Limnol. Oceanogr., 56(6), 2282–2292, doi:10.4319/lo.2011.56.6.2282, 2011.

Bauer, J. E. and Bianchi, T. S.: Dissolved Organic Carbon Cycling and Transformation, Elsevier Inc., 2011.

Berger, S., Jung, E., Köpp, J., Kang, H. and Gebauer, G.: Monsoon rains, drought periods and soil texture as drivers of soil N_2O fluxes – Soil drought turns East Asian temperate deciduous forest soils into temporary and unexpectedly persistent N_2O sinks, Soil Biol. Biochem., 57, 273–281, doi:10.1016/j.soilbio.2012.09.026, 2013.

Bianchi, T. S.: The role of terrestrially derived organic carbon in the coastal ocean: A changing paradigm and the priming effect, Proc. Natl. Acad. Sci., 108(49), 19473–19481, doi:10.1073/pnas.1017982108, 2011.

Borken, W. and Matzner, E.: Nitrate leaching in forest soils: an analysis of long-term monitoring sites in Germany, J. Plant Nutr. Soil Sci., 167(3), 277–283, doi:10.1002/jpln.200421354, 2004.

Butzen, V., Seeger, M., Wirtz, S., Huemann, M., Mueller, C., Casper, M. and Ries, J. B.: Quantification of Hortonian overland flow generation and soil erosion in a Central European low mountain range using rainfall experiments, Catena, 113, 202–212, doi:10.1016/j.catena.2013.07.008, 2014.

Camino-Serrano, M., Gielen, B., Luysaert, S., Ciais, P., Vicca, S., Guenet, B., de Vos, B., Cools, N., Ahrens, B., Arain, M. A., Borken, W., Clarke, N., Clarkson, B., Cummins, T., Don, A., Pannatier, E. G., Laudon, H., Moore, T., Nieminen, T. M., Nilsson, M. B., Peichl, M., Schwendenmann, L., Siemens, J. and Janssens, I.: Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type, Global Biogeochem. Cycles, 497–509, doi:10.1002/2013GB004726.Received, 2014.

Canham, C. D., Pace, M. L., Weathers, K. C., McNeil, E. W., Bedford, B. L., Murphy, L. and Quinn, S.: Nitrogen deposition and lake nitrogen concentrations: a regional analysis of terrestrial controls and aquatic linkages, Ecosphere, 3(7), 66, doi:10.1890/ES12-00090.1, 2012.

Chen, Z., Hu, C., Conmy, R. N., Muller-Karger, F. and Swarzenski, P.: Colored dissolved organic matter in Tampa Bay, Florida, Mar. Chem., 104(1-2), 98–109, doi:10.1016/j.marchem.2006.12.007, 2007.

Clark, J. M., Van Der Heijden, G. M. F., Palmer, S. M., Chapman, P. J. and Bottrell, S. H.: Variation in the sensitivity of DOC release between different organic soils following H_2SO_4 and sea-salt additions, Eur. J. Soil Sci., 62(2), 267–284, doi:10.1111/j.1365-2389.2010.01344.x, 2011.

Compton, J. E., Church, M. R., Larned, S. T. and Hogsett, W. E.: Nitrogen export from forested watersheds in the oregon coast range: The role of N_2-fixing Red alder, Ecosystems, 6(8), 773–785, doi:10.1007/s10021-002-0207-4, 2003.

Dhillon, G. S. and Inamdar, S.: Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering uncharted waters?, Geophys. Res. Lett., 40(7), 1322–1327, doi:10.1002/grl.50306, 2013.

Don, A. and Kalbitz, K.: Amounts and degradability of dissolved organic carbon from foliar litter at different decomposition stages, Soil Biol. Biochem., 37(12), 2171–2179, doi:10.1016/j.soilbio.2005.03.019, 2005.

FAO-Food and Agriculture Organization of the United Nations: World reference base for soil resources 2014 international soil classification system for naming soils and creating legends for soil maps. Rome. 2014

Fellman, J. B., Hood, E. and Spencer, R. G. M.: Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review, Limnol. Oceanogr., 55(6), 2452–2462, doi:10.4319/lo.2010.55.6.2452, 2010.

Frank, H., Patrick, S., Peter, W. and Hannes, F.: Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments - The significance of water flow paths, Biogeochemistry, 50(2), 137–161, doi:10.1023/A:1006398105953, 2000.

Hansson, K., Olsson, B. A., Olsson, M., Johansson, U. and Kleja, D. B.: Differences in soil properties in adjacent stands of Scots pine, Norway spruce and silver birch in SW Sweden, For. Ecol. Manage., 262(3), 522–530, doi:10.1016/j.foreco.2011.04.021, 2011.

Hilton, R. G., Galy, A., Hovius, N., Kao, S.-J., Horng, M.-J. and Chen, H.: Climatic and geomorphic controls on the erosion of terrestrial biomass from subtropical mountain forest, Global Biogeochem. Cycles, 26(3), GB3014, doi:10.1029/2012GB004314, 2012.

Hur, J. and Cho, J.: Prediction of BOD, COD, and total nitrogen concentrations in a typical urban river using a fluorescence excitation-emission matrix with PARAFAC and UV Absorption Indices, Sensors, 12(12), 972–986, doi:10.3390/s120100972, 2012.

Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H. and McHale, P.: Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, J. Geophys. Res. Biogeosciences, 116, doi:10.1029/2011JG001735, 2011.

Inamdar, S., Dhillon, G., Singh, S., Parr, T. and Qin, Z.: Particulate nitrogen exports in stream runoff exceed dissolved nitrogen forms during large tropical storms in a temperate, headwater, forested watershed, J. Geophys. Res. G Biogeosciences, 120(8), 1548–1566, doi:10.1002/2015JG002909, 2015.

