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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

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Abstract

Lakes nested in forested watersheds play important roles in mediating the concentrations and fluxes of dissolved organic matter. We compared long-term patterns of concentrations and fluxes of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved inorganic nitrogen (DIN) in the Arbutus Lake Watershed to evaluate how a lake nested in a forested watershed affects the dynamics of DOC and DON in the Adirondack Mountains of New York State, USA. We observed no significant long-term changes of concentrations and fluxes of DOC and DON in the Lake outlet since 1983 and 1994, respectively. However, the temporal patterns of DOC and DON concentrations in the Lake inlet showed significant seasonality such as increases during the vegetation-growing season along with notable decreases in the dormant season. A comparison of mass-balances between inlet and outlet for the period from 2000 to 2009 suggested that the Lake was a sink of DOC (mean of influx minus outflux: $+1140\,\mathrm{mol\,C\,ha^{-1}\,yr^{-1}}$). In contrast, the difference of discharge-weighted DON concentrations (mean of inlet minus outlet: $-1.0\,\mathrm{\mu mol\,N\,L^{-1}}$) between inlet and outlet was much smaller than the discharge-weighted DOC concentrations (average of inlet minus outlet: $+87\,\mathrm{\mu mol\,C\,L^{-1}}$). DON fluxes showed considerable variation among years (mean of influx minus outflux: $+8\,\mathrm{mol\,N\,ha^{-1}\,yr^{-1}}$; range of differences: -15 to $27\,\mathrm{mol\,N\,ha^{-1}\,yr^{-1}}$). DON exhibited low % retention ((influx – outflux) / influx) (mean: 6.9 %, range: -34.8 to $+31.2$) compared to DOC (mean: 30.1 %, range: $+9.2$ to $+44.1$). The resultant increase of DON within the lake was closely linked with a net decrease of DIN through monthly Pearson correlation analysis, suggesting the importance of biotic factors in mediating a lake DON dynamics. Our results show different relative retentions of DOC compared with DON, along with a larger retention of DIN than DON, suggesting that DOC and DON might display substantially different biogeochemical relationships in oligo-mesotrophic lakes nested forested watersheds and therefore different roles for a sink behavior for DOC compared to a producer of DON.

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1   Introduction

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

There has been considerable discussion on the mechanisms driving recent increases of DOC in acid-sensitive surface waters in North America and Europe (Driscoll et al., 2007; Erlandsson et al., 2011; Evans et al., 2007; Monteith et al., 2007, 2015). For example, Monteith et al. (2007) suggested that the recovery of the previous acidi-
fication of surface water in response to decreased acidic deposition might result from an increase in the solubility of soil organic matter due to the change of pH, aluminum and ionic strength (Kalbitz et al., 2000; Mulder et al., 2001). Erlandsson et al. (2011) suggested the importance of understanding the effects of acidification on reexamining DOC reference levels. Other possible mechanisms driving this increase in DOC
concentrations include increasing temperatures (Freeman et al., 2001), changing hydrology associated with increases in precipitation and runoff (Schindler et al., 1997), changes in land uses (Worrall et al., 2004), alteration of dry and rewetting cycles (von Schiller et al., 2015), increasing primary production induced by increases of atmo-

spheric CO_2 (Freeman et al., 2004) and increased occurrences of droughts (Worrall and Burt, 2005).

While many studies have explored the dynamics and fate of DOC in aquatic ecosystems (e.g., Findlay and Sinsabaugh, 2003), very few have simultaneously investigated the changes in DON. The short-term studies that have compared DOC vs. DON changes indicate that DOC export from forested lakes in Adirondack Mountains was negatively related to hydraulic residence time but not for DON, suggesting that different biogeochemical responses for DOC and DON (Ito et al., 2005). Evaluating the causes of these differences is important for understanding spatial and temporal patterns of DOC and DON in surface waters including the role of within-lake processes. The generation of organic matter by autochthonous processes is an important factor for the formation of DOC and DON within lakes. Generally DOC and DON concentrations increase in eutrophic lakes due to the relative high autochthonous contributions in spite of enhanced microbial transformations to consume DOC and DON, while for oligotrophic lakes with low DOC and DON concentrations show a net decrease due to microbial decomposition, sedimentation, and photolysis (e.g., Thurman, 1985). Within-lake processes can affect nutrient dynamics including changes in C : N ratios (Ito et al., 2007). Previous studies have shown differences in lability of DON and DOC (Kang and Mitchell, 2013; Gregorich et al., 2003; Kirchman, 2003; Petrone et al., 2009). DOM from drainage lakes can alter the amount and the chemical characteristics of the DOM and the processing of other elements in downstream surface waters.

Arbutus Lake, an oligotrophic/mesotrophic lake, in the Adirondack Mountains of New York State, is the one of the original Adirondack Long-Term Monitoring program (ALTM) lakes established in 1982 (Driscoll et al., 2003; Kelting and Laxson, 2014; Owen et al., 1999). Arbutus Lake watershed has been the site of various hydrologic and biogeochemical studies of DOC and DON. Piatek et al. (2009) showed that wetlands in the inlet (Archer Creek) catchment played an important role in controlling DOC concentrations within the Arbutus Lake watershed. Mitchell et al. (2006) reported on relationships between precipitation patterns and the export of DOC after late summer storms

due to increases in water derived from upper soil layers and concomitant decrease in the proportion of ground water contributions. DOC export corresponded to interannual changes of temperature, precipitation and discharge in the winter (Park et al., 2005). The export of DON constituted 47 % to the total solute N flux in the Arbutus

5 Lake watershed for the period from 1985 to 1998 (Mitchell et al., 2001), and was enhanced by biotic processes affecting dissolved inorganic nitrogen (DIN) transformations at higher temperature in summer (Park et al., 2003). Ito et al. (2005) suggested that the decrease of the C : N ratios among Adirondack lakes including Arbutus Lake was related to the contribution of autochthonous sources with low C : N ratio, compared

10 with allochthonous terrestrial sources. Most recently Kang and Mitchell (2013) studied DOM characteristics in the Arbutus Watershed in the Adirondack Mountains as water passed from upland streams, through a wetland, to the lake inlet and finally the lake outlet. There was a net export of high concentrations of aromatic, refractory and high-molecular-weight (HMW) DOC and DON produced from the wetland into the lake.

15 Also they observed the decomposition of refractory HMW DOC and the increase of bioavailable DOC and DON within the lake.

    The objectives of our current study were to (1) evaluate long-term changes in DOC concentrations and fluxes at the outlet of Arbutus Lake using monthly based ALTM data, (2) compare DOC, DON, and DIN concentrations and fluxes between inlet and

20 outlet in Arbutus Lake using weekly observations from ongoing hydrobiogeochemical investigations in the Arbutus Watershed, and (3) evaluate the role of within-lake processes in affecting the dynamics (i.e., sources and sinks) of DOC and DON in the lake. This study contributes to a further evaluating how a lake nested in a forest watershed affected dynamics of DOC and DON.

