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Characterizing Headwater Stream Hydrology and Nitrogen Export During Storms Across a Gradient of Watershed Development

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Characterizing Headwater Stream Hydrology and Nitrogen Export During Storms Across a Gradient of Watershed Development

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Abstract

Nitrogen (N) is a critical element for aquatic ecosystem function that can degrade water quality and cause eutrophication if in excess of natural levels. Anthropogenic nonpoint sources contribute more than 90% of total N added to major watersheds in the U.S, in excess of natural levels, and they are increasing with land development. Storms mobilize N from anthropogenic sources and generate periods of high N export to aquatic ecosystems. In this thesis, I explore how a gradient of watershed development affects the volume-weighted load, composition, and timing of N exported from first-order streams in New England during storms. I find that volume-weighted loads of total N and total organic N increase with increasing watershed development, and that volume-weighted loads of ammonium and nitrate during storms increase with watershed impervious cover. I also find that, for all levels of watershed development, total organic N composes more than 60% of total N exported during storms. Finally, I find that, for all levels of watershed development, N export increases with increasing stream discharge volume during storms. There are significant seasonal differences in the relationships between watershed development and N export, perhaps affected by factors such as watershed septic system prevalence, snowmelt contributions, and summer drought. These factors should be taken into account when estimating parameters of N export across watersheds of varying degrees of development.

Introduction

Humans have increased global nitrogen (N) fixation to more than double the natural rate (Vitousek 1997). Increased N fixation has been linked to increases in N loading to streams and rivers (Vitousek 1997), the eutrophication of coastal waters (Nixon 1992, National Research Council 1993), and the acidification of freshwater lakes and streams (Driscoll et al. 1987, Henriksen et al. 1988, Kelly et al. 1990), among a host of other environment and ecosystem effects (Howarth et al 1996). Nitrogen enters surface waters primarily via atmospheric deposition, runoff from fertilizer, and disposal of wastewater (Valiela et al. 2002).

Sources of N entering surface waters are divided into two broad categories: point and nonpoint sources. Point sources are discrete sources of N, such as wastewater treatment plants or industrial discharges. Nonpoint sources are diffuse sources of N, such as excess fertilizer from agricultural or residential areas, or N from livestock, pet waste, or faulty septic systems. Early controls on N loading to streams, since the passage of the 1972 Federal Water Pollution Control Act, focused primarily on point sources even though nonpoint sources contribute 95.3% of total N added to major watersheds in the U.S. (Pucket 1994). Indeed, nonpoint sources of N are the primary causes of coastal eutrophication across U.S. (Welch 1992), and of river, lake, and reservoir eutrophication in parts of the U.S. (Puckett 1994). Thus, there is a critical management need to exert greater controls over nonpoint sources of N in order to protect coastal and estuarine systems (Yang 2012).

Nonpoint sources of N increase with human population growth in watersheds globally. Howarth et al. (1996) found that watersheds experiencing disturbance by humans tend to exhibit higher overall N export than forested watersheds. In a study of U.S. watersheds exhibiting a gradient of forestation and development, concentrations of N in streams increased with watershed development (Mueller et al. 2006). Human population density also correlates highly with river concentrations of nitrate (NO_3^--N) and explains 76% of the variation in NO_3^--N load export among 42 major world rivers that account for 37% of global freshwater discharge to the ocean (Peierls et al. 1991).

Many studies have shown higher N export from watersheds dominated by urban and/or agricultural land relative to forested watersheds (Beaulac et al. 1982, Basnyat et al. 1999, Biggs et al. 2004, Groffman et al. 2004, Yang 2012). Groffman et al. (2004), in a 4-year study of watersheds in Baltimore, Maryland, found the mean N yield of urban and suburban watersheds (6.7 kg N ha^{-1}) was more than 10 times that of completely forested watersheds (0.52 kg N ha^{-1}). Annual variation in yields was greatest in urban watersheds and least in forested watersheds (Groffman et al. 2004). Further, a Wickham et al. (2002) model of the mid-Atlantic region of the U.S. found that areas with forest:agriculture ratios of 6:1 and projected urbanization rates of ≥ 20% of watershed land cover were at risk of increasing N exports.

Differences in human-associated nonpoint sources of N in developed watersheds may account for the differences in N export from forested watersheds. Nitrogen export from sources such as fertilizer, landfills, construction activities, and pet waste all increase with increasing development (Carey et al. 2013). Nitrogen from partially or untreated sewage from septic systems, used by approximately 20% of homes in the US (USEPA 2008), contributes substantially to N loads in streams draining developed watersheds (Castro et al. 2003). Turf grass, a common installed feature in exurban and suburban developments, can be either a net sink or net source of N during storms and snowmelt periods, depending on the type, rate, and timing of fertilization application (Carey et al. 2013).

The prevalence of different forms of N in streams may also be related to watershed development. Nitrogen in streams draining more highly forested watersheds tends to be dominated by organic nitrogen (ON; Hedin et al. 1995, Scott et al. 2007). Nitrogen in streams draining urban and suburban watersheds tends to be dominated by inorganic N, particularly NO_3^--N (Howarth et al. 1996, Groffman et al. 2004), though Groffman et al. (2004) also found that the NO_3^--N fraction was low for both highly urbanized and highly forested watersheds. Biggs et al. (2004) found several large urban watersheds (~1000 – 3000 km^3) in Brazil that showed higher total dissolved N concentrations than watersheds dominated by small pastures. Regression models developed in a study of Seattle watersheds experiencing a gradient of development indicated that converting 10% of catchment area from forest to urban land cover would result in increases in

average stream water concentrations of TN, NO_3^--N, and ammonium (NH_4^+-N) (Brett et al. 2005).

Watershed development can also substantially alter watershed and stream hydrology. The proliferation of impervious cover (i.e., roads, roofs, and parking lots) increases diversion of water away from subsurface flow to runoff (Wolman 1967, Leopold 1968, Hollis 1975). Runoff is found to increase in direct proportion to watershed rooftop and road extent (Roesner et al. 2001). The removal of forest cover and the compaction and stripping of soils can lower the perviousness and storage capacity of a watershed, which leads to increased watershed runoff (Dunne et al. 1978). These common watershed alterations can increase the volume of discharge that reaches streams as well as the rate of water delivery to streams (Ferguson et al. 1990). Streams draining developed watersheds can display greater peak discharge volumes and lower baseflow discharge volumes than streams draining forested and relatively undeveloped watersheds (Hollis 1975, Paul et al. 2001, Turner et al. 1975). The effects of development (i.e., roads) on local stream hydrology can extend 50-200 meters downstream (Forman et al. 1998).

Storms may increase or decrease N concentrations in streams, but nonetheless tend to cause the export of higher N loads than during baseflow conditions. Some studies show that storms increase the concentration and load of N above baseflow conditions (Correll et al. 1999, Inamdar 2006), while other studies show storms decrease concentrations of

N but still increase N load (Wiegner et al. 2009, Taylor et al. 2015). Nitrogen export during storms can be disproportionately high compared to export during baseflow conditions for the same length of time (Inamdar et al. 2006, Taylor et al. 2015, Wiegner et al. 2009). In a study in Hawaii, the majority of particulate N export occurred during stormflow rather than baseflow (Wiegner et al. 2009). A single storm (Tropical Storm Irene) in a forested watershed in Maryland contributed nearly a third of annual N export (Inamdar et al. 2015).

There also appear to be seasonal controls on N export from watersheds, and even potential interactions between seasonal controls and watershed development. Studies that examine seasonal differences in N export in streams show spring and fall pulses, where the increase in N concentrations during the spring are attributed to contributions from snowmelt, while the increase in concentration of N in the fall is attributed to greater amounts of precipitation and decreased biological assimilation (Arheimer et al. 1996, Campbell et al. 2000, Clark et al. 2004, Inamdar et al. 2006, McHale et al. 2000). Watersheds with N inputs in excess of biological demand can experience increases in stream concentrations of N across all seasons, and this increased N input may attenuate the differences between stream concentrations of N between seasons (Aber et al. 1997, Hedin et al. 1995, Hood et al. 2003, Stoddard 1994).

Watershed development may alter the role of storms in N export dynamics. Previous research suggests increasing watershed development increases stream water

discharge volumes and volume-weighted loads of N in stormwater runoff (Sonzogni et al. 1980; Chui et al. 1982; Graves et al. 2004; Kayhanian et al. 2007). Several other studies have focused on how watershed development alters N concentration during storms, with some studies reporting decreased concentrations during storms compared to baseflow conditions (Janke et al. 2014) and others reporting no differences in N concentrations between baseflow and stormflow conditions (Taylor et al. 2005, Duncan 2004). Increasing watershed development has also been associated with increased contribution of N export during storms to total annual budgets (Shields et al. 2008, Turner et al. 1975). However, the overall magnitude of annual N export may not be related to watershed development (Shields et al. 2008). Thus, it remains unclear how watershed development alters stream discharge and N export from headwater streams during storms. The specific objectives in this study were to determine how a gradient of watershed development affects:

1) Stream discharge across seasons, stream discharge during stormflow periods, and the duration of stormflow periods in headwater streams; and
2) The load of N (NO_3^--N, NH_4^+-N, TON, TN) and Cl^- across seasons and during stormflow periods from headwater streams.

Methods

Site Description

This study was conducted in the Farmington River Basin, located to the west and north of Hartford, which ultimately drains into the Connecticut River (Figure 1). The

Connecticut River is a major source of N to the Long Island Sound (LIS), where N loading is the primary cause of seasonal hypoxia (Long Island Sound Study 2016). The Connecticut Department of Energy and Environmental Protection (DEEP) has expressed interest in reducing N loads from nonpoint sources: a 2011 report from their Nonpoint Source Management program states that "identifying the causes of nonpoint source pollution and the relationship to human activities to the health of Long Island Sound is a priority area of concern for CT DEEP and the Long Island Sound estuary partnership" (Connecticut DEEP 2011). Continued development of N management practices then warrants a better understanding of the interplay between watershed development, storms, and nonpoint sources of N in watersheds that drain to the LIS.

Mean annual spring, summer, and fall temperatures are 10.9° C, 20.9° C, and 8.5° C at the National Oceanic and Atmospheric Admiration (NOAA) monitoring station closest to the centroid of my study area in Burlington, CT (NOAA 2016a). The mean monthly precipitation across Connecticut is 19.4-25.9 centimeters, but the probability of large storms in a given month is high and these large storms can cause a month's precipitation to rise substantially above the average (Miller et al. 2010). The year 2015 (during which I collected my samples) was drier than the 30-year average in Connecticut, with annual precipitation at 79% of average, and with August and September rainfall in the Hartford area only averaging 56% and 69% of average rainfall, respectively, according to the NOAA (2016b). Average spring, summer, and fall temperatures for the year 2015 in Hartford were 9.44° C, 21.7° C, and 12.8° C,

respectively, according to the National Weather Service (2016), which are within one standard deviation of the 30-year average (NOAA 2016a).

Four headwater streams (first order) were selected within the Farmington River Basin (Figure 1). These sites were selected for their similar watershed sizes (average: 3.3775 ± 0.2516 km^2), a gradient of developed land cover (4.15-59.08% of watershed area), and absence of standing water or wetlands (Table 1). Developed land cover, as defined by Center for Land Use Education and Research (CLEAR 2010), consists of “high-density built-up areas typically associated with commercial, industrial and residential activities and transportation routes.” Watershed boundaries were delineated in ArcMap 10.3 using the Hydrology toolset and Connecticut LiDAR 10-foot digital elevation models (Center for Land Use Education and Research) (CLEAR 2014). Percent of watershed area land cover was derived from CLEAR land cover data (2010), and average impervious cover from the National Land Cover Database Percent Developed Imperviousness dataset (Xian et al. 2011).

The two least developed study sites drained protected forested areas. The majority of the watershed draining to Tain is owned by the Wildlife Conservation Fund (known as the Taine Mountain Preserve), and is stewarded by the Burlington Land Trust. The watershed draining to Tunx is contained entirely within the Tunxis State Forest of Connecticut. Hop and Bris were on private properties and drained watersheds consisting mostly of houses, apartments, and a few small businesses.

Field methods

From April 12, 2015 to October 5, 2015 sites were monitored for continuous stream stage, and stream samples were collected during both baseflow and stormflow periods. Stream stage was monitored using pressure transducers (Teledyne Isco Inc., Lincoln, NE) that generated records every fifteen minutes from April to June, and then every five minutes from June to October. Pressure transducers were anchored into the streambed at each site. Due to equipment failure or conflicts with property owners, continuous stream stage was not recorded at all sites throughout the study period (Table 2).

Stream water grab samples were collected from each site bi-weekly from April until October, with the exception of one sampling date in July when samples were lost due to improper storage. Samples were collected in acid-washed HDPE bottles that were triple-rinsed in the field. Samples were transported to the lab on ice, filtered through 0.7 μm GF/F Whatman glass fiber filters in syringe holders, and filtered and unfiltered aliquots of each sample were frozen within 24 hours of collection until analysis.

Samples were collected during storm events from the four sites using automated water sampling units (Teledyne Isco Inc., Lincoln, NE) from April to October (except for Tunx, where collection began on May 24, 2015; Table 2). The automated samplers were triggered during storm events when the pressure transducer showed that stream stage had risen 0.010 m in a 30-minute period, and thereafter collected discrete samples once every hour into acid-washed 500 mL bottles for the subsequent 24 hours. In the event of

rainfall continuing beyond this 24-hour period, the automated sampler was set to sample once every hour for another 24-hour period, and so on until rainfall above the site had ceased. Storm samples were collected from the automated samplers within 24 hours of automated collection, transported to the lab on ice, and refrigerated in the lab. Within 48 hours of automated collection, samples were filtered through 0.7 μm GF/F Whatman glass fiber filters in syringe holders, and filtered and unfiltered aliquots were stored in acid-washed and sampled-rinsed HDPE bottles and frozen until analysis.