IPCC: Summary for Policymakers, in Climate Change 2013 - The Physical Science Basis, edited by T. F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Doschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley, pp. 1–30, Cambridge University Press, Cambridge., 2013.

Janeau, J.-L., Gillard, L.-C., Grellier, S., Jouquet, P., Le, T. P. Q., Luu, T. N. M., Ngo, Q. A., Orange, D., Pham, D. R., Tran, D. T., Tran, S. H., Trinh, A. D., Valentin, C. and Rochelle-Newall, E.: Soil erosion, dissolved organic carbon and nutrient losses under different land use systems in a small catchment in northern Vietnam, Agric. Water Manag., 146, 314–323, doi:10.1016/j.agwat.2014.09.006, 2014.

Jeong, J. J., Bartsch, S., Fleckenstein, J. H., Matzner, E., Tenhunen, J. D., Lee, S. D., Park, S. K. and Park, J. H.: Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements, J. Geophys. Res. Biogeosciences, 117(3), 1–13, doi:10.1029/2012JG001999, 2012.

Johnson, M. S., Lehmann, J., Selva, E. C., Abdo, M., Riha, S. and Couto, E. G.: Organic carbon fluxes within and streamwater exports from headwater catchments in the southern Amazon, Hydrol. Process., 20, 2599–2614, doi:10.1002/hyp.6218, 2006.

Jung, B. J., Lee, H. J., Jeong, J. J., Owen, J., Kim, B., Meusburger, K., Alewell, C., Gebauer, G., Shope, C. and Park, J. H.: Storm pulses and varying sources of hydrologic carbon export from a mountainous watershed, J. Hydrol., 440-441, 90–101, doi:10.1016/j.jhydrol.2012.03.030, 2012.

Jung, B.-J., Jeanneau, L., Alewell, C., Kim, B. and Park, J.-H.: Downstream alteration of the composition and biodegradability of particulate organic carbon in a mountainous, mixed land-use watershed, Biogeochemistry, 122(1), 79–99, doi:10.1007/s10533-014-0032-9, 2015.

Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B. and Matzner, E.: Controls on the dynamics of dissolved organic matter in soils: a review, Soil Sci., 165, 277–304, 2000.

Kao, S.-J. and Liu, K.-K.: Fluxes of dissolved and nonfossil particulate organic carbon from an Oceania small river (Lanyang Hsi) in Taiwan, Biogeochemistry, 39(1996), 255–269, doi:10.1023/A:1005864605382, 1997.

Katsuyama, M. and Ohte, N.: Determining the sources of stormflow from the fluorescence properties of dissolved organic carbon in a forested headwater catchment, J. Hydrol., 268(1-4), 192–202, doi:10.1016/S0022-1694(02)00175-0, 2002.

Kaushal, S. S. and Lewis, W. M.: Patterns in the chemical fractionation of organic nitrogen in Rocky Mountain streams, Ecosystems, 6(5), 483–492, doi:10.1007/s10021-003-0175-3, 2003.

Kiikkilä, O., Smolander, A. and Kitunen, V.: Degradability, molecular weight and adsorption properties of Dissolved Organic Carbon and nitrogen leached from different types of decomposing litter, Plant Soil, 373, 787–798, doi:10.1007/s11104-013-1837-3, 2013.

Kim, S. J., Kim, J. and Kim, K.: Organic carbon efflux from a deciduous forest catchment in Korea, Biogeosciences, 7(4), 1323–1334, doi:10.5194/bg-7-1323-2010, 2010.

Korea forest research institute: Distribution of main tree species in South Korea - 1:5,000 based on the map of forest type (한국의 주요 수종분포-1:5,000 임상도 기반), 김경민 이승호., Korea Forest Research Institute. [online] Available from: http://book.nifos.go.kr/ebook/Links/kfri/151027151648704_6__self, 2013.

Korean meteorological administration. www.kma.go.kr.

Lee, J.-Y., Kim, J.-K., Owen, J. S., Choi, Y., Shin, K., Jung, S. and Kim, B.: Variation in carbon and nitrogen stable isotopes in POM and zooplankton in a deep reservoir and relationship to hydrological characteristics, J. Freshw. Ecol., 28(1), 47–62, doi:10.1080/02705060.2012.689999, 2013.

Lloret, E., Dessert, C., Pastor, L., Lajeunesse, E., Crispi, O., Gaillardet, J. and Benedetti, M. F.: Dynamic of particulate and dissolved organic carbon in small volcanic mountainous tropical watersheds, Chem. Geol., 351, 229–244, doi:10.1016/j.chemgeo.2013.05.023, 2013.

MacDonald, J. A., Dise, N. B., Matzner, E., Armbruster, M., Gundersen, P. and Forsius, M.: Nitrogen input together with ecosystem nitrogen enrichment predict nitrate leaching from European forests, Glob. Chang. Biol., 8(10), 1028–1033, doi:10.1046/j.1365-2486.2002.00532.x, 2002.

McGlynn, B. L. and McDonnell, J. J.: Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, Water Resour. Res., 39(4), SWC31–SWC318, doi:10.1029/2002WR001525, 2003.

Michalzik, B., Kalbitz, K., Park, J. H., Solinger, S. and Matzner, E.: Fluxes and concentrations of dissolved organic carbon and nitrogen - A synthesis for temperate forests, Biogeochemistry, 52, 173–205, doi:10.1023/A:1006441620810, 2001.

Moldan, F., Hruška, J., Evans, C. D. and Hauhs, M.: Experimental simulation of the effects of extreme climatic events on major ions, acidity and dissolved organic carbon leaching from a forested catchment, Gårdsjön, Sweden, Biogeochemistry, 107(1-3), 455–469, doi:10.1007/s10533-010-9567-6, 2012.

