Ecological Engineering 91 (2016) 506–514

Contents lists available at ScienceDirect

Ecological Engineering

journal homepage: www.elsevier.com/locate/ecoleng

# Environmental drivers of seasonal variation in green roof runoff water quality

Ishi Buffam[a,b,*], Mark E. Mitchell[a], Richard D. Durtsche[c]

[a] Department of Biological Sciences, University of Cincinnati, 318 Clifton Ct., Cincinnati, OH 45221, United States
[b] Department of Geography, University of Cincinnati, Cincinnati, OH 45221, United States
[c] Department of Biological Sciences, Northern Kentucky University, 148 Science Center, Nunn Dr., Highland Heights, KY 41099, United States

ARTICLE INFO

*Article history:*
Received 8 August 2015
Received in revised form 6 February 2016
Accepted 27 February 2016

*Keywords:*
Vegetated roof
Stormwater runoff
Nutrient concentrations
Green infrastructure
Nitrate

ABSTRACT

Green (vegetated) roofs provide many beneficial environmental services but can also pose a disservice by leaching nutrients and metals, via storm water runoff, to downstream aquatic ecosystems. Current estimates of water quality impacts rely on limited samples (snapshots in time) and may not accurately reflect the true influence of green roof ecosystems, which likely vary temporally as do natural ecosystems. Using a 46 $m^2$ green roof in Cincinnati, OH, we analyzed runoff from >80 events over two years for pH, conductivity, and concentrations of dissolved nutrients, base cations, and metals. We related the variation in water chemistry to environmental variables including air temperature, storm event magnitude, and estimated antecedent moisture. We observed strong seasonal patterns in bioactive elements, with carbon, nitrogen, phosphorus, and base cation concentrations highest in the summer, and positively correlated with temperature. This suggests temperature-mediated processes such as microbial mineralization of organic matter, desorption or weathering, rather than plant uptake or hydrologic variation among storms, are the major controlling mechanisms for runoff water quality in this newly constructed green roof. The large temporal variation in green roof effluent water quality supports the need for long-term studies to characterize the complexity of these engineered ecosystems and their responsiveness to environmental variation.



## 1. Introduction

Green roofs (roofs with vegetation and soil-like substrate overlain on a waterproof membrane) now comprise more than 20% of the flat roof area in cities like Stuttgart, Germany, and are expected to continue to proliferate in the near future with stated goals of 20% coverage of large buildings in Washington, D.C. by the year 2025 and 50–70% coverage of city owned buildings in Toronto and Portland (Carter and Laurie, 2008; Deutsch et al., 2005). The increasing implementation of green roofs can be explained in large part by the ecosystem services they provide. Green roofs provide reduced heating and cooling costs, improved air quality (Clark et al., 2008), noise reduction (Van Renterghem and Botteldooren, 2009) and wildlife habitat (Brenneisen, 2006). They also reduce stormwater runoff, often by 50% or more relative to impervious surfaces (Mentens et al., 2006), a crucial service for many cities dealing with combined sewer overflow problems.

However, despite their ability to reduce runoff water amount, green roofs may degrade local water quality by leaching out nutrients and metals during storm events. Previous studies have identified green roofs as sources of phosphorus (P), organic carbon (C), nitrogen (N) copper, and iron (Berndtsson et al., 2006; Buffam and Mitchell, 2015; Monterusso et al., 2004). The dynamics of phosphorus in runoff are of particular concern, since excess phosphorus in receiving water bodies can result in eutrophication (Carpenter et al., 1998). At this point, little is known about the temporal dynamics of this leaching from full-scale green roofs, since most studies of green roof water quality have involved snapshots in time with only a few samples (reviewed in Buffam and Mitchell, 2015). These studies may not accurately reflect the water quality impacts of green roof ecosystems, which are likely to vary temporally as natural ecosystems do among events and across seasons, in response to variation in precipitation and temperature. Because of the limited understanding of these dynamics in green roof ecosystems, it is not known how the potentially large-scale implementation of green roofs in urban watersheds could impact regional water quality.

* Corresponding author at: Department of Biological Sciences, University of Cincinnati, 318 Clifton Ct., Cincinnati, OH 45221, United States.
*E-mail address:* ishi.buffam@uc.edu (I. Buffam).

http://dx.doi.org/10.1016/j.ecoleng.2016.02.044
0925-8574/

Although some green roof studies have noted variations in runoff water quality among rain events and across seasons, very little is known or understood about these patterns or the processes underlying them. One study found lower levels of conductivity in green roof runoff following larger precipitation events while another found higher concentrations of total phosphorus and $PO_4^{3-}$ and lower $NO_3^-$ in green roof runoff during large events (Berghage et al., 2009; Teemusk and Mander, 2007). A study of a Connecticut green roof, on the other hand, found no effect of event size on total phosphorus concentrations (Gregoire and Clausen, 2011). Researchers have also observed seasonal variability. One study observed increased copper and nitrate concentrations in the summer months compared to fall and winter samples (Van Seters et al., 2009). Other studies have found higher levels of phosphorus in snowmelt vs. rain event runoff (Gregoire and Clausen, 2011), annually variable $NO_3^-$ concentrations in green roof runoff attributable to shifting pollution input levels (Teemusk and Mander, 2007), and reduced green roof retention of heavy metals such as copper and lead during the Fall and Winter seasons (Steusloff, 1998). With more long-term observation, the seasonal patterns and key mechanisms that are controlling these patterns may become apparent.

Like natural vegetated ecosystems, green roof ecosystems may be expected to exhibit seasonal fluctuations in runoff water chemistry due to variation in plant productivity, microbial activity, and other temperature or light-dependent processes. While little is known about the mechanisms controlling green roof ecosystems and runoff water quality, seasonal patterns in stream water chemistry in runoff from natural ecosystems have been attributed to physical processes including hydrologic variability (Agren et al., 2008; Welter et al., 2005) physicochemical processes including weathering (Likens et al., 1977), chemical processes including heightened reaction rates (Freeman et al., 2001; Gardner and Jones, 1973), and biological processes including enhanced mineralization and uptake (Likens et al., 1977; Wang et al., 2012). Determining the seasonal patterns of green roof water quality runoff and the primary mechanisms responsible for these patterns will improve green roof runoff models, green roof design and management, and our understanding of how these systems will impact urban water quality and respond to impending changes in temperature and precipitation patterns.

In this study, we investigated the temporal dynamics of green roof runoff water quality to address the following questions: (1) is there seasonal variation in the concentrations of dissolved nutrients, cations and metals in runoff from a green roof ecosystem? if so, is the seasonal variation correlated with measurable environmental parameters (e.g., air temperature); (2) is there among-event variation in the concentrations of dissolved nutrients, cations and metals in runoff from a green roof ecosystem? if so, are these differences correlated with measurable event characteristics like precipitation amount, event duration and antecedent moisture conditions? (3) are seasonally-varying factors (e.g., temperature) or shorter-term event-related factors (e.g., amount of precipitation) stronger drivers of variation in green roof runoff water quality? We addressed these questions by analyzing water chemistry from incoming precipitation and runoff samples from a 46 $m^2$, sloped green roof and an adjacent, 37 $m^2$, sloped shingled roof, for the majority of the precipitation events from April 2011 to February 2013. We hypothesized that the concentrations of bioactive compounds (dissolved N, P, C and base cations) would be elevated in green roof runoff relative to precipitation and control roofs, due to the presence of these elements in green roof substrate; but would decrease during summer due to uptake by plants within the green roof ecosystem, particularly N which is commonly the limiting nutrient in terrestrial ecosystems (Chapin et al., 2011). We also expected that concentrations of all elements would be diluted during larger storm events.

