CONTAMINATION OF URBAN SURFACE WATER BY VEHICLE EMISSIONS

Final Report

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16. Abstract

Combined sewer overflows (CSOs) are a water management issue for Onondaga County and the city of Syracuse, NY. To reduce them, the County is investing in green infrastructure (GI). GI technologies such as green roofs, rain gardens, and bioswales are designed to reduce runoff from impervious urban surfaces, which can decrease the number of CSO events. However, effects of GI on the amount of pollutants in the runoff remain unknown. Thus, the objective of this research is to assess the impact on the water chemistry of installing green roofs and other GI in Syracuse as a means to reduce stormwater runoff. This will also involve experimental studies with atmospheric deposition to quantify pollutants in the water originating from the ambient air due to emissions from construction projects and automobiles. Current work is targeted towards the green roof on downtown Pirro convention center and an adjacent traditional roof on the War Memorial. Both of these roofs have easily accessible drains that allow for runoff sampling during rainstorms. In addition, precipitation barrels are set up concurrently to sample for precipitation. These are taken back to the laboratory for analysis of anions, specifically chloride, fluoride, carbonate, phosphate, and sulfate concentrations using ion chromatography (IC). Eight storms spanning from June-September 2014 have been sampled. The specific dates are 6/17, 6/25, 7/3, 7/14, 7/23, 8/31, 9/13, and 9/21. Runoff samples have been collected for the latter seven storms from the traditional roof. Results show that average concentrations for each anion vary from storm to storm. Sulfate and nitrate have the highest average concentrations in runoff from the roof for each storm. The average concentration of fluoride does not exceed 5 umol/L for all storms. Average phosphate concentrations are less than the method detection limit (MDL) in runoff.

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This report summarizes the work conducted by the authors at Syracuse University for the TranLive Project "Contamination of Urban Surface Water by Vehicle Emissions". The overall goal of this project was to develop and test methods for determining the amount of airborne contaminant particles depositing in cities and contributing to water pollution, focusing on chemical species emitted from motor vehicles. Previous work on this topic has been hampered by the challenges in estimating deposition of contaminants from the atmosphere in cities, where aerodynamics are complex and modeling results are highly uncertain. The approach taken in this project was to develop a new and more accurate method for experimentally determining atmospheric deposition of each contaminant of interest. The method would then be used with several other types of samples to quantify the various mechanisms that contribute vehicle-emitted contaminants to surface water.

There are several ways airborne contaminants from vehicles can get into surface water in cities. Rain contains some of these contaminants, acquiring them through in-cloud scavenging during formation of cloud droplets. Some of these contaminants serve as nuclei, and thus are incorporated into rain when cloud droplets come together to form raindrops. Other contaminants are scavenged as wind carries them through clouds and the particles collide with the droplets. In addition, contaminant particles can be scavenged by raindrops as they fall to the earth's surface. All of these mechanisms together are responsible for wet deposition, and it is quantified by taking the concentration in rain (ug/Liter) and multiplying it by the total liters of rain falling in a given area over the time period of the storm.

Another way contaminants can get into surface water is through dry deposition. This is more difficult to quantify. Dry deposition refers to many mechanisms by which particles reach surfaces, which can involve several steps. Aerodynamic transport refers to particles carried by the wind from the atmosphere into the boundary layer just above the surface. Once they are close to the surface, particles must traverse the boundary layer of relatively quiescent air to come into contact with the surface. This can occur by such mechanisms as Brownian diffusion, turbulent bursts in the boundary layer, inertial deposition, impaction, and settling by gravity. Diffusiophoresis, thermophoresis, and electrostatic forces can also play a role. After a particle comes into contact with the surface, it can stick or it can be entrained back into the airflow. In some cases, particles may undergo several re-entrainments before finally coming to rest on a surface.

Most measurements of dry deposition have been conducted over fields of vegetation where there is adequate fetch (upwind distance) so that steady-state conditions have been achieved. Several mathematical models for dry deposition to different types of vegetation have been developed, and they are often used to estimate deposition to large areas of uniform vegetative canopies. Examples include deciduous forests, coniferous forests, natural grassland, and agricultural fields. In contrast to large expanses of vegetation, deposition to surfaces in cities cannot be estimated reliably. The aerodynamic complexity of cities prevents reliable modeling, and the variation in building shapes and sizes in a city makes it difficult to account for boundary layer transport. Unfortunately, estimating contamination of surface water in cities requires a way to estimate dry deposition, since rainstorms can wash deposited particles off surfaces and into storm sewers or bodies of water.

Several innovations have been incorporated to account for the dry deposition component of particle transport to surface water in cities. The Principal Investigator of the project previously developed a means of measuring dry deposition to controlled surfaces using symmetric airfoils (two U.S patents issued). These devices enable turbulence to be minimized over the surface so that a reliable lower limit to deposition onto natural surfaces can be obtained. These airfoils have been used in Western U.S. cities where long periods of dry weather enable enough material to accumulate to permit chemical analysis. It was discovered that the airborne concentrations of contaminant particles in the city of Syracuse were too small to enable reliable deposition measurements in short periods between rainstorms. As a result, it was necessary to develop a much larger surface to permit measurements over periods of 2-3 days. A considerable effort went into experimenting with different artificial surfaces to arrive at a final design that appears to work well. This is a 4-foot diameter circular disk made of 1/8 inch thick high density polyethylene coated with a 1-mil FEP Teflon film. The disk is positioned horizontally on a metal stand coated with epoxy paint to prevent corrosion which would produce contaminant particles. Two such disks are positioned a few meters apart so that replication can be obtained, thus demonstrating reliable data.

A few experiments were conducted to compare the airfoil deposition with deposition onto the disks. Preliminary results suggest that the disks can be reliably used to estimate a lower limit to deposition, just like the airfoils, although deposition to the disks is usually slightly smaller than that to the airfoils. Experiments were also conducted by isolating different regions of the disk surface to show that deposition to the disks is most likely uniform over the surface. This greatly simplifies collecting the samples and interpreting the results.

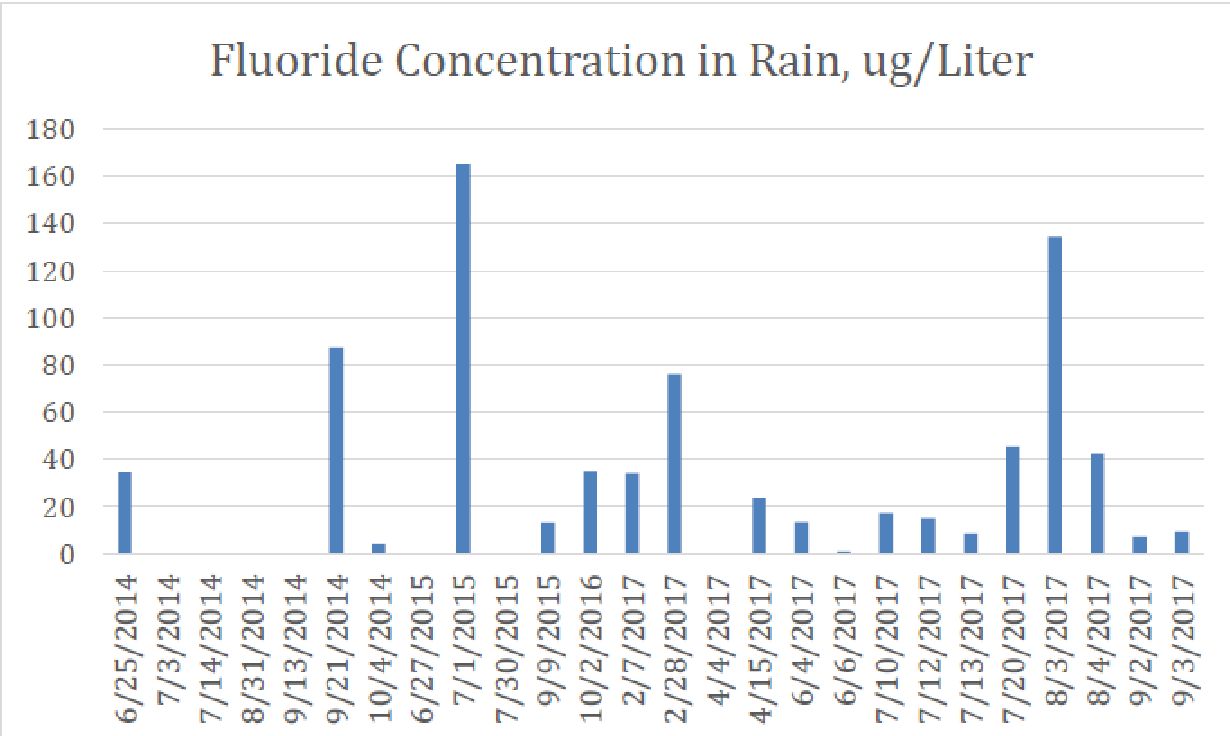
Experiments were also conducted to examine rain washoff of deposited particles from a vegetated surface (a large green roof on the Onondaga County Convention Center) and from a smooth traditional roof surface (a roof of roughly the same size on the War Memorial Arena across the street from the green roof). The experiments on the green roof show that infiltration of rainwater through the growth medium has a marked effect on the chemical contaminants in the runoff, although rainwater draining from the roof of the War Memorial are likely to be useful to estimate dry deposition onto that traditional roof. The concentrations in War Memorial roof drainage are initially high at the beginning of a storm ("first flush" sampling), then decrease down to the concentration in the rain. Sampling roof drainage is thus likely to become a new and fairly simple way to estimate dry deposition to buildings in a city.

Several representative graphs of anion data are shown in the Figures below. The graphs show concentrations of several anions in rain as well as concentrations of the same chemical species in runoff from the green roof. Note that for the four species fluoride, chloride, sulfate, and nitrate, concentrations in the green roof runoff are generally much greater than those in the rain. This is most likely due to chemical additives to the growth medium and roof membrane.

Representative graphs of data for two trace metals are also shown. The copper and lead data are for rain, control roof runoff (War Memorial traditional roof), and green roof runoff. The copper concentrations are enhanced in the green roof runoff, probably due to additives in the growth medium, while the lead concentrations are decreased relative to rain.

A wealth of deposition data are also available, using the disks as a controlled surface. By comparing the chemical concentrations in rain with the concentrations from dry deposition, estimates of the relative importance of wet and dry deposition are being made. Most of the runoff from the city of Syracuse ends up in Onondaga Lake, which has a long history of contamination from industry. Due to extensive cleaning efforts over the past two decades, Onondaga Lake is now much cleaner, but contaminants contributed by vehicle emissions are now a primary concern. The new methods developed here are being used to estimate the inputs to the Lake.

One peer reviewed manuscript has been prepared for the International Conference on Sustainable Infrastructure in October 2017. The paper is attached to this summary. The paper indicates that trace metals as well as anions have been measured in wet and dry deposition using the new methods developed here, although only a small fraction of the available data are shown. The results are in the process of being written for other conferences and for journal publication.


Fluoride Concentration in Rain, ug/Liter
180
160
140
120
100
80
60
40
20
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/28/2017
4/4/2017
4/15/2017
6/4/2017
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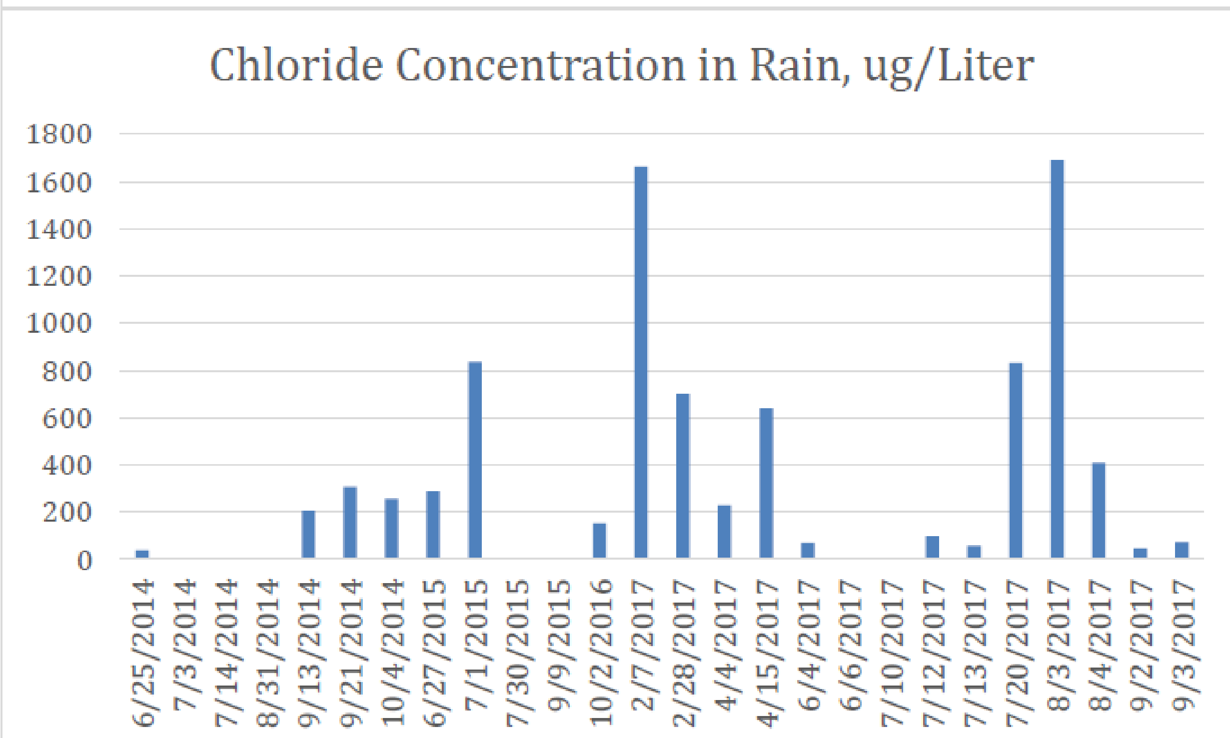
9/2/2017
9/3/2017


Chloride Concentration in Rain, ug/Liter
1800
1600
1400
1200
1000
800
600
400
200
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/28/2017
4/4/2017
4/15/2017
6/4/2017
6/6/2017
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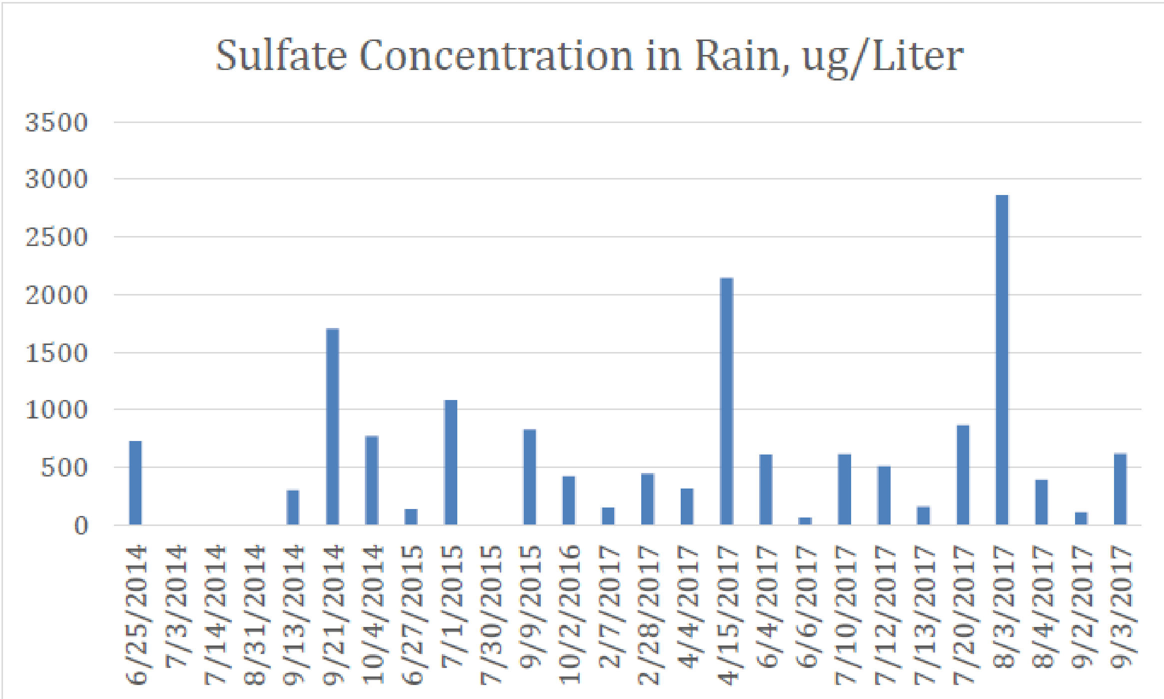
9/2/2017
9/3/2017


