Chemical Analysis of Precipitation and Stormwater Runoff from a Large Green Roof

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ABSTRACT
The growth medium of a green roof is likely to affect the chemistry of the rainwater passing through it, which may impact the receiving waters. Currently only limited data exist on the changes in rain chemistry caused by green roofs. The objectives of this project are to determine the differences in concentration of several contaminants in rain and in runoff from a green roof in downtown Syracuse, NY, and to explore reasons for the observed differences. A few samples were collected in 2014 and 2016, but most of the data are from 2017. Collection of precipitation uses funnels, while collection of runoff takes place using a drainpipe that connects to several roof drains. Both types of samples are analyzed by ion chromatography for chloride, sulfate, and nitrate. Preliminary tests show that chloride concentrations in the green roof runoff are generally greater than or equal to those in precipitation. Sulfate in the runoff is greatly enhanced compared with precipitation. Nitrate concentrations do not show a clear pattern. Engineered soil greatly influences the chemistry of the incoming rain, and additional research is needed to better understand this chemistry.

KEYWORDS
Green Roof, Stormwater, Ion Chromatography, Precipitation Chemistry, Runoff Chemistry

INTRODUCTION
Widespread urbanization has shown an increase in impermeable surfaces where there was once soil and plants to absorb the precipitation. The lack of area for infiltration can lead to flooding, and in cities with combined sewers, it can lead to combined sewer overflow where raw sewage enters the receiving waters. To reduce flooding and discharge of untreated sewage, green infrastructure such as green roofs can be installed to delay and store rain runoff. Previous work has shown that rainwater flowing through the growth medium of a green roof (engineered soil) can experience changes in chemistry. For example, Vijayaraghavan et al. (2012) report higher concentrations of nitrate, phosphate, and sulfate in runoff compared to the incident rain using green roof test plots in Singapore. The plots incorporated growth medium with the trade name “universal garden soil” and were planted with sedum. Czemiel Berndtsson (2010) presents a literature review of green roof studies, some of which include chemical analysis of runoff. The data show that levels of nitrogen and phosphorus species in green roof runoff by different authors are quite variable, in part due to different roof characteristics.

The primary objective of this project is to compare the concentrations of chloride (Cl\textsuperscript{−}), sulfate (SO\textsubscript{4}\textsuperscript{2−}), and nitrate (NO\textsubscript{3}\textsuperscript{−}) in fresh precipitation and in rainwater that has passed through a large, extensive green roof. A second objective is to explore the reasons for these changes. Chemicals such as sulfate and nitrate, which contribute to acid deposition, are especially

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important. Excess nitrogen in the runoff can have an adverse effect on the receiving waters by enhancing algae growth and eutrophication. The roof used in this study is on the Onondaga County Convention Center (OnCenter) in Syracuse, NY.

**METHODS**

The green roof, installed in 2011, is 0.56 hectares with growth medium 7.6 cm deep planted with six types of sedum. There are 25 roof drains, and samples are collected from a pipe connected to eight of these drains. Precipitation is collected on the roof of the Biological Research Laboratories on the Syracuse University campus, about 1.6 km east of the green roof. Sample bottles are secured in a wooden frame with funnels. Field blanks are obtained at each location. All samples are analyzed for chloride, sulfate, and nitrate using an ion chromatograph (IC). No fertilizer or other chemicals have been added to the roof since it was installed in 2011, although characteristics of the growth medium have undoubtedly changed over time. Only limited chemistry data from runoff were obtained prior to 2017.

**RESULTS**

Figure 1. a, b, c shows average net concentrations for Cl\(^-\), SO\(_4\)^{2-}, and NO\(_3\)^- in the precipitation and green roof runoff. Each bar represents a separate rain event from 2014 to 2017.

**DISCUSSION**

Figure 1a shows that chloride concentrations in the runoff are usually equal to or greater than concentrations in the incoming rain. In storms 4/15/2017 and 7/20/2017, the opposite is observed, but the number of samples in these storms is small. The reason for the high chloride concentration in runoff on 6/4/2017 is unknown. This concentration is not likely due to contamination, as all three samples of runoff show similar high concentrations.

Sulfate concentrations shown in Figure 1b are consistently significantly higher in the runoff than in the precipitation. The data support the green roof being a source of sulfate. Investigations of the source of this sulfate are underway.

The nitrate concentrations from the runoff represented in Figure 1c show no dominant pattern when compared to the rain concentrations. About half of the rain events have runoff concentrations greater than precipitation, while the other half of the runoff concentrations are less than those in precipitation.

The highest nitrate concentration in runoff occurs on 8/3-4/2017. The precipitation data shown in the graph is an average of five samples, one from an event on 8/3 and four from an event on 8/4. The storm on 8/3 had a nitrate concentration of 5.7 mg/L, while the storm on 8/4 had a concentration of 1.4 mg/L. The first storm had an intensity of 15.6 mm/hr and lasted for 10 minutes, a brief but intense cloudburst. In contrast, the second storm the next day had an intensity of 2.4 mm/hr and lasted two hours. The differences in concentrations in the precipitation from these storms is notable.

No runoff from the green roof occurred during the cloudburst on 8/3, as the total rainfall was only 2.6 mm. However, runoff occurred the next day when the total rainfall reached 4.6 mm. The concentration in the runoff averaged 5.0 mg/L, much greater than the concentration in the rain on that day. The runoff on 8/4 most likely included some of the high concentration rain on 8/3. Hence one cannot conclude that the nitrate in the growth medium was responsible for the elevated levels in runoff on 8/4.
Figure 1. Average concentrations of chloride, sulfate, and nitrate, measured in precipitation and green roof runoff from selected storms. Error bars show one standard deviation from the mean. Each bar represents the average of the indicated number of samples, ranging from 1 to 24.
Johnson and Davidson (2017) note that fertilizer was applied to the green roof at the time of its installation in 2011. It is not known whether the nitrate concentrations in Figure 1c were influenced by this fertilizer. However, it is of interest that events on 6/25/14, 9/9/15, and many events in 2017 had runoff nitrate levels less than those in incoming rain. Rowe (2011) reports high nutrient concentrations in green roofs that have been fertilized. Age of green roof and vegetation type can factor in to the leeching of nitrate into the runoff (Czemiel Berndtsson, 2010).

Comparing patterns for the three analytes in Figure 1 shows that the storm on 4/15/2017 is unique in that concentrations in precipitation exceeded those in runoff for all three analytes. Further investigation of this event is underway.

Data collection is continuing and will expand to include other chemicals in future work. Arrangements are also being made to sample a nearby traditional roof as a control.

CONCLUSIONS
Concentrations of chloride, sulfate, and nitrate in fresh precipitation and runoff from a green roof in several events show a number of patterns. Concentrations of chloride in the runoff are generally equal to or greater than levels in the incoming rain. The same is true for sulfate. However, concentrations of nitrate showed more complex results: nitrate levels in runoff exceeded levels in rain for roughly half of the events, while the opposite was observed for the other half. One especially intense storm produced the highest levels of nitrate in rain observed throughout the study; runoff from a storm the next day most likely included some of the previous day’s rainwater and showed similarly high concentrations. Chemical analysis of rain and runoff will continue in future work.

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