Laboratory methods

Filtered samples were analyzed for NO_3^--N and Cl^- by ion chromatography on a Dionex ICS-1100 (Thermo Fisher Scientific, Waltham, MA), and for NH_4^+-N by the phenate method (APHA 1998) on a SmartChem 200 discrete analyzer (Westco Scientific Instruments, Brookfield, CT). Unfiltered samples were analyzed for TN by persulfate digestion (APHA 1998), which oxidizes all N species to NO_3^--N. Digested samples were analyzed on the SmartChem by colormetric determination of NO_3^--N plus nitrite (NO_2^--N) by enzymatic reduction (Campbell et al. 1997; Patton et al. 2011). In this method, NO_3^--N is reduced to NO_2^--N with nontoxic, soluble NO_3^--N reductase rather than toxic, granular, copperized cadmium used in longstanding standard methods (e.g., APHA 1998). Colorimetric reagents used to determine resulting NO_2^--N are identical to those used in standard cadmium reduction methods (e.g., APHA 1998). Commercially available enzyme, AtNaR (available from the Nitrate Elimination Company, www.nitrate.com) along with the method ("Method for Nitrate Reductase Nitrate-

Nitrogen Analysis"; NECi Method N07-0003), recently approved by the Environmental Protection Agency, were used for this analysis. Dissolved inorganic nitrogen (DIN) concentrations were estimated by adding NO_3^--N and NH_4^+-N. Dissolved organic nitrogen (DON) concentrations were estimated by subtracting DIN from TN.

Limits of detection (LOD) for all analyses were calculated by the following formula:

$$LOD = \frac{3\sigma_{standard}}{\sqrt{n_{standard} + 1}}$$

In the case that analysis yielded a concentration lower than the LOD, its value was set to one half the LOD.

Stream discharge calculations

Discharge at each site was determined via a rating curve that related stream discharge and stream stage, as per standard USGS methods (Sauer 2002). Stream cross sections and stages, along with discharge every 15.2 cm (six inches) across streams, were collected throughout the study period, during both baseflow and stormflow conditions. These measurements were then used to establish a relationship between stream stage—measured continuously during the study period by the pressure transducers installed in the streams—and stream discharge at all corresponding times of stage measurement. In the cases of Bris and Tain, baseflow during July diminished to the point that pressure transducers had to be moved to a new location downstream, where the stream was narrower and the stage higher. In the case of Hop, due to a conflict with

the property owner, the pressure transducer at this site was also moved farther downstream. In all cases, the move was less than 30 yards from the initial site. The pressure transducer at Tunx was never moved. Consequently, two separate rating curves were developed for Bris, Tain, and Hop (one for prior to the move and one for after) and only one was developed for Tunx. Power relationships between stage and discharge produced the best-fit lines for all locations for Bris, Hop, and Tain; an exponential relationship for Tunx (Table 3).

Stormflow period identification

Storm events were classified as having begun at 15 minutes before the collection of the first sample, which was collected whenever there was rainfall and the stream stage had risen 0.010 m in a 30-minute period. Samples were then collected by the automated sampler, typically for 23 hours following initial collection, depending on duration of storm event. Because the streams often exhibited multiple distinguishable stage peaks during collection periods, and because the Farmington River watershed experienced frequent scattered showers (as opposed to uniform storm events), a set of criteria were developed to determine the start and end points of storms within collection periods. The storm start was identified as 30 minutes before the first automated sample collection. The storm end was identified as either eight hours after the stage peak or when the stage returned to within 5% of pre-storm stage—whichever came first. An exception was made to these criteria when, before storm end criteria was met, and at least 30 minutes after a stage peak, the stage rose again for a minimum of 30 minutes by a minimum of

0.010 cm. When this exception was met, a storm end was declared 30 minutes after the first stage peak and a storm start was declared 30 minutes before the second stage peak. Thus, one collection event can be divided into multiple storms, without any storms overlapping in time.

Flux and load calculations

Nitrogen and Cl^- concentrations for the study period (except for time periods identified in Table 2) were interpolated using methods included in the loadflex package (Appling et al. 2015) and LOADEST package (Runkel et al. 2004) in R. These methods provide point predictions of concentrations at 15- or 5-minute intervals according to whichever time interval stream stage was being collected. The best fit among the potential models was the composite method described in Appling et al. (2015). This method (Appling et al. 2015) generates point predictions of concentrations by adding a piecewise linear interpolation of the residuals of observed data to a regression model (loadReg2; Runkel et al. 2004). Durbin-Watson d statistics and auto-correlation ρ for the calibration residuals were all less than 2 and greater than 0, respectively, indicating positive auto-correlation. Durbin-Watson d statistics and auto-correlation ρ for the interpolation residuals were less than and greater than, respectively, the calibration residuals, indicating that autocorrelation of my interpolated results are desirably different and strong enough to reasonably extrapolate from observations.

Flux rates (kg/d) were calculated for N species and Cl^- at all times stream stage was collected by multiplying interpolated concentrations by discharge. Raw load (kg) was calculated for N species and Cl^- by multiplying the flux rates by the stream stage collection intervals and summing these values over a period of interest (Table 8). Load (kg ha^{-1}) was calculated by dividing raw load by watershed area. Flow-weighted load (kg m^{-3}) was calculated for each N species and Cl^- by dividing the calculated raw load of that constituent over a period of interest by the total volume of water that moved past the pressure transducers over the period of interest. Flux rates, raw loads, and flow-weighted loads were calculated for each site for the full sampling period ("full interval"), for each season (spring, summer, and fall), and for each storm event. Spring storm events were those that occurred between the start of the collection period and May 31st; summer storm events between June 1st and August 31st, and fall storm events between September 1st and the end of the study period.

Statistical analysis

Differences in the parameters of interest between the study sites were compared using max-*t* tests for multiple comparisons that allow for unequal group sizes, non-normality, and heteroscedasticity (R functions 'aov()', 'glht()'; R packages 'sandwich' and 'multcomp'; see: Herberich et al. 2010, Hothorn et al. 2008). This method, by asymptotic control of the familywise error rate, allows for the comparison of the means of multiple treatments without increasing the chance for type I errors typical of standard methods (Hothorn et al. 2008). Once ANOVA analysis confirmed that there were significant

differences between the means samples with different treatments ($p < 0.05$), this method (Herberich et al. 2010, Hothorn et al. 2008) allowed us to compare the mean loads, mean volume-weighted loads and mean duration of storms that occurred throughout the full interval and storms that occurred during each season (spring, summer, and fall) by site. We also ran the same analysis to compare sites grouped into "high development" (> 40% developed land cover (i.e., Bris and Hop) and "low development" (< 19% developed land cover (i.e., Tain and Tunx)). For loads of N and Cl^- exported during storm flow periods, Shapiro-Wilk tests (R function 'shapiro.test()') were performed to examine the normality of the data, and then simple linear regressions (R function 'lm()') were used to examine how much discharge volume explained loads over the study period (referred to in tables as "full interval"). For mean volume-weighted loads of N and Cl^- exported during storm flow periods, Shapiro-Wilk tests were performed to examine the normality of the data, and then simple linear regressions were used to examine how much percent watershed development and average watershed impervious cover explained volume-weighted loads over the study period (referred to in tables as "full interval") and seasons. Mean-volume weighted loads were also log-transformed and their normality was examined using Shapiro-Wilk tests. Simple linear regressions were used to examine how much percent watershed development and average watershed impervious cover explained log-transformed volume-weighted loads over the study period and seasons. All statistical analysis was performed in R version 3.2.5 (R Core Team 2016), via the R Studio interface version 0.99.902 (R Studio Team 2015).

Result*s*

Hydrology

Among the four watersheds, 103 storm events were identified over the study period: 12 storms at Tunx (4.19% developed), 22 at Tain (18.56% developed), 36 at Hop (40.29% developed), and 33 at Bris (59.08% developed; Tables 2, 4).

The contribution of observed stormflow period discharge volume to the study period (baseflow and stormflow periods) discharge volume was highest for the site with the lowest development (Tunx; Table 5). Stormflow periods contributed almost 40% of the entire study period discharge volume at the site with the lowest development (Tunx), but less than 19% of the entire study period discharge volume for the three other sites (Bris, Hop, Tain). The majority of the storm contribution for the site with the lowest development (Tunx) derived from summer storm contributions, in particular one storm at the beginning of the season (the outlier in Fig. 2). This single storm event contributed 81% of observed summer storm discharge volumes in this watershed, and 32% of study period discharge volume.

There was not a clear relationship between watershed development and mean stormflow period discharge volume. Stormflow periods at the site with the second highest watershed development (Hop) yielded the greatest mean discharge volume for the full interval and spring ($p < 0.05$), but no one site was significantly different from the others during the summer or fall. When sites were lumped into high watershed

development and low watershed development, spring was the only interval when stormflow period discharge volume was significantly different ($t = -2.46$, $p < 0.05$), with high development sites having a higher mean than low development sites (Fig 2b).

Sites with greater watershed development tended to experience shorter mean stormflow period durations, indicating that sites with greater watershed development were "flashier," though this finding was not true for all seasons (Fig. 3; Tables 6, 7). The site with the highest watershed development (Bris) exhibited significantly shorter stormflow period durations than the site with the second lowest watershed development (Tain) for the full and summer intervals (full: $t = 3.136$, $p < 0.05$; summer: $t = 2.741$, $p < 0.05$; Fig. 3a; Table 6). When sites were grouped by low and high percent watershed development, storms at sites with low percent watershed development had significantly longer mean durations during the full interval ($t = 2.984$, $p < 0.05$) and summer ($t = 2.850$, $p < 0.05$; Tables 8,9; Fig. 3b). For the full interval, mean stormflow period duration of low development sites was 60% greater than that of high development sites.

Nitrogen and chloride

Load

Stormflow period export of all species of N significantly increased with increasing stormflow period discharge volumes (Figs. 4a-d). However, it is worth noting that Shapiro-Wilk tests for normality indicated that we must reject the null hypothesis that N and Cl^- loads exported from sites were normally distributed (data not shown). The same was true even when loads were log-transformed (data not shown). For observed

stormflow periods, the site with the second highest development (Hop) exported the greatest total TN, TON, and NO_3^--N loads while the site with the lowest development (Tunx) exported the greatest total NH_4^+-N load (Table 10).

As with N loads, stormflow period export of Cl^- increased with increasing discharge volumes (Fig. 4e). Chloride loads during storms were greatest at the more developed watersheds (Bris and Hop) for all intervals except for summer, when Tunx experienced the very large storm (Table 11). For all intervals other than summer, the site with the second highest development (Hop) exported the greatest load of Cl^-, coinciding with its greater discharge volume (Table 11).

Volume-weighted loads: Baseflow periods

During baseflow periods, simple linear regression analysis showed no significant relationship between volume-weighted loads of TN, TON, or NO_3^--N and watershed development or impervious cover during any interval over the study period (Fig. 5). Shapiro-Wilk tests of data did not indicate that the null hypothesis that the data came from a normal distribution could be rejected except in the case of Cl^- during the summer ($p > 0.05$; Table 12). However, volume-weighted loads of NH_4^+-N significantly increased with watershed development in the spring ($R^2 = 0.99$, $p < 0.05$; Fig. 5) and watershed impervious cover over the full interval ($R^2 = 0.99$, $p < 0.05$; Fig. 6). Volume-weighted loads of Cl^- significantly increased with watershed impervious cover in the spring (R^2 >

0.96, $p < 0.05$) and summer (R^2 = 0.99, $p < 0.05$; Fig. 7), but were not significantly related to percent watershed development for any interval.

Volume-weighted loads: Observed stormflow periods

Sites with higher development generally had greater mean volume-weighted loads during observed stormflow periods than sites with lower development, though this result varied by season. For the full interval and fall, both sites with the highest developments (Bris, Hop) had significantly greater ($p < 0.05$) mean volume-weighted loads for all N species during stormflow periods than the site with the lowest development (Tunx; Figs. 8, 9; Tables 13, 14). Further, during the summer, the site with the highest development had a significantly greater volume-weighted load of all N species than the site with the lowest development (Figs. 8,9; Tables 13, 14). The site with the highest development (Bris) also had greater mean volume-weighted loads of TN and TON than the site with the second-lowest development (Tain) in the fall (TN: t = 2.736, $p < 0.05$; TON: t = 2.821, $p < 0.05$; Figs. 9a, 9b; Tables 13, 14), NH_4^+-N in the spring (t = 4.034, $p < 0.05$; Fig. 8b; Tables 13, 14), and NO_3^--N over the full interval (t = 3.475, $p < 0.05$, Fig. 8a; Tables 13, 14).

The site with the highest watershed development (Bris), had significantly greater mean volume-weighted loads of Cl^- ($p < 0.05$) during stormflow periods than all sites for all intervals except the spring, when no watershed was significantly different from any other (Tables 13, 14). The site with the second highest development (Hop) had significantly

greater mean volume-weighted loads of Cl^- than the site with the second lowest over the full interval (Tain; $t = 4.483$, $p < 0.05$) and during the fall ($t = 5.131$, $p < 0.05$; Tables 13, 14).

When sites were grouped into high development and low development, the high development group generally had significantly greater volume-weighted loads during stormflow periods, though this varied by season (Figs. 10, 11; Tables 15, 16). For the full interval, sites with high development exported significantly greater ($p < 0.05$) mean volume-weighted loads of all N species. During the spring and fall, sites with high development exported significantly greater ($p < 0.05$) mean volume-weighted loads of TN and TON (Fig. 11; Tables 15, 16).

