Comments from referees

In blue font color the reply of the authors to the referee comments with line numbers referring to the manuscript version with the yellow-marked changes

General comments

The manuscript presented very useful information on forms and flows of carbon and nitrogen in an upland fluvial system. The planning and coverage of sampling and parameters are good. The results will improve our understanding of material flows in terrestrial fluvial systems based on nature of tree types and water flows. The results deserve to be published but not in the present form. The basic problem is with the presentation and the way they dealt with scientific and technical issues. I recommend encouraging the authors for submitting a revised version after they work on some of the issues mentioned and improve the presentation for clarity.

Specific Comments

Title: manuscript is not really studying the 'response of carbon and nitrogen components IN RUNOFF to storm events' but addresses the influence of storms on carbon and nitrogen components in runoff. The appropriate title for the manuscript seems to be (from lines 32-33 on page 2): Influence of tree species and episodic discharges on the fluxes of dissolved and particulate carbon and nitrogen from two watersheds OR Changes in fluxes of dissolved and particulate carbon and nitrogen from two watersheds of different tree types during heavy discharge periods.

Reply: *title has been changed accordingly to 'Changes in fluxes of dissolved and particulate carbon and nitrogen from two watersheds of different tree species during intense storm events'.*

Page 3: Lines 4-5 – The sentence 'the annual air temperature ranges from 10-15oC with -6oC in January and 26oC in August' does not make sense to me.

Reply: *it has been clarified as 'The average annual temperature of the Lake Soyang watershed in western Gangwon-province is 11^{o}C with monthly average temperature ranging from -5^{o}C in January to 24^{o}C in August'. See line 11-13 on page 3.*

Page 3: Line 7 –Is the 47% broadleaved forest 'the deciduous'? Here the comparison is between deciduous and mixed types and so appropriate type to be named than the description (broadleaved).

Reply: *it has been clarified as 'Korean mountainous forests are mostly composed of deciduous forests representing 47% of the total forested area (38% coniferous forest, 12% mixed coniferous and deciduous forest)'. See line 15-16 on page 3.*

Page 3: Lines 12-14 – Are the slopes at two sampling points MC and MD oriented in different directions in the mixed watershed? If they are oriented in one direction then fluxes from the upper can definitely influence the other during floods. This question also pertains to slope comparisons between two watershed sampling points. Figure 1 and info on page 3 shows that deciduous sampling point is at a higher altitude than that in the mixed watershed. What if both the watersheds (and hence the sampling points) slope in the same direction? If yes, the flow from deciduous sampling point would

influence the composition at MC and MD!! This is quite possible as the two watersheds are nearby. The authors should clarify on this issue of slopes and possible interference between sampling points.
Reply: *we have described the effect of slope direction in the methods: new text: 'The slope direction of the coniferous part at the mixed watershed is towards the MD plot. Lateral flow from the coniferous part to the MD plot can only influence deeper soil solution characteristics as near surface flow was never observed. Our data (see results) indicate significant quality differences of soil solutions between the MD and MC plots which suggest only a minor influence on soil solution chemistry at the MD plot from lateral flows. Furthermore, the quality parameters of soil solutions at the MD plot were similar to those of the DD plot, the latter being not influenced by lateral flows from coniferous sites. Thus, it is unlikely that the MC plot did affect the MD plot'. See line 27-32 on page 3.*

Page 4: Line 5 – 'were collected after each storm event': maximal flows/fluxes must have occurred during the peak flow. When the maximal speeds subsided the original peak signals (of concentrations/fluxes) of the flood may have been lost!! This can be

exemplified using the data in Table 2 for deciduous station. On July 8 (say first flood studied) DOC, DON, POC, PON values are higher than the following flood event on 14
July. Obviously, the first flood water carried more C & N than the second one since the first/fresh rain/flood can dissolve/scoop more of materials accumulated during the preceding dry or intervening periods in the soils. This was also noticed by the authors on Page 6 Line 15.
Reply*: we have clarified this as 'During storm events in July 2013, throughfall, forest floor leachate and soil solution was collected after each storm event so that these samples represent cumulative water samples during the entire storm event'. See line 17-19 on page 4.*

Page 4: Line 5 – 'runoff samples were collected every 1 or 2 h in the weir' – were these also collected after the storm events (coinciding with throughfall, forest floor leachate and soil solution sampling) or during the event or both? This information is crucial for making the right comparisons and assessing changes.
Reply: *we have clarified this as 'In case of runoff, samples were taken in July 2013 at the weir using automatic collectors (6712 Portable Sampler, Teledyne Isco Inc., Lincoln, NE, USA) before, during, and after each rain event at intervals of 1 or 2 h'. See line 19-20 on page 4.*

Page 6: line 3 – In the absence of clear definitions of Oi, Oe and Oa it is hard to understand the significance of percentages of these fractions, as also in relevant Figures.
Reply: *the definition and thickness of horizons have been given: new text: '(Oi: slightly decomposed recognizable litter, Oe: moderately decomposed fragmented litter, Oa: highly decomposed humus material)' and 'The average thickness of Oi and Oe+Oa was 1.2 and 1.5 cm at the MC plot, 2.5 and 3 cm at the MD plot, and 2.3 and 2 cm at the DD plot, respectively', See line 28-29 and line 29-31 on page 4.*

Page 6: Lines 17-21 – I am not convinced of the 'threshold value' since there are not enough data points to show a consistent increase in concentrations. Relatively higher concentrations in POC and PON are found (Fig 2d,e) RANDOMLY during discharges from _1 to 9 mm/h.
Reply: *the reviewer is right, text has been changed accordingly to 'At discharges from ~1 to 9 mm h^{-1}, higher*

concentrations of POC and PON in runoff were found (Figure 3d,e). For example, the POC concentration in runoff from the mixed watershed was as high as 10.7 mg C L^{-1} at the largest discharge of 9 mm h^{-1}. At the deciduous watershed, the POC concentration in runoff reached a maximum of 8.6 mg C L^{-1} already at 3 mm h^{-1} discharge during the first storm event (Figure 3d, Table 2)'. See line 7-10 on page 7.

Page 6: Lines 22-23 – DOC rise with increasing flood and fall with decreasing flood is convincing and is, indeed a good observation.
Reply: *thank you for your comment; no reply needed.*

Page 8: in the entire page of this discussion, the authors did not seem to have paid much attention to (a) nature of litter, (b) altitude and (c) substratum of the two watersheds. I understood that the deciduous watershed was at higher altitude with hard rock below 40 cm whereas that of mixed was at lower height laden with soils upto or below 50 cm. Presumably the hard rock might have occurred deeper in the mixed watershed. The nature off litter (seasonally fallen parts of the trees) would be relatively freshly fallen in the deciduous watershed that could easily be broken/decomposed by physical/microbial activities that could leach more DOC or dissolvable OM. This fresh DOM can be easily be flushed by flowing water. The hard substratum and high altitude facilitate flow of water at higher speeds (as it cannot seep deep) in the deciduous wa-tershed than in the mixed watershed. The rapidly draining flood facilitates easy mixing of forest floor and soil solutions with surface runoff.
Although logical in their statement of "i) In the deciduous litter layer the leaves are overlapping and are partly impermeable which may cause more surface near flow (lines 23-25)" this does support their observation that 'a larger proportion of the DOC in runoff results from forest floor leachates at the deciduous (lines 17-18)'. If the top layer is impermeable how would one explain high DOC in runoff to have come from mixing with forest floor leachates? It is also possible for high DOC formation at the surface itself as the fresher litter is weathered or decomposed on the floor of the deciduous watershed.
Reply: *we agree with the last statement and our argumentation in the discussion has been modified for more clarity. Your comments have been incorporated in more detailed discussion. New text: 'As the deciduous watershed is located at a higher altitude the soils might be more shallow than at the mixed watershed which will add to the larger near surface flow paths'. and 'Faster decomposition of the deciduous litter leaches relatively more DOM and both factors result in higher DOC export fluxes at the deciduous than at the mixed watershed. Based on our data set of this study, one cannot quantify the relative importance of these factors for the differences between the watersheds'. See line 20-22 and line 23-26 on page 9.*