## 2. Study site and methods

### 2.1. Location, climate and study site

The vegetated roof and non-vegetated, traditional roof used in this study are located at the Civic Garden Center in Cincinnati, Ohio. Cincinnati lies in a transition zone between the humid subtropical and humid continental climate zones, with a long-term (1961–1990) average high temperature of 31 °C in July and 4 °C in January (National Weather Service, Wilmington, Ohio). Precipitation averages 1080 mm per year and is typically relatively evenly distributed throughout the year, with slightly higher average precipitation amounts during spring and summer (March–August, 97–120 mm $month^{-1}$) than fall and winter (September–February, 67–84 mm $month^{-1}$). Short, intense thunderstorms are common during the warmer months. The climate during the 22-month sampling period for this study included one wetter than average year (1360 mm of precipitation during 2011) and one drier than average year (763 mm of precipitation during 2012).

The 46 $m^2$ extensive, 20° sloped vegetated roof was installed by Tremco Inc. (Cincinnati, OH) in April 2010 using Tremco's standard aggregate-based extensive green roof substrate, at a depth of 10 cm. A soil stabilization system was installed along with a pre-vegetated sedum mat with commonly used green roof plants including *Sedum album*, *S. sexangulare*, *S. acre*, *S. spurium*, *S. rupestre, S. floriferum*, *S. kamtschaticum*, *S. immergrunchen*, and *S. hispanicum.* Management of the roof includes occasional weeding by hand, and in May 2012, treatment with corn gluten meal, an organic weed preventer. The 37 $m^2$ traditional, 20° sloped roof is composed of asphalt shingles. Approximately 30% of the green roof is shaded by *Magnolia acuminata* and *Magnolia grandiflora* trees while approximately 10% of the traditional roof is shaded by *M. grandiflora* and *Fagus sylvatica* trees. Both roofs have gutters which direct roof runoff into a PVC pipe and ultimately into a 4.7 l high-density polyethylene (HDPE) runoff collection bucket positioned to overflow into a rain barrel.

### 2.2. Sampling

Runoff water samples for water quality analyses were collected from both roofs for the majority of precipitation events that induced green roof runoff from 4/12/2011 to 2/13/2013, using acid-washed 500 ml HDPE containers. Samples were either collected directly from the gutter downspout during the event or, if runoff had ceased, from the corresponding runoff collection bucket. Because samples were taken as grab samples at the end of runoff events, concentrations are instantaneous concentrations and do not necessarily capture the full behavior of each storm event or its contribution to local waterways. A pilot study was performed which confirmed that our measured end of event concentrations were on average approximately 10% different than the event mean concentrations (EMC) for all variables, and up to 30% for some analytes. An atmospheric deposition sample was also collected from each runoff-inducing rain event using a 19 l HDPE collection bucket positioned on a nearby flat conventional roof located 45 m from the vegetated and traditional test roofs. These samples are termed "precipitation" samples but include both wet deposition from the event, as well as dry deposition from the between-event time period. Since the green roof frequently generated no runoff following small rain events, in practice the sampling regime involved a cutoff where we only sampled events of >ca. 5 mm precipitation, depending on antecedent conditions. This approach resulted in samples taken from a total of 88 unique events (defined in Section 2.4 below), including 88 green roof runoff samples, 86 traditional roof runoff samples, and 61 precipitation samples. The reduced number of traditional roof samples was a result of equipment failure for two events, while the reduced number of precipitation samples resulted from a lack of sufficient sample volume for analysis from smaller events. All samples, immediately after collection, were transported back to the laboratory and refrigerated until filtration and analysis.

### 2.3. Water quality analyses

A portion of each runoff sample was analyzed for pH (Orion Ross Ultra Combination pH, Thermo Fisher Scientific, Waltham, MA) and conductivity (Orion Conductivity Cell; Thermo Fisher Scientific, Waltham, MA). The remaining sample was filtered through a 0.45 μm filter (Millipore MF™ membrane filter; Millipore, Billerica, MA) within 48 h of the precipitation event and was subdivided for individual analyses. All subsamples were frozen until they could be analyzed, except those analyzed for metals which were acidified to a final concentration of 2% ultrapure nitric acid and refrigerated.

Samples were analyzed for: $PO_4^{3-}$ using the ascorbic acid method (Murphy and Riley, 1962) adapted for a microplate reader (Biotek® Synergy H1Hybrid Microplate reader; Biotek, Winooski, VT); $NH_4^+$ using the phenol-hypochlorite reaction (Weatherburn, 1967) adapted for a microplate reader; $NO_3^-$ using a spectrophotometric method (Doane and Horwath, 2003) adapted for a microplate reader; total nitrogen (TN) and dissolved organic carbon (DOC) using a Shimadzu TOC-$V_{CPH}$ equipped with TNM-1 (Shimadzu, Kyoto, Japan); and base cations and metals (aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), phosphorus (P), potassium (K), sodium (Na), strontium (Sr), and zinc (Zn)) using ICP-OES (Thermo-Electron iCAP 6300 Duo ICP-OES; Thermo Fisher Scientific, Waltham, MA). Dissolved Organic Nitrogen (DON) concentration was calculated as $TN - NH_4^+ - NO_3^-$, in units of mg N $l^{-1}$. Trace metals (Ag, Co, Cr, Cu, Li, Mn, and Ni) were also analyzed using ICP-OES, but were excluded from further statistical analysis and are not reported herein because for each of these elements, the mean measured concentrations for all locations were below the instrument detection limit, which ranged from 0.006 to 0.031 ppm for the different trace metals. Finally, two elements (Sr and P) were excluded from further statistical analysis because they provided redundant information. Sr was extremely highly correlated ($r = 0.99$) with Ca concentration. The P analysis gave values essentially identical to the $PO_4^{3-}$ analysis, with high correlation ($r = 0.94$) and the difference between the two (representing dissolved organic phosphorus (DOP) concentrations) indistinguishable from zero. We retained the $PO_4^{3-}$ data rather than P data due to higher precision and reliability of the $PO_4^{3-}$ data.

### 2.4. Climate data

Hourly air temperature and precipitation data were obtained from the National Oceanic and Atmospheric Administration (NOAA) weather station at the Lunken Regional Airport, which is located approximately 8 km from the study site. Discrete precipitation events were defined as periods of precipitation bracketed both before and after by at least 12 consecutive hours without precipitation. By this definition, during the 22 month sampling period there were 172 total events including 95 events with total precipitation >5 mm. We collected runoff samples from the green roof for 88 events total, including over 2/3 of the larger events ($n = 65$ of 95). Many of the smaller events did not generate runoff from the green roof, thus did not fit our criteria for sampling. Using the hourly climate data, we calculated the following climate variables associated with each event: total antecedent precipitation in the 7 day period prior to the beginning of the event ($P_{ANT}$, mm), total event precipitation ($P_{TOT}$, mm), precipitation event duration ($P_{DUR}$, h), maximum hourly precipitation rate for the event ($P_{MAX}$, mm $h^{-1}$), mean hourly precipitation rate for the event ($P_{AVE}$, mm $h^{-1}$), air temperature at the time of sampling ($T_{SAMP}$, °C), mean air temperature during the event up to the time of sampling ($T_{EVENT}$, °C), and mean air temperature for the 7 days prior to sampling ($T_{WEEK}$, °C). An additional categorical variable (YEAR) was defined for each event to indicate whether the event occurred in year 1 or year 2 of the study, with the dividing date set to May 10, 2012. This date approximately halfway through the study corresponded to a management action – addition of corn gluten to the roof as a weed suppressant – that gave an opportunity to study the effect on runoff water quality of the addition of a nitrogen-containing organic fertilizer.

