

*This file contains the responses to Referee #1 and #2.*

Dear Referee#1,

Thank you for your comments. We have responded to your general and detailed comments for the manuscript entitled “Importance of within-lake processes in affecting the dynamics of dissolved organic carbon and dissolved organic and inorganic nitrogen in an Adirondack forested lake/watershed”.

Included in this communication are our comments and tables with responses.

Please, let me know if you require anything else regarding this revision.

Sincerely yours,

Phil-Goo Kang

## 1. Responses to general comments.

**#A. (Referee's comment)** This paper describes long-term data series of dissolved organic carbon (DOC, years 1984-2009) and dissolved organic and inorganic nitrogen (DON and DIN, years 1994-2009) concentrations, and comparison of calculated mass balances (2000-2009) of these species between in- and outlets of a lake belonging to the Adirondack Long-term Monitoring Program. Data seems to be of high quality, rather frequent, and continuous. Input-output comparison based on concentrations measured on weekly basis. Authors found that the lake is sink of DOC and DIN (retention), but varying between a small sink or source of DON. No long-term trends were found in concentrations or input or output fluxes. The data may be valuable to document even though no long-term changes in flux patterns were seen.

==> Thanks for your comments. This is consistent with the focus of this paper.

**#B. (Referee's comment)** However, the within-lake processes determining the output to input ratio were only discussed on literature basis.

==> There are several ways to estimate unknown specific processes, e.g., direct measurements, modeling, statistical analysis, etc. In this paper, we combined results obtained from previous studies with new measurements to help evaluate within-lake processes.

**#C. (Referee's comment)** I let the editors decide whether the Biogeosciences could be the forum for this paper. The manuscript would benefit from a revision.

==> You will note that we have completed a number of changes in the manuscript that should improve the clarity and importance of the findings of our study.

**#D. (Referee's comment)** Inorganic carbon was not included nor much discussed in this study, opposite to inorganic nitrogen. However it could have significant role when pondering the meaning of lake as a DOC sink. Many lakes are known to emit substantial amounts of carbon as CO<sub>2</sub> to the atmosphere.

==> As we mentioned in Introduction and Conclusion, many studies have focused on DOC but few have also included evaluation of DON. Also the end product of DOC due to retention/decomposition is certainly DIC. Due to length considerations we did not focus on DIC dynamics. The evaluation of DIC would necessitate a different set of analyses and goals. The DIC of Arbutus Lake has a mean of ~115  $\mu\text{mol C L}^{-1}$  and DIC ranges from ~50 to 250  $\mu\text{mol C L}^{-1}$ . DIC constitutes about 25% of total dissolved carbon. The reviewer is correct. Across the ALTM lakes they are uniformly oversaturated with respect to the solubility of atmospheric CO<sub>2</sub>. This was summarized in another paper for Adirondack lakes, which included Arbutus Lake (Fakhraei and Driscoll, 2015). For further details see: The Adirondack Long-Term Monitoring Lakes: A Compendium of Site Descriptions, Recent Chemistry and Selected Research Information. 2011. NYSERDA Report 11-12. Albany, NY, USA.

We added paragraphs about DIC in the end of Introduction and Discussion.

**#E. (Referee's comment)** I am also concerned how relevant some of the statistical testing was, particularly if not testing a hypothesis. Therefore hypothesis formulation and modification of the

text (introduction, discussion) accordingly could improve the readability and make the text more interesting.

==> We have added more details on specific hypotheses. Regarding modification of the text the editor's comments will be helpful in revising the paper.

For example, we added in the Introduction:

“We hypothesized that both monthly and yearly changes of DOC and DON within the Lake differ due to the relative importance of different internal processes between these two solutes, i.e., DOC is decomposed to dissolved inorganic carbon (DIC) which may be released to the atmosphere as carbon dioxide or retained as DIC in the lake, while DON is decomposed to DIN which may be utilized by a range of biotic processes including uptake, denitrification, etc.”

Also, we added supportive statement in the 2.3 Calculation in the Methods

**#F. (Referee's comment)** I feel that the paper is lengthy relative to its content, but cannot give exact advice how to organize it.

==> Overall we reduced a length of the manuscript. We removed one table and three figures and created one table (As a result, three figures were deleted). On the other hand, some of the comments by the editor and the referees ask for additional information that we added in the manuscript. We feel that we have considered the balance between length, information covered and detailed.

## 2. Responses to detailed comments

### #2.1

(Referee's comments) Abstract l. 5. in aquatic systems?

(Revision) **Accepted**

Original version: dissolved inorganic nitrogen (DIN) in the Arbutus Lake Watershed to evaluate how

Modified version: dissolved inorganic nitrogen (DIN) in aquatic ecosystems of the Arbutus Lake Watershed to evaluate how

(Page/line) 17287/5

### #2.2

(Referee's comments) Abstract l. 7. be more specific.

(Revision) **Accepted**

Original: how a lake nested in a forested watershed affects the dynamics of DOC and DON

Modified: how a lake nested in a forested watershed affects the source (i.e., production) and sinks (i.e., retention) of DOC and DON

(Page/line) 17287/7

### #2.3

(Referee's comments) P. 17291, l. 24. Delete palustrine

(Revision) **Accepted**

Original: The wetland, a palustrine peatland (Greenwood Mucky peats)

Modified: The wetland (Greenwood Mucky peats)

(Page/line) 17291/24

#2.4

(Referee's comments) Could you give dominant vegetation also for the peatland?

(Revision) **Accepted(added)**

Speckled Alder (*Alnus incana* ssp. *rugosa*) is the dominant vegetation in the wetland (Bischoff et al., 2001).

(Page/line) 17297/25

#2.5

(Referee's comments) P. 17292, chapters 2.2, 2.3. 2.4 could be combined. ALTM in the heading is not very informative.

(Revision) **Accepted**

Three subsections have been combined as recommended.

Original:

2.2 Hydrological data

2.3 ALTM measurements of DOC

2.4 Chemistry data collected by SUNY-ESF

Modified:

2.2 Hydrological and chemistry data

(Page/line) 17292

#2.6

(Referee's comments) p. 17293, l. 12. How many inlets there are in total or do you mean here some other water and matter input routes? Unclear.

(Revision) (**Comments**) The inlet site is a major source of water to the Lake. Please see p17291.

L15. There are less important ephemeral water sources that we assumed have the same chemistry of the major lake inlet. We provided this information in the statement of L12 in p17293.

#2.7

(Referee's comments) p. 17294. l. 22. Why the monthly discharge-weighted concentrations were tested? See my general comments.

(Revision) (**Comments**) This statistical analysis is linked to Figure 5.

Since we used weekly samples, in order to evaluate monthly variation of DOC, DON, and DIN in the inlet and outlet, respectively, we analyzed discharged-weighted concentrations.

Also we added statements in 2.3 Calculation in the Methods to address the usage of the discharge-weighted concentration.

#2.8

(Referee's comments) p. 17297, l. 5-10, move to the discussion

(Revision) **Accepted (changed)**

We moved the sentence that you pointed out to the Discussion to replace other sentence (p17304, l. 7 to 9).

Original: The decrease of the molar C:N ratio from the inlet (mean: 55) to the outlet (mean: 40) is consistent with the pattern for other studies of Adirondack Lakes (Ito et al., 2005, 2007).

Modified: The pattern of decreasing C:N ratios in our study with an inlet value of 55 and an

outlet value of 40 is consistent with previous studies of Adirondack Lakes (including Arbutus Lake) (Ito et al., 2005, 2007) and lakes in other regions of the world (Kopáček et al., 2003; Schindler et al., 1992; Wetzel, 2001).

(Page/line) P17304/7-9

#2.9

(Referee's comments) P. 173021, l. 10-15. Discuss what is the fate of decomposition end products and how much actually is retained in the lake?

(Revision) As stated previously for our study we wanted to focus on DOC, DON and DIN. Our paper is one of the few papers that includes analyses of DOC, DIN and DON for a lake/watershed system. Note DOC has received more attention than DON in the evaluation of DOM (Please see the last sentence in Conclusions).

All ALTM lakes are oversaturated with respect to the solubility of atmospheric CO<sub>2</sub>. This was summarized in another study for this group of Adirondack lakes, which include Arbutus (Fakhraei and Driscoll, 2015).

We added a paragraph in the end of the Discussion. Also, we added the retention amounts in the Table 4 to address how much is retained in the lake.

#2.10

(Referee's comments) Table 1. "with r value 0.5 or greater"

(Revision) ***Partly accepted***

In the first sentence in the title, the abbreviation of "r" is the correlation coefficient and we wanted to focus on those results with relatively high "r" values.

Original: Note that correlation results with 0.5 or greater in monthly analysis are shown.

Modified: Note that r values with 0.5 or greater in monthly analysis are shown to emphasize the most important correlations.

#2.11

(Referee's comments) Table 4. You may consider leaving the I-O column away, because you also give the retention%.

(Revision) ***Accepted***

#2.12

(Referee's comments) Figure 2. Show discharge data also as a scatter plot.

(Revision) ***Figure 2 is deleted.***

#2.13

(Referee's comments) Figure 6. . . .and share of the annual flux (%).

(Revision) ***Accepted***

**Original: Figure 6.** Monthly average flux (circle, left horizontal axis; error bars, SE) and monthly % flux of the annual flux (bar, right horizontal axis) of DOC, DON, and DIN at the inlet and outlet of Arbutus Lake

**Modified: Figure 6.** Monthly average flux (circle, left horizontal axis; error bars, SE) and share of the annual flux (%); bar, right horizontal axis) of DOC, DON, and DIN at the inlet and outlet of Arbutus Lake

#2.14

(Referee's comments) Modify the y-axis title (%)

(Revision) **Accepted**

Original: % DOC flux            % DON flux            % DIN flux  
Modified: DOC flux (%)        DON flux (%)            DIN flux (%)

#2.15

(Referee's comments) Figure 7. ...significant difference from the zero?

(Revision) **Accepted**

Original: Asterisk indicated significant difference with zero

Modified: Asterisk indicated significant difference from the zero

#2.16

(Referee's comments) Figure 8. Part of the DIC is likely released from the system to the atmosphere. Shall you include that direction too.

(Revision) **Accepted**

#2.17

(Referee's comments) Potentially useful reference Sarkkola, S., Nieminen, M., Koivusalo, H., Laurén, A., Kortelainen, P., Mattsson, T., Palviainen, M., Piirainen, S., Starr, M. & Finér, L. 2012: Trends in concentrations and export of nitrogen in boreal forest streams. *Boreal Env. Res.* 17: 85–101.

(Revision) **Accepted** We added this reference in the "Introduction". Thanks for letting us know about this paper. It will be helpful for future studies as well.

Original: very few have simultaneously investigated the changes in DON.

Modified: very few have simultaneously investigated the changes in DON (*Sarkkola et al., 2012*).

(Page/line) P17289/5

Dear Referee #2,

Thank you for your comments. We have responded to your general and detailed comments (Title: Importance of within-lake processes in affecting the dynamics of dissolved organic carbon and dissolved organic and inorganic nitrogen in an Adirondack forested lake/watershed).

Included with this communication are our comments and tables with responses.

Please, let me know if you require anything else regarding this revision.

Sincerely yours,

Phil-Goo Kang

## 1. Responses to general comments.

**#A. (Referee's comment)** This paper provides valuable information on long-term C and N processes within a lake. Specifically, DOC, DIN and DON data is presented together in a long-term data set which makes possible interesting comparisons across time and seasons. The objectives and the structure of the work are well presented.

==> Thanks for your comments. This comment is consistent with the major goals of our paper.

**#B. (Referee's comment)** However, the study mostly relies on the description of the dataset and statically analyses are rather scarce (or not well supported). The application of other statistical tools, such as, cross-correlation between inlet and outlet to take into accounted water residence time, will help to provide a more robust discussion based on more explicit objectives.

==> Following your suggestion, we analyzed data using other statistical analyses including step-wise regression, multiple correlation, etc. including hydraulic residence time as a parameter and also using year periods (growing, dormant, and ice-cover). Unfortunately, we did not find any significant results when hydraulic residence time was included as a variable. However, we did find significant and important results when we performed analyses of hydraulic retention (%) in relation to solute retention (%) of DOC, DON and DIN (e.g., Note Table 5 shows Pearson correlation results) using monthly analysis This issue also relates to detailed comment #9 and our response as given below).

Although we did not include all of these results in our manuscript, the relationship between water residence time and hydraulic retention was not significant ( $p=0.57$ ,  $r^2=0.04$ ). We could add this result if it is considered to be important.

Also, with respect to solute's retention (%), the consistent usage of the same equation for hydraulic retention compared to solute's retention is reasonable. Hence we used retention (%) not residence time (This issue is also related to detailed comment #1 provided below).

**#C. (Referee's comment)** Consider to reduce the number of figures/tables according to a more specific predictions.

==> Table 3 has been merged into Table 4.

Figures 2 and 3 have been merged into the new Table 1.

Figures 5 and 6 have been merged into Figure 3.

As a result, 3 figures were deleted.

## 2. Responses to detailed comments.

### #2.1

(Referee's comments) P. 17294 L. 14: Is it possible to consider residence water time for retention estimates? That is compare the "same" water mass at the inlet to the outlet (after 0.6 yr<sup>-1</sup>)

(Revision) (*comment*) Please see our previous comment regarding the usage of hydraulic retention (%) versus water residence time.



#2.2

(Referee's comments) P. 17294 L. 19-20: which software was use for Seasonal Kendall trend analyses?

(Revision) (**Accepted**) A DOS executable program that runs under Windows operating system was used. Detailed information is provided in the reference (Helsel et al., 2006).

Original: A Seasonal Kendall trend analysis was used to determine temporal changes in monthly discharge-weighted DOC and DON concentrations at the inlet and outlet sites (Helsel et al., 2006).

Modified: A Seasonal Kendall trend analysis (a DOS executable program) was used to determine temporal changes in monthly discharge-weighted DOC and DON concentrations at the inlet and outlet sites (Helsel et al., 2006).

#2.3

(Referee's comments) P. 17295 L. 6: How precipitation data from 1941 was obtained?

(Revision) (**comment**) Thanks for your comment. The title of Table 1 has been changed as below:

Original: Annual precipitation and temperature at AEC site and yearly discharge at the Arbutus Lake outlet since 1941.

Modified: Annual precipitation and temperature at Adirondack Ecological Center site since 1941 (available at: [http://www.esf.edu/aec/research/ALTEMP\\_projects.htm](http://www.esf.edu/aec/research/ALTEMP_projects.htm), 2016) and yearly discharge at the Arbutus Lake outlet since 1983.

#2.4

(Referee's comments) P. 17295 L. 6-14: This section shows that there no significant trend in precipitation, temperature or DOC concentration during the temporal period studied. Why you do not related these variables directly? Moreover, temperature and rainfall are not further discussed.

(Revision) (**comment**) Thanks for your comment. As indicated, there were no significant relationships among precipitation, temperature and DOC over the long term. Similarly in the more detailed analyses section for which we had weekly measurements there were no long-term changes, but some interesting patterns become apparent, especially for DON and DIN.

#2.5

(Referee's comments) P. 17298 L. 21: substitute “,” to “.”

(Revision) **Accepted**. Thanks for your correction.

Original: inlet to the outlet, For the calendar...

Modified: inlet to the outlet. For the calendar...

(Page/line) 17298/21

#2.6

(Referee's comments) P.17306 L.7: remove dot.

(Revision) **Accepted**

Original: of Redfield's ratio. calculated from...

Modified: of Redfield's ratio: calculated from...

(Page/line) 17306/7

#2.7

(Referee's comments) Table 1 Not sure which is the basis to provide correlations within months.

Biological periods might make more sense, such as vegetative/growing periods or ice cover.  
(Revision) Please see our comment of #1.B and #2.9.

#2.8

(Referee's comments) Fig. 2 As far as it is presented now; I do not think this figure is needed.  
(Revision) Figures 2 and 3 have been merged into the new Table 1.

#2.9

(Referee's comments) Fig. 5, 6 and 7 Consider to draw important year periods which are further discussed (vegetative/growing period; snowmelt).  
(Revision) Figures were changed as you recommended.