Park, J.-H., Duan, L., Kim, B., Mitchell, M. J. and Shibata, H.: Potential effects of climate change and variability on watershed biogeochemical processes and water quality in Northeast Asia, Environ. Int., 36, 212–225, doi:http://dx.doi.org/10.1016/j.envint.2009.10.008, 2010.

Pellerin, B. A., Kaushal, S. S. and McDowell, W. H.: Does anthropogenic nitrogen enrichment increase organic nitrogen concentrations in runoff from forested and human-dominated watersheds?, Ecosystems, 9(5), 852–864, doi:10.1007/s10021-006-0076-3, 2006.

Richey, J. E.: Global River Carbon Biogeochemistry, in Encyclopedia of Hydrological Sciences, pp. 1–13, John Wiley & Sons, Ltd, Chichester, UK., 2005.

Sanderman, J., Lohse, K. A., Baldock, J. A. and Amundson, R.: Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed, Water Resour. Res., 45(3), W03418, doi:10.1029/2008WR006977, 2009.

Singh, S., Inamdar, S., Mitchell, M. and McHale, P.: Seasonal pattern of dissolved organic matter (DOM) in watershed sources: influence of hydrologic flow paths and autumn leaf fall, Biogeochemistry, 118(1-3), 321–337, doi:10.1007/s10533-013-9934-1, 2014.

Singh, S., Inamdar, S. and Mitchell, M.: Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow, Hydrol. Process., 29(6), 1505–1520, doi:10.1002/hyp.10286, 2015.

Smolander, A. and Kitunen, V.: Comparison of tree species effects on microbial C and N transformations and dissolved organic matter properties in the organic layer of boreal forests, Appl. Soil Ecol., 49(1), 224–233, doi:10.1016/j.apsoil.2011.05.002, 2011.

Trum, F., Titeux, H., Ranger, J. and Delvaux, B.: Influence of tree species on carbon and nitrogen transformation patterns in forest floor profiles, Ann. For. Sci., 68(4), 837–847, doi:10.1007/s13595-011-0080-4, 2011.

von Schiller, D., Graeber, D., Ribot, M., Timoner, X., Acuña, V., Martí, E., Sabater, S. and Tockner, K.: Hydrological transitions drive dissolved organic matter quantity and composition in a temporary Mediterranean stream, Biogeochemistry, 123, 1–18, doi:10.1007/s10533-015-0077-4, 2015.

Yates, C. A. and Johnes, P. J.: Nitrogen speciation and phosphorus fractionation dynamics in a lowland Chalk catchment, Sci. Total Environ., 444, 466–479, doi:10.1016/j.scitotenv.2012.12.002, 2013.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B. and Saccomandi, F.: Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying, Chemosphere, 38(1), 45–50, doi:10.1016/S0045-6535(98)00166-0, 1999.

Biogeosciences Discuss., doi:10.5194/bg-2016-92, 2016
Manuscript under review for journal Biogeosciences
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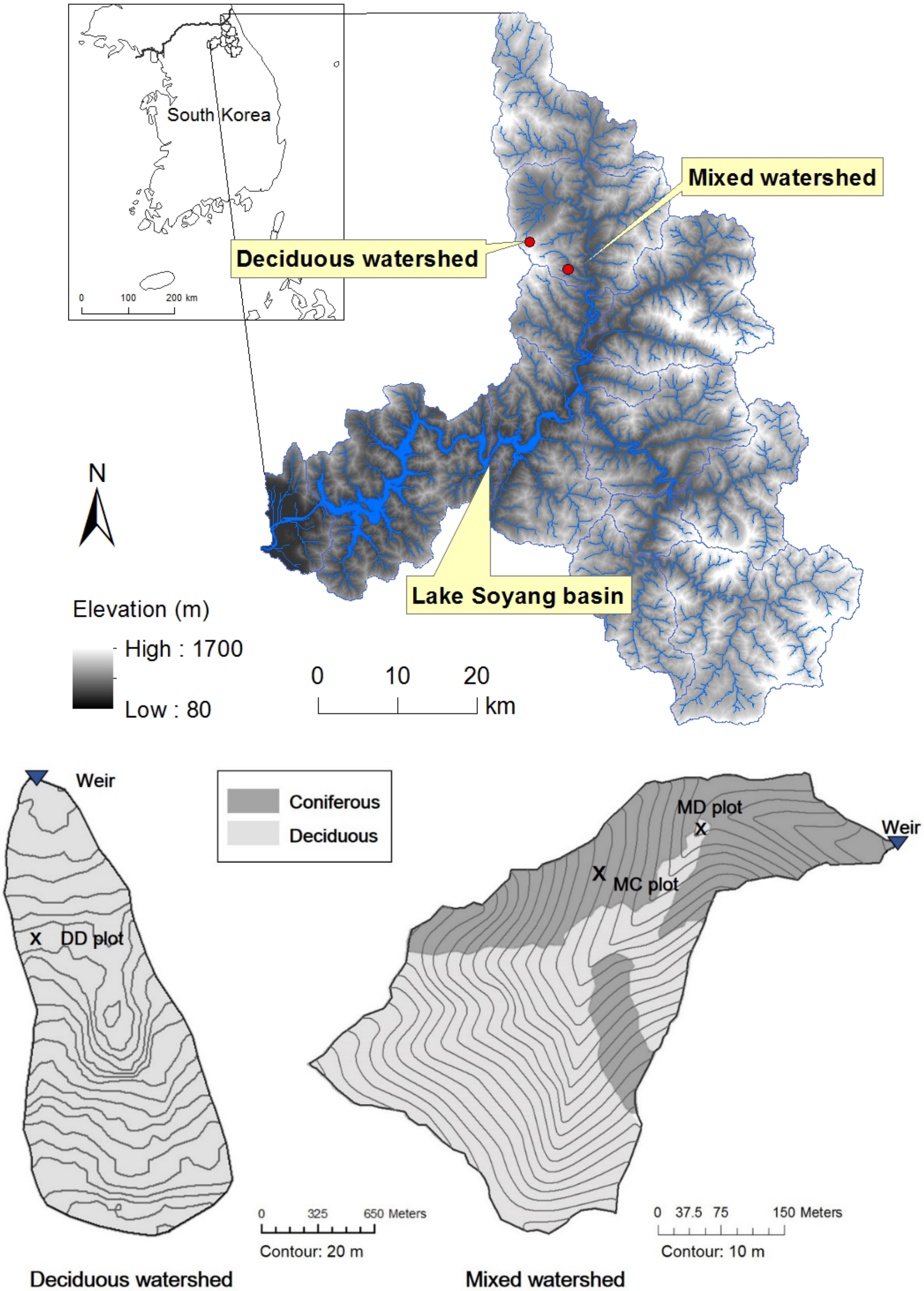