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2   Methods

2.1   Site description of Arbutus Lake

The Arbutus Lake watershed (43°58′48″ N, 74°13′48″ W) is located within the Huntington Wildlife Forest in the Adirondack Mountains of New York State. Arbutus Lake has a surface area of 50 ha, an average depth of 3.0 m, and a maximum depth of 8.4 m (Driscoll and van Dreason, 1993). The lake has been classified as a medium till drainage lake by Newton and Driscoll (1990). For the period from 2001 to 2010 the total phosphorus concentrations ranged from 11 to 14 $\mu g\,L^{-1}$ and chlorophyll *a* concentrations ranged from 2.2 to 4.4 $mg\,m^{-3}$ during the summer (Kelting and Laxson, 2014), indicating a trophic status within the oligo and meso range (OECD, 1982). The Arbutus Lake watershed has an area of 352 ha and the elevations range from 513 to 748 m (Park et al., 2005). The annual temperature averaged 5.1 °C from 1984 to 2013 and total annual precipitation averaged 1086 mm from 1981 to 2013 in Newcomb, NY (3 km distance from Huntington Wildlife forest) (NYSERDA, 2015).

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

2.2 Hydrological data

The stage height and discharge at the outlet of Arbutus Lake have been measured using a V-notch weir since 1991 (Fig. 1). The inlet, located in the Archer Creek catchment, has been monitored using an H-flume equipped with an automated discharge logging device since October 1994 (Mitchell et al., 2001) (Fig. 1). To calculate annual discharge-weighted DOC concentration at the outlet using ALTM data, we estimated monthly discharge at the lake outlet from 1984 to1990 using modeled discharge values and measured values for subsequent periods (Mitchell et al., 1996).

2.3 ALTM measurements of DOC

The outlet of Arbutus Lake has been monitored monthly by the ALTM program since February 1983 including DOC concentrations, and the analytical method described in Driscoll and van Dreason (1993). For the long-term change of DOC at Arbutus Lake, we used the monthly ALTM data from February 1983 to December 2012.

2.4 Chemistry data collected by SUNY-ESF

The inlet has been sampled weekly for chemical analyses, including DON concentrations since October 1994 and DOC concentration since May 1999. The outlet has been monitored weekly for chemical analyses, including DON concentrations since October 1991 and DOC concentration since May 1999. Water samples were kept on ice in the field transported to the Biogeochemistry Laboratory at SUNY ESF in Syracuse, NY, filtered through a precombusted glassfiber filter (Whatman GF/F) within one week after collection, and stored at 4 °C until further analysis. The Biogeochemistry Laboratory, which is a participant in the USGS QA/QC program, analyzed C and N solutes as follows: NO_3^- using a Dionex IC; NH_4^+ with an autoanalyzer using the Berthelot Reaction followed by colorimetric analysis; total dissolved nitrogen (TDN) using the persulfate oxidation procedure, followed by colorimetric analysis on an autoanalyzer; and

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DOC using the Tekmar–Dohrmann Phoenix 8000 TOC analyzer®. DON concentrations were calculated as the difference between TDN and DIN ($NO_3^- + NH_4^+$) (Inamdar and Mitchell, 2007). If DIN exceeded or equaled TDN (< 2.5 and < 1.4 % of all samples in inlet and outlet, respectively), the value of DON was treated as zero. The lowest DON concentrations in the inlet and outlet were −7.0 and −17.1 µmol N L^{-1}, respectively. The calculated error for DON concentrations was ±6.6 % square root of the sum of the squared analytical precision of TDN (±4.2 %), NH_4^+ (±3.2 %), and NO_3^- (±3.9 %) (Kang and Mitchell, 2013).

2.5   Calculations

To calculate mass balances of DOC, DON, and DIN for Arbutus Lake, we used the same period (2000–2009) for the inlet and outlet chemistry. We assumed that the Archer Creek inlet chemistry was representative of all surface and ground water sources to Arbutus Lake. We assumed that direct DOC (e.g., 1600 mol C ha^{-1} yr^{-1} in Ithaca, NY; Likens et al., 1983) and DON (e.g., 93 to 135 mol N ha^{-1} yr^{-1} in New England, US; Campbell et al., 2000) inputs via precipitation to the Lake would be small as for other northeastern US forests. We also used the results from the NADP/NTN site for wet only deposition directly to Arbutus Lake (http://nadp.sws.uiuc.edu/nadpdata/annualReq.asp?site=NY20).

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

Residence time (years) = V/Q,

where V is the lake volume (134.5 × 10^4 m^3) and Q is the yearly outlet discharge (unit: m^3 yr^{-1}).

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

$$\text{MDWC} = \sum (Q_j \times C_j) \Big/ \sum Q_i,$$

where Q_j and C_j are Q (daily discharge) and C (concentration), respectively, for the jth weekly sample in a given month and Q_i is daily Q in a given month.

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

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

where Q_i is monthly Q in a given year.

Fluxes from the inlet and the outlet from 2000 to 2009 were also computed per unit area as follows:

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

where A is a watershed area (inlet = 135 ha and outlet = 352 ha).

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.

2.6 Statistical approaches

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). All linear regression was analyzed based on $\alpha = 0.05$ using Sigma-Plot (Version 11.0, Systat Software, Inc.). To compare differences of discharge-weighted concentrations among months, one-way analysis of variance (ANOVA) with posthoc

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Tukey HSD test ($\alpha = 0.05$) was performed using Minitab (Version 16, Minitab Inc.). Pearson correlation was analyzed for significance levels of $p < 0.05$ using Minitab (Version 16, Minitab Inc.).

3 Results

3.1 The long-term climatic factors and monthly DOC trend using ALTM data

Precipitation increased significantly from 1941 to 2009 (Fig. 2). However, there was no significant change in precipitation ($p = 0.08$) or temperature ($p = 0.07$) from 1983 to 2009 during the period of DOM investigation (Fig. 2). There was a significant relationship between precipitation and discharge during the same period (Fig. 2). An analysis of the Arbutus ALTM data set from 1983 to 2012 showed no significant change in DOC concentrations at the Lake outlet (mean 398.4 ± 61.1 SD μmol C L^{-1}, $n = 304$, slope: $0.06\,\mu$mol C L^{-1} yr^{-1}, tau: 0.009, $p = 0.91$) (Fig. 3). Annual DOC influx for Arbutus Lake ranged from 1620 to 4028 mol C ha^{-1} yr^{-1} and averaged 2527 (± 122 SE) mol C ha^{-1} yr^{-1}.

3.2 Trends of weekly DOC, DON, and DIN concentrations using SUNY-ESF data set

The DOC and DON concentrations at the inlet and outlet using weekly concentration data from SUNY-ESF are given in Fig. 4. The inlet DOC concentrations (mean 480 ± 202 SD μmol C L^{-1}, $n = 541$) showed higher mean and greater monthly variation than the outlet (mean 402 ± 93 SD μmol C L^{-1}, $n = 545$). In contrast, the DON concentrations showed similar values at the inlet (mean 10.1 ± 5.4 SD μmol N L^{-1}, $n = 751$) and the outlet (mean 11.5 ± 5.0 SD μmol N L^{-1}, $n = 727$). The Seasonal Kendall test did not show any significant changes over time in DOC or DON concentrations: inlet DOC (slope: $1.8\,\mu$mol C L^{-1} yr^{-1}, tau: 0.04, $p = 0.68$), inlet DON (slope: $-0.03\,\mu$mol N L^{-1} yr^{-1}, tau:

−0.05, $p = 0.53$), outlet DOC (slope: $1.07\,\mu mol\,C\,L^{-1}\,yr^{-1}$, tau: 0.04, $p = 0.81$), and outlet DON (slope: $-0.11\,\mu mol\,N\,L^{-1}\,yr^{-1}$, tau: −0.09, $p = 0.22$).