## 1 Abstract

2 Lakes nested in forested watersheds play important roles in mediating the concentrations and  
3 fluxes of dissolved organic matter. We compared long-term patterns of concentrations and  
4 fluxes of dissolved organic carbon (DOC) ~~and~~ dissolved organic (DON) and inorganic  
5 nitrogen (DON), and dissolved inorganic nitrogen (DIN) in aquatic ecosystems of the Arbutus  
6 Lake Watershed to evaluate how a lake nested in a forested watershed affects the sources  
7 (e.g.i.e. production) and sinks (e.g.i.e. retention) dynamics of DOC and DON in the  
8 Adirondack Mountains of New York State, USA. We observed no significant long-term  
9 changes of ~~concentrations and fluxes of~~ DOC and DON in the Lake outlet since 1983 and  
10 1994, respectively. However, the temporal patterns of DOC and DON concentrations in the  
11 Lake inlet showed significant seasonality such as increases during the vegetation-growing  
12 season along with notable decreases in the dormant season. A comparison of mass-balances  
13 between inlet and outlet for the period from 2000 to 2009 suggested that the Lake was a sink  
14 of DOC (mean of influx minus outflux: +1,140 mol C ha<sup>-1</sup> yr<sup>-1</sup>). In contrast, the difference of  
15 discharge-weighted DON concentrations (mean of inlet minus outlet: -1.0 μmol N L<sup>-1</sup>)  
16 between inlet and outlet was much smaller than the discharge-weighted DOC concentrations  
17 (average of inlet minus outlet: + 87 μmol C L<sup>-1</sup>). DON fluxes showed considerable variation  
18 among years (mean of influx minus outflux: +8 mol N ha<sup>-1</sup> yr<sup>-1</sup>; range of differences: -15 to  
19 27 mol N ha<sup>-1</sup> yr<sup>-1</sup>). DON exhibited low % retention ((influx-outflux)/influx) (mean: 6.9%,  
20 range: -34.8 to +31.2) compared to DOC (mean: 30.1%, range: +9.2 to +44.1). The resultant  
21 increase of DON within the lake was closely linked with a net decrease of DIN through  
22 monthly Pearson correlation analysis, suggesting the importance of biotic factors in mediating  
23 ~~a~~-lake DON dynamics. Our results show different relative retentions of DOC compared with  
24 DON, along with a larger retention of DIN than DON, suggesting that DOC and DON might  
25 display substantially different biogeochemical relationships in oligo-mesotrophic lakes nested  
26 forested watersheds and therefore different roles for a sink behavior for DOC compared to a  
27 producer of DON.

28

## 29 1 Introduction

1 Dissolved organic matter (DOM) produced from terrestrial (Aitkenhead-Peterson et al., 2003)  
2 and aquatic (Bertilsson and Jones, 2003) sources plays an important role in supporting  
3 microbial activity, contributing to energy flux, and influencing material cycling (Findlay and  
4 Sinsabaugh, 2003; Wetzel, 2001). DOM interactions with toxic Al and Hg (Driscoll et al.,  
5 1988) and the creation of disinfection by-products (Siddiqui et al., 1997) affect water quality  
6 and general ecosystem health. Dissolved organic carbon (DOC) also plays a role in the  
7 protection of aquatic biota due to the attenuation of ultraviolet-B radiation (Williamson, 1995).  
8 Dissolved organic nitrogen (DON) is an important component of the total solute N loss in  
9 some ecosystems, especially those with low concentrations of total dissolved N (TDN)  
10 (Campbell et al., 2000; Hedin et al., 1995; Mitchell et al., 2001; Neff et al., 2003). Little  
11 attention has been paid to differences in the transport and transformations of DOC, DON, and  
12 DIN along different compartments of forested watersheds, except a few recent studies that  
13 compared differential storm responses of DOC and DON (Inamdar et al., 2008; Goodman et  
14 al., 2011).

15 There has been considerable discussion on the mechanisms driving recent increases of DOC  
16 in acid-sensitive surface waters in North America and Europe (Driscoll et al., 2007;  
17 Erlandsson et al., 2011; Evans et al., 2007; Monteith et al., 2007; 2015). For example,  
18 Monteith et al. (2007) suggested that the recovery of the previous acidification of surface  
19 water in response to decreased acidic deposition might result from an increase in the solubility  
20 of soil organic matter due to the change of pH, aluminum and ionic strength (Kalbitz et al.,  
21 2000; Mulder et al., 2001). Erlandsson et al. (2011) suggested the importance of  
22 understanding the effects of acidification on reexamining DOC reference levels. Other  
23 possible mechanisms driving this increase in DOC concentrations include increasing  
24 temperatures (Freeman et al., 2001), changing hydrology associated with increases in  
25 precipitation and runoff (Schindler et al., 1997), changes in land uses (Worrall et al., 2004),  
26 alteration of dry and rewetting cycles (von Schiller et al., 2015), increasing primary  
27 production induced by increases of atmospheric CO<sub>2</sub> (Freeman et al., 2004) and increased  
28 occurrences of droughts (Worrall and Burt, 2005).

29 While many studies have explored the dynamics and fate of DOC in aquatic ecosystems (e.g.,  
30 Findlay and Sinsabaugh, 2003), very few have simultaneously investigated the changes in  
31 DON ([Sarkkola et al., 2012](#)). The short-term studies that have compared DOC versus DON  
32 changes indicate that DOC export from forested lakes in Adirondack Mountains was

1 negatively related to hydraulic residence time but not for DON, suggesting that different  
2 biogeochemical responses for DOC and DON (Ito et al., 2005). Evaluating the causes of these  
3 differences is important for understanding spatial and temporal patterns of DOC and DON in  
4 surface waters including the role of within-lake processes. The generation of organic matter  
5 by autochthonous processes is an important factor for the formation of DOC and DON within  
6 lakes. Generally DOC and DON concentrations increase in eutrophic lakes due to the relative  
7 high autochthonous contributions in spite of enhanced microbial transformations to consume  
8 DOC and DON, while for oligotrophic lakes with low DOC and DON concentrations show a  
9 net decrease due to microbial decomposition, sedimentation, and photolysis (e.g., Thurman,  
10 1985). Within-lake processes can affect nutrient dynamics including changes in C:N ratios  
11 (Ito et al., 2007). Previous studies have shown differences in lability of DON and DOC (Kang  
12 and Mitchell, 2013; Gregorich et al., 2003; Kirchman, 2003; Petrone et al., 2009). DOM from  
13 drainage lakes can alter the amount and the chemical characteristics of the DOM and the  
14 processing of other elements in downstream surface waters.

15 Arbutus Lake, an oligotrophic/mesotrophic lake, in the Adirondack Mountains of New York  
16 State, is the one of the original Adirondack Long-Term Monitoring program (ALTM) lakes  
17 established in 1982 (Driscoll et al., 2003; Kelting and Laxson, 2014; Owen et al., 1999).  
18 Arbutus Lake watershed has been the site of various hydrologic and biogeochemical studies  
19 of DOC and DON. Piatek et al. (2009) showed that wetlands in the inlet (Archer Creek)  
20 catchment played an important role in controlling DOC concentrations within the Arbutus  
21 Lake watershed. Mitchell et al. (2006) reported on relationships between precipitation patterns  
22 and the export of DOC after late summer storms due to increases in water derived from upper  
23 soil layers and concomitant decrease in the proportion of ground water contributions. DOC  
24 export corresponded to interannual changes of temperature, precipitation and discharge in the  
25 winter (Park et al., 2005). The export of DON constituted 47% to the total solute N flux in the  
26 Arbutus Lake watershed for the period from 1985 to 1998 (Mitchell et al., 2001), and was  
27 enhanced by biotic processes affecting dissolved inorganic nitrogen (DIN) transformations at  
28 higher temperature in summer (Park et al., 2003). Ito et al. (2005) suggested that the decrease  
29 of the C:N ratios among Adirondack lakes, including Arbutus Lake, was related to the  
30 contribution of autochthonous sources with low C:N ratio, compared with allochthonous  
31 terrestrial sources. Most recently Kang and Mitchell (2013) studied DOM characteristics in  
32 the Arbutus Watershed in the Adirondack Mountains as water passed from upland streams,

1 through a wetland, to the lake inlet and finally the lake outlet. There was a net export of high  
2 concentrations of aromatic, refractory and high-molecular-weight (HMW) DOC and DON  
3 produced from the wetland into the lake. Also they observed the decomposition of refractory  
4 HMW DOC and the increase of bioavailable DOC and DON within the lake.

5 The objectives of our current study were to 1) evaluate long-term changes in DOC  
6 concentrations and fluxes at the outlet of Arbutus Lake using monthly based ALTM data, 2)  
7 compare DOC, DON, and DIN concentrations and fluxes between inlet and outlet in Arbutus  
8 Lake using weekly observations from ongoing hydrobiogeochemical investigations in the  
9 Arbutus Watershed, and 3) evaluate the role of within-lake processes in affecting the  
10 dynamics (i.e., sources and sinks) of DOC and DON in the lake. ~~This study contributes to a~~  
11 ~~further evaluating how a lake nested in a forest watershed affected dynamics of DOC and~~  
12 ~~DON. We hypothesized that both monthly and yearly changes of DOC and DON within the~~  
13 ~~Lake differ due to the relative importance of different internal processes between these two~~  
14 ~~solutes, i.e., DOC is decomposed to dissolved inorganic carbon (DIC) which may be released~~  
15 ~~to the atmosphere as carbon dioxide or retained as DIC in the lake, while DON is decomposed~~  
16 ~~to DIN which may be utilized by a range of biotic processes including uptake, denitrification,~~  
17 ~~etc. Our study evaluates how a lake nested in a forest watershed affects dynamics of DOC and~~  
18 ~~DON and provides new information on long-term DOC and DON processes within a lake~~  
19 ~~with a particular focus on linking internal processes between DIN and DON based on data~~  
20 ~~collected in our study as well as information from previous studies on the Arbutus Lake.~~

## 22 **2 Methods**

### 23 **2.1 Site description of Arbutus Lake**

24 The Arbutus Lake watershed (43°58'48"N, 74°13'48"W) is located within the Huntington  
25 Wildlife Forest in the Adirondack Mountains of New York State. Arbutus Lake has a surface  
26 area of 50 ha, an average depth of 3.0 m, and a maximum depth of 8.4 m (Driscoll and van  
27 Dreason, 1993). The lake has been classified as a medium till drainage lake by Newton and  
28 Driscoll (1990). For the period from 2001 to 2010 the total phosphorus concentrations ranged  
29 from 11 to 14  $\mu\text{g L}^{-1}$  and chlorophyll-a concentrations ranged from 2.2 to 4.4  $\text{mg m}^{-3}$  during

1 the summer (Keltling and Laxson, 2014), indicating a trophic status within the oligo and meso  
2 range (OECD, 1982). The Arbutus Lake watershed has an area of 352 ha and the elevations  
3 range from 513 to 748 m (Park et al., 2005). The annual temperature averaged 5.1 °C from  
4 1984 to 2013 and total annual precipitation averaged 1,086 mm from 1981 to 2013 in  
5 Newcomb, NY (3 km distance from Huntington Wildlife forest) (NYSERDA, 2015).

6 The Archer Creek catchment (135 ha) represents a major source of water (45%) to Arbutus  
7 Lake (McHale et al., 2000). The overstory vegetation in the upper slopes consists of mixed  
8 northern hardwoods including American beech (*Fagus grandifolia*), sugar maple (*Acer*  
9 *saccharum*), red maple (*Acer rubrum*), yellow birch (*Betula alleghaniensis*), and white pine  
10 (*Pinus strobus*). Lower slopes close to the lake are dominated by conifer stands such as  
11 eastern hemlock (*Tsuga canadensis*), red spruce (*Picea rubens*), and balsam fir (*Abies*  
12 *balsamea*) (Park et al., 2005). The surficial geology consists of thin to medium deposits of  
13 glacial till with a high sand content; the bedrock geology is largely composed of igneous  
14 rocks with some calcium-rich minerals (Driscoll et al., 1993). The wetland, ~~a palustrine~~  
15 ~~peatland~~ (Greenwood Mucky peats), is located in valley bottom and is 4% of the entire  
16 subcatchment area, and speckled alder (*Alnus incana* ssp. *rugosa*) is the dominant vegetation  
17 in the wetland (Bischoff et al., 2001).

## 18 **2.2 Hydrological and chemistry data**

19 The stage height and discharge at the outlet of Arbutus Lake have been measured using a V-  
20 notch weir since 1991 (Figure 1). The inlet, located in the Archer Creek catchment, has been  
21 monitored using an H-flume equipped with an automated discharge logging device since  
22 October 1994 (Mitchell et al., 2001) (Figure 1). To calculate annual discharge-weighted DOC  
23 concentration at the outlet using ALTM data, we estimated monthly discharge at the lake  
24 outlet from 1984 to 1990 using modeled discharge values and measured values for subsequent  
25 periods (Mitchell et al., 1996).

## 26 **~~2.3 ALTM measurements of DOC~~**

27 The outlet of Arbutus Lake has been monitored monthly by the ALTM program since  
28 February 1983 including DOC concentrations, and the analytical method described in Driscoll

1 and van Dreason (1993). For the long-term change of DOC at Arbutus Lake, we used the  
2 monthly ALTM data from February 1983 to December 2012.

### 3 **2.4 Chemistry data collected by SUNY-ESF**

4 The inlet has been sampled weekly for chemical analyses, including DON concentrations  
5 since October 1994 and DOC concentration since May 1999. The outlet has been monitored  
6 weekly for chemical analyses, including DON concentrations since October 1991 and DOC  
7 concentration since May 1999. Water samples were kept on ice in the field transported to the  
8 Biogeochemistry Laboratory at SUNY ESF in Syracuse, NY, filtered through a precombusted  
9 glassfiber filter (Whatman GF/F) within one week after collection, and stored at 4 °C until  
10 further analysis.

11 The Biogeochemistry Laboratory, which is a participant in the USGS QA/QC program,  
12 analyzed C and N solutes as follows:  $\text{NO}_3^-$  using a Dionex IC;  $\text{NH}_4^+$  with an autoanalyzer  
13 using the Berthelot Reaction followed by colorimetric analysis; total dissolved nitrogen  
14 (TDN) using the persulfate oxidation procedure, followed by colorimetric analysis on an  
15 autoanalyzer; and DOC using the Tekmar–Dohrmann Phoenix 8000 TOC analyzer®. DON  
16 concentrations were calculated as the difference between TDN and DIN ( $\text{NO}_3^- + \text{NH}_4^+$ )  
17 (Inamdar and Mitchell, 2007). If DIN exceeded or equaled TDN (<2.5% and <1.4% of all  
18 samples in inlet and outlet, respectively), the value of DON was treated as zero. The lowest  
19 DON concentrations in the inlet and outlet were -7.0 and -17.1  $\mu\text{mol N L}^{-1}$ , respectively. The  
20 calculated error for DON concentrations was  $\pm 6.6\%$  [square root of the sum of the squared  
21 analytical precision of TDN ( $\pm 4.2\%$ ),  $\text{NH}_4^+$  ( $\pm 3.2\%$ ), and  $\text{NO}_3^-$  ( $\pm 3.9\%$ )] (Kang and  
22 Mitchell, 2013).

### 23 **2.35 Calculations**

24 To calculate mass balances of DOC, DON, and DIN for Arbutus Lake, we used the same  
25 period (2000-2009) for the inlet and outlet chemistry. We assumed that the ~~Archer Creek inlet~~  
26 chemistry of Archer Creek inlet (a major source of water to the lake) was representative of all  
27 surface and ground water sources to Arbutus Lake. We assumed that direct DOC [e.g., 1,600  
28  $\text{mol C ha}^{-1} \text{ yr}^{-1}$  in Ithaca, NY; Likens et al., 1983] and DON [e.g., 93 to 135  $\text{mol N ha}^{-1} \text{ yr}^{-1}$  in  
29 New England, US; Campbell et al., 2000] inputs via precipitation to the Lake would be small



1 as for other northeastern U.S. forests. We also used the results from the NADP/NTN site for  
2 wet only deposition directly to Arbutus Lake  
3 (<http://nadp.sws.uiuc.edu/nadpdata/annualReq.asp?site=NY20>).

4 ~~The annual residence time of the lake was calculated as follows:~~

5 ~~$$\text{Residence time (years)} = V/Q,$$~~

6 ~~where V is the lake volume ( $134.5 \times 10^4 \text{ m}^3$ ) and Q is the yearly outlet discharge (unit:~~  
7  ~~$\text{m}^3/\text{year}$ ).~~

8 To calculate and compare fluxes of DOC, DON and DIN between the inlet and outlet, firstly

9 ~~t~~The monthly discharge-weighted concentrations (MDWC) of DOC, DON and DIN were  
10 calculated using weekly concentration data as follows:

11 
$$MDWC = \sum (Q_j \times C_j) / \sum Q_i,$$

12 where  $Q_j$  and  $C_j$  are  $Q$  (daily discharge) and  $C$  (concentration), respectively, for the  $j^{\text{th}}$  weekly  
13 sample in a given month and  $Q_i$  is daily  $Q$  in a given month. MDWC was also used to  
14 compare the monthly differences between the inlet and outlet.

15 To calculate annual discharge-weighted concentration (ADWC), ~~monthly discharge-weighted~~  
16 ~~concentration~~MDWC (for ALTM data, monthly concentrations were used) and monthly  
17 discharges were ~~determined-used~~ as follows:

18 
$$ADWC = \sum (MDWC \times Q_i) / \sum Q_i,$$

19 where  $Q_i$  is monthly  $Q$  in a given year.

20 Finally, fFluxes from the inlet and the outlet from 2000 to 2009 were also computed per unit  
21 area as follows:

22 
$$\text{Flux (mol ha}^{-1} \text{ yr}^{-1}) = \sum (ADWC \times Q_i) / A,$$

23 where  $A$  is the a watershed area of either the major lake (inlet=135 ha) or the entire Arbutus  
24 watershed (outlet=352 ha).

To quantitatively understand how much any solute was retained or decomposed due to the within-lake process, The annual % retention of lake water (hydraulic retention), DOC, DON, and DIN within the lake was also computed:

$$Retention (\%) = (influx - outflux) / influx \times 100,$$

where influx and outflux are fluxes of lake water and solutes at the inlet and the outlet, respectively. Positive values indicated a sink, and negative values indicated a source within the Lake.