Figure 1: Location and tree species composition of the two studied forested watersheds. Lake Soyang map was modified from Jung et al. (2015).

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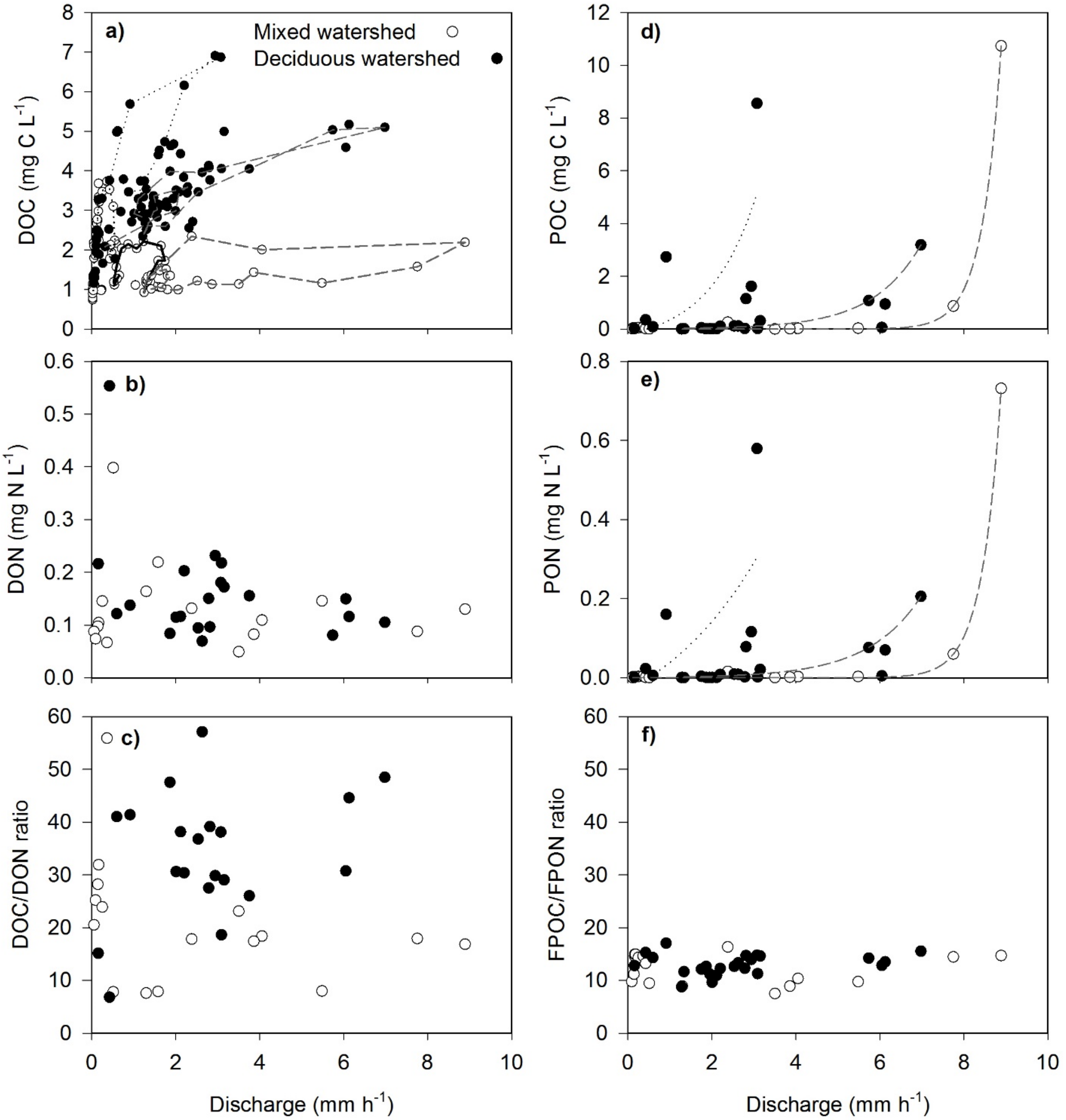

Figure 2: Concentrations of a) dissolved organic carbon (DOC) and b) nitrogen (DON), d) particulate organic carbon (POC) and e) nitrogen (PON) and the ratios of c) DOC/DON and f) POC/PON in runoff with discharge during monsoon storm events. Doted, solid and dashed lines correspond to the storm event of July 8th 2013, July 11th 2013 and July 14th 2013, respectively.