### 2.5. Statistical analysis

Statistical analyses were run using 88 green roof runoff samples, 86 traditional roof runoff samples, and 61 precipitation samples, corresponding to 88 discrete runoff events. Most analytes were approximately normally distributed but data for $NH_4^+$, $NO_3^-$, DON, K, Na, Zn, $P_{ANT}$, $P_{TOT}$, $P_{DUR}$, $P_{MAX}$, and $P_{AVE}$, were log-normally distributed and were therefore natural log-transformed prior to statistical analysis. After transformation, skewness for all variables was between −1 and +2.

In order to determine the overall mean effect of the roof type on runoff water quality in the face of among-event variability, we first compared the concentrations for each analyte among green roof runoff (GR), traditional roof runoff (TR), and precipitation (P), using three paired *t*-tests (i.e., GR v. TR; GR v. P; TR v. P) (SPSS v.21, IBM, Armonk, NY). Each discrete runoff event was treated as an independent replicate. Bonferroni correction was applied for multiple comparisons, giving overall $\alpha = 0.05$ for each analyte. Second, we segmented the data by season with Spring (March–May), Summer (June–August), Fall (September–November) and Winter (December–February), to examine the differences in analyte concentrations among seasons for each location.

The relationship between water chemistry ($n = 14$ parameters described in Section 2.3) and time-varying environmental predictor variables ($n = 9$ variables described in Section 2.4) was first tested using multivariate Redundancy Analysis (RDA) in the program CANOCO (v.5). This analysis was run separately for each of the three locations (green roof runoff, traditional shingled roof runoff, and precipitation). For samples with 1 or 2 missing chemistry parameter values, the missing data were replaced with the median for the respective parameter for that location. Samples with more than 2 missing parameter values were excluded from analysis. This approach resulted in the replacement of ca. 1% of the data values and exclusion of 1 sample from each location. Forward selection was used to construct parsimonious models with high explanatory power, using only predictor variables that significantly improved the model ($p < 0.05$ for inclusion). Partial RDA (pRDA) analysis was also performed in order to calculate the degree of shared explained variance between the different selected environmental predictors (Okland and Eilertsen, 1994).

Environmental predictor variables that were significant in the green roof RDA analysis were also examined for their relationship with individual water quality variables using multiple linear regression (MLR) using R v 3.03 (R Core Team, 2015). Only environmental variables that were very weakly or un-correlated with one another ($p > 0.01$ and $R^2 < 0.10$) were used in the models. In a first step, leading candidate MLR models were selected using the Bayesian Information Criteria (BIC) in stepwise backward selection (*step* command in *stats* package in *R*). Temporal autocorrelation in the data was then tested using the Durbin Watson test and plotting semivariograms with the residuals of the best-fit models. Autocorrelation was detected in model residuals for several of the analytes, with a range of up to 36 days. To account for this, an autocorrelation term (AC) was added to these models, using autocovariate regression (*spdep* package in R) (Dormann et al., 2007) adapted for temporal data. Following inclusion of the autocorrelation term when significant, final best MLR models were selected using the Bayesian Information Criteria (BIC) from a set of all regression subsets (*regsubsets* command in leaps package in R). Finally, the Durbin Watson test was again applied to ensure lack of temporal autocorrelation in the residuals of the final models. The unique contribution of each environmental predictor in the models was determined from the squared semipartial correlation ($sr^2$), which is calculated as the proportion of explained variance lost (change in $R^2$ value) when that independent variable is removed from the best model.

## 3. Results and discussion

### 3.1. Impact of green roof on runoff chemistry

Our research with a detailed, 22-month study of runoff water quality from a 46 $m^2$ green roof in Cincinnati revealed that green roof runoff chemistry was distinctly different than precipitation or traditional roof runoff (Table 1), and also exhibited striking seasonal patterns (Table 2, Fig. 1). Most analytes were lowest in precipitation, intermediate in traditional roof runoff, and highest in green roof runoff, with median values at least 10-fold higher in green roof runoff than in precipitation (Table 1). The inorganic nitrogen species nitrate and ammonium were exceptions to this rule. Ammonium was highest in precipitation, intermediate in traditional roof runoff, and lowest in green roof runoff, suggesting that the green roof serves as a sink for $NH_4^+$. Although the green roof runoff peaked at relatively high concentrations of nitrate (>10 mg N $l^{-1}$) compared to the other locations, nitrate was not significantly different between green roof runoff and precipitation, and was lowest in the traditional roof runoff. The overall lack of significant difference in nitrate concentration between green roof and precipitation can be attributed to the fact that green roof runoff nitrate concentrations were seasonally variable, substantially higher than precipitation in the summer but lower than precipitation in the winter (Table 2, Table S1), suggesting seasonal variation in N processing rates. Green roof runoff nitrate concentrations were also much higher in year 2, following the organic N fertilization. For most analytes, the traditional roof runoff was more similar to precipitation than to green roof runoff chemistry—that is, the green roof imparted a large change in runoff chemistry as compared to the shingled traditional roof.

The observation of higher concentrations of DOC, $NO_3^-$, $PO_4^{3-}$ and inorganic salts in runoff from the Civic Garden Center green roof as compared to the control roof, generally align with results from other studies of green roof runoff (Berndtsson, 2010; Rowe, 2011; Buffam and Mitchell, 2015). The consistency of these patterns among published studies suggests that the leaching of nutrients (especially $PO_4^{3-}$) from green roofs is of concern, particularly in the first several years after construction if compost or other high-nutrient organic matter is integrated into the substrate (Berndtsson 2010; Buffam and Mitchell, 2015). Although runoff volume was not directly measured in this study, average annual runoff reduction is about 50–60% for extensive green roofs (Gregoire and Clausen, 2011; Carter and Rasmussen, 2006). Thus, a mean concentration in green roof runoff of greater than about 2× the control roof value, would suggest that the green roof is a relative source of that particular analyte. With a median of 1.8 mg $l^{-1}$ of P as $PO_4^{3-}$ (about 20-fold higher than the runoff from the traditional roof), this represents a substantial flux of P even after accounting for the 50–60% runoff reduction by the green roof. For comparison, wastewater typically has a concentration of 3–10 mg $l^{-1}$ of P as phosphate (Metcalf and Eddy, 1991). The actual impact on downstream water quality of green roof effluent will depend on the degree to which the runoff volume is reduced, the timing and magnitude of the nutrient pulse, and the way the system is “plumbed” downstream, i.e., whether the runoff water is directed into sewers, surface waters, or other green infrastructure elements.