Simple linear regressions of volume-weighted loads of N and Cl^- during stormflow periods with percent watershed development and percent impervious cover revealed seasonally significant relationships (Figs. 12-14). A Shapiro-Wilk test was performed on the mean volume-weighted loads of N species, and the null hypothesis that these values came from a normal distribution could not be rejected (Table 17). Mean volume-weighted loads of TN and TON significantly increased with increasing development over the full interval (TN: $R^2 = 0.89$, TON: $R^2 = 0.94$) and in the fall (TN: $R^2 = 0.92$, $p < 0.05$; TON: $R^2 = 0.89$, $p < 0.05$) (Fig 12). Mean volume-weighted loads of TN but not TON significantly increased with increasing development in the spring ($R^2 = 0.90$, $p < 0.05$; Fig 12). Changes in watershed development were not significantly related to NH_4^+-N or

NO_3^--N; however, changes in area-weighted watershed impervious cover were. Mean volume-weighted loads of NO_3^--N increased with increasing area-weighted impervious cover during the full interval ($R^2 = 0.88$, $p < 0.05$) and the spring ($R^2 = 0.95$, $p < 0.05$) (Fig. 13). Mean volume-weighted loads of NH_4^+-N increased in the spring ($R^2 = 0.89$) with increasing area-weighted impervious cover (Fig. 13). Furthermore, a Shapiro-Wilk test was performed on the mean volume-weighted load of Cl^-, and the null hypothesis that these values came from a normal distribution could be rejected in two cases: the full interval and spring (Table 17). Linear regressions of this data (including for the full interval and spring) indicated that mean volume-weighted loads of Cl^- increased with area-weighted percent impervious cover for all intervals ($R^2 > 0.92$; Fig. 14). Changes in area-weighted impervious cover were not significantly related to TN or TON.

When volume-weighted loads of N species and Cl^- were log-transformed, normality of their distributions was improved, and linear regressions with percent watershed development and percent impervious cover revealed mostly the same seasonally significant relationships (Figs. 15-17). A Shapiro-Wilk test was performed on the log-transformed mean volume-weighted loads of N species, and the null hypothesis that these values came from a normal distribution could not be rejected (Table 18). Further, the p-values for the Shapiro-Wilk test of the log-transformed were greater than those of the non-transformed data in 10 out of 16 cases (data not shown). Log-transformed mean volume-weighted loads of TN and TON significantly increased with increasing development over the full interval (TN: $R^2 = 0.88$, TON: $R^2 = 0.87$) and in the fall (TN: R^2

= 0.88, $p < 0.05$; TON: $R^2 = 0.89$, $p < 0.05$) (Fig 15). Changes in watershed development were not significantly related to NH_4^+-N or NO_3^--N. Linear regressions comparing log-transformed mean volume-weighted loads of N showed no significant increases with percent impervious cover for any species (Fig. 16. Furthermore, a Shapiro-Wilk test was performed on the mean volume-weighted load of Cl^-, and the null hypothesis that these values came from a normal distribution could be rejected during any interval—unlike the case of non-transformed data, where a Shapiro-Wilk test indicated that normality could be rejected for the full interval and summer (Table 18). Linear regressions of this data indicated that mean volume-weighted loads of Cl^- increased with area-weighted percent impervious cover during the full interval (R^2 = 0.92, $p < 0.05$) and summer ($R^2 > 0.8$, $p < 0.05$; Fig. 17).

Composition of total nitrogen

Simple linear regression analysis did not reveal a significant relationship between composition of mean volume-weighted load of N—which is the percent of TN volume-weighted load made up by either inorganic N (NO_3^--N and NH_4^+-N) or TON—and development or impervious cover ($p > 0.05$; data not shown). However, the fraction of the mean volume-weighted load of TN composed of TON was high for all sites: TON composed > 55% of TN during baseflow periods for all intervals and > 60% of TN during stormflow periods for all intervals ($p < 0.05$; Table 19).

Discussion

Mean TN and TON volume-weighted loads increased with increasing watershed development during observed stormflow periods. Studies show that, broadly, watershed development increases N loading to watersheds, primarily by increasing human waste inputs, increasing NO_x inputs, and increasing fertilizer application to lawns (Valiela and Brown 2002). Hatt et al. (2004) specifically linked elevated volume-weighted loads of TN, during both baseflow and stormflow conditions, to the proliferation of septic systems in more developed watersheds. Further, increased impervious cover, as a result of increased development, reduces the residence time of water in a watershed (Dunne and Leopold 1978). This can cause an elevated proportion of N in runoff from a watershed to be exported rather than being retained and processed.

Land cover and land use data available for the sites in my study were insufficient to determine which if any of these sources may have been causes for increasing watershed TN or TON volume-weighted export. However, it seems unlikely that the cause was fertilizer inputs: simple linear regressions of TN and TON volume-weighted loads and percent watershed turf and grass land cover showed no significant relationships ($p>0.05$). High year-round levels of Cl^- may indicate significant contributions of waste from septic systems, but this phenomenon may instead be the result of legacy Cl^- in groundwater being mobilized year-round. Salinity in groundwater has increased dramatically in CT over the last 100 years (Cassanelli et al. 2013). Data on septic system prevalence at the sites in my study were not available by the time of its

study's completion, so its relationship to N export in my study's watersheds could not be examined.

My finding that mean TN and TON volume-weighted loads increased with increasing watershed development during observed stormflow periods on volume-weighted loads and percent watershed development contrasts with that of Brezonik et al. (2002), a study on storms in watersheds in the Twin Cities metropolitan area (MN, USA), that showed no relation between volume-weighted loads during storms of TN, NO_3^--N plus NO_2^--N, or total Kjeldahl nitrogen (TKN) and residential land use. Brezonik et al. (2002) also found that that increasing impervious cover was inversely related to TN volume-weighted loads during storms, but in my study that relationship was insignificant.

Watershed development explained more of the variation in volume-weighted loads of TN and TON during storms over the full interval, spring, and fall than over summer. The lack of correlation during the summer may be the result of the persistent drought conditions experienced by all sites during the summer months of this study. Previous studies have shown that dry antecedent conditions before storms are correlated to higher volume-weighted loads of TKN (Driver et al. 1990, Brezonik 2004), as well as higher volume-weighted loads of NO_3^--N, NO_2^--N, and TN in streams (Shields et al. 2008), but none discuss how degree of watershed development might affect these results. It may be that TN and TON build up in watersheds at similar rates during dry periods regardless of development. Shields et al. (2008) have argued that their data on

N export from developed watersheds suggest a decoupling from and increased upslope retention of N from septic sources during drought periods. It may then be that septic systems were the major contributing factor to the elevated volume-weighted loads of N in the developed watersheds of this study.

Furthermore, looking forward in time, and depending on precipitation trends such as decreasing summer rainfall in New England (Brown et al. 2011, Hayhoe et al. 2006), there may arise a trend of higher and lower development sites looking more alike in terms of storm N runoff as septic systems are decoupled from streams during droughts. My findings highlight the need for further studies on the sources of TN and TON across a gradient of development during dry period storm events.

Mean volume-weighted load of NO_3^--N increased with increasing watershed impervious cover, but not watershed development, during stormflow periods. NO_3^--N and NH_4^+-N increased with impervious cover during the full interval and spring but showed no significant change during summer or fall. Further research on flow path (i.e., subterranean flow, throughfall, precipitation, and overland flow) in the watersheds in this study needs to be done in order to better understand the mechanisms behind the relationship with impervious cover, and behind the increase—or lack thereof—with impervious cover across seasons. Of further note, my finding for stormflow period volume-weighted loads contrasts with the Brezonik (2004) finding that showed no linear

relationship between impervious cover and NO_3^--N during storm events occurring in any seasons.

Inamdar et al. (2013) found that relative contributions of water from these various flow paths in developed watersheds can vary with storm event magnitude, intensity, and antecedent watershed moisture conditions, which can in turn significantly alter the volume-weighted loads of N species in streams. Furthermore, watersheds in my study experienced drought conditions during the summer, which can lower the water table and reduce contributions of N from groundwater during storms and cause overland flow to be the dominant N contributor (Inamdar 2013). Concentrations of NO_3^--N have been found to be particularly high in the spring, owing to snowpack contributions and accumulation of NO_3^--N in soils while they are metabolically more dormant in winter (Inamdar et al. 2006). It is unlikely that the more-developed sites in my study accumulated more snowpack during winter than the less-developed ones, so they may have instead accumulated more NO_3^--N in soils during the winter months than the less-developed ones. Differences between NO_3^--N and NH_4^+-N in more- and less-developed watersheds may then be expected to become less significant as winter snow pack is reduced and snowmelt is expected to occur earlier in the northern hemisphere with climate change (Brown et al. 2011).

Organic nitrogen was the dominant form of N (56-96% of TN) for all sites during the study period, during both baseflow and stormflow conditions. This finding is consistent

with some studies that show organic N as the dominant N species in stormflow (Hedin et al. 1995, Janke et al. 2014, Schindler et al. 1980) but contrasts with others that show dominance of other species like NO_3^--N (Brett et al. 2005, Kaushal et al. 2011). Scott et al. (2007) found that TON was the dominant N species in streams nationwide, but did not find as high of a fraction of TON in the New England region. Rather, fractions of TON in my study, especially those in summer and fall, were more similar to the elevated fractions found in the Pacific Northwest than anywhere in New England. This difference in TON fractions may be the result of site selection in the Scott et al. (2007) dataset, as it drew from USGS monitoring stations, which in many parts of New England are scarcer in headwater streams than they are in higher order streams. This difference in TON fractions may also be the result of a lack of sampling in my study conducted during the winter, when lesser amounts of TON may be produced and exported. In order to produce more accurate regional estimations of the TON fractions in New England, more thorough exploration of TON sources and processing in headwater streams must be conducted.

Less developed sites tended to exhibit longer storm duration. This finding contrasts with that of one study (Barker et al. 1991), which showed that developed watersheds could exhibit longer stormflow period durations, of any given discharge magnitude, by factors of 5 to 10 over forested watersheds. This finding is however consistent with the findings of Ferguson et al. (1990), which showed that watershed development increased the rate of delivery of runoff to streams. One might expect periods of stormflow in more-

developed watersheds to be shorter than those in less-developed watersheds because a greater proportion of precipitation will enter the stream by overland flow, which is a quicker mode of conveyance than subterranean flow.

Loads (raw loads, not volume-weighted loads) of all N species and Cl^- increased with increasing stream discharge volume. Generally, the greatest loads of all chemical species occurred during spring stormflow periods, when stream discharge was already high from spring snowmelt, and the smallest loads occurred during fall stormflow periods. This seasonal bias may also be due to this study being conducted in a year that experienced summer drought. Both the positive correlation between N species storm loads and stream discharge volume, and that most N species discharge occurs in the spring are consistent with the findings of Kappel et al. (1986), which showed that 40% of their watersheds' annual TKN load was exported in the spring during a period of high snowmelt and runoff. Additionally, there may be a synergistic effect between high spring runoffs and higher concentrations of TN found in snowmelt (as opposed to those found in precipitation; Wilson 1993)—that is, the primary driver of discharge during this season is a particularly TN-rich source. My finding emphasizes the importance of further research on N export during storms for water quality management purposes, as periods of high discharge driven by storms can be major drivers of N export from watersheds across a gradient of development.

Elevated Cl^- loads in the spring may also owe to the heavy application of road salts during the winter months. As the year progressed, and successive storms flushed Cl^- from winter salt applications, there may have been less Cl^- retained by the watersheds in my study to export, regardless of discharge volume.

Conclusions

Results of this study showed elevated volume-weighted N loads from streams draining watersheds with higher percent developed land cover. I found that volume-weighted TN and TON loads were more strongly related to increased percent watershed development whereas volume-weighted NO_3^--N load was more strongly related to watershed impervious cover. I also found that greater than 60% of volume-weighted loads of TN were made up of TON, with less developed sites generally having a larger fraction of TON during the study period and observed storms. These relationships varied by season, likely caused by septic system prevalence, contributions from snowmelt, and summer drought conditions. Thus, further research on N export from watersheds experiencing different forms of urbanization (i.e., whether they employ septic systems or sewers) and under varying climatic conditions is needed.

Discharge volume was strongly correlated with total N and Cl^- loads, with the majority of N and Cl^- exported in the spring, likely due to snowmelt contribution to watershed discharge volumes. Although there was not a significant relationship between watershed development and discharge volume or watershed development and loads of N or Cl^-,

the duration of stormflow in streams was lower in more developed than in less developed watersheds. This suggests that watershed development may increase the intensity of N and Cl^- export in streams during stormflow periods. I propose that efforts to reduce N export from developed watersheds include robust strategies to remove N from stormwater.

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Table 1. Watershed characteristics.

Site	Lat/Long	Total Area (km^2)	Percent Watershed Cover Developed	Turf & Grass	Forest	Average Impervious Cover
Bris	41°55'30.97"N 73°3'35.55"W	3.50	59.08%	13.86%	26.40%	21.67%
Hop	41°51'44.10"N 72°48'31.29"W	3.37	40.29%	4.86%	54.57%	6.51%
Tain	41°46'3.34"N 72°55'23.61"W	3.03	18.56%	11.63%	65.93%	2.51%
Tunx	42° 0'57.03"N 72°55'12.79"W	3.61	4.15%	0.59%	95.25%	2.07%

Table 2. Intervals for which stream stage was collected. Order of sites from most developed to least developed: Bris, Hop, Tain Tunx.

Site	Interval Start	Interval End	Total Interval (Days)	Gap Start	Gap End	Days Missing
Bris	4/15/15 12:45	10/2/15 23:55	170.423	5/20/15 12:30	5/24/15 17:45	4.219
				6/2/15 12:15	6/12/15 15:15	10.125
				6/19/15 11:55	6/23/15 9:35	3.903
				7/1/15 7:25	7/13/15 15:05	12.319
				7/16/15 21:45	7/24/15 12:50	7.628
		Total Days Recorded	**132.229**		Total Days Missing	38.194
Hop	4/12/15 14:30	10/4/15 23:55	175.400	5/19/15 13:30	5/23/15 15:00	4.063
				6/2/15 17:00	6/15/15 16:50	13.000
				7/20/15 20:55	7/23/15 16:45	2.826
				7/26/15 12:50	**8/11/15 18:15**	**16.226**
		Total Days Recorded	**139.285**		Total Days Missing	36.115
Tain	4/12/2015 16:00	10/4/2015 23:55	175.330	5/20/15 11:30	**5/24/15 17:00**	**4.229**
		Total Days Recorded	**162.427**		Total Days Missing	12.903
Tunx	5/24/15 16:00	10/4/2015 23:55	133.326	6/12/15 18:45	6/16/15 15:45	3.875
				7/16/15 0:00	7/24/15 15:40	8.653
		Total Days Recorded	**120.798**		Total Days Missing	12.528

Table 3. Rating curves for each site. y is discharge (m^3/s), x is stream stage (is the number of discharge measurements taken to generate the rating curve equation.

