The Effect of
Vegetated Roofs on
Acid Precipitation
Runoff

Abstract of

a thesis presented to the Faculty

of the University at Albany, State University of New York

in partial fulfillment of the requirements

for the degree of

Master of Science

College of Arts and Sciences

Department of Atmospheric and Environmental Sciences

Jennifer Gillen
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Abstract

Vegetated, or “green” roofs are used in urban architecture and sustainable building to capture stormwater and enhance urban wildlife. Most research to date has focused on their water retention capabilities, but green roofs also have the potential to treat anthropogenic acid precipitation in urban environments. More specifically, green roofs could reduce sulfate, nitrate and hydrogen ion concentrations in runoff. One previous study has demonstrated that nitrate was reduced in water draining from a green roof (Berndtsson, et al. 2006), but this unpublished thesis appears to be the first comprehensive study of the effects of vegetated roof materials on major ions and acidity in runoff. The objective of this current research was to test whether green roofs could significantly modify acidified precipitation. Experiments were conducted using a variety of materials commonly used in modern green roof design.

Twenty different experimental roof surfaces, each with an area of 0.5 m^2, were constructed and exposed to ambient rainfall during the 2008 growing season. Twenty of these plots simulated green roof constructions varying by vegetation, drainage material and soil (substrate) depth and composition. Substrate types included one commercially available topsoil and three hydroponic soils; low density, inorganic materials commonly used in green roofing. Runoff samples were collected from the green roof plots and a control, a traditional asphalt-shingled roof plot. Precipitation was collected in a funnel-style bulk precipitation collector. Collections followed ten precipitation events that occurred between June and October, 2008. Water samples were measured for pH and alkalinity and analyzed via ion chromatography for concentrations of 10 major ions.

As a group, the experimental green roofs effectively lowered nitrate ion concentrations in runoff and raised pH to near-neutral values (from 6.8 to 7.8, varying with roof construction), compared to a mean pH in precipitation of 5.3. The weighted average of nitrate concentrations in precipitation was 0.03 meq/L while average concentrations in the three types of hydroponic substrate plots were one-third lower, at 0.02 meq/L for each substrate type. In contrast, roofs with topsoil substrates had the opposite effect; average nitrate concentration was 0.40 meq/L. This increase could be due to nutrients leaching from the topsoil.

Sulfate ion concentrations were increased in water captured from all green roofs. The weighted average sulfate concentration of precipitation was 0.03 meq/L. Topsoil substrate plots had average concentrations between 0.46-0.86 meq/L, while hydroponic plots had lower increases in sulfate concentration with values ranging between 0.04-0.19 meq/L. The effects of vegetation, substrate thickness, and drainage material on ion concentrations in runoff were insignificant.

In addition to these results, this study indicates that the geographic origins and pathways of weather can control sulfate and nitrate ion concentrations and pH of precipitation falling in the northeastern United States. In precipitation from two tropical systems (Tropical Storm Hanna and Hurricane Kyle), sulfate and nitrate concentrations were at their lowest values (≤0.01 meq/L) and pH reached the highest levels measured throughout the experiment (6.9 for Hanna and 6.1 for Kyle) as compared to all other precipitation events. These results are likely due to the absence of sulfur and nitrogen emitters in the path of these two weather systems.

Although sulfate wet deposition in the northeastern United States has declined since the passage of the Clean Air Act in 1970 and amendments in 1990, concentrations of reactive forms of nitrogen remain high, and pH remains low. This study is one of the first to demonstrate that, in addition to intercepting stormwater, many green roof materials can improve stormwater quality, enhancing their environmental value as elements of sustainable urban building design.

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> "Twenty years from now you will be more
> disappointed by the things that you didn't do
> than by the ones you did do.
>
> So throw off the bowlines.
> Sail away from the safe harbor.
> Catch the trade winds in your sails.
>
> Explore. Dream.
> Discover."
>
> ~ Attributed to Mark Twain

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Chapter One: Acid Deposition

Sulfur Dioxide and Nitrogen Oxides

In the past fifty years, acid deposition has caused many problems in the United States and throughout the world. Studies have shown that deposition has significantly altered surface water and soil biology and chemistry, decreased biodiversity, eroded infrastructure and damaged automobile coatings (U.S. Environmental Protection Agency 2007). Wet deposition, or acid rain, is precipitation below the natural level of 5.6 pH. Natural precipitation has a pH far below neutral (7.0 pH) due to the interaction of carbon dioxide and water in the atmosphere. As indicated in Equation 1.1, carbon dioxide and water react to form carbonic acid, a weak acid which dissolves into hydrogen and bicarbonate ions (Seinfeld and Pandis 2006).

EQUATION 1.1

$$CO_2 + H_2O \rightarrow H_2CO_{3\,(aq)}$$
$$H_2CO_{3\,(aq)} \rightarrow H^+ + HCO_3^-$$

Acid deposition occurs when sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are introduced into the atmosphere. These compounds react with oxygen and hydrogen to form acids and are eventually deposited as sulfate and nitrate ions (U.S. Environmental Protection Agency 2008). Although SO_2 and NO_x do enter the atmosphere through natural processes, two-thirds of global SO_2 emissions (Lucas and Akimoto 2007) and just over half of global NO_x emissions (Graedel et al. 1995) are anthropogenic. In the United States, electricity generation and fossil fuel combustion were the greatest emitters of SO_2 in 2002, during which time electricity generation released five times more SO_2 than other forms of fossil fuel combustion (U.S. Environmental Protection Agency 2007).

Nitrogen oxides are commonly anthropogenically released by high temperature burning of fuels during combustion in vehicles and power plants. In 1999, an air quality trends report showed that 55.5% of all anthropogenic NO_x in the United States was emitted by transportation sources and 39.5% was from non-mobile fuel combustion (U.S. Environmental Protection Agency 2008).

Sulfur dioxide and nitrogen oxides become relevant to acid deposition after they enter the atmosphere as gases and react with hydroxyl radicals. Reactions such as those portrayed in Equations 1.2 and 1.3 (Seinfeld and Pandis 2006) convert SO_2 and NO_x to sulfuric and nitric acid and then sulfate and nitrate ions, respectively.

EQUATION 1.2

$$SO_2 + OH \rightarrow HOSO_2$$
$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

EQUATION 1.3

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + NO_2 \rightarrow N_2O_5$$
$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Sulfate and nitrate ions are byproducts of these oxidations and thus can be associated with acid content when analyzing precipitation samples. This method has been previously employed by Wigington et. al (1996) and Summers and Barrie (1986).

Clean Air Act

The 1990 amendments of the Clean Air Act incorporated a program to reduce acid rain by reducing emissions of SO_2 and NO_x. A multi-phase plan set permanent caps on the amount of SO_2 emissions allowed by electricity-producing power plants in the United States (U.S. Environmental Protection Agency 2008). If plants exceed these caps (approximately 50% of 1980 levels) without purchasing allowances beforehand, they are subject to significant financial penalties (U.S. Environmental Protection Agency 2008).

Although the Clean Air Act does briefly address NO_x issues, emissions have shown very little change since the law was originally passed in 1970 (Krajick 2001). Fortunately, sulfur dioxide emissions have experienced a near 40% reduction from the 28.8 tonne peak in 1973 (Krajick 2001). However, despite the efforts of the Clean Air Act, acid deposition still exists in the United States. This is especially true in the Northeast, where acidity levels are highest (Menz and Seip 2004)

Geography

In the continental United States, the jet stream generally moves air masses from the Southwest to the Northeast. Pollution is essentially picked up and carried with these air masses as they pass over heavy industry in the Midwest and Ohio River Valley. By the time the reactions necessary to produce acid deposition have occurred and precipitation forms, pollutants may have traveled several hundred miles from their source (Menz and Seip 2004). This effect is illustrated in Figure 1.1. It is for this reason that many lakes in the secluded Adirondack Mountains of New York State are unnaturally acidic.

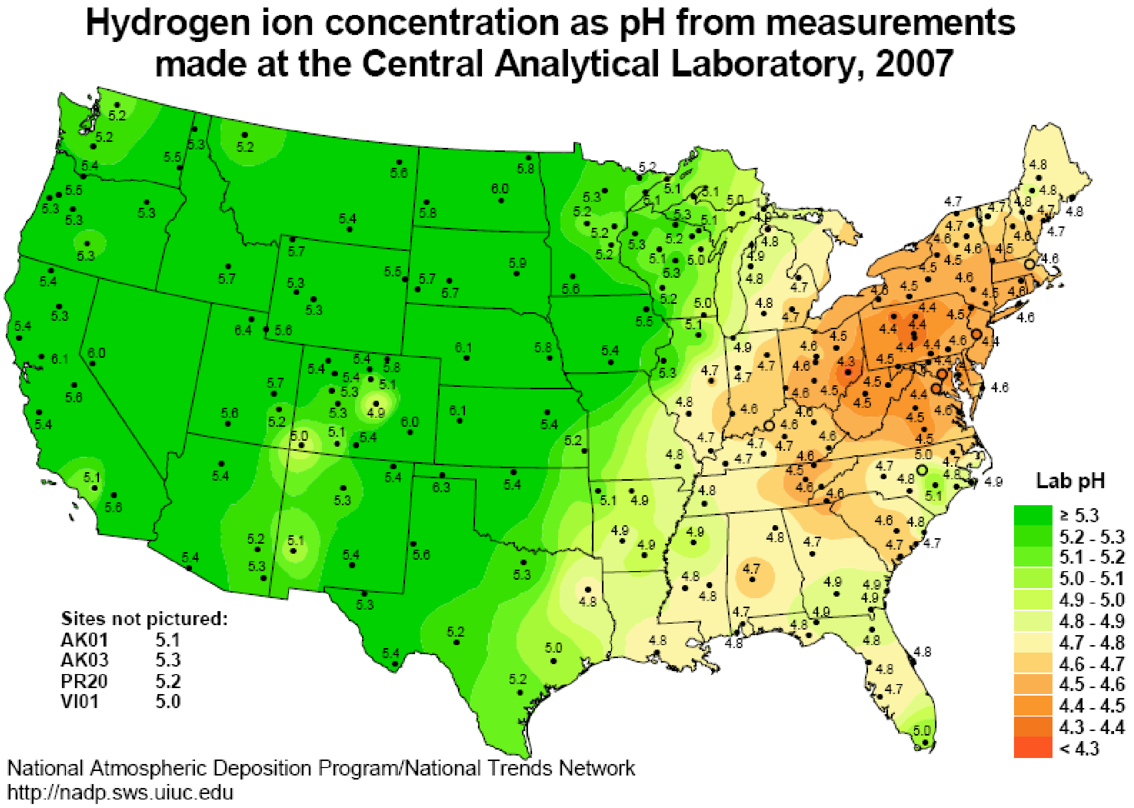


FIGURE 1.1. Laboratory measurements of pH of precipitation made by the National Atmospheric Deposition Program (NADP, 2009).

Though there have been efforts to decrease the overall anthropogenic acidification in the United States from the source, specifically by the passage of the Clean Air Act, there have not been many attempts to decrease the acidity already in the precipitation. However, several studies have proposed that green roofs have the ability to reduce hydrogen and nitrate ion concentrations in acidified runoff (Berndtsson et al. 2006; Pennsylvania State University, 2008).

Hypothesis

Following evidence from other studies (Berndtsson et al. 2006), I’ve proposed that green roofs will help to counteract the negative effects of acid rain runoff. Hydrogen, sulfate and nitrate ion concentrations, the most destructive components of acid rain, will be lower in green roof runoff as compared to conventional roof runoff and unfiltered precipitation. Nitrate and sulfate will be absorbed by vegetation and soil materials. In addition to this, the acidity of the green roof runoff will be neutralized by the filtering effect of the vegetation and cation exchange, adsorption, and dissolution reactions in the soil processes illustrated in Figure 1.2. Variation in green roof construction and vegetation will result in varying runoff compositions and pH values.

A secondary prediction is that green roof runoff composition will depend on geographic origin of air masses that bring precipitation. Weather traveling along the jet stream will collect pollution as it moves across the United States. However, storm systems originating in the Atlantic Ocean and traveling up the United States’ Eastern Seaboard to New England will not be exposed to heavy pollution like that produced in the Midwest. For this reason, it is predicted that green roof runoff associated with tropical systems will have smaller concentrations of nitrate and sulfate and more neutral acidities as compared to runoff related to Gulf Stream systems.

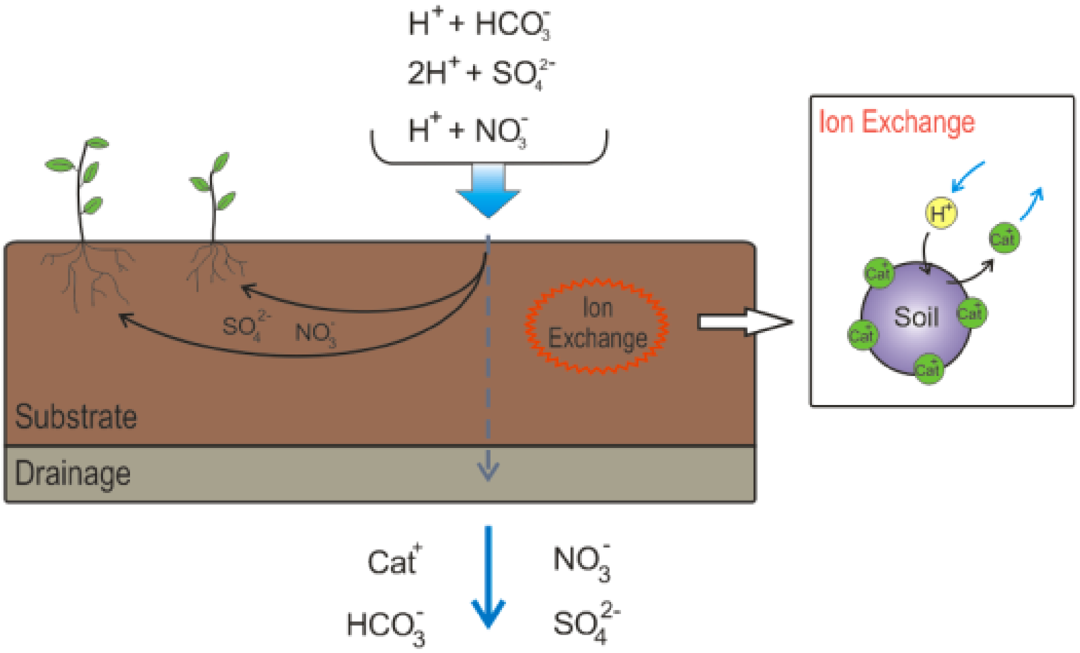


FIGURE 1.2. Paths of ions introduced by acid precipitation through the green roof. pH is altered by exchange of H^+ with other cations on soil particles. "Cat^+" represents cations such as sodium, calcium, magnesium, potassium and ammonium.

Chapter Two: History, Current Uses and Benefits

Intensive and Extensive

Green roofs fall into two major classifications: intensive or extensive. Intensive roofs are comparable to roof gardens. While accommodating a wide variety of plant species and sizes they also are used mainly for aesthetic and recreational purposes. Intensive roofs require an especially stable structure, as soil depths typically vary between 15cm and one meter. This depth becomes very heavy after saturation, thus necessitating substantial support.

Extensive green roofs are most commonly used for practical purposes such as water retention. Soil depths generally run between 3-15cm, so plants with shallow root systems are favored. Extensive green roofs are typically built on roofs that are not easily accessible, making regular maintenance difficult, if not impossible. For this reason, it is wise to use vegetation tolerant to harsh environmental conditions. Succulent plants are often chosen for green roof construction because of their ability to retain water and survive in arid climate and soil conditions. Succulents from the genus *Sedum* are one of the most commonly used extensive green roof plants in the United States (Dunnett and Kingsbury 2004). The shallow root systems and tolerances to heat, cold, Sun, shade and drought possessed by *Sedum* help to create green roofs that are practically self-sustaining. These plants also thrive in hydroponic soils. Hydroponics are manufactured soils advantageous to extensive green roofing due to their low densities and high nutrient and water retention capabilities.