### 3.2. Patterns of temporal variation in green roof runoff chemistry

The green roof runoff chemistry had high temporal variability. Concentrations of all major base cations (Ca, K, Mg, Na) and bioactive elements (C, N and P) as well as specific conductivity were highest in summer, and generally lowest in winter, with spring and autumn intermediate (Fig. 1, Table 2). In contrast, the dissolved metals (Al, Fe, Zn) and pH exhibited little or no seasonal variation (Fig. 1, Table 2). Relative to the green roof runoff, there was considerably less seasonal variation in the traditional roof runoff and precipitation chemistry (Fig. 1, Tables S1, S2). Most of the analytes also had much lower concentrations in precipitation than in green roof runoff, particularly during summer, with the exception of $NH_4^+$. The median $NO_3^-$ concentration for example was about 5 times higher in green roof runoff than precipitation during summer, while the median K, Mg and Zn concentrations were all more than 10-fold higher in green roof runoff than in precipitation during summer. For $NH_4^+$, concentrations in precipitation were higher than in green roof runoff, and there was a weak positive correlation between the two, suggesting a possible direct influence of precipitation ($N$ = 61 events, $R^2$ = 0.19). For $NO_3^-$ however, there was no correlation. Thus, variation in precipitation chemistry can be ruled out as a main contributor to temporal variation in green roof runoff chemistry, except possibly for $NH_4^+$.

### 3.3. Relationship between water chemistry and environmental predictor variables

The variation in green roof runoff chemistry was strongly correlated with environmental variables, especially temperature (Fig. 2). In total, four environmental variables were selected in the best-fit multivariate RDA model and explained 39% of the temporal variance in runoff chemistry. The strongest variable was air temperature during the preceding week ($T_{WEEK}$) at 26–32% of the total variance, followed by antecedent moisture conditions ($P_{ANT}$) and total event precipitation ($P_{TOT}$) which together explained 3–7%, and the difference among years (YEAR) which explained 4–5%. The shared variance ranges extended from unique explained variance (lower end) to maximum explained variance (upper end) for a given variable. The major effect, of $T_{WEEK}$, reflected a tendency for high concentrations of most solutes in green roof runoff during warmer periods (i.e., summer). The relationship was particularly strong (loadings >0.5 on principal RDA axis) for conductivity, $PO_4^{3-}$, $NO_3^-$, DON, DOC, Ca, K, Mg, and Na.

In contrast, the temporal variation in traditional roof runoff and precipitation were only weakly correlated with the seven environmental variables tested. Only $T_{WEEK,}$ explaining 5% of the total variance, was significant in the best-fit RDA model of traditional roof runoff. For precipitation chemistry, three variables (total precipitation ($P_{TOT}$) 7–8%, air temperature ($T_{WEEK}$) 5–6%, and antecedent conditions ($P_{ANT}$) 3–4%, explaining 16% of the temporal variance were significant in the RDA. The major effect, of total event precipitation ($P_{TOT}$), reflected a tendency for most analytes to be more dilute in the precipitation from larger rain events.

Variation in green roof runoff chemistry was highly correlated with temperature for most of the individual analytes, with additional variance explained by event size and antecedent moisture conditions for many parameters (Table 3). Temperature ($T_{WEEK}$) uniquely explained >20% of the variance for 9 of the 14 analytes,

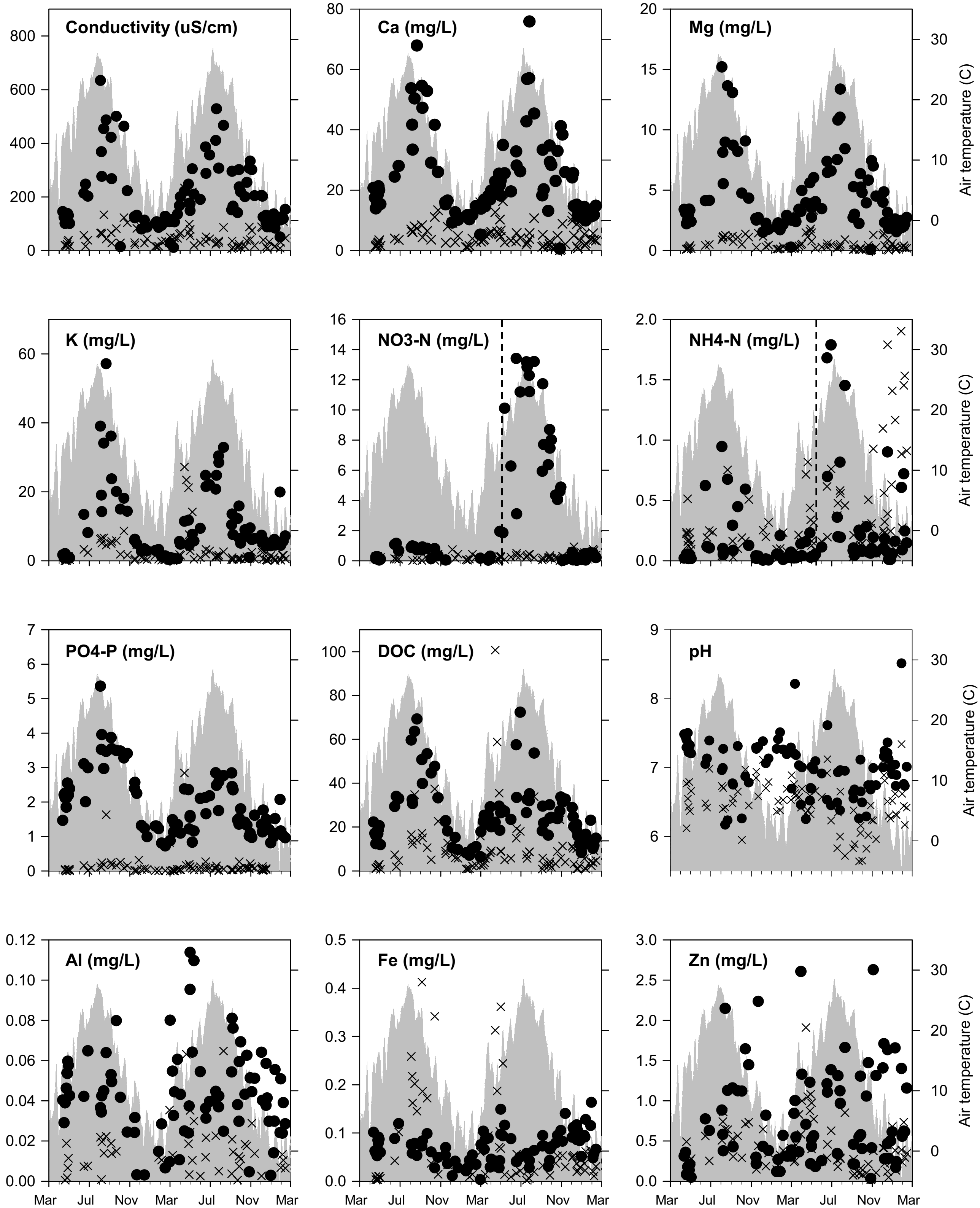


**Fig. 1.** Seasonal variation (2011–2013) in water quality parameters in runoff from the green roof (●) and traditional roof (X), together with weekly mean air temperature (grey area fill). $Na^+$ and DON (not shown) had patterns very similar to $K^+$ and DOC, respectively. Dotted lines on $NO_3^-$ and $NH_4^+$ panels indicate the date of the organic N addition.