The annual retention amount of DOC, DON and DIN was calculated as follows:

$$Retention\ amount\ (mol) = (influx - outflux) \times 50 / (lake\ surface\ area).$$

The annual residence time of the lake was also calculated as follows:

$$Residence\ time\ (years) = V / Q,$$

where V is the lake volume ( $134.5 \times 10^4 \text{ m}^3$ ) and Q is the yearly outlet discharge (unit:  $\text{m}^3/\text{year}$ ).

## **2.46 Statistical approaches and hypothesis testing**

To determine temporal changes in MDWC of monthly discharge-weighted DOC and DON concentrations at the inlet and outlet sites, a Seasonal Kendall trend analysis (a DOS executable program) was used to determine temporal changes in monthly discharge-weighted DOC and DON concentrations at the inlet and outlet sites (Helsel et al., 2006). All linear regression was analyzed based on  $\alpha=0.05$  using Sigma Plot (Version 11.0, Systat Software, Inc.). To compare differences of MDWC between the inlet and outlet discharge-weighted concentrations among months, one-way analysis of variance (ANOVA) with posthoc Tukey HSD test ( $\alpha=0.05$ ) was performed using Minitab (Version 16, Minitab Inc.). To evaluate correlation among DOC, DON and DIN concentration and climatic variables (temperature and discharge) in the inlet and outlet and % retention of lake water and fluxes and concentrations in DOC, DON and DIN of Arbutus Lake, Pearson correlation was analyzed for

1 significance levels of  $p < 0.05$  using Minitab (~~Version 16, Minitab Inc.~~). We hypothesized that  
2 the dynamics of DON and DOC including changes in concentrations and mass balances will  
3 differ due to the relative importance of biogeochemical processes affecting each solute.

### 4 5 **3 Results**

#### 6 **3.1 The long-term climatic factors and monthly DOC trend using ALTM data set**

7 Precipitation increased significantly from 1941 to 2009 (Table 1~~Figure 2~~). However, there  
8 was no significant change in precipitation ( $p=0.08$ ) or temperature ( $p=0.07$ ) from 1983 to  
9 2009 during the period of DOC and DON~~M~~ investigation (Table 1~~Figure 2~~). There was a  
10 significant relationship between precipitation and discharge during the same period (Table  
11 1~~Figure 2~~). An analysis of the Arbutus ALTM data set from 1983 to 2012 showed no  
12 significant change in DOC concentrations at the Lake outlet (mean ~~408.1~~398.4  $\pm$  ~~31.3~~61.1 SD  
13  $\mu\text{mol C L}^{-1}$ , ~~n=304, slope: 0.06  $\mu\text{mol C L}^{-1} \text{ year}^{-1}$ , tau: 0.009, p=0.91;~~) (Table 1~~Figure 3~~).  
14 Annual DOC influx for Arbutus Lake ~~ranged from 1,620 to 4,028 mol C ha<sup>-1</sup> yr<sup>-1</sup> and~~  
15 averaged ~~2,501~~27 ( $\pm$  ~~602~~22 SDE)  $\text{mol C ha}^{-1} \text{ yr}^{-1}$ .

#### 16 **3.2 Trends of ~~weekly~~ DOC, DON, and DIN concentrations using SUNY-ESF data** 17 **set**

18 The DOC and DON concentrations at the inlet and outlet using weekly concentration data  
19 from SUNY-ESF are given in Figure 24. The inlet DOC concentrations (mean  $480 \pm 202$  SD  
20  $\mu\text{mol C L}^{-1}$ ,  $n=541$ ) showed higher mean and greater monthly variation than the outlet (mean  
21  $402 \pm 93$  SD  $\mu\text{mol C L}^{-1}$ ,  $n=545$ ). In contrast, the DON concentrations showed similar values  
22 at the inlet (mean  $10.1 \pm 5.4$  SD  $\mu\text{mol N L}^{-1}$ ,  $n=751$ ) and the outlet (mean  $11.5 \pm 5.0$  SD  $\mu\text{mol}$   
23  $\text{N L}^{-1}$ ,  $n=727$ ). The Seasonal Kendall test did not show any significant changes over time in  
24 DOC or DON concentrations: inlet DOC (slope:  $1.8 \mu\text{mol C L}^{-1} \text{ year}^{-1}$ , tau: 0.04,  $p=0.68$ ),  
25 inlet DON (slope:  $-0.03 \mu\text{mol N L}^{-1} \text{ year}^{-1}$ , tau: -0.05,  $p=0.53$ ), outlet DOC (slope:  $1.07 \mu\text{mol}$   
26  $\text{C L}^{-1} \text{ year}^{-1}$ , tau: 0.04,  $p=0.81$ ), and outlet DON (slope:  $-0.11 \mu\text{mol N L}^{-1} \text{ year}^{-1}$ , tau: -0.09,  
27  $p=0.22$ ).

1 The monthly concentrations of DOC, DON, and DIN and the monthly discharge values are  
2 shown in Figure 35. At the inlet there was a strong seasonality of DOC, DON, and DIN  
3 concentrations. DOC and DON concentrations enhanced during a growing season and  
4 reduced during winter while DIN concentrations increased during winter and decreased from  
5 May to October. At the outlet the monthly DOC patterns that decreased from April and  
6 reaching a minimum in the fall (i.e., October) were substantially different than the temporal  
7 patterns of inlet DOC concentrations. At the inlet, DON concentrations showed a similar  
8 seasonal pattern to that of DOC concentrations; however, at the outlet the patterns were not  
9 similar, suggesting differences in the mechanisms regulating DOC and DON dynamics in the  
10 Lake. Outlet DIN concentrations increased from January to April and decreased from May  
11 through November, indicative of DIN uptake ~~by the aquatic biota~~ and/or DIN reduction ~~by~~  
12 ~~biogeochemical processes such as plant and microbial uptake or denitrification including~~  
13 ~~dissimilatory nitrate reduction in the Lake.~~

14 The statistical correlations among DOC, DON, DIN, monthly average temperature, and  
15 monthly total discharge for every month and for entire years are provided in Table 24. For the  
16 inlet, DOC was positively correlated with DON, temperature, and discharge, and DON  
17 showed a positive relationship with temperature and discharge as also found for the inlet DOC.  
18 We observed a significantly negative relationship between DON and DIN concentrations. At  
19 the outlet, DOC was not correlated with DON, and the significantly negative relationships  
20 (May to December) between DON and DIN in the Lake was found.

### 21 3.3 Fluxes and mass balances of DOC, DON, and DIN in Arbutus Lake

22 Based on weekly samples from 2000 to 2009, we calculated the mass-balances of DOC, DON,  
23 and DIN ~~using annual discharge weighted concentrations and fluxes~~ at the inlet and the outlet  
24 (Tables 32 ~~and to~~ 43). Our calculation of average residence time of  $0.66 \text{ yr}^{-1}$  was almost same  
25 as that value estimated to be  $0.6 \text{ yr}^{-1}$  in a previous study of Driscoll and van Dreason (1993)  
26 (Table 32). ~~ADWC~~~~Average of discharge weighted concentrations~~ of DOC and DIN decreased  
27 from the inlet to the outlet, while DON increased, ~~resulting~~. ~~The increase of DON resulted~~ in  
28 a decrease in ~~C:N molar~~ C:N ratios of DOM as water was transported through in the Lake  
29 (Table 43). ~~The pattern of decreasing C:N ratios in our study with an inlet value of 55 and an~~  
30 ~~outlet value of 40 is consistent with previous studies of Adirondaack Lakes (including Arbutus~~  
31 ~~Lake) (Ito et al., 2005; 2007) and lakes in other regions of the world (Kopáček et al., 2003;~~

1 ~~Schindler et al., 1992; Wetzel, 2001~~. For Arbutus Lake the mean DOC outflux of 2,477  $\pm$   
2 ~~180 SE (n=10)~~ mol C ha<sup>-1</sup> yr<sup>-1</sup> using weekly observations was similar (i.e., difference of 2%)  
3 to the average flux calculated using the monthly ALTM data (2,501.27 ( $\pm$  602.122 SDE) mol C  
4 ha<sup>-1</sup> yr<sup>-1</sup>) for the period from 1983 to 2012 (Figure 3, Tables 1 and 43).

5 The difference between the inlet and ~~the~~ outlet of ~~ADWC of annual~~ DOC ~~concentrations~~  
6 averaged 93  $\mu$ mol C L<sup>-1</sup>, ranging from -5 (in 2007) to 161 (in 2001)  $\mu$ mol C L<sup>-1</sup>. The  
7 difference between inlet and outlet fluxes averaged 1,140 mol C ha<sup>-1</sup> yr<sup>-1</sup> with the range of  
8 236 to 2,100 mol C ha<sup>-1</sup> yr<sup>-1</sup> (Table 4), indicating that DOC was decomposed or retained in  
9 the Lake. The ~~retention (%) proportion~~ of DOC ~~decreases for concentrations and fluxes from~~  
10 ~~the inlet to the outlet~~ ranged ~~from -1.2 to 29.4% (mean: 18.4%) and~~ from 9.2 to 44.1% (mean:  
11 30.1%), ~~respectively, of inlet values~~. Hence, for all years there was a net decrease of DOC  
12 between the inlet and ~~the~~ outlet.

13 For DON ~~annual~~ differences of ~~annual discharge weighted concentrations~~ ADWC and fluxes  
14 between ~~the~~ inlet and outlet ranged from -3.5 to 1.1  $\mu$ mol N L<sup>-1</sup> (mean: -1.0  $\mu$ mol N L<sup>-1</sup>) and  
15 from -15 to 27 mol N ha<sup>-1</sup> yr<sup>-1</sup> (mean: 8 mol N ha<sup>-1</sup> yr<sup>-1</sup>), respectively (Table 4). This analysis  
16 suggests that within-lake processes sometimes (particularly 2007) resulted in a net increase in  
17 DON through the Lake in contrast to the routine net decrease in DOC. Net retention of DOC  
18 within the Lake was smallest in 2007 and there was a net increase in DON during the same  
19 year (Table 34). The fraction of DON input concentrations and fluxes that changed in the  
20 Lake based on fluvial DON exports ranged from -50.0 to 12.7% (mean: -10.0%) and from -  
21 35.7 to 31.0% (mean: 11.2%), respectively.

22 For DIN annual differences in concentrations and fluxes between inlet and outlet ranged from  
23 7 to 28  $\mu$ mol N L<sup>-1</sup> (mean: 16  $\mu$ mol N L<sup>-1</sup>) and from 60 to 183 mol N ha<sup>-1</sup> yr<sup>-1</sup> (mean: 120 mol  
24 N ha<sup>-1</sup> yr<sup>-1</sup>), respectively (Table 4s 3 and 4), indicating the removal of DIN in the Lake. The  
25 fraction of DIN concentrations and fluxes from inlet values that were retained in the Lake  
26 ranged from 42.1 to 64.3% (mean: 57.1%) and from 45.9 to 69.4% (mean: 61.5%),  
27 respectively. In brief, ~~fluxes of~~ DOC, DON, and DIN decreased in the Lake (~~mean: 57,050,~~  
28 ~~405 and 5,985 mol, respectively; Table 4~~), but the ~~retention amount~~ ~~proportion~~ of DON  
29 decreases in the Lake (~~mean: 11.2%~~) was less than that of DIN (~~mean: 61.5%~~ Table 4).

### 30 3.4 Factors affecting changing fluxes of DOC, DON, and DIN

1 The patterns of DOC, DON, and DIN fluxes were similar for the inlet and outlet, although the  
2 concentration patterns of those solutes were different (Figure 53), indicating that flux changes  
3 were largely caused by hydrological changes (Figure 63, Table 5). The monthly variation of  
4 the differences in DOC, DON, and DIN concentrations and fluxes between inlet and outlet is  
5 shown in Figure 74. ~~Although there were annual differences in fluxes particularly driven by~~  
6 ~~variation during the snowmelt period, most of the differences in fluxes between inlet and~~  
7 ~~outlet were positive, indicative of the retention or loss of these solutes within Arbutus Lake.~~  
8 The net retention of DOC flux through the Lake was caused by both a decrease in discharge  
9 ~~from the inlet to the outlet~~, particularly during snowmelt, and a decrease in DOC  
10 concentrations ~~from the inlet to the outlet~~. In contrast DON concentrations showed no  
11 significant difference between the inlet and outlet in months except in January and December  
12 which exhibited increases in DON concentration ~~from the inlet to the outlet~~. For the calendar  
13 year the differences of DIN concentration between the inlet and outlet increased through April  
14 after which concentrations were markedly reduced within the Lake ~~likely due to both~~  
15 ~~assimilatory and dissimilatory N reduction by the biota.~~

16 Results of Pearson correlation comparing % retention of lake water and fluxes and  
17 concentrations of DOC, DON, and DIN are shown in Table 45. The % retention of DOC was  
18 significantly related to hydraulic ~~retentionsidence time (%)~~, but not for DON, indicating that  
19 the decrease of DOC in the Lake was related to the hydraulic changes, whereas DON  
20 retention was less affected, indicating that other factors including biotic processes were likely  
21 important. Although a significant relationship between % retention of DOC and DON was  
22 shown, the range of DON retention ranged from negative to positive while the % retention of  
23 DOC was always positive. Box-plots of the yearly retention of DOC, DON, and DIN in fluxes  
24 are shown in Figure 8a, and potential sources and sinks for solutes are described in Figure 8b.

25

## 26 **4 Discussion**

27 Our study suggests that annual DOC and DON mass balances were strikingly uncoupled as  
28 we hypothesized, and Arbutus Lake generally acted as a sink for DOC but a periodic source  
29 for DON (Table 4, Figure 85). For DON, internal recycling between DIN and DON might be  
30 important in affecting DON concentrations in the Lake. Few studies have compared

1 simultaneously the long-term DOC and DON dynamics in lakes. Our work indicated that the  
2 sink strength of DOC in Arbutus Lake, an oligo-mesotrophic lake, was a function of hydraulic  
3 residence (Table 5). ~~For DON, internal recycling between DIN and DON might be important~~  
4 ~~in affecting DON concentrations in the Lake.~~

#### 5 **4.1 Long-term change of DOC export from the Lake**

6 Our results indicated that DOC concentrations and mass balances in Arbutus Lake varied  
7 among years but did not show significant long-term trend. These results are similar to Driscoll  
8 et al. (2007) who also found no significant trend in DOC concentrations for Arbutus Lake.  
9 However, Driscoll et al. (2007) did report that 10 of the original 16 ALTM lakes showed  
10 increased concentrations of DOC from 1982 to 2004 with a mean increase of  $4.5 \pm 3.8 \mu\text{mol}$   
11  $\text{C L}^{-1} \text{ yr}^{-1}$ . The actual mechanisms causing changes of DOC concentration are not specifically  
12 known but could include biological and chemical processes (e.g., a decrease in soil DOC  
13 partitioning) and factors associated with climatic change (e.g., the hydrological change and  
14 the dry and rewetting cycle) (Driscoll et al., 2007; Fellman et al., 2011; Singh et al., 2014;  
15 von Schiller et al., 2015). Monteith et al. (2007) suggested that increases in surface water  
16 DOC are linked to decreases in sulfur deposition due to decreases in the partitioning of  
17 organic matter by soil associated with the change in pH, aluminum and ionic strength  
18 (Ekstrom et al., 2011; Erlandsson et al., 2011; Evans et al., 2012; Mulder et al., 2001). Most  
19 of the Adirondack lakes including Arbutus Lake have shown significant decreases in sulfate  
20 concentration (Park et al., 2003; Driscoll et al., 2007). The effects of changes of acidic  
21 deposition on surface water, including trends in DOC concentrations, have been documented  
22 in North America (Driscoll et al., 2007) and Europe (Erlandsson et al., 2011; Evans et al.,  
23 2007; Kalbitz et al., 2000; Monteith et al., 2007; Monteith et al., 2015; Mulder et al., 2001).  
24 However, for Arbutus Lake the effects of changes in acidic deposition may be less evident  
25 due to its relatively high pH ( $\sim 6.7$ ) and ANC ( $\sim 77 \mu\text{eq L}^{-1}$ ) values and base status (Foster et  
26 al., 1992; Johnson and Lindberg, 1992; Mitchell et al., 2001; Chen et al., 2004; NYSERDA,  
27 2011).

#### 28 **4.2 Temporal patterns of DOC and DON concentrations in forested catchments**

29 Our study suggests the importance of biotic processes in affecting the seasonality of DOC and  
30 DON concentrations in forested watersheds. We observed the seasonal variation of DOC and

1 DON concentrations such as the increase in inlet DOC and DON concentrations of the Lake  
2 during the growing season with notable decreases in the dormant season (i.e., December to  
3 March) (Figure 53). The seasonality of dissolved organic matter dynamics in forested  
4 watersheds has been shown in various studies (e.g., Aitkenhead-Peterson et al. 2003; Levia et  
5 al., 2011; Park et al., 2003). In addition, our study indicated that at the lake outlet increases in  
6 DON concentration coincided with decreases in DIN, suggesting that some DIN was  
7 converted to DON (Table 42). The monthly concentrations of DIN increased during winter  
8 and decreased from May to October, likely indicating the uptake of nitrogen as a nutrient by  
9 the biota during warmer periods of the year (Bischoff et al., 2001). Our observation of the  
10 negative relationship of DIN with DON at the inlet was consistent with the study of McHale  
11 et al. (2000) (Figure 53, Table 42). Regarding a quality of DOC and DON from the inlet,  
12 Kang and Mitchell (2013) in this catchment showed the production of refractory and HMW  
13 DOC and DON in upland regions of the catchment, which was followed by a large increase of  
14 DOC concentrations as water was transported through downstream wetland areas. Hence, the  
15 import of the high concentrations of aromatic, refractory and HMW DOM from the inlet  
16 would likely be an important source of DOC and DON for lakes (Kang and Mitchell, 2013;  
17 Piatek et al., 2009; Reddy and DeLaune, 2008).