Extensive green roofs are much more common in Scandinavia and Germany than the United States. However, like the sod roofs of ancestral Vikings, modern

European green roofs commonly use sod as a growing medium instead of succulents and hydroponics (Dunnett and Kingsbury 2004). Although effective, sod roofs are much denser than other systems and thus demand greater structural support.

"Brown" roofs are an emerging form of extensive green roof. The major difference is that brown roof soils consist of broken-down construction material such as crushed brick or concrete. These materials are often harvested from the demolition of old structures in the construction area. The primary objective of brown roofs is to increase biodiversity in highly developed areas. Instead of planting or seeding the roof with specific species, the brown roof is left to naturally colonize (Kadas 2006).

Although they have several important differences, all green (and brown) roofs have the same basic stratigraphic composition. The top three layers are dedicated solely to the vegetated aspect of the roof. These layers consist of vegetation, soil and drainage. Layers found below these vary by structure but are all in place to protect the roof and underlying structure. Typical layers of this portion include (from top down) a moisture retention surface, root barrier, waterproofing substance and the roof deck itself (Carter and Rasmussen 2006).

Uses and Benefits

The greatest potential benefit green roofs can have on a region is to diminish increased stormwater runoff volume and peak flows, an increasing problem in urbanized areas. Excess water falls from a solid or gravel roof onto streets, sidewalks or other impermeable surfaces. This water is then free to flow into a nearby ocean, lake, river or stream, picking up and carrying whatever pollutants are encountered

(Carter and Rasmussen 2006). More importantly, this large, uncontrolled discharge of water amplifies any possible flooding situations by entering sewage systems instead of recharging into the groundwater. This situation is especially hazardous when a municipality employs a combined sewage system, such as the one used in New York City.

Eighty percent of sewers in New York City combine storm and sewage waters in the same pipes running to treatment plants. These treatment plants can handle only a limited volume of water. When this capacity is reached, any excess water, including raw sewage, is flushed into the environment (Tillinger et al. 2003). As of 2004, combined sewage systems were used by over 740 communities in the US including major cities such as Boston, MA, Philadelphia, PA, Chicago, IL, and Seattle, WA (U.S. Environmental Protection Agency 2004). A 2000 congressional amendment to the Clean Water Act mandated compliance with a 1994 EPA policy for such communities to improve, reduce or eliminate overflows resulting from combined sewage systems (Federal Water Pollution Control Act 2007). Many developers in the United States are now looking to green roofs to mitigate these problems. Carter and Rasmussen (2006) found an extensive green roof in Athens, Georgia to reduce runoff by 88% in storms producing less than 2.54cm of rain (Carter and Rasmussen 2006) while an experiment at Pennsylvania State University found extensive green roofs to reduce runoff by an average of 80% for storms of all intensities (Tillinger et al. 2003).

Beyond decreasing stormwater runoff, studies have shown that green roofs actually provide thermal and noise insulation for underlying rooms. Although dependent on weather and climate, extensive green roofs have been found to improve insulation by 25% and lower room temperatures an average of 3-4ºC (Porsche and Köhler 2003). In addition to this, a green roof thickness of 20cm can lower sound absorption by up to 46dB (Porsche and Köhler 2003). However, no noise measurements have been made for studies involving soil shallower than 20cm.

FIGURE 2.1. A recreationally-focused intensive green roof on the Evening Star Building in NW Washington, DC. Photograph by author.

Chapter Three: Methods

Construction Overview

The University at Albany is located on the western edge of the city of Albany in Eastern New York State. The city has a humid continental climate and receives an average of 98 cm of precipitation annually (National Oceanic and Atmospheric Administration 2007). Over 45% of precipitation falls from June through October, the duration of the study period.

To evaluate the potential acid-neutralizing capabilities of green roofs, twenty-one simulated roofs were constructed. These plots included one control, consisting of a conventional, asphalt-shingled roof. In addition to this control plot, a funnel-style bulk precipitation collector was used to obtain unfiltered precipitation samples for chemical analysis.

The project was setup in a 0.25 ha courtyard between the Biology and Life Science buildings on the campus of the University at Albany in Albany, New York (42°41'4.41"N, 73°49'18.07"W). Surrounded by buildings and enclosed walkways on all sides, this site was safe from unsolicited human interaction but still widely exposed to the elements. The plots rested on 3.0m x 0.5m rectangular frame supports. In turn, these frames were held approximately 0.9m above the ground by sawhorses. The position of each plot on the structure was decided by a random number generator. However, topsoil plots had to be setup 3 weeks prior to hydroponic plots because the sod required daily watering for 14 days after implantation. For this reason, topsoil plot positions were still randomly arranged but were limited to the same row, while hydroponic varieties took up the other four rows.

The twenty-one plots were constructed using 62-liter polypropylene storage boxes. These boxes have an area of $0.52m^2$ and a 17.8cm depth. A 1.3cm diameter drainage hole was drilled in a corner of each box and covered with plastic screening to prevent soil particles from clogging the tubing. This was especially important for plots using modular drainage systems due to the difficulty in maintaining a tight seal between the drainage panel and box. From the drainage hole, water flowed through polypropylene tubing into a 3.79L polyethylene sample bottle. A loop was made in this tubing and in the tubing from the bulk precipitation collector to trap water and minimize evaporation.

The one-gallon sample bottle for the bulk precipitation collector was connected with the same polypropylene tubing via a poly-outlet lid to a 125ml HDPE Nalgene bottle. The tubing extended into the bottle and was submerged in deionized water. This step was taken in an effort to further reduce evaporation from the 3.79L bottle. Unlike the green roof plots, the bulk precipitation collector did not have a saturated soil horizon to act as a humidified barrier against evaporation. The water in the Nalgene bottle saturated the air in the tube, keeping any sample water in the one-gallon bottle. A diagram of the bulk precipitation collector is shown in Figure 3.1.

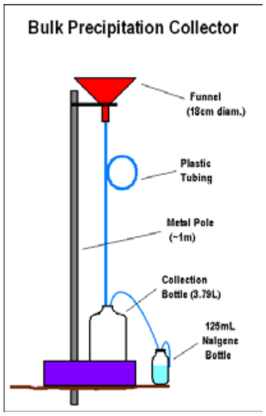


FIGURE 3.1. Diagram of the funnel-style bulk precipitation collector used in the experiment.

The conventional roof plot was a relatively simplistic design consisting of asphalt shingles nailed to a board of plywood which had been cut to the area of the box. The remaining 20 plots were designed to simulate the most common green roof models and therefore varied by several different factors. Figure 3.2 is a drawing of the twenty-one roof plots as they were arranged in the courtyard.

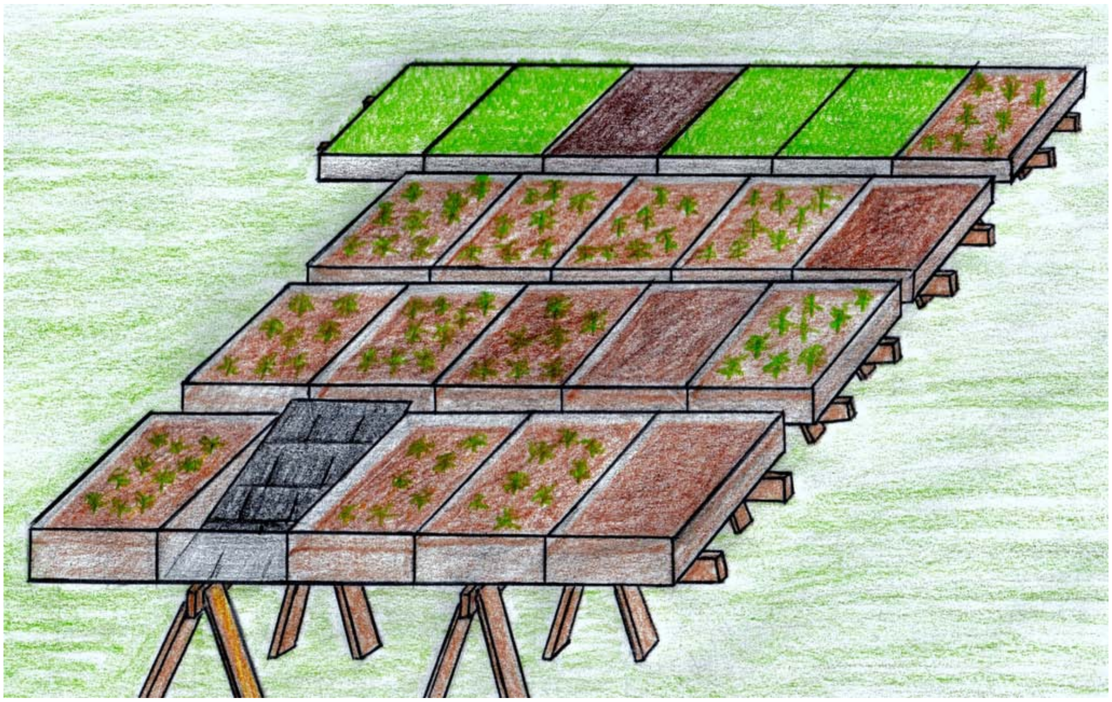


FIGURE 3.2. A diagram of the twenty-one roof plots, including the twelve green roof plots with *sedum acre*, four green roof plots with Kentucky Bluegrass sod, four green roof plots with no vegetation, and the one conventional (asphalt shingled) roof.

Drainage

The bottommost layer of these plots was responsible for drainage. Two commonly used green roof drainage systems were tested: aggregate and modular. Plots using an aggregate system contained a 2.54cm layer of coarse gravel (with diameters between 1.27-2.54cm). Although quite heavy (each 2.54cm layer weighed approximately 20kg), the aggregate system provides a relatively inexpensive way to keep excess water away from root systems, thus maintaining plant health. However, unlike a modular system, aggregate draining may require maintenance due to settling of the gravel (Dunnett and Kingsbury 2004).

The modular drainage panels used in this project were purchased from Bright Green Roofs, a green roof and living wall distributor based out of Hartland, Michigan. Made from high-density polyethylene (HDPE), these lightweight panels have an egg-carton shape. They work by elevating roots and soil approximately 1.5 inches above the roof foundation (or as in this case, the polypropylene box). Excess water drains through quarter-inch diameter holes drilled into the panels. A "bio blanket" is attached to the top of the panels. Approximately 0.5cm thick, it is made of natural fibers and works to anchor roots, prevent soil erosion and evenly distribute water among the root system and drainage holes.

Soil Type

The most important variable in this experiment was soil type. Four distinct soils were used; a basic, unfertilized topsoil and three hydroponic soils. The term "hydroponic" usually refers to gardening without any soil. Instead, plant roots are submerged into a mineral nutrient solution. However, common green roof practices employ chemically inert, soil-like hydroponic materials created by exposing specific media to great temperatures. These hydroponics are quite advantageous to green roofing due to their light weight and great water and nutrient holding capacities

(Dunnett and Kingsbury 2004). The three hydroponics used in this experiment were light expanded clay aggregate (LECA), perlite and vermiculite.

LECA is manufactured by baking pure clay to 1200ºC for approximately three hours. This creates uniform, low-density pellets with diameters between 0.6-1.27cm. LECA is non-biodegradable and has a neutral pH value. Due to the many tiny pores created in the pellets during the heating process, LECA is a very porous material. This creates a favorable environment for absorption of water and nutrients by plant roots as solution is held by the clay pellets. In addition to this benefit, the large grain size allows oxygen to enter the spaces between pellets and promotes plant health (Expanded Shale, Clay and Slate Institute 2008). However, the relatively large size of the pellets allows for some settling and compaction.

Perlite begins as a volcanic glass that softens and greatly expands when heated to approximately 870°C. Natural perlite is formed by the hydration of obsidian, a common igneous glass. Like LECA, perlite has a neutral pH, low density and high porosity but has a smaller and less uniform grain size (Perlite Institute 2005). Perlite's white, Styrofoam-like pellets are often included in store bought potting soils.

Vermiculite is a clay mineral formed from the weathering of igneous rock, specifically that containing biotite. Globally, the majority of raw vermiculite is mined from rock dating back to Precambrian time. The mineral expands into an accordion shaped grain with a high porosity and neutral pH when heated to between 1200-1350°C (Dunnett and Kingsbury 2004). The vermiculite grains used in this experiment were much smaller than both the LECA and perlite pellets and had the lowest density.

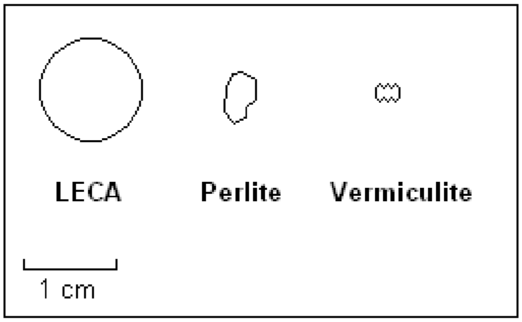


FIGURE 3.3. Grain sizes of hydroponic soils expanded clay (LECA), Perlite and Vermiculite.

The three hydroponics were mixed with Coco Peat at a ratio of 1:4 to provide additional nitrogen and water holding capacity. Unlike the more commonly used sphagnum peat moss, Coco Peat has a neutral to slightly acidic pH as well as the ability to retain water. Coco Peat is made by harvesting the outer material of coconut shells. Essentially, it is a combination of shell fibers and the substance holding these fibers to the husk. The most important advantage of Coco Peat is that it is made from a renewable resource and does not contribute to the destruction of wetlands unlike the harvesting of sphagnum peat.

A quarter of the plots used standard, unfertilized topsoil as soil. Relative to the hydroponics, this is a very dense soil and therefore not ideal for green roofing. The added weight means an additional obstacle during construction and necessitates a stronger structure. Despite these limitations, topsoil and sod are frequently employed in extensive green roofing. For this reason, topsoil was one of the tested soils.

Soil Depth

The third variable tested by the project was soil depth. Two common green roof soil depths were chosen: three and nine cm. In most cases, three cm is the absolute shallowest possible green roof depth and is used for buildings unable to structurally support more intensive systems. While this shallower depth is advantageous because it is lighter and requires less material (and therefore less financial strain), it also retains less water than larger depths. Because water retention is the most beneficial reason for having a green roof, this can be a major drawback. Additionally, the shallow depth also leaves the builder with less flexibility in vegetation selection. Drought resistant plants with shallow root systems are one of the few that can flourish at this depth.

The nine centimeter soil depth is heavier and more costly but can support a much wider variety of vegetation as well as increased water retention. Based on soil type, the added weight could increase subsidence, slightly impeding drainage.

Vegetation Type

The fourth and final variable tested was vegetation presence and type. Four plots containing topsoil were planted with Kentucky bluegrass (*Poa pratensis*) sod. Kentucky bluegrass is a shallow-rooted grass very common to the Northern United States and Canada (Kleber 1992).

Twelve hydroponic plots were planted with *Sedum acre*. Plants of the sedum genus are extremely common to green roofing due to their shallow root systems and high tolerances for both sun and shade. These perennials are also drought tolerant, storing water in their fleshy leaves. In fact, the only major requirement for healthy Sedums is a well-drained soil area which is more than adequately provided by the hydroponics and drainage layers (Wells 2008). *Sedum acre* grows to a maximum height of only two inches. However, it rapidly spreads to cover open ground, another desirable characteristic when green roofing (Wells 2008).

The final four plots contained no vegetation in order to test the effects of only soil on runoff acidity and composition. Due to space and budget concerns, the lack of vegetation was not tested on all drainage and depth variables. Instead, each soil type was tested with the most common green roof drainage system and soil depth: modular drainage and nine centimeter depths (Dunnett and Kingsbury 2004). Table 3.1 summarizes all the plots and their characteristics.