while neither $P_{TOT}$ nor $P_{ANT}$ ever explained >20%. Chemistry variables with particularly high variance explained by $T_{WEEK}$ ($sr^2 > 0.4$) were conductivity, DOC, DON, $NO_3^-$, $PO_4^{3-}$, $Ca^{2+}$, and $Mg^{2+}$. In all cases, $T_{WEEK}$ indicated higher concentrations at warmer temperatures. Antecedent moisture conditions were moderately important based on the inclusion of $P_{ANT}$ in 5 of the 14 models, though secondary to temperature. In all cases, $P_{ANT}$ indicated higher solute concentrations in green roof runoff during periods with

**Table 1**
Summary (median, 10–90th percentiles) of concentrations in green roof runoff, traditional roof runoff, and atmospheric deposition during 88 rain events over 22 months of study.

| Analyte | Units | Green Roof (N = 88) | Trad. Roof (N = 86) | Precip. (N = 61) |
|---|---|---|---|---|
| pH | pH units | **7.0 (6.5–7.4)** | 6.5 (6.0–6.9) | *5.7 (4.9–6.6)* |
| Conductivity | mS/cm | **152 (88–411)** | 37 (15–108) | *15 (8–46)* |
| DOC | mg C $L^{-1}$ | **23.0 (10.5–47.9)** | 5.9 (1.0–24.2) | *2.2 (1.1–7.1)* |
| DON | mg N $L^{-1}$ | **1.6 (0.7–14.5)** | 0.6 (0.1–4.5) | *0.1 (−0.2–0.6)* |
| $NO_3-$ | mg N $L^{-1}$ | **0.4 (0.0–10.2)** | *0.2 (0.0–0.5)* | **0.4 (0.2–0.9)** |
| $NH_4^+$ | mg N $L^{-1}$ | *0.1 (0.0–0.7)* | 0.2 (0.0–1.0) | **0.3 (0.1–0.7)** |
| $PO_4^{3-}$ | mg P $L^{-1}$ | **1.6 (1.0–3.4)** | *0.1 (0.0–0.2)* | *0.0 (0.0–0.1)* |
| Ca | mg $L^{-1}$ | **19.9 (11.2–47.9)** | 3.8 (1.2–10.0) | *1.0 (0.2–2.8)* |
| K | mg $L^{-1}$ | **5.7 (0.9–24.7)** | 1.0 (0.1–6.4) | *0.3 (0.0–1.0)* |
| Mg | mg $L^{-1}$ | **3.3 (1.8–8.8)** | *0.3 (0.1–1.4)* | *0.1 (0.0–0.4)* |
| Na | mg $L^{-1}$ | **2.5 (1.0–5.2)** | *0.4 (0.1–2.2)* | *0.2 (0.1–1.2)* |
| Al | mg $L^{-1}$ | **0.040 (0.003–0.066)** | *0.005 (−0.025–0.029)* | *0.004 (−0.019–0.022)* |
| Fe | mg $L^{-1}$ | **0.070 (0.027–0.113)** | **0.022 (−0.009–0.193)** | *0.003 (−0.015–0.034)* |
| Zn | mg $L^{-1}$ | **0.56 (0.16–1.63)** | 0.30 (0.09–0.84) | *0.02 (0.00–0.05)* |

Boldface text indicate locations significantly higher than other locations for the given analyte, and italicized text indicate locations significantly lower than other locations (paired t-tests, $\alpha = 0.05$).

**Table 2**
Summary (median, 10–90th percentiles) of green roof runoff chemistry, organized by season.

| Analyte | Units | Spring (N = 24) | Summer (N = 17) | Fall (N = 22) | Winter (N = 25) |
|---|---|---|---|---|---|
| pH | pH units | 7.2 (6.5–7.5) | 7.0 (6.2–7.4) | *6.7 (6.3–7.3)* | 7.1 (6.7–7.5) |
| Conductivity | μS/cm | 134 (64–234) | **356 (200–549)** | 229 (123–451) | *107 (81–173)* |
| DOC | mg C $L^{-1}$ | 21.0 (12.7–28.4) | **33.4 (25.9–69.8)** | 28.4 (18.1–49.7) | 12.1 (7.6–23.7) |
| DON | mg N $L^{-1}$ | 1.6 (1.1–7.2) | **10.3 (2.6–35.8)** | 1.6 (0.1–19.3) | *1.2 (0.7–2.0)* |
| $NO_3^-$ | mg N $L^{-1}$ | 0.1 (0.0–1.9) | **3.1 (0.7–13.2)** | 2.5 (0.0–8.5) | *0.1 (−0.1–0.5)* |
| $NH_4^+$ | mg N $L^{-1}$ | *0.0 (0.0–0.1)* | **0.6 (0.1–1.7)** | 0.1 (0.0–0.5) | 0.1 (0.0–0.7) |
| $PO_4^{3-}$ | mg P $L^{-1}$ | 1.6 (0.9–2.4) | **2.8 (1.7–4.2)** | 2.3 (1.0–3.5) | *1.2 (0.8–1.6)* |
| Ca | mg $L^{-1}$ | 18.3 (13.9–25.5) | **42.2 (23.0–70.3)** | 28.7 (13.7–51.1) | *11.8 (9.6–18.8)* |
| K | mg $L^{-1}$ | 1.1 (0.5–9.5) | **23.4 (9.0–44.4)** | 9.3 (5.0–22.6) | *4.5 (1.3–7.3)* |
| Mg | mg $L^{-1}$ | 3.3 (2.3–5.3) | **7.8 (3.9–14.1)** | 4.8 (2.3–9.0) | *2.2 (1.5–3.5)* |
| Na | mg $L^{-1}$ | 2.0 (0.9–4.3) | 4.8 (2.7–10.7) | 2.6 (1.1–4.8) | 1.9 (0.6–3.6) |
| Al | mg $L^{-1}$ | 0.05 (0.02–0.10) | 0.04 (0.03–0.06) | 0.05 (0.00–0.08) | 0.03 (−0.01–0.06) |
| Fe | mg $L^{-1}$ | 0.08 (0.03–0.11) | 0.06 (0.04–0.10) | 0.07 (0.03–0.10) | 0.07 (0.02–0.12) |
| Zn | mg $L^{-1}$ | 0.36 (0.06–1.28) | 1.04 (0.31–1.81) | 0.82 (0.21–2.06) | 0.50 (0.15–1.64) |

Boldface text indicate seasons with exceptionally high values (10th percentile > another season's 90th percentile), while italicized text indicate seasons with exceptionally low values (90th percentile < another season's 10th percentile).