The monthly concentrations of DOC, DON, and DIN and the monthly discharge values are shown in Fig. 5. At the inlet there was a strong seasonality of DOC, DON, and DIN concentrations. DOC and DON concentrations enhanced during a growing season and reduced during winter while DIN concentrations increased during winter and decreased from May to October. At the outlet the monthly DOC patterns that decreased from April and reaching a minimum in the fall (i.e., October) were substantially different than the temporal patterns of inlet DOC concentrations. At the inlet, DON concentrations showed a similar seasonal pattern to that of DOC concentrations; however, at the outlet the patterns were not similar, suggesting differences in the mechanisms regulating DOC and DON dynamics in the Lake. Outlet DIN concentrations increased from January to April and decreased from May through November, indicative of DIN uptake by the aquatic biota and/or DIN reduction by biogeochemical processes such as plant and microbial uptake or denitrification including dissimilatory nitrate reduction in the Lake. The statistical correlations among DOC, DON, DIN, monthly average temperature, and monthly total discharge for every month and for entire years are provided in Table 1. For the inlet, DOC was positively correlated with DON, temperature, and discharge, and DON showed a positive relationship with temperature and discharge as also found for the inlet DOC. We observed a significantly negative relationship between DON and DIN concentrations. At the outlet, DOC was not correlated with DON, and the significantly negative relationships (May to December) between DON and DIN in the Lake was found.

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

Based on weekly samples from 2000 to 2009, we calculated the mass-balances of DOC, DON, and DIN using annual discharge-weighted concentrations and fluxes at the inlet and the outlet (Tables 2 to 4). Our calculation of average residence time of

0.66 yr^{-1} was almost same as that value estimated to be 0.6 yr^{-1} in a previous study of Driscoll and van Dreason (1993) (Table 2). Average of discharge-weighted concentrations of DOC and DIN decreased from the inlet to the outlet, while DON increased. The increase of DON resulted in a decrease in C : N molar ratios of DOM as water was transported through the Lake (Table 3). 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). For Arbutus Lake the mean DOC outflux of 2477±180 SE (n = 10) mol C ha^{-1} yr^{-1} using weekly observations was similar (i.e., difference of 2 %) to the average flux calculated using the monthly ALTM data (2527 (±122 SE) mol C ha^{-1} yr^{-1}) for the period from 1983 to 2012 (Fig. 3, Table 3).

The difference between the inlet and the outlet of annual DOC concentrations averaged 93 µmol C L^{-1}, ranging from −5 (in 2007) to 161 (in 2001) µmol C L^{-1}. The difference between inlet and outlet fluxes averaged 1140 mol C ha^{-1} yr^{-1} with the range of 236 to 2100 mol C ha^{-1} yr^{-1} (Tables 3 and 4), indicating that DOC was decomposed or retained in the Lake. The proportion of DOC decreases for concentrations and fluxes from the inlet to the outlet ranged from −1.2 to 29.4 % (mean: 18.4 %) and from 9.2 to 44.1 % (mean: 31.5 %), respectively, of inlet values. Hence, for all years there was a net decrease of DOC between the inlet and the outlet.

For DON annual differences of annual discharge-weighted concentrations and fluxes between inlet and outlet ranged from −3.5 to 1.1 µmol N L^{-1} (mean: −1.0 µmol N L^{-1}) and from −15 to 27 mol N ha^{-1} yr^{-1} (mean: 8 mol N ha^{-1} yr^{-1}), respectively (Tables 3 and 4). This analysis suggests that within-lake processes sometimes (particularly 2007) resulted in a net increase in DON through the Lake in contrast to the routine net decrease in DOC. Net retention of DOC within the Lake was smallest in 2007 and there was a net increase in DON during the same year (Table 4). The fraction of DON input concentrations and fluxes that changed in the Lake based on fluvial DON exports ranged from −50.0 to 12.7 % (mean: −10.0 %) and from −35.7 to 31.0 % (mean:

11.2 %), respectively. For DIN annual differences in concentrations and fluxes between inlet and outlet ranged from 7 to 28 $\mu mol\,N\,L^{-1}$ (mean: 16 $\mu mol\,N\,L^{-1}$) and from 60 to 183 $mol\,N\,ha^{-1}\,yr^{-1}$ (mean: 120 $mol\,N\,ha^{-1}\,yr^{-1}$), respectively (Tables 3 and 4), indicating the removal of DIN in the Lake. The fraction of DIN concentrations and fluxes from inlet values that were retained in the Lake ranged from 42.1 to 64.3 % (mean: 57.1 %) and from 45.9 to 69.4 % (mean: 61.5 %), respectively. In brief, fluxes of DOC, DON, and DIN decreased in the Lake, but the proportion of DON decreases in the Lake (mean: 11.2 %) was less than that of DIN (mean: 61.5 %).

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

Results of Pearson correlation comparing % retention of lake water and fluxes and concentrations of DOC, DON, and DIN are shown in Table 5. The % retention of DOC was significantly related to hydraulic residence time, but not for DON, indicating that the decrease of DOC in the Lake was related to the hydraulic changes, whereas DON retention was less affected, indicating that other factors including biotic processes were

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likely important. Although a significant relationship between % retention of DOC and DON was shown, the range of DON retention ranged from negative to positive while the % retention of DOC was always positive. Box-plots of the yearly retention of DOC, DON, and DIN in fluxes are shown in Fig. 8a, and potential sources and sinks for solutes are described in Fig. 8b.

4 Discussion

Our study suggests that annual DOC and DON mass balances were strikingly uncoupled, and Arbutus Lake generally acted as a sink for DOC but a periodic source for DON (Fig. 8). Few studies have compared simultaneously the long-term DOC and DON dynamics in lakes. Our work indicated that the sink strength of DOC in Arbutus Lake, an oligo-mesotrophic lake, was a function of hydraulic residence (Table 5). For DON, internal recycling between DIN and DON might be important in affecting DON concentrations in the Lake.

4.1 Long-term change of DOC export from the Lake

Our results indicated that DOC concentrations and mass balances in Arbutus Lake varied among years but did not show significant long-term trend. These results are similar to Driscoll et al. (2007) who also found no significant trend in DOC concentrations for Arbutus Lake. However, Driscoll et al. (2007) did report that 10 of the original 16 ALTM lakes showed increased concentrations of DOC from 1982 to 2004 with a mean increase of $4.5 \pm 3.8\,\mu mol\,C\,L^{-1}\,yr^{-1}$. The actual mechanisms causing changes of DOC concentration are not specifically known but could include biological and chemical processes (e.g., a decrease in soil DOC partitioning) and factors associated with climatic change (e.g., the hydrological change and the dry and rewetting cycle) (Driscoll et al., 2007; Fellman et al., 2011; Singh et al., 2014; von Schiller et al., 2015). Monteith et al. (2007) suggested that increases in surface water DOC are linked to decreases

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in sulfur deposition due to decreases in the partitioning of organic matter by soil associated with the change in pH, aluminum and ionic strength (Ekstrom et al., 2011; Erlandsson et al., 2011; Evans et al., 2012; Mulder et al., 2001). Most of the Adirondack lakes including Arbutus Lake have shown significant decreases in sulfate concentration (Park et al., 2003; Driscoll et al., 2007). The effects of changes of acidic deposition on surface water, including trends in DOC concentrations, have been documented in North America (Driscoll et al., 2007) and Europe (Erlandsson et al., 2011; Evans et al., 2007; Kalbitz et al., 2000; Monteith et al., 2007, 2015; Mulder et al., 2001). However, for Arbutus Lake the effects of changes in acidic deposition may be less evident due to its relatively high pH (~ 6.7) and ANC ($\sim 77\,\mu eq\,L^{-1}$) values and base status (Foster et al., 1992; Johnson and Lindberg, 1992; Mitchell et al., 2001; Chen et al., 2004; NYSERDA, 2011).