Page 9: Lines 2-8 – higher DOC/DON ratio at deciduous basin is possible when organic matter with less or no nitrogen but rich in carbon is weathered and is leached. Nitrogen compounds are perhaps enriched in litter or particulates. However, Fig 2 depicts lower PON than DON, in general in both watersheds, implying that nitrogen might be remaining with the deposited litter in the watersheds!
Reply: *we explained the larger DOC/DON ratios at the deciduous watershed in lines 14-16 on page 8. The mobilization of particulate organic matter is attributed to the erosion or river benches and no conclusion on N retention in litter is possible. See line 17-18 on page 10.*

Page 9: Statements in lines 11-13 (‘Substantial fluxes of NO3-N and the dominance of NO3-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)’) and lines 20-21 (‘Overall, it seems that a larger N uptake by the deciduous trees at the deciduous watershed could explain the differences in NO3-N fluxes’) are arbitrary and not supported by any data.
Reply: *true, the conclusion is speculative and that is why it is formulated as a suggestion. However, other reasons for the higher* NO_3 *fluxes at the coniferous site are not likely.*

Technical Comments Page 3: Lines 11 and 21 – Are the latitude and longitude positions accurate to the decimals mentioned?
Reply: *the positions of watershed at the weir have been corrected as 38°12´N, 128°11´E for the mixed watershed in Seohwa and 38°15´N, 128°7´E for the deciduous watershed in Haean. See line 19 on page 3 and line 1-2 on page 4.*

Page 3: Line 30: Does ‘throughfall’ refer to precipitation or rainwater?
Reply: *the sentence has been written as ‘Throughfall collectors (n=5) under the canopy were equipped with filters to prevent large particles from entering’. See line 12 on page 4.*

Page 4: Line 13 – define Oi, Oe and Oa.
Reply: *as mentioned earlier, the definitions of Oi, Oe and Oa have been added in line 28-29 on page 4.*

Page 4: Lines 26-27 – ‘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’. The storm events should be identified based on meteorological observations of wind and rainfall. However, one should keep in mind that the present study is made in summer monsoon. During monsoon season the rainfall may not be continuous on all days but with intermittent gaps (breaks) or spells of rain. I guess the authors are referring to these spells, or at the most the episodic rainfall events (which are normal during summer monsoon) of variable duration as ‘storms’. This requires authors clarification for what they meant by ‘storm’. This point, however, was rightly stated by the authors on page 8 line 4 – ‘four heavy rainfall events of the monsoon season at both watersheds’ but not elsewhere in the manuscript.
Reply: *as you suggested, the rainfall characteristic during monsoon has been referred as ‘During the monsoon season the rainfall was not continuous on all days but with intermittent gaps. The most lasting rainfall events were identified as storm events with more than a day interval between each storm event’. The term ‘rainfall’ has been used to explain ‘storms’ in the method part of this manuscript. See line 13-15 on page 5.*

Page 5: Lines 4 and 8 – (i) unmatched DOC and POC cutoff limits! (ii) 0.7 micron cutoff limit for POC is quite on higher side since most of the fine sized particulate materials are lost through the filter paper.
Reply: *we do not agree that the fraction from 0.45 to 0.7 micron represents most of the fine sized material. DOM is commonly defined as organic matter in water samples smaller than 0.45µm (Thurman, 1985). 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). Consequently, DOC and POC cutoff limits are unmatched as you pointed. However, prior tests (Doyle 2013) showed that materials between 0.45 and 0.7 µm comprised a minor fraction in*

total organic matter.

Therefore, we have made a comment on that in the methods section: new text: 'DOC and POC cutoff limits as 0.45 and 0.7 µm were unmatched in this study because of practical reasons and the unmatched fraction is considered negligible'. See line 2 on page 6.

-Thurman, E. M. (1985). Organic geochemistry of natural waters. Nordrecht, The Netherlands: Martinus Nijhoff/Junk Publisher.

-Bauer, J.E., and Bianchi, T.S. (2011). 5.02—dissolved organic carbon cycling and transformation. Treatise on estuarine and coastal science, 5, 7-67.

-Mostofa, K.M., Liu, C.Q., Minakata, D., Wu, F., Vione, D., Mottaleb, M.A., ... and Sakugawa, H. (2013). Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters. In Photobiogeochemistry of Organic Matter. Springer Berlin Heidelberg, 273-364

-Doyle, C. B. (2013). Contribution of bacterial cells to the fluorescence spectra of natural organic matter in freshwaters, University of North Carolina, master thesis.

Page 5: Line 6 – was nitrite in water analysed? It should be included in mineral-N.
Reply: *nitrite was not measured because it was negligible in soil solutions and runoff from test measurement. We have made a comment on that in the methods section: new text: 'Nitrite was not measured because concentrations were negligible in soil solutions and runoff'. See line 24-25 on page 5.*

Fig 2 – what are FPOC/FPON in Fig. 2f?
Reply: *technical comment: it has been changed to POC/PON in figure 3 on page 19.*

Fig. 3. Upper panel in the left column – DON and PON should be corrected to DOC and POC.
Reply: *technical comment: it has been corrected to DOC and POC in figure 4 on page 20.*

Figures 5 & 6: Alphabets (a, b: : :.) need to be explained in more detail. For instance what does it mean by ab or abcd. In the captions it is mentioned "Different alphabet letters indicate the significant difference between groups". I could not understand what is the difference and what are the groups mentioned.
Reply: *technical comment: the meaning of alphabets has been explained in detail as 'Statistically significant differences between sample types (throughfall, forest floor leachates, soil solution, and runoff) are indicated by different letters in the box plots, significance level of p<0.05'. See in caption of figure 6 and 7 on page 23 and 24, respectively.*

Fig. 6 – DTN is dissolved total nitrogen?
Reply: *technical comment: it has been changed to total dissolved nitrogen (TDN) in the manuscript.*

Anonymous Referee #1

Received and published: 26 June 2016

Lee et al. in this manuscript have tried to understand the effect of storm events on dissolved and particulate carbon and nitrogen in runoff from two different watersheds dominated with different species of vegetation. In general, study of this kind can provide an improved understanding of nutrients and material transfer from different terrestrial set up under monsoon condition. It is understandable that it requires a lot of effort to carry out study of this nature; it would have been better if there were more sampling events. Keeping aside the limitation in numbers of sampling events, the manuscript in present form is very poorly written with lots of mistakes in presentation of results and figures. I believe it is not suitable for publication in Biogeosciences. Below are some of my specific observations:

* Abstract does not clearly bring out the findings of the study. It merely describes the variability in results. I think they should modify it to include the processes involved for such observation.

Reply: *the abstract has been revised to highlight major findings, including watershed-specific differential storm responses of DOC vs. POC (PON) and DON vs. DIN. We already suggested differences in hydrologic flow paths as a major mechanism for the differential storm responses observed in the two watersheds. This proposed mechanism has been complemented with more detailed descriptions of the interplay between hydrology and species differences affecting litter and SOM chemistry. See the changes in line 17-27 in the abstract.*

* Introduction is poorly written with no focus. It wanders from one topic to other other without gravitating towards the focus of the work. The first line of the introduction itself appears confusing to me.

Reply: *the introduction has been extended with connections and references so that the focus of the paper became clearer. The first line of the introduction has been deleted. We have focused on three main topics: heavy rainfall effects, tree species effects and the relation among DOC, DON, DIN, POC, and PON.*

* One common observation throughout the manuscripts is regarding the references. I think it should be chronologically arranged.

Reply: *we followed manuscript preparation guidelines for authors in Biogeosciences webpage (source: http://www.biogeosciences.net/for_authors/manuscript_preparation.html), which regulate that 'In terms of in-text citations, the order can be based on relevance, as well as chronological or alphabetical listing, depending on the author's preference'.*

* Framing of the sentences from previous works is such that they appear as if they are from the present study (line 15-20).