**Table 3**
Results of multiple linear regression (MLR) relating green roof runoff chemistry variables to environmental explanatory variables.

| Response variable | Explanatory variables: variance explained ($sr^2$) | | | | | Model fit | | |
|---|---|---|---|---|---|---|---|---|
| | $P_{TOT}$ | $P_{ANT}$ | $T_{WEEK}$ | YEAR | AC | $R^2_{adj.}$ | P value | F-statistic |
| pH | | 0.09 | (0.13) | | | 0.15 | <0.001 | $F_{2,84} = 8.87$ |
| Cond | (0.04) | (0.09) | **0.55** | | | 0.61 | <0.001 | $F_{3,84} = 37.03$ |
| $PO_4^{3-}$ | | | **0.41** | (0.07) | 0.19 | 0.66 | <0.001 | $F_{3,83} = 55.56$ |
| $NH_4^+$ | | (0.11) | **0.17** | 0.04 | | 0.31 | <0.001 | $F_{3,82} = 13.51$ |
| $NO_3^-$ | | | **0.42** | **0.36** | 0.03 | 0.80 | <0.001 | $F_{3,80} = 111.40$ |
| DON | (0.02) | | **0.41** | (0.03) | **0.29** | 0.68 | <0.001 | $F_{4,77} = 42.65$ |
| DOC | (0.05) | (0.04) | **0.56** | | 0.07 | 0.59 | <0.001 | $F_{4,83} = 32.17$ |
| Al | | | **0.16** | | | 0.15 | <0.001 | $F_{1,85} = 15.68$ |
| $Ca^{2+}$ | (0.03) | | **0.47** | | 0.10 | 0.59 | <0.001 | $F_{3,83} = 42.21$ |
| $Fe^{3+}$ | | | | 0.06 | | 0.13 | 0.026 | $F_{1,85} = 5.11$ |
| $K^+$ | | | **0.23** | 0.05 | **0.26** | 0.59 | <0.001 | $F_{3,83} = 42.59$ |
| $Mg^{2+}$ | (0.04) | (0.03) | **0.48** | | 0.06 | 0.58 | <0.001 | $F_{4,82} = 30.69$ |
| $Na^+$ | | | **0.20** | | **0.28** | 0.45 | <0.001 | $F_{2,84} = 36.15$ |
| $Zn^{2+}$ | (0.14) | | | | 0.12 | 0.26 | <0.001 | $F_{2,84} = 16.50$ |

Values in parentheses indicates a negative correlation between explanatory and response variable, all others are positive. Bolded cells indicate environmental variables with >20% explained variance in the given model. PANT: antecedent precipitation in the 7 day period prior to the beginning of the event; PTOT: total event precipitation; TWEEK: mean air temperature for 7 days prior to the event; YEAR: categorical variable, with first year (prior to fertilization with corn gluten) vs. second year (post-fertilization); AC: autocovariate regression term to account for temporal autocorrelation

drier antecedent conditions. Total event precipitation ($P_{TOT}$) was included in 6 of the 14 models, had relatively low values for uniquely explained variance, and indicated higher concentrations in green roof runoff during smaller events (lower total precipitation amounts). Year-to-year differences were significant for 6 of the analytes, but explained very little variance, except for in the case of $NO_3^-$ which was considerably higher in the second year. Green roof runoff $NO_3^-$ concentrations were almost equally strongly affected by both temperature, and by the differences among years, presumably due to the fertilization with corn gluten meal (Fig. 3). Many of the analytes also had temporal autocorrelation, with the resulting autocovariance regression terms explaining up to 29% of the variance (Table 3). In summary, runoff chemistry from this green roof was highly seasonal, and also varied among events based on

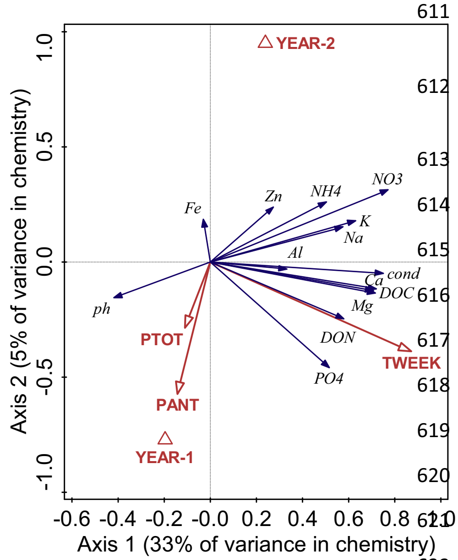


**Fig. 2.** Multivariate Redundancy Analysis (RDA) of green roof runoff chemistry, depicting ordination of 14 water quality variables during 87 distinct runoff events as a function of four significant environmental predictor variables. Mean air temperature during the week preceding the runoff event ($T_{WEEK}$) was highly correlated with RDA axis 1, and explained the most variance in chemistry.

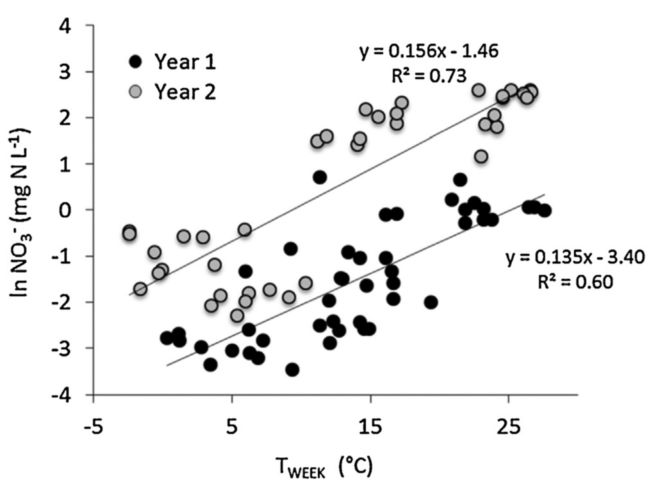


**Fig. 3.** Nitrate concentrations in green roof runoff as a function of mean weekly temperature, for year 1 (pre-fertilization) and year 2 (post-fertilization with corn gluten meal). *Note*: natural-log transformation of response variable.

event size and antecedent wetness. Most elements had higher concentrations during summer, during small rain events, and during events following dry periods. This was typified by the behavior of conductivity (Table 3, Fig. 1).

### 3.4. Potential mechanisms affecting temporal variation in green roof runoff chemistry

We observed variation in green roof runoff chemistry on three discrete timescales: among-event variation related to event size and antecedent conditions, seasonal variation correlated with mean weekly temperature, and among-year variation likely related to the addition of corn gluten (containing organic N) in May 2012. The seasonal variation was most pronounced and explained the majority of environmentally-related temporal variation in green roof runoff water chemistry for all bioactive analytes. We have identified several hypothesized mechanisms with potential to cause seasonal variation in green roof runoff water quality, that could be tested in future studies:

1. Plant-mediated nutrient cycling is altered during the growing season, either through direct plant uptake, or by release of soil exudates which influence the rate of microbial/decomposer activity in the substrate matrix.
2. Chemical dissolution of minerals (weathering) or ion desorption in the green roof substrate are more rapid at higher temperatures.
3. Microbial mineralization rates of substrate organic matter increase as a function of temperature, releasing dissolved inorganic N and P and solubilizing DOC.
4. Green roof hydrodynamics vary seasonally, due to variation in evapotranspiration rates and rainfall event size and duration. For instance, higher evapotranspiration rates in the summer lead to rapid drying, and short-duration high-intensity thunderstorms are more common in the warmer months, leading to a more rapid, episodic flow-through dynamic than in winter.