Sulfate Concentration in Rain, ug/Liter
3500
3000
2500
2000
1500
1000
500
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/28/2017
4/4/2017
4/15/2017
6/4/2017
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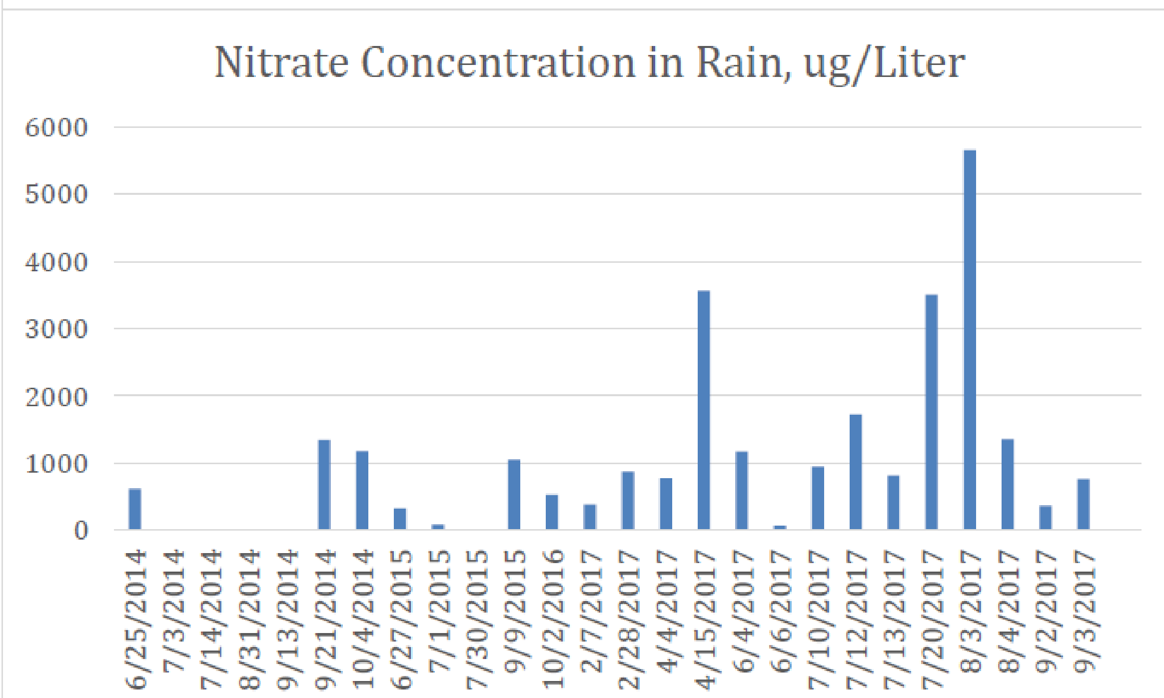
8/4/2017
9/2/2017
9/3/2017


Nitrate Concentration in Rain, ug/Liter
6000
5000
4000
3000
2000
1000
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/28/2017
4/4/2017
4/15/2017
6/4/2017
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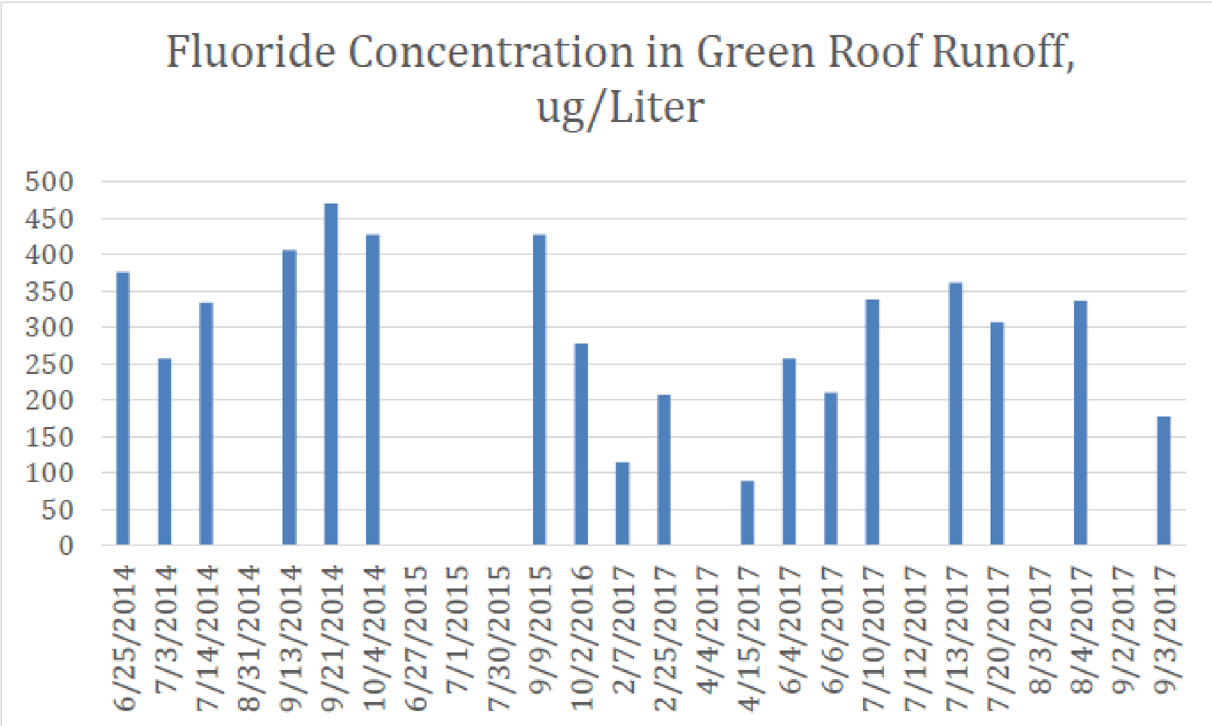
9/2/2017
9/3/2017


Fluoride Concentration in Green Roof Runoff, ug/Liter
500
450
400
350
300
250
200
150
100
50
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/25/2017
4/4/2017
4/15/2017
6/4/2017
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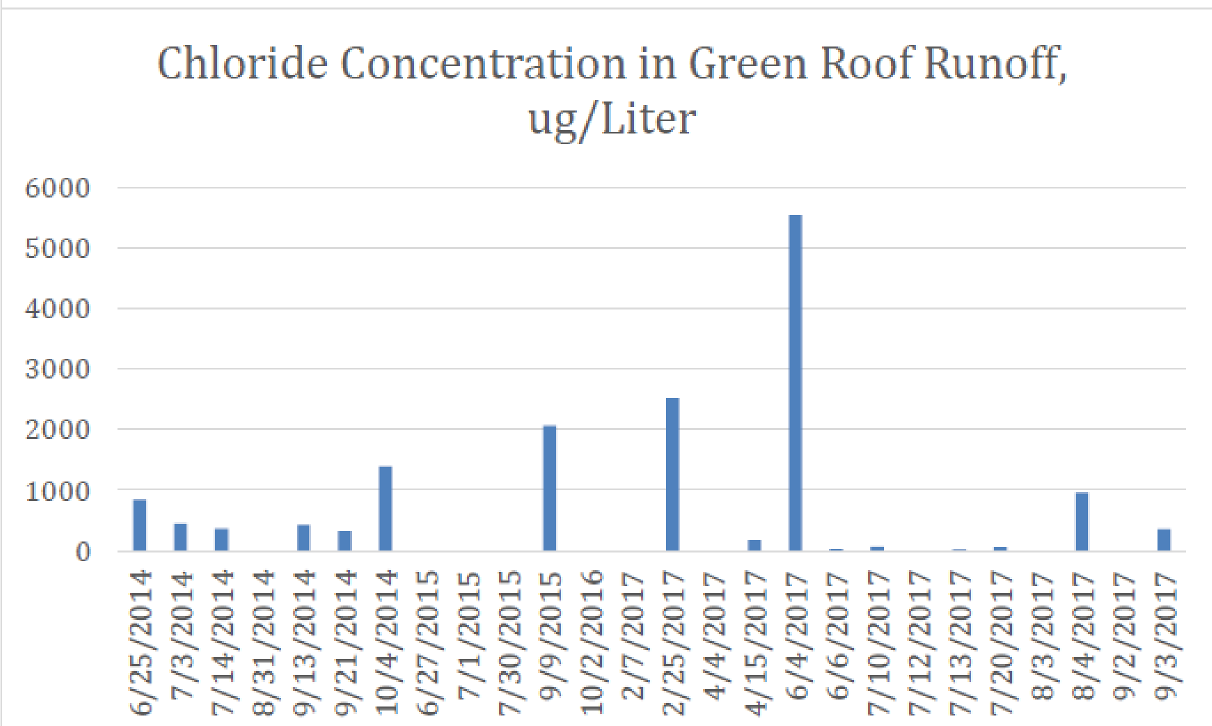
9/2/2017
9/3/2017


Chloride Concentration in Green Roof Runoff, ug/Liter
6000
5000
4000
3000
2000
1000
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/25/2017
4/4/2017
4/15/2017
6/4/2017
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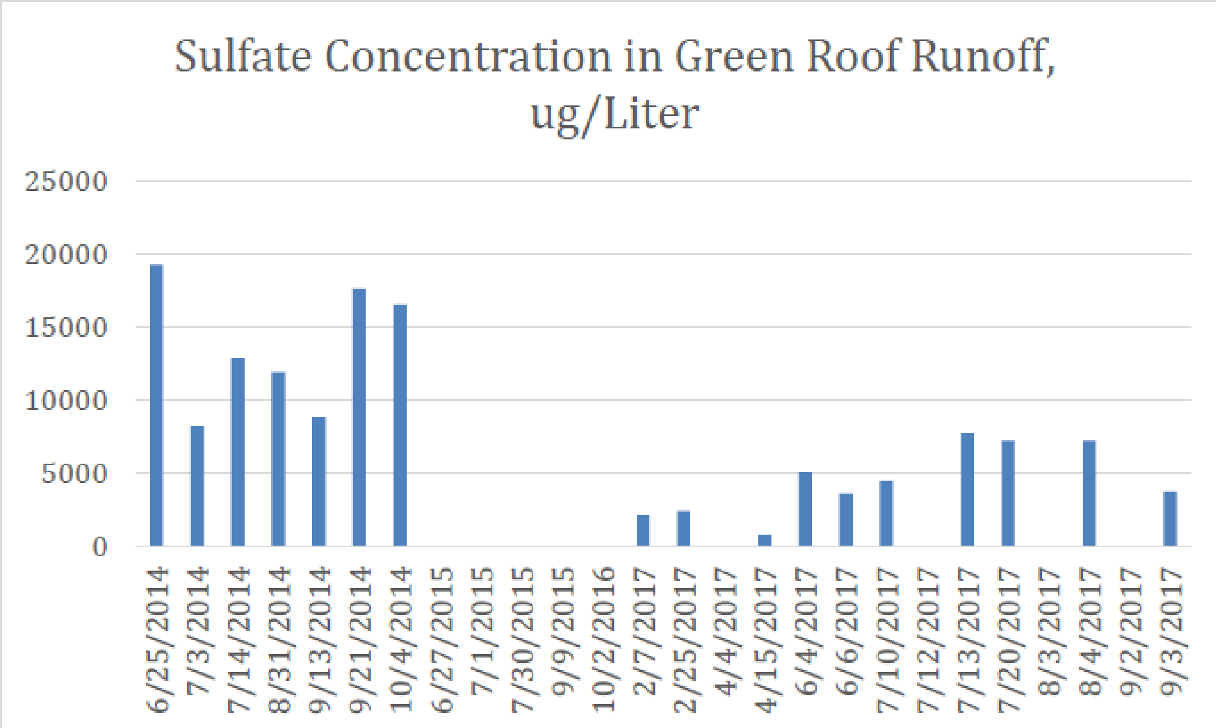
9/2/2017
9/3/2017


Sulfate Concentration in Green Roof Runoff, ug/Liter
25000
20000
15000
10000
5000
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/25/2017
4/4/2017
4/15/2017
6/4/2017
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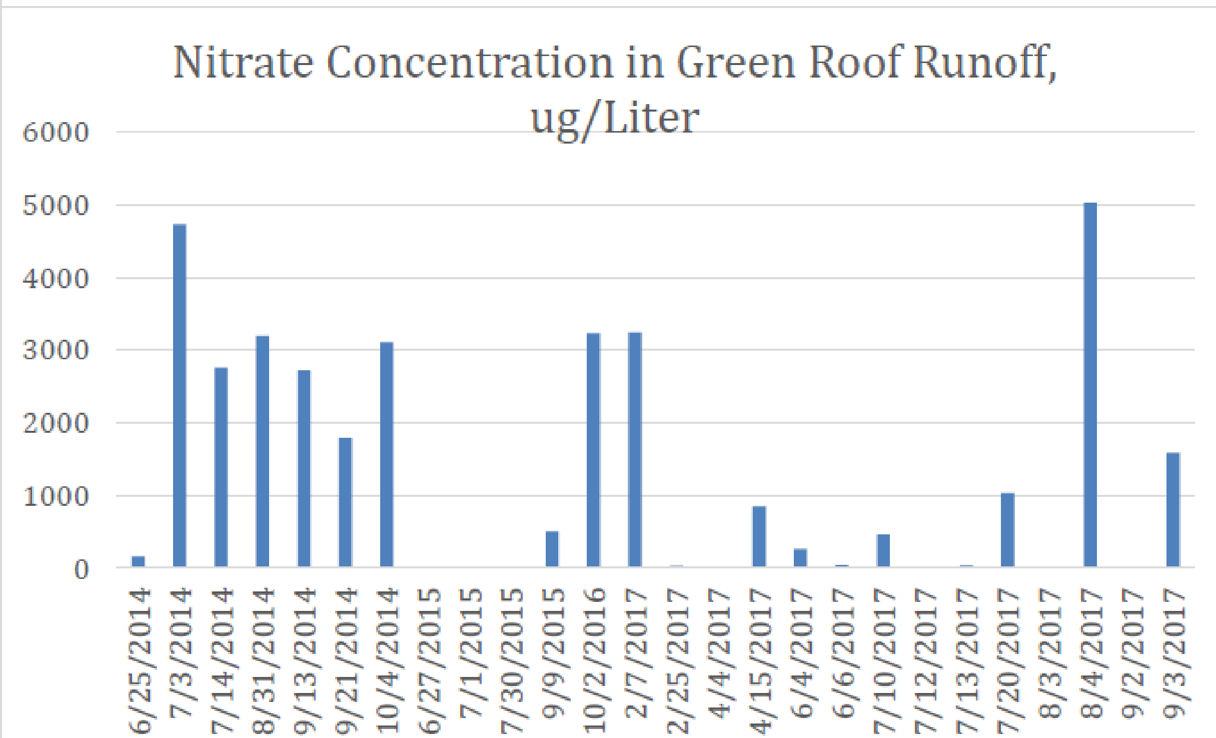
8/4/2017
9/2/2017
9/3/2017