18 Annual DOC fluxes and concentrations from the inlet (Table 4) were similar to ranges  
19 reported from other studies of Adirondack lakes (Canham et al., 2004) and across United  
20 States [580 to 6,200 mol C ha<sup>-1</sup> yr<sup>-1</sup> and 41 to 2,567 μmol C L<sup>-1</sup>] (Aitkenhead and McDowell,  
21 2000; Tate and Meyer, 1983; Webster et al., 2006). We observed marked increases of DOC  
22 and DON influxes during snow melt (April to May) that accounted for 35.8 and 36.7% of the  
23 annual inputs, respectively (Figure 63). The importance of the snowmelt period has been  
24 shown in other studies of forested catchments (Hornberger et al., 1994; Boyer et al., 1997;  
25 Goodman et al., 2011; Park et al., 2005). These studies also suggest that as groundwater table  
26 rises during snow melt, high concentration of DOC and DON from pore water in upper soil  
27 horizons including the forest floor are flushed into adjacent surface waters. The export of  
28 DOM during snowmelt provides a substantial contribution to the yearly DOM mass fluxes.  
29 The export of DOC from soils to surrounding waters is controlled by many factors including  
30 hillslope connectivity (McGlynn and McDonnell, 2003), wetland area (Piatek et al., 2009),  
31 topography and the snow melt pattern (Boyer et al., 1997; Hornberger et al., 1994). At the  
32 inlet of Arbutus Lake, the increased discharge associated with snowmelt begins in early



1 spring (e.g., March and April) resulting in increased DOC and DON concentrations that  
2 continue to increase to maximum mid-summer concentrations (Figure 53).

3 Our study also showed positive relationships between discharge and the concentrations of  
4 DOC and DON during the growing season from the inlet catchment (Table 42). Previous  
5 analyses of the resultant influx of DOC and DON in the Archer Creek watershed during the  
6 growing season have shown close linkages with watershed wetness with notable increases in  
7 DOC during storms after dry antecedent periods (Inamdar et al., 2008; von Schiller et al.,  
8 2015). Studies of other lake/watersheds have found lower DOC concentrations under dry  
9 conditions (Schindler et al., 1997) with elevated DOC concentrations under wetter conditions  
10 (Hinton et al., 1997; Inamdar et al., 2011; Singh et al., 2014; Tranvik and Jansson, 2002). The  
11 increase in DOC concentrations in surface waters with increases in wetness of catchments has  
12 been attributed to the generation of flow paths through organic rich soil, including the forest  
13 floor (Inamdar et al., 2008), and Park et al. (2003) also showed seasonal increases of DON  
14 due to soil microbial production from December 1996 to May 1996 in the Lake inlet.

#### 15 **4.3 Importance Role of within-lake processes**

16 Our observations of decreasing DOC fluxes from March to November in the Lake support the  
17 role of the Lake as a sink of DOC (Figure 74). Similarly subalpine lakes have been found to  
18 be a DOC sink during spring snowmelt (Goodman et al., 2011). During the warm summer,  
19 autochthonous generation of DOC might contribute to slight increases in Lake DOC (Figures  
20 5-3 and 74). Nevertheless, our observations support the role of the Lake as a net sink for DOC.  
21 The retention and loss of DOC within lakes may occur by microbial decomposition (Kang and  
22 Mitchell, 2013), sedimentation (Owen et al., 1999) and photolysis (Bertilsson and Tranvik,  
23 2000; Molot and Dillon, 1997).

24 Our observation of the increase of DON compared to DOC within the Lake indicated the  
25 importance of the DON generation processes in the N mass balance of this Lake. When DON  
26 is mineralized to ammonium, some of the ammonium may be nitrified. This nitrate can then  
27 be utilized in assimilatory and dissimilatory reduction. Some of the organic N formed by  
28 assimilatory nitrate reduction can be found as DON (Figure 5b). Regarding the differences in  
29 DON formation versus DOC formation in the Lake, it is important to ascertain whether the  
30 rate of DON decomposition was substantially less than that of DOC or the DON generation

1 from DIN was the major factor in maintaining relatively high concentrations of DON in the  
2 Lake. From the one-year study of Kang and Mitchell (2013) in the Arbutus Lake,  
3 approximately 10% ( $39.9 \mu\text{mol C L}^{-1}$ ) of the total DOC was microbially decomposed,  
4 whereas 20% ( $2.2 \mu\text{mol N L}^{-1}$ ) of the total DON was estimated to be bioavailable.

5 The removal of seston due to sedimentation can contribute to losses of DOC and DON within  
6 lake waters. Owen et al. (1999) studied seston sedimentation using traps in Arbutus Lake  
7 from September, 1992 to November, 1993, excluding the period from December to April.  
8 They reported on average sedimentation rate of  $1.4 \text{ g dry mass m}^{-2} \text{ d}^{-1}$  and seston C and N  
9 concentrations of  $16.8 \text{ mmol C g}^{-1}$  and  $1.4 \text{ mmol N g}^{-1}$  with sedimentation fluxes of  $85,848$   
10  $\text{mol C ha}^{-1} \text{ yr}^{-1}$  and  $7,154 \text{ mol N ha}^{-1} \text{ yr}^{-1}$ . These relatively high sedimentation fluxes can  
11 easily account for the fluxes of DOC and DON retained in the Lake observed in our study  
12 ( $1,140 \text{ mol C ha}^{-1} \text{ yr}^{-1}$  and  $8 \text{ mol N ha}^{-1} \text{ yr}^{-1}$ , respectively; Table 34) and support the  
13 mechanism of removal of DOC and DON through the sedimentation of seston within the Lake.  
14 Further understanding including the contribution of PON to DON increases is needed.

15 Since terrestrial DOM consists of HMW aromatic, chromophoric compounds (Kang and  
16 Mitchell, 2013), DOM entering the Lake could also be oxidized by photolysis (Sinsabaugh  
17 and Findlay, 2003). Photochemical reactions upon exposure to ultraviolet (UV) radiation due  
18 to increased residence time in the lake can result in a considerable decrease of chromophoric  
19 DOM and the resultant modification of chemical properties of DOM (Bertilsson and Tranvik,  
20 2000; Molot and Dillon, 1997). Kang and Mitchell (2013) observed a decrease in aromatic  
21 compounds observed from ~~SUVA (specific ultra violet absorbance)~~ and HMW DOC  
22 concentration in the Lake suggesting the possibility of the importance of photolysis. ~~In spite~~  
23 ~~of the potential for photolysis as a mechanism removing DOM in lakes (e.g., Wetzel, 2003),~~  
24 ~~the quantitative determination of the relative importance of this process has been difficult.~~ We  
25 observed that during the ice-covered period (December to March), ~~the outlet concentrations~~  
26 ~~and fluxes of DOC and DON were greater than the inlet, resulting in~~ a net increase of DOC  
27 and DON in the outlet compared to the inlet. The exception to this occurred during March  
28 when increased discharge resulted in a large increase in DOC and DON flux into the Lake  
29 (Figure 74). Our results support the hypothesis of Pace and Cole (2002) that a decrease of  
30 photolysis during ice-cover can result in a buildup of DOC in lakes. ~~However, future research~~  
31 ~~should consider the effect of allochthonous DOM entering lakes during the growing season on~~

~~the net increase of DOC and DON in lakes during ice cover and quantify the photolysis of DOM [e.g., approximately 10% of total respiration based on the study of Granéli et al. (1996)].~~

Like DOC the greatest difference in monthly DON fluxes between inlet and outlet occurred during the spring snowmelt. However, the magnitude of the differences in monthly fluxes between the inlet and outlet was relatively small for DON [ $-1.0 \mu\text{mol N L}^{-1}$  ~~for discharge-weighted concentrations~~ and  $8 \text{ mol N ha}^{-1} \text{ yr}^{-1}$  ~~of fluxes~~] compared to DOC [ $93.0 \mu\text{mol C L}^{-1}$  and  $1,140 \text{ mol C ha}^{-1} \text{ yr}^{-1}$ ] likely indicating a contribution by autotrophs to the generation of DON in the Lake over the annual cycle compared to DOC (Table 42, Figure 74). ~~We observed differences of discharge-weighted concentrations and fluxes of DIN between inlet and outlet ranging from 7 to 28  $\mu\text{mol L}^{-1}$  and from 60 to 183  $\text{mol ha}^{-1} \text{ yr}^{-1}$ , respectively, indicating that~~ Our observation of the decrease of DIN in the Lake may ~~support~~ be due in part to biological uptake and assimilation of DIN by algae (e.g., assimilatory nitrate reduction). The assimilation of DIN is also supported by our analysis showing the negative relationship between DIN and DON especially during the growing season (May to September) in the Lake (Table 42). Our results concurred with a one year (June 1995 to May 1996) study of McHale et al. (2000) who also found a net loss of DIN and net increase of DON between the inlet and outlet of Arbutus Lake. McHale et al. (2000) also showed that changes in  $\text{NO}_3^-$  concentrations and fluxes were greater than for DON during the growing season (June to September).

The pattern of decreasing C:N ratios in our study with an inlet value of 55 and an outlet value of 40 is consistent with previous studies of Adirondack Lakes (including Arbutus Lake) (Ito et al., 2005; 2007) and lakes in other regions of the world (Kopáček et al., 2003; Schindler et al., 1992; Wetzel, 2001). ~~The decrease of the molar C:N ratio from the inlet (mean: 55) to the outlet (mean: 40) is consistent with the pattern for other studies of Adirondack Lakes (Ito et al., 2005; 2007).~~ Autochthonous DOM (with a C:N ratio of  $\sim 12$ ; Wetzel, 2001) has been known to contribute to a pattern of decreasing the C:N ratios from the inlet to the outlet of lakes. For Arbutus Lake, Owen et al. (1999) suggested that autochthonous production was the major contributor to seston with C:N ratios varying from (11.6 to 11.9) and hence has values substantially lower than C:N ratios of DOM from terrestrial sources such as leaf litter (53 to 62) and B horizon soil organic matter (22 to 29). Similarly, in a forested mid-Atlantic watershed, a decrease of C:N ratios from litter to groundwater were observed largely due to a loss of DOC compared to DON (Inamdar et al., 2011). Goodman et al. (2011) also observed high temporal variability of C:N ratios and a decrease of the C:N ratios between inlet and

1 outlet in five out of seven lakes studied. Other studies have suggested that changes in DON  
2 concentrations can be attributed to hydrological factors (Kaiser and Zech, 2000; Kaushal and  
3 Lewis, 2003), internal N cycles (Caraco and Cole, 2003; Kaushal and Lewis, 2005), and high  
4 DON uptake in N-limited systems (Kaushal and Lewis, 2005; Stepanauskas et al., 2000a).  
5 The increase of DON in Arbutus Lake might also be due to the production of DON from  
6 macrophyte stands (Stepanauskas et al., 2000b) which are abundant (Heady, 1942).

7 In the current study, one of the major findings is the observation of different retention  
8 amounts of DOC versus DON within the Lake (Table 4, Figure 8a5a). The lowest retention,  
9 we observed, for both DOC and DON in 2007 could likely be attributed to the biotic  
10 contributions. Although we would require measurements of primary productivity to quantify  
11 the contribution of internal biological production within the Lake, the large amounts of DIN  
12 removal in the Lake suggests the importance of DIN uptake and DON production in  
13 regulating TDN in the Lake (Figure 8b). In 2003, the year with highest hydraulic retention in  
14 the Lake, we observed the highest retention of DOC and a high level of retention of DON  
15 (Table 4). In comparing results among years, there was a positive relationship between  
16 hydraulic retention and DOC retention, but not for DON retention (Table 5).

#### 17 **4.4 Limitation and further study**

18 ~~Our observation of the increase of DON compared to DOC within the Lake indicated the~~  
19 ~~importance of the DON generation processes in the N mass balance of the Lake. When DON~~  
20 ~~is mineralized to ammonium some of the ammonium may be nitrified. This nitrate can then be~~  
21 ~~utilized in assimilatory and dissimilatory reduction. Some of the organic N formed by~~  
22 ~~assimilatory nitrate reduction can be found as DON (Figure 8b5b). Regarding the differences~~  
23 ~~in DON formation versus DOC formation in the Lake, it is important to ascertain whether the~~  
24 ~~rate of DON decomposition was substantially less than that of DOC or the DON generation~~  
25 ~~from DIN was the major factor in maintaining relatively high concentrations of DON in the~~  
26 ~~Lake. From the 1-year study of Kang and Mitchell (2013) in the Arbutus Lake, approximately~~  
27 ~~39.9  $\mu\text{mol C L}^{-1}$  in DOC (10% of the total DOC) was microbially decomposed, whereas 2.2~~  
28  ~~$\mu\text{mol N L}^{-1}$  in DON (20% of the total DON) was estimated to be bioavailable. Considering~~  
29 ~~the concentration difference of DOC and DON between inlet and outlet in this study [93  $\mu\text{mol}$~~   
30  ~~$\text{C L}^{-1}$  and 1  $\mu\text{mol N L}^{-1}$ , respectively; calculated from Table 44], the bioavailable DON was~~  
31 ~~greater than the difference between the inlet and outlet, indicating that DON was likely~~

1 produced within the Lake ([Kang and Mitchell, 2013](#)). In contrast, larger amounts of DOC  
2 were retained in the Lake than values of biodegradable DOC, indicating that DOC might be  
3 more readily decomposed due to different processes with DON changes in the Lake.  
4 Therefore, we suggest that DON generated from internal production from DIN is important.  
5 Further study is needed to understand the [primary productivity](#)~~algal production rate for~~  
6 [estimating of](#) DOC and DON, [the microbial uptake rate of DOC \(i.e., glucose\) and DON \(i.e.,](#)  
7 [dissolved free amino acid\)](#) and the quantification of DON decomposition and retention.

8 Wet DIN deposition was estimated to account for 21.3% (range: 14.3 to 29.2 %) of the DIN  
9 input to Arbutus Lake from 2000 to 2009 [for example, in 2009 allochthonous DIN input  
10 from the inlet catchment,  $26,878 \text{ mol N yr}^{-1} = 89 \text{ mol N ha}^{-1} \text{ yr}^{-1}$  (inlet DIN flux in 2009;  
11 [Table 34](#))  $\times 302 \text{ ha}$  (entire watershed area – lake area) and wet deposition input of DIN,  
12  $11,071 \text{ mol N yr}^{-1} = 221 \text{ mol N ha}^{-1} \text{ yr}^{-1}$  (NADP, 2009)  $\times 50 \text{ ha}$  (lake area)]. If the direct  
13 deposition of DIN in the Lake is included in the N budget, N mass balances in the retention of  
14 DIN in Arbutus Lake is even greater [mean of DIN retention including wet DIN deposition:  
15 64.3%]. Arbutus Lake is considered P-limited based on its molar N:P ratio of 25 [more than 7  
16 of Redfield's ratio; calculated from TP concentration data ( $0.44 \mu\text{mol P L}^{-1}$ ) from Kelting and  
17 Laxson (2014) and average TDN data ( $23 \mu\text{mol N L}^{-1}$ ) in this study]. Whereas in N-limited  
18 lakes, lake productivity is dependent on atmospheric DIN inputs that contribute to algal  
19 productivity and DON concentrations. In those N-limited lakes, the recycling of DON might  
20 play an important role in N availability. Additionally, in lentic systems, since DOM  
21 bioavailability may regulate secondary production in the microbial loop  
22 (DOM→bacteria→protozoa→zooplankton), we should reconsider the importance of DON  
23 recycling.

24 [DIC is the end product of DOC due to retention/decomposition with other fates of DOC](#)  
25 [including sedimentation, photolysis and direct uptake for biotic production. The DIC of](#)  
26 [Arbutus Lake has a mean of  \$\sim 115 \mu\text{mol C L}^{-1}\$  and DIC ranges from  \$\sim 50\$  to  \$250 \mu\text{mol C L}^{-1}\$](#)   
27 [\(NYSERDA, 2011\) and DIC constitutes about 25% of total dissolved carbon. Fakhraei and](#)  
28 [Driscoll \(2015\) summarized across the ALTM lakes which included Arbutus Lake that DIC is](#)  
29 [uniformly oversaturated with respect to the solubility of atmospheric  \$\text{CO}\_2\$ . The importance of](#)  
30 [DIC as a DOC sink needs to be studied further. Also in spite of the potential for photolysis as](#)  
31 [a mechanism removing DOC and producing DIC in lakes \(e.g., Wetzel, 2003\), the](#)

1 quantitative determination of the relative importance of this process has been difficult.  
2 Therefore, future research should consider the effect of allochthonous DOM entering lakes  
3 during the growing season on the net increase of DOC and DON in lakes during ice-cover and  
4 quantify the photolysis of DOM [e.g., approximately 10% of total respiration based on the  
5 study of Granéli et al. (1996)].