Site (Location)	Rating Curve Equation	R^2	n
Bris (1)	$y = 0.2124x^{1.5428}$	0.89	6
Bris (2)	$y = 24.487x^{5.9653}$	0.60	10
Hop (1)	$y = 75.447x^{4.9323}$	0.84	11
Hop (2)	$y = 2.0551x^{2.5872}$	0.99	12
Tain (1)	$y = 0.3361x^{1.6850}$	0.91	4
Tain (2)	$y = 92.187x^{4.0582}$	0.94	12
Tunx	$y = 4 \cdot 10^{-6} e^{51.3410x}$	0.94	14

Table 4. Number of observed storms at each site for a given interval. Order o sites from most developed to least developed: Bris, Hop, Tain Tunx.

	Number of Observed Storms			
Site	Full Interval	Spring	Summer	Fall
Bris	36	5	13	15
Hop	33	9	11	16
Tain	22	8	10	4
Tunx	12	0	6	6

Table 5. Percent contribution of stormflow period discharge to study period discharge at each site, by interval. Order of sites from most developed to lea developed: Bris, Hop, Tain Tunx.

Interval	Bris	Hop	Tain	Tunx
Full	6.00%	10.07%	18.20%	39.55%
Spring	6.42%	10.88%	24.64%	
Summer	3.42%	7.29%	14.53%	41.07%
Fall	23.58%	15.33%	10.19%	11.06%

Table 6. F statistics for ANOVA tests comparing mean storm durations by interval. Included intervals and statistics indicate significant differences between the populations being compared ($p < 0.05$); missing intervals and values indicate insignificance ($p \geq 0.05$).

Interval	F Statistic
Full	3.841
Summer	4.239

Table 7. *t* values for max-*t* tests comparing mean storm durations, by interval. Included comparisons and statistics indicate significantly different means between compared sites ($p < 0.05$); missing comparisons and statistics indicate insignificance ($p \geq 0.05$). Order of sites from most developed to least developed: Bris, Hop, Tain Tunx.

Interval	Comparison	Duration
Full	Tain-Bris	3.136
Summer	Tain-Bris	2.741

Table 8. F statistics for ANOVA tests comparing mean storm durations for high- and low-development designations (>40% developed land cover and < 19% developed land cover, respectively). Included intervals and statistics indicate significant differences between the populations being compared ($p < 0.05$); missing intervals and statistics indicate insignificance ($p \geq 0.05$).

Interval	F Statistic
Full	8.906
Summer	8.067

Table 9. *t* values for max-*t* tests comparing mean mean storm durations for high- and low-development designations (> 40% developed land cover and < 19% developed land cover, respectively), by interval. Included comparisons and statistics indicate significantly different means ($p < 0.05$); missing comparisons and statistics indicate insignificance ($p \geq 0.05$).

Interval	Comparison	Duration
Full	Low-High	2.984
Summer	Low-High	2.840

Table 10. Sum of loads (kg) of N and Cl^- exported from sites during the whole study period (both baseflow and stormflow periods), by site and interval. Order of sites from most developed to least developed: Bris, Hop, Tain Tunx.

Site	Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Bris	Full	6.030	2.395	23.94	32.36	9269
Hop	Full	53.74	6.362	132.1	192.2	18760
Tain	Full	2.952	0.9108	14.24	18.10	744.6
Tunx	Full	0.7030	2.446	49.16	52.27	1951
Bris	Spring	5.265	1.401	17.56	24.22	7016
Hop	Spring	46.83	5.466	81.14	133.4	15910
Tain	Spring	1.479	0.3369	4.409	6.225	374.8
Tunx	Spring	0.0024	0.0031	0.1601	0.1655	30.63
Bris	Summer	0.6629	0.9422	5.862	7.467	2132
Hop	Summer	6.771	0.7964	48.35	55.91	2613
Tain	Summer	1.316	0.4760	8.743	10.54	3150
Tunx	Summer	0.6791	2.426	48.55	51.62	1841
Bris	Fall	0.1016	0.0514	0.5152	0.6681	115.1
Hop	Fall	0.1322	0.0989	2.571	2.802	236.3
Tain	Fall	0.1569	0.0979	1.080	1.335	54.60
Tunx	Fall	0.0215	0.0175	0.4495	0.4885	79.06

Table 11. Sum of loads of (kg/ha) of N and Cl^- exported from sites during all observed stormflow periods during a given interval, by site. Order of sites from most developed to least developed: Bris, Hop, Tain Tunx. Missing values for Tunx during the spring are due to a lack of observed storms.

Site	Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Bris	Full	0.000592	0.004068	0.005959	1.28828	5.510757
Hop	Full	0.000903	0.034358	0.038342	1.881694	53.57434
Tain	Full	0.000556	0.008191	0.009842	0.435878	15.3937
Tunx	Full	0.001438	0.032087	0.033847	1.163931	88.05476
Bris	Spring	0.000481	0.002576	0.004191	1.064622	3.7111
Hop	Spring	0.000655	0.022853	0.026001	1.210597	37.23598
Tain	Spring	0.000275	0.003993	0.004824	0.260912	9.07724
Tunx	Spring					
Bris	Summer	5.50E-05	0.00098	0.001126	0.139256	1.053537
Hop	Summer	0.000159	0.008334	0.008964	0.382938	11.57115
Tain	Summer	0.000168	0.003477	0.00408	0.129773	4.861566
Tunx	Summer	0.001432	0.031609	0.033353	1.144439	87.00205
Bris	Fall	5.55E-05	0.000513	0.000642	0.084402	0.746119
Hop	Fall	8.81E-05	0.003172	0.003378	0.288159	4.767206
Tain	Fall	0.000113	0.000721	0.000938	0.045193	1.454894
Tunx	Fall	6.30E-06	0.000478	0.000494	0.019492	1.052709

Table 12. Shapiro-Wilk W statistics for mean flow-weighted loads of N and Cl^- during baseflow conditions. Included W statistics indicate acceptance of the null hypothesis that data are normally distributed ($p \geq 0.05$); missing W statistics indicate rejection of the null hypothesis that data are normally distributed ($p < 0.05$).

Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	0.9960	0.8281	0.8207	0.9245	0.8391
Spring	0.9950	0.9882	0.9704	0.7981	0.9735
Summer	0.8991	0.9105	0.8707	0.9249	
Fall	0.9334	0.9785	0.8533	0.9585	0.8352

Table 13. F statistics for ANOVA tests comparing comparing mean volume-weighted loads during stormflow periods. Included intervals and statistics indicate significantly different means between compared sites (p < 0.05); missing intervals and statistics indicate insignificance (p ≥ 0.05).

Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	65.41	8.007	13.70	21.16	25.70
Spring		9.575		3.750	
Summer	27.41	10.85	9.950	16.39	16.18
Fall	33.09	14.34	9.377	8.781	28.45

Table 14. t values for max-*t* tests comparing mean volume-weighted loads during stormflow periods. Included t values indicate significantly different means between compared sites (p < 0.05); missing values indicate insignificance (p ≥ 0.05). Order of sites from most developed to least developed: Bris, Hop, Tain Tunx.

Interval	Comparison	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	Hop-Bris	-4.358	-4.333			-6.214
Full	Tain-Bris	-3.475				-7.597
Full	Tunx-Bris	-7.563	-4.690	-4.636	-6.239	-7.035
Full	Tain-Hop					-4.483
Full	Tunx-Hop	-8.289		-5.918	-6.891	
Full	Tunx-Tain	-8.884		-3.899	-5.366	
Spring	Hop-Bris		-4.368			
Spring	Tain-Bris		-4.034			
Spring	Tain-Hop					
Summer	Hop-Bris		-5.267			-6.241
Summer	Tain-Bris		-3.810			-6.749
Summer	Tunx-Bris	-5.625	-3.581	-3.632	-5.015	-6.493
Summer	Tain-Hop					
Summer	Tunx-Hop	-4.704		-4.736	-5.437	
Summer	Tunx-Tain	-5.422		-4.886	-6.106	
Fall	Hop-Bris	-3.527				-4.673
Fall	Tain-Bris			-2.821	-2.736	-8.108
Fall	Tunx-Bris	-7.466	-2.833	-3.063	-3.695	-5.991
Fall	Tain-Hop		2.674	-4.208	-2.962	-5.131
Fall	Tunx-Hop	-5.088	-4.008	-3.615	-4.260	
Fall	Tunx-Tain	-4.819	-5.106			

Table 15. F statistics for ANOVA tests comparing mean volume-weighted loads during stormflow periods for high- and low-development designations (>40% developed land cover and < 19% developed land cover, respectively). Included intervals and statistics indicate significant differences between the populations being compared ($p < 0.05$); missing intervals and statistics indicate insignificance ($p \geq 0.05$).

Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	14.39	5.709	18.11	23.39	43.18
Spring			5.205	6.238	
Summer		4.638			20.21
Fall	9.857		18.06	18.56	34.54

Table 16. t values for max-*t* tests comparing mean volume-weighted loads during stormflow periods for high- and low-development designations (>40% developed land cover and < 19% developed land cover, respectively). Included comparisons and values indicate significant differences between the populations being compared ($p < 0.05$); missing intervals and statistics indicate insignificance ($p \geq 0.05$).

Interval	Comparison	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	Low-High	-3.794	-2.389	-4.256	-4.836	-6.571
Spring	Low-High			-2.281	-2.498	
Summer	Low-High		-2.153			-4.495
Fall	Low-High	-3.140		-4.250	-4.308	-5.877

Table 17. Shapiro-Wilks W statistics for mean flow-weighted loads of N and Cl^- during stormflow conditions. Included W statistics indicate acceptance of the null hypothesis that data are normally distributed ($p \geq 0.05$); missing W statistics indicate rejection of the null hypothesis that data are normally distributed ($p < 0.05$).

Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	0.869	0.775	0.982	0.972	
Spring	0.767	0.834	0.957	0.939	
Summer	0.882	0.904	0.920	0.953	0.769
Fall	0.935	0.824	0.852	0.993	0.920

Table 18. Shapiro-Wilk W statistics for log-transformed flow-weighted loads of N and Cl^- during stormflow conditions. Included W statistics indicate acceptance of the null hypothesis that data are normally distributed ($p \geq 0.05$); missing W statistics indicate rejection of the null hypothesis that data are normally distributed ($p < 0.05$).

Interval	NO_3^--N	NH_4^+-N	TON	TN	Cl^-
Full	0.903	0.862	0.949	0.979	0.904
Spring	0.791	0.935	0.934	0.975	0.790
Summer	0.792	0.918	0.861	0.886	0.939
Fall	0.936	0.873	0.857	0.974	0.985

Table 19. Percent contribution of TON volume-weighted loads to TN volume-weighted loads, during baseflow and stormflow periods.

Interval	Site	Baseflow	Storm Flow
Full	Bris	74.4%	68.3%
Full	Hop	67.2%	89.6%
Full	Tain	77.8%	83.2%
Full	Tunx	93.7%	94.8%
Spring	Bris	73.2%	61.5%
Spring	Hop	58.9%	87.9%
Spring	Tain	67.2%	82.8%
Spring	Tunx	96.7%	
Summer	Bris	78.0%	87.0%
Summer	Hop	86.1%	93.0%
Summer	Tain	82.7%	85.2%
Summer	Tunx	93.8%	94.8%
Fall	Bris	76.9%	79.9%
Fall	Hop	90.3%	93.9%
Fall	Tain	82.0%	76.9%
Fall	Tunx	78.1%	96.7%

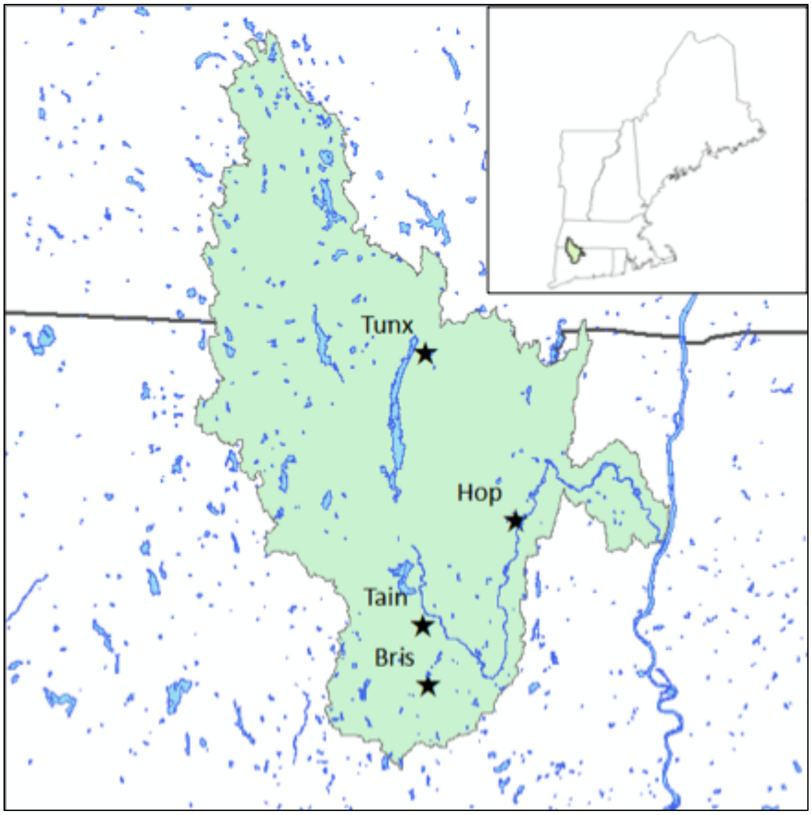

Figure 1. Sampling locations (stars) within the Farmington River Watershed (green) and the New England region (inset). Watersheds at sampling locations are too small to appear noticeably in this map.