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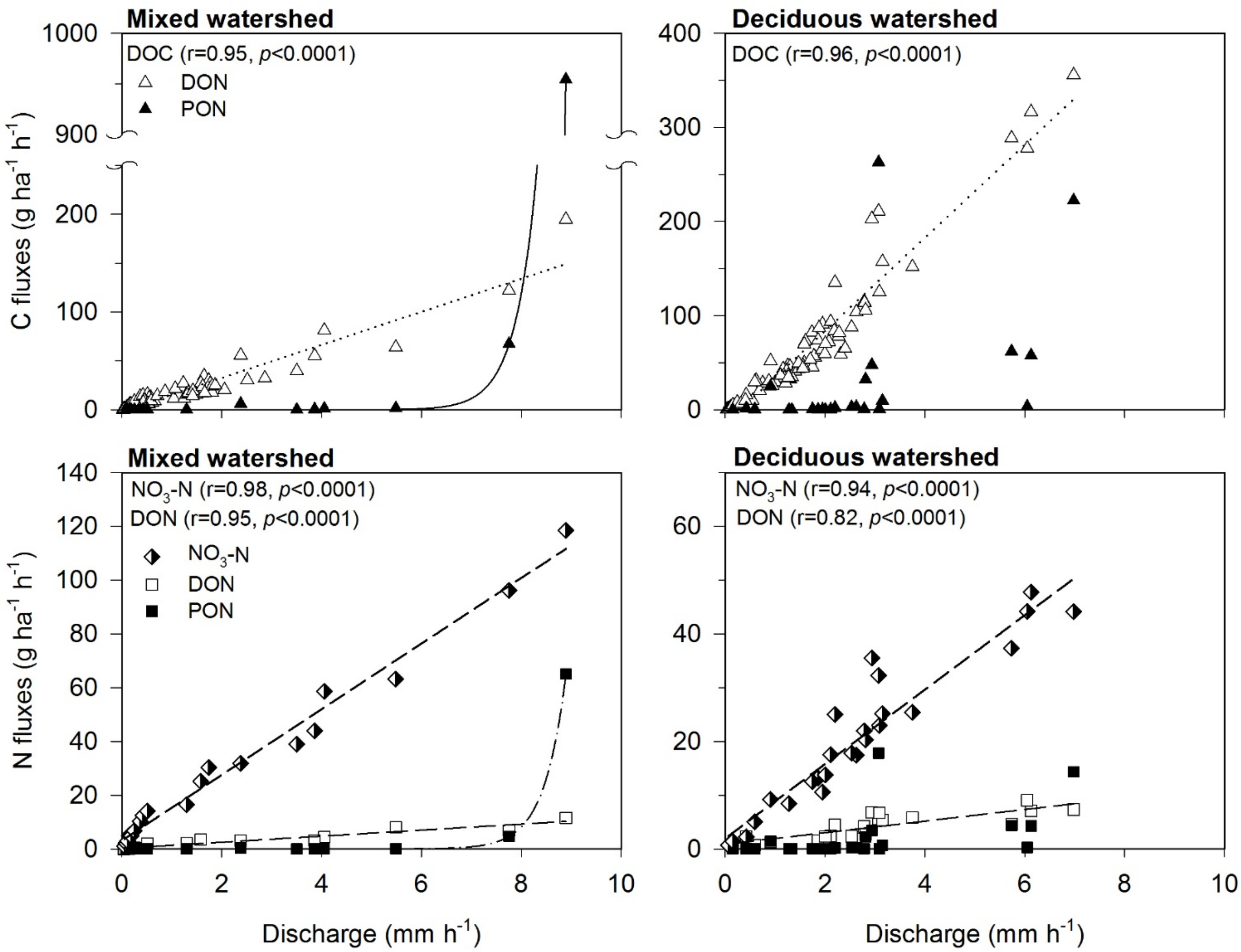

Figure 3: Fluxes of carbon (dissolved organic carbon (DOC) and particulate organic carbon (POC) and nitrogen (dissolved organic nitrogen (DON), and particulate organic nitrogen (PON) and nitrate (NO_3-N) in runoff with discharge during monsoon storm events.