4.2   Temporal patterns of DOC and DON concentrations in forested catchments

Our study suggests the importance of biotic processes in affecting the seasonality of DOC and DON concentrations in forested watersheds. We observed the seasonal variation of DOC and DON concentrations such as the increase in inlet DOC and DON concentrations of the Lake during the growing season with notable decreases in the dormant season (i.e., December to March) (Fig. 5). The seasonality of dissolved organic matter dynamics in forested watersheds has been shown in various studies (e.g., Aitkenhead-Peterson et al., 2003; Levia et al., 2011; Park et al., 2003). In addition, our study indicated that at the lake outlet increases in DON concentration coincided with decreases in DIN, suggesting that some DIN was converted to DON (Table 1). The monthly concentrations of DIN increased during winter and decreased from May to October, likely indicating the uptake of nitrogen as a nutrient by the biota during warmer periods of the year (Bischoff et al., 2001). Our observation of the negative relationship of DIN with DON at the inlet was consistent with the study of McHale et al. (2000) (Fig. 5, Table 1). Regarding a quality of DOC and DON from the inlet, Kang and Mitchell (2013) in this catchment showed the production of refractory and HMW DOC and DON

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in upland regions of the catchment, which was followed by a large increase of DOC concentrations as water was transported through downstream wetland areas. Hence, the import of the high concentrations of aromatic, refractory and HMW DOM from the inlet would likely be an important source of DOC and DON for lakes (Kang and Mitchell, 2013; Piatek et al., 2009; Reddy and DeLaune, 2008).

Annual DOC fluxes and concentrations from the inlet (Tables 3 and 4) were similar to ranges reported from other studies of Adirondack lakes (Canham et al., 2004) and across United States (580 to 6200 mol C ha^{-1} yr^{-1} and 41 to 2567 µmol C L^{-1}) (Aitkenhead and McDowell, 2000; Tate and Meyer, 1983; Webster et al., 2006). We observed marked increases of DOC and DON influxes during snow melt (April to May) that accounted for 35.8 and 36.7 % of the annual inputs, respectively (Fig. 6). The importance of the snowmelt period has been shown in other studies of forested catchments (Hornberger et al., 1994; Boyer et al., 1997; Goodman et al., 2011; Park et al., 2005). These studies also suggest that as groundwater table rises during snow melt, high concentration of DOC and DON from pore water in upper soil horizons including the forest floor are flushed into adjacent surface waters. The export of DOM during snowmelt provides a substantial contribution to the yearly DOM mass fluxes. The export of DOC from soils to surrounding waters is controlled by many factors including hillslope connectivity (McGlynn and McDonnell, 2003), wetland area (Piatek et al., 2009), topography and the snow melt pattern (Boyer et al., 1997; Hornberger et al., 1994). At the inlet of Arbutus Lake, the increased discharge associated with snowmelt begins in early spring (e.g., March and April) resulting in increased DOC and DON concentrations that continue to increase to maximum mid-summer concentrations (Fig. 5).

Our study also showed positive relationships between discharge and the concentrations of DOC and DON during the growing season from the inlet catchment (Table 1). Previous analyses of the resultant influx of DOC and DON in the Archer Creek watershed during the growing season have shown close linkages with watershed wetness with notable increases in DOC during storms after dry antecedent periods (Inamdar et al., 2008; von Schiller et al., 2015). Studies of other lake/watersheds have found

lower DOC concentrations under dry conditions (Schindler et al., 1997) with elevated DOC concentrations under wetter conditions (Hinton et al., 1997; Inamdar et al., 2011; Singh et al., 2014; Tranvik and Jansson, 2002). The increase in DOC concentrations in surface waters with increases in wetness of catchments has been attributed to the generation of flow paths through organic rich soil, including the forest floor (Inamdar et al., 2008), and Park et al. (2003) also showed seasonal increases of DON due to soil microbial production from December 1996 to May 1996 in the Lake inlet.

4.3 Role of within-lake processes

Our observations of decreasing DOC fluxes from March to November in the Lake support the role of the Lake as a sink of DOC (Fig. 7). Similarly subalpine lakes have been found to be a DOC sink during spring snowmelt (Goodman et al., 2011). During the warm summer, autochthonous generation of DOC might contribute to slight increases in Lake DOC (Figs. 5 and 7). Nevertheless, our observations support the role of the Lake as a net sink for DOC. The retention and loss of DOC within lakes may occur by microbial decomposition (Kang and Mitchell, 2013), sedimentation (Owen et al., 1999) and photolysis (Bertilsson and Tranvik, 2000; Molot and Dillon, 1997).

The removal of seston due to sedimentation can contribute to losses of DOC and DON within lake waters. Owen et al. (1999) studied seston sedimentation using traps in Arbutus Lake from September 1992 to November 1993, excluding the period from December to April. They reported on average sedimentation rate of $1.4\,g\,dry\,mass\,m^{-2}\,d^{-1}$ and seston C and N concentrations of $16.8\,mmol\,C\,g^{-1}$ and $1.4\,mmol\,N\,g^{-1}$ with sedimentation fluxes of $85\,848\,mol\,C\,ha^{-1}\,yr^{-1}$ and $7154\,mol\,N\,ha^{-1}\,yr^{-1}$. These relatively high sedimentation fluxes can easily account for the fluxes of DOC and DON retained in the Lake observed in our study ($1140\,mol\,C\,ha^{-1}\,yr^{-1}$ and $8\,mol\,N\,ha^{-1}\,yr^{-1}$, respectively; Table 3) and support the mechanism of removal of DOC and DON through the sedimentation of seston within the Lake.