Nitrate Concentration in Green Roof Runoff, ug/Liter
6000
5000
4000
3000
2000
1000
0
6/25/2014
7/3/2014
7/14/2014
8/31/2014
9/13/2014
9/21/2014
10/4/2014
6/27/2015
7/1/2015
7/30/2015
9/9/2015
10/2/2016
2/7/2017
2/25/2017
4/4/2017
4/15/2017
6/4/2017
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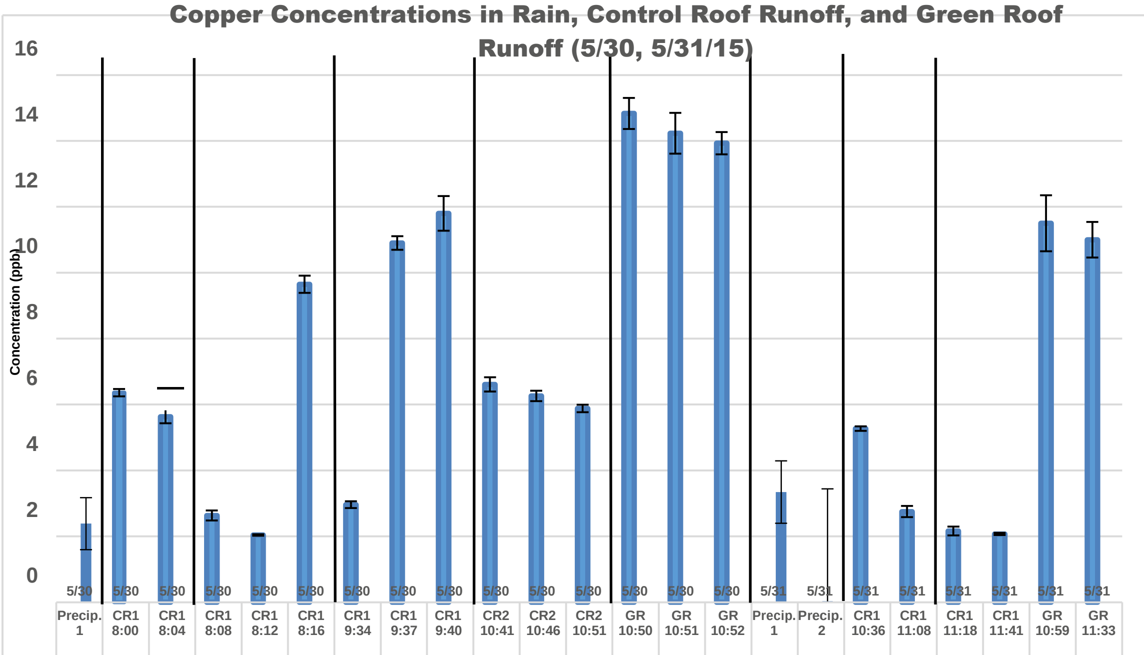
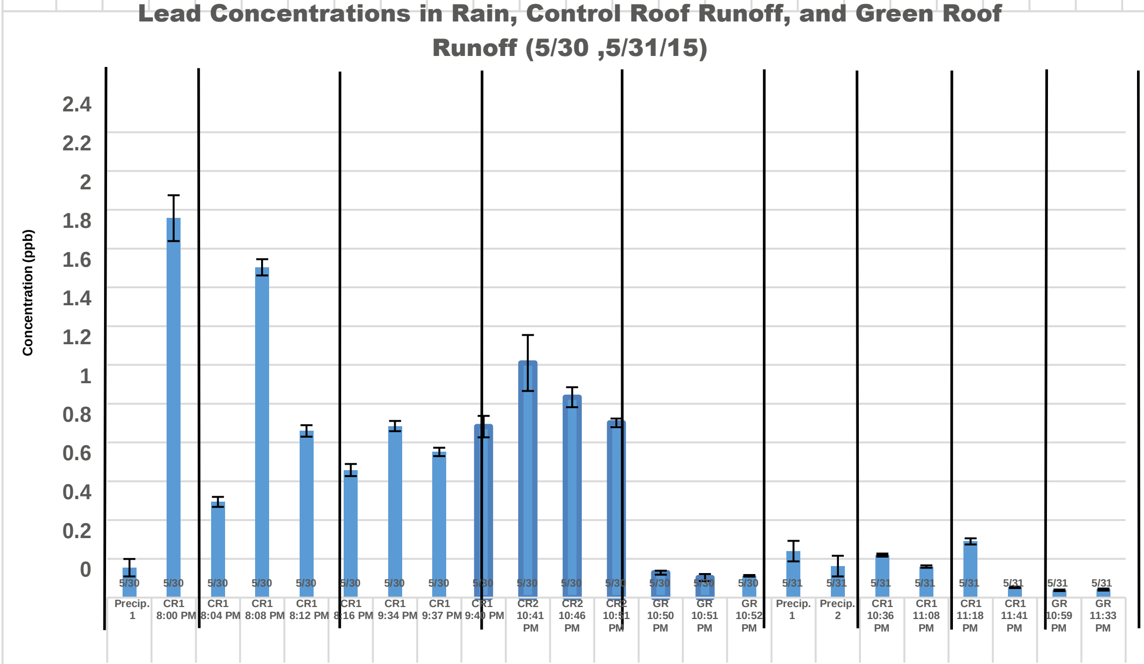
9/2/2017
9/3/2017


Copper Concentrations in Rain, Control Roof Runoff, and Green Roof Runoff (5/30, 5/31/15)
Concentration (ppb)
0
2
4
6
8
10
12
14
16
5/30 Precip. 1
5/30 CR1 8:00
5/30 CR1 8:04
5/30 CR1 8:08
5/30 CR1 8:12
5/30 CR1 8:16
5/30 CR1 9:34
5/30 CR1 9:37
5/30 CR1 9:40
5/30 CR2 10:41
5/30 CR2 10:46
5/30 CR2 10:51
5/30 GR 10:50
5/30 GR 10:51
5/30 GR 10:52
5/31 Precip. 1
5/31 Precip. 2
5/31 CR1 10:36
5/31 CR1 11:08
5/31 CR1 11:18
5/31 CR1 11:41
5/31 GR 10:59
5/31 GR 11:33


Lead Concentrations in Rain, Control Roof Runoff, and Green Roof Runoff (5/30 ,5/31/15)
Concentration (ppb)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
2.4
5/30 Precip. 1
5/30 CR1 8:00 PM
5/30 CR1 8:04 PM
5/30 CR1 8:08 PM
5/30 CR1 8:12 PM
5/30 CR1 8:16 PM
5/30 CR1 9:34 PM
5/30 CR1 9:37 PM
5/30 CR1 9:40 PM
5/30 CR2 10:41 PM
5/30 CR2 10:46 PM
5/30 CR2 10:51 PM
5/30 GR 10:50 PM
5/30 GR 10:51 PM
5/30 GR 10:52 PM
5/31 Precip. 1
5/31 Precip. 2
5/31 CR1 10:36 PM
5/31 CR1 11:08 PM
5/31 CR1 11:18 PM
5/31 CR1 11:41 PM
5/31 GR 10:59 PM
5/31 GR 11:33 PM

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Chemistry of Stormwater Runoff from a Large Green Roof in Syracuse, NY

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Abstract
A green roof can provide a wide variety of ecological benefits in urban environments such as reducing the amount of stormwater runoff. In addition, the growth medium may filter contaminated rainwater, providing runoff that is cleaner than the incoming rain. However, the growth medium might contribute other contaminants, thereby increasing the concentration relative to the rainwater. Thus, field experiments are needed to determine which contaminants are filtered out and which are leached from the growth medium during large rainstorms. It is also possible that some contaminants deposited from the atmosphere are picked up by the runoff.

To investigate these issues, we determined the chemistry of stormwater runoff from two adjacent rooftops: a 1.5 acre extensive green roof on the Onondaga County Convention Center and a similarly sized gray roof on the War Memorial Sports Arena, both located in downtown Syracuse, New York. We assumed that the same atmospheric contaminants depositing on the green roof are also depositing on the gray roof. This allowed us to compare concentrations of chemical species in the rain, green roof runoff, and gray roof runoff to determine which contaminants are contributed by the rain, by leaching from the growth medium, and by atmospheric deposition. Results from storms sampled in 2014, 2015, and 2016 suggest that sulfate and copper are leached from the growth medium while lead is filtered. Additional experiments will be conducted to better understand the leaching potential of the green roof.

Introduction
Urbanization has replaced natural vegetation with impervious surfaces, such as building roofs, streets, and parking lots that do not absorb incoming rainwater. Instead, the incoming rainwater flows over these surfaces as stormwater runoff and reaches storm sewers. Stormwater runoff can pick up contaminants from these surfaces including soil particles, pollutants, and pathogens. After entering the sewers, the stormwater flows to a local wastewater treatment plant. However, in

combined sewers where stormwater and raw sewage flow in the same pipes, the mixture may exceed the capacity of the treatment plant. The untreated mixture must then be discharged directly into the receiving water body as combined sewer overflow.

Green infrastructure, including green roofs, is installed to reduce stormwater runoff, potentially reducing the loads of contaminants from entering storm sewers and natural water bodies. Many studies have evaluated the capabilities of green roofs to reduce stormwater runoff, but there are far fewer studies on whether green roofs are capable of removing contaminants from stormwater. A few studies have demonstrated that green roofs may retain heavy metals originating from wet deposition such as copper (Cu) and zinc (Zn) (Gnecco et al. 2013; Steusloff, 1998). However, certain materials in the growth medium and/or in the drainage pipes may be leached, and therefore contribute metals into runoff. For example, presence of water-soluble copper-based fertilizers in the growth medium may result in leaching of copper in the runoff (Gregoire et al. 2011). Other studies have found high concentrations of nitrate (NO_3^-) and phosphate (PO_4^{3-}) in green roof runoff (Gregoire et al. 2011; Hathaway et al. 2008). It should be emphasized that since green roofs are able to retain incoming precipitation, the total export of these contaminants in green roof runoff may be lower in comparison to that in runoff from gray roofs.

The purpose of this study is to compare concentrations of inorganic anions and trace metals in runoff samples collected from both an extensive green roof and an adjacent gray roof in downtown Syracuse, New York. This is to determine which contaminants in rainfall are retained within the green roof growth medium and which are leached from it during rainstorms.

<u>*Site Descriptions*</u>

Figure 1 shows the extensive green roof located on the Nicholas J. Pirro Convention Center in downtown Syracuse, New York. The depth of the growth medium is 7.6 cm (3 inches), and the surface area of the roof is 0.56 hectares (1.5 acres). The roof was installed in 2011, and during this time, fertilizers of unknown composition were added. On the roof, there are 8 drain pipes that connect to a single pipe where stormwater is sampled inside the building. Figure 2 depicts the east side of the gray (control) roof on the War Memorial Sports Arena. Samples are taken from a drain pipe connected to the roof.

Figure 1: South view of the Oncenter green roof in late June.

Fresh precipitation was collected on the quad of Syracuse University (SU) prior to the 10/2/16 storm (Figure 3). Large trash barrels were deployed with the lids cut at the centers where funnels were positioned to collect rainwater. Plastic tubing was used to connect each funnel to a sample bottle, which was secured inside the barrel. For the 10/2/16 storm, precipitation was collected on the roof of the Biological Research Laboratories (BRL) on the SU campus. Bottles were secured in a wooden apparatus with funnels attached to increase the surface area of collection. The apparatus is shown in Figure 4.

Figure 2: Section of War Memorial roof viewing toward Southwest.

Experimental Design

There were 6 rainstorms analyzed for contaminants in fresh precipitation ("Precip."), control roof runoff ("CR Pipe"), and green roof runoff ("GR Pipe") from 2014-2016. Sample sizes and the number of field blanks prepared were different across rainstorms as seen in Table 1 due to numerous constraints on equipment and logistics.

Field blanks for precipitation collection were prepared before the rain began. However, blanks for the control and green roofs were sometimes prepared before and during active rainfall. Before sampling from both roofs, old water that had accumulated in pipes from previous rainstorms was drained. Precipitation and control roof runoff were collected during active rainfall but not necessarily simultaneously. In addition, no first flush samples were

Figure 3: Precipitation sampling on SU quad.

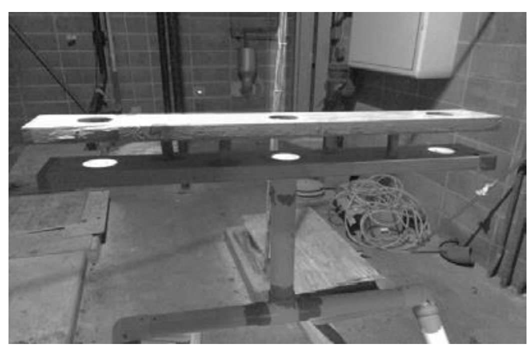


Figure 4: Precipitation sampler used for 10/2/16 rainstorm.

collected from the control roof. Also, sampling of green roof runoff was delayed to allow the roof to become saturated. Therefore, there were a few storms where sampling from the green roof occurred after it stopped raining.

Sulfate (SO_4^{2-}) and nitrate were analyzed in samples collected in the rainstorms on 6/25/14, 9/21/14, 9/9/15, and 10/2/16. Copper and lead were analyzed in samples collected in storms on 5/30/15, 5/31/15, and 9/9/15. After collection, samples and field blanks were brought back to the laboratory and were stored at 5 ˚C until analyzed. Sulfate and nitrate were analyzed using ion chromatography (IC) while copper and lead were analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

The same general data analysis procedure was used for each event. For each sample type and analyte, the average concentration in the blanks was computed along with the standard deviation. The average blank concentration was subtracted from each sample concentration, and an average of these "net" values was then computed along with the standard deviation. For each individual sample, the standard deviation was computed by compounding the standard deviation values of the blank and original sample concentrations. All calculations were performed in Microsoft Excel.

A variation of this procedure was used for the 9/9/15 rainstorm for the control roof. Sampling was conducted six times over a one hour period. After correcting for blank levels, the two "CR Pipe" samples collected at each time interval were averaged. The six resulting values were then averaged again to obtain the value that is reported in this paper along with the standard deviation.

Table 1: Number of field blanks and number of samples for each storm. As mentioned in the text, the samples refer to those analyzed by ICP for some storms and by IC for other storms except for 9/9/15, which had both.

Storm	Precip Blanks	Precip Samples	CR Pipe Blanks	CR Pipe Samples	GR Pipe Blanks	GR Pipe Samples
6/25/14	1	2	2	6	2	6
9/21/14	4	4	3	6	3	3
5/30/15	4	3	3	8	2	3
5/31/15	3	2	1	4	0	2
9/9/15	3 IC 3 ICP	3 IC 3 ICP	3 IC 3 ICP	12 IC 12 ICP	2 IC 2 ICP	3 IC 6 ICP
10/2/16	3	3	3	3	3	6

Preliminary Analysis

Average net concentrations of SO_4^{2-} and NO_3^- are shown in Figures 5 and 6, respectively. Concentration in µg/L is plotted on the y-axis. The error range on each bar is the standard deviation (i.e. analytical uncertainty in the measurement) as discussed in the previous section.

From Figure 5, it is clear that the average sulfate concentrations are much higher in the runoff from the green roof (by roughly an order of magnitude) compared to that in the precipitation and control roof runoff. Therefore, the green roof appears to be a source of sulfate for reasons not yet investigated. One hypothesis is that the sulfate is leached from fertilizer in the growth medium, but the composition of the fertilizer has yet to be studied. It is also evident that the concentrations in the precipitation and control roof runoff are comparable. Thus, the control roof (surface, pipes, fittings, etc.) does not significantly contribute contamination of the runoff, assuming that all sulfate in the falling rain reaches the roof surface, which is washed off completely during the storm. It is hypothesized that the slightly greater concentrations of SO_4^{2-} in the control roof runoff may originate from dry deposition of sulfate particles prior to the rainstorm, although more data are needed to verify this.