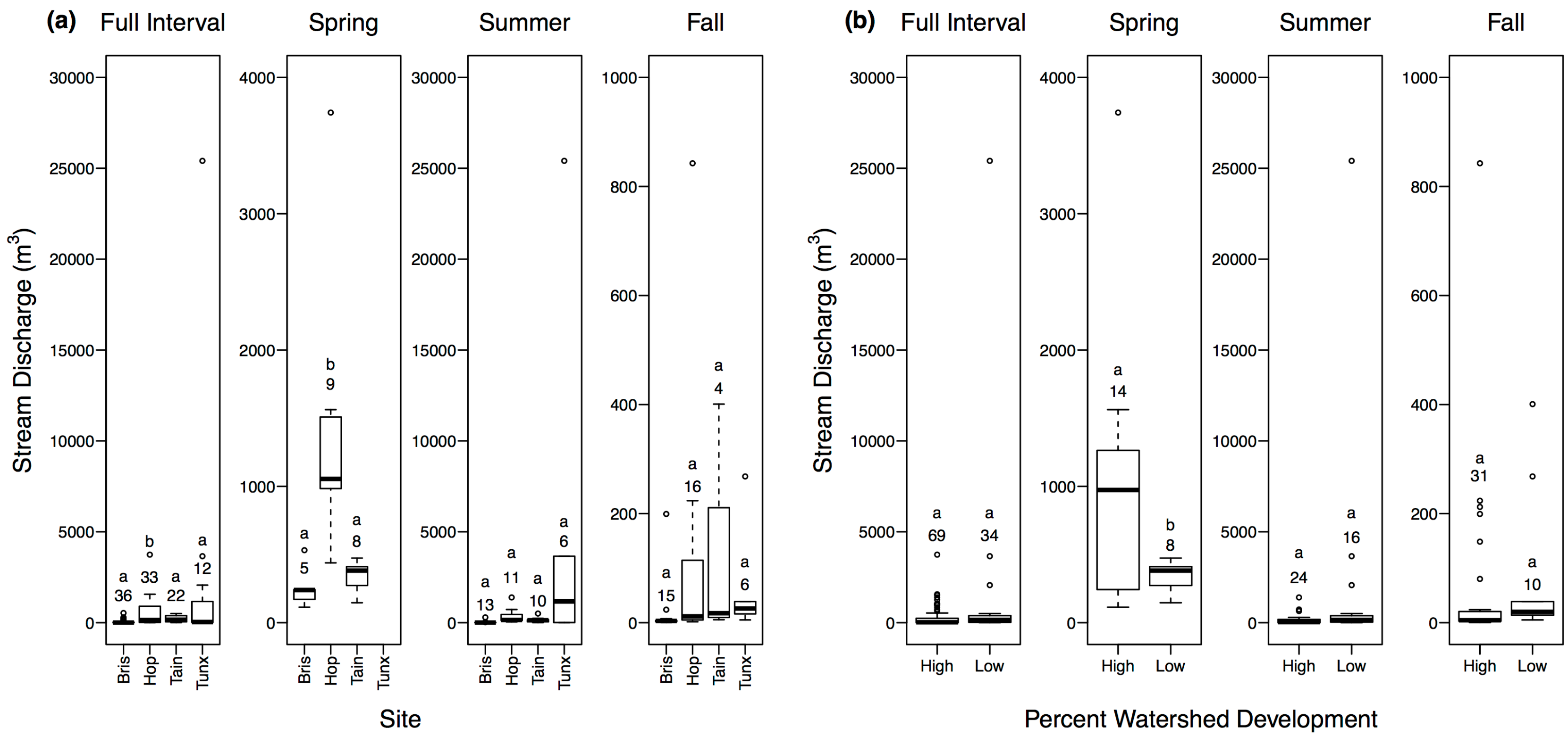

Figure 2. Boxplots of stormflow period discharge volume by site, where the numbers above boxes indicate number of observed storms for that site during that interval. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

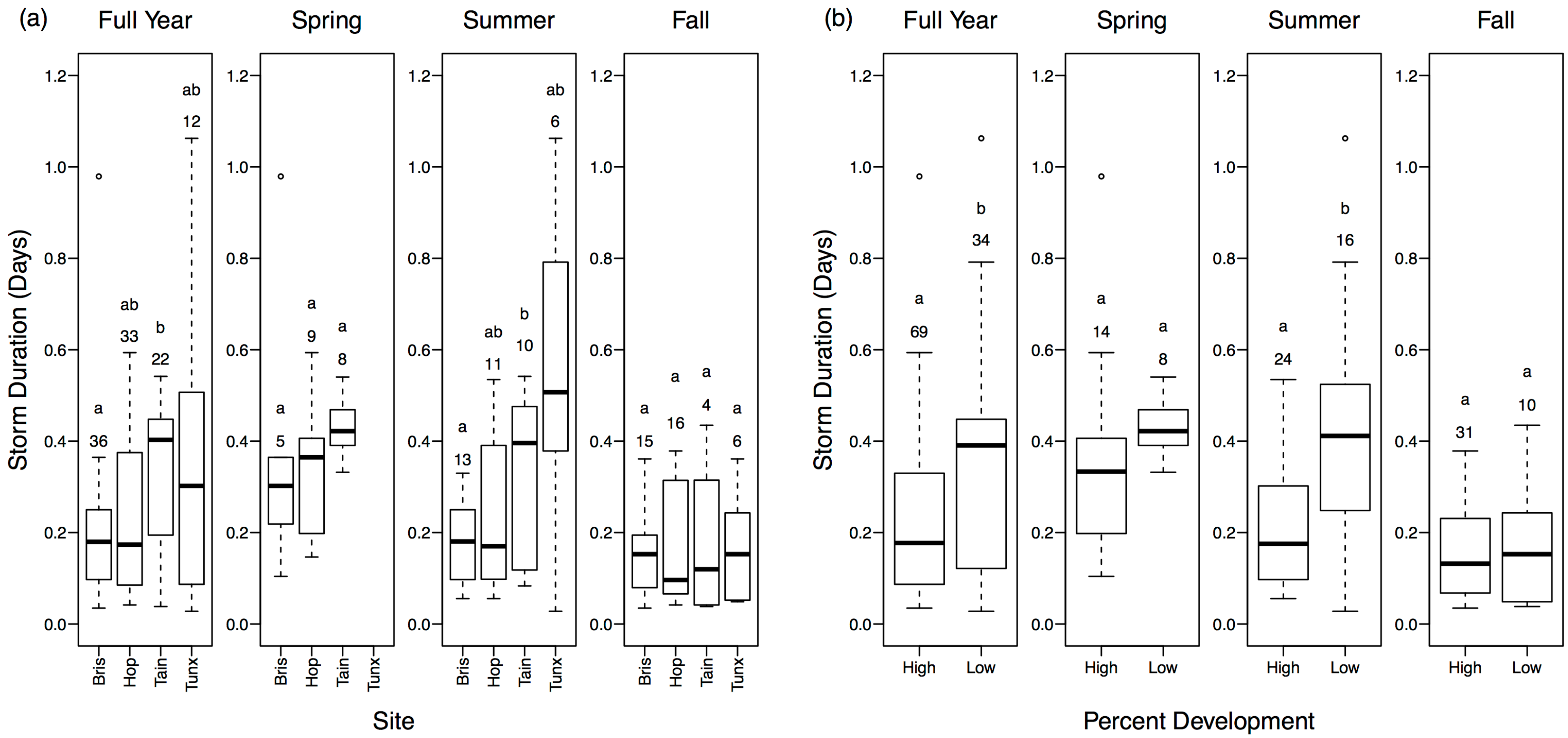

Figure 3. Boxplots of stormflow period durations by (a) site and (b) low and high percent watershed development, where the numbers above boxes indicate number of observed storms for that site during that interval.. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

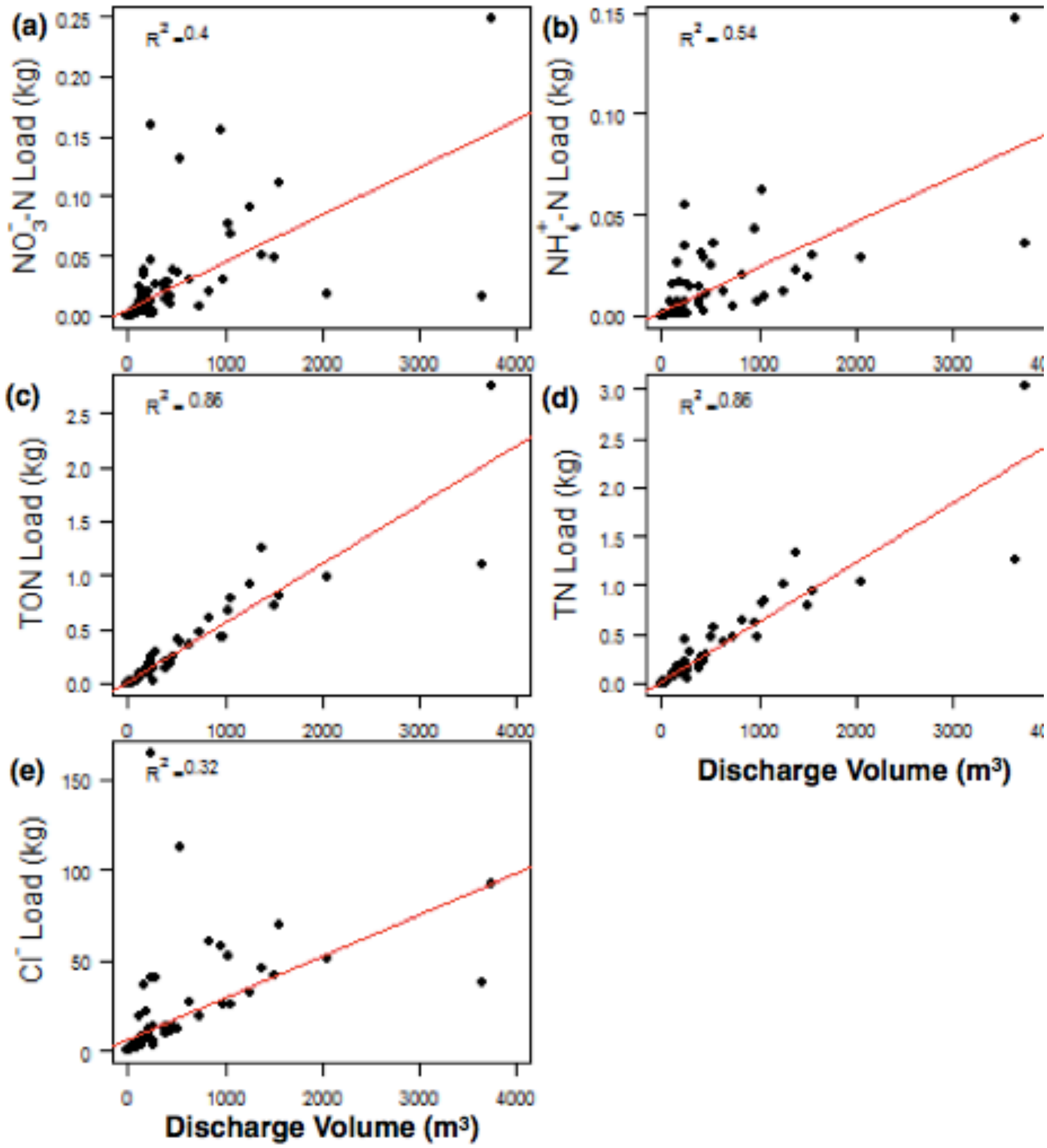

Figure 4. (a) NO_3^--N, (b) NH_4^+-N, (c) TON, (d) TN, (e) Cl^- loads versus discharge volume during stormflow periods (does not include outlier storm from Tunx in the summer, see Fig 3). Simple linear regressions (red lines) were all signific (p < 0.05).

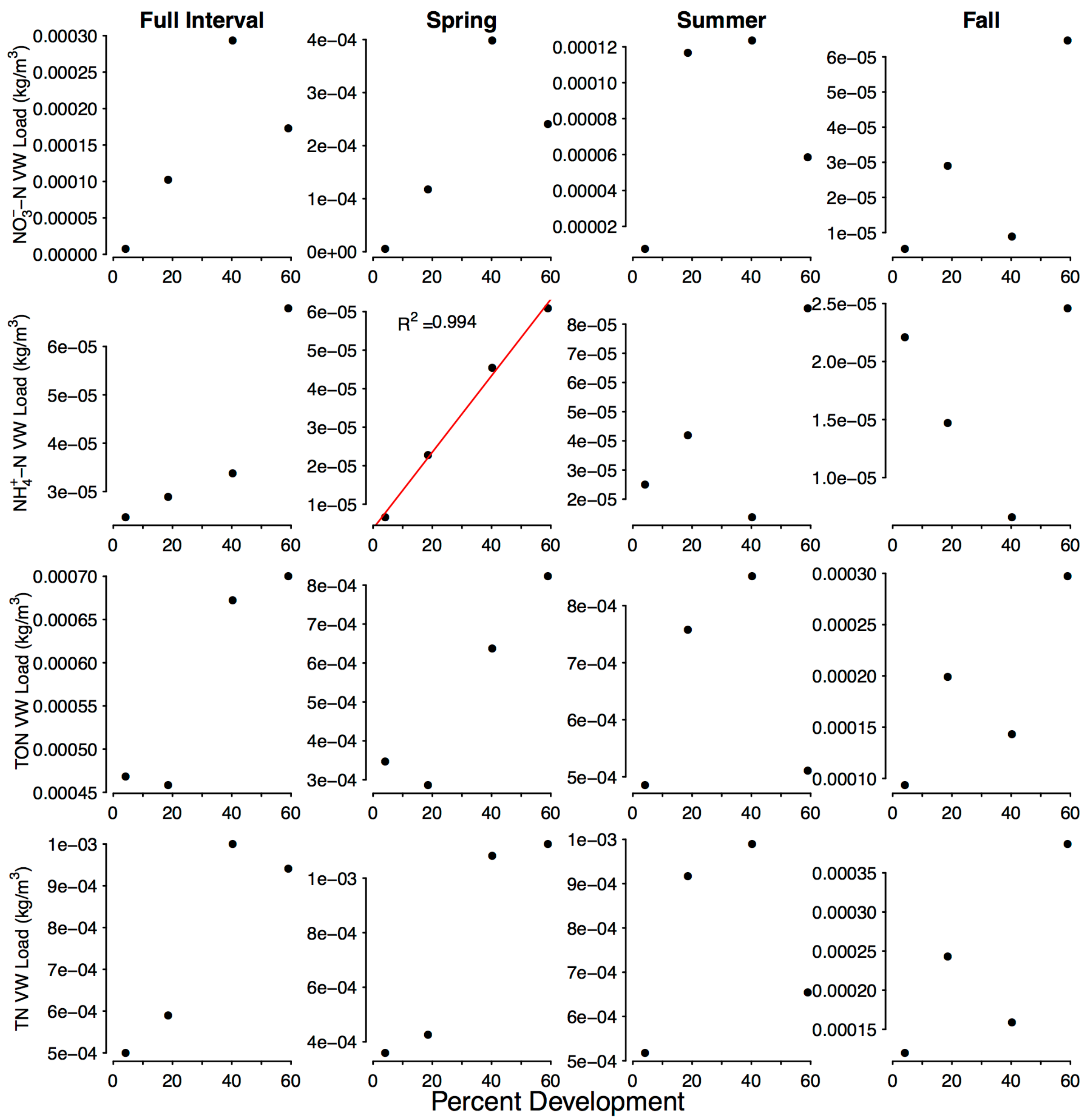

Figure 5. Simple linear regressions of mean volume-weighted N load during baseflow periods versus percent watershed development, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significance.