Plot ID	**Drainage System**	**Soil Type**	**Soil Depth (cm)**	**Vegetation Type**
C1	Aggregate	LECA	3	*Sedum acre*
C2	Modular	LECA	3	*Sedum acre*
C3	Aggregate	LECA	9	*Sedum acre*
C4	Modular	LECA	9	*Sedum acre*
C5	Modular	LECA	9	No Vegetation
P1	Aggregate	Perlite	3	*Sedum acre*
P2	Modular	Perlite	3	*Sedum acre*
P3	Aggregate	Perlite	9	*Sedum acre*
P4	Modular	Perlite	9	*Sedum acre*
P5	Modular	Perlite	9	No Vegetation
V1	Aggregate	Vermiculite	3	*Sedum acre*
V2	Modular	Vermiculite	3	*Sedum acre*
V3	Aggregate	Vermiculite	9	*Sedum acre*
V4	Modular	Vermiculite	9	*Sedum acre*
V5	Modular	Vermiculite	9	No Vegetation
T1	Aggregate	Topsoil	9	*Poa pratensis*
T2	Modular	Topsoil	3	*Poa pratensis*
T3	Modular	Topsoil	9	No Vegetation
T4	Modular	Topsoil	9	*Poa pratensis*
T5	Aggregate	Topsoil	3	*Poa pratensis*

TABLE 3.1. Characteristics of all green roof plots.

Collection and Cleaning

Samples were collected from ten precipitation events from June through October 2008. Samples were collected as soon as possible (typically within 60-90 minutes) after a precipitation event in an effort to maintain accurate pH levels. Previous studies indicate that weathering reactions could occur as a result of exposure of sample in the bulk precipitation collector to the atmosphere for several days. These reactions may underestimate the amount of H+ ions and in turn underestimate the acidity of the sample (Likens et al. 1977). Although ten sample collections were made throughout the experimental period, no samples from the collection on June 16th, 2008, which followed three days of heavy rain, were used in the study due to non-reproducible pH, alkalinity and ion concentration measurements. It is thought that either vessel contamination or a long collection period (three days) during the heavy rain events created contaminated and therefore unusable samples.

After collection, samples were taken to the lab and weighed on an analog balance. Relative mass was the important factor in this case because these measurements were only compared to other mass measurements in this study and not external studies. After net mass of each sample was obtained, samples were transferred to 250ml HDPE bottles for pH measurement and refrigerated storage. Approximately 20ml of each sample were filtered through 0.45 micron membranes into scintillation vials and refrigerated. These samples were later used for ion chromatography.

After the collection and transfer of samples to 250ml bottles, the one-gallon bottles were thoroughly rinsed twice with tap water and twice with 18.3 MΩ deionized water. The tap water removed any material left behind from the previous collection while the deionized water removed any contaminants from the tap water. No detergents were used in this process due to washing frequency as well as the large size and abnormal shape of the bottles. After washing and air drying, these bottles were ready for the next collection. Because this process took several days to complete, two 22-bottle sets were used to expedite collection.

The 250ml HDPE bottles and the 20ml scintillation vials were soaked overnight in a detergent solution (Citranox) and scrubbed to remove particles. Bottles and vials were then rinsed with tap water three times, once with deionized water, then filled with deionized water to soak overnight. They were then emptied, rinsed once more with deionized water and dried in a drying oven. After this process, bottles and vials were ready for use.

Analysis: pH and Alkalinity

After collection and weighing of each sample set, pH measurements were taken using a Thermo Orion glass-bulb electrode and benchtop meter. The electrode was filled with Ag/AgCl solution. Before measurement, the meter was calibrated with buffer solutions of pH 4, 7 and 10.

The ion chromatograph uses a carbonate-bicarbonate eluent and thus cannot distinguish between bicarbonate concentrations in samples and eluent. Total alkalinity measurements were taken to estimate the concentration of bicarbonate in each sample. It was assumed that bicarbonate alkalinity was equal to total alkalinity. This was done by using the pH electrode and meter along with a Hach digital titrator as well as a magnetic stirring plate to promote homogeneity. Samples were measured to 100mL in a graduated cylinder and then poured into a 250ml beaker for titration. Each titration digit is equivalent to 1.25×10^{-3}ml of 1.6N H_2SO_4. Samples were titrated with 1.6 N

H_2SO_4 to an endpoint of pH 4.50, following the “Phenolphthalein and Total Method,” (Hach Company 2006).

Geochemical Analysis

Ion chromatography was used to determine concentrations of major ions fluoride, chloride, nitrate, phosphate and sulfate. Anion concentrations were measured using a method modified from US EPA method 300.1A, “Determination of inorganic anion in drinking water by ion chromatography” (US Environmental Protection Agency 1997). A similar method was used to measure concentrations of cations lithium, sodium, ammonium, potassium, magnesium and calcium.

The process begins by diluting 0.5mL aliquots of sample to 5.0mL with deionized water (18.3MΩ-cm) in 5.0mL Dionex Poly-Vials. Aliquots of direct precipitation (denoted as “R” in data) were not diluted. All aliquots were analyzed by Dionex ion chromatograph; the ICS-90 for cation analysis and the DX-120 for anion analysis. The anion eluent used is 3.5mM/1mM sodium carbonate-sodium bicarbonate. The cation eluent used was 20mM methanesulfonic acid with a tetrabutylammonium hydroxide regenerant solution. Samples were loaded via an AS-40 automated sampler and Chromeleon version 6.5 software was used on a Dell PC.

Quality Control and Assurance

Standard solutions of known concentrations were used to calibrate the ion chromatograph. For each sample set, accuracy was assured by analyzing a 6 cation standard solution and a 5 anion standard solution from Dionex as well as a 5 ion standard solution made in the laboratory. The 5 ion standard contains sodium, potassium, chloride, nitrate and sulfate. Two samples in each set were fortified with this solution to measure analyte recovery. Two samples in each set were also duplicated to determine analytical precision. The laboratory fortified matrices contained 0.5mL of samples, 0.5mL of the 5 ion standard and 4.0mL of 18.3MΩ-cm deionized water.

Percent recovery of the 5 ion standard solution was determined using the following formula:

$$\% \text{ Recovery} = 100([\text{LFM}] - [\text{sample}])/[\text{std}]),$$

where “LFM” is the ionic concentration in the laboratory fortified matrix, “sample” is the mean ionic concentration of the unfortified aliquot and its duplicate, and “std” is the ionic concentration of the 5 ion standard solution.

An aliquot each of the 6 cation standard and the 5 anion standard were analyzed with each sample set. Percent recoveries were determined using the formula:

$$\% \text{ Recovery} = 100[\text{measured}]/[\text{std}],$$

where “measured” is the ionic concentration of each standard analyzed in the laboratory and “std” is the ionic concentration of each standard determined by the Dionex Corporation. Percent recovery analyses of all standards are show in Appendix I.

Analytical precision was determined by calculating the mean and standard deviation of sample duplicates. Precision is reported as percent relative standard deviation using the following formula:

$$\%RSD = 100(\sigma)/(x)$$

Where "σ" is the standard deviation of the sample and duplicate ionic concentrations and "x" is the mean ionic concentration of the sample and duplicate. Each sample set contained two sets of samples and duplicates, so each sample set also produced two percent relative standard deviations for each ion. Percent relative standard deviation analyses are shown in Appendix II.

In an effort to identify any major inaccuracies, percent error was determined for every sample analyzed by the ion chromatograph throughout the experiment. This totaled 251 calculations using the formula:

$$\%\ \text{Error} = 100 \times |([\sum\text{cations}]-[\sum\text{anions}])/([\sum\text{cations}]+[\sum\text{anions}])|,$$

where "∑cations" is the sum of all cation concentrations in meq/L for each sample and "∑anions" is the sum of all anion concentrations in meq/L for each sample. Percent error analyses are shown in Appendix III.

The minimum detection limit (MDL) was set as 3x the standard deviation of "initial" 18.3MΩ-cm deionized water laboratory blank ionic concentrations. "Initial" deionized water laboratory blanks are defined as those that did not follow standards (and thus did not risk contamination by standards) in the ion chromatography run sequence. Deionized water analyses are shown in Appendix IV.

Chapter Four: Results

Potassium-Chloride Contamination

Some samples were contaminated by residual potassium chloride solution (KCl) during pH measurement. During storage, the glass bulb of the pH electrode was stored in a KCl solution to extend life and increase accuracy. However, even after rinsing the bulb with deionized water, some KCl remained and was transferred to samples in 250mL bottles. Aliquots were taken from these bottles to be analyzed in the ion chromatograph. Concentrations of potassium and chloride ions were abnormally high in many samples. Figure 4.1 indicates the potassium-chloride contamination in bulk precipitation. One collection set (8/7/2008) was not contaminated by KCl because aliquots for ion chromatography were removed before pH was measured. These data were used to examine relationships between the green roofs and potassium and chloride ions. All potassium and chloride ion data can be found in Appendix III**.**

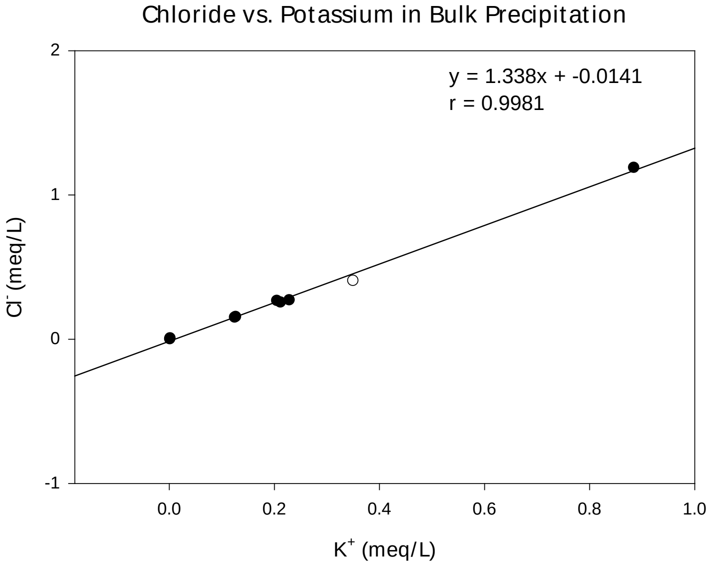


FIGURE 4.1. The correlation of chloride and potassium indicates contamination.

Precipitation

The fundamental data for this study came from the funnel-style bulk precipitation collector. To determine the influence of the green roofs on acid precipitation, one most know exactly what is entering the treated plots. The bulk precipitation collector also gave a fairly accurate measurement of the total volume of rain that fell during a particular collection period. Figure 4.2 shows pH, dissolved ion concentrations and the volume of bulk precipitation collected throughout the experiment. A significant (α>0.05), positive correlation exists between pH and precipitation volume. In contrast, nitrate and sulfate ion concentration have significantly negative correlations with both pH and precipitation volume. Correlation matrices are found in Figures 5.3-5.5, chapter five.

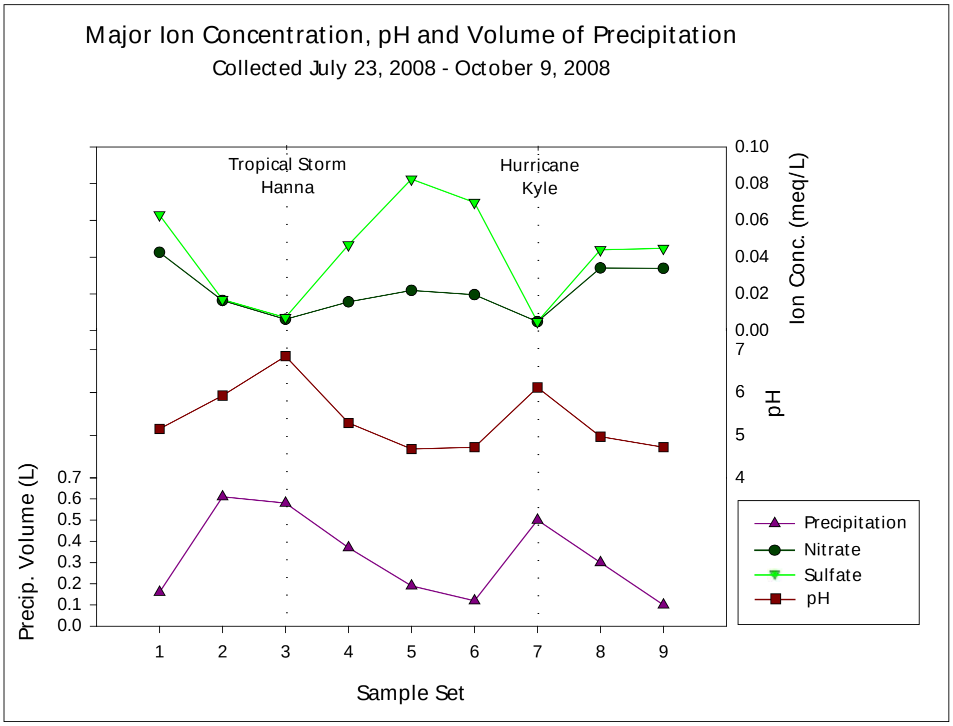


FIGURE 4.2. Total volume, pH and nitrate and sulfate concentrations of precipitation for the 9 collections in sequential order.

Alkalinity

Bicarbonate concentration (HCO_3^-) in green roofs showed a very distinct and intriguing pattern. Average HCO_3^- is illustrated in Figure 4.3. In hydroponic plots (C, P and V), HCO_3^- varied little by type of soil (vermiculite plots have slightly higher values than perlite and expanded clay) and even less by depth of soil. However, a clear difference exists between hydroponic plots with modular drainage and those with aggregate (gravel) drainage. Modular drainage plot HCO_3^- was roughly half those of aggregate drainage plots. After further consideration, it was determined that the gravel used in the experiment was made of limestone and thus released carbonate when exposed to weak acids from precipitation and soil water. This carbonate reacted with hydrogen ions to form the dissolved HCO_3^- solution.

Sod roofs had the opposite relationship; while aggregate plots had comparatively high HCO_3^- (more than double even the aggregate hydroponic plots), modular sod plot concentrations were between 13% and 35% higher than the aggregate sod plot concentrations. This is likely due to a high calcium carbonate content in the topsoil. However, it is unknown why HCO_3^- in modular drainage topsoil plots is even higher than the aggregate topsoil plots.

Controls R and CR had the lowest HCO_3^- levels which were 0.08 meq/L and 0.43 meq/L, respectively. The conventional roof was made of asphalt shingles which most likely contributed some HCO_3^- to runoff. This accounts for the more than quadrupled concentration of HCO_3^- in CR as compared to R.