## 7 **5 Conclusions**

8 Our study found no significant long-term changes in annual mean concentrations of DOC and  
9 DON. However, mass-balances for DOC and DON between the Lake inlet and outlet revealed  
10 that the Lake was generally a sink for DOC (range: 11,800 to 105,000 mol) and DIN (range:  
11 3,000 to 9,150 mol), but functioned as a sink or source for DON (range: -750 to 1,350 mol);  
12 ~~depending the time of the year~~. Annual concentrations and fluxes showed strong variation  
13 ~~among years~~ as a function of the hydraulic retention time of the Lake.

14 Our study suggests a complex interplay of both hydrological and biological factors in  
15 affecting DOC dynamics of a lake (Goodman et al., 2011), and that newly formed DON from  
16 DIN within a lake plays an important role in lake N dynamics (Stepanauska et al., 2000b).  
17 The enrichment of N in DOM could be a source of nutrient N for downstream aquatic  
18 ecosystems. This DON may also serve as a link in the supply of a limiting N nutrient and  
19 subsequently contribute to productivity of N limited systems. Our study provides new  
20 information~~indicates~~ that DOC and DON may display substantially different biogeochemical  
21 relationships in oligo/mesotrophic lakes nested in forested watersheds, and therefore different  
22 roles for a sink behavior for DOC (which has received more attention) ~~versus and~~ a producer  
23 of DON.

## 25 **Acknowledgments**

26 We thank David Lyon (SUNY-ESF) for sampling and analytical assistance. This research was  
27 supported by U.S. National Science Foundation (Ecosystem Studies, LTER, Hubbard Brook)  
28 and the New York State Energy Research and Development Authority (NYSERDA).

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## 2 **References**

3 Aitkenhead, J. A. and McDowell, W. H.: Soil C:N ratio as a predictor of annual riverine DOC  
4 flux at local and global scales, *Global Biogeochem. Cy.*, 14, 127–138,  
5 doi:10.1029/1999GB900083, 2000.

6 Aitkenhead-Peterson, J. A., McDowell, W. H., and Neff, J. C.: Sources, production, and  
7 regulation of allochthonous dissolved organic matter inputs to surface waters, in: *Aquatic  
8 ecosystems: interactivity of dissolved organic matter*, edited by Findlay, S. E. G. and  
9 Sinsabaugh, R. L., Academic Press San Diego, 26–70, 2003.

10 Bertilsson, S. and Jones, J. B.: Supply of dissolved organic matter to aquatic ecosystems:  
11 autochthonous sources, in: *Aquatic ecosystems: interactivity of dissolved organic matter*,  
12 edited by Findlay, S. E. G. and Sinsabaugh, R. L., Academic Press San Diego, 3–24, 2003.

13 Bertilsson, S. and Tranvik, L.: Photochemical transformation of dissolved organic matter in  
14 lakes, *Limnol. Oceanogr.*, 45, 753–762, 2000.

15 Bischoff, J. M., Bukaveckas, P., Mitchell, M. J., and Hurd, T.: N storage and cycling in  
16 vegetation of a forested wetland: implications for watershed N processing, *Water Air Soil  
17 Poll.*, 128, 97–114, 2001.

18 Boyer, E. W., Hornberger, G. M., Bencala, K. E., and McKnight, D. M.: Response  
19 characteristics of DOC flushing in an alpine catchment, *Hydrol. Process.*, 11, 1635–1647,  
20 doi:10.1002/(SICI)1099-1085(19971015)11:12<1635::AID-HYP494>3.0.CO;2-H, 1997.

21 Campbell, J. L., Hornbeck, J. W., McDowell, W. H., Buso, D. C., Shanley, J. B., and Likens,  
22 G. E.: Dissolved organic nitrogen budgets for upland, forested ecosystems in New England,  
23 *Biogeochemistry*, 49, 123–142, 2000.

24 Canham, C. D., Pace, M. L., Papaik, M. J., Primack, A. G. B., Roy, K. M., Maranger, R. J.,  
25 Curran, R. P., and Spada, D. M.: A spatially explicit watershed-scale analysis of dissolved  
26 organic carbon in Adirondack lakes, *Ecol. Appl.*, 14, 839–854, 2004.

- 1 Caraco, N. F. and Cole, J. J.: The importance of organic nitrogen production in aquatic  
2 systems: A landscape perspective, in: *Aquatic ecosystems: interactivity of dissolved organic*  
3 *matter*, edited by Findlay, S. E. G. and Sinsabaugh, R. L., Academic Press San Diego, 263–  
4 279, 2003.
- 5 Chen, L., Driscoll, C. T., Gbondo-Tugbawa, S. S., Mitchell, M. J., and Murdoch, P. S.: The  
6 application of an integrated biogeochemical model (PnET-BGC) to five forested watersheds  
7 in the Adirondack and Catskill regions of New York, *Hydrol. Process.*, 18, 2631–2650, 2004.
- 8 Driscoll, C. T. and van Dreason, R.: Seasonal and long-term temporal patterns in the  
9 chemistry of Adirondack lakes, *Water Air Soil Poll.*, 67, 319–344, 1993.
- 10 Driscoll, C. T., Fuller, R. D., and Simone, D. M.: Longitudinal variations in trace metal  
11 concentrations in a northern forested ecosystem, *J. Environ. Qual.*, 17, 101–107, 1988.
- 12 Driscoll, C. T., Driscoll, K. M., Roy, K. M., and Mitchell, M. J.: Chemical response of lakes  
13 in the Adirondack region to declines in acidic deposition, *Environ. Sci. Technol.*, 37, 2036–  
14 2042, 2003.
- 15 Driscoll, C. T., Driscoll, K. M., Roy, K. M., and Dukett, J.: Changes in the chemistry of lakes  
16 in the Adirondack region of New York following declines in acidic deposition, *Appl.*  
17 *Geochem.*, 22, 1181–1188, doi:10.1016/j.apgeochem.2007.03.009, 2007.
- 18 Ekstrom, S. M., Kritzberg, E. S., Kleja, D. B., Larsson, N., Nilsson, P. A., Graneli, W., and  
19 Bergkvist, B.: Effect of acid deposition on quantity and quality of dissolved organic matter in  
20 soil-water, *Environ. Sci. Technol.*, 45, 4733–4739, doi:10.1021/es104126f, 2011.
- 21 Erlandsson, M., Cory, N., Fölster, J., Köhler, S., Laudon, H., Weyhenmeyer, G. A., and  
22 Bishop, K.: Increasing dissolved organic carbon redefines the extent of surface water  
23 acidification and helps resolve a classic controversy, *Bioscience*, 61, 614–618,  
24 doi:10.1525/bio.2011.61.8.7, 2011.
- 25 Evans, C. D., Monteith, D. T., Reynolds, B., and Clark, J. M.: Buffering of recovery from  
26 acidification by organic acids, *Sci. Total Environ.*, 404, 316–325, 2007.



- 1 Evans, C. D., Jones, T. G., Burden, A., Ostle, N., Zieliński, P., Cooper, M. D. A., Peacock, M.,  
2 Clark, J. M., Oulehle, F., Cooper, D., and Freeman, C.: Acidity controls on dissolved organic  
3 carbon mobility in organic soils, *Glob. Change Biol.*, 18, 3317–3331, doi:10.1111/j.1365-  
4 2486.2012.02794.x, 2012.
- 5 [Fakhraei, H. and Driscoll, C. T.: Proton and aluminum binding properties of organic acids in](#)  
6 [surface waters of the Northeastern U.S., \*Environ. Sci. Technol.\*, 49, 2939–2947,](#)  
7 [doi:10.1021/es504024u, 2015.](#)
- 8 Fellman, J. B., Dogramaci, S., Skrzypek, G., Dodson, W., and Grierson, P. F.: Hydrologic  
9 control of dissolved organic matter biogeochemistry in pools of a subtropical dryland river,  
10 *Water Resour. Res.*, 47, doi:10.1029/2010WR010275, 2011.
- 11 Findlay, S. E. G. and Sinsabaugh, R. L. (Eds.): *Aquatic ecosystems: interactivity of dissolved*  
12 *organic matter*, Academic Press San Diego, 2003.
- 13 Foster, N. W., Mitchell, M. J., Morrison, I. K., and Shepard, J. P.: Nutrient cycling in  
14 Huntington Forest and Turkey Lakes deciduous stands: acid and base cations, *Can. J. Forest*  
15 *Res.*, 22, 167–174, 1992.
- 16 Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B., and Fenner, N.: Export of organic  
17 carbon from peat soils, *Nature*, 412, 785, 2001.
- 18 Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A.,  
19 Sleep, D., Hughes, S., and Hudson, J.: Export of dissolved organic carbon from peatlands  
20 under elevated carbon dioxide levels, *Nature*, 430, 195–198, 2004.
- 21 Goodman, K. J., Baker, M. A., and Wurtsbaugh, W. A.: Lakes as buffers of stream dissolved  
22 organic matter (DOM) variability: Temporal patterns of DOM characteristics in mountain  
23 stream-lake systems, *J. Geophys. Res.*, 116, G00N02, doi:10.1029/2011JG001709, 2011.
- 24 Granéli, W., Lindell, M., and Tranvik, L.: Photo-oxidative production of dissolved inorganic  
25 carbon in lakes of different humic content, *Limnol. Oceanogr.*, 41, 698–706, 1996.

- 1 Gregorich, E. G., Beare, M. H., Stoklas, U., and St-Georges, P.: Biodegradability of soluble  
2 organic matter in maize-cropped soils, *Geoderma*, 113, 237–252, doi:10.1016/S0016-  
3 7061(02)00363-4, 2003.
- 4 Heady, H. F.: Littoral vegetation of the lakes on the Huntington Forest, *Roosevelt Wildlife*  
5 *Bulletin*, 8, 1–37, 1942.
- 6 Hedin, L. O., Armesto, J. J., and Johnson, A. H.: Patterns of nutrient loss from unpolluted,  
7 old-growth temperate forests: evaluation of biogeochemical theory, *Ecology*, 76, 493–509,  
8 1995.
- 9 Helsel, D. R., Mueller, D. K., and Slack, J. R.: Computer program for the Kendall family of  
10 trend tests, U.S. Geological Survey Scientific Investigations Report 2005-5275; 4, 2006.
- 11 Hinton, M. J., Schiff, S. L., and English, M. C.: The significance of storms for the  
12 concentration and export of dissolved organic carbon from two Precambrian Shield  
13 catchments, *Biogeochemistry*, 36, 67–88, 1997.
- 14 Hornberger, G. M., Bencala, K. E., and McKnight, D. M.: Hydrological controls on dissolved  
15 organic carbon during snowmelt in the Snake River near Montezuma, Colorado,  
16 *Biogeochemistry*, 25, 147–165, doi:10.1007/BF00024390, 1994.
- 17 Inamdar, S. P. and Mitchell, M. J.: Storm event exports of dissolved organic nitrogen (DON)  
18 across multiple catchments in a glaciated forest watershed, *J. Geophys. Res.*, 112, G02014,  
19 doi:10.1029/2006JG000309, 2007.
- 20 Inamdar, S. P., Rupp, J., and Mitchell, M. J.: Differences in dissolved organic carbon (DOC)  
21 and nitrogen (DON) responses to storm-event and groundwater conditions in a forested  
22 western New York, *J. Am. Water Resour. As.*, 44, 1–16, 2008.
- 23 Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H., and McHale, P.:  
24 Fluorescence characteristics and sources of dissolved organic matter for stream water during  
25 storm events in a forested mid-Atlantic watershed, *J. Geophys. Res.*, 116, G03043,  
26 doi:10.1029/2011JG001735, 2011.

- 1 Ito, M., Mitchell, M. J., Driscoll, C. T., and Roy, K. M.: Nitrogen input-output budgets for  
2 lake-watersheds in the Adirondack region of New York, *Biogeochemistry*, 72, 283–314, 2005.
- 3 Ito, M., Mitchell, M. J., Driscoll, C. T., Newton, R. M., Johnson, C. E., and Roy, K. M.:  
4 Controls on surface water chemistry in two lake-watersheds in the Adirondack region of New  
5 York: differences in nitrogen solute sources and sinks, *Hydrol. Process.*, 21, 1249–1264, 2007.
- 6 Johnson, D. W. and Lindberg, S. E.: *Atmospheric Deposition and Forest Nutrient Cycling*,  
7 Springer-Verlag New York, 1992.
- 8 Kaiser, K. and Zech, W.: Sorption of dissolved organic nitrogen by acid subsoil horizons and  
9 individual mineral phases, *Eur. J. Soil Sci.*, 51, 403–411, doi:10.1046/j.1365-  
10 2389.2000.00320.x, 2000.
- 11 Kalbitz, K., Solinger, D., Park, J. H., and Matzner, E.: Controls on the dynamics of dissolved  
12 organic matter: A review, *Soil Sci.*, 165, 277–304, 2000.
- 13 Kang, P. and Mitchell, M. J.: Bioavailability and size-fraction of dissolved organic carbon,  
14 nitrogen, and sulfur at the Arbutus Lake watershed, Adirondack Mountains, NY,  
15 *Biogeochemistry*, 115, 213–234, doi:10.1007/s10533-013-9829-1, 2013.
- 16 Kaushal, S. S. and Lewis, W. M.: Patterns in the chemical fractionation of organic nitrogen in  
17 Rocky Mountain streams, *Ecosystems*, 6, 483–492, doi:10.1007/s10021-003-0175-3, 2003.
- 18 Kaushal, S. S. and Lewis, W. M.: Fate and transport of organic nitrogen in minimally  
19 disturbed montane streams of Colorado, USA, *Biogeochemistry*, 74, 303–321,  
20 doi:10.1007/s10533-004-4723-5, 2005.
- 21 Kelting, D. L. and Laxson, C. L.: *Adirondack Lake Assessment Program: 2013 Report*,  
22 *Arbutus Lake, Adirondack Watershed Institute of Paul Smith’s College. Report No. PSCAWI*  
23 *2014-56; 24*, 2014.
- 24 Kirchman, D. L.: The contribution of monomers and other low-molecular weight compounds  
25 to the flux of dissolved organic material in aquatic ecosystems, in: *Aquatic ecosystems:*

- 1 interactivity of dissolved organic matter, edited by Findlay, S. E. G. and Sinsabaugh, R. L.,  
2 Academic Press San Diego, 217–241, 2003.
- 3 Kopáček, J., Hejzlar, J., Kana, J., Porcal, P., and Klementová, S.: Photochemical and  
4 biological degradation of dissolved organic carbon and its impact on alkalinity production in  
5 acidified lakes, *Limnol. Oceanogr.*, 43, 106–117, 2003.
- 6 Levia, D. F., Carlyle-Moses, D., and Tanaka, T. (Eds.): *Forest hydrology and*  
7 *biogeochemistry: synthesis of past research and future directions*, Springer Netherlands, 2011.
- 8 Likens, G. E., Edgerton, E. S., and Galloway, J. N.: The composition and deposition of  
9 organic carbon in precipitation, *Tellus*, 35B, 16–24, 1983.
- 10 McGlynn, B. L. and McDonnell, J. J.: Role of discrete landscape units in controlling  
11 catchment dissolved organic carbon dynamics, *Water Resour. Res.*, 39, 1090,  
12 doi:10.1029/2002WR001525, 2003.
- 13 McHale, M. R., Mitchell, M. J., McDonnell, J. J., and Cirimo, C.: Nitrogen solutes in an  
14 Adirondack forested watershed: importance of dissolved organic nitrogen, *Biogeochemistry*,  
15 48, 165–184, doi:10.1023/A:1006121828108, 2000.
- 16 Mitchell, M. J., Driscoll, C. T., and Raynal, D. J.: Temporal changes and Solute Mass  
17 Balances in an Adirondack Forested watershed, *Water Air Soil Poll.*, 88, 355–369, 1996.
- 18 Mitchell, M. J., McHale, P. J., Inamdar, S. P., and Raynal, D. R.: Role of within-lake  
19 processes and hydrobiogeochemical changes over 16 years in a watershed in the Adirondack  
20 Mountains of New York State, USA, *Hydrol. Process.*, 15, 1951–1965, 2001.
- 21 Mitchell, M. J., Piatek, K. B., Christopher, S., Mayer, B., Kendall, C., and McHale, P.: Solute  
22 sources in stream water during consecutive fall storms in a northern hardwood forest  
23 watershed: a combined hydrological, chemical and isotopic approach, *Biogeochemistry*, 78,  
24 217–246, 2006.
- 25 Molot, L. A. and Dillon, P. J.: Photolytic regulation of dissolved organic carbon in northern  
26 lakes, *Global Biogeochem. Cy.*, 11, 357–365, 1997.