Reply: *this sentence has been changed to 'Only few data are available on the partitioning of DON and PON fluxes in runoff from forested watersheds, like Inamdar et al. (2015)'. See line 20-22 on page 2.*

* Introduction last sentence: What is measuring campaign?

Reply: *technical comment: the term has been deleted. Also, the sentence has been simply written to '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 in South Korea during the 2013 monsoon season'. See line 4-7 on page 3.*

* How can annual air temperature range from 10 - 15 oC with -6oC in January and 26 oC in August?
Reply: *it has been clarified as 'The average annual temperature of the Lake Soyang watershed in western Gangwon-province is 11^{o}C with monthly average temperature ranging from -5^{o}C in January to 24^{o}C in August'. See line 11-13 on page 3.*

* Page 3: Line 20: '(deciduous watershed) (Figure 1)' should be replace with (deciduous watershed; Figure 1).
Reply: *technical comment: the format has been changed to '(mixed watershed; Figure 1) or '(deciduous watershed; Figure 1)'. See line 18 and 1 on page 3 and 4, respectively.*

Page 4: The text suddenly jumps to Oi and Oe+Oa layers without providing any context to it.
Reply: *the definition of horizons has been given: new text: '(Oi: slightly decomposed recognizable litter, Oe: moderately decomposed fragmented litter, Oa: highly decomposed humus material)'. See line 28-29 on page 4.*

Page 4: What do you mean by partly below detection limit. Please provide the number of samples or occasions when it went below detection limit.
Reply: *the detection limits were already stated in the text; line 11 on page 5. The new text in the methods section has been given as 'Concentrations less than detection limit were observed in 5-8% of the measurements in runoff during the July events'. See line 9 on page 5.*

* The authors mention the statistical methods followed for analysis but it hardly comes during discussion.
Reply: *the statistical significance was already mentioned for figure 6 and 7. See the caption of figure 6 and 7 on page 23 and 24.*

* Page 5: Line 25: Elaborate on the meaning of freeze drying the samples for mass spectrometric analysis or rephrase the sentence.
Reply: *the sentence has been changed to 'After filtration (0.45 µm, Whatman), water samples were freeze-dried to measure ^{13}C and ^{15}N isotope abundances of DOC and TDN…'. See line 14-15 on page 6.*
Water samples were freeze dried to measure isotope abundance because freeze drying is widely used as pre-treatment of water samples for isotope analysis (Lee et al. 2013, Lamber et al. 2014).

-J.-Y. Lee et al. (2013) Variation in carbon and nitrogen stable isotopes in POM and zooplankton in a deep reservoir and relationship to hydrological characteristics, Journal of Freshwater Ecology, 28(1):47–62.

- Lambert T. et al. (2014) DOC sources and DOC transport pathways in a small headwater catchment as revealed by carbon isotope fluctuation during storm events. Biogeosciences, 11:3043-3056.

* Should not mineral N include nitrite?
Reply: *nitrite was not measured because it was negligible in soil solutions and runoff from test measurement. We have made a comment on that in the methods section: new text: 'Nitrite was not measured because concentrations were negligible in soil solutions and runoff'. See line 24-25 on page 5.*

* Authors state that 'the soil _13C and soil_15N values significantly increased with soil depth from -29 to -24‰

and from 0 to 8‰ respectively". However, it would be nice to see the vertical profiles of such data. Was the surface _15N always near 0 ‰
Reply: *New figure of soil profiles of ^{13}C and ^{15}N isotope abundance has been added. See new figure 2 on page 18*

* I could not make the sense out of the sentence 'In the study period, the highest precipitation coincided with the maximum precipitation intensity, the highest precipitation intensity and the maximum discharge at the 10 mixed watershed and at the deciduous watershed on July 14th, 2013"
Reply: *technical comment: this sentence has been deleted*.

* While the difference in DOC concentrations with discharge between deciduous and mixed watershed appears to be convincing (Fig 2a), the POC and PON increase with discharge relies heavily on one data point from high discharge. I do not doubt the increase but I believe that to make unequivocal conclusion more points would have been an asset.
Reply: *the discussion was changed. The "threshold" interpretation has been weakened. See the discussion section 4.3 on page 10.*

* Please rephrase the sentence "The fluxes of DOC and NO3-N increased with a much steeper slope at the deciduous and at the mixed watershed, respectively".
Reply: *the sentence was rephrased as 'The DOC fluxes at the deciduous watershed increased with a much steeper slope in response to discharge than at the mixed, while the NO_3-N fluxes at the mixed watershed more steeply increased with increasing discharge than at the deciduous'. See line 21-23 on page 7.*

* There is problem with the symbols and its representation in Figure 3. I think authors should be careful with these kinds of mistakes before submitting their manuscript for review. It is very tiring to review a manuscript with these kinds of mistakes.
Reply: *sorry for the confusion: the mistakes have been corrected in the new figure.*

* Result section discussing Chemical properties of DOM and POM in runoff should be modified with proper emphasis on isotopic data. At present the isotopic data has just been mentioned as passing comment.
Reply: *we have descried the isotopic signatures in the result section: new text: 'Also, the ^{13}C data in runoff, being more negative at the deciduous watershed, point to a larger proportion of forest floor leachates in runoff than at the coniferous watershed'. See line 23-13 on page 8.*

* In the discussion, authors have admitted that the numbers of events are rather low in the study and observations made by them have already been observed before by Dhillon and Inamdar (2013). I am wondering what novel finding they are discussing which warrants publication in a journal like Biogeosciences.
Reply: *Most of previous studies focused on the fluxes of organic matter at one watershed for one year or more. In our case, the novelty lies in comparing differential storm responses of DOC/DON and POC/PON with a particular reference to watershed properties and storm response patterns*.

* Discussion section needs to be re-written with proper emphasis on the major findings

C3 from this work. The mechanisms and processes behind the differences in observation need to be discussed properly. The effect of altitude, nature of littler and specific nature of the two watersheds needs to be take in account.
Reply: in t*he discussion, we have addressed other watershed characteristics as you suggested (altitude, nature of litters and specific nature of the two watersheds) for example, v) As the deciduous watershed is located at a higher altitude the soils might be more shallow than at the mixed watershed which will add to the larger near surface flow paths. vi) Faster decomposition of the deciduous litter leaches relatively more DOM and both factors result in higher DOC export fluxes at the deciduous than at the mixed watershed. Based on our data set of this study, one cannot quantify the relative importance of these factors for the differences between the watersheds'. See line 20-26 on page 9.*

*Fig 2: What are FPOC/FPON?
Reply: *technical comment: it has been changed to POC/PON in figure 3 on page 19.*

Fig 5: A succinct Fig 5 will be better.

Reply: The design of the figure has been changed, especially 1) the compartments at the y axis are rearranged downwards. 2) the x axis description is only once to the two graphs 3) PLF/FLF in figure 5 is removed. See new figure 6 and

Changes in fluxes of dissolved and particulate carbon and nitrogen from two watersheds of different tree species during intense storm events

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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 pointing to changing flow paths from deeper to upper soil layers at high discharge, whereas nonlinear responses of POC and PON fluxes were observed likely due to the origin of particulate matter from the erosion of mineral soil along the stream benches. 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 of 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}). The latter suggests a larger N uptake by deciduous trees. Cumulative fluxes of POC and PON were similar at both watersheds. Quality parameters of organic matter in soils and runoff indicate 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 particulate and dissolved C and N in runoff to storm events as a combined effect of tree species composition and watershed specific flow paths.

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

1 Introduction

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 (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).

In case of organic N export, 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, like Inamdar et al. (2015). They reported that particulate N composed 39-87% of the storm event N export. 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 weak relationships were found (Singh et al., 2015).

Considering an effect of watershed characteristic, tree species might influence the export of DOM 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). Amiotte-Suchet et al. (2007) found higher annual DOC concentrations and fluxes in runoff at a deciduous forested watershed than at a watershed dominated by coniferous species.