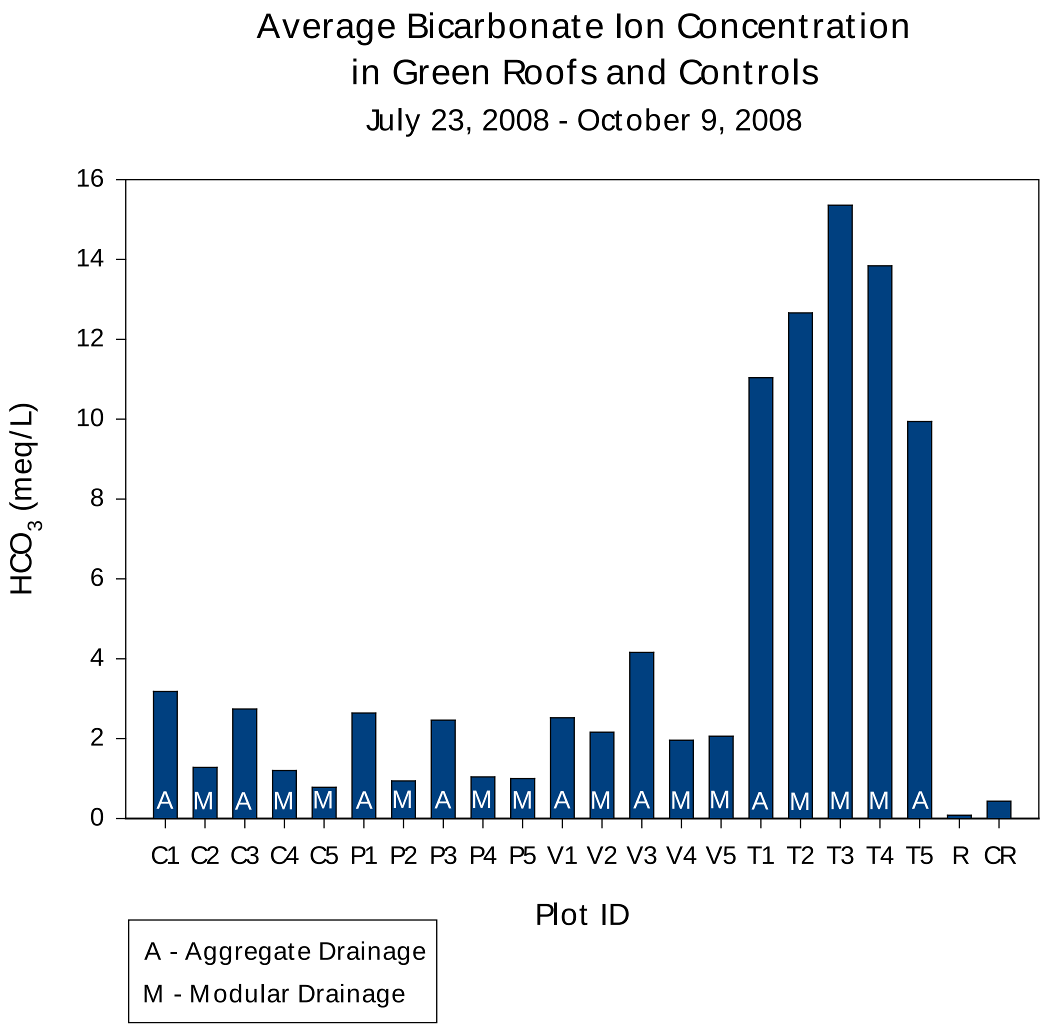


FIGURE 4.3. Average HCO_3^- of all plots and controls. Drainage type of each plot is indicated by "A" (aggregate) or "M" (modular).

pH in Precipitation

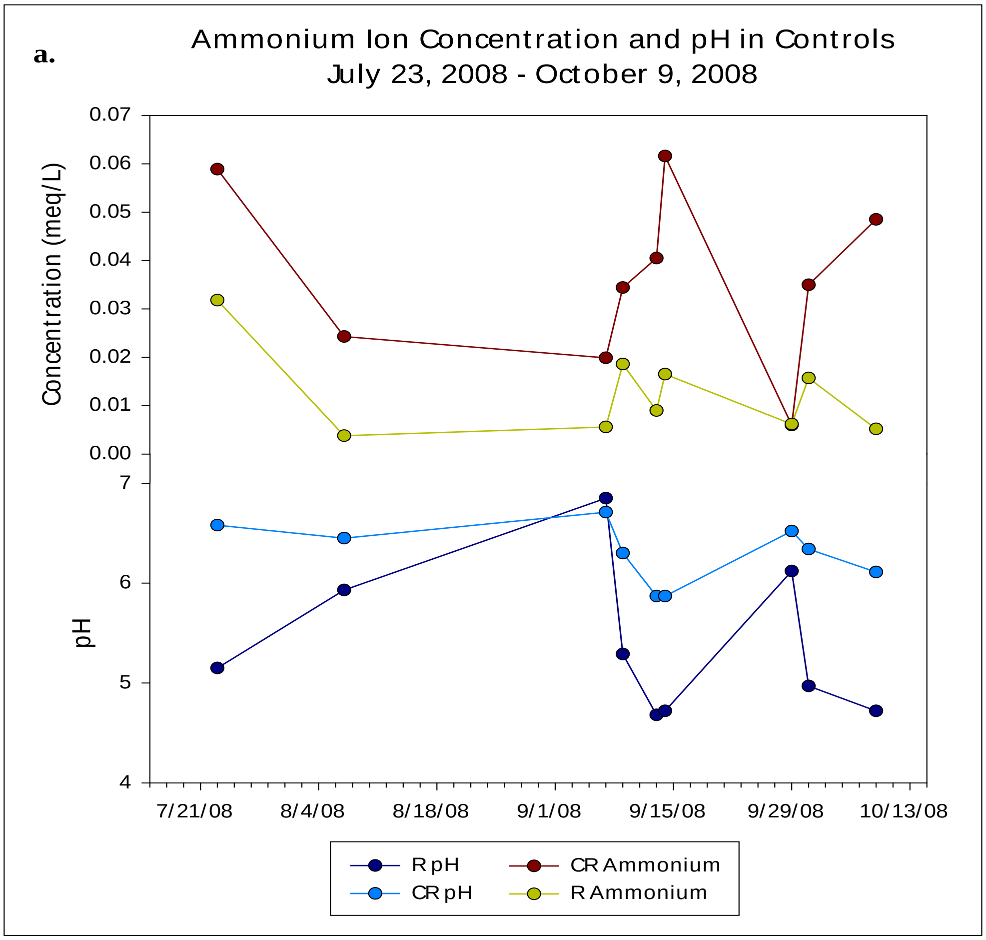
The most obvious difference between treated plots and bulk precipitation (R) is level of acidity. The results of this experiment show that green roofs were more successful in lowering the pH of anthropogenically acidified precipitation than conventional roofs (Table 4.1). Green roof runoff pH levels ranged from 6.79 to 7.80. Sod plots had the highest average pH level while Perlite plots had the lowest.

Plot Type	**Average pH**	**S.D.**	**n**
Expanded Clay	7.28	0.28	9
Perlite	7.15	0.34	9
Vermiculite	7.33	0.20	9
Sod (Topsoil)	7.75	0.04	9
Bulk Precipitation	5.38	0.76	9
Conventional Roof	6.31	0.30	9

TABLE 4.1. Average pH values of the four soil types and controls. “S.D.” is standard deviation and “n” is number of collections included.

The higher pH levels for the sod plots are likely due to an alkaline topsoil composition. While all green roof plot acidities hovered around neutral, the conventional roof average pH was 6.31 and average pH of bulk precipitation was 5.38, which is below typical precipitation levels (Seinfeld and Pandis 2006). There was no significant difference between the pH of plots with vegetation and the pH of those without.

Although bulk precipitation (R) and the conventional roof plot runoff (CR) were expected to have almost duplicate results, this was not the case. Though pH of CR and R have a significant positive correlation ($r = 0.81$: $p<0.05$), CR was a full pH unit higher than R throughout the study. Further research suggests this is due to the asphalt shingles used to make the conventional roof. Noguchi et al. (1995)showed that asphalt dust in the atmosphere decreases acidity in precipitation. This may account for the greater neutrality in CR samples. In addition to this, Figure 4.4 shows a significantly negative correlation between CR ammonium ion concentration and pH in R ($r = -0.77$: $p<0.05$). Along with information from the Noguchi study, this correlation suggests that a cation exchange in which hydrogen ions take the place of ammonium ions in the shingles occurs and the ammonium ions are flushed away in runoff. This raises the ammonium concentration in CR and raises the pH of CR runoff.



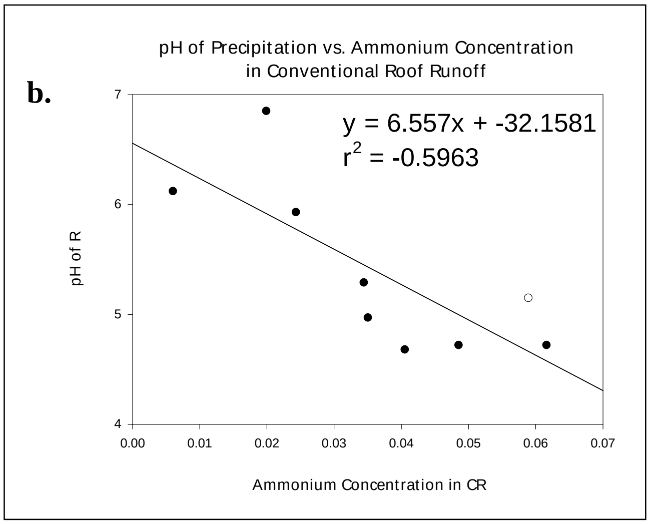


FIGURE 4.4. (a) Ammonium ion concentration and pH in runoff from the conventional (shingled) roof and bulk precipitation collector throughout the experimentation period. (b) Negative correlation between pH of precipitation and ammonium concentration in conventional roof runoff.

A discernable pattern in Figure 4.5 is that pH in hydroponic plots is slightly higher for those employing aggregate drainage than those with modular. This result is likely due to the consumption of hydrogen ions in the precipitation as the acids react with the calcium carbonate in the limestone gravel (Equation 4.1).

EQUATION 4.1

$$\mathrm{CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3}$$

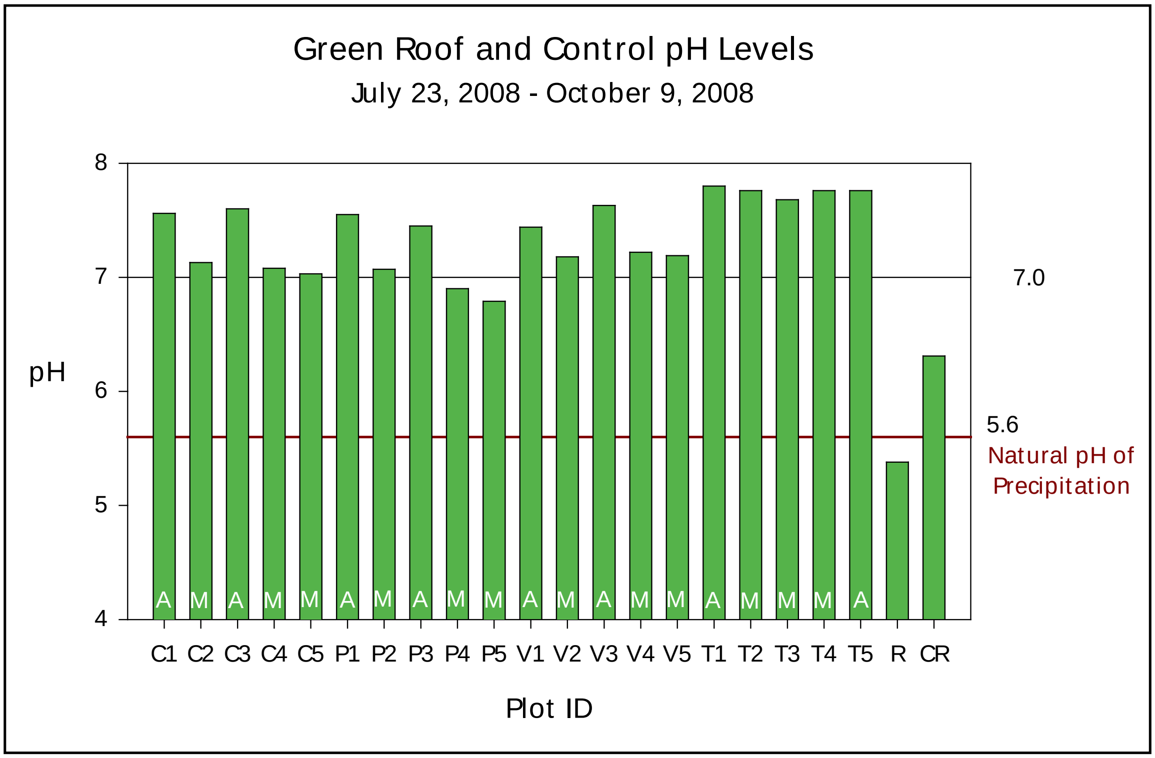


FIGURE 4.5. Average pH of all plots and controls throughout the experiment. The reference line at 7.0 represents neutral pH while the line at 5.6 shows the typical pH of precipitation, according to Seinfeld and Pandis (2006).

Dissolved Nitrate Ion Concentrations

Average nitrate concentrations in all sod plots were above that of bulk precipitation. In fact, plot T5 had almost 60% more nitrate whereas the plot with no vegetation (T3) had the lowest average nitrate concentration. It was predicted that the vegetation would consume nitrate as a nutrient. This was probably the case, but unexpectedly high levels of nitrogen in the topsoil likely contributed to the high nitrate concentrations and overshadowed any effect the vegetation may have had. Nitrate concentrations in sod plots are shown in Figure 4.6.

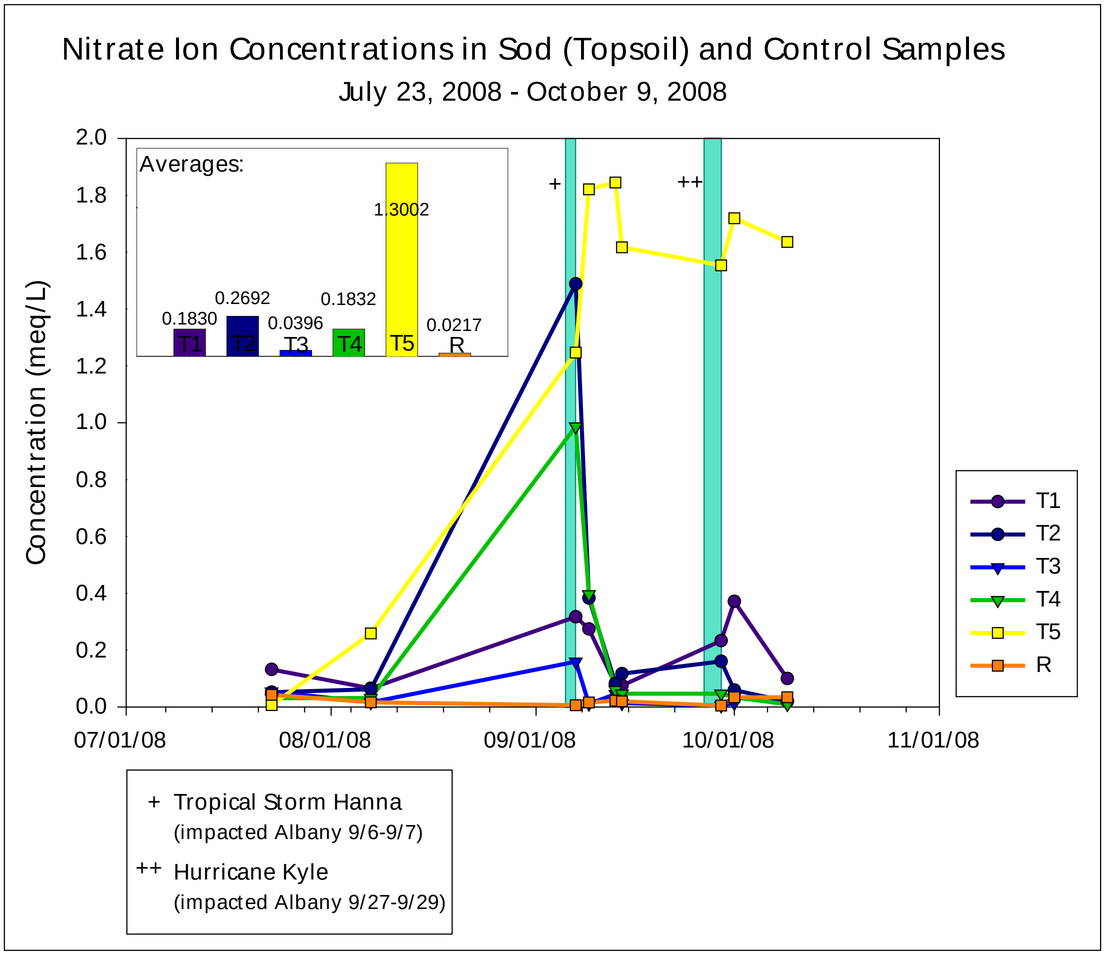


FIGURE 4.6. Nitrate ion concentrations in runoff from plots with sod soils. The two blue columns represent the periods in which Tropical Storm Hanna and Hurricane Kyle influenced weather in Albany. The inset shows the concentration averages in precipitation and runoff of each sod plot for all nine collections.