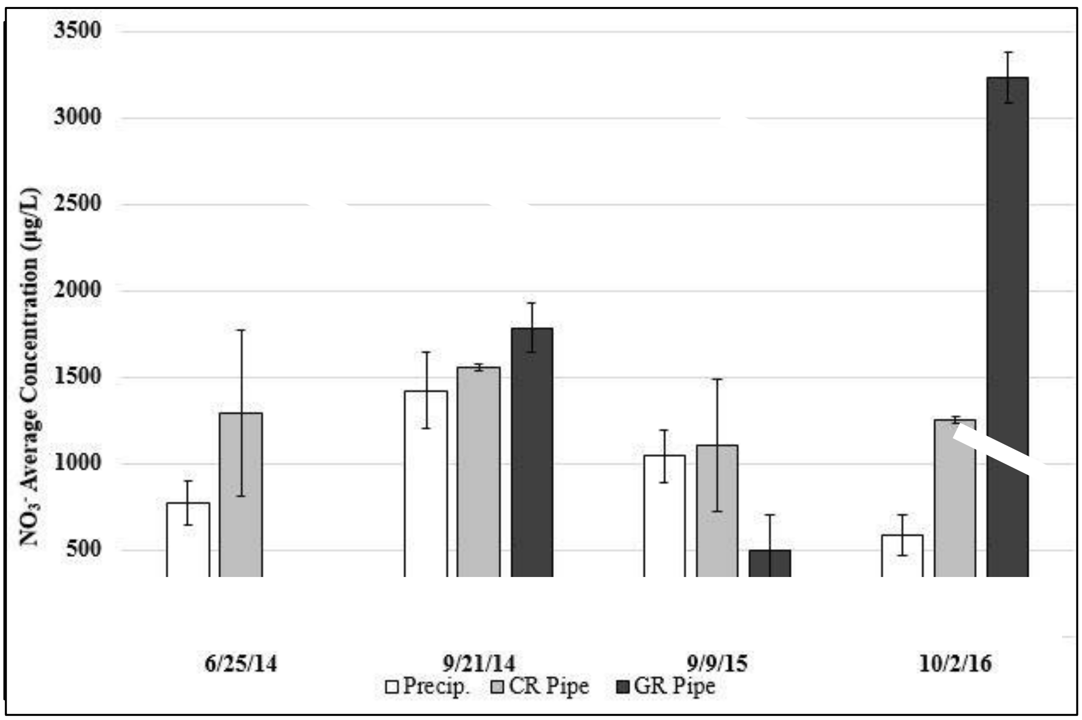


Figure 6: Average net NO_3^- concentrations in "Precip.," "CR Pipe," and "GR Pipe" samples.

Table 2: Average net Cu concentrations in “Precip.,” “CR Pipe”, and “GR Pipe” samples

Cu Conc. (µg/L)	Precip.		CR Pipe		GR Pipe	
Date	**Avg.**	**σ**	**Avg.**	**σ**	**Avg.**	**σ**
5/30/2015	2.39	0.79	6.5	3.88	14.33	0.46
5/31/2015	3.34	3.41	3.06	1.5	11.25	0.35
9/9/2015	1.03	0.38	7.46	0.65	14.93	0.19

Table 3: Average net Pb concentrations in “Precip.,” “CR Pipe,” and “GR Pipe” samples.

Pb Conc. (µg/L)	Precip.		CR Pipe		GR Pipe	
Date	**Avg.**	**σ**	**Avg.**	**σ**	**Avg.**	**σ**
5/30/2015	0.78	0.045	1.02	0.52	0.12	0.013
5/31/2015	0.24	0.053	0.18	0.1	0.04	0.003
9/9/2015	0.17	0.009	0.44	0.1	0.11	0.005

On the other hand, the average nitrate concentrations in the green roof runoff do not show a consistent trend in Figure 6. Concentrations in samples collected from 6/25/14 and 9/9/15 suggest that the green roof is a sink for nitrate, but those from 9/21/14 and 10/2/16 suggest that it is a source. One would expect decreasing concentrations over time after the initial fertilization, but this is not apparent within the dataset. As with sulfate, the control roof does not appear to be a significant source of nitrate.

The average net concentrations for Cu and Pb are shown in Table 2 and Table 3, respectively. The analytical uncertainties are also included in both tables. For all rainstorms, Cu concentrations were higher in the green roof runoff compared to those in the precipitation and the control roof runoff. Thus, the green roof appears to be a source of Cu. On the other hand, the green roof appears to be a sink for Pb, as concentrations in the green roof runoff are lower. It is likely that there is net sorption of lead onto particles in the growth medium.

The Cu concentrations in the control roof runoff for 5/30/15 and 9/9/15 are higher than in the precipitation. This suggests that the control roof is also a source of copper. The average concentrations of lead are more comparable. The rainstorm on 5/31/15 followed directly after the one on 5/30/15, and the trace metal concentrations are slightly lower in the control roof runoff than in the precipitation. This may suggest complete washout of particles that deposited during antecedent dry period and may also suggest that negligible additional particles were deposited between the 5/30/15 and 5/31/15 rainstorms.

The high analytical uncertainties in some trace metal concentrations from control roof runoff and precipitation samples should be recognized as this limits the conclusions. However, the uncertainty in the green roof runoff concentrations is quite low, which gives confidence in the observations reported for the green roof.

Conclusions

Average concentrations measured in samples collected from the control roof, green roof, and fresh precipitation from rainstorms in 2014-2016 suggest that the green roof may be a source of SO_4^{2-} and Cu while it may be a sink for Pb. In addition, the concentrations of the analytes are comparable in the control roof runoff and collected precipitation, suggesting that the control roof is neither absorbing nor contributing chemical species to the runoff.

References

Gnecco, I., Palla, A., Lanza, L.G., P., La Barbera. (2013). "The Role of Green Roofs as a Source/sink of Pollutants in Storm Water Outflows." *Water Resour Manage*, 27 (14), 4715-4730.

Gregoire, B.G., and Clausen, J.C. (2011). "Effect of a modular extensive green roof on stormwater runoff and water quality." *Ecol. Eng.*, 37 (6), 963-969.

Hathaway, A.M., Hunt W.F., and Jennings, G.D. (2008). "A field study of green roof hydrologic and water quality performance." *Trans. ASABE*, 51 (1), 37-44.

Steusloff, S. (1998). "Input and output of airborne aggressive substances on green roofs in Karlsruthe." In: Breuste, J., Feldmann, H., Uhlmann, O. (Eds.), *Urban Ecology.* Springer-Verlag, Berlin.

APPENDIX

Deposition and Washoff of Atmospheric Trace Metals and Anions from Two Large Building Roofs

Alex Johnson, Cliff I. Davidson

Department of Civil and Environmental Engineering, Syracuse University

AAAR 35th Annual Conference
October 19, 2016

Background

Urban surfaces (streets, building roofs, etc.) accumulate aerosol dry deposition from atmosphere

Stormwater washes off deposited aerosol

- Stormwater becomes contaminated

Stormwater is discharged to receiving waters, e.g., lakes, rivers, oceans

- Contributes to contamination of these waters

Onondaga Lake

Objectives

Estimate dry deposition of contaminants onto urban surfaces

Estimate wash off by stormwater runoff from building roofs

- Building roofs are a representative urban surface
- Large receptor of dry deposited contaminants

Determine time constants for wash off process

Experimental Methods

Measured airborne concentrations and dry deposition fluxes

Note: no denuder used

Measured contaminant concentrations in fresh precipitation and roof runoff (green roof and control roof)

Conducted analysis for nitrate and sulfate using IC

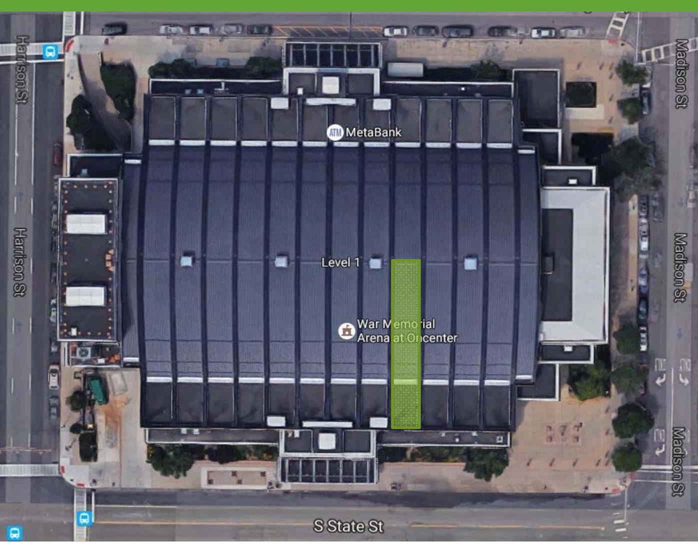
Also consider trace metals using ICP-MS

Dry Deposition Site on SU Campus

Control Roof on War Memorial Hockey Arena

Size: 1.3 acres

Source: Google Maps



Green Roof on Convention Center

Size: 1.5 acres

Plantings: Six varieties of sedum

Soil Thickness: 3 inches

Data Needed for Model Example

Dry deposition flux, duration of antecedent dry period

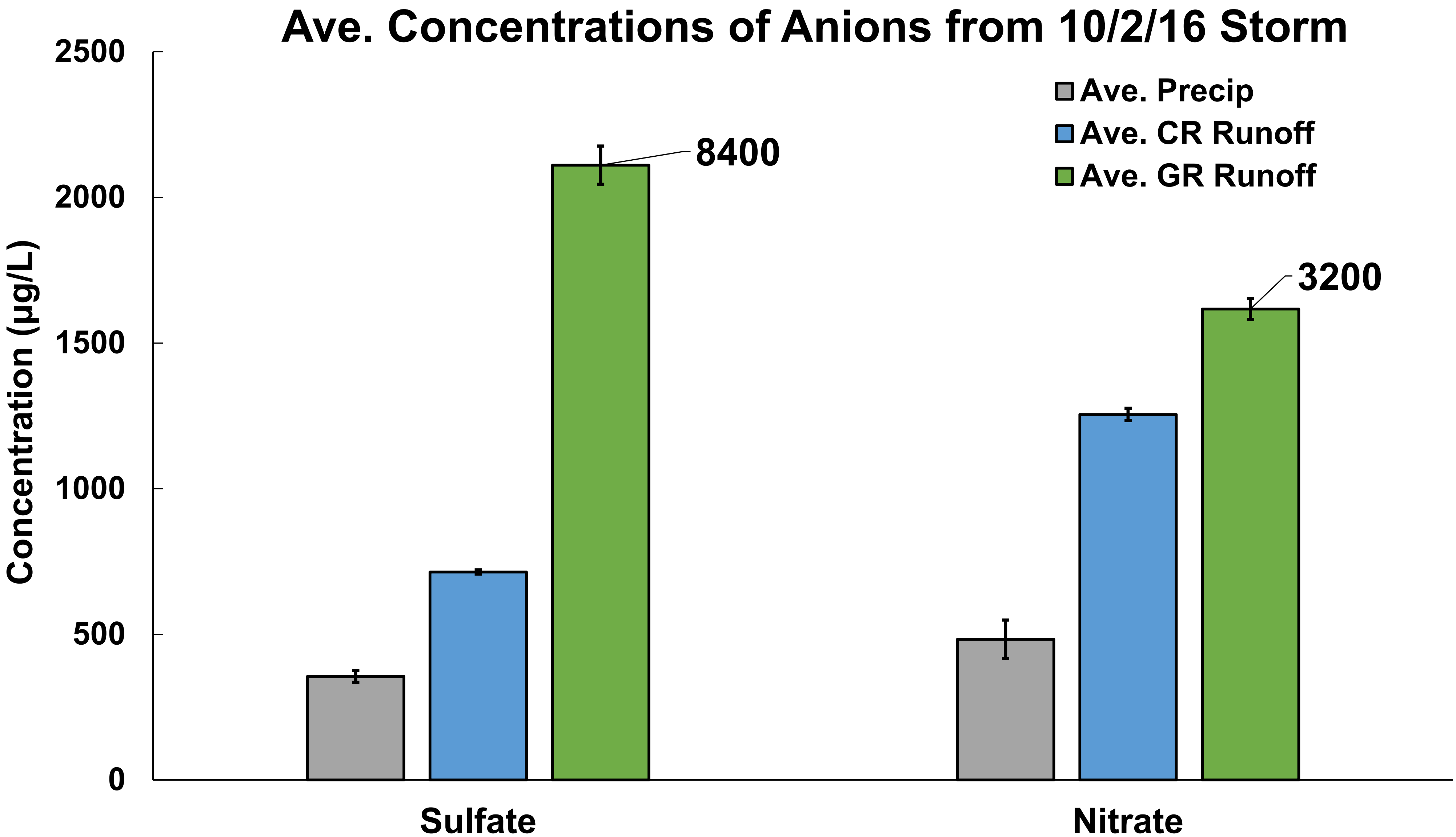
Precipitation amount & concentration, duration of storm

Volume of runoff, concentrations in runoff from control roof & green roof

Results from 10/2/16 Storm

Parameter	Sulfate	Nitrate
Airborne Conc. ($\mu g/m^3$)	0.75 +/- 0.32	0.672 +/- 0.2
Dry Deposition Flux ($\mu g/m^2 day$)	77 +/- 6	211 +/- 19
Dry Deposition Velocity (cm/s)	0.12	0.36
Fresh Precip. Conc. ($\mu g/L$)	355 +/- 21	483 +/- 66
Scavenging Ratio (x 10^6)	0.47	0.72

Model Parameters:
Exposure time: 13 days
Total Rainfall: 0.37 inches
Control Roof Area: 230 m^2



Ave. Concentrations of Anions from 10/2/16 Storm
Concentration (µg/L)
2500
2000
1500
1000
500
0
Ave. Precip
Ave. CR Runoff
Ave. GR Runoff
8400
3200
Sulfate
Nitrate

Model Calculations for Control Roof

Compute the amount of contaminant dry deposited prior to storm

M = flux x exposure time x roof area

Develop Mass Balance

Convert precip. & runoff concentrations into mass loads

Compute M - mass in runoff = Remaining mass

Compute time constant

Remaining mass = M x e^{-rt}

Conclusions

Rain can remove dry deposited aerosol from roof surfaces

- Washoff rates are currently being investigated

Need additional data for more realistic modeling

Experiments with comparisons of dry deposition fluxes from the airfoils and disks are currently being conducted

Acknowledgments

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Technical staff in the College of Engineering

Questions?