- 1 Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T.,  
2 Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopáček, J., and  
3 Vesely, J.: Dissolved organic carbon trends resulting from changes in atmospheric deposition  
4 chemistry, *Nature*, 450, 537–540, 2007.
- 5 Monteith, D. T., Henrys, P. A., Evans, C. D., Malcolm, I., Shilland, E. M., and Pereira, M. G.:  
6 Spatial controls on dissolved organic carbon in upland waters inferred from a simple  
7 statistical model, *Biogeochemistry*, 123, 363–377, doi:10.1007/s10533-015-0071-x, 2015.
- 8 Mulder, J., De Wit, H. A., Boonen, H. W. J., and Bakken, L. R.: Increased levels of aluminum  
9 in forest soils: effects on the stores of soil organic carbon, *Water Air Soil Poll.*, 130, 989–994,  
10 2001.
- 11 NADP: National Atmospheric Deposition Program, 2009.
- 12 Neff, J. C., Chapin, F. S. III, and Vitousek, P. M.: Breaks in the cycle: dissolved organic  
13 nitrogen in terrestrial ecosystems, *Front. Ecol. Environ.*, 1, 205–211, 2003.
- 14 Newton, R. M. and Driscoll, C. T.: Classification of ALSC Lakes, in: *Adirondack Lakes  
15 Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984-87,*  
16 *Adirondack Lakes Survey Corporation, Ray Brook pp. 2-70-2-91, 1990.*
- 17 NYSERDA: The Adirondack Long-Term Monitoring Lakes: A Compendium of Site  
18 Descriptions, Recent Chemistry and Selected Research Information, New York State Energy  
19 Research and Development Authority Report. No. 11-12, 251–252, 2011.
- 20 NYSERDA: Importance of Acidic and Mercury Deposition in Relation to Climate Change in  
21 the Adirondack Mountains: Biogeochemical Responses, New York State Energy Research  
22 and Development Authority Report. No. 15-04s, 2015.
- 23 OECD: Eutrophication of waters: Monitoring, assessment and control, Organisation for  
24 Economic Co-operation and Development, Paris, 1982.
- 25 Owen, J. S., Mitchell, M. J., and Michener, R. H.: Stable nitrogen and carbon isotopic  
26 composition of seston and sediment in two Adirondack lakes, *Can. J. Fish. Aquat. Sci.*, 56,  
27 2186–2192, 1999.

- 1 Pace, M. L. and Cole, J. J.: Synchronous variation of dissolved organic carbon and color in  
2 lakes, *Limnol. Oceanogr.*, 47, 333–342, doi:10.4319/lo.2002.47.2.0333, 2002.
- 3 Park, J. H., Mitchell, M. J., McHale, P. J., Christopher, S. F., and Myers, T. P.: Interactive  
4 effects of changing climate and atmospheric deposition on N and S biogeochemistry in a  
5 forested watershed of the Adirondack Mountains, New York State, *Glob. Change Biol.*, 9,  
6 1602–1619, 2003.
- 7 Park, J. H., Mitchell, M. J., and Driscoll, C. T.: Winter-time climatic control on dissolved  
8 organic carbon export and surface water chemistry in an Adirondack forested watershed,  
9 *Environ. Sci. Technol.*, 39, 6993–6998, 2005.
- 10 Petrone, K. C., Richards, J. S., and Grierson, P. F.: Bioavailability and composition of  
11 dissolved organic carbon and nitrogen in a near coastal catchment of south-western Australia,  
12 *Biogeochemistry*, 92, 27–40, doi:10.1007/s10533-008-9238-z, 2009.
- 13 Piatek, K. B., Christopher, S. F., and Mitchell, M. J.: Spatial and temporal dynamics of stream  
14 chemistry in a forested watershed, *Hydrol. Earth Syst. Sci.*, 13, 423–439, 2009.
- 15 Reddy, K. R. and DeLaune, R. D. (Eds.): *Biogeochemistry of wetlands: Science and*  
16 *applications*, CRC Press, 2008.
- 17 [Sarkkola, S., Nieminen, M., Koivusalo, H., Laurén, A., Kortelainen, P., Mattsson, T.,](#)  
18 [Palviainen, M., Piirainen, S., Starr, M. and Finér, L.: Trends in concentrations and export of](#)  
19 [nitrogen in boreal forest streams, \*Boreal Env. Res.\*, 17, 85–101, 2012.](#)
- 20 Schindler, D. W., Stainton, M. P., Kelly, C. A., Bayley, S. E., Curtis, P. J., and Parker, B. R.:  
21 Natural and man-caused factors affecting the abundance and cycling of dissolved organic  
22 substances in Precambrian Shield lakes, *Hydrobiologia*, 229, 1–21, 1992.
- 23 Schindler, D. W., Curtis, P. J., Bayley, S. E., Parker, B. R., Beaty, K. G., and Stainton, M. P.:  
24 Climate-induced changes in the dissolved organic carbon budgets of boreal lakes,  
25 *Biogeochemistry*, 36, 9–28, 1997.
- 26 Siddiqui, M. S., Amy, G. L., and Murphy, B. D.: Ozone enhanced removal of natural organic  
27 matter from drinking water sources, *Water Res.*, 31, 3098–3106, 1997.

- 1 Singh, S., Inamdar, S., Mitchell, M., and McHale, P.: Seasonal pattern of dissolved organic  
2 matter (DOM) in watershed sources: influence of hydrologic flow paths and autumn leaf fall,  
3 *Biogeochemistry*, 118, 321–333, 2014.
- 4 Sinsabaugh, R. L. and Findlay, S.: Dissolved organic matter: Out of the black box into the  
5 mainstream, in: *Aquatic ecosystems: interactivity of dissolved organic matter*, edited by  
6 Findlay, S. E. G. and Sinsabaugh, R. L., Academic Press San Diego, 479–498, 2003.
- 7 Stepanauskas, R., Laudon, H., and Jorgensen, N. O. G.: High DON bioavailability in boreal  
8 streams during a spring flood, *Limnol. Oceanogr.*, 45, 1298–1307,  
9 doi:10.4319/lo.2000.45.6.1298, 2000a.
- 10 Stepanauskas, R., Farjalla, V. F., Tranvik, L. J., Svensson, J. M., Esteves, F. A., and Granéli,  
11 W.: Bioavailability and sources of DOC and DON in macrophyte stands of a tropical coastal  
12 lake, *Hydrobiologia*, 436, 241–248, 2000b.
- 13 Tate, C. M. and Meyer, J. L.: The influence of hydrologic conditions and successional state  
14 on dissolved organic-carbon export from forested watersheds, *Ecology*, 64, 25–32,  
15 doi:10.2307/1937325, 1983.
- 16 Thurman, E. M.: *Organic geochemistry of natural waters*, Martinus Nijhoff/Dr W. Junk  
17 Publishers: Dordrecht, p. 51, 1985.
- 18 Tranvik, L. J. and Jansson, M.: Climate change-terrestrial export of organic carbon, *Nature*,  
19 415, 861–862, 2002.
- 20 von Schiller, D., Graeber, D., Ribot, M., Timoner, X., Acuña, V., Martí, E., Sabater, S., and  
21 Tockner, K.: Hydrological transitions drive dissolved organic matter quantity and  
22 composition in a temporary Mediterranean stream, *Biogeochemistry*, 123, 429–446,  
23 doi:10.1007/s10533-015-0077-4, 2015.
- 24 Webster, J. R., Wallace, J. B., and Benfield, E. F.: Chapter 6. Organic processes in streams of  
25 the eastern United States, in: *River and stream ecosystems of the world*, edited by Cushing, C.  
26 E., Cummins, K. W., and Minshall, G. W., University of California Press, 117–187, 2006.

- 1 Wetzell, R. G.: *Limnology: Lake and River Ecosystems*, 3rd edn., Academic Press New York,  
2 2001.
- 3 Wetzell, R. G.: Dissolved organic carbon: Detrital energetics, metabolic regulators, and drivers  
4 of ecosystem stability of aquatic ecosystems, in: *Aquatic ecosystems: interactivity of*  
5 *dissolved organic matter*, edited by Findlay, S. E. G. and Sinsabaugh, R. L., Academic Press  
6 San Diego, 455–478, 2003.
- 7 Williamson, C. E.: What role does UV-B radiation play in freshwater ecosystems?, *Limnol.*  
8 *Oceanogr.*, 40, 386–392, 1995.
- 9 Worrall, F. and Burt, T.: Predicting the future DOC flux from upland peat catchments, *J.*  
10 *Hydrol.*, 300, 126–39, 2005.
- 11 Worrall, F., Burt, T., and Adamson, J.: Can climate change explain increases in DOC flux  
12 from upland peat catchments?, *Sci. Total Environ.*, 326, 95–112, 2004.



1 | Table 1. Means and linear regression results (slope and p value) of annual precipitation and atmospheric temperature at Adirondack  
 2 | Ecological Center site since 1941 and 1983 (available at: [http://www.esf.edu/aec/research/ALTEMP\\_projects.htm](http://www.esf.edu/aec/research/ALTEMP_projects.htm), 2016) and annual  
 3 | discharge, DOC concentration, and DOC flux at the Arbutus Lake outlet since 1983 using ALTM data set

	<u>Period</u>	<u>Mean (SD)</u>	<u>Slope</u>	<u>p value</u>	<u>Unit</u>
<u>Precipitation*</u>	<u>1941-2009</u>	<u>1046.2 (152.0)</u>	<u>2.1</u>	<u>0.02</u>	<u>mm</u>
	<u>1983-2009</u>	<u>1109.8 (125.8)</u>	<u>5.4</u>	<u>0.08</u>	
<u>Temperature</u>	<u>1941-2009</u>	<u>5.2 (1.0)</u>	<u>-0.01</u>	<u>0.79</u>	<u>°C</u>
	<u>1983-2009</u>	<u>5.5 (0.7)</u>	<u>0.03</u>	<u>0.07</u>	
<u>Lake Discharge*</u>	<u>1983-2009</u>	<u>619.4 (118.2)</u>	<u>-0.2</u>	<u>0.95</u>	<u>mm ha<sup>-1</sup></u>
<u>DOC concentration</u>	<u>1983-2012</u>	<u>408.1 (31.3)</u>	<u>0.1</u>	<u>0.91</u>	<u>mol C L<sup>-1</sup></u>
<u>DOC flux</u>	<u>1983-2012</u>	<u>2,501 (602)</u>	<u>-2.8</u>	<u>0.84</u>	<u>mol C ha<sup>-1</sup> yr<sup>-1</sup></u>

4 | \* Determination coefficient ( $r^2$ ) between precipitation and lake discharge from 1983 to 2009 is 0.51 ( $p < 0.0001$ ).  
 5 |

1 Table 2. Monthly and yearly Pearson correlation results (r) among DOC, DON and DIN concentrations as well as climatic variables  
 2 (Huntington Forest) at the inlet and outlet of Arbutus Lake. Note that r values correlation results with 0.5 or greater in monthly analysis  
 3 are shown to emphasize the most important correlations. A statistically significant correlation is indicated with asterisks (p<0.001<sup>\*\*\*</sup>,  
 4 p<0.01<sup>\*\*</sup>, p<0.05<sup>\*</sup>).

		Jan - Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
DOC vs. DON	Inlet	0.26 <sup>***</sup>							0.55 <sup>***</sup>					
	Outlet													
DON vs. DIN	Inlet	-0.28 <sup>***</sup>								-0.68 <sup>***</sup>				-0.41 <sup>**</sup>
	Outlet	-0.29 <sup>***</sup>					-0.50 <sup>***</sup>		-0.61 <sup>***</sup>	-0.57 <sup>***</sup>	-0.66 <sup>***</sup>		-0.53 <sup>***</sup>	-0.54 <sup>***</sup>
DOC vs. DIN	Inlet	-0.28 <sup>***</sup>	0.57 <sup>***</sup>	0.62 <sup>***</sup>										
	Outlet													
DOC vs. Temp	Inlet	0.35 <sup>***</sup>	0.56 <sup>***</sup>											
	Outlet	-0.24 <sup>***</sup>												
DON vs. Temp	Inlet	0.29 <sup>***</sup>												
	Outlet													
DIN vs. Temp	Inlet	-0.55 <sup>***</sup>												
	Outlet	-0.34 <sup>***</sup>												
DOC vs. Discharge	Inlet	0.15 <sup>**</sup>	0.61 <sup>***</sup>	0.75 <sup>***</sup>	0.64 <sup>***</sup>		0.77 <sup>***</sup>		0.66 <sup>***</sup>	0.62 <sup>***</sup>				
	Outlet	0.11 <sup>**</sup>					0.50 <sup>***</sup>		0.57 <sup>***</sup>					
DON vs. Discharge	Inlet	0.11 <sup>**</sup>										0.50 <sup>***</sup>		
	Outlet													
DIN vs. Discharge	Inlet	0.38 <sup>***</sup>	0.62 <sup>***</sup>	0.71 <sup>***</sup>										
	Outlet	0.27 <sup>***</sup>												

5

1 | Table 32. Annual precipitation, inlet and outlet discharge, residence time, and hydraulic retention from 2000 to 2009 in Arbutus Lake.

Year	Precipitation (mm yr <sup>-1</sup> )	Inlet discharge (mm yr <sup>-1</sup> )	Outlet discharge (mm yr <sup>-1</sup> )	Residence time (year)	Hydraulic retention (%)
2000	1,323	885	733	0.52	17.2
2001	901	572	476	0.80	16.9
2002	902	545	541	0.71	0.9
2003	1,094	860	632	0.60	26.5
2004	972	635	567	0.67	10.8
2005	1,296	728	539	0.71	26.0
2006	1,174	820	712	0.54	13.2
2007	1,199	604	542	0.70	10.2
2008	1,395	830	756	0.51	8.9
2009	1,153	641	471	0.81	26.5
Mean	1,141	720	597	0.66	15.7

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3

1 | Table 3. Means ( $\pm$ SE, n=10) of annual discharge-weighted concentrations, fluxes, and retention of DOC, DON, and DIN and molar  
 2 | DOC:DON ratios at the inlet and outlet sites from 2000 to 2009.

		Inlet	Outlet	Retention
Discharge-weighted concentration ( $\mu\text{mol L}^{-1}$ )	DOC	506 (16)	413 (14)	
	DON	10 (1)	11 (1)	
	DIN	28 (3)	12 (2)	
DOC:DON (molar ratio)		55 (6)	40 (3)	
Flux ( $\text{mol ha}^{-1} \text{yr}^{-1}$ )	DOC	3,617 (257)	2,477 (180)	30.1% (3.3)
	DON	71 (8)	63 (2)	-6.9% (6.9)
	DIN	195 (19)	75 (8)	61.1% (3.1)

4  
5

1 | Table 4. Annual average of discharge-weighted concentrations, molar DOC:DON ratio, annual flux, and retention (% and amount) of  
 2 | DOC, DON, and DIN at the inlet (In) and outlet (Out) of Arbutus Lake from 2000 to 2009 (I-O: Input-Output).

3

Year	DOC ( $\mu\text{mol C L}^{-1}$ )		DON ( $\mu\text{mol N L}^{-1}$ )		DIN ( $\mu\text{mol N L}^{-1}$ )		C:N		DOC ( $\text{mol C ha}^{-1} \text{ yr}^{-1}$ )		DON ( $\text{mol N ha}^{-1} \text{ yr}^{-1}$ )		DIN ( $\text{mol N ha}^{-1} \text{ yr}^{-1}$ )		Retention (%)			<u>Retention Amount (mol)</u>		
	In	Out	In	Out	In	Out	In	Out	In	Out I-O	In	Out I-O	In	Out I-O	DOC	DON	DIN	<u>DOC</u>	<u>DON</u>	<u>DIN</u>
2000	486	392	11	12	29	12	44	33	4,303	2,875 <del>1,428</del>	96	85 <del>-12</del>	259	92 <del>+67</del>	33.2	12.0	64.5	<u>71,400</u>	<u>-550</u>	<u>8,350</u>
2001	547	386	11	9	38	18	50	44	3,130	1,838 <del>1,292</del>	60	42 <del>-18</del>	220	84 <del>+36</del>	41.3	30.0	61.8	<u>64,600</u>	<u>900</u>	<u>6,800</u>
2002	476	354	9	10	29	15	53	35	2,599	1,911 <del>-688</del>	51	52 <del>-2</del>	159	85 <del>-74</del>	26.5	-3.2	46.5	<u>34,400</u>	<u>-50</u>	<u>3,700</u>
2003	554	421	11	10	24	11	50	42	4,761	2,661 <del>2,100</del>	93	66 <del>-26</del>	209	64 <del>+45</del>	44.1	28.5	69.4	<u>105,000</u>	<u>1,350</u>	<u>7,250</u>
2004	562	438	6	8	26	14	94	55	3,570	2,481 <del>1,089</del>	40	47 <del>-7</del>	165	80 <del>-85</del>	30.5	-17.6	51.5	<u>54,450</u>	<u>-350</u>	<u>4,250</u>
2005	524	449	8	10	22	8	66	45	3,812	2,420 <del>1,392</del>	60	54 <del>-7</del>	157	42 <del>+15</del>	36.5	11.2	73.2	<u>69,600</u>	<u>300</u>	<u>5,750</u>
2006	558	496	9	11	28	10	62	45	4,579	3,529 <del>1,050</del>	75	78 <del>-3</del>	230	71 <del>+59</del>	22.9	-4.7	69.1	<u>52,500</u>	<u>-150</u>	<u>7,950</u>
2007	424	429	7	10	49	21	61	43	2,562	2,326 <del>-236</del>	42	57 <del>-15</del>	295	112 <del>+83</del>	9.2	-34.8	62.0	<u>11,800</u>	<u>-750</u>	<u>9,150</u>
2008	487	398	13	12	19	11	37	33	4,042	3,012 <del>1,030</del>	109	91 <del>-18</del>	159	86 <del>-73</del>	25.5	16.6	45.9	<u>51,500</u>	<u>900</u>	<u>3,650</u>
2009	439	364	14	13	13	6	31	28	2,817	1,712 <del>1,105</del>	87	60 <del>-27</del>	89	29 <del>-60</del>	39.2	31.2	67.4	<u>55,250</u>	<u>1,350</u>	<u>3,000</u>
<u>Mean</u>	<u>506</u>	<u>413</u>	<u>10</u>	<u>11</u>	<u>28</u>	<u>12</u>	<u>55</u>	<u>40</u>	<u>3,617</u>	<u>2,477</u>	<u>71</u>	<u>63</u>	<u>195</u>	<u>75</u>	<u>30.1</u>	<u>6.9</u>	<u>61.1</u>	<u>57,050</u>	<u>405</u>	<u>5,985</u>