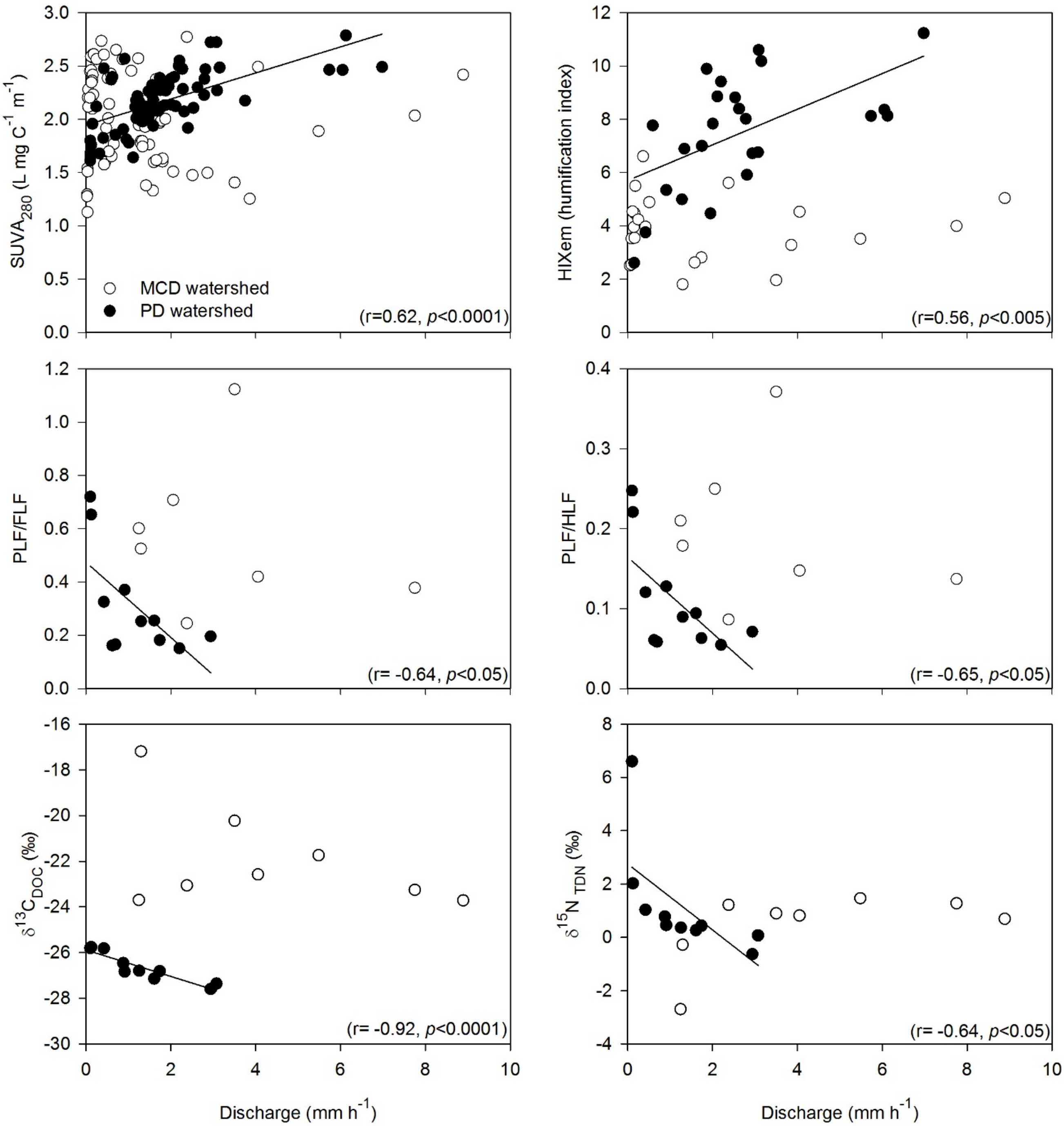

Figure 4: Specific ultraviolet absorbance ($SUVA_{280}$), humification index (HIXem), protein-like fluorescence/humic-like fluorescence (PLF/HLF), protein-like fluorescence/fulvic-like fluorescence (PLF/FLF), ^{13}C isotope abundance of dissolved organic carbon ($\delta^{13}C_{DOC}$) and ^{15}N isotope abundance of dissolved total nitrogen ($\delta^{15}N_{DTN}$) in runoff with discharge during monsoon storm events. Only significant regressions are shown.

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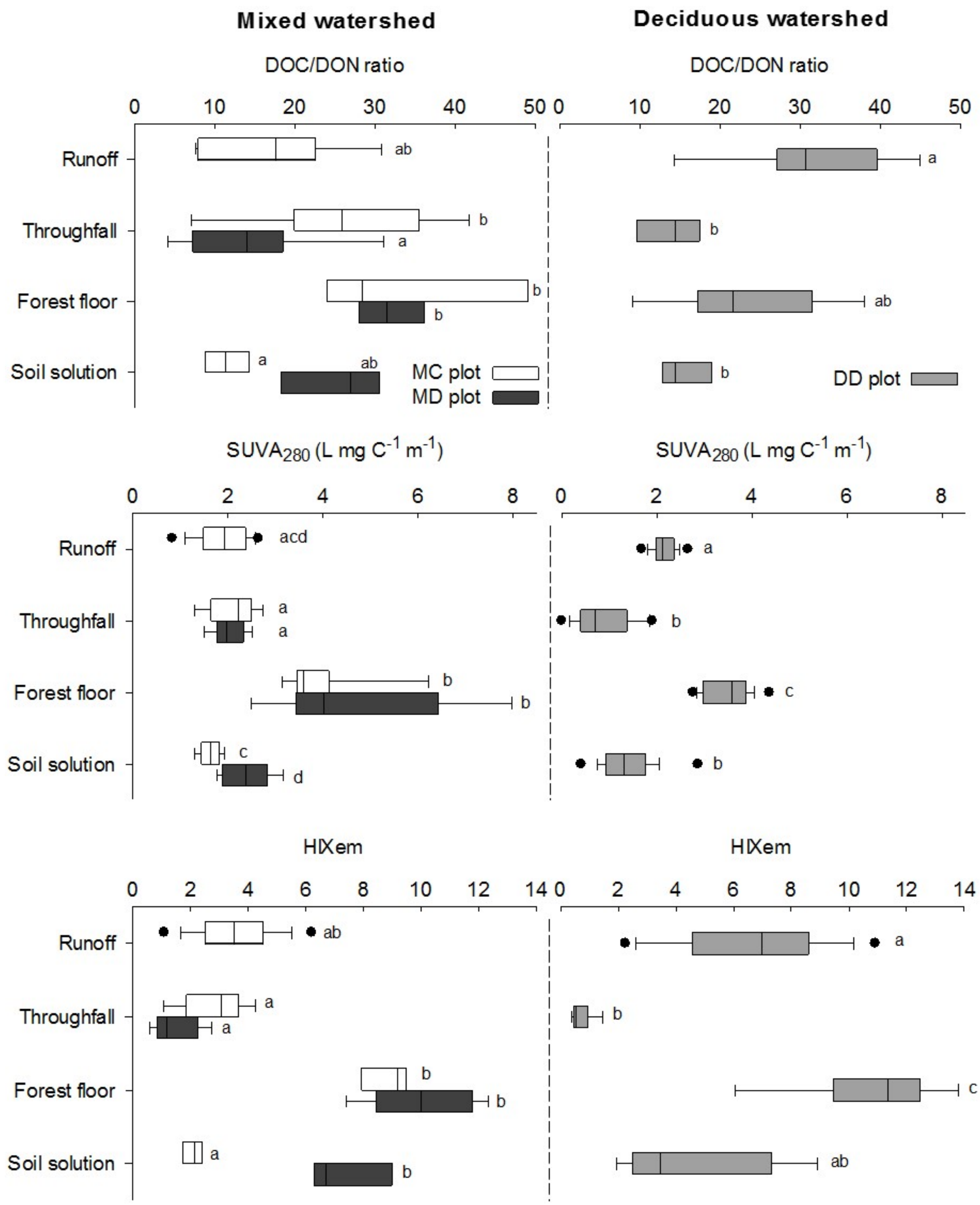