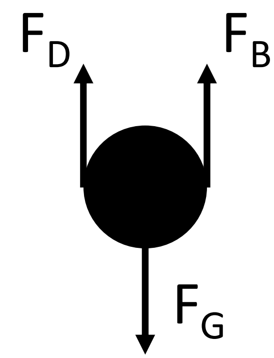
SYRACUSE UNIVERSITY ENGINEERING & COMPUTER SCIENCE

Influence of Urban Aerosols on the Chemistry of Stormwater Runoff from Building Roofs

Alex Johnson

Environmental Seminar
December 7, 2015

Background



Problem Background

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Stormwater washes off deposited aerosol from surfaces

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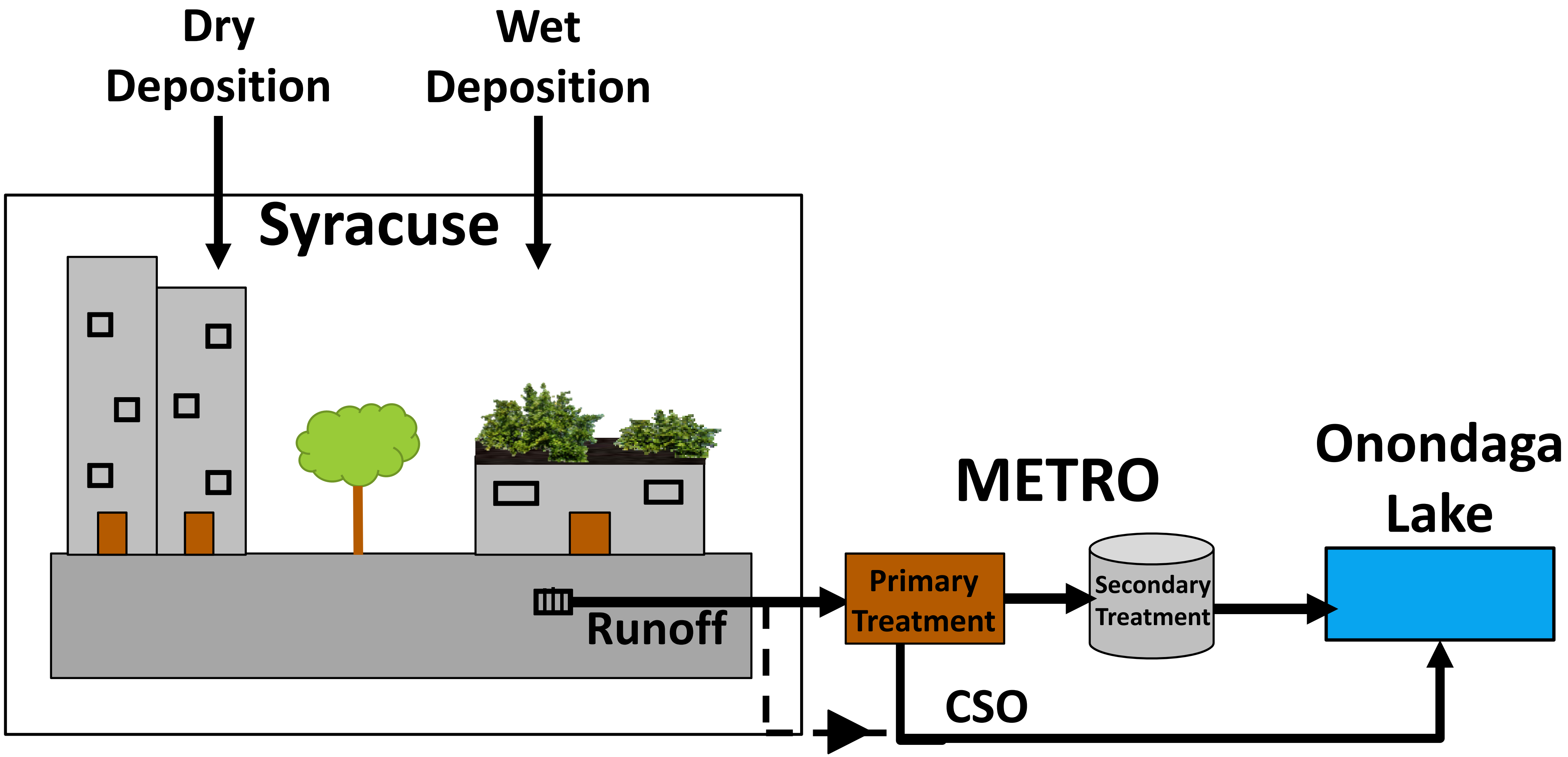

Dry
Deposition
Wet
Deposition
Syracuse
Runoff
METRO
Primary
Treatment
Secondary
Treatment
Onondaga
Lake
CSO

Dry Deposition Inputs

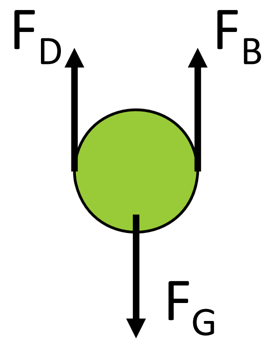
Gravitational Settling

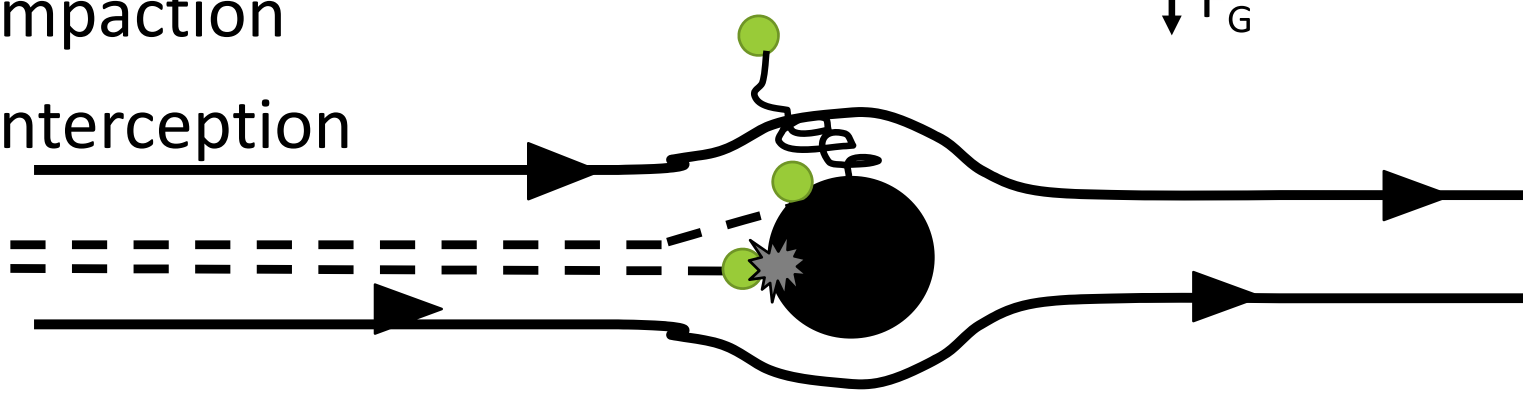
Brownian Diffusion

Turbulent Bursts

Impaction

Interception



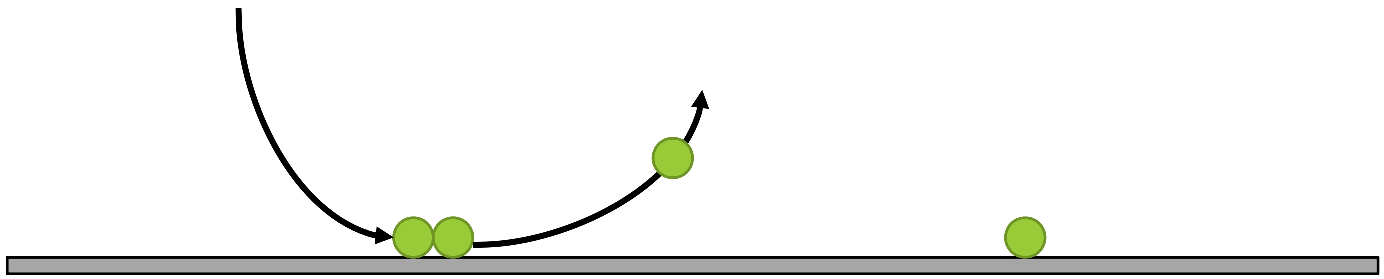


Resuspension

Lift force is greater than forces keeping particle at surface

Reduces dry deposition

Empirical resuspension rates ($time^{-1}$)



Dry Deposition Measurements

Fluxes

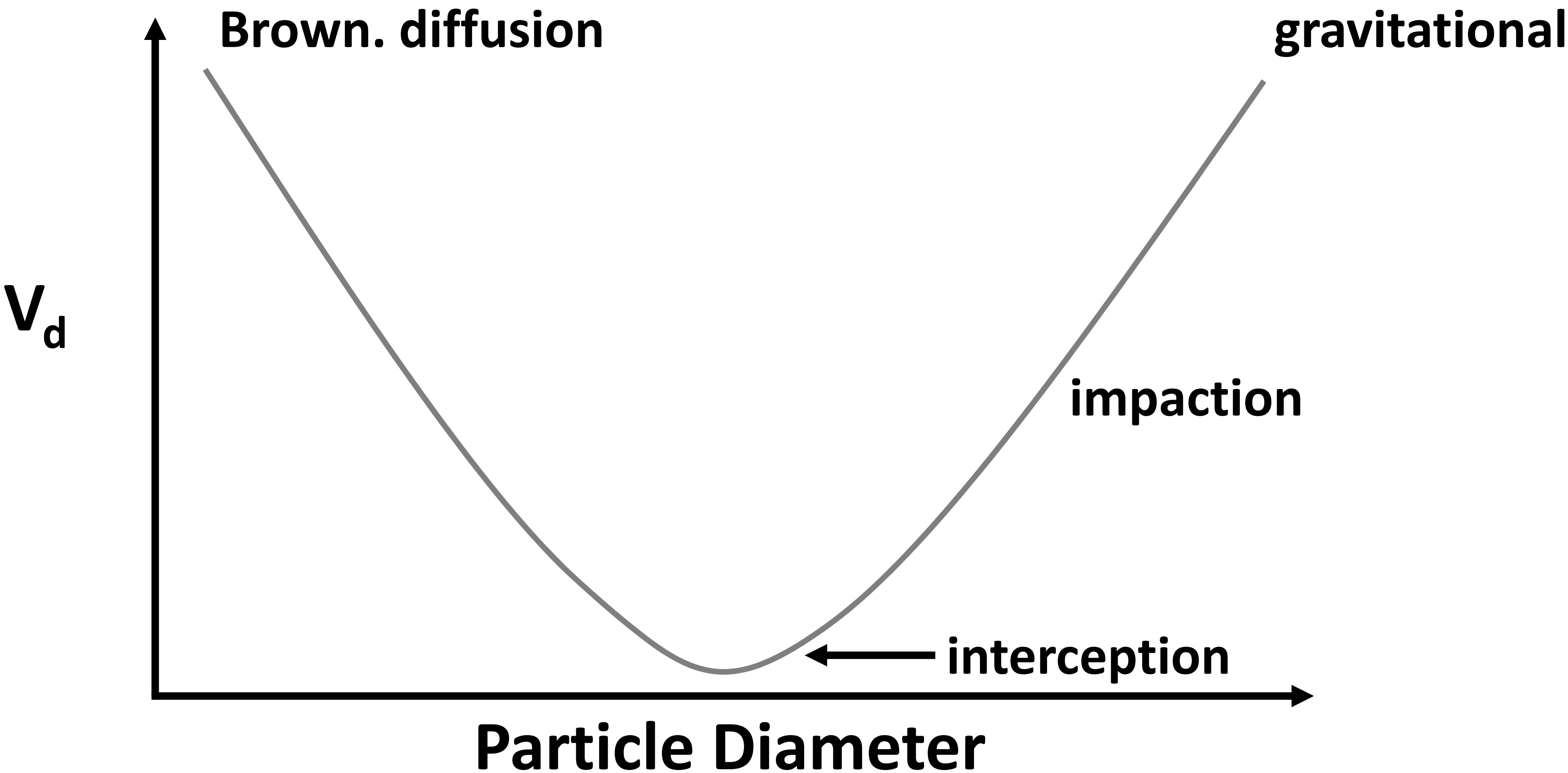
- Surface Analysis Techniques (e.g., surrogate surfaces)
- Micromet. Techniques (e.g., concentration gradients, eddy covariance)

Airborne Concentrations

Dry Deposition Velocities

- Ratio of Flux to Airborne Concentration

Additional parameters (e.g., particle size distributions)


Brown. diffusion
gravitational
V_d
impaction
interception
Particle Diameter

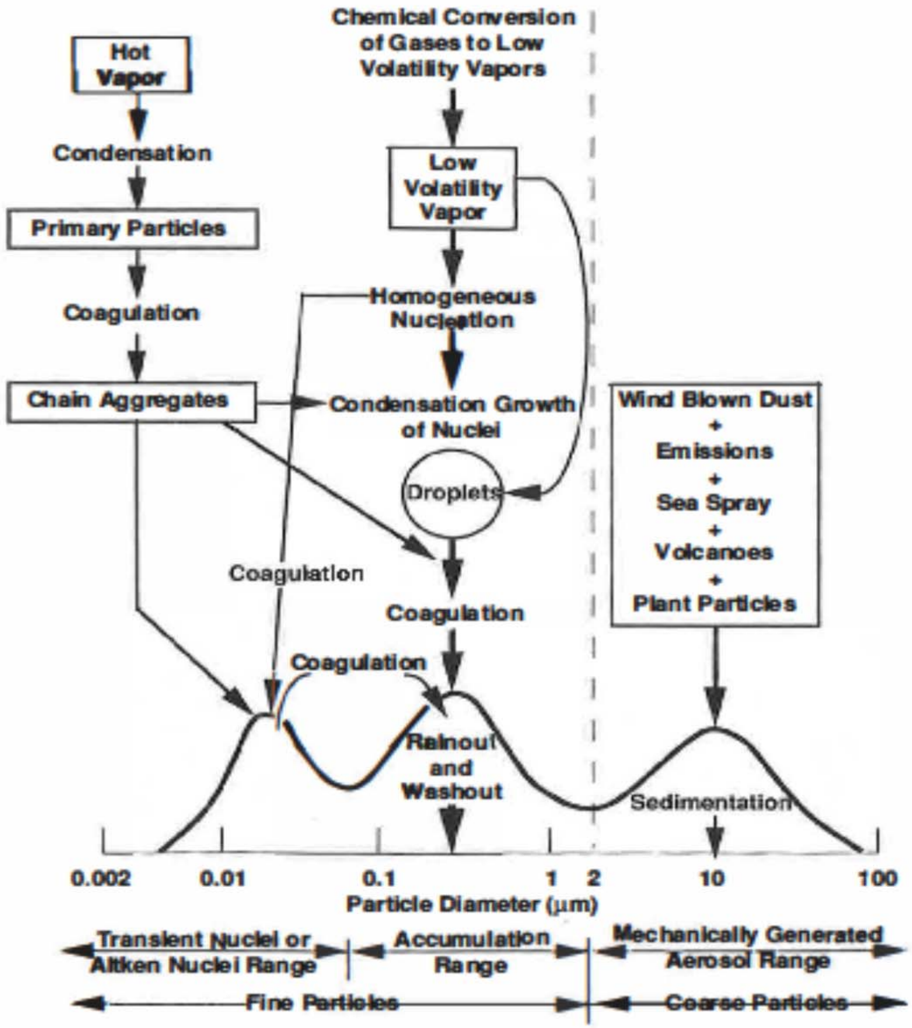
Wet Deposition

Condensation Nucleation

Favors soluble particles (e.g., sulfate, nitrate)