The results of this study suggest that the dominant mechanism(s) responsible for seasonality in runoff water quality from this green roof are most closely linked to variation in temperature (i.e., #2 and #3 above), rather than hydrology (event size/type) or growing season (plant activity). The direct uptake of nutrients by plants would lead to reduced availability of nutrients for export during the growing season, as seen for nitrate in streams draining watersheds with aggrading forest (Aber et al., 1997; Likens et al., 1977; Vitousek and Reiners, 1975). Nutrient concentrations in green roof runoff, however, were highest throughout the growing season (Fig. 1), suggesting other more important controlling processes are at work. Nevertheless, plant activity may have an indirect effect on water quality by influencing microbial mineralization via the release of soil exudates (Hamilton and Frank, 2001). Plant activity is also likely to become a more dominant process in terms of regulating water quality and nutrient dynamics for older green roofs with aged, lower-nutrient substrate in the absence of fertilization and in general whenever nutrient supply is scarce relative to plant demand (Buffam and Mitchell, 2015; Chapin et al., 2011).

Although event size was only weakly correlated with green roof runoff water quality in this study, it is important to note that our model was based on precipitation amount and runoff concentrations, rather than measured roof runoff amount and fluxes out of the system. Thus, there is still uncertainty with respect to the importance of event size. For example, increased evapotranspiration during warm periods will decrease runoff relative to incoming precipitation, potentially resulting in evapotranspirative concentration of soil solution ions. This effect may have contributed to the elevated concentrations of chemicals in green roof runoff during the summer, and requires further study with the establishment of a complete water balance and calculation of chemical fluxes.

The remaining potential mechanisms #2 and #3 above, involving the direct temperature dependence of chemical or biological process rates, are strong candidates as central processes explaining green roof seasonal runoff patterns. The chemical dissolution of minerals (weathering) and desorption of ions are chemical processes which can be directly related to temperature using the Arrhenius equation (Arrhenius, 1889). For example, a chemical reaction will proceed toward equilibrium at a rate approximately 10 times faster at a typical July daily high temperature in Cincinnati of 30 °C than at a typical January daily high temperature of 5 °C. Using a mechanistic model, researchers have shown 4-fold increases in phosphorus desorption when temperature is increased from 10 °C to 42 °C (Barrow, 1983). Likewise, in soils from Idaho, investigators observed increases in phosphorus desorption with higher temperatures (Gardner and Jones, 1973).

Microbial mineralization, like weathering and desorption, is influenced by temperature and thus a viable process for explaining the observed seasonal fluctuations in green roof runoff water quality. Many controlled experiments and models have confirmed that mineralization rates increase with temperature, with reaction rates typically doubling for every ca. 10 °C increase (Davidson and Janssens, 2006). Field observations of seasonal fluctuations in runoff chemistry have attributed higher phosphorus and DOC levels to the influence of temperature on mineralization (Freeman et al., 2001; Grierson et al., 1999; Wang et al., 2012). These observations, coupled with our own observations of seasonal variation in runoff chemistry from green roofs, suggest that microbial mineralization is likely to play important functional role in the release and export of solutes from green roofs, and is worth investigating in greater detail.

Although most analytes showed similar patterns during the two years of record in our study, year-to-year differences in $NO_3^-$ concentrations (Fig. 1) were striking. This variation was likely a result of management activity on the roof-specifically application of corn gluten meal, an organic weed preventer which contains high levels of organic nitrogen, in May 2012. Interestingly, this action apparently resulted in a more than 6-fold year to year increase in $NO_3^-$ concentrations released from the green roof, indicating that fertilization of a green roof, even with an organic N source, can have immediate negative effects on runoff water quality—presumably through microbial mineralization and subsequent nitrification of the added N. Similar observations of release of N via runoff following fertilizer amendments have been observed for both full-scale and plot-scale green roofs (Emilsson et al., 2007; Teemusk and Mander, 2011). We cannot rule out the potential impact of increased N availability from the corn gluten meal application on other water quality parameters, which could be impacted in the second year of this study due to alterations in plant or microbial processes, for example. However, apart from the increase in $NO_3^-$ and to a lesser degree $NH_4^+$ concentrations during year two, we saw no other strong year-to-year differences that would indicate a fertilization effect. Additionally, even though the concentration of nitrate in runoff from the green roof increased substantially in the second year following the corn gluten application, the positive relationship between temperature ($T_{WEEK}$) and nitrate concentrations was maintained (Fig. 3), suggesting the main processes responsible for $NO_3^-$ leaching rates were similar during both years.

### *3.5. Conclusions and future directions*

Our findings confirm results from other recent studies showing that runoff from green roofs, particularly when newly constructed, can contain high levels of leached bioactive solutes (especially $PO_4^{3-}$ and DOC) that could negatively impact water quality downstream (Berndtsson, 2010; Buffam and Mitchell, 2015). Fertilization with organic N halfway through our study had a direct and almost immediate impact on export of $NO_3^-$ in runoff, and this effect lasted through at least one growing season. Green roof effluent water quality varied greatly over time and among seasons in this study, particularly winter to summer (e.g., median $PO_4^{3-}$ concentration was 2.5 times as high, and median $Ca^{2+}$ concentration was nearly 4 times as high, in summer vs. winter). The multiple samples over this long-term study fleshed out these differences where shorter duration investigations would not adequately characterize runoff water quality, emphasizing the need for long-term studies in these ecosystems.

Contrary to our predictions, bioactive solute concentrations (including inorganic nutrients, nitrate and phosphate) in green roof runoff were higher in the summer growing season than any other season. As this pattern was not found for the incoming precipitation or the adjacent shingled control roof, this intriguing result suggests that temperature-driven dynamics internal to the green roof ecosystem play a large role in controlling effluent water quality. We suggest that microbial mineralization of nutrient-rich organic matter in the substrate is a likely source of the main variation in nutrient concentrations (Berndtsson et al., 2006; Buffam and Mitchell, 2015), but isolation of contributing processes remains a goal for future studies. As expected, concentrations of many elements tended to be lower during larger rain events, both for the incoming precipitation, and for the roof runoff. Concentrations of many elements also tended to be higher during events following dry antecedent conditions. However, both of these effects were minor for green roof runoff, relative to temperature-associated seasonal variation.

A better understanding of within-roof processes is essential to model the expected behavior of green roofs under a range of design and climate conditions, and to provide for more informed green roof design and management. Future experimental studies on temperature and moisture dependence are recommended, and may help to isolate the factors controlling green roof runoff and elucidate the basic biological, physical, and chemical processes at work. Our observations reinforce the need for longer-term studies of green roofs. This study focused on a relatively "young" roof, ranging from 1 to 3 years post-construction during the time of measurement. The high effluent C, P and base cation concentrations are consistent with a within-roof source of these elements, presumably the soil-like substrate; and many of these elements are expected to decrease over time due to a gradual leaching out and/or uptake by plants on the roof (Berndtsson, 2010; Buffam and Mitchell, 2015; Köhler et al., 2002). Quantifying the role of these processes would require a longer-term study and/or detailed studies of roofs of varying ages. As green roofs are long-lived structures, understanding how they behave and change throughout the year and their lifetime is essential to design and manage these ecosystems to support healthy plant communities, minimize storm water runoff, and improve regional water quality.