Since terrestrial DOM consists of HMW aromatic, chromophoric compounds (Kang and Mitchell, 2013), DOM entering the Lake could also be oxidized by photolysis (Sins-

abaugh and Findlay, 2003). Photochemical reactions upon exposure to ultraviolet (UV) radiation due to increased residence time in the lake can result in a considerable decrease of chromophoric DOM and the resultant modification of chemical properties of DOM (Bertilsson and Tranvik, 2000; Molot and Dillon, 1997). Kang and Mitchell (2013) observed a decrease in aromatic compounds observed from SUVA (specific ultra violet absorbance) and HMW DOC concentration in the Lake suggesting the possibility of the importance of photolysis. In spite of the potential for photolysis as a mechanism removing DOM in lakes (e.g., Wetzel, 2003), the quantitative determination of the relative importance of this process has been difficult. We observed that during the ice-covered period (December to March), the outlet concentrations and fluxes of DOC and DON were greater than the inlet, resulting in a net increase of DOC and DON. The exception to this occurred during March when increased discharge resulted in a large increase in DOC and DON flux into the Lake (Fig. 7). Our results support the hypothesis of Pace and Cole (2002) that a decrease of photolysis during ice-cover can result in a buildup of DOC in lakes. However, future research 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 ($-1.0\,\mu\mathrm{mol\,N\,L^{-1}}$ for discharge-weighted concentrations and $8\,\mathrm{mol\,N\,ha^{-1}\,yr^{-1}}$ of fluxes) compared to DOC ($93.0\,\mu\mathrm{mol\,C\,L^{-1}}$ and $1140\,\mathrm{mol\,C\,ha^{-1}\,yr^{-1}}$) likely indicating a contribution by autotrophs to the generation of DON in the Lake over the annual cycle compared to DOC (Table 1, Fig. 7). We observed differences of discharge-weighted concentrations and fluxes of DIN between inlet and outlet ranging from 7 to $28\,\mu\mathrm{mol\,L^{-1}}$ and from 60 to $183\,\mathrm{mol\,ha^{-1}\,yr^{-1}}$, respectively, indicating that the decrease of DIN in the Lake may be due in part to biological uptake and assimilation of DIN by algae (e.g., assimilatory nitrate reduction). The assimilation of DIN is supported by our analysis

showing the negative relationship between DIN and DON especially during the growing season (May to September) in the Lake (Table 1). 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 NO_3^- concentrations and fluxes were greater than for DON during the growing season (June to September).

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

In the current study, one of the major findings is the observation of different retention amounts of DOC vs. DON within the Lake (Table 4, Fig. 8a). The lowest retention, we observed, for both DOC and DON in 2007 could likely be attributed to the biotic contributions. Although we would require measurements of primary productivity to quantify the contribution of internal biological production within the Lake, the large amounts of

DIN removal in the Lake suggests the importance of DIN uptake and DON production in regulating TDN in the Lake (Fig. 8b). In 2003, the year with highest hydraulic retention in the Lake, we observed the highest retention of DOC and a high level of retention of DON (Table 4). In comparing results among years, there was a positive relationship between hydraulic retention and DOC retention, but not for DON retention (Table 5).

Our observation of the increase of DON compared to DOC within the Lake indicated the importance of the DON generation processes in the N mass balance of the Lake. When DON is mineralized to ammonium some of the ammonium may be nitrified. This nitrate can then be utilized in assimilatory and dissimilatory reduction. Some of the organic N formed by assimilatory nitrate reduction can be found as DON (Fig. 8b). Regarding the differences in DON formation vs. DOC formation in the Lake, it is important to ascertain whether the rate of DON decomposition was substantially less than that of DOC or the DON generation from DIN was the major factor in maintaining relatively high concentrations of DON in the Lake. From the 1 year study of Kang and Mitchell (2013) in the Arbutus Lake, approximately $39.9\,\mu mol\,C\,L^{-1}$ in DOC (10 % of the total DOC) was microbially decomposed, whereas $2.2\,\mu mol\,N\,L^{-1}$ in DON (20 % of the total DON) was estimated to be bioavailable. Considering the concentration difference of DOC and DON between inlet and outlet in this study ($93\,\mu mol\,C\,L^{-1}$ and $-1\,\mu mol\,N\,L^{-1}$, respectively; calculated from Table 4), the bioavailable DON was greater than the difference between inlet and outlet, indicating that DON was likely produced within the Lake. In contrast, larger amounts of DOC were retained in the Lake than values of biodegradable DOC, indicating that DOC might be more readily decomposed due to different processes with DON changes in the Lake. Therefore, we suggest that DON generated from internal production from DIN is important. Further study is needed to understand the algal production rate of DOC and DON and the quantification of DON decomposition and retention.

Wet DIN deposition was estimated to account for 21.3 % (range: 14.3 to 29.2 %) of the DIN input to Arbutus Lake from 2000 to 2009 (for example, in 2009 allochthonous DIN input from the inlet catchment, $26\,878\,mol\,N\,yr^{-1} = 89\,mol\,N\,ha^{-1}\,yr^{-1}$ (inlet DIN flux

in 2009; Table 4) × 302 ha (entire watershed area – lake area) and wet deposition input of DIN, $11\,071\,\mathrm{mol\,N\,yr^{-1}} = 221\,\mathrm{mol\,N\,ha^{-1}\,yr^{-1}}$ (http://nadp.sws.uiuc.edu/nadpdata/annualReq.asp?site=NY20) $\times 50\,\mathrm{ha}$ (lake area)). If the direct deposition of DIN in the Lake is included in the N budget, N mass balances in the retention of DIN in Arbutus Lake is even greater (mean of DIN retention including wet DIN deposition: 64.3 %). Arbutus Lake is considered P-limited based on its molar N : P ratio of 25 (more than 7 of Redfield's ratio. calculated from TP concentration data ($0.44\,\mathrm{\mu mol\,P\,L^{-1}}$) from Kelting and Laxson, 2014 and average TDN data ($23\,\mathrm{\mu mol\,N\,L^{-1}}$) in this study). Whereas in N-limited lakes, lake productivity is dependent on atmospheric DIN inputs that contribute to algal productivity and DON concentrations. In those N-limited lakes, the recycling of DON might play an important role in N availability. Additionally, in lentic systems, since DOM bioavailability may regulate secondary production in the microbial loop (DOM → bacteria → protozoa → zooplankton), we should reconsider the importance of DON recycling.

5 Conclusions

Our study found no significant long-term changes in annual mean concentrations of DOC and DON. However, mass-balances for DOC and DON between the Lake inlet and outlet revealed that the Lake was generally a sink for DOC and DIN, but functioned as a sink or source for DON, depending the time of the year. Annual concentrations and fluxes showed strong variation among years as a function of the hydraulic retention time of the Lake. Our study suggests a complex interplay of both hydrological and biological factors in affecting DOC dynamics of a lake (Goodman et al., 2011), and that newly formed DON from DIN within a lake plays an important role in lake N dynamics (Stepanauska et al., 2000b). The enrichment of N in DOM could be a source of nutrient N for downstream aquatic ecosystems. This DON may also serve as a link in the supply of a limiting N nutrient and subsequently contribute to productivity of N limited systems. Our study indicates that DOC and DON may display substantially different

biogeochemical relationships in oligo/mesotrophic lakes nested forested watersheds, and therefore different roles for a sink behavior for DOC (which has received more attention) vs. a producer of DON.

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Table 1. Monthly and yearly Pearson correlation results (r) among DOC, DON and DIN concentrations as well as climatic variables (Huntington Forest) at the inlet and outlet of Arbutus Lake. Note that correlation results with 0.5 or greater in monthly analysis are shown. A statistically significant correlation is indicated with asteriks ($p < 0.001$[***], $p < 0.01$[**]).

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

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Table 2. Annual precipitation, inlet and outlet discharge, residence time, and hydraulic retention from 2000 to 2009 in Arbutus Lake.