Ice Nucleation

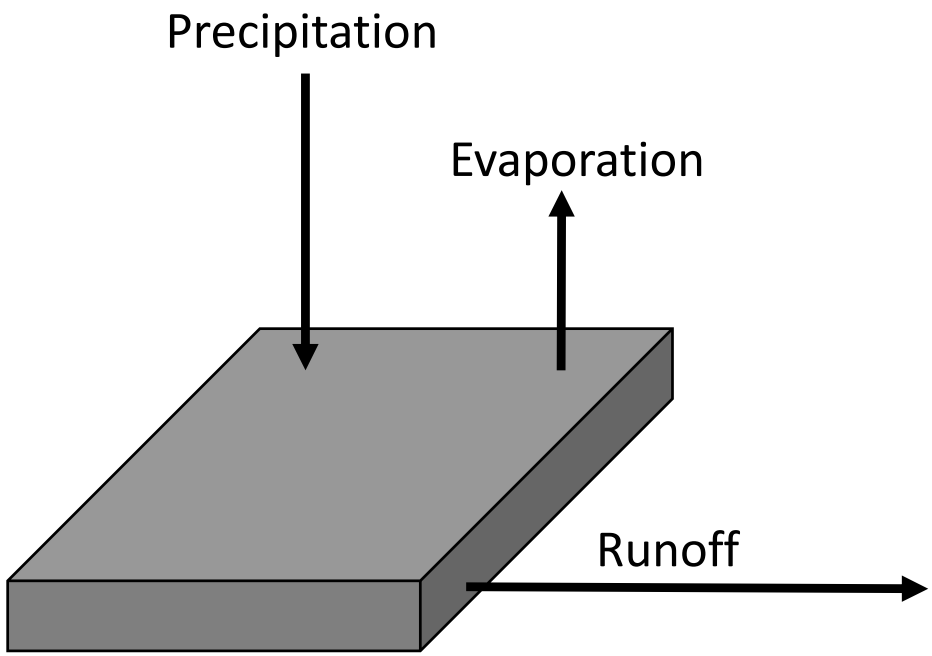
Minerals with crystal properties resembling ice



Source: Acidic Deposition: State of Science and Technology, *NAPAP*

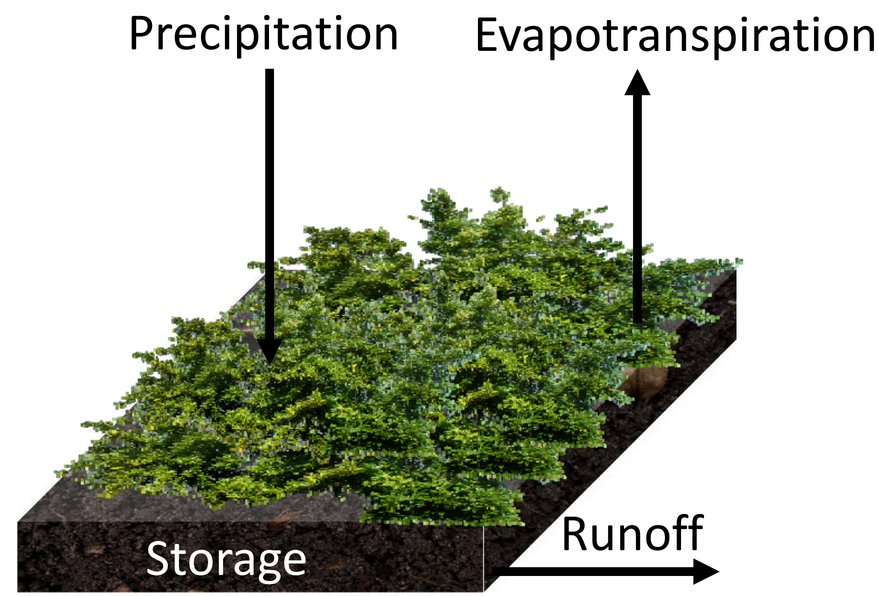
Rooftop Water Balances

Traditional Roof

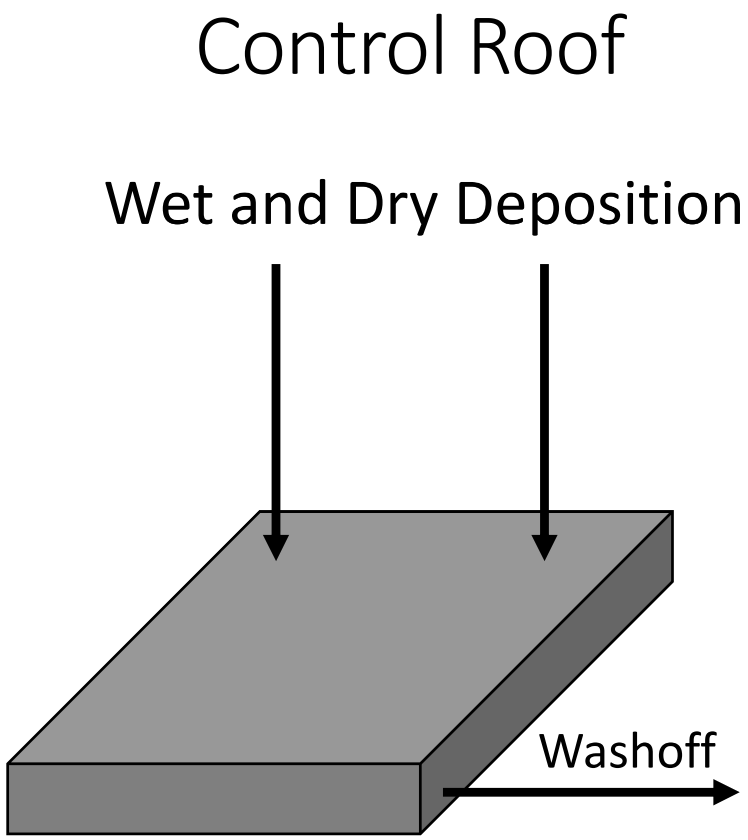


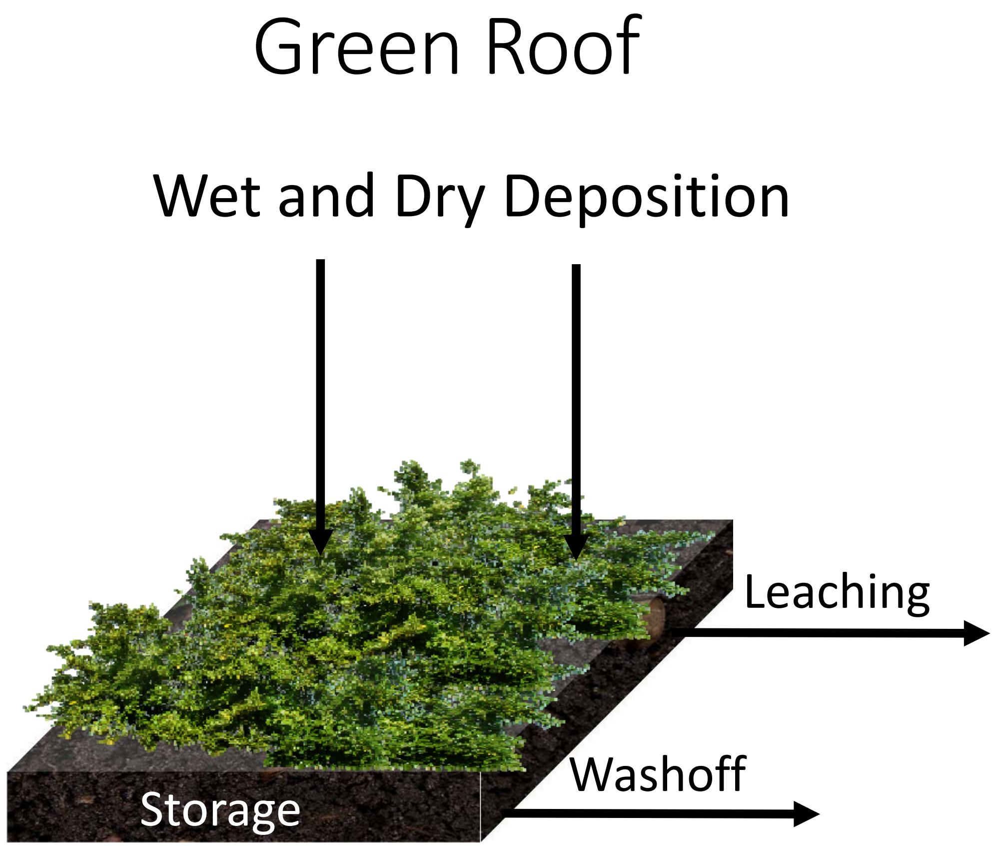
Green Roof

$$\frac{dS}{dt} = P - R - ET$$

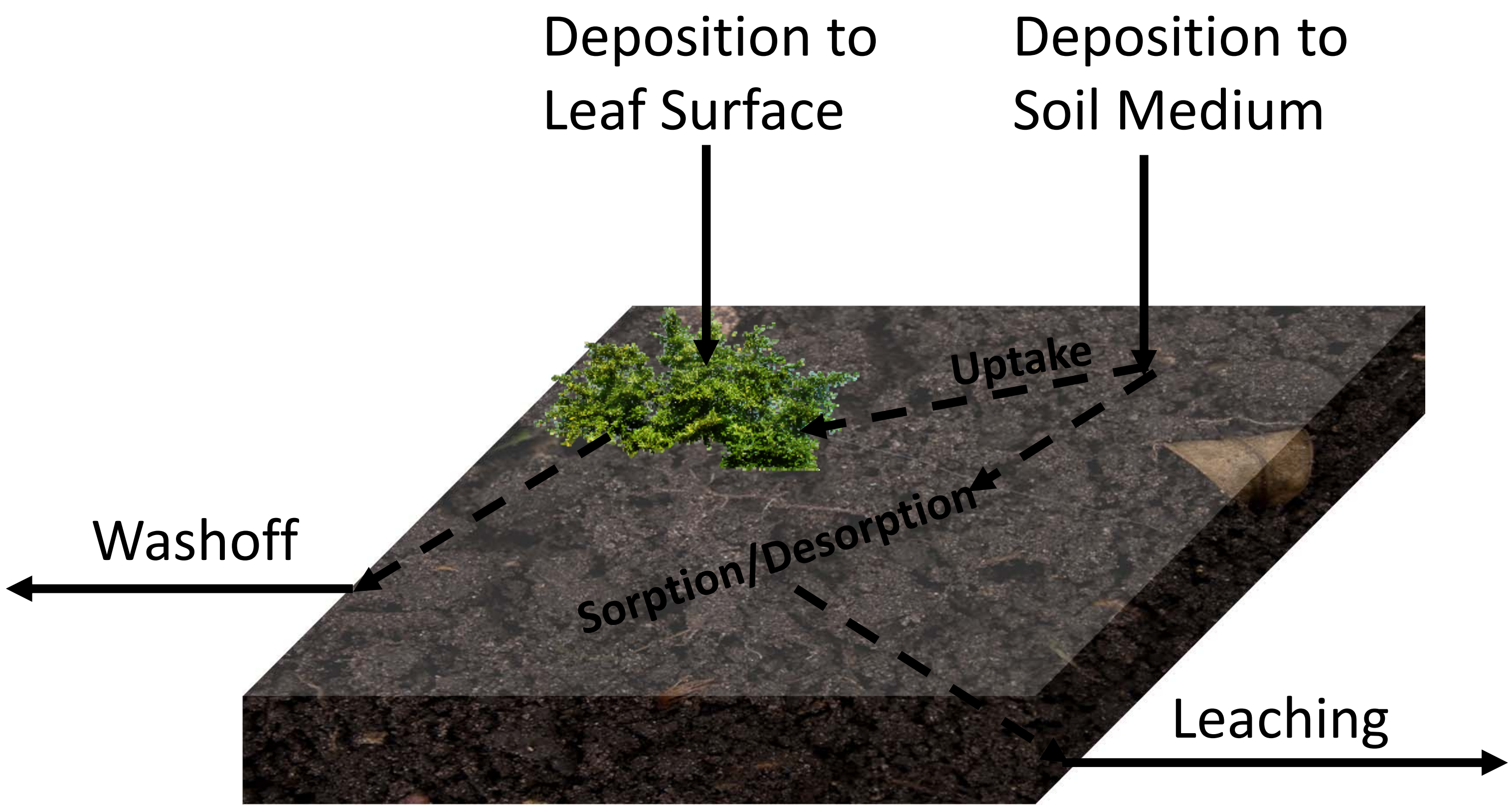


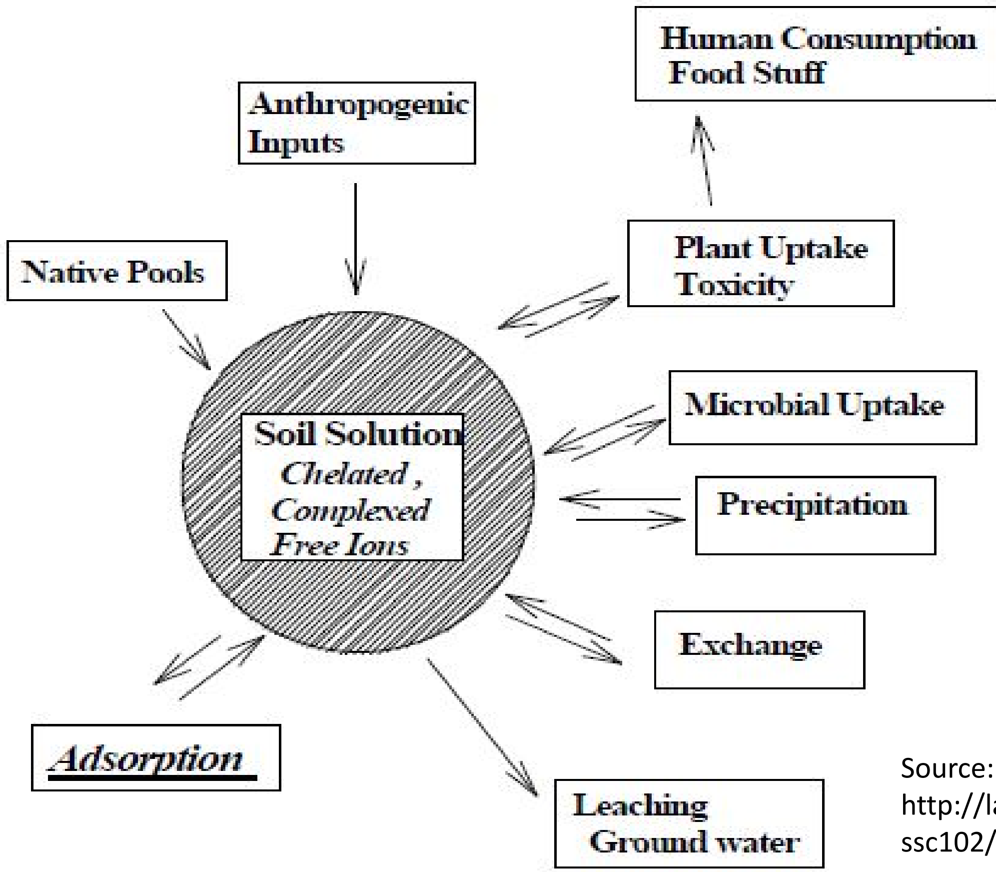
Rooftop Pollutant Mass Balances



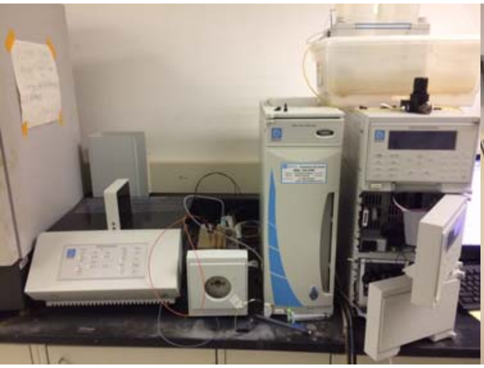


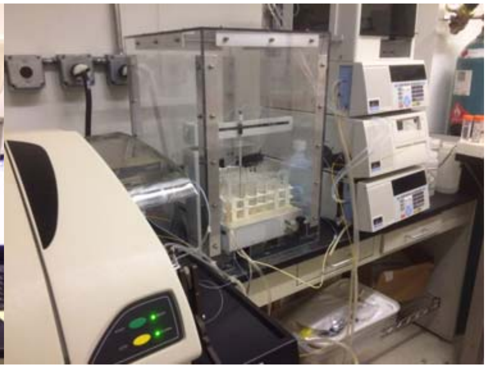
Interactions on Green Roof Surface



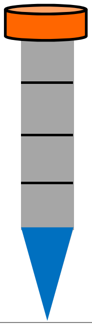


Source:
http://lawr.ucdavis.edu/classes/ssc102/Section7.pdf





Analyses



Experimental Methods

Measured airborne concentrations and dry deposition fluxes

Measured contaminant concentrations in fresh precipitation and roof runoff (green roof and control roof)