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. Understanding the influence of both drivers is needed for a better prediction of 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 in South Korea during the 2013 monsoon season.

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). The average annual temperature of the Lake Soyang watershed in western Gangwon-province is 11^{o}C with monthly average temperature ranging from -5^{o}C in January to 24^{o}C in August (Korean meteorological administration). Annual precipitation ranges from 1200 to 1500 mm and the summer monsoon usually accounts for 50 to 60% of the annual precipitation (Park et al., 2010; Seo et al., 2011). Korean mountainous forests are mostly composed of deciduous forests representing 47% of the total forested area (38% coniferous forest, 12% mixed coniferous and deciduous forest) 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 (38°12´N, 128°11´E, 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 slope direction of the coniferous part at the mixed watershed is towards the MD plot. Lateral flow from the coniferous part to the MD plot can only influence deeper soil solution characteristics as near surface flow was never observed. Our data (see results) indicate significant quality differences of soil solutions between the MD and MC plots which suggest only a minor influence on soil solution chemistry at the MD plot from lateral flows. Furthermore, the quality parameters of soil solutions at the MD plot were similar to those of the DD plot, the latter being not influenced by lateral flows from coniferous sites. Thus, it is unlikely that the MC plot did affect the MD plot.

The deciduous forested watershed (deciduous watershed; Figure 1) is located in Haean, the Gangwon province (38°15´N, 128°7´E, 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 average age of trees in the two watersheds is about 35 years. 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) under the canopy 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.

Before storm events in June 2013, throughfall, forest floor leachate and soil solution were collected at about weekly intervals, and runoff samples were collected 2-3 times per week. During storm events in July 2013, throughfall, forest floor leachate and soil solution was collected after each storm event so that these samples represent cumulative water samples during the entire storm event. In case of runoff, samples were taken in July 2013 at the weir using automatic collectors (6712 Portable Sampler, Teledyne Isco Inc., Lincoln, NE, USA) before, during, and after each rain event at intervals of 1 or 2 h. Discharge at the outlet of the watersheds was measured by a v-notch weir. During routine runoff sampling, water temperature, pH and electrical conductivity was measured in situ. Water samples were cooled at 4^{o}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.

Precipitation data (total and hour unit; Table 2) at the study area were used from the automatic weather station of the Korean meteorological administration at the point ‘Seohwa 594’ and ‘Haean 518’ for the mixed watershed and for the deciduous watershed, respectively. Those data were also comparable to our from bulk precipitation measurements at the field sites.

2.2.2 Soil sampling

The total stock of organic horizons (Oi: slightly decomposed recognizable litter, Oe: moderately decomposed fragmented litter, Oa: highly decomposed humic material) was collected at each plot in a 20 × 20 cm frame with 10 replicates. The average thickness of Oi and Oe+Oa was 1.2 and 1.5 cm at the MC plot, 2.5 and 3 cm at the MD plot, and 2.3 and 2 cm at the

DD plot, respectively. 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 deeper 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

In June 2013, before the monsoon storm events, 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. Concentrations less than detection limit were observed in 5-8% of the measurements in runoff during the July events. The detection limits were applied to the calculation of 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 the corresponding discharge. During the monsoon season the rainfall was not continuous on all days but with intermittent gaps. The most lasting rainfall events were identified as storm events 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 assured, the Holm-Sidak Test was used for both pairwise comparisons and comparisons versus a control group. When the normality 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 total dissolved nitrogen (TDN) in water samples were measured by a total organic carbon analyzer (TOC-CPH, Shimadzu, Japan). 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 (FIA-LAB; MLE, Dresden, Germany). Nitrite was not measured because concentrations were negligible in soil solutions and runoff.

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). DOC and POC cutoff limits as 0.45 and 0.7 µm were unmatched in this study because of practical reasons and the unmatched fraction is considered negligible.

The absorption spectra of DOM were obtained at wavelengths from 200 to 600 nm using a UV-visible spectrophotometer (DR5000, HACH). 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-55, Perkin-Elmer, USA) 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), water samples were freeze-dried to measure ^{13}C and ^{15}N isotope abundances of DOC and TDN 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 morphology of the organic layers at the MC, MD, and DD plots were similar, representing a moder-like organic layer, with distinct Oi-layers and less distinct Oe and Oa-layers. However, the depth of O-layer in the MC plot (ca. 3 cm) was thinner than in the MD and DD plot (ca. 4-5 cm). The typical soil type at both watersheds is 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 (Figure 2).

The average discharge in June 2013 before storm events was 0.03 mm h^{-1} at the mixed watershed and 0.06 mm h^{-1} at the deciduous watershed (data not shown). The total amount of precipitation in July was slightly higher at the deciduous watershed (367 mm) than at the mixed watershed (313 mm; Table 2). Also, the intensity of precipitation in July was larger at the deciduous watershed than at the mixed watershed. Similar to precipitation data, the mixed watershed had less maximum discharge and also slightly lower discharge before start of a storm event than the deciduous watershed.

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 3a). In contrast, the DON concentrations in runoff from both watersheds were independent of discharge (Figure 3b). The highest concentration of DOC and DON in runoff was observed during the earlier storm events (Table 2). The NH_4-N concentrations were at any time negligible (< 0.05 mg N L^{-1}).

At discharges from ~1 to 9 mm h^{-1}, higher concentrations of POC and PON in runoff were found (Figure 3d,e). For example, the POC concentration in runoff from the mixed watershed was as high as 10.7 mg C L^{-1} at the largest discharge of 9 mm h^{-1}. At the deciduous watershed, the POC concentration in runoff reached a maximum of 8.6 mg C L^{-1} already at 3 mm h^{-1} discharge during the first storm event (Figure 3d, Table 2). 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 3a). No hysteretic loops were observed for DON, POC and PON (Figure 3b,d,e).

The DOC/DON ratio in runoff ranged from 5 to 60 (Figure 3c). The DON concentrations lower than 0.05 mg N L^{-1} were not considered for calculation of the DOC/DON ratios. In response to increased discharge, the DOC/DON ratios were stable at the mixed watershed, while there was a tendency for increasing in the 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 the DOC/DON ratio, the POC/PON ratio ranged narrowly from 10 to 20 at both watersheds (Figure 3f) 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 4). The DOC fluxes at the deciduous watershed increased with a much steeper slope in response to discharge than at the mixed, while the NO_3-N fluxes at the mixed watershed more steeply increased with increasing discharge than at the deciduous. The POC fluxes were generally much lower than the DOC fluxes, but the POC and PON fluxes increased in a non-linear response to discharge. Only 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 the PON and DON fluxes. At the deciduous watershed, only one event caused slightly larger POC than DOC fluxes.

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. The NO_3-N fluxes as the dominant N flux form represented 93% and 82% of the total N flux in runoff at the mixed and the deciduous watershed, respectively. The cumulative fluxes of NO_3-N were about twice as high (5.2 kg N ha^{-1}) at the mixed watershed than at the deciduous watershed (2.9 kg N ha^{-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 5). At the deciduous watershed, $SUVA_{280}$ and HIXem increased with increased discharge, while PLF/FLF, PLF/HLF, $\delta^{13}C_{DOC}$ and $\delta^{15}N_{TDN}$ 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 and PLF/HLF in runoff corresponded more to those in forest floor percolates (Figure 6). In contrast, at the deciduous watershed, these parameters in runoff were closely related to the quality of forest floor leachates. Also, the ^{13}C data in runoff, being more negative at the deciduous watershed, point to a larger proportion of forest floor leachates in runoff than at the coniferous watershed.

The patterns of DOC/DON ratios in response to discharge were also different at the two watersheds (Figure 3c). Large DOC/DON ratios at high discharge at the deciduous watershed resulted from the positive response of DOC concentration and the stable DON concentration to discharge. The DOC/DON ratios at the coniferous watershed were stable in response to discharge.

The range of the POC/PON ratio in runoff was similar to that of the POC/PON ratio of mineral soil layers at both watersheds (Figure 7). 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.