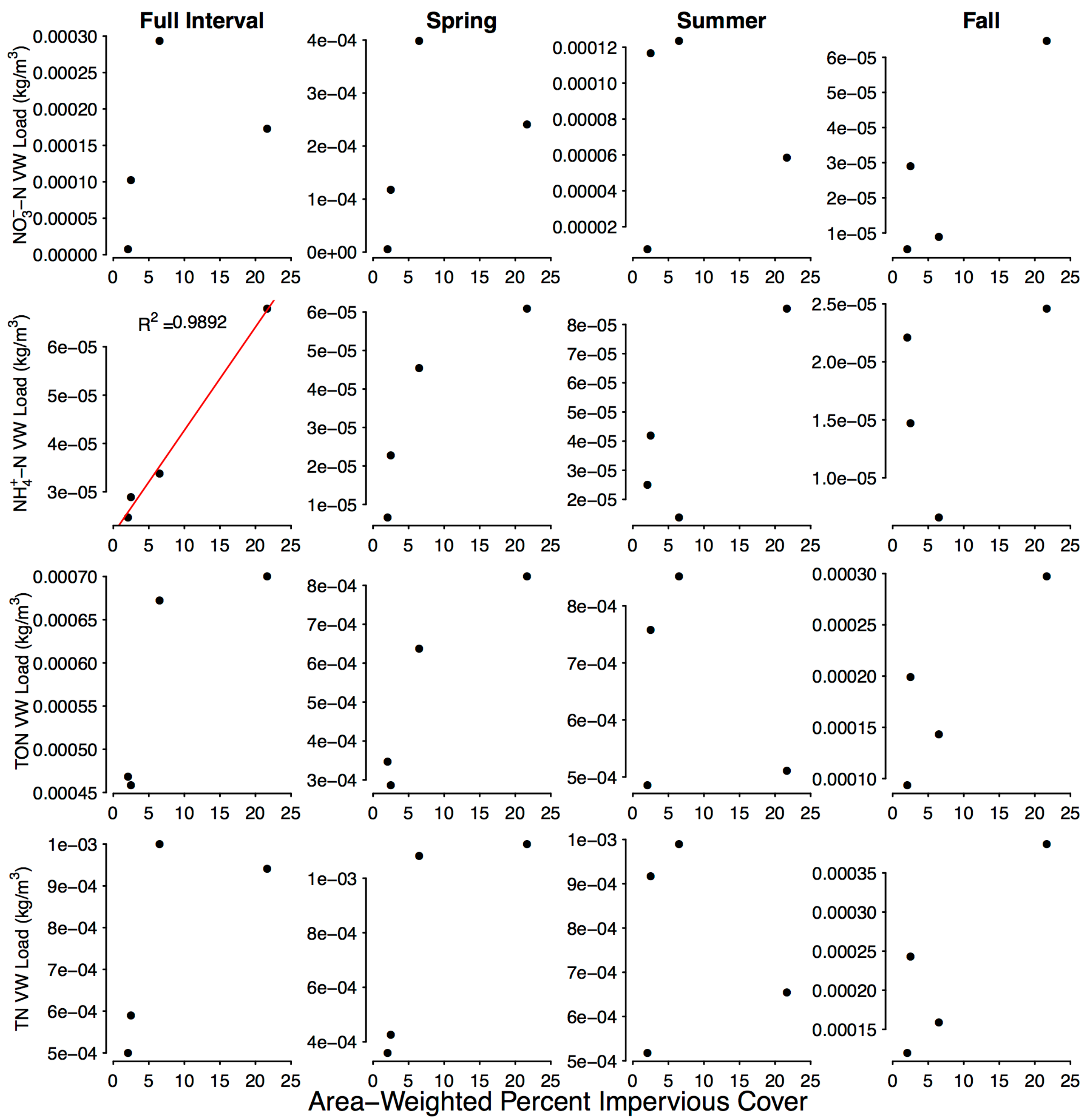

Figure 6. Simple linear regressions of mean volume-weighted load during baseflow periods versus area-weighted percent impervious cover of watershed, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant results from simple linear regressions.

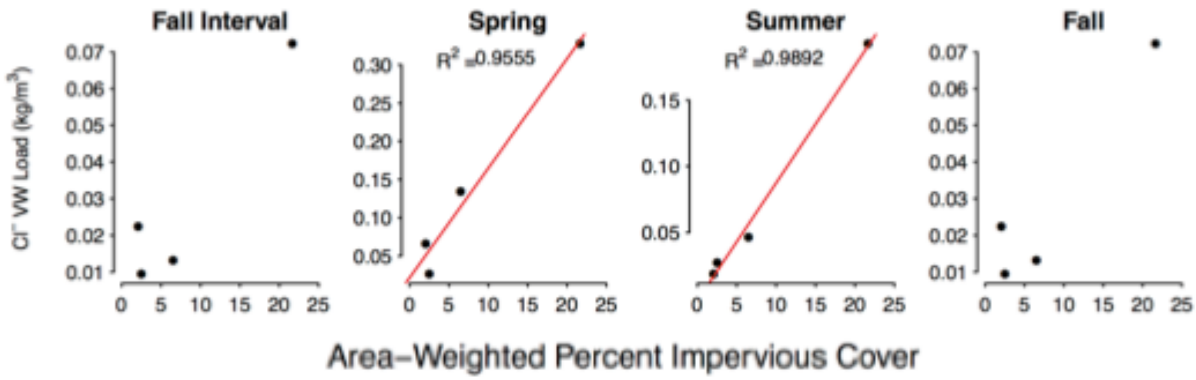

Figure 7. Simple linear regressions of mean volume-weighted Cl^- load during baseflow periods versus area-weighted percent impervious cover of watershed, by interval. R^2 is adjusted R^2. Red lines and R^2 values indicate significant results from simple linear regressions.

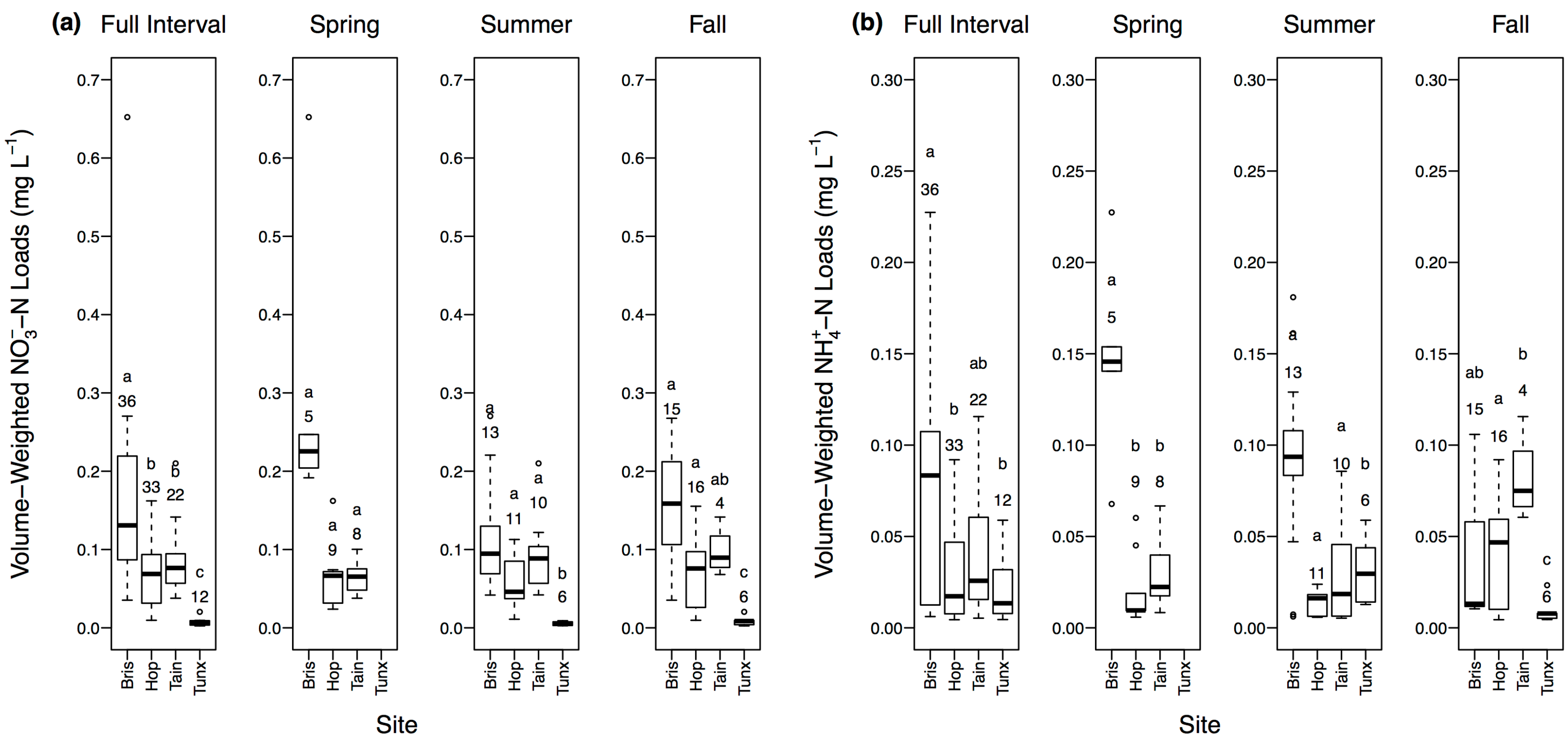

Figure 8. Boxplots of volume-weighted stormflow period loads by interval and sites for (a) NO_3^-N and (b) NH_4^+-N, where the numbers above boxes indicate number of observed storms for that site during that interval. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. No storms were collected at Tunx during spring. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

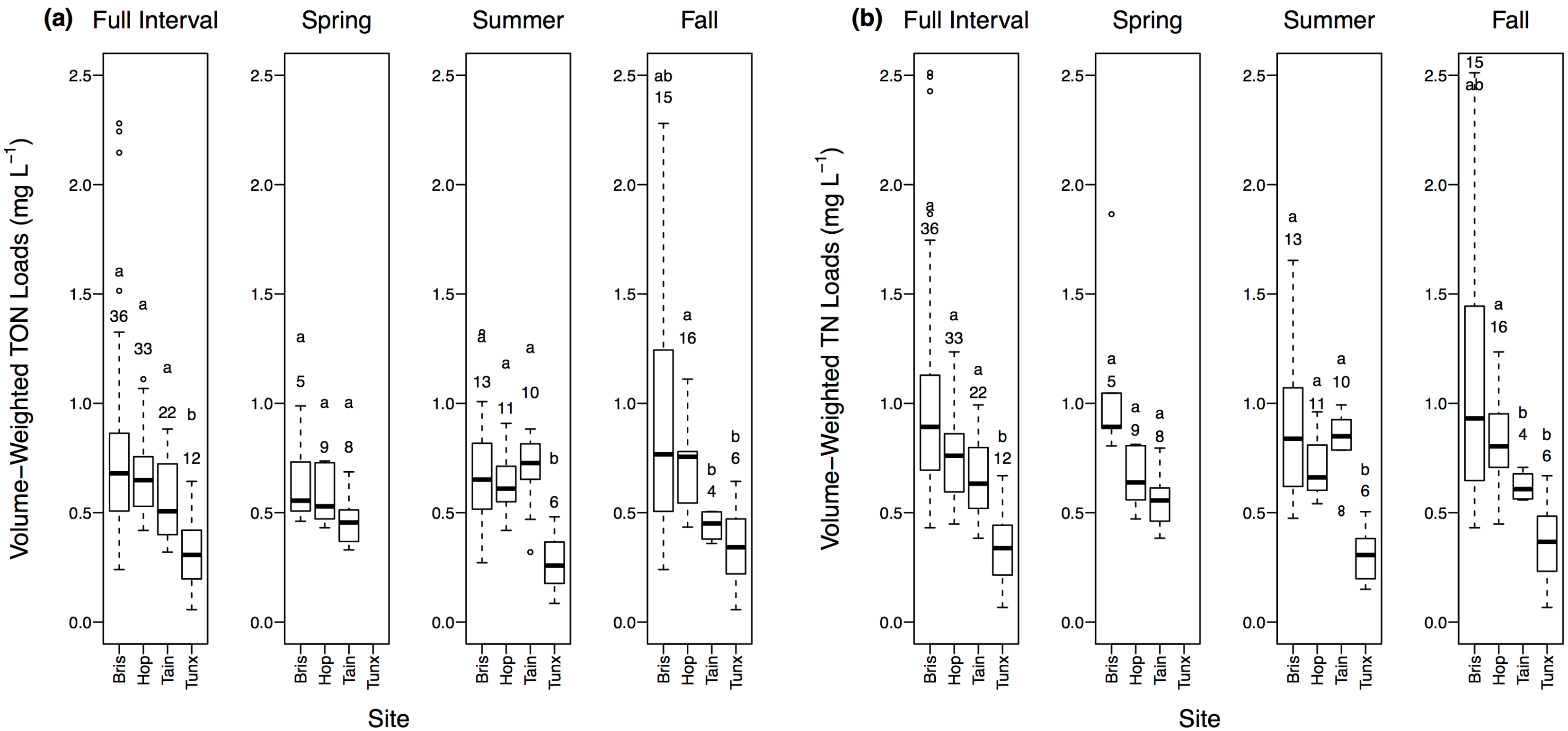

Figure 9. Boxplots of volume-weighted stormflow period loads by interval and sites for (a) TON and (b) TN, where the numbers above boxes indicate number of observed storms for that site during that interval. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. No storms were collected at Tunx during spring. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