Year	Precipitation (mm yr^{-1})	Inlet discharge (mm yr^{-1})	Outlet discharge (mm yr^{-1})	Residence time (year)	Hydraulic retention (%)
2000	1323	885	733	0.52	17.2
2001	901	572	476	0.80	16.9
2002	902	545	541	0.71	0.9
2003	1094	860	632	0.60	26.5
2004	972	635	567	0.67	10.8
2005	1296	728	539	0.71	26.0
2006	1174	820	712	0.54	13.2
2007	1199	604	542	0.70	10.2
2008	1395	830	756	0.51	8.9
2009	1153	641	471	0.81	26.5
Mean	1141	720	597	0.66	15.7

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

		Inlet	Outlet	Retention
Discharge-weighted concentration ($\mu mol\,L^{-1}$)	DOC	506 (16)	413 (14)	
	DON	10 (1)	11 (1)	
	DIN	28 (3)	12 (2)	
	DOC : DON (molar ratio)	55 (6)	40 (3)	
Flux ($mol\,ha^{-1}\,yr^{-1}$)	DOC	3617 (257)	2477 (180)	30.1 % (3.3)
	DON	71 (8)	63 (2)	6.9 % (6.9)
	DIN	195 (19)	75 (8)	61.1 % (3.1)

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

Year	DOC ($\mu mol\,C\,L^{-1}$)		DON ($\mu mol\,N\,L^{-1}$)		DIN ($\mu mol\,N\,L^{-1}$)		C : N		DOC ($mol\,C\,ha^{-1}\,yr^{-1}$)			DON ($mol\,N\,ha^{-1}\,yr^{-1}$)			DIN ($mol\,N\,ha^{-1}\,yr^{-1}$)			Retention (%)		
	In	Out	In	Out	In	Out	In	Out	In	Out	$I - O$	In	Out	$I - O$	In	Out	$I - O$	DOC	DON	DIN
2000	486	392	11	12	29	12	44	33	4303	2875	1428	96	85	12	259	92	167	33.2	12.0	64.5
2001	547	386	11	9	38	18	50	44	3130	1838	1292	60	42	18	220	84	136	41.3	30.0	61.8
2002	476	354	9	10	29	15	53	35	2599	1911	688	51	52	−2	159	85	74	26.5	−3.2	46.5
2003	554	421	11	10	24	11	50	42	4761	2661	2100	93	66	26	209	64	145	44.1	28.5	69.4
2004	562	438	6	8	26	14	94	55	3570	2481	1089	40	47	−7	165	80	85	30.5	−17.6	51.5
2005	524	449	8	10	22	8	66	45	3812	2420	1392	60	54	7	157	42	115	36.5	11.2	73.2
2006	558	496	9	11	28	10	62	45	4579	3529	1050	75	78	−3	230	71	159	22.9	−4.7	69.1
2007	424	429	7	10	49	21	61	43	2562	2326	236	42	57	−15	295	112	183	9.2	−34.8	62.0
2008	487	398	13	12	19	11	37	33	4042	3012	1030	109	91	18	159	86	73	25.5	16.6	45.9
2009	439	364	14	13	13	6	31	28	2817	1712	1105	87	60	27	89	29	60	39.2	31.2	67.4

Table 5. Pearson correlation results (r) among % retention of lake water and fluxes and concentrations (conc.) in DOC, DON, and DIN of Arbutus Lake. A statistically significant correlation is indicated with asterisks ($p < 0.001$[***], $p < 0.01$[**], $p < 0.05$[*]). % Retention of concentrations was calculated using the same equation for flux retention described in Sect. 2.