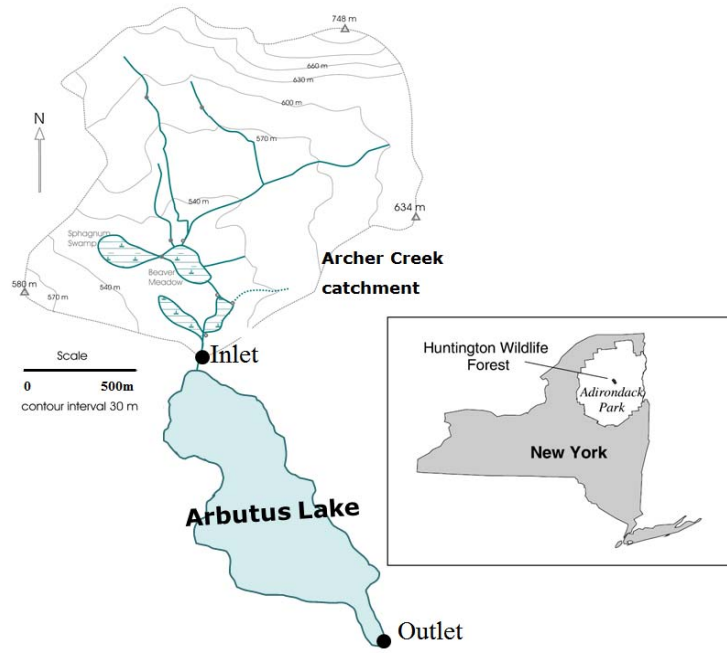
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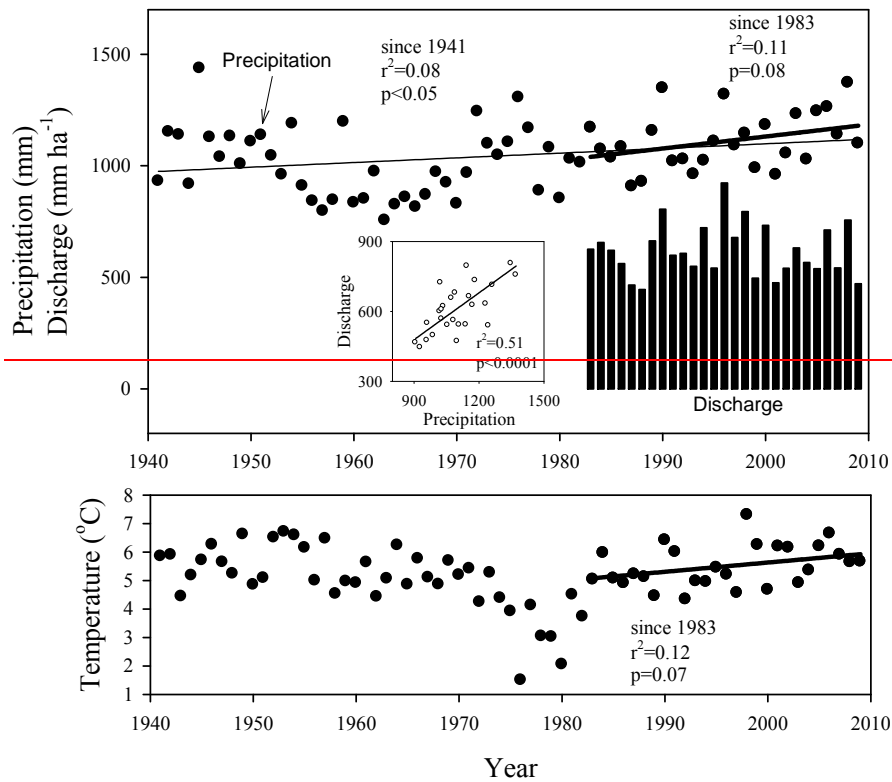
1 | Table 5. Pearson correlation results (r) among % retention of lake water and fluxes and concentrations (conc.) in DOC, DON, and DIN  
 2 | of Arbutus Lake. A statistically significant correlation is indicated with asterisks (p<0.001<sup>\*\*\*</sup>, p<0.01<sup>\*\*</sup>, p<0.05<sup>\*</sup>). % retention of  
 3 | concentrations was calculated using the same equation for flux retention described in Methods.  
 4 |

<b>% Retention</b>	Lake water	DOC flux	DOC conc.	DON flux	DON conc.	DIN flux
DOC flux	0.68 <sup>*</sup>	--				
DOC conc.		0.75 <sup>*</sup>	--			
DON flux		0.86 <sup>***</sup>		--		
DON conc.		0.70 <sup>*</sup>	0.69 <sup>**</sup>	0.92 <sup>***</sup>	--	
DIN flux	0.83 <sup>***</sup>					--
DIN conc.						0.87 <sup>***</sup>

5 |



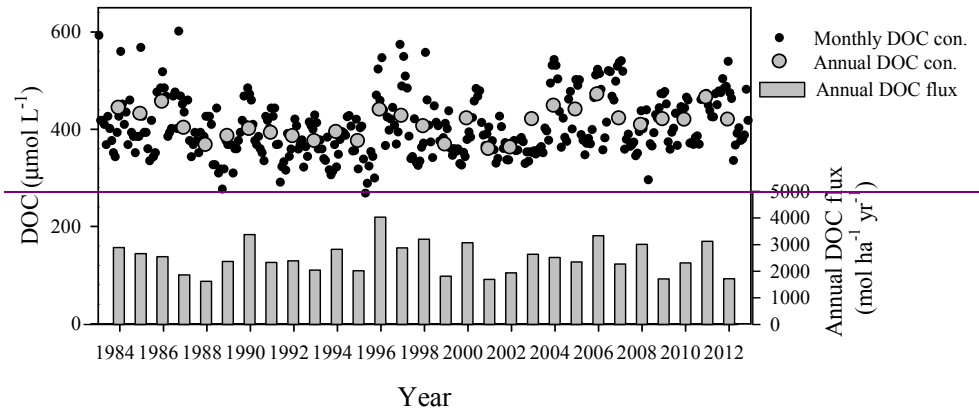
1  
2 Figure 1. Study sites in the Arbutus Lake watershed in Huntington Wildlife Forest,  
3 Adirondack Park, New York, USA.



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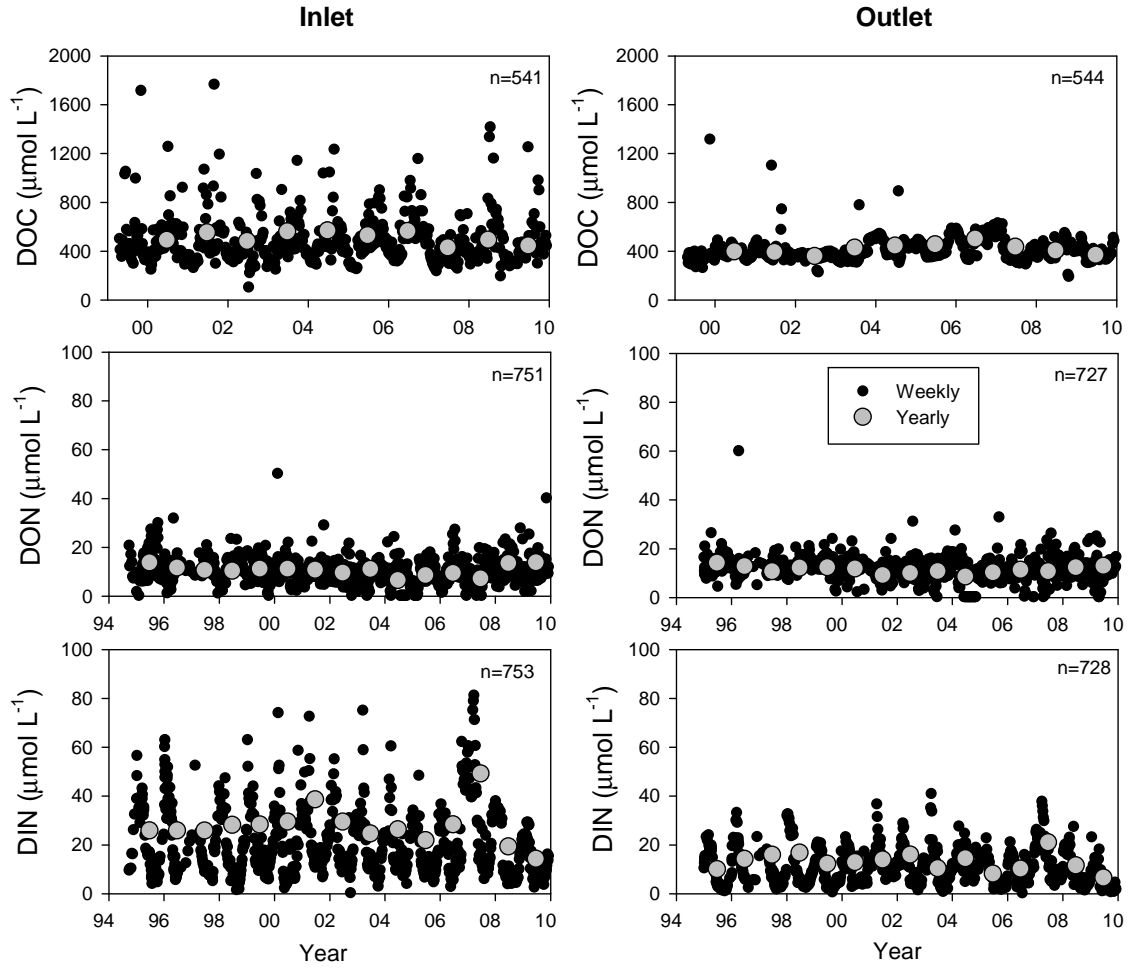
Figure 2. Annual precipitation and temperature at Adirondack Ecological Center site since 1941 (available at: [http://www.esf.edu/aec/research/ALTEMP\\_projects.htm](http://www.esf.edu/aec/research/ALTEMP_projects.htm), 2016) and yearly discharge at the Arbutus Lake outlet since 1983. Annual precipitation and temperature at AEC site and yearly discharge at the Arbutus Lake outlet since 1941. Relationship between precipitation and discharge is embedded in the upper panel.





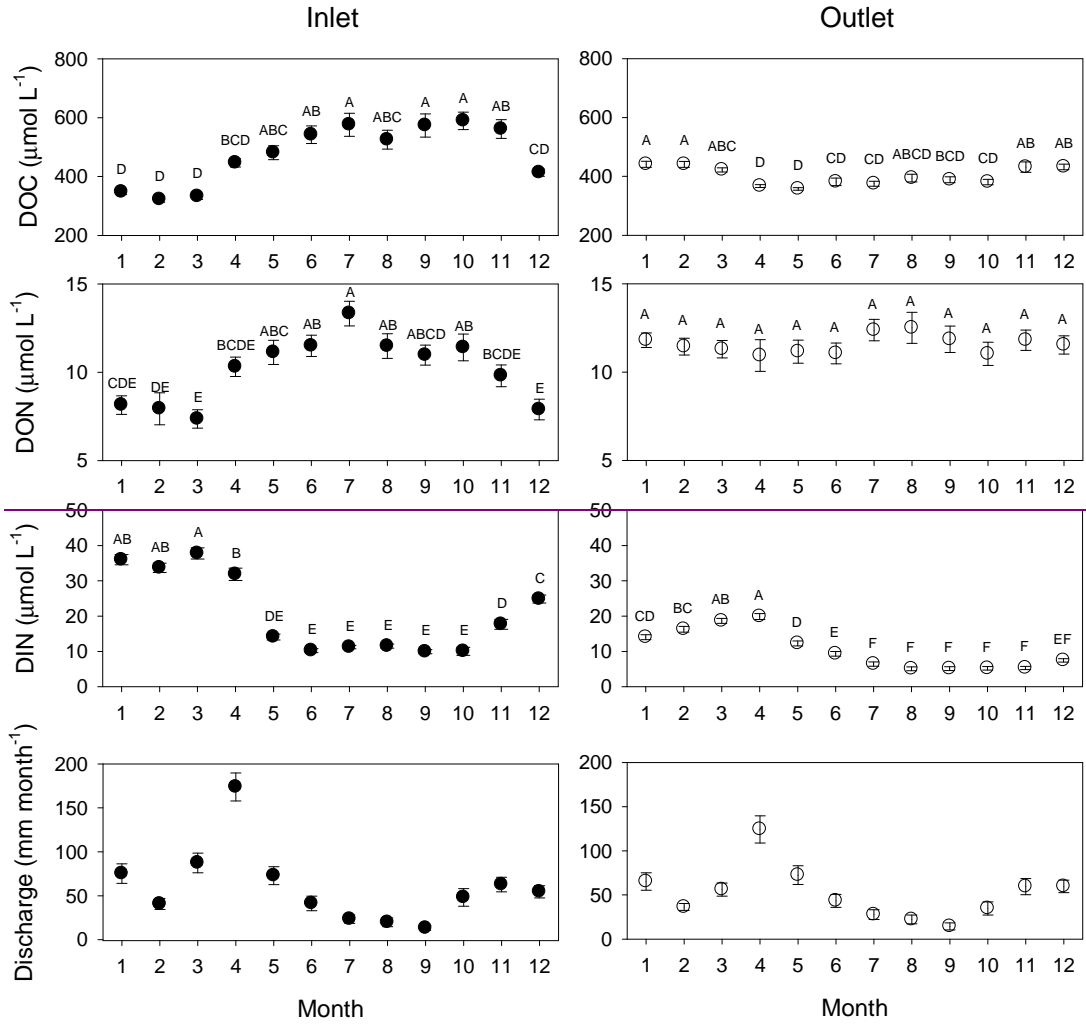
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Figure 3. Monthly (small black circles) and annual (larger gray circle) variation of DOC concentrations and annual DOC flux (gray bars) at Arbutus Lake (outlet) from 1983 (February) to 2012 (December) using ALTM data set.



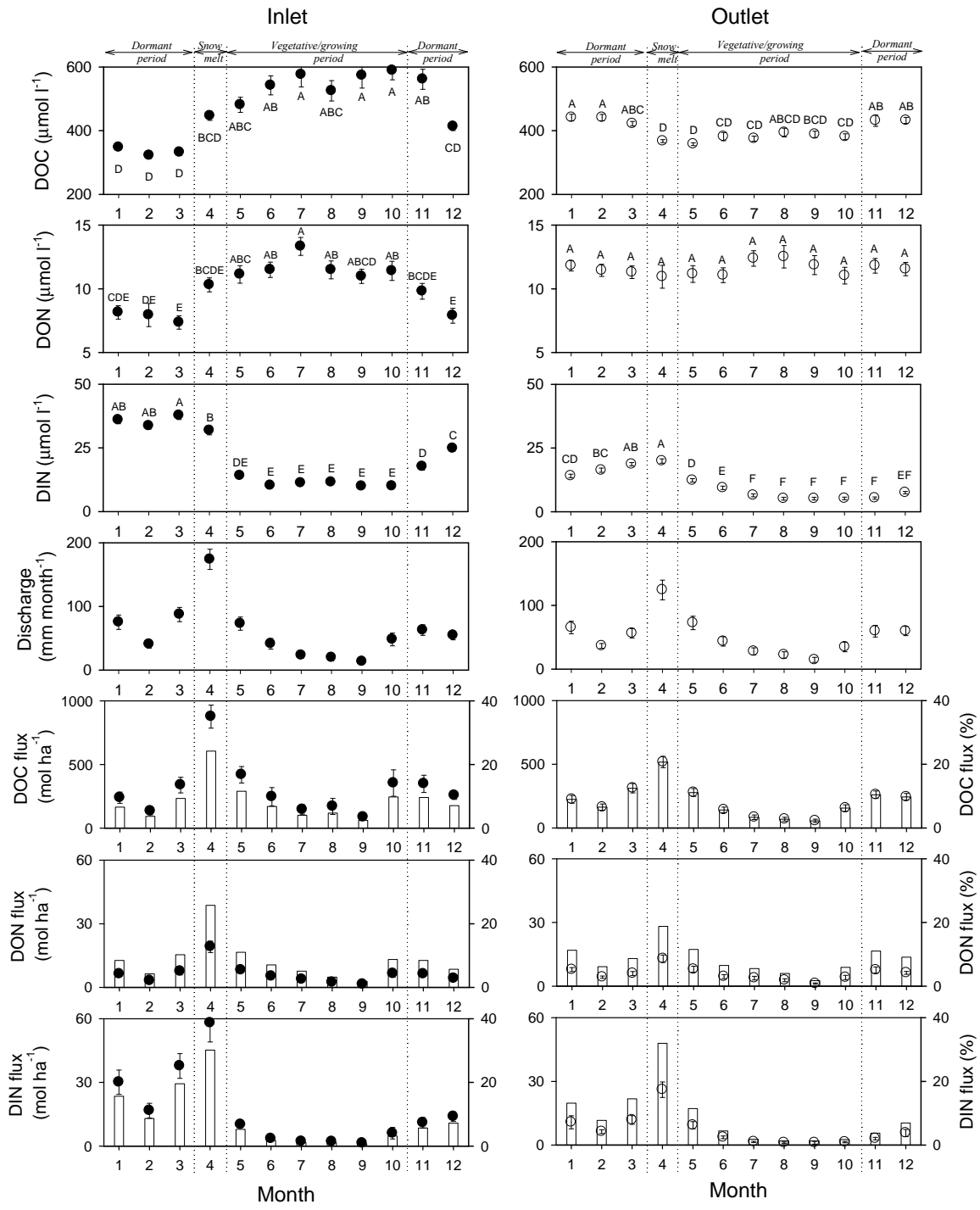
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2 | Figure 24. Weekly and annual yearly variation of DOC concentrations from 1999 to 2009  
 3 | and DON and DIN concentrations from 1994 to 2009 at the inlet and outlet of Arbutus  
 4 | Lake. Annual values are discharged-weighted concentrations.