4 Discussion

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

We intensively sampled 4 heavy rainfall events during the monsoon season, the events representing a substantial proportion of the annual precipitation in the region. While the number of events was rather small, consistent patters emerged documenting the response of N and C fluxes to precipitation and discharge changes. The increase of DOC concentrations and fluxes in runoff induced by heavy storm events with increased 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. Similar to our results, larger annual DOC fluxes at a deciduous forested catchment than at a mixed coniferous catchment were reported by Amiotte-Suchet et al. (2007).

The different response of DOM to discharge between the two watersheds, such as the large response of runoff DOC concentration to discharge at the deciduous watershed (Figure 3a) and the significant change in runoff DOC quality parameters (Figure 5), are likely caused by a shift of hydrological flow paths to more surficial layers at the deciduous watershed. Also, the comparison of DOC quality parameters in runoff with those in forest floor leachates and soil solution at the deciduous watershed (Figure 6) indicated that a larger proportion of the DOC in runoff from forest floor leachates at the deciduous. Previous studies have also reported a positive relationships between discharge and DOM concentrations in runoff as a consequence of 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 several watershed characteristics (slope and soil textures) and the precipitation regime at both watersheds were similar, 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 partly impermeable, which may cause more surface near flow than in coniferous litter layers with relatively large pore spaces in between needles. 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. 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 $\mu S\ cm^{-1}$) than at the DD plot (pH 6.1±0.2, 10.3±6.3 $\mu S\ cm^{-1}$) and the MD plot (pH 5.8±0.4, 9.0±6.3 $\mu S\ cm^{-1}$). Acidity and ionic strength are negatively related to DOC release from soils (Clark et al., 2011; Michalzik et al., 2001; Moldan et al., 2012). iv) In stream generation of DOC from litter might be involved (Johnson et al., 2006) if more leaf than needle litter enters the stream. v) As the deciduous watershed is located at a higher altitude the soils might generally be shallower than at the mixed watershed, which will add to the larger near surface flow paths under high precipitation. vi) Faster decomposition of the deciduous litter leaches relatively more DOM resulting in higher DOC export fluxes at the deciduous than at the mixed watershed. Based on our data set of this study, one cannot quantify the relative importance of these factors causing the differences between the watersheds.

4.2 Organic and inorganic nitrogen in runoff

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 flux 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 the 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 exceeded their dissolved fractions only for short time during heavy storm events with more than 100 mm precipitation except one storm event at the deciduous watershed on 2013 July 14 (Table 2). Previous studies in the nearby region considered 100 mm precipitation as a threshold that would induce large POC fluxes (Jeong et al., 2012; Jung et al., 2012). Our finding indicates that POM fluxes from forested watershed are unlikely regulated solely by precipitation amount, but slope and river bench characteristics will interfere. The small proportion of particulate fluxes in our study seems to be mainly caused by the relatively moderate precipitation events during the study period. 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 watershed 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 heavy precipitation events and vegetation cover for the export fluxes of particulate and dissolved organic C and N with runoff from forested watersheds. Our results suggest that changes of the precipitation regime, with more severe monsoon storms in the future as predicted, will increase the export of dissolved and particulate organic matter from these watersheds. 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 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.

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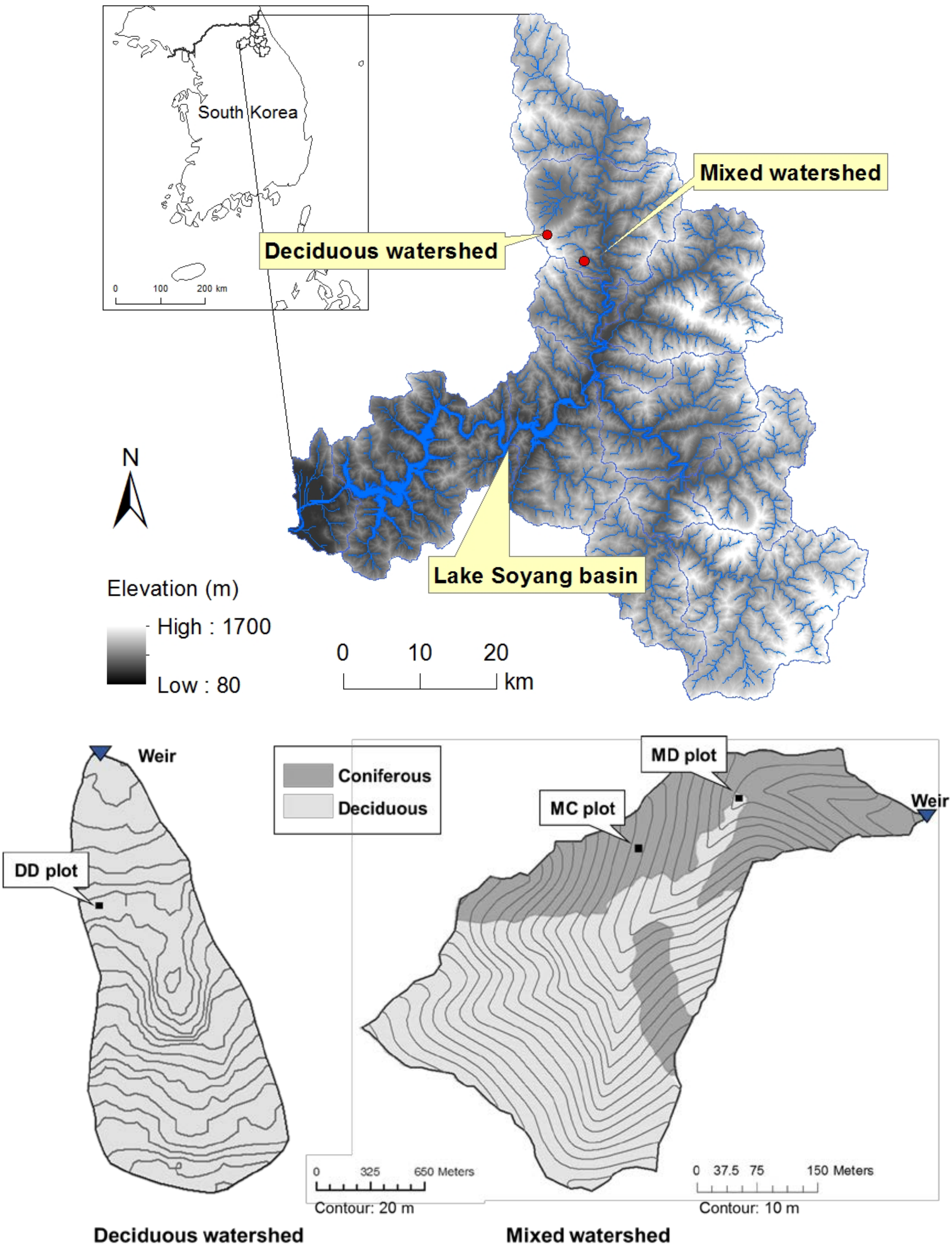


Figure 1: Location and tree species composition of the two studied forested watersheds. Lake Soyang map was modified from Jung et al. (2015).