% Retention	Lake water	DOC flux	DOC conc.	DON flux	DON conc.	DIN flux
DOC flux	0.68[*]	–				
DOC conc.		0.75[*]	–			
DON flux		0.86[***]		–		
DON conc.		0.70[*]	0.69[**]	0.92[***]	–	
DIN flux	0.83[***]					–
DIN conc.						0.87[***]
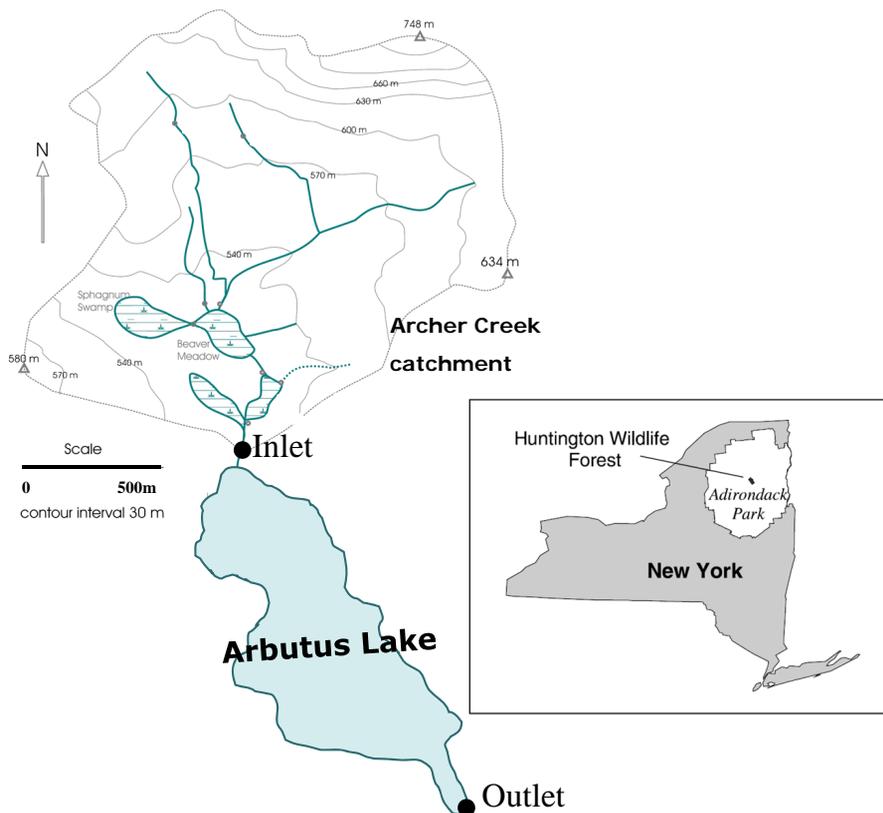
Figure 1. Study sites in the Arbutus Lake watershed in Huntington Wildlife Forest, Adirondack Park, New York, USA.
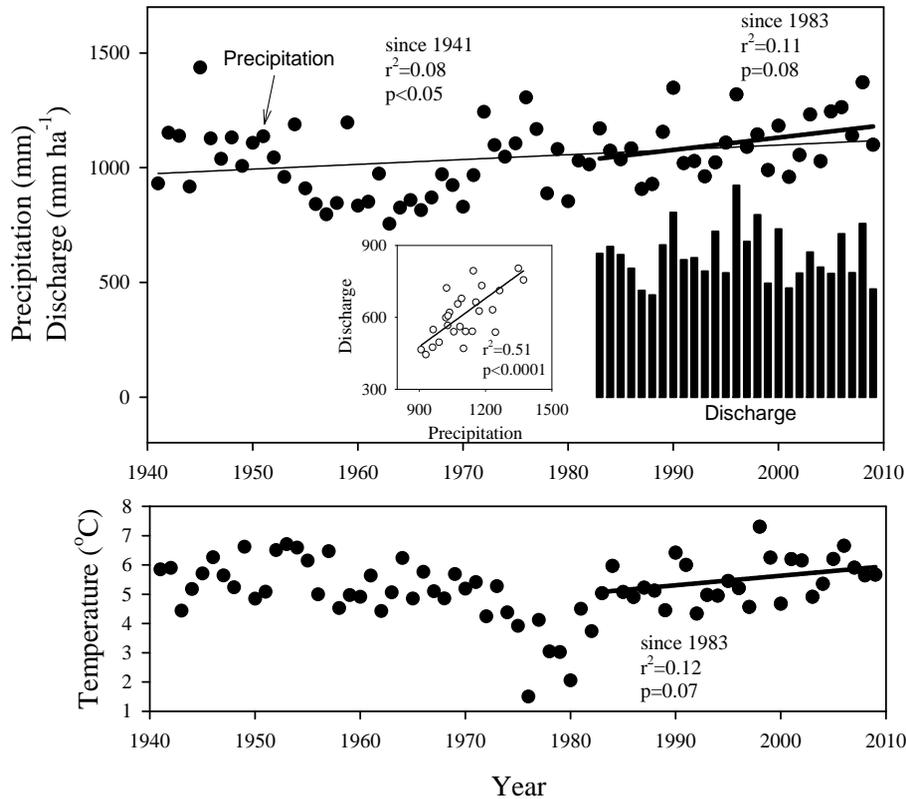
Figure 2. Annual precipitation and temperature at AEC site and yearly discharge at the Arbutus Lake outlet since 1941. Relationship between precipitation and discharge is embedded in the upper panel.
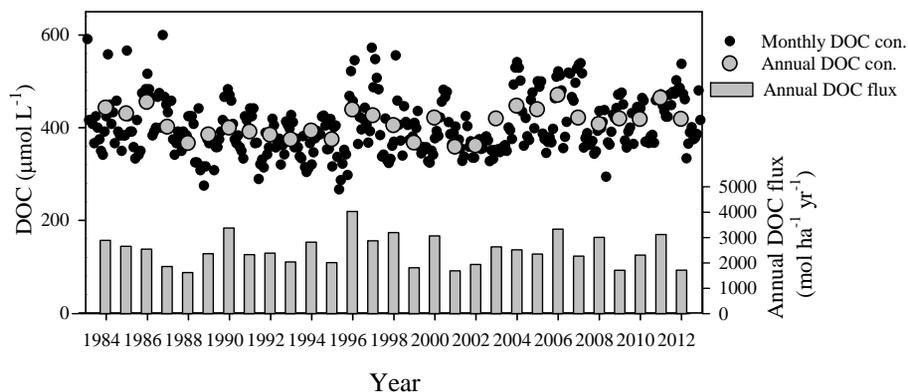
Figure 3. Monthly (small black circles) and annual (larger gray circle) variation of DOC concentrations and annual DOC flux (gray bars) at Arbutus Lake (outlet) from 1983 (February) to 2012 (December) using ALTM data set.
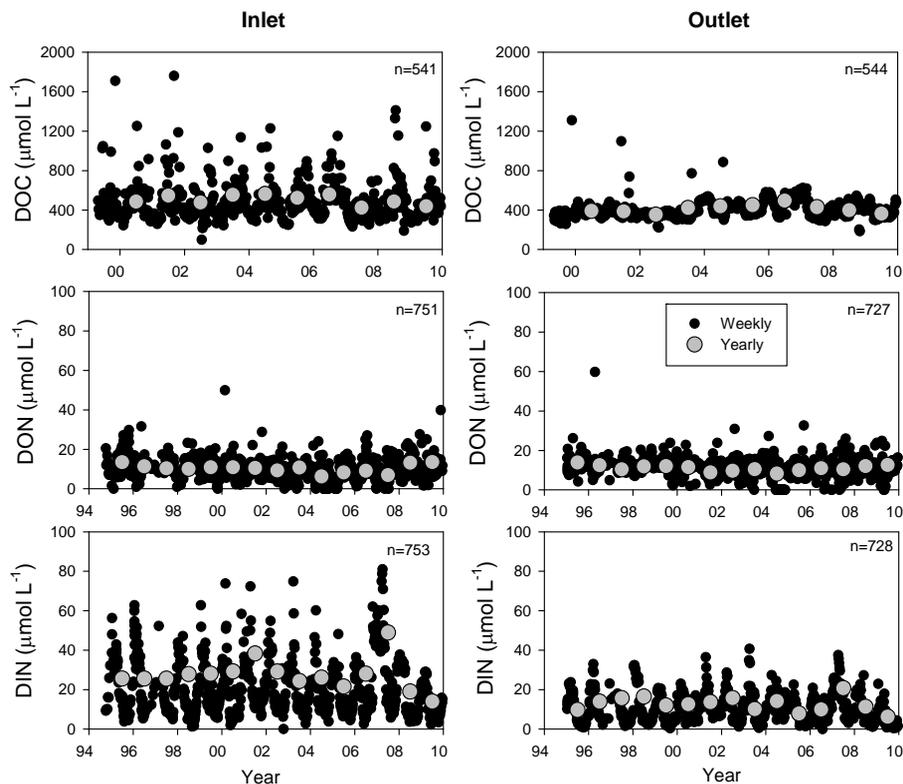
Figure 4. Weekly and annual yearly variation of DOC concentrations from 1999 to 2009 and DON and DIN concentrations from 1994 to 2009 at the inlet and outlet of Arbutus Lake. Annual values are discharged-weighted concentrations.
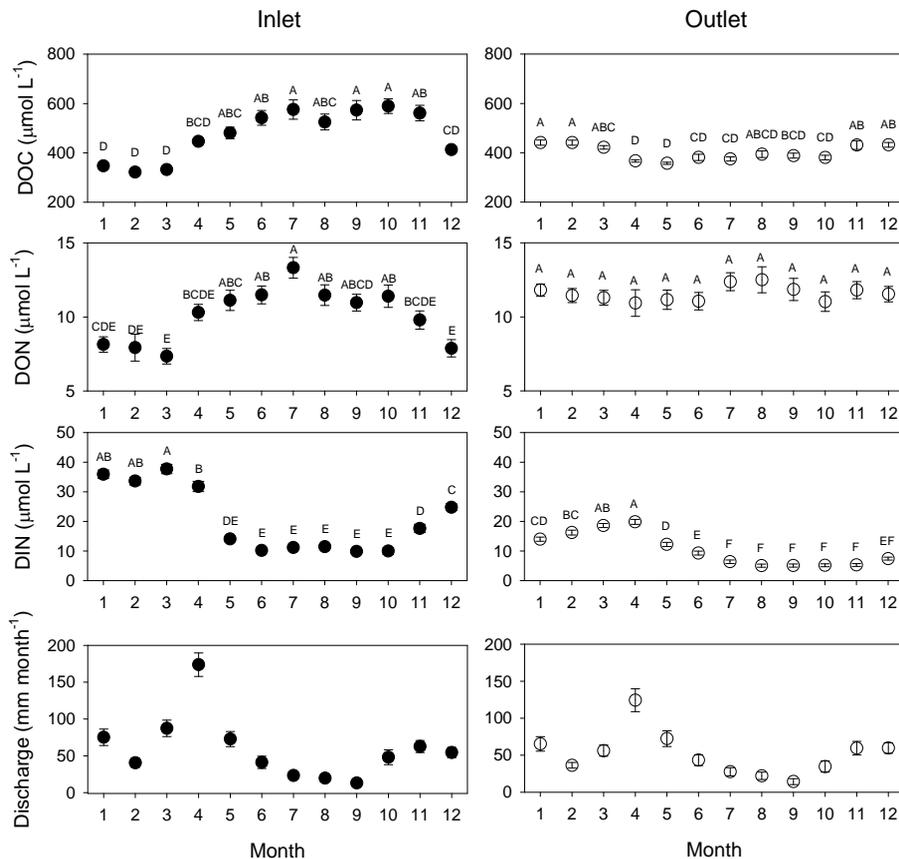
Figure 5. Monthly average discharged-weighted concentrations (error bar: SE) of DOC, DON, and DIN in the inlet and outlet of Arbutus Lake. Letters indicate results of posthoc Tukey HSD test ($\alpha = 0.05$) in one-way ANOVA and the same letter among months means no significant difference.