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1



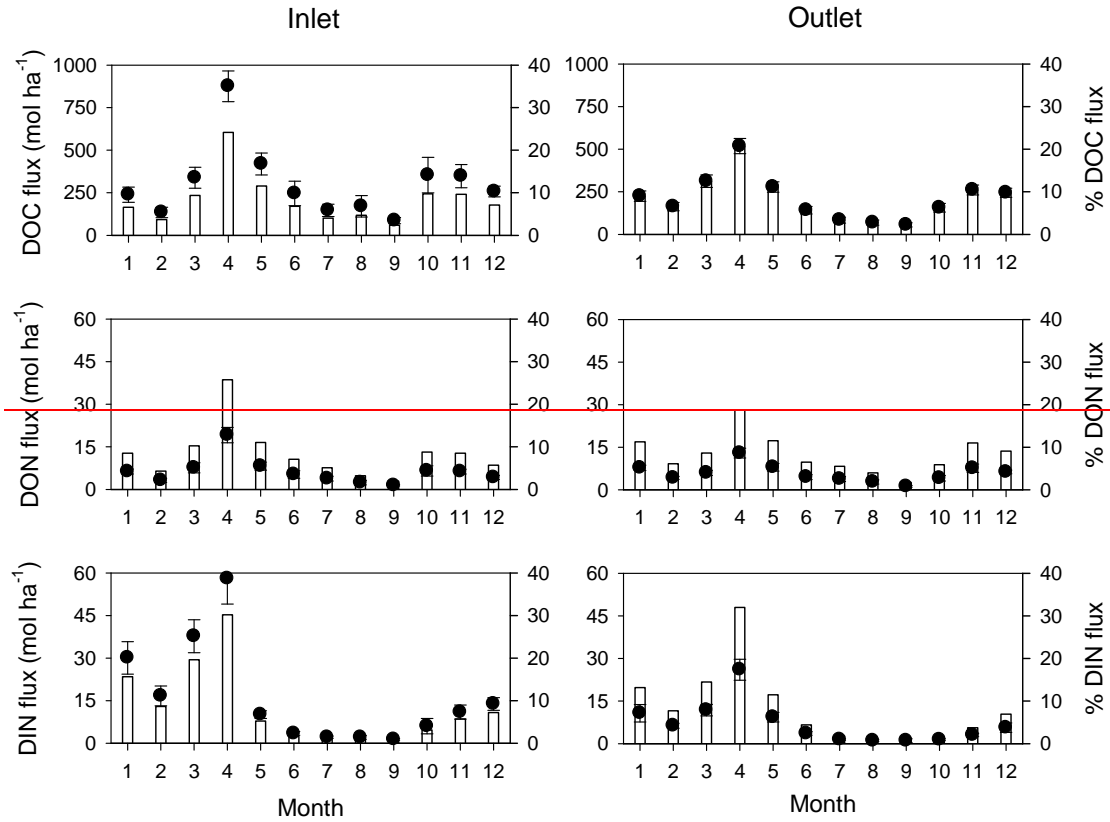
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4 Figure 35. Monthly average discharged-weighted concentrations (error bar: SE) of DOC,

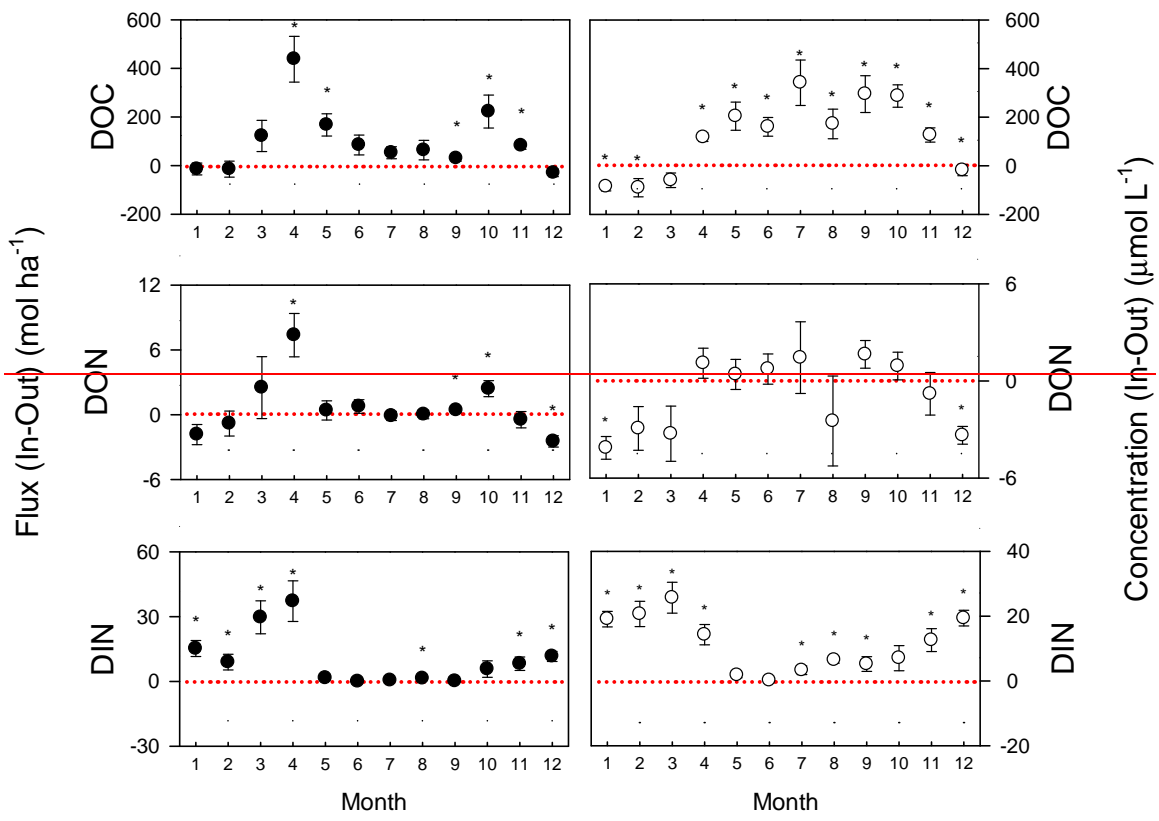
5 DON, and DIN in the inlet and outlet of Arbutus Lake and monthly average flux (circle,

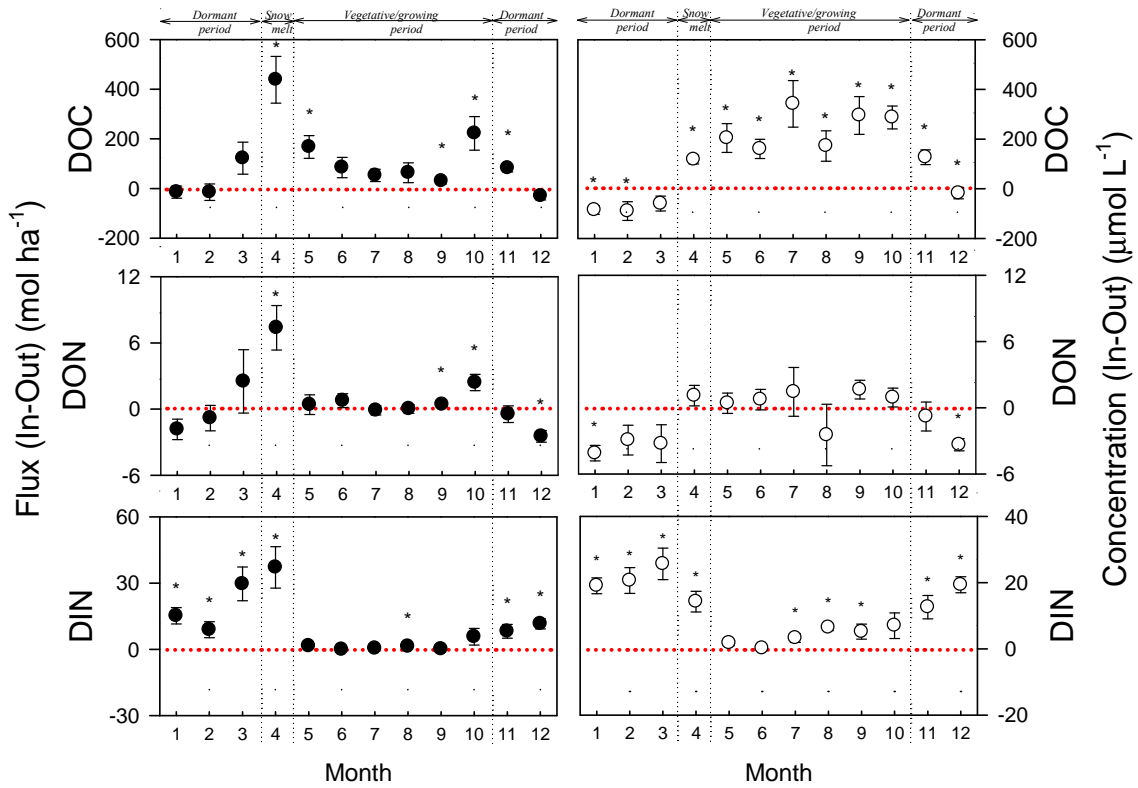
1 left horizontal axis; error bars, SE) and share of the annual flux (bar, right horizontal  
2 axis) of DOC, DON, and DIN at the inlet and outlet of Arbutus Lake. Letters in upper  
3 panels indicate results of posthoc Tukey HSD test ( $\alpha=0.05$ ) in one-way ANOVA and the  
4 same letter among months means no significant difference. Note that specific periods that  
5 were compared are provided on the top of the figure panels.  
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Figure 6. Monthly average flux (circle, left horizontal axis; error bars, SE) and share of monthly % flux of the annual flux (bar, right horizontal axis) of DOC, DON, and DIN at the inlet and outlet of Arbutus Lake.

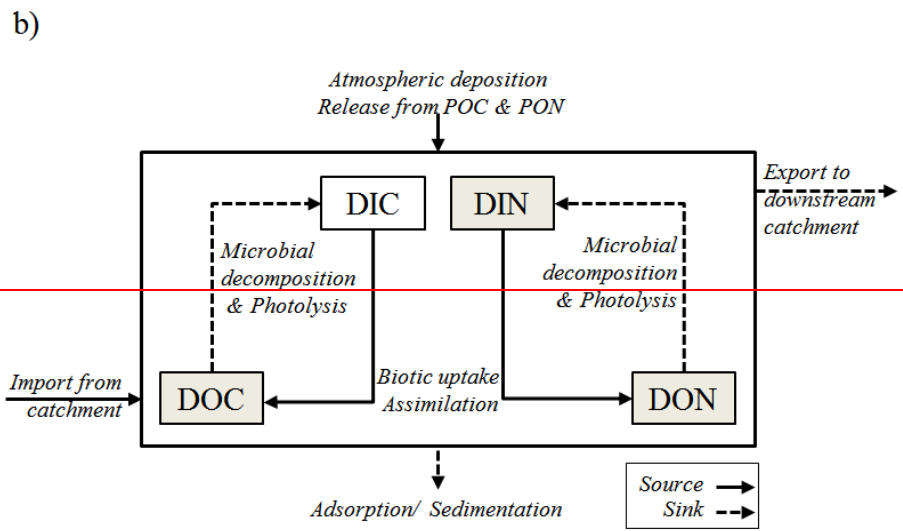
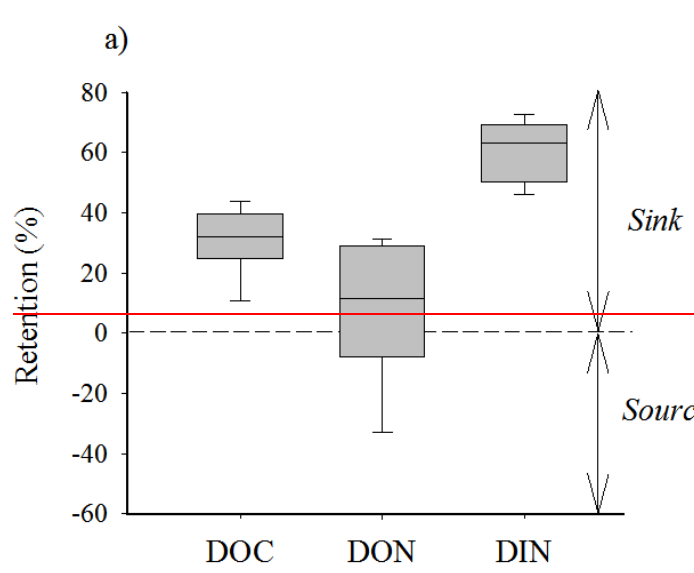




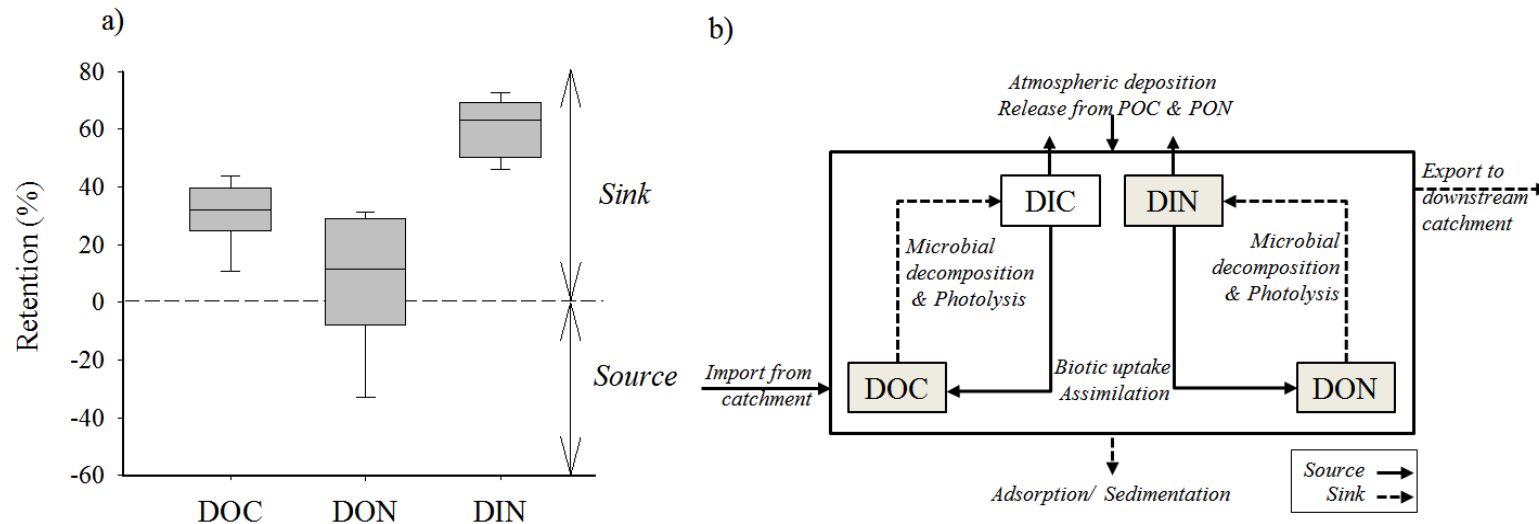
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2 Figure 47. Monthly differences (error bars: SD) of DOC, DON, and DIN in fluxes and  
 3 discharge-weighted concentrations between inlet and outlet of Arbutus Lake from 2000  
 4 to 2009. Asterisk indicates significant difference with from the zero (paired t-test  
 5 between inlet and outlet at  $\alpha=0.05$ ). Note that specific periods that were compared are  
 6 provided on the top of the figure panels.





1



1  
 2 Figure 58. a) A box plot showing annual retention ((influx-outflux)/influx) of DOC, DON, and DIN at Arbutus Lake from 2000 to 2009.  
 3 Whisker caps indicated 10<sup>th</sup> and 90<sup>th</sup> percentiles and a box showed the 25<sup>th</sup>, 50<sup>th</sup> (median), and 75<sup>th</sup> percentiles from the bottom to the top. b) a  
 4 diagram indicating processes of sources and sinks in DOC and DON in Arbutus Lake (DIC: dissolved inorganic carbon).