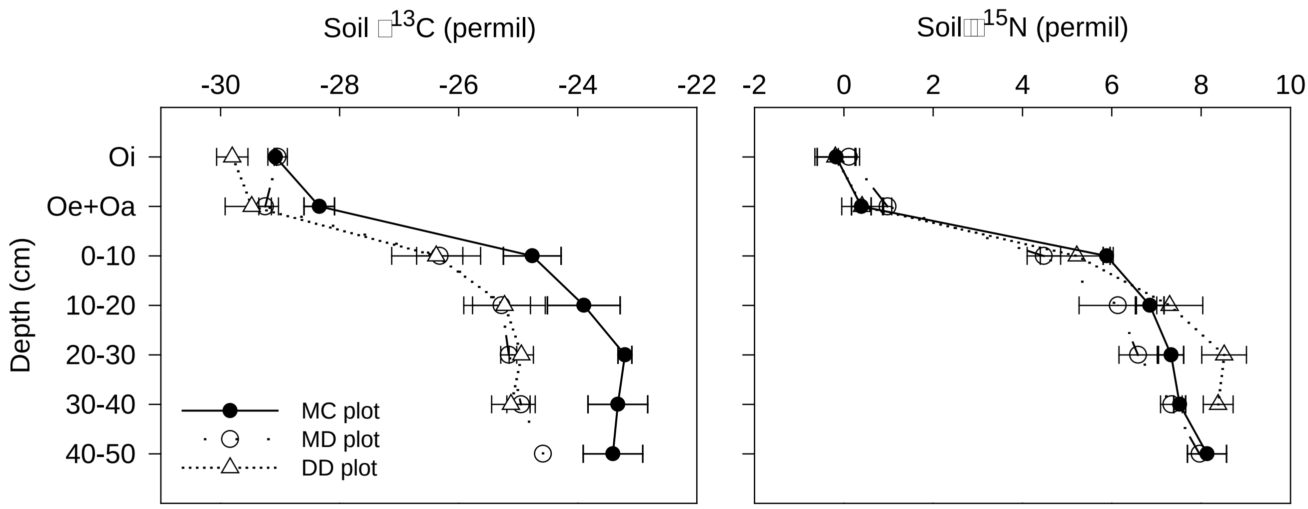


Figure 2: Soil profiles of ^{13}C and ^{15}N isotope abundance at the MC, MD, and DD plot. Error bars represent standard deviation (n=3).

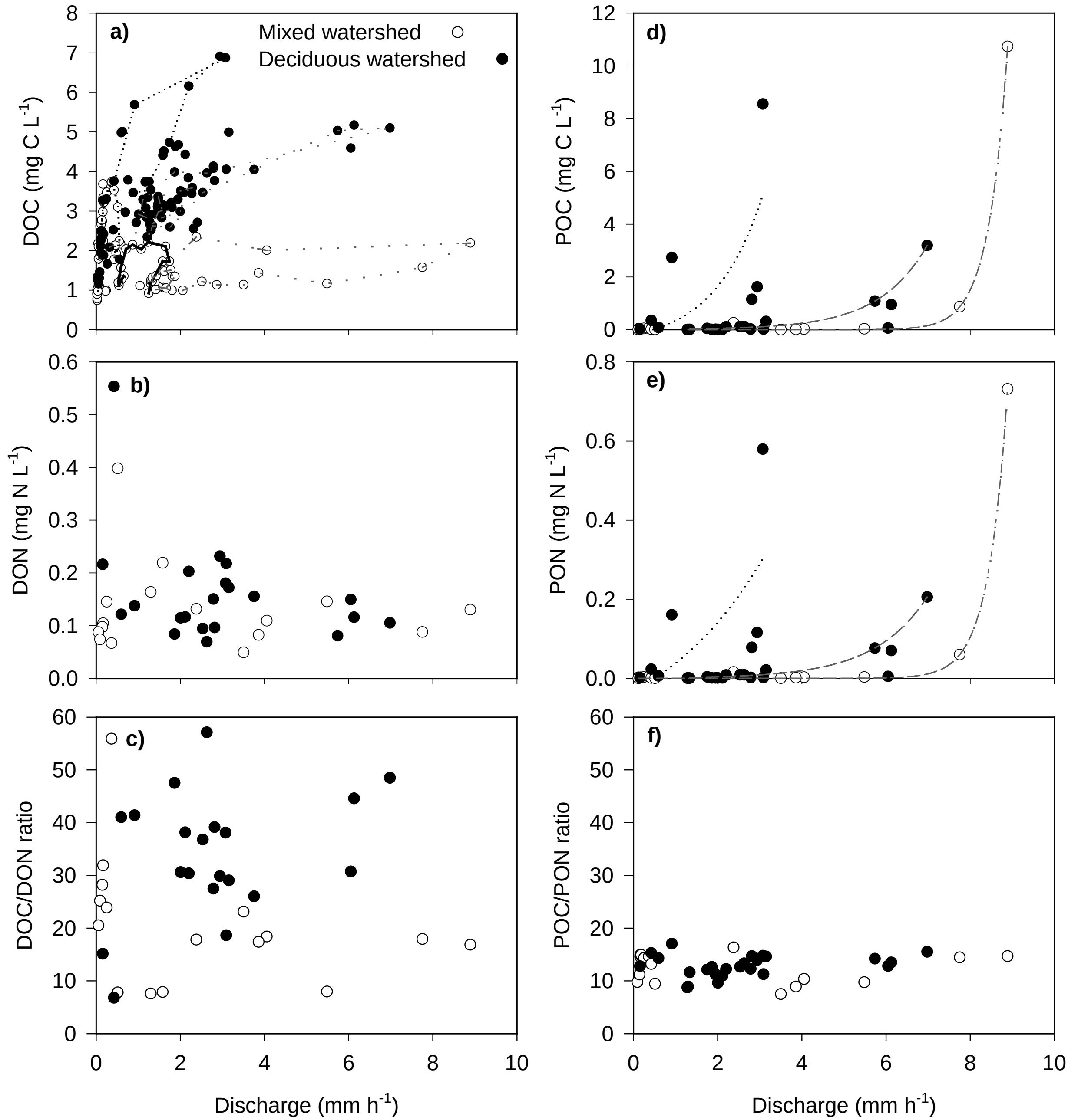


Figure 3: Concentrations of a) dissolved organic carbon (DOC) and b) nitrogen (DON), d) particulate organic carbon (POC) and e) nitrogen (PON) and the ratios of c) DOC/DON and f) POC/PON in runoff with discharge during monsoon storm events. Doted, solid and dashed lines correspond to the storm event of July 8th 2013, July 11th 2013 and July 14th 2013, respectively.