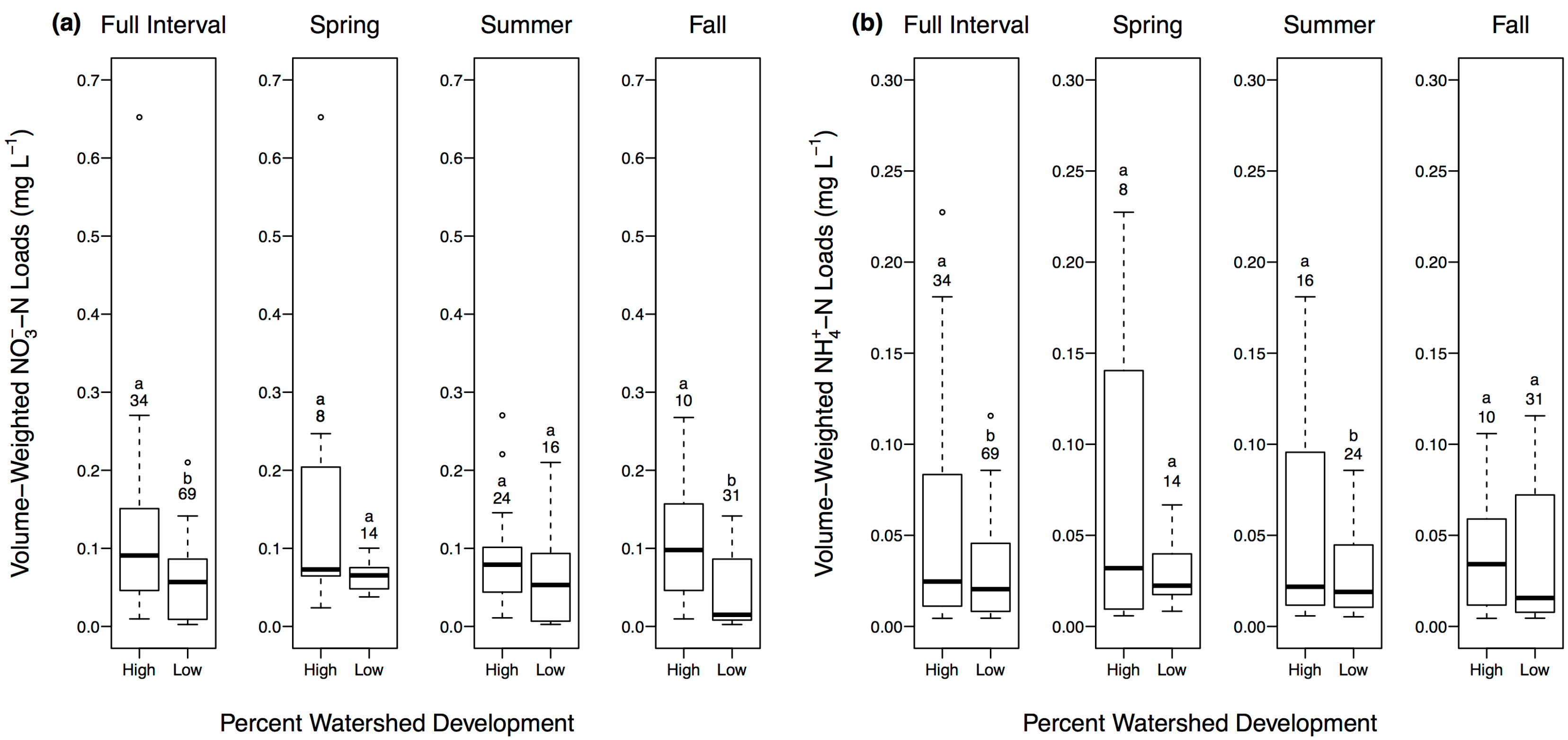

Figure 10. Boxplots of volume-weighted stormflow period loads by interval and percent development for (a) NO_3^-N and (b) NH_4^+-N, where the numbers above boxes indicate number of observed storms for that site during that interval. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

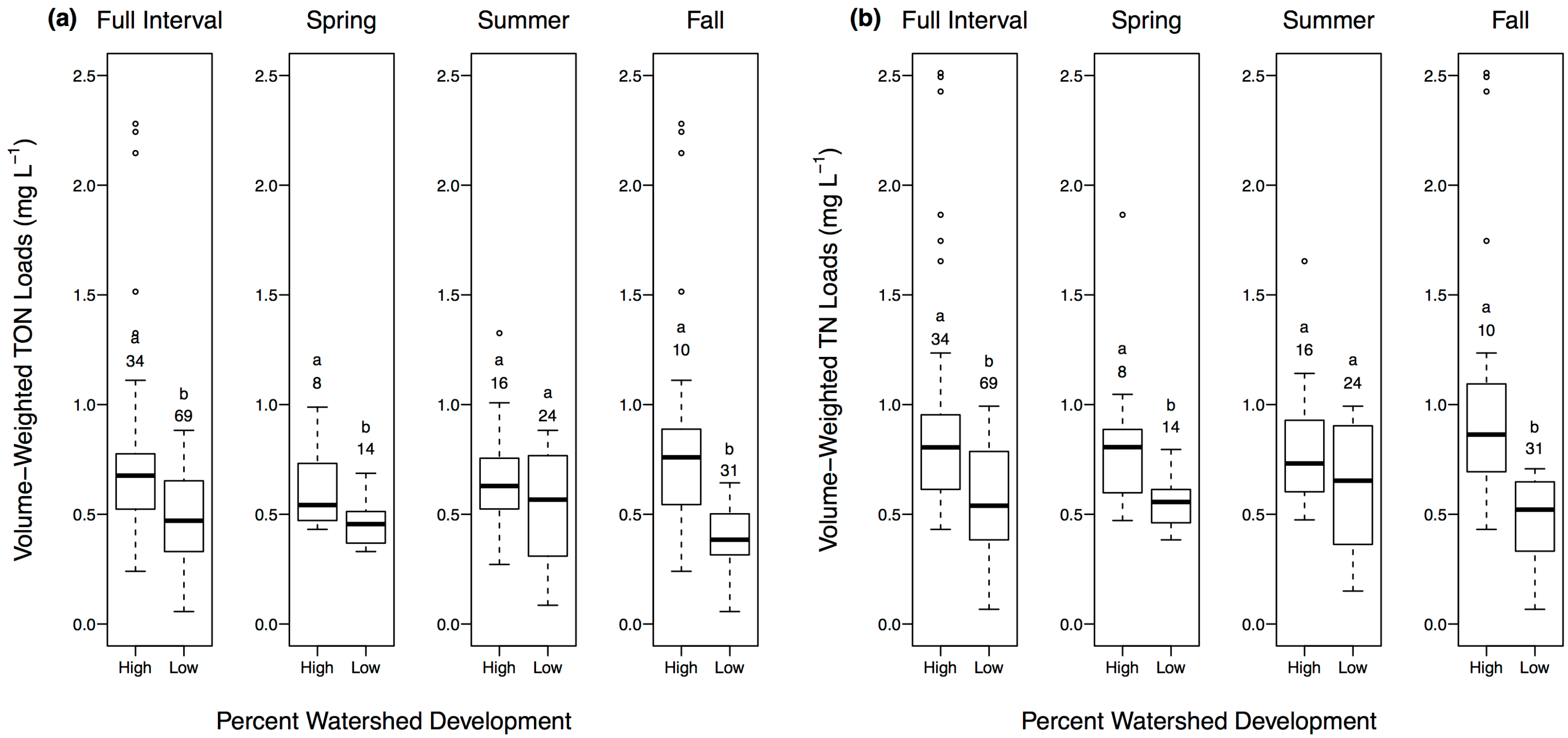

Figure 11. Boxplots of volume-weighted storm loads by interval and percent development for (a) TON and (b) TN, where the numbers above boxes indicate number of observed storms for that site during that interval. Boxes show median and interquartile range. Outliers (open circles) are identified as points outside 1.5 times the interquartile range. Letters above number of storms indicate significance ($p < 0.05$) during the interval of interest (e.g., full, spring, summer or fall) by max t-test post hoc comparisons.

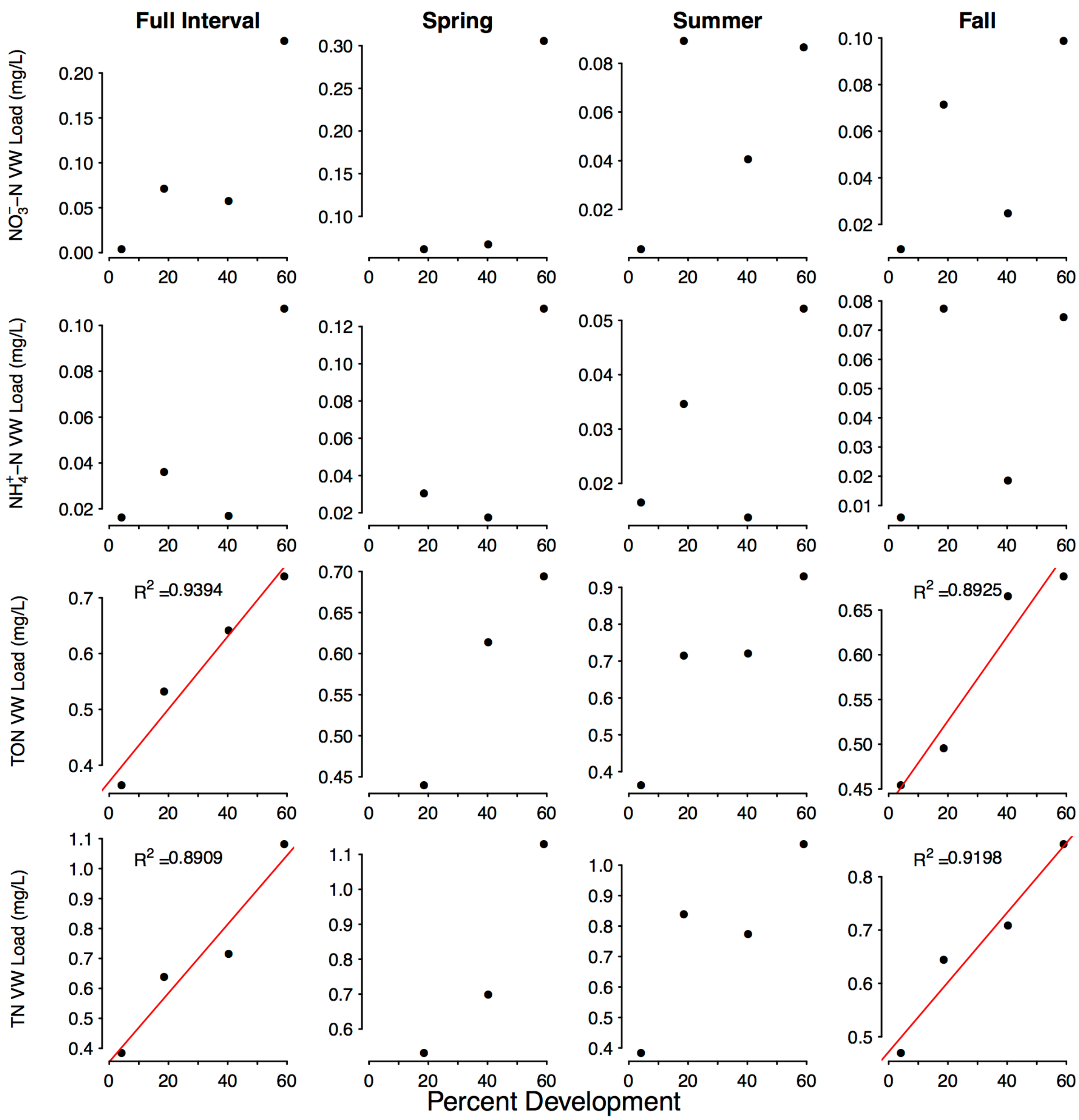

Figure 12. Simple linear regressions of volume-weighted load during stormflow periods versus percent watershed development, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.