## Acknowledgements

We thank Dan Divelbiss, Jill Bader, Kate Johnson, Kati Massey, Aaron McCoy, Denis Bailey, Scott Nichting, Magdalena Wiedermann, Ryan Mooney-Bullock and the Civic Garden Center of Greater Cincinnati for their help, advice, and resources. Thanks also to two anonymous reviewers who provided helpful comments that improved the manuscript. Funding was provided in part by a University Research Council Grant from the University of Cincinnati.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2016.02.044.

## References

Aber, J.D., Ollinger, S.V., Driscoll, C.T., 1997. Modeling nitrogen saturation in forest ecosystems in response to land use and atmospheric deposition. Ecol. Modell. 101 (1), 61–78.

Agren, A., Jansson, M., Ivarsson, H., Bishop, K., Seibert, J., 2008. Seasonal and runoff-related changes in total organic carbon concentrations in the River Ore Northern Sweden. Aquat. Sci. 70 (1), 21–29.

Arrhenius, S.Z., 1889. Uber die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Sauren. Zeitschrift fur Physikalische Chemie 4, 226–248.

Barrow, N.J., 1983. A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. 34 (4), 733–750.

Berghage, R.D., Beattie, D., Jarrett, A.R., Thuring, C., Razei, F., O'Connor, T., 2009. Green Roofs for Stormwater Runoff Control, edited, EPA Publication No. 600-R-09-026. U.S. Environmental Protection Agency, Cincinnati, OH.
Berndtsson, J.C., 2010. Green roof performance towards management of runoff water quantity and quality: a review. Ecol. Eng. 36 (4), 351–360.
Berndtsson, J.C., Emilsson, T., Bengtsson, L., 2006. The influence of extensive vegetated roofs on runoff water quality. Sci. Total Environ. 355 (1–3), 48–63.
Brenneisen, S., 2006. Space for urban wildlife: designing green roofs as habitats in Switzerland. Urban Habitats 4 (1), 27–33.
Buffam, I., Mitchell, M.E., 2015. Nutrient cycling in green roof ecosystems. In: Sutton, R. (Ed.), Green Roof Ecosystems. Springer, New York.
Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8 (3), 559–568.
Carter, T., Laurie, F., 2008. Establishing green roof infrastructure through environmental policy instruments. Environ. Manage. 42, 151–164.
Carter, T., Rasmussen, T., 2006. Evaluation of the hydrologic behavior of green roofs. J. Am. Water Resour. Assoc. 42, 1261–1294.
Chapin, F.S., Matson, P.A., Vitousek, P.M., 2011. Fundamentals of Terrestrial Ecosystem Ecology, 2nd ed. Springer, New York.
Clark, C., Adriaens, P., Talbot, F.B., 2008. Green roof valuation: a probabilistic economic analysis of environmental benefits. Environ. Sci. Technol. 42 (6), 2155–2161.
Davidson, E.A., Janssens, I.A., 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature 440 (7081), 165–173.
Deutsch, B., Whitlow, H., Sullivan, M., Saveneau, A., 2005. Re-greening Washington, DC: a green roof vision based on quantifying storm water and air quality benefits. In: Technical Rep. Casey Trees Endowment Fund & Limno-Tech, Inc., Washington, D.C, 15 pp.
Doane, T.A., Horwath, W., 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36 (12), 2713–2722.
Dormann, C.F., et al., 2007. Methods to account for spatial autocorrelation in the analysis of species distributional data: a review. Ecography 30 (5), 609–628.
Emilsson, T., Berndtsson, J.C., Mattsson, J.E., Rolf, K., 2007. Effect of using conventional and controlled release fertiliser on nutrient runoff from various vegetated roof systems. Ecol. Eng. 29 (3), 260–271.
Freeman, C., Evans, C.D., Monteith, D.T., Reynolds, B., Fenner, N., 2001. Export of organic carbon from peat soils. Nature 412 (6849), 785.
Gardner, B.R., Jones, J.P., 1973. Effects of temperature on phosphate sorption isotherms and phosphate desorption. Commun. Soil Sci. Plant Anal. 4 (2), 83–93.
Gregoire, B.G., Clausen, J.C., 2011. Effect of a modular extensive green roof on stormwater runoff and water quality. Ecol. Eng. 37 (6), 963–969.
Grierson, P.F., Comerford, N.B., Jokela, E.J., 1999. Phosphorus mineralization and microbial biomass in a Florida Spodosol: effects of water potential temperature and fertilizer application. Biol. Fertil. Soils 28 (3), 244–252.
Hamilton, E.W., Frank, D.A., 2001. Can plants stimulate soil microbes and their own nutrient supply? Evidence from a grazing tolerant grass. Ecology 82 (9), 2397–2402.
Köhler, M., Schmidt, M., Grimme, F.W., Laar, M., Assunção Paiva, V.L., Tavares, S., 2002. Green roofs in temperate climates and in the hot-humid tropics-far beyond the aesthetics. Environ. Manage. Health 13 (4), 382–391.
Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., Johnson, N.M., 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York, 146 pp.
Mentens, J., Raes, D., Hermy, M., 2006. Green roofs as a tool for solving the rainwater runoff problem in the urbanized 21st century? Landsc. Urban Plann. 77 (3), 217–226.
Metcalf, Eddy, I., 1991. Wastewater Engineering: Treatment, Disposal, and Reuse. McGraw-Hill, New York.
Monterusso, M.A., Rowe, D.B., Rugh, C.L., Russell, D.K., 2004. Runoff water quantity and quality from green roof systems. Expanding Roles for Horticulture in Improving Human Well-Being and Life Quality 639, 369–376.
Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. 27, 31–36.
Okland, R.H., Eilertsen, O., 1994. Canonical correspondence-analysis with variation partioning—some comments and an application. J. Veg. Sci. 5 (1), 117–126.
R Core Team, 2015. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, URL http://www.R-project.org/.
Rowe, B., 2011. Green roofs as a means of pollution abatement. Environ. Pollut. 159 (8–9), 2100–2110.
Steusloff, S., 1998. Input and output of airborne aggressive substances on green roofs in Karlsruhe. Urban Ecol., 144–148.
Teemusk, A., Mander, U., 2007. Rainwater runoff quantity and quality performance from a greenroof: the effects of short-term events. Ecol. Eng. 30 (3), 271–277.
Teemusk, A., Mander, U., 2011. The Influence of green roofs on runoff water quality: a case study from Estonia. Water Resour. Manage. 25 (14), 3699–3713.
Van Renterghem, T., Botteldooren, D., 2009. Reducing the acoustical facade load from road traffic with green roofs. Build. Environ. 44 (5), 1081–1087.
Van Seters, T., Rocha, L., Smith, D., MacMillan, G., 2009. Evaluation of green roofs for runoff retention runoff quality, and leachability. Water Qual. Res. J. Can. 44 (1), 33–47.
Vitousek, P.M., Reiners, W.A., 1975. Ecosystem succession and nutrient retention—hypothesis. Bioscience 25 (6), 376–381.
Wang, S., et al., 2012. Effects of warming and grazing on soil N availability species composition, and ANPP in an alpine meadow. Ecology 93 (11), 2365–2376.
Weatherburn, M.W., 1967. Phenol-hypochlorite reaction for determination of ammonia. Anal. Chem. 39, 971–974.
Welter, J.R., Fisher, S.G., Grimm, N.B., 2005. Nitrogen transport and retention in an arid land watershed: influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76 (3), 421–440.