Average nitrate concentrations in the expanded clay plots were all below the average concentration in bulk precipitation. Expanded clay was the only soil type to achieve this. However, the ratio of the clay plot nitrate concentrations to precipitation nitrate concentrations varied by collection (Figure 4.7a). Data also shows that average concentration in aggregate clay plots was higher than in modular plots.

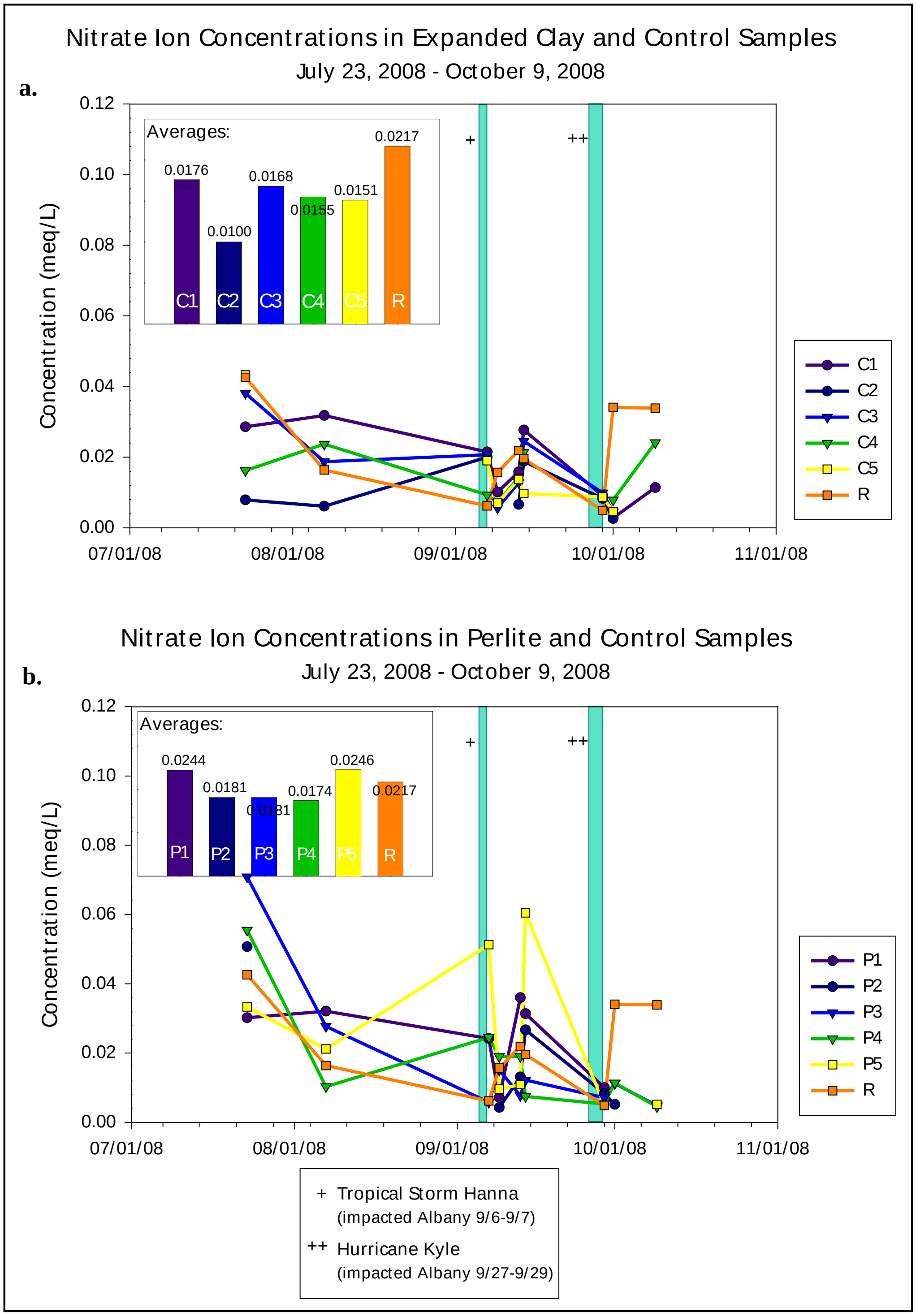


FIGURE 4.7. Nitrate ion concentrations in runoff from plots with expanded clay (a) and Perlite (b) soils. The two blue columns represent the periods in which Tropical Storm Hanna and Hurricane Kyle influenced weather in Albany. The insets show the concentration averages in precipitation and runoff of each plot for all nine collections.

Perlite nitrate concentrations also varied by collection, indicated in Figure 4.7b. Average concentrations in plots P2, P3 and P4 were all below the precipitation average while plots P1 and P5 were above.

Nitrate concentrations in vermiculite plots again varied by collection and had only one plot (V5) with an average below the average nitrate concentration in precipitation (Figure 4.8a). While nitrate concentrations for plots V1, V2, and V3 were not too far above the average for R (15%, 5% and 4%, respectively), plot V4's average was 40% higher. It should also be noted that throughout the experiment, plot V4 experienced several problems with sample collection. This plot only yielded measurable sample in five out of the nine collections. No major drainage or sealing issues could be identified so these difficulties were attributed to rapid evaporation from the thin layer of low density soil in V4.

All hydroponic green roofs showed a similar pattern for the final two collections. While nitrate concentration in precipitation jumped to 0.03 meq/L on 10/1/08 and 10/09/08, all hydroponic nitrate concentrations did not reach higher than 0.02 meq/L.

The conventional roof's nitrate concentration has a significant positive correlation with nitrate concentration in precipitation. The only abnormality came from the 9/7/08 Tropical Storm Hanna collection; CR's nitrate concentration spiked instead of falling as expected. This can be seen in Figure 4.8b. The 9/7/08 sample was run through the ion chromatograph twice in an attempt to find an analytical error but both sequences produced similar results. The spike may be the result of contamination.

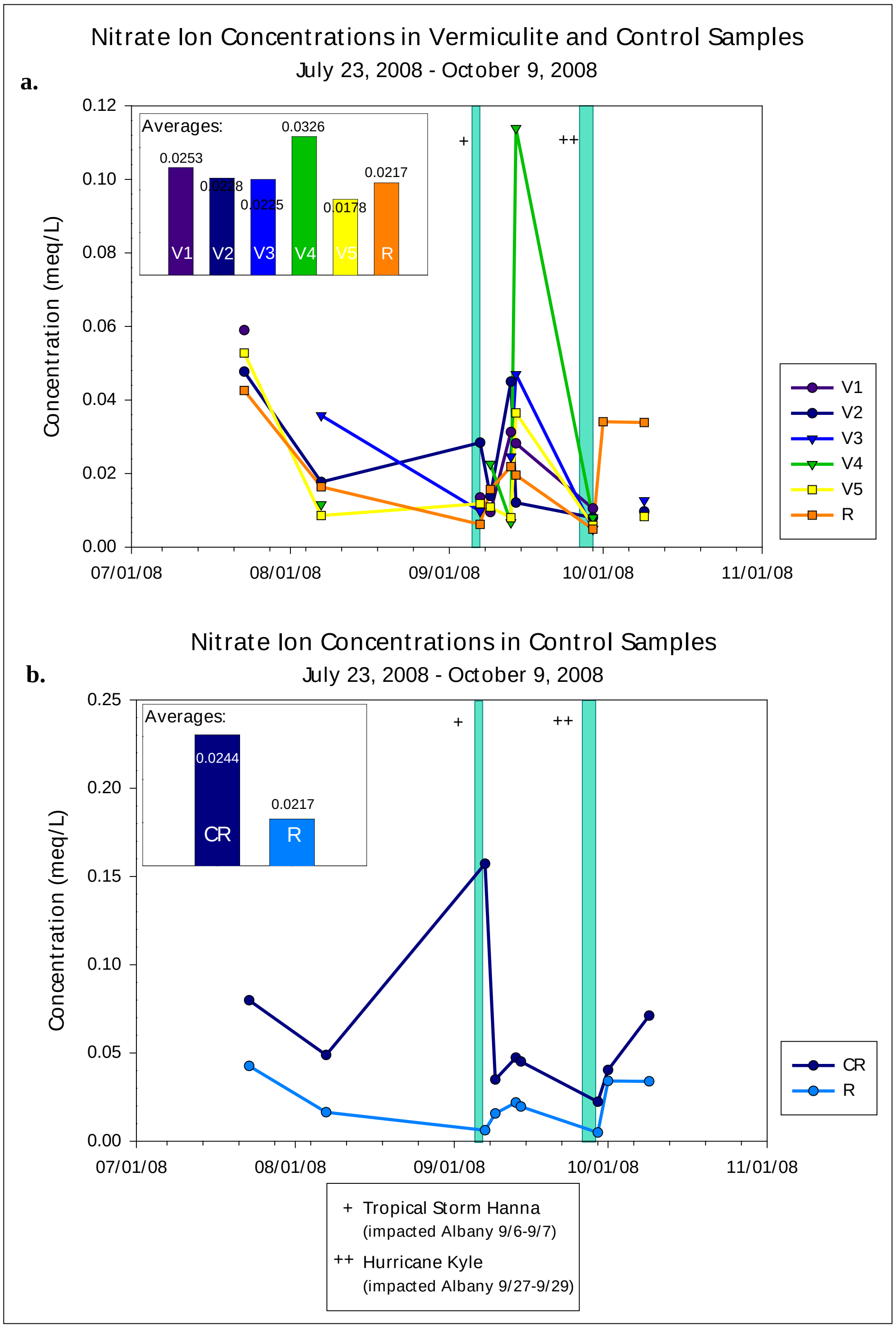
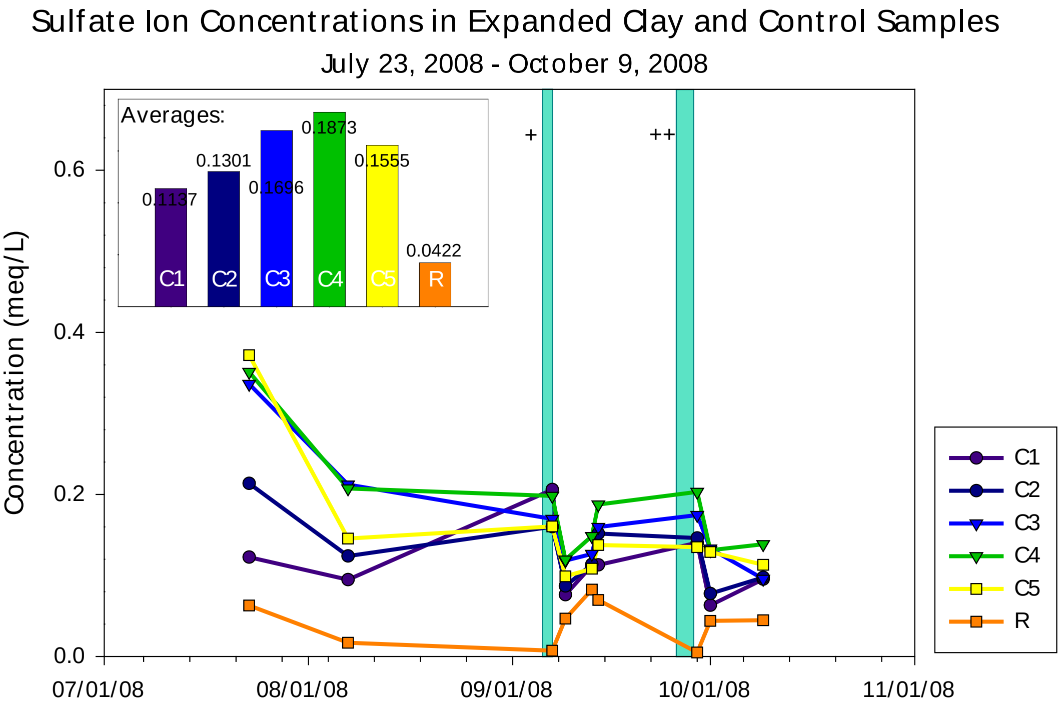


FIGURE 4.8. Nitrate ion concentrations in runoff from the vermiculite plot (a) and the conventional roof (b). The two blue columns represent the periods in which Tropical Storm Hanna and Hurricane Kyle influenced weather in Albany. The insets show the concentration averages in precipitation and runoff of each plot for all nine collections.

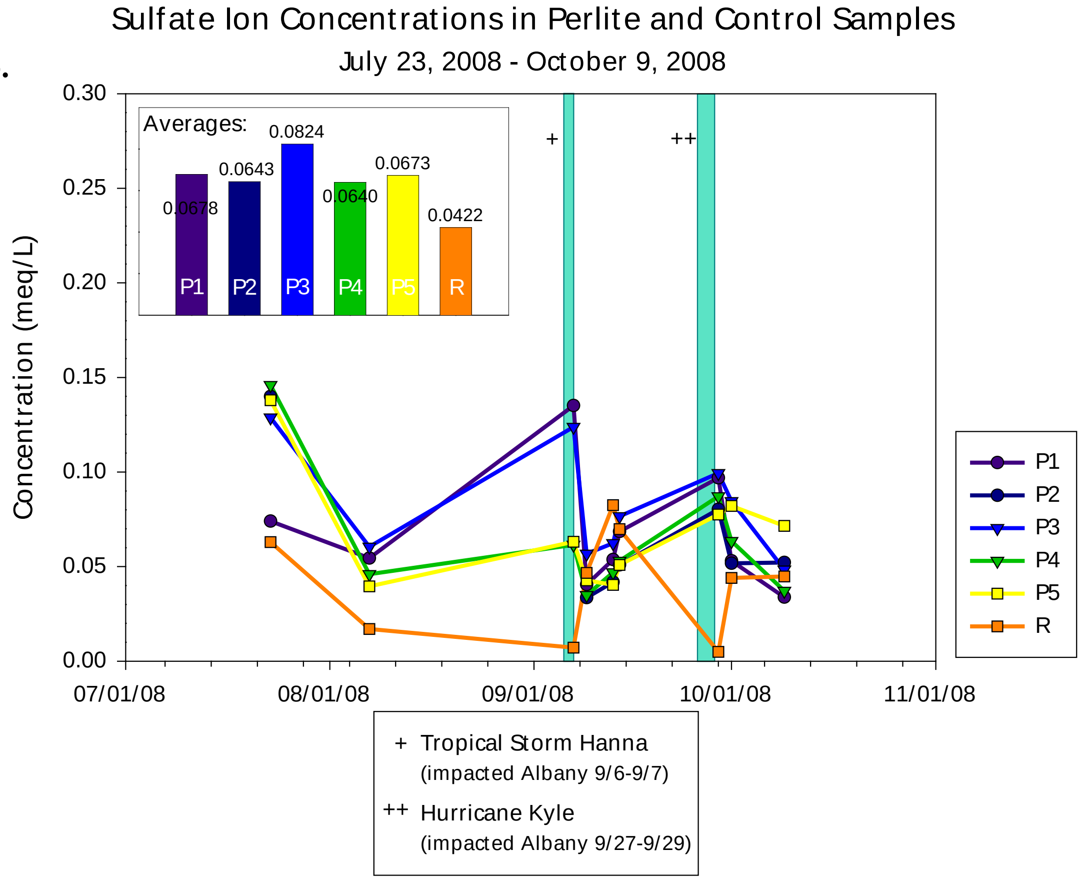
Dissolved Sulfate Ion Concentrations

Average sulfate concentration for all treated plots was above that of precipitation. The green roofs did not have the effect on sulfate that was hypothesized. In fact, the green roofs and conventional roof plot actually added sulfate to the runoff. The sod plots contributed the most sulfate to runoff followed by expanded clay, Vermiculite, Perlite and the conventional roof. The averages of all Perlite plots and the average of the conventional roof were comparable, being 0.07 meq/L and 0.06 meq/L, respectively. Figure 4.11a-4.11e illustrates sulfate ion concentrations in the treated plots compared with concentration in precipitation.