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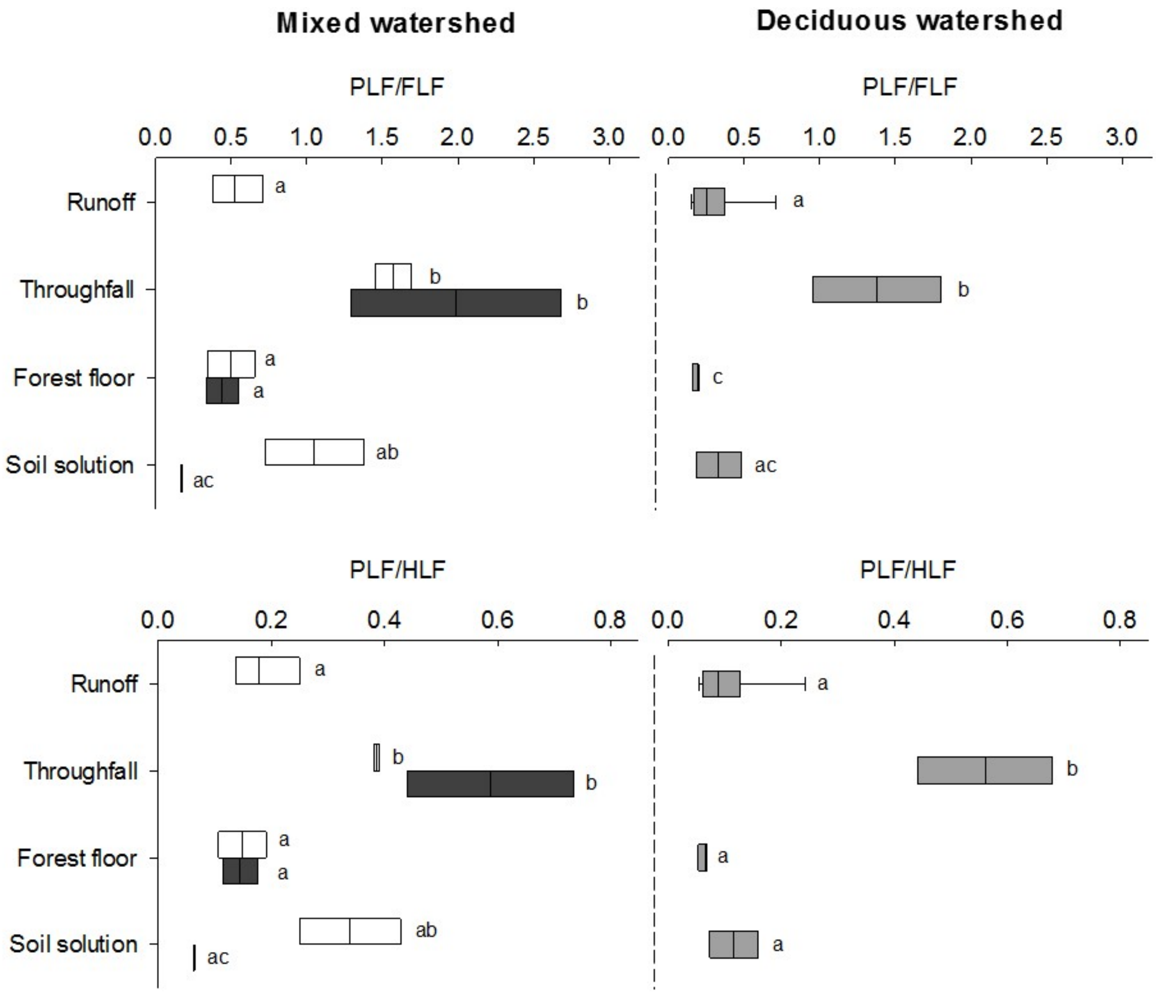
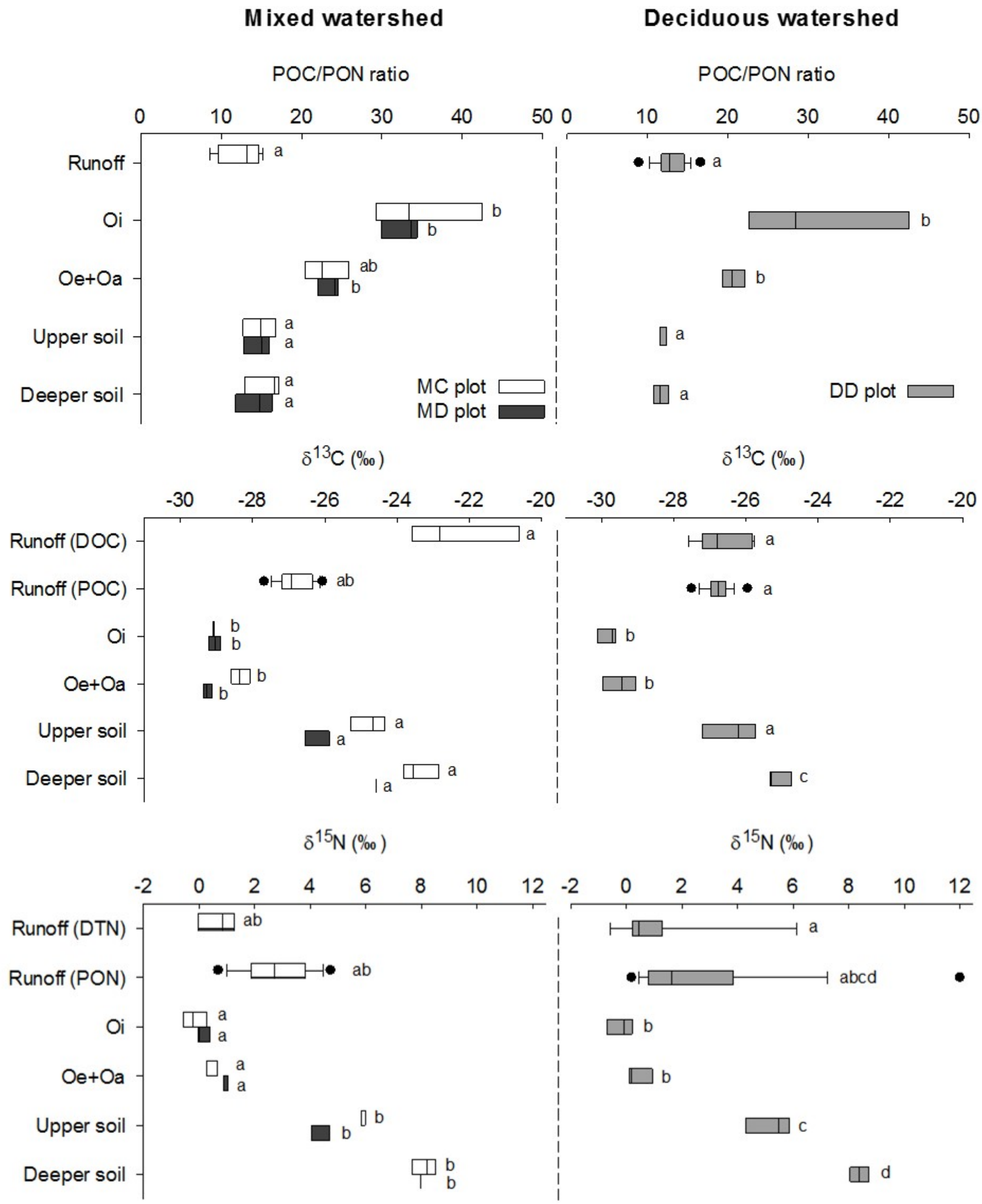