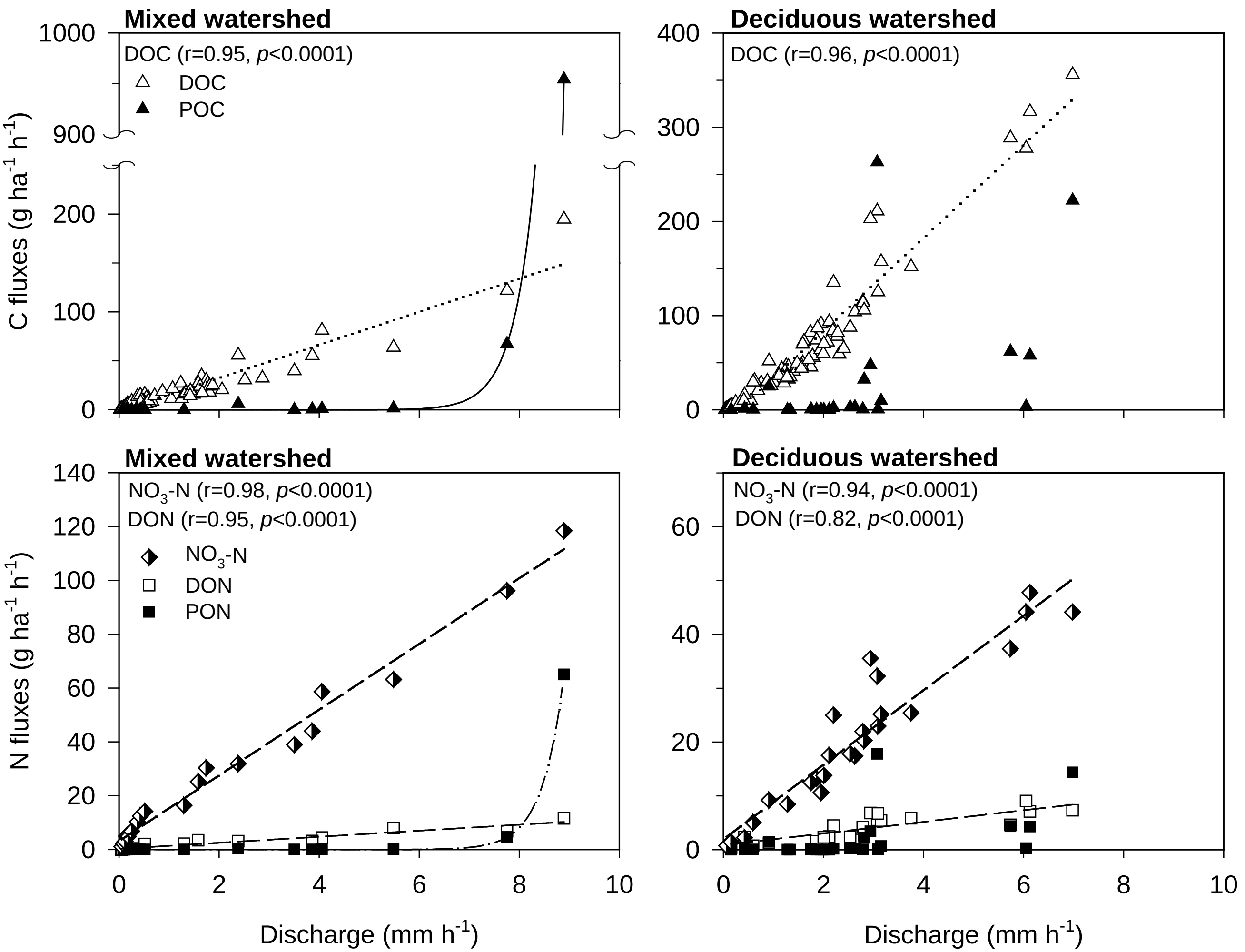


Figure 4: Fluxes of carbon (dissolved organic carbon (DOC) and particulate organic carbon (POC) and nitrogen (dissolved organic nitrogen (DON), and particulate organic nitrogen (PON) and nitrate (NO_3-N) in runoff with discharge during monsoon storm events.

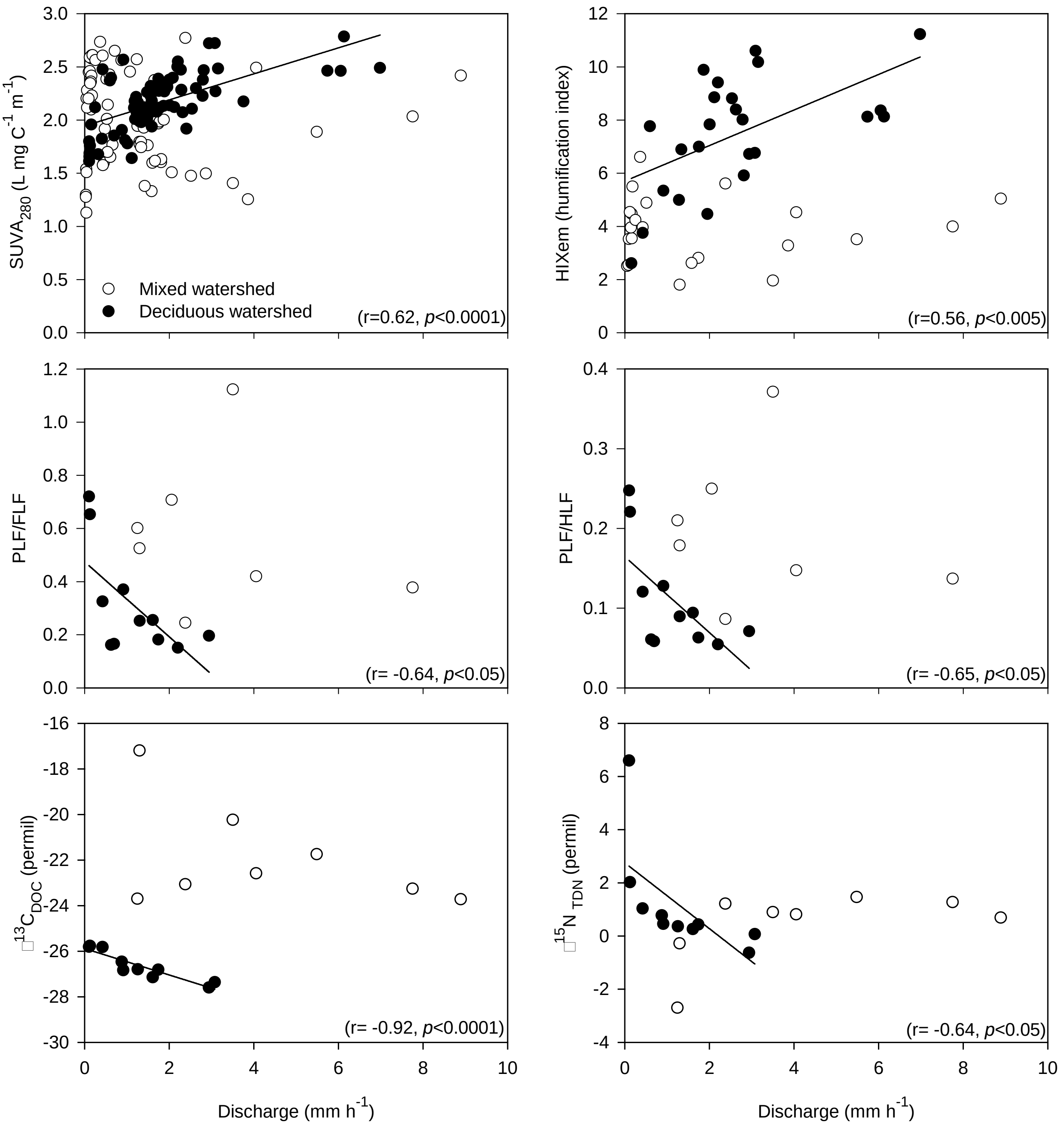
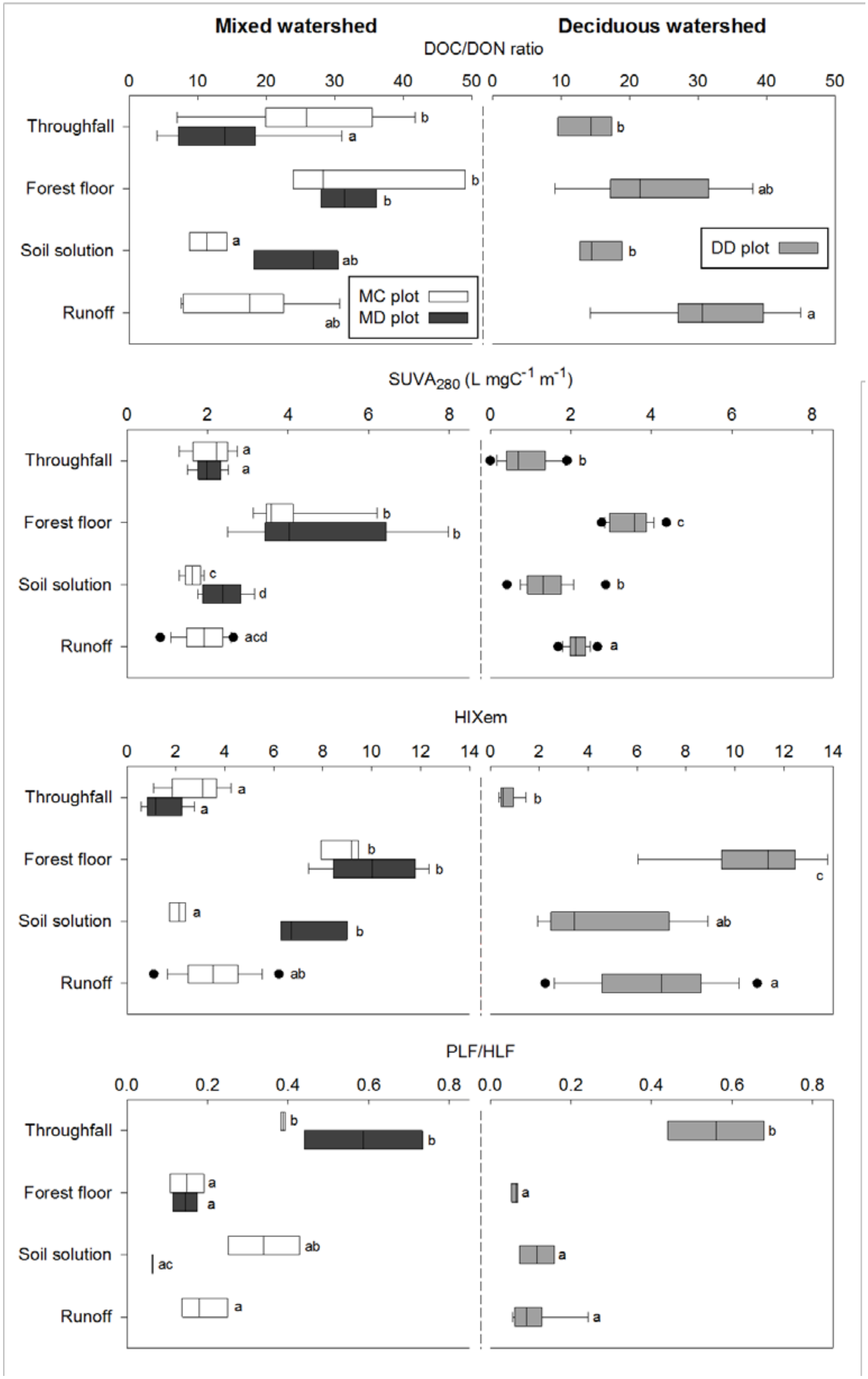