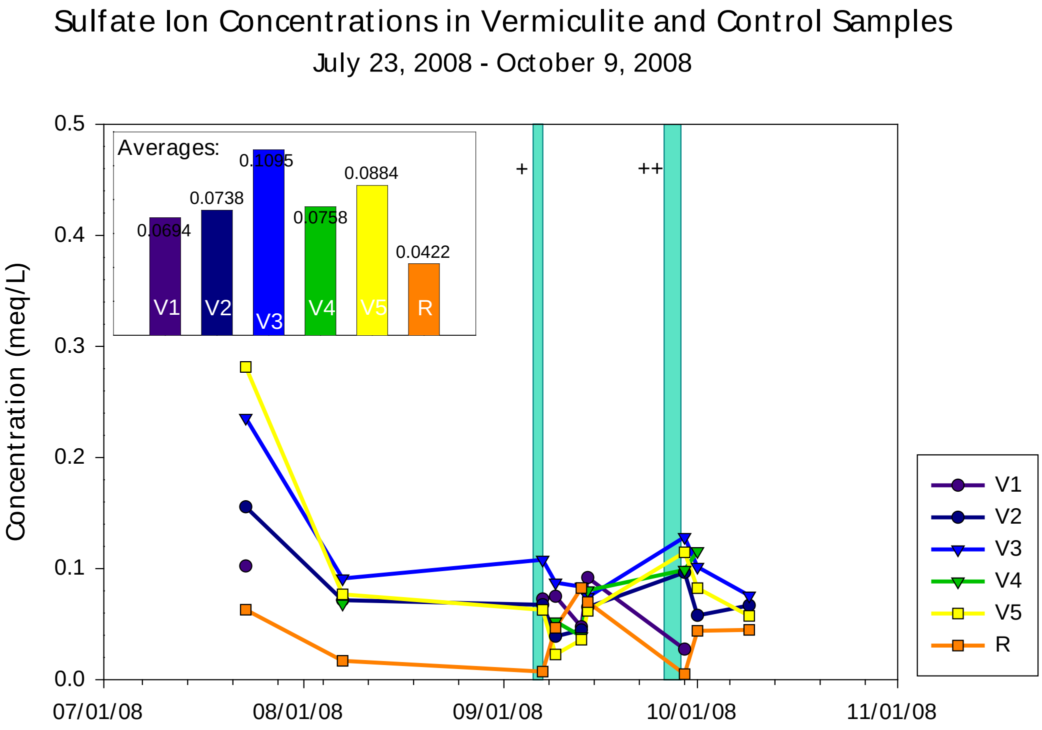
a.


Sulfate Ion Concentrations in Expanded Clay and Control Samples
July 23, 2008 - October 9, 2008
Averages:
0.1137
0.1301
0.1696
0.1873
0.1555
0.0422
C1
C2
C3
C4
C5
R
+
++
Concentration (meq/L)
0.0
0.2
0.4
0.6
07/01/08
08/01/08
09/01/08
10/01/08
11/01/08
C1
C2
C3
C4
C5
R

b.

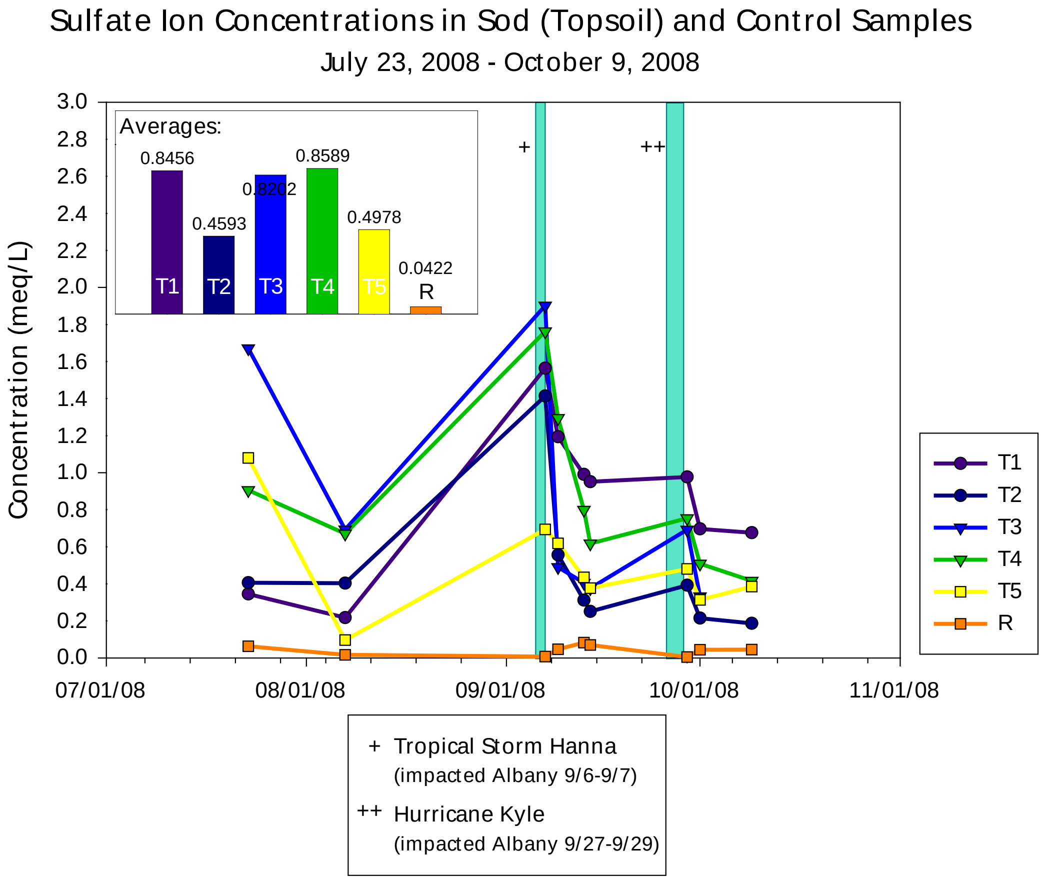

Sulfate Ion Concentrations in Perlite and Control Samples
July 23, 2008 - October 9, 2008
Averages:
0.0678
0.0643
0.0824
0.0640
0.0673
0.0422
P1
P2
P3
P4
P5
R
+
++
Concentration (meq/L)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
07/01/08
08/01/08
09/01/08
10/01/08
11/01/08
P1
P2
P3
P4
P5
R
+ Tropical Storm Hanna
(impacted Albany 9/6-9/7)
++ Hurricane Kyle
(impacted Albany 9/27-9/29)

c.



Sulfate Ion Concentrations in Vermiculite and Control Samples
July 23, 2008 - October 9, 2008

d.



Sulfate Ion Concentrations in Sod (Topsoil) and Control Samples
July 23, 2008 - October 9, 2008

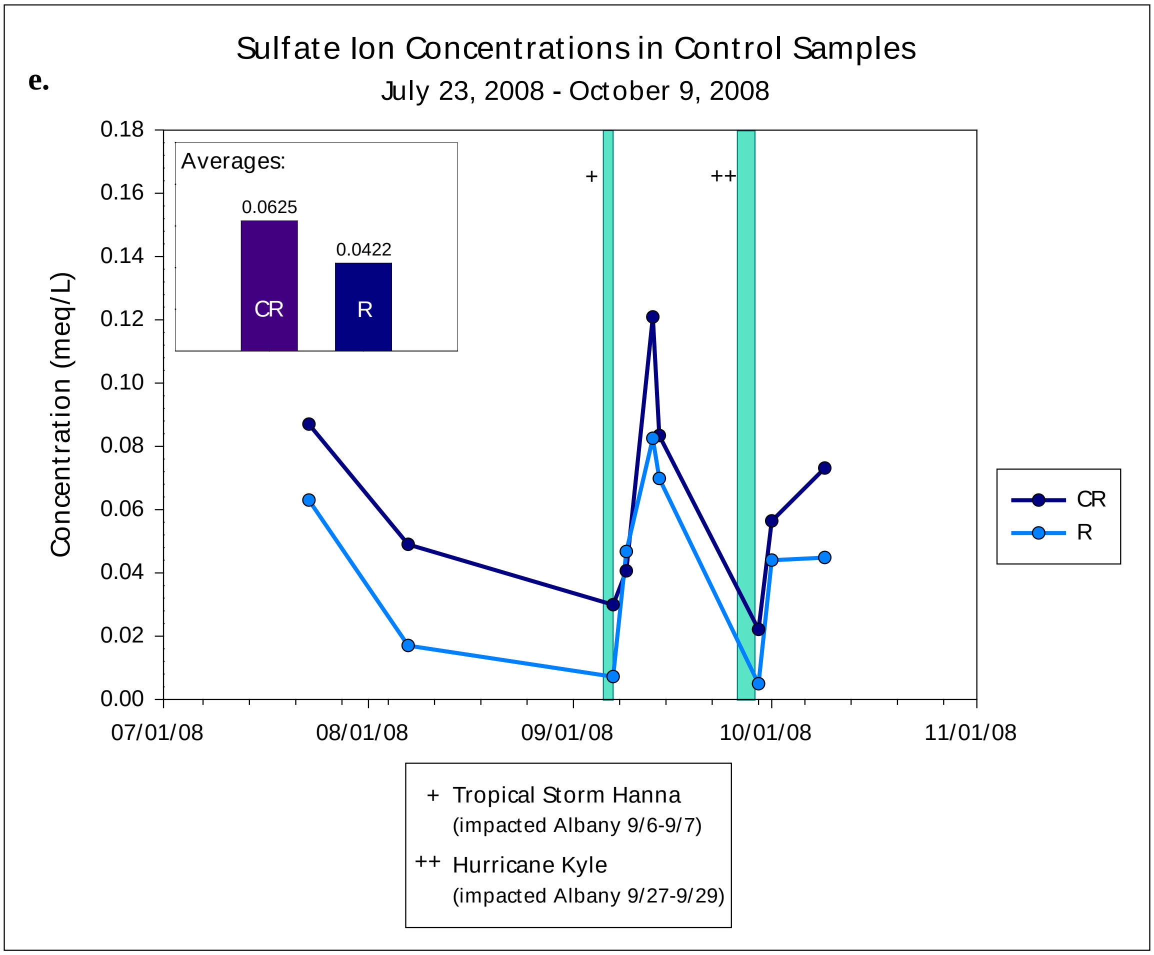


FIGURE 4.9. Pages 39-41. Sulfate ion concentrations in runoff from plots with expanded clay (a), Perlite (b), vermiculite (c) and sod (d) soils and the conventional roof (e). The two blue columns represent the periods in which Tropical Storm Hanna and Hurricane Kyle influenced weather in Albany. The insets show the concentration averages in precipitation and runoff of each plot for all nine collections.

Other Dissolved Ions

Fluoride and lithium ions were found to be present in relatively low concentrations (Appendix V). Most average plot concentrations were in orders of magnitude of 10^{-3} meq/L. For both ions, average concentrations were highest in expanded clay plots and lowest in Perlite and sod plots. The most obvious difference was between soil types and no significant difference was found between soil depth, drainage type or plant presence.

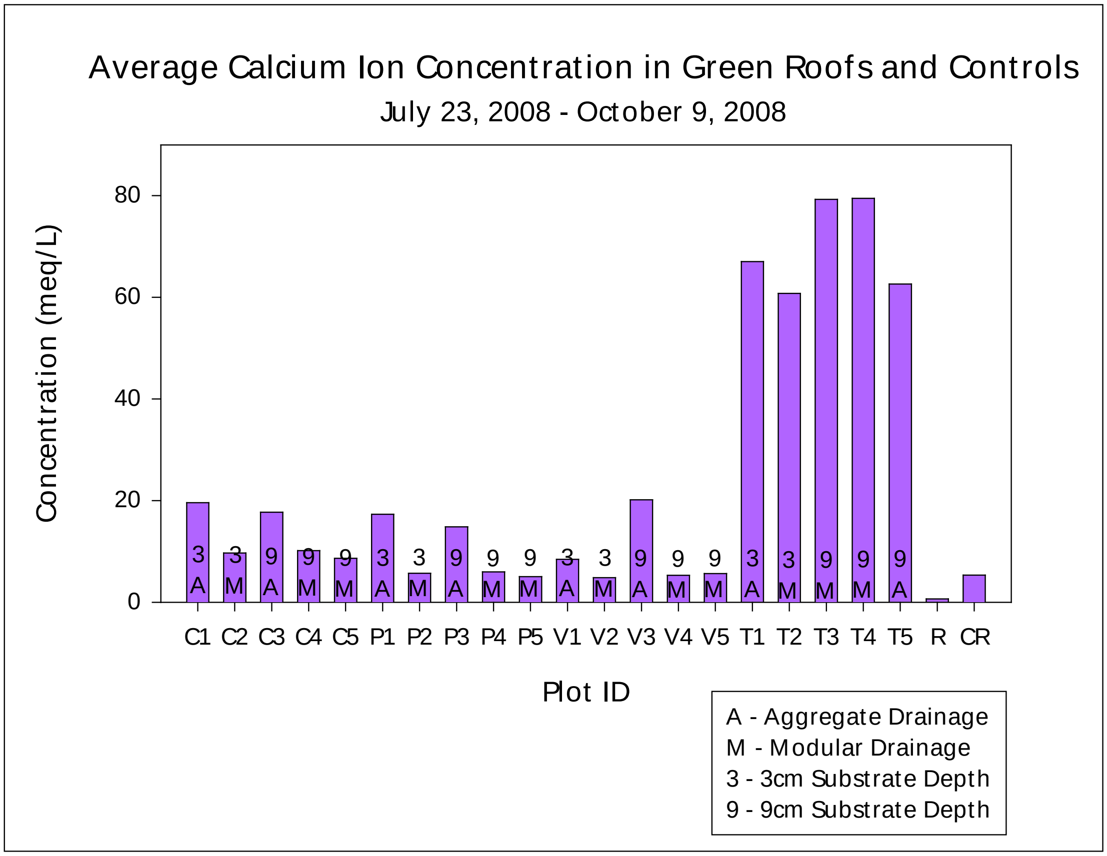


FIGURE 4.10. Average calcium ion concentrations in all plots throughout the experiment. Drainage type of each plot is indicated by “A” (aggregate) or “M” (modular) while soil depth is indicated by “3” (3cm) and “9” (9cm).

Average calcium ion concentrations differed in two major respects. First, plots consisting of the three hydroponic soils had similar values, ranging from 5.0377 meq/L (plot P5) to 20.17 meq/L (plot V3). However, though average concentrations from hydroponic plots were similar, a distinct pattern is evident in Figure 4.10 indicating modular drainage plot runoff had about half the calcium than aggregate drainage plots.

The second major difference is that the sod plots had much higher values than the hydroponic; sod runoff concentrations ranged between 3-4 times greater. Neither plant presence nor drainage type appeared to have an influence on calcium concentration. The controls had the lowest average concentration, with CR’s values near the lowest of the hydroponic plots and R almost one-tenth of CR’s concentration.