Figure 5: Range of dissolved organic carbon and nitrogen ratio (DOC/DON ratio), specific ultraviolet absorbance ($SUVA_{280}$), humification index (HIXem), protein-like fluorescence/humic-like fluorescence (PLF/HLF), protein-like fluorescence/fulvic-like fluorescence (PLF/FLF) of runoff, throughfall, forest floor leachates and soil solutions during monsoon storm events. Box plots display minimum, lower quartile, median, upper quartile, maximum and outliers. Different alphabet letters indicate the significant difference between groups.



5 **Figure 6: Range of particulate organic carbon and nitrogen ratio (POC/PON ratio), $\delta^{13}C$ and $\delta^{15}N$ in runoff, Oi, Oe+Oa, upper soil (0-10 cm depth) and deeper soil (40-50 cm depth at the MC and MD plot, 30-40 cm depth at the DD plot). Box plots display minimum, lower quartile, median, upper quartile, maximum and outliers. Different alphabet letters indicate the significant difference between groups.**

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Table 1: Tree species composition and geomorphological characteristics of the studied forested watersheds.

Watershed	Major tree species	Area (ha)	Average Slope (°)	Altitude (m a.s.l.)
Mixed				
Coniferous	Larch and Pine	6.1		
Deciduous	Walnut, Maple, Oak, Lime, Elm	9.5		
		(Total 15.6)	27.9	368-682
Deciduous	Walnut, Maple, Oak, Ash	39	24.0	586-1005

a.s.l.: above sea level

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Table 2: Hydrological characteristics of sampled storm events and maximum concentration of dissolved organic carbon (DOC) and nitrogen (DON), particulate organic carbon (POC) and nitrogen (PON) in runoff.

Watershed	Start time		Duration	Number of samples	Total precipitation	Maximum intensity	Average intensity	Maximum discharge	Discharge before start of a storm event	Maximum DOC	Maximum DON	Maximum POC	Maximum PON
			(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})
Mixed	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	41	26	172.5	34.0	10.6	8.89	1.21	2.4	0.2	10.7	0.730
Deciduous	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	42	23	148.5	32.0	9.5	7.39	1.07	5.1	0.2	3.2	0.21
	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

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Table 3: Total precipitation, total runoff and cumulative fluxes of dissolved organic carbon (DOC) and nitrogen (DON), nitrate (NO_3-N) and particulate organic carbon (POC) and nitrogen (PON) in June and July 2013.

Watershed	Period	Total precipitation (mm)	Total runoff (mm)	DOC fluxes (kg C ha^{-1})	DON fluxes (kg N ha^{-1})	NO_3-N fluxes (kg N ha^{-1})	POC fluxes (kg C ha^{-1})	PON fluxes (kg N ha^{-1})
Mixed	June[a]	86.0	21.8	0.22	0.02	0.43	0.001	0.0001
	July[b]	508.0	380.7	6.74	0.26	5.20	2.22	0.15
Deciduous	June[a]	70.5	52.4	0.85	0.1	0.52	0.01	0.001
	July[b]	498.0	439.5	16.13	0.52	2.87	1.46	0.11

[a] Before heavy storm events from June 1st to June 30th, 2013

[b] Heavy storm events from July 1st to July 20th, 2013