Conducted analysis for lead and copper using ICP-MS and for nitrate and sulfate using IC

Dry Deposition Site on SU Campus

Control Roof on War Memorial Hockey Arena

Size: 1.3 acres

Source: Google Maps

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Size: 1.5 acres

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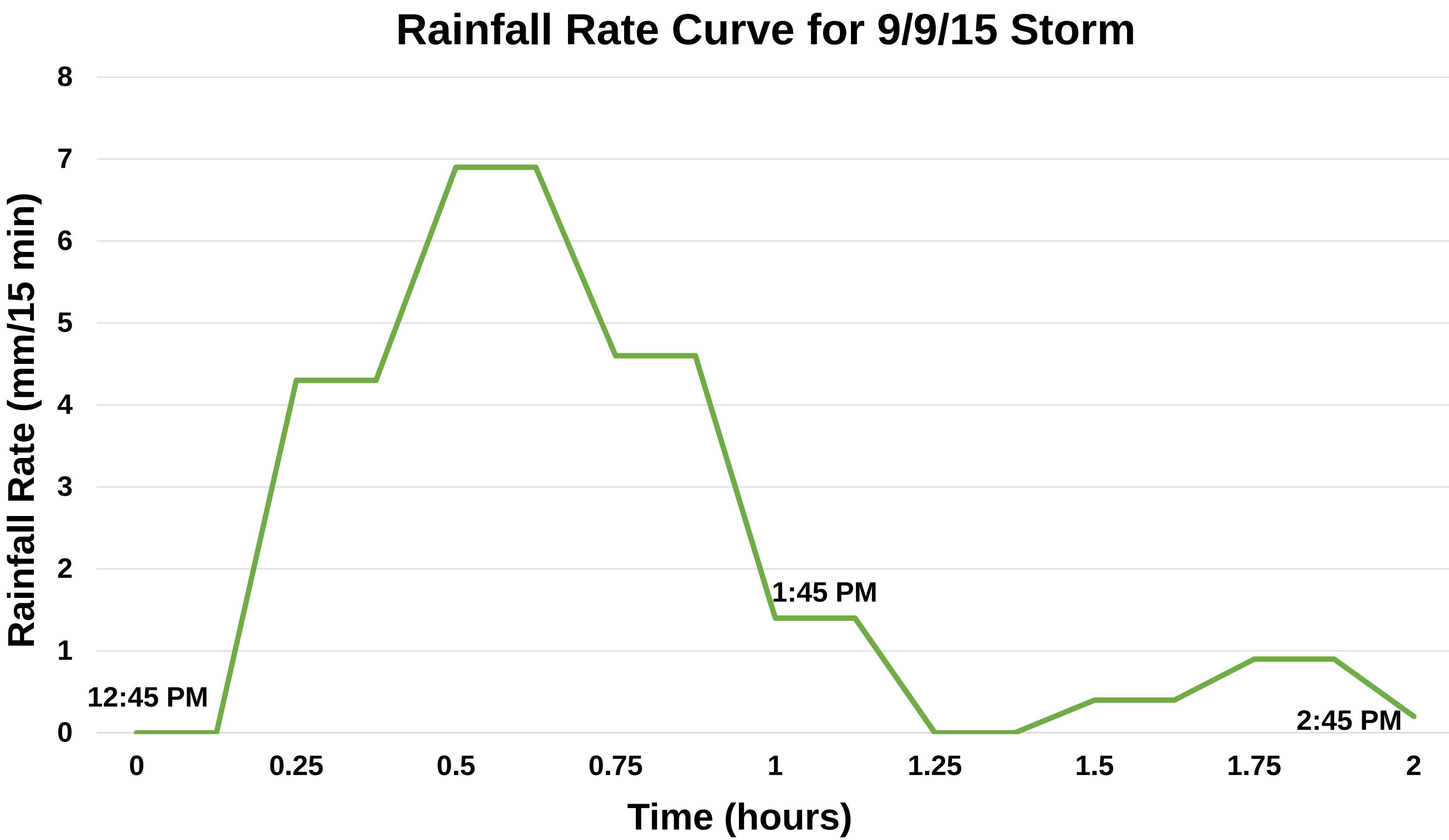
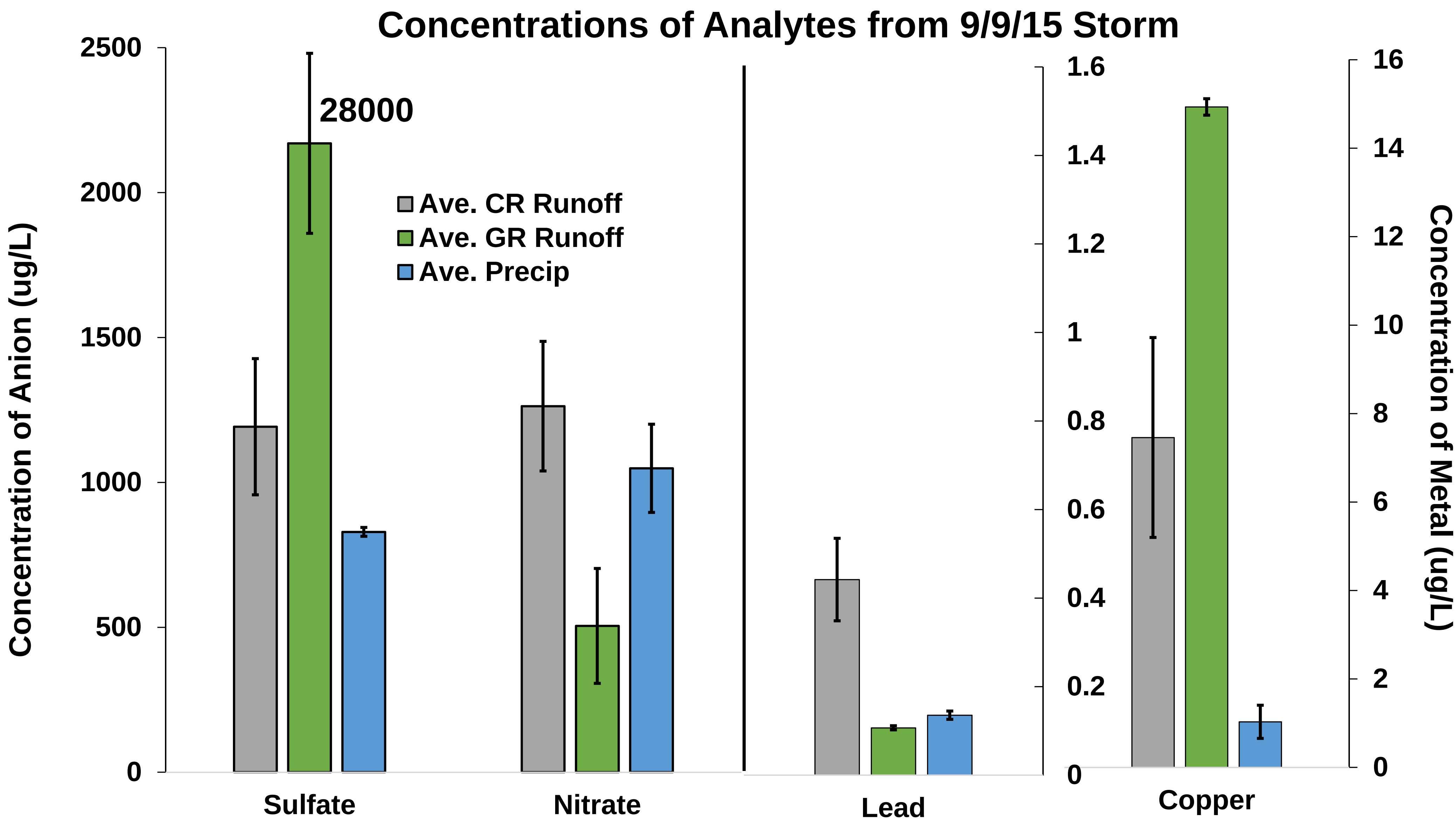
Soil Thickness: 3 inches


Rainfall Rate Curve for 9/9/15 Storm
Rainfall Rate (mm/15 min)
8
7
6
5
4
3
2
1
0
12:45 PM
1:45 PM
2:45 PM
0
0.25
0.5
0.75
1
1.25
1.5
1.75
2
Time (hours)



Concentrations of Analytes from 9/9/15 Storm
Concentration of Anion (ug/L)
Concentration of Metal (ug/L)
28000
Ave. CR Runoff
Ave. GR Runoff
Ave. Precip
2500
2000
1500
1000
500
0
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
16
14
12
10
8
6
4
2
0
Sulfate
Nitrate
Lead
Copper

Conclusions

Rain can remove dry deposited aerosol from roof surfaces
- Washoff rates are currently being investigated

Growth medium on green roof may remove some contaminants but could be a source for others, e.g., copper

Collection of hydrologic data is underway- combine with aerosol chemistry data to understand green roof behavior

Acknowledgments

Onondaga County (Save the Rain Project)

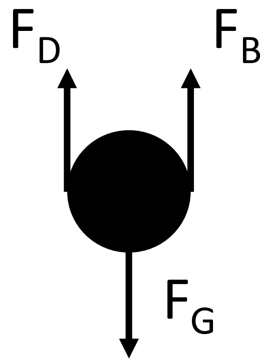
Syracuse University Water Initiative

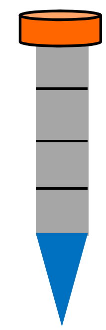
Numerous undergraduate and M.S. students

Mario Montesdeoca and Nick Glick

Richard Chave and William Dossert

Questions?





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Alex Johnson, Cliff I. Davidson

Department of Civil and Environmental Engineering, Syracuse University

AAAR 35th Annual Conference
October 19, 2016

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Estimate wash off by stormwater runoff from building roofs

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Note: no denuder used

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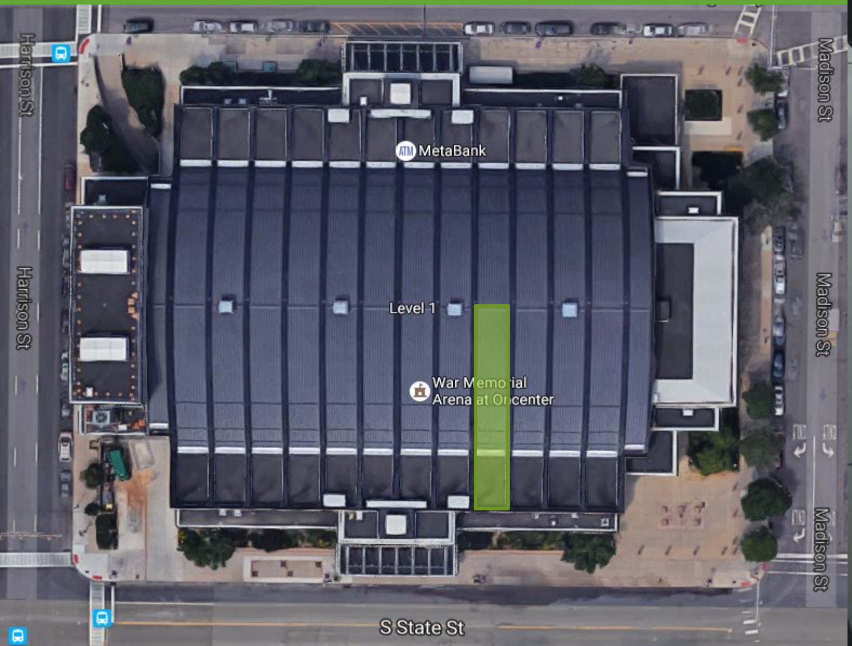

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Volume of runoff, concentrations in runoff from control roof & green roof

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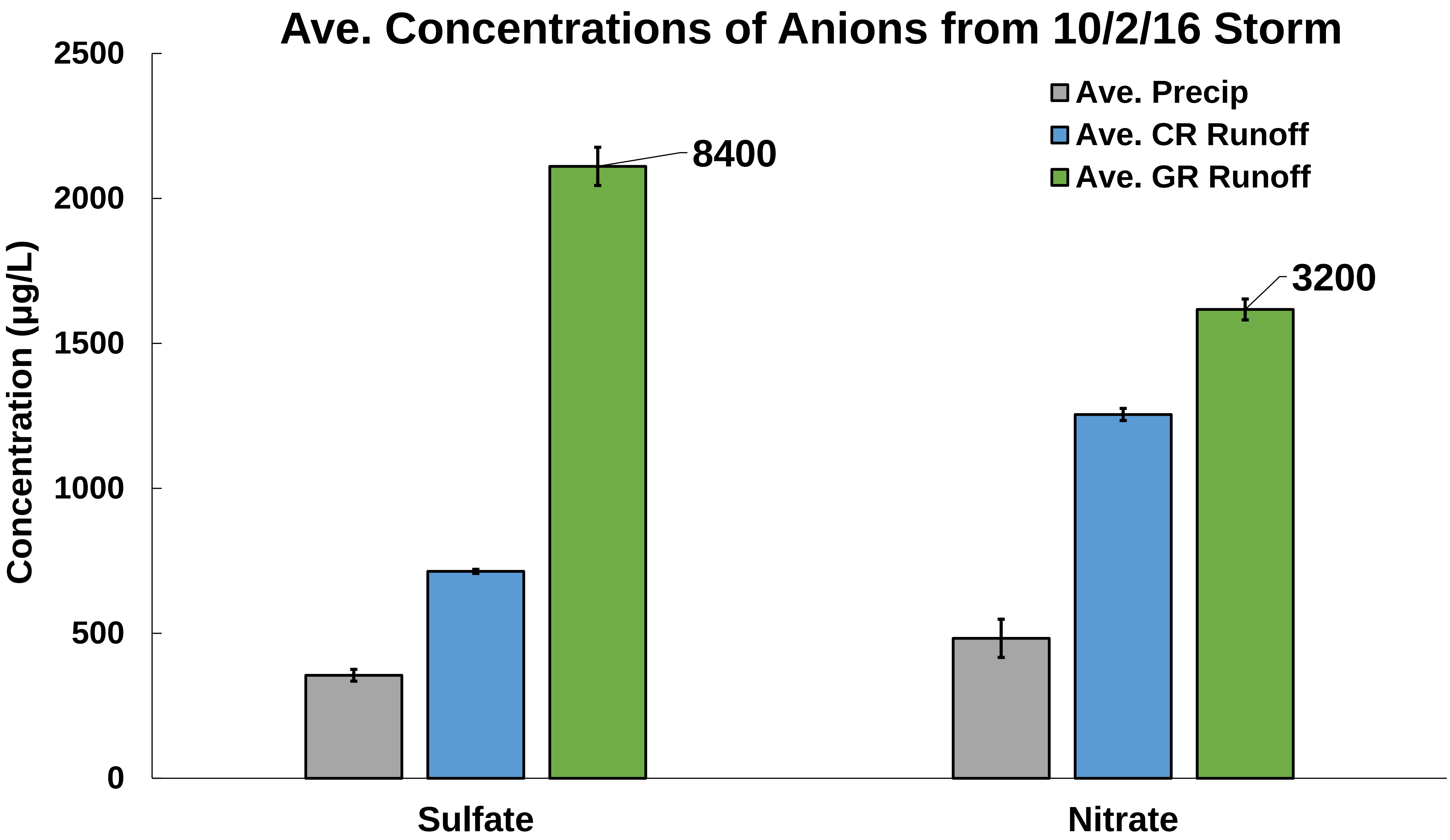
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SYRACUSE UNIVERSITY

EMPOWER

Education Model Program on Water-Energy Research

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Numerous undergraduates and M.S. students

Technical staff in the College of Engineering

Save the Rain

www.savetherain.us

Questions?