Average magnesium ion concentrations followed a similar pattern to calcium in that hydroponic runoff values were about 3-4x less than in sod runoff. The control values were also comparable; average CR concentration fell just below lower hydroponic concentrations and R concentration was just over one-tenth of CR. As demonstrated in Figure 4.11a, no major distinctions can be made between soil depth, drainage type or plant presence.

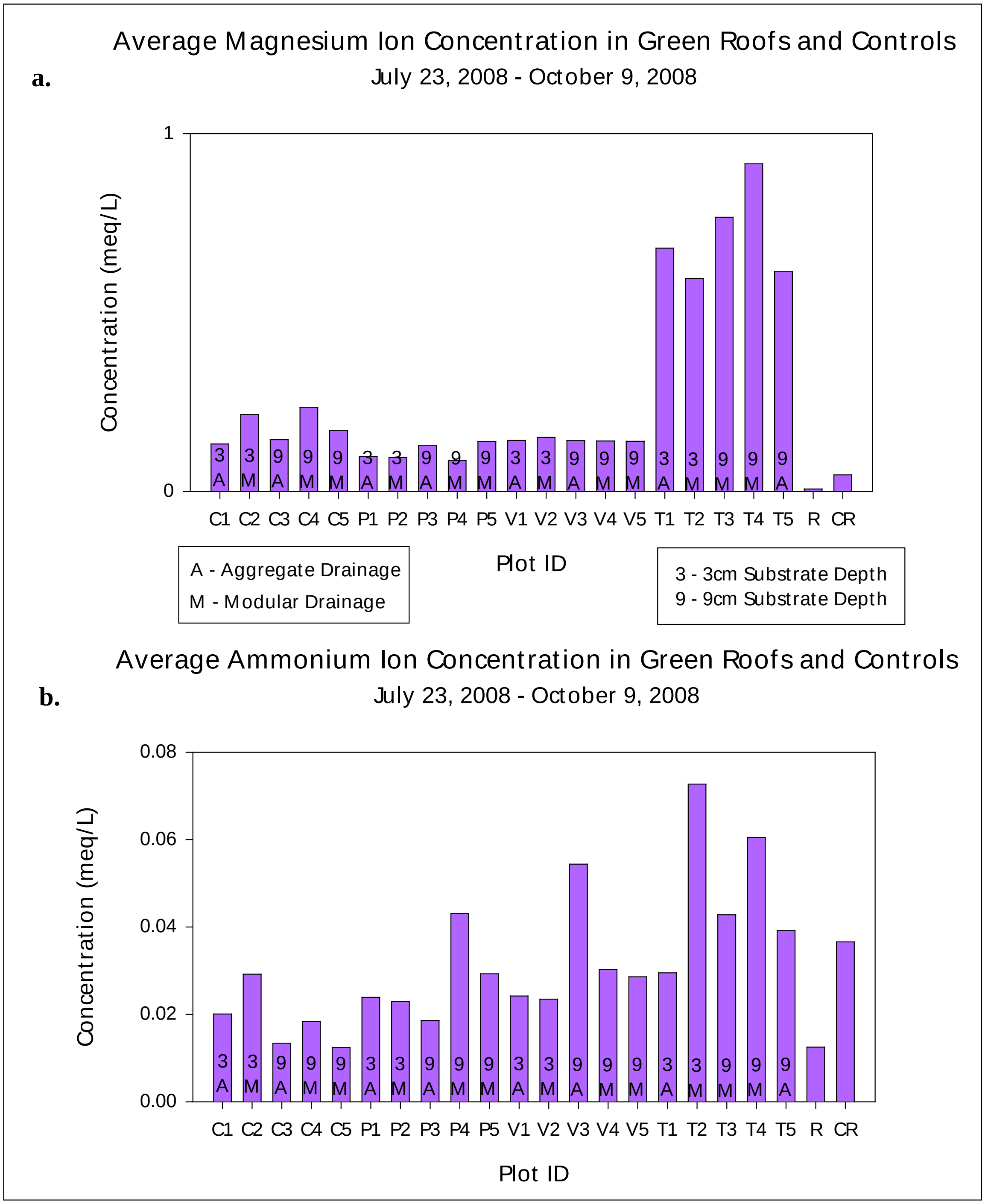


FIGURE 4.11. (a) Average magnesium ion concentrations in runoff from all plots throughout the experiment. (b) Average ammonium ion concentrations in all plots throughout the experiment. Drainage type of each plot for (a) and (b) is indicated by “A” (aggregate) or “M” (modular) and soil depth is indicated by “3” (3cm) and “9” (9cm).

Average ammonium ion concentrations differ from the other secondary ions in that CR has a relatively high value. In fact, it is higher than the average ammonium concentrations of 80% of hydroponic plots and one of the sod plots (T1), which have the highest concentrations. The only distinguishable pattern in Figure 4.11b is a difference in ammonium concentration based on soil type.

Figure 4.12a indicates average sodium ion concentrations differed by soil type. Vermiculite plots had the highest concentrations followed by sod, Perlite and expanded clay plots. Additionally, plots with 3cm of Perlite, clay and topsoil soil and modular drainage had the lowest sodium concentration while plots of other depths and drainage types of these same soils showed no patterns.

Finally, the uncontaminated chloride and potassium data from August 7, 2008 shows that chloride concentration again differed by soil type, with topsoil plots having the highest concentrations of both ions (Figure 4.12b). Additionally, perlite plots had the lowest concentrations of both ions, though expanded clay and vermiculite plot concentrations were comparatively low as well. No significant correlations were found between ion concentration and drainage type or depth for either chloride nor potassium but topsoil plots showed much lower concentrations of both ions in the non-vegetated plot. As expected, the controls were both very low as compared to green roof plots.

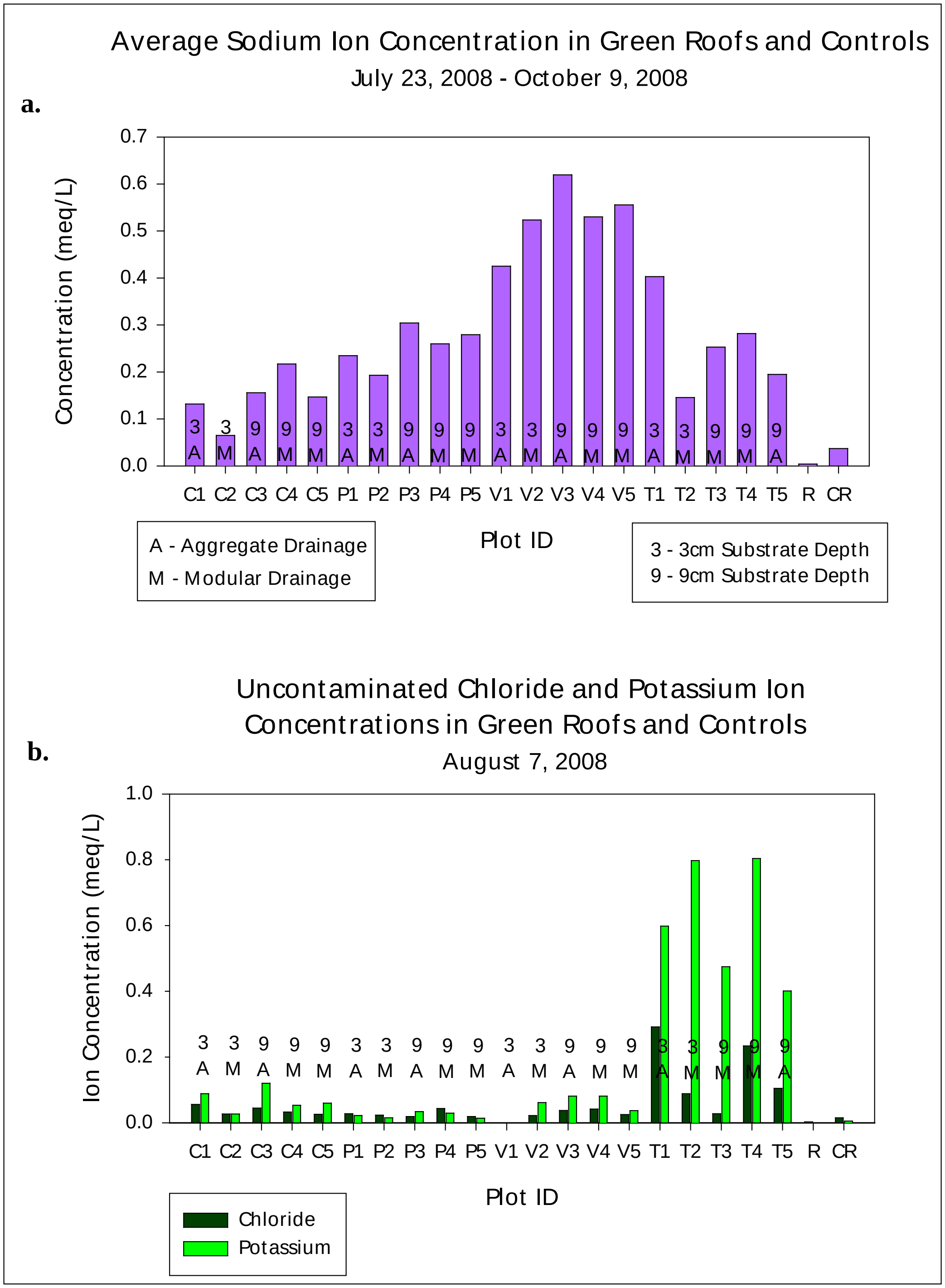


FIGURE 4.12. (a) Average sodium ion concentrations in runoff from all plots throughout the experiment. (b) Chloride and potassium ion concentrations in all plots except V1. The samples are from the 8/7/2008 collection, the only one which was not contaminated by KCl solution from the pH meter. Drainage type of each plot for (a) and (b) is indicated by “A” (aggregate) or “M” (modular) and soil depth is indicated by “3” (3cm) and “9” (9cm).

Chapter Five: Discussion

Comparative Data

Ion concentrations and pH data from three sites in New England (Table 5.1) were compared to measured values obtained in this study. The first set of data is from the Hubbard Brook Ecosystem Study (Likens et al.1977). This benchmark study used a funnel-style bulk precipitation collector (the model for this study) to collect samples between 1963 and 1974. The Hubbard Brook Experimental Forest is located in Central New Hampshire, about 200 kilometers north-northwest of Boston, MA. The study period took place during and just after the creation of the Clean Air Act and thus nitrate and sulfate concentrations are higher than present day average values.

The other two sets of data were collected by the National Atmospheric Deposition Program (NADP) in Bennington, VT and Frost Valley, NY between 1981-2006 and 1983-2006, respectively. Bennington, VT is approximately 60 kilometers east-northeast of Albany and Frost Valley, NY is approximately 100 kilometers southwest of Albany in the Catskill Mountains. Again, these studies began as the Clean Air Act was coming into affect, and as acidity and precipitation ion concentrations levels were readily decreasing as time progressed. Nitrate and sulfate dissolved ion concentrations and pH of precipitation from the two NADP sites is illustrated in Figure 5.1.

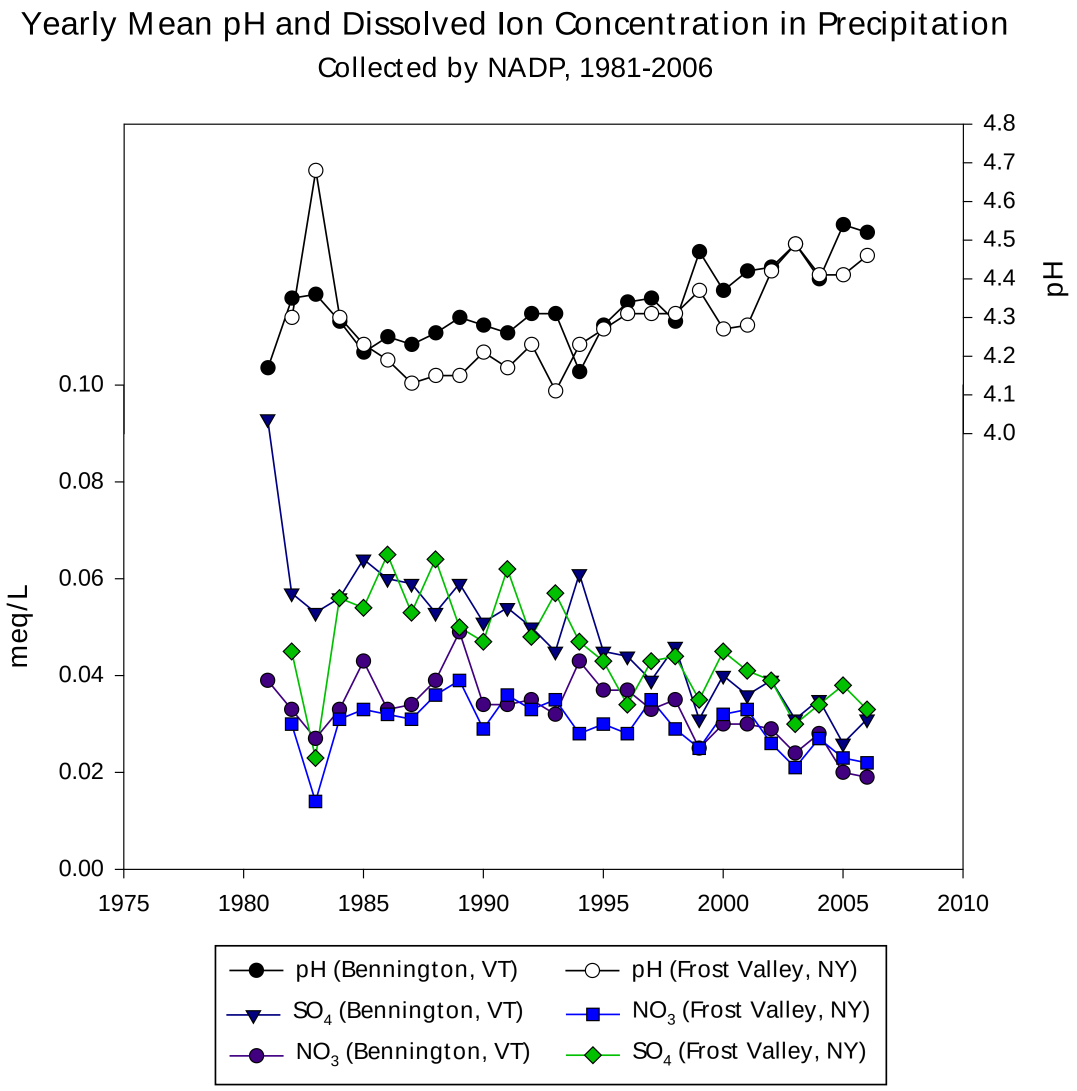


FIGURE 5.1. pH and nitrate and sulfate ion concentrations measured in precipitation collected by the National Atmospheric Deposition Program (NADP) in Bennington, VT and Frost Valley, NY between 1981-2006 and 1983-2006, respectively. Source: (NADP 2008).

As expected, nitrate and sulfate concentrations are slightly higher in the older studies than this study while pH is slightly lower. These differences could also be associated with differences in geographic location. Nonetheless, averages are comparable and thus support data from this study.

Location	NO_3^- (meq/L)	SO_4^{3-} (meq/L)	Date
Hubbard Brook	0.0237	0.0603	1963-1974
Vermont	0.033	0.048	1981-2006
Catskills	0.030	0.045	1983-2006
UAlbany	0.03	0.03	7/2008-10/2008

TABLE 5.1. Weighted averages of nitrate and sulfate concentrations in precipitation collected in Central New Hampshire, Bennington, VT, Frost Valley, NY and Albany, NY. Sources: (National Atmospheric Deposition Program 2008) and (Likens et al. 1977, 32).

Tropical Systems

During the experimentation period, Albany was impacted by two tropical systems. The first was Tropical Storm Hanna, which dropped a total of approximately 2.1cm of rain on the collection site between September 6th and 7th.