Figure 5: Specific ultraviolet absorbance ($SUVA_{280}$), humification index (HIXem), protein-like fluorescence/humic-like fluorescence (PLF/HLF), protein-like fluorescence/fulvic-like fluorescence (PLF/FLF), ^{13}C isotope abundance of dissolved organic carbon ($\delta^{13}C_{DOC}$) and ^{15}N isotope abundance of total dissolved nitrogen ($\delta^{15}N_{TDN}$) in runoff with discharge during monsoon storm events. Only significant regressions are shown.



Mixed watershed
Deciduous watershed
DOC/DON ratio
Throughfall
Forest floor
Soil solution
Runoff
MC plot
MD plot
DD plot
SUVA280 (L mgC-1 m-1)
HIXem
PLF/HLF

Figure 6: Range of dissolved organic carbon and nitrogen ratio (DOC/DON ratio), specific ultraviolet absorbance ($SUVA_{280}$), humification index (HIXem), and protein-like fluorescence/humic-like fluorescence (PLF/HLF) of throughfall, forest floor leachates, soil solutions, and runoff during monsoon storm events. Box plots display minimum, lower quartile, median, upper quartile, maximum and outliers. Statistically significant differences between sample types (throughfall, forest floor leachates, soil solution, and runoff) are indicated by different letters in the box plots, significance level of p<0.05.

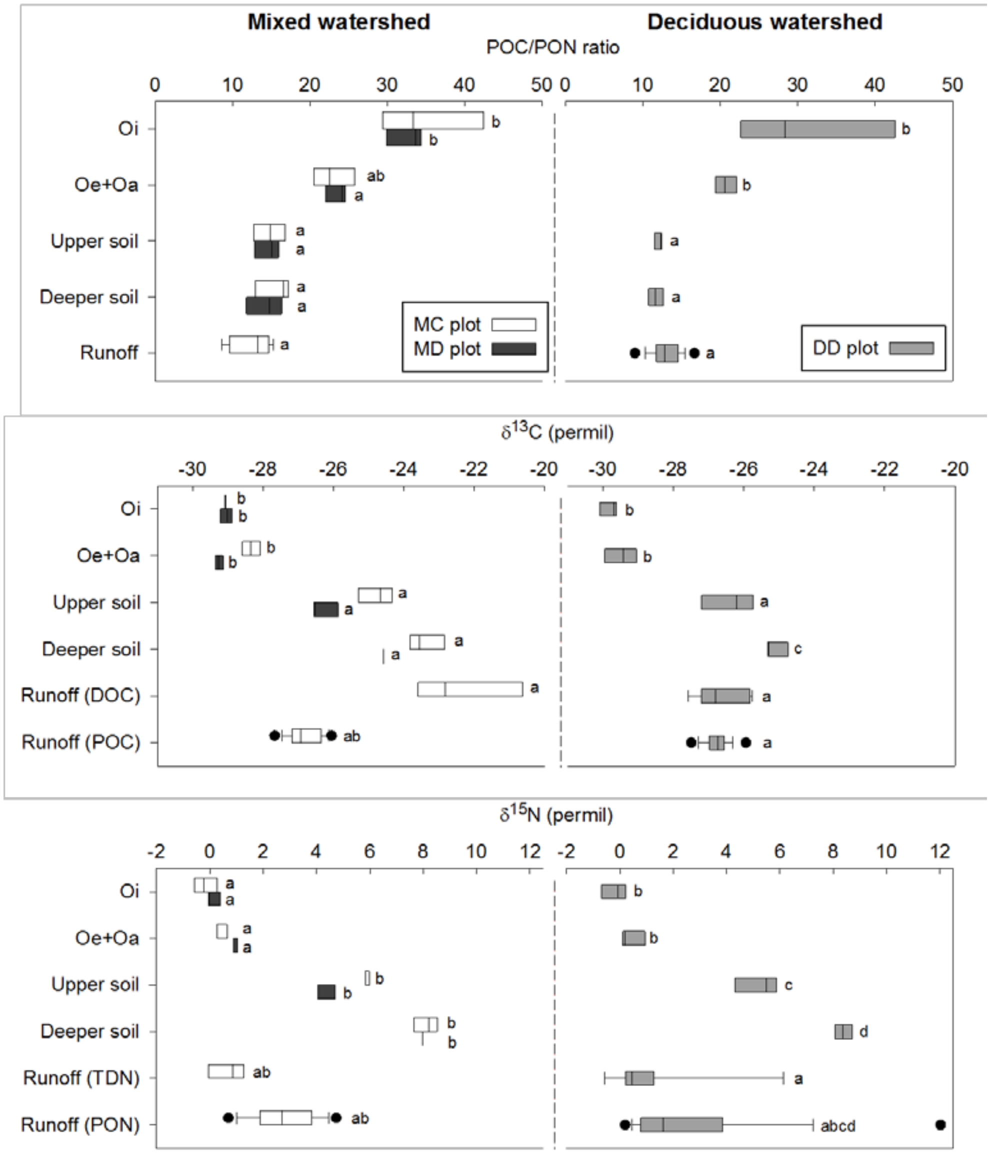


Figure 7: Range of particulate organic carbon and nitrogen ratio (POC/PON ratio), $\delta^{13}C$ and $\delta^{15}N$ in Oi, Oe+Oa, upper soil (0-10 cm depth), deeper soil (40-50 cm depth at the MC and MD plot, 30-40 cm depth at the DD plot), and runoff. Box plots display minimum, lower quartile, median, upper quartile, maximum and outliers. Statistically significant differences between sample types (throughfall, forest floor leachates, soil solution, and runoff) are indicated by different letters in the box plots, significance level of $p<0.05$.

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		(Total 15.6)	27.9	368-682
Coniferous	Larch and Pine	6.1		
Deciduous	Walnut, Maple, Oak, Lime, Elm	9.5		
Deciduous	Walnut, Maple, Oak, Ash	39	24.0	586-1005

a.s.l.: above sea level

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 precipitation intensity	Average precipitation 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	2.3	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	4.2	8.89	1.21	2.4	0.2	10.7	0.730
					(total 313.5)	(avg. 16)	(avg. 3.2)	(avg.2.8)	(avg. 0.45)				
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	3.5	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
					(total 367.5)	(avg. 20)	(avg. 4.1)	(avg. 5.1)	(avg. 0.52)				

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