Estimating Dry Deposition of Aerosols to Building Roofs Using Data on Contaminants in Rain and Runoff

Alex Johnson, Cliff I. Davidson

Department of Civil and Environmental Engineering, Syracuse University

NEGSWS 2017
September 9th, 2017

Background

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Stormwater washes off deposited aerosol

- Stormwater becomes contaminated

Stormwater is discharged to receiving waters, e.g., lakes, rivers, oceans

- Contributes to contamination of these waters

Onondaga Lake

Objectives

Estimate dry deposition onto a traditional building roof

Measure washoff of dry deposition from a traditional building roof

- Construct time series of runoff concentrations for each storm

Compare total mass load of contaminant in runoff to dry deposition estimate

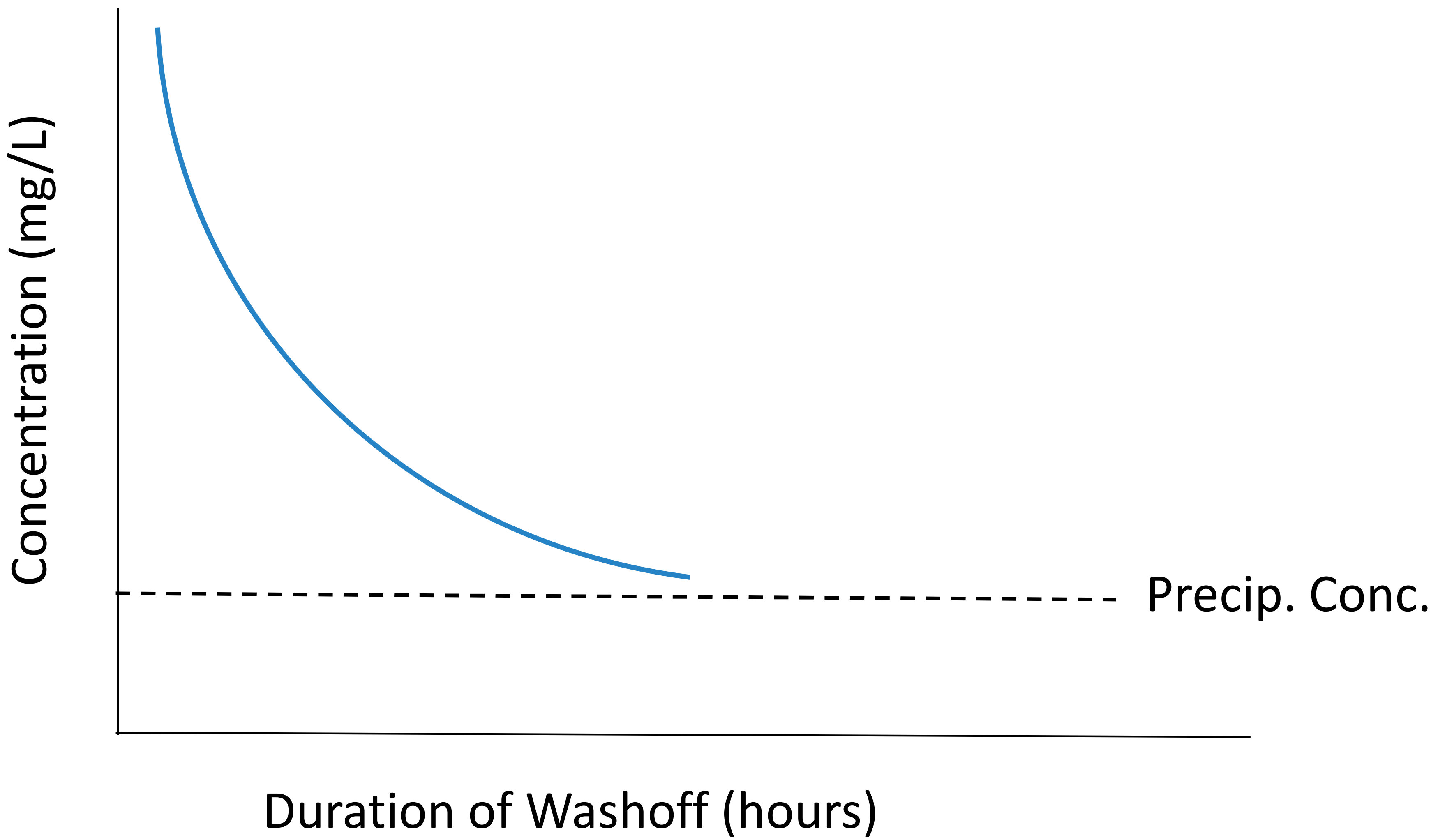
Data Needed

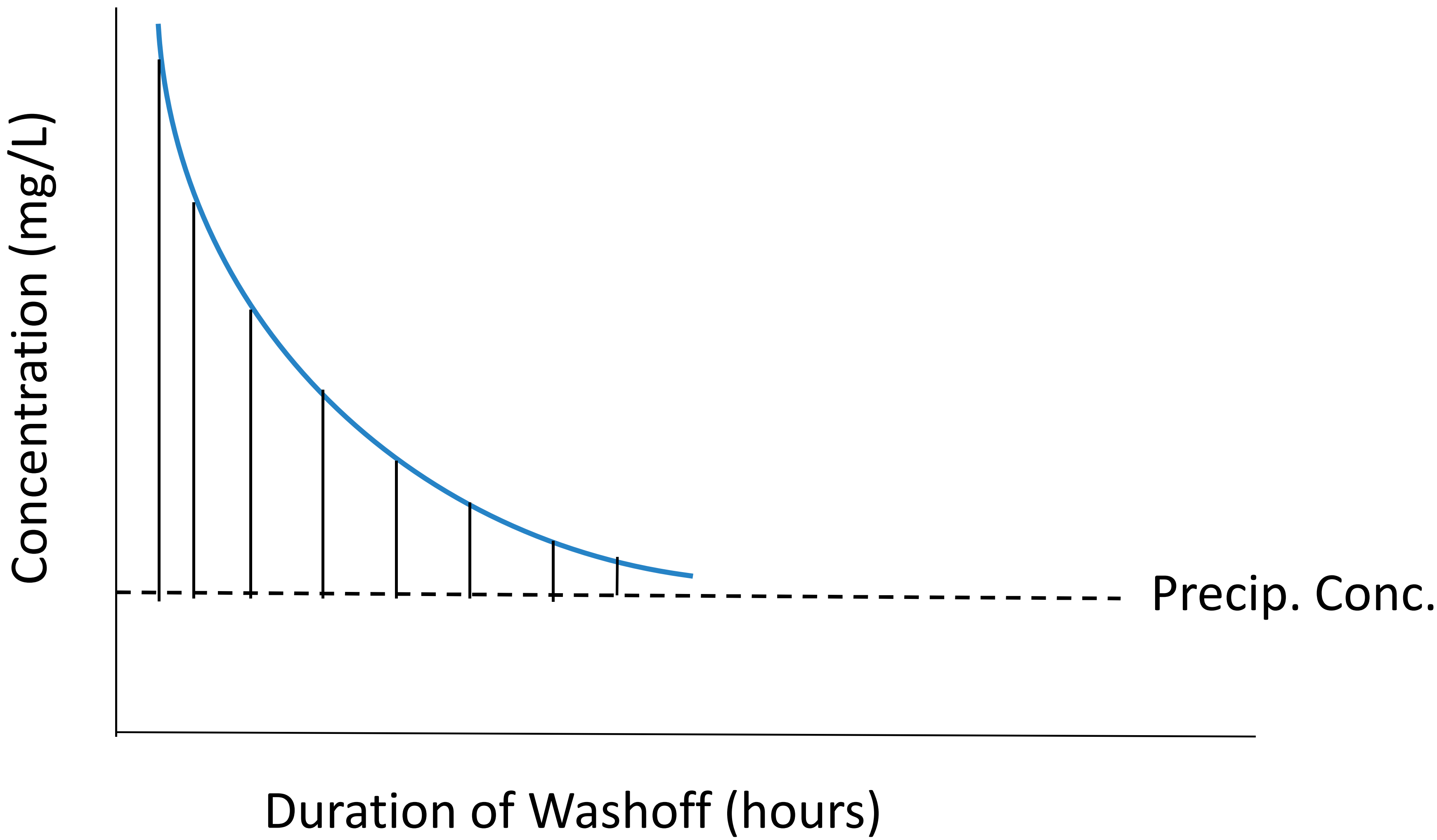
Dry deposition flux, duration of antecedent dry period (ADP)

Precipitation intensity & concentration, duration of washoff

Volume of runoff & concentrations of contaminants in runoff throughout storm

Inorganic anions (i.e. sulfate) are of interest

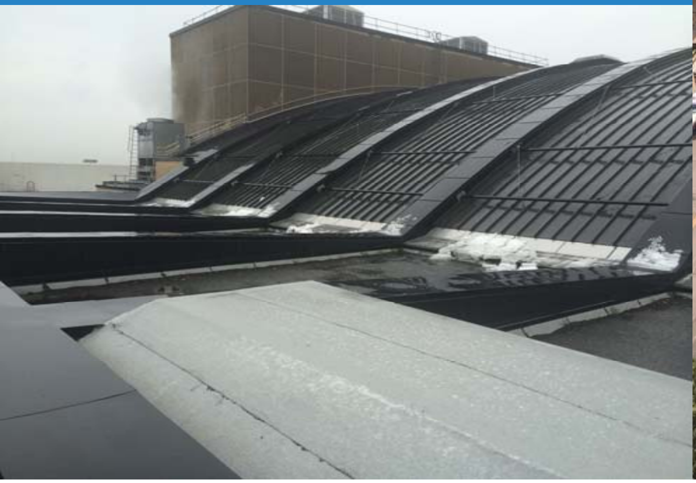

Concentration (mg/L)
Precip. Conc.
Duration of Washoff (hours)


Concentration (mg/L)
Precip. Conc.
Duration of Washoff (hours)

Control Roof on War Memorial Hockey Arena

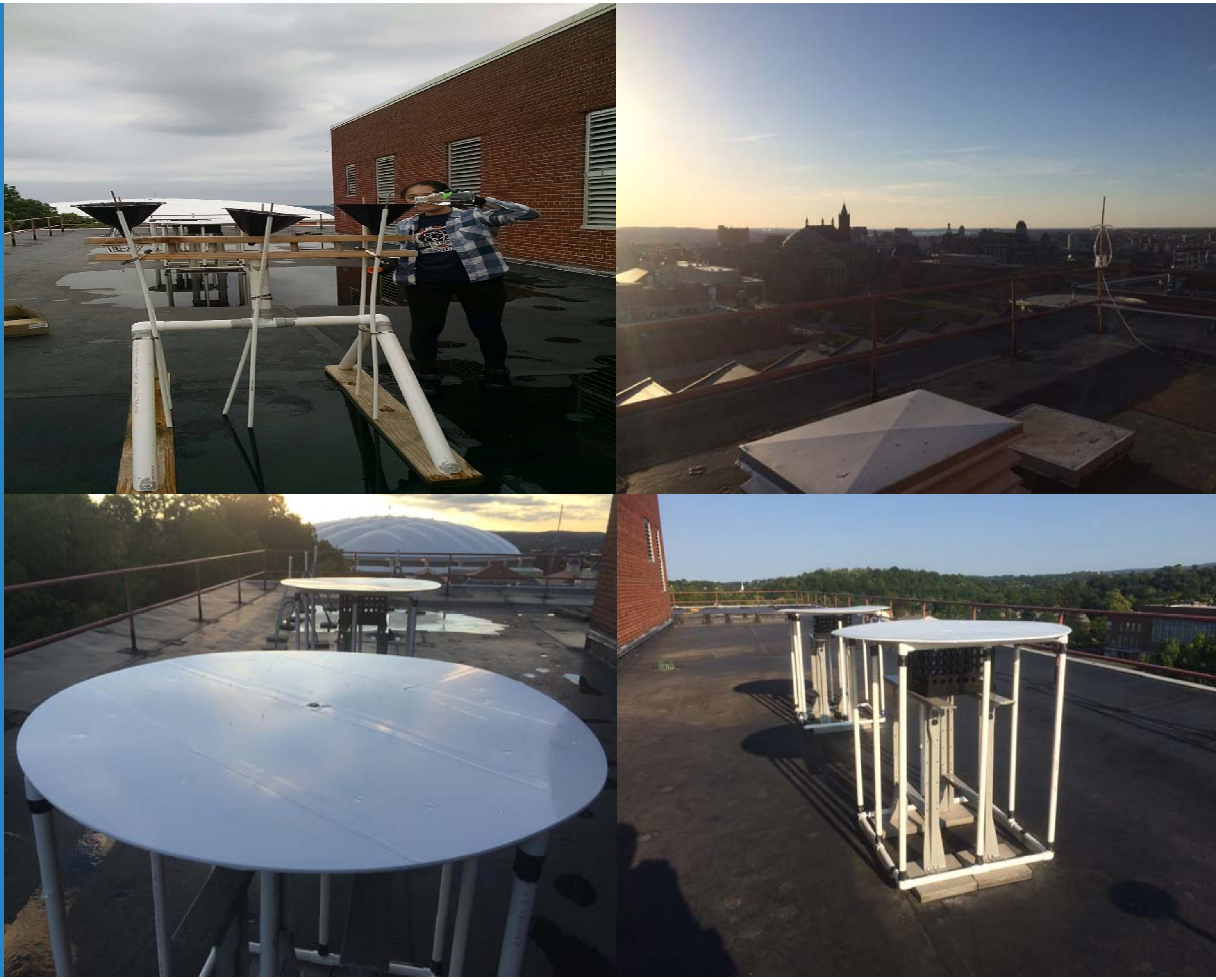
Total Size: 1.3 acres

Drainage area for drain pipe: 0.29 acres



Field Site on
SU Campus

1.6 km away
from roof



Data for Ideal Storm

Analyte	Dry Deposition Flux (µg/m^2 day)	Airborne Concentration (µg/m^3)	Dry Deposition Velocity (cm/s)
Sulfate	**73 +/- 7.9**	**0.62 +/- 0.004**	**0.14**

Additional Information:

Contributing Roof Area: 1176 m^2

ADP: 2.5 days

Duration of washoff: 0.17 hours (or 10 minutes)

Rain Intensity: 1 mm/hour

Precip. Concentration: 0.61 mg/L

Estimate Dry Deposition onto Roof

<u>Compute Mass of Dry Deposition onto Contributing Area:</u>

Roof Contributing Area x ADP x Flux = Total Deposition (mg)

1176 m^2 x 2.5 days x 73 µg m^{-2} day^{-1} = 210 mg SO_4^{2-}

Washoff Calculation

Need to figure out amount of SO_4^{2-} in rain:

Precip. Concentration x Volume of Runoff = Mass Load

0.61 mg/L x (1176 m^2 x 0.17 hours x 1 mm/hour) = 120 mg SO_4^{2-}

Precip. mass load < total deposition

✓ Can See Dry Deposition in Runoff Concentration

Assume no debris in runoff

Washoff Calcuation

What is the concentration of sulfate in runoff?

Total dry deposition / volume of runoff = concentration

210 mg / (1 mm/hr x 1176 m^2 x 0.17 hours) = 1.1 mg/L

So we expect an initial concentration of 1.7 mg/L (1.1 + 0.61 mg/L) to decrease to 0.61 mg/L

Conclusions

Flux data from disks can be used to estimate dry deposition onto building roofs

Can potentially measure washoff of dry deposition

Plan to create time series of contaminant concentrations in roof runoff over duration of storm

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