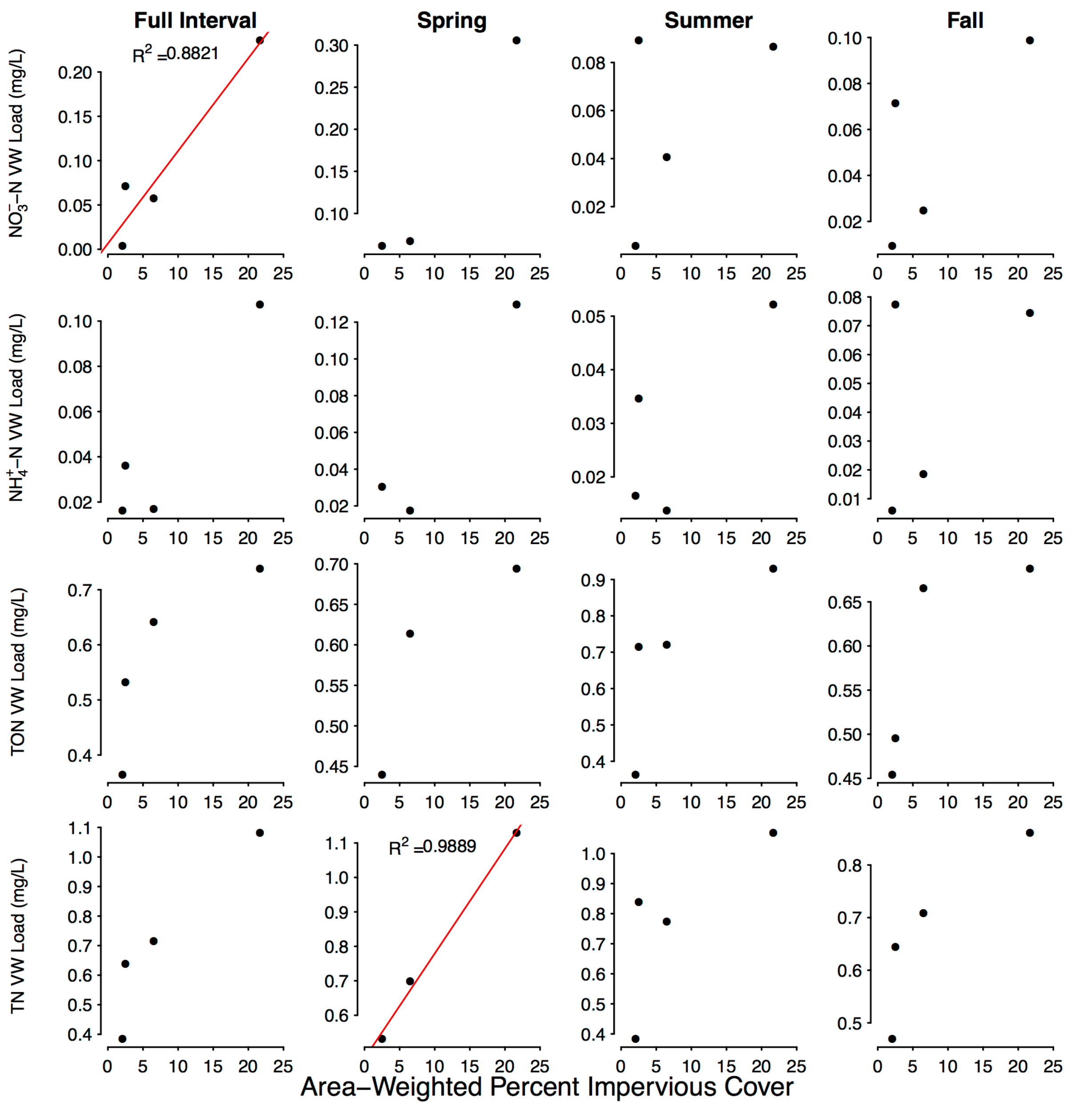

Figure 13. Simple linear regressions of volume-weighted load during stormflow periods versus area-weighted percent impervious cover of watershed, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.

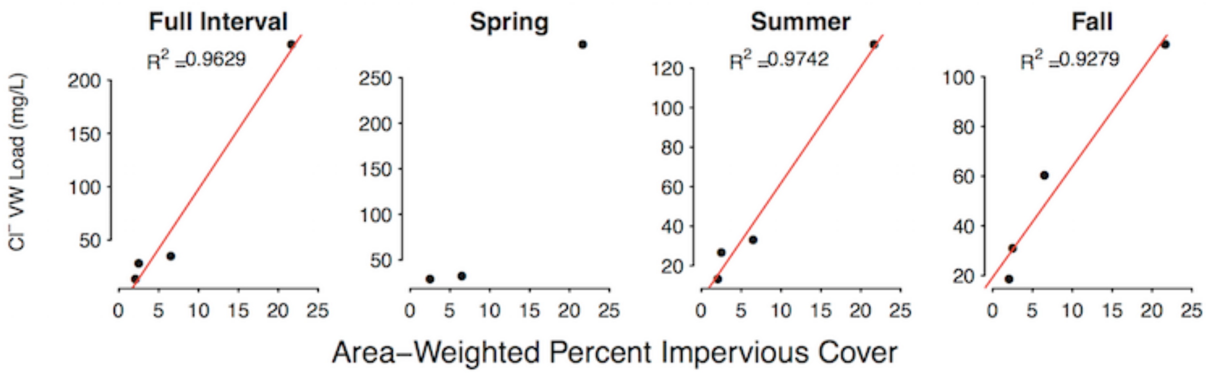

Figure 14. Simple linear regressions of volume-weighted Cl^- load during stormflow periods versus area-weighted percent impervious cover of watershed, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.

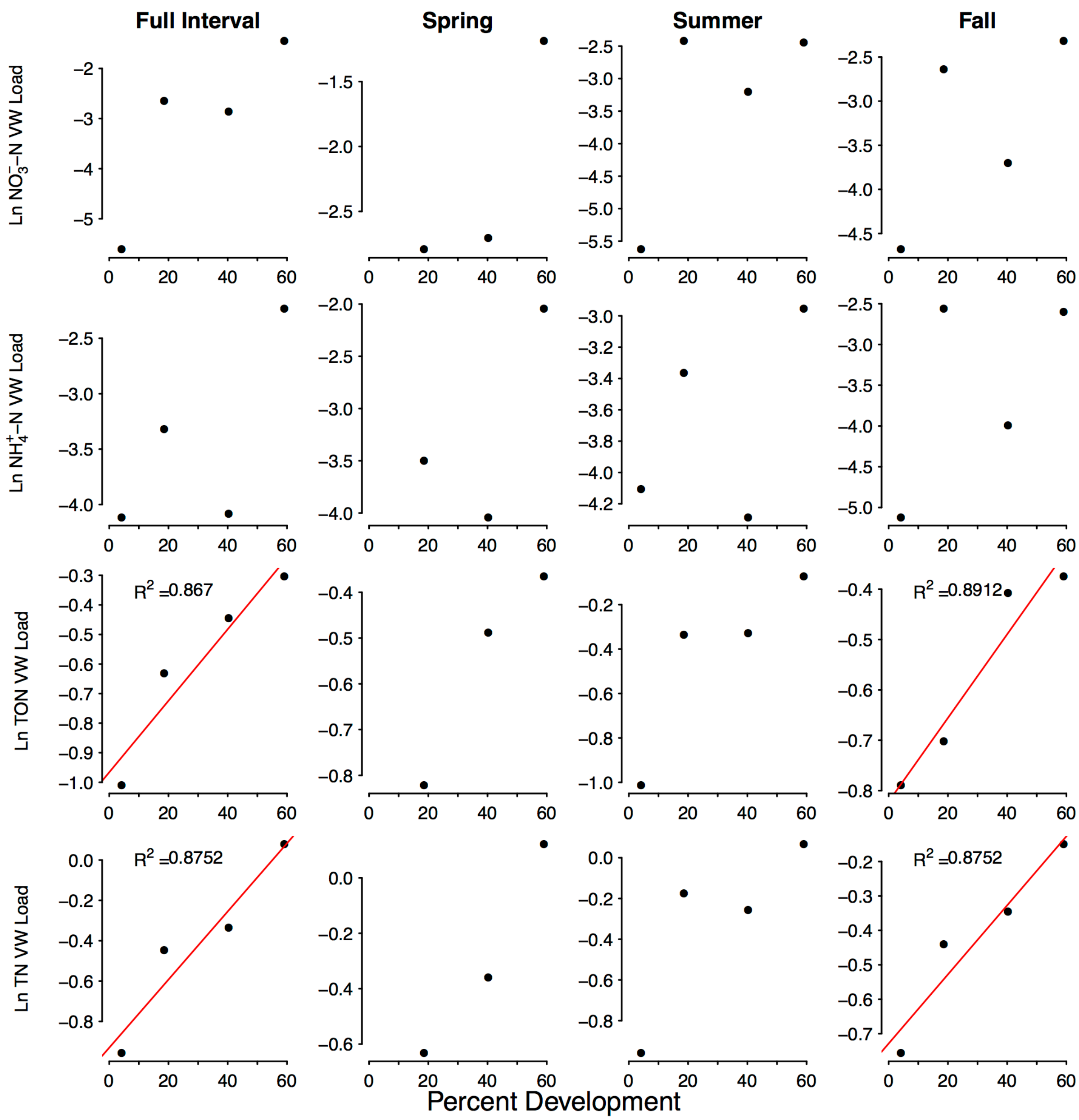

Figure 15. Simple linear regressions of log-transformed volume-weighted load during stormflow periods versus percent watershed development, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.

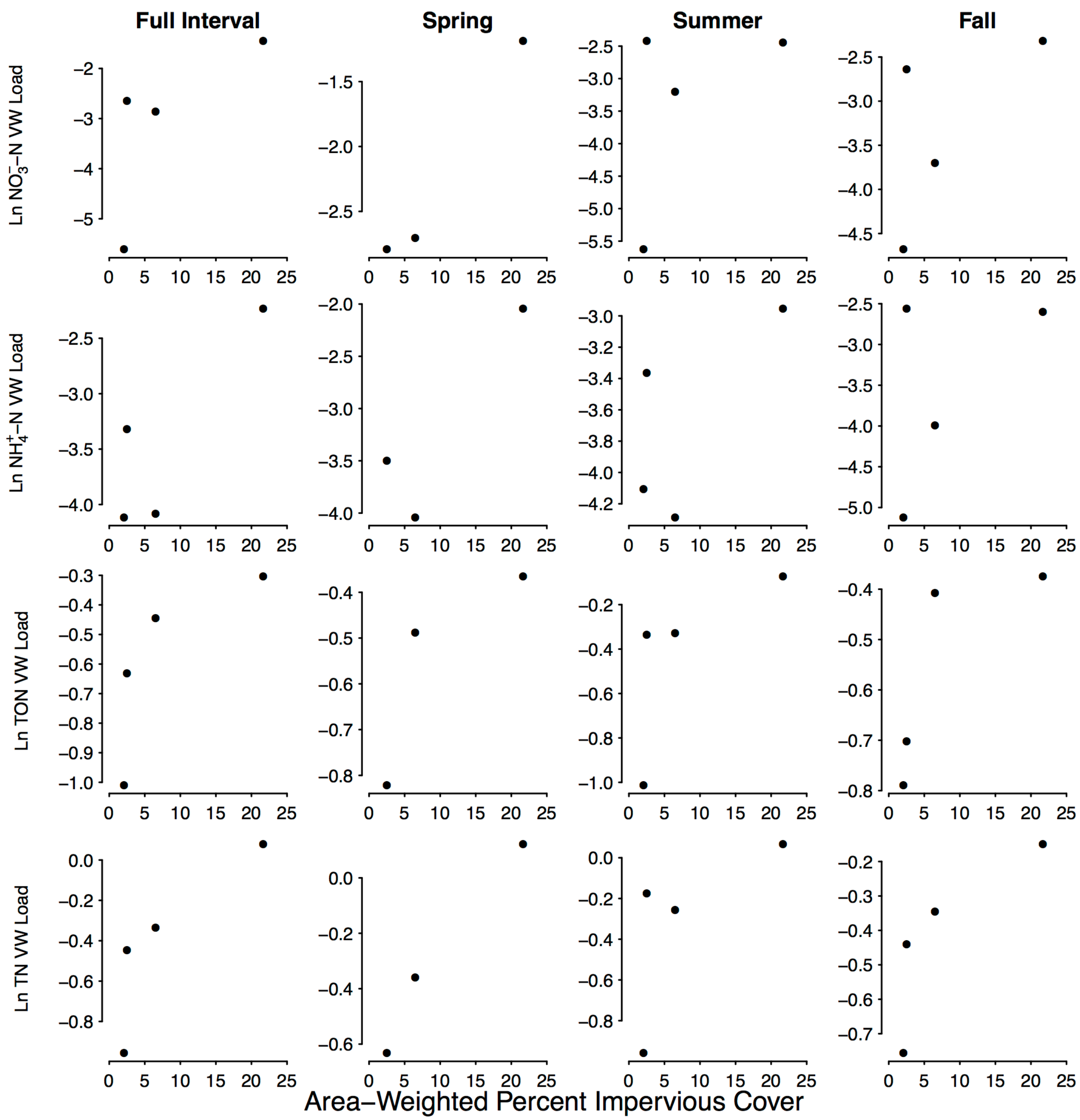

Figure 16. Simple linear regressions of log-transformed volume-weighted load during stormflow periods versus area-weighted percent impervious cover of watershed, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.

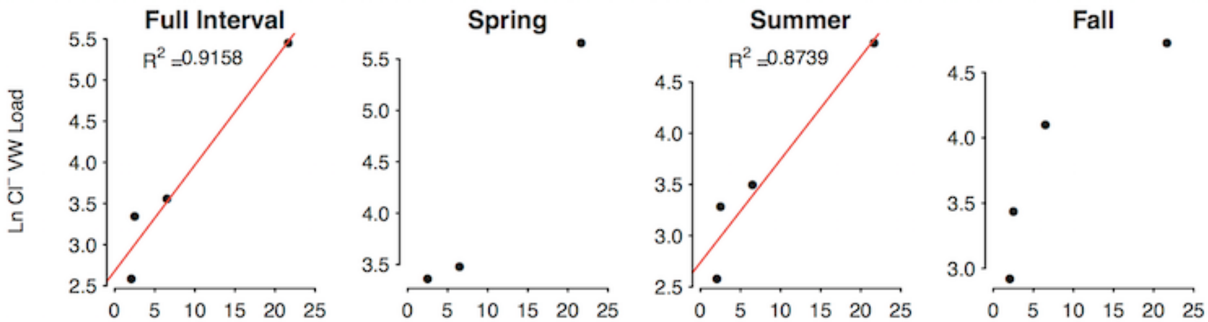

Figure 17. Simple linear regressions of log-transformed volume-weighted Cl^- load during stormflow periods versus area-weighted percent impervious cover of watershed, by interval and N species. R^2 is adjusted R^2. Red lines and R^2 values indicate significant simple linear regressions.