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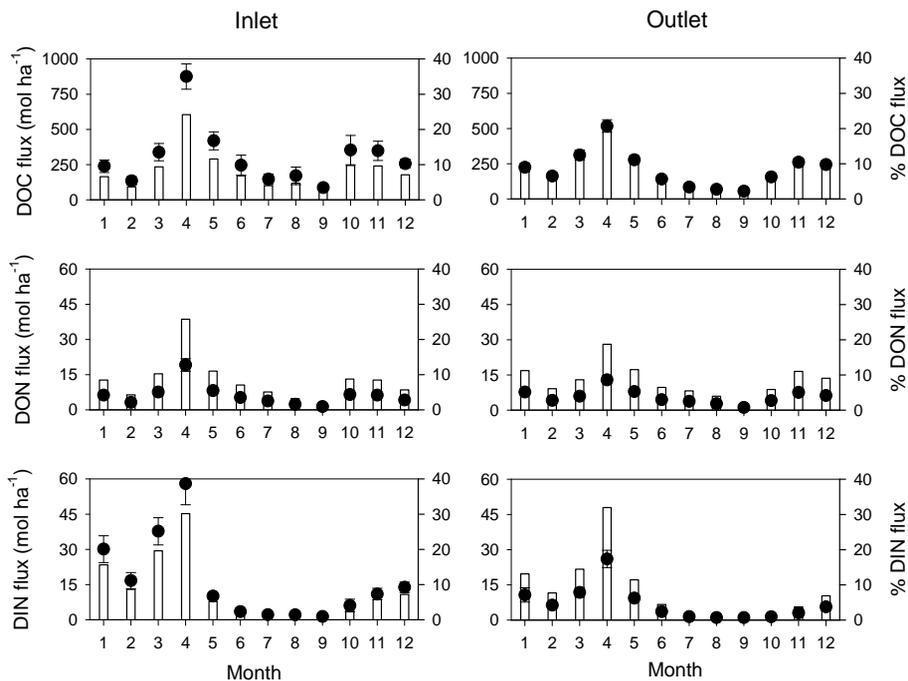
Figure 6. Monthly average flux (circle, left horizontal axis; error bars, SE) and monthly % flux of the annual flux (bar, right horizontal axis) of DOC, DON, and DIN at the inlet and outlet of Arbutus Lake.
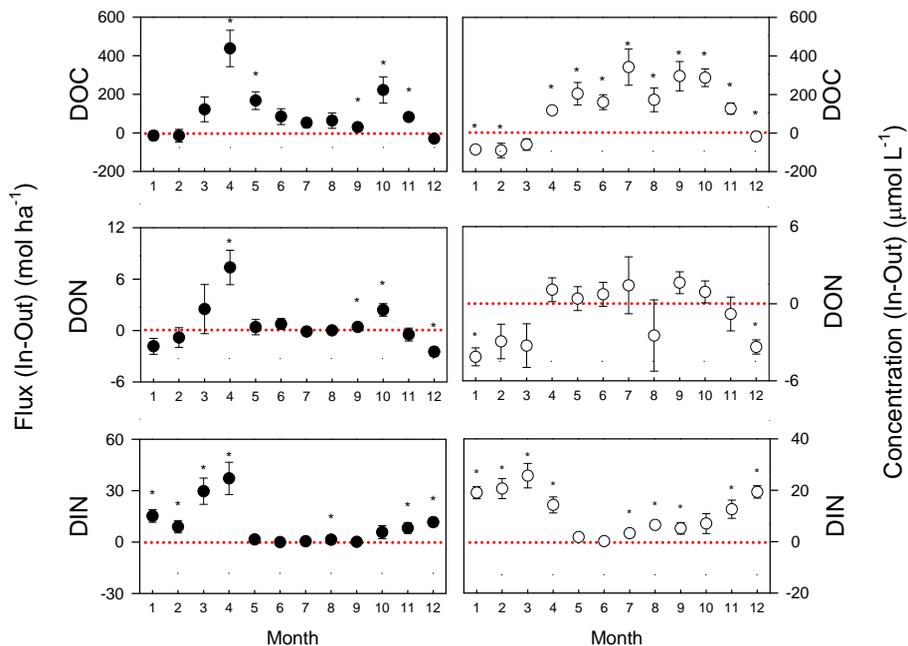
Figure 7. Monthly differences (error bars: SD) of DOC, DON, and DIN in fluxes and discharge-weighted concentrations between inlet and outlet of Arbutus Lake from 2000 to 2009. Asterisk indicates significant difference with zero (paired t test between inlet and outlet at $\alpha = 0.05$).
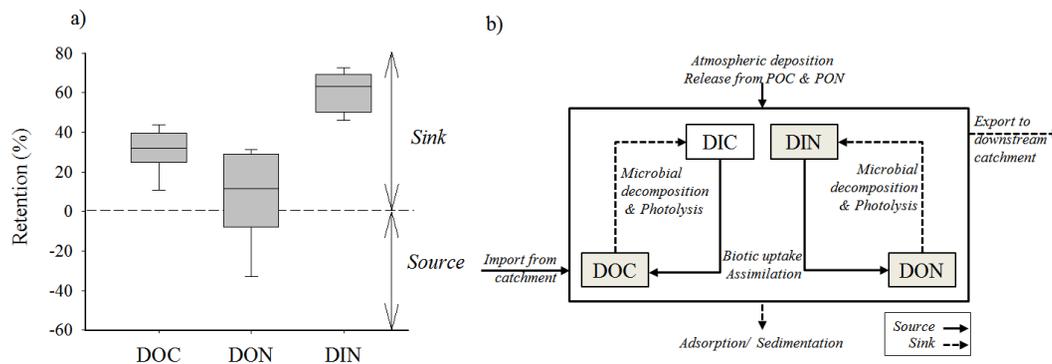
Figure 8. (a) A box plot showing annual retention ((influx – outflux) / influx)) of DOC, DON, and DIN at Arbutus Lake from 2000 to 2009. Whisker caps indicated 10th and 90th percentiles and a box showed the 25th, 50th (median), and 75th percentiles from the bottom to the top. **(b)** a diagram indicating processes of sources and sinks in DOC and DON in Arbutus Lake (DIC: dissolved inorganic carbon).