The second tropical system was Hurricane Kyle. Between September 27th and 29th, Kyle released 1.8cm of rain on the collection site. Track positions of Hurricane Kyle and Tropical Storm Hanna provided by the National Weather Service are shown in Figure 5.2.

As predicted in chapter one, these storms produced precipitation with higher pH and lower nitrate and sulfate ion concentrations. Plots showing this data have quite distinctive peaks during these tropical events. The storms are denoted by blue stripes in such plots.

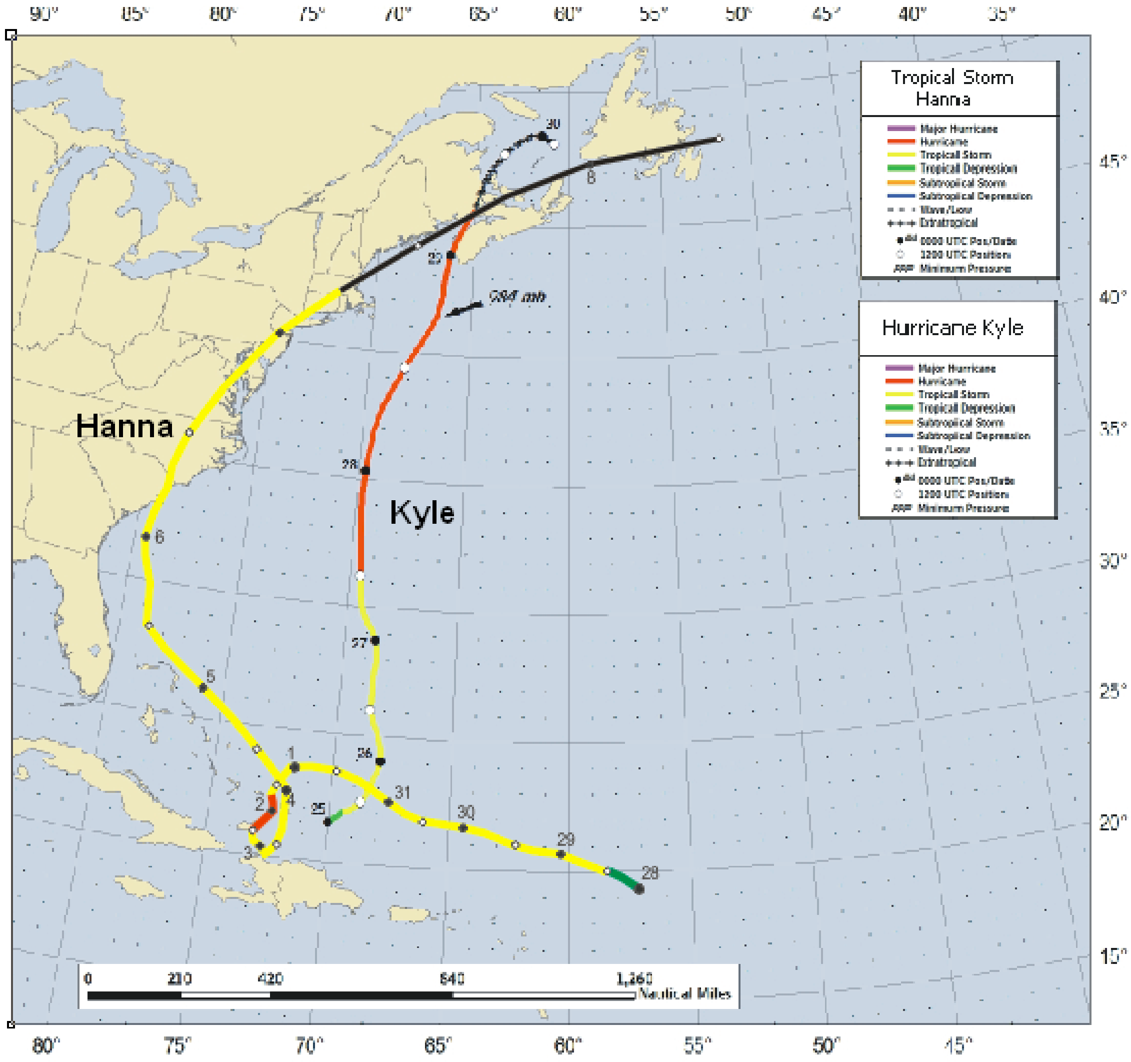


FIGURE 5.2. Paths of Tropical Storm Hanna and Hurricane Kyle during the 2008 hurricane season.

Source: (National Oceanic and Atmospheric Administration 2009).

Trends in Acidity of Green Roof Runoff

The most important control on pH in green roof runoff was soil type. Perlite plots had the most neutral (nearest to 7.00) average pH and the most neutral Perlite plot held sedums, modular drainage and a 3cm soil depth (P2). Expanded clay plots had the second-most neutral average pH and the most neutral plot contained modular drainage, a 9cm soil depth and no vegetation (C5).

Within Perlite and expanded clay soil categories, acidity varied the most by drainage type. Modular drainage runoff was more neutral than aggregate drainage runoff. This is likely due to an alkaline effect of the calcium carbonate in the gravel aggregate creating a more basic solution. There is no observable relationship between soil depth and acidity with Perlite soils but possibly between plant presence and acidity. Plots lacking vegetation with both Perlite and expanded clay soils had the lowest pH values in their respective soil groups.

Vermiculite ranked third in average neutrality. This soil's most neutral plot was V2, which had modular drainage, a 3cm soil depth and sedums. Plot V5 (modular drainage, 9cm depth and no vegetation) was just one-hundredth of a pH unit above V2. Like Perlite and expanded clay plots, average vermiculite plot pH varied by drainage type with the modular plots having more neutral values than aggregate plots.

The fourth soil type, topsoil, had much higher average pH levels than the three hydroponic groups. Acidity levels showed no clear difference by drainage type or soil depth but a small difference in plant presence; the plot without vegetation (V3) had a slightly lower pH than those with vegetation. A correlation matrix for pH of all plots is shown in Figure 5.3.

These results indicate that the best means to create neutral pH green roof runoff is to use a hydroponic soil and modular drainage. However, all green roofs produced significantly more neutral runoff than from bulk precipitation and the conventional roof.

	C1	C2	C3	C4	C5	P1	P2	P3	P4	P5	V1	V2	V3	V4	V5	T1	T2	T3	T4	T5	R	CR	Volume (L)
Precip. Volume (L)																							1.00
CR																						1.00	0.68
R																					1.00	0.81	0.90
T5																				1.00	-0.78	-0.68	-0.61
T4																			1.00	0.81	-0.94	-0.77	-0.87
T3																		1.00	0.67	0.25	-0.67	-0.28	-0.81
T2																	1.00	0.64	0.79	0.81	-0.83	-0.56	-0.72
T1																1.00	0.84	0.63	0.94	0.88	-0.97	-0.75	-0.89
V5															1.00	0.60	0.57	0.48	0.39	0.40	-0.60	-0.15	-0.49
V4														1.00	0.52	0.94	0.53	0.34	0.78	0.77	-0.86	-0.80	-0.86
V3													1.00	0.30	0.53	0.83	0.76	0.84	0.82	0.71	-0.76	-0.34	-0.77
V2												1.00	0.72	0.89	0.80	0.84	0.80	0.69	0.73	0.59	-0.85	-0.49	-0.87
V1											1.00	0.45	0.61	0.14	0.62	0.31	-0.07	0.56	0.19	-0.07	-0.24	0.19	-0.48
P5										1.00	0.66	0.90	0.67	0.89	0.87	0.82	0.62	0.46	0.63	0.62	-0.77	-0.42	-0.75
P4									1.00	0.90	0.64	0.88	0.56	0.93	0.71	0.72	0.50	0.46	0.65	0.45	-0.72	-0.41	-0.77
P3								1.00	0.68	0.65	0.02	0.89	0.45	0.70	0.63	0.65	0.79	0.53	0.58	0.47	-0.73	-0.51	-0.69
P2							1.00	0.75	0.33	0.35	-0.10	0.56	-0.15	0.44	0.48	0.30	0.34	0.31	0.15	-0.09	-0.55	-0.47	-0.38
P1						1.00	0.24	0.76	0.49	0.57	0.07	0.78	0.71	0.40	0.61	0.65	0.91	0.68	0.58	0.57	-0.62	-0.23	-0.61
C5					1.00	0.68	0.39	0.84	0.88	0.76	0.22	0.87	0.48	0.92	0.57	0.67	0.67	0.37	0.61	0.53	-0.66	-0.44	-0.72
C4				1.00	0.95	0.68	0.29	0.74	0.88	0.85	0.35	0.86	0.49	0.89	0.67	0.70	0.65	0.36	0.55	0.56	-0.64	-0.39	-0.71
C3			1.00	0.77	0.83	0.64	0.41	0.76	0.85	0.71	0.60	0.87	0.60	0.91	0.56	0.59	0.54	0.71	0.57	0.25	-0.62	-0.26	-0.82
C2		1.00	0.59	0.60	0.63	0.70	0.36	0.69	0.71	0.76	0.37	0.83	0.79	0.65	0.74	0.88	0.82	0.67	0.86	0.70	-0.90	-0.54	-0.73
C1	1.00	0.51	0.51	0.70	0.67	0.91	0.16	0.69	0.43	0.56	0.03	0.68	0.54	0.28	0.61	0.48	0.78	0.35	0.33	0.52	-0.40	-0.03	-0.39

FIGURE 5.3. Correlation matrix for acidity of all plots. Significance exists when the r-value is greater than or equal to the critical value (±0.66). This value was calculated by applying degrees of freedom (df = n-2) to a sample set of 9 (df =7) and a 95% confidence interval (p = 0.05) to the table of critical values for Pearson correlation in a two-tailed test.

Trends in Nitrate Concentrations in Green Roof Runoff

Soil type again proved to be the most important control on nitrate concentration in green roof runoff. Expanded clay plots had the lowest average nitrate concentration followed by Perlite, vermiculite and topsoil plots. Similar to pH results, topsoil values were much higher than hydroponic values. While this variable was obvious across the board, effectiveness of other variables differed by soil type.

Expanded clay plots were affected by drainage type; aggregate plots produced runoff with greater nitrate concentrations than modular plots. Perlite and vermiculite plots do not appear to have been influenced by drainage type or soil depth. Interestingly enough, any difference caused by plant presence is inverted in these two soil types; the Perlite plot with modular drainage and a 9cm soil depth had 29% less nitrate than the same plot with no vegetation. For the same two plots in the vermiculite category, the plot with no vegetation had 45% less nitrate than the plot with vegetation. With an expanded clay or topsoil soil, these same two plots had approximately equal nitrate concentrations. The conclusion here is that if there is an effect of plant presence, it drastically varies by soil type.

The topsoil plot with the lowest nitrate concentration had modular drainage, 9cm soil depth and no vegetation. The four other topsoil plots had approximately equal nitrate concentration, suggesting the only variable to potential influence nitrate concentration in sod and topsoil runoff is plant presence.

The conventional roof average nitrate concentration is nearly three times that of bulk precipitation. Like the unexpectedly high ammonium concentration in CR runoff, this is due to the asphalt in the shingles acting as a source of nitrate (Noguchi et al. 1995 2361).

Expanded clay is clearly the best soil choice if intentions are to reduce nitrate concentration in runoff. Expanded clay and Perlite were the only soils to have averages below that of bulk precipitation. A correlation matrix for nitrate concentration of all plots is shown in Figure 5.4.

	C1	C2	C3	C4	C5	P1	P2	P3	P4	P5	V1	V2	V3	V4	V5	T1	T2	T3	T4	T5	R	CR	Volume (L)	pH
pH																								1.00
Precip. Volume (L)																							1.00	0.90
CR																						1.00	0.21	0.52
R																					1.00	-0.08	-0.72	-0.69
T5																				1.00	-0.27	-0.26	-0.23	-0.29
T4																			1.00	0.09	-0.52	0.78	0.50	0.69
T3																		1.00	0.84	-0.16	-0.20	0.98	0.28	0.58
T2																	1.00	0.88	0.99	0.06	-0.55	0.82	0.52	0.74
T1																1.00	0.50	0.25	0.53	0.31	-0.20	0.20	0.39	0.41
V5															1.00	-0.24	-0.19	0.01	-0.20	-0.52	0.62	0.11	-0.49	-0.31
V4														1.00	1.00	-0.31	-0.07	-0.23	-0.12	0.18	0.34	0.26	-0.63	-0.53
V3													1.00	0.72	0.00	-0.62	-0.25	-0.39	-0.24	0.15	-0.14	-0.33	-0.10	-0.34
V2												1.00	-0.26	-0.33	0.43	-0.14	0.07	0.43	0.07	-0.39	0.44	0.34	-0.21	-0.12
V1											1.00	0.75	-0.08	0.40	0.84	-0.66	-0.45	0.00	-0.47	-0.78	0.95	0.08	-0.73	-0.50
P5										1.00	0.24	0.15	0.39	0.96	0.58	0.02	0.45	0.48	0.39	-0.23	-0.06	0.52	-0.03	0.17
P4									1.00	0.25	0.78	0.81	-0.46	-0.35	0.70	0.01	0.15	0.41	0.18	-0.62	0.43	0.40	-0.15	0.05
P3								1.00	0.84	0.16	0.86	0.56	-0.25	-0.07	0.78	-0.24	-0.25	-0.02	-0.24	-0.84	0.56	0.07	-0.16	-0.08
P2							1.00	0.88	0.80	0.61	0.94	0.58	-0.18	0.88	0.96	-0.59	-0.47	0.70	-0.40	-0.90	0.62	0.89	-0.65	-0.22
P1						1.00	0.59	0.27	0.22	0.44	0.69	0.59	0.55	0.25	0.36	-0.76	-0.19	0.20	-0.26	-0.38	0.49	0.23	-0.36	-0.35
C5					1.00	0.44	0.92	0.89	0.95	0.24	0.86	0.75	-0.52	-0.12	0.75	-0.35	0.04	0.40	0.02	-0.96	0.51	0.46	-0.26	0.06
C4				1.00	0.33	0.71	0.68	0.12	-0.27	-0.02	0.60	-0.32	0.48	0.35	0.10	-0.86	-0.47	-0.29	-0.54	-0.35	0.20	-0.15	-0.25	-0.26
C3			1.00	0.55	0.88	0.59	0.99	0.75	0.70	0.63	0.85	0.53	-0.12	0.71	0.88	-0.52	0.04	0.35	-0.02	-0.75	0.39	0.45	-0.29	0.01
C2		1.00	0.39	0.08	0.04	-0.07	0.34	-0.23	-0.02	0.87	-0.39	-0.28	0.20	0.98	0.16	-0.04	0.68	0.58	0.66	0.12	-0.47	0.61	0.04	0.34
C1	1.00	0.42	0.83	0.56	0.69	0.75	0.88	0.54	0.39	0.68	0.73	0.34	0.48	0.45	0.59	-0.63	0.08	0.24	0.04	-0.74	0.00	0.32	0.08	0.16

FIGURE 5.4. Correlation matrix for nitrate concentration of all plots. Significance exists when the r-value is greater than or equal to the critical value (±0.66). This value was calculated by applying degrees of freedom (df = n-2) to a sample set of 9 (df =7) and a 95% confidence interval (p = 0.05) to the table of critical values for Pearson correlation in a two-tailed test.

Trends in Sulfate Concentrations in Green Roof Runoff

Unlike pH and nitrate concentration, green roofs did not neutralize sulfate concentrations. In fact, average sulfate concentrations in all green roof plot runoff samples were above that measured in bulk precipitation. This unexpected data could be attributed to low sulfate uptake by plants due to a lack of widespread vegetation cover. The *Sedum acre* lacked an extended period of time to spread and thus more sulfate could have been released by drainage than expected. Combine this with the likelihood that there were already small, natural sources of sulfur in the plots and this hypothesis could explain slightly higher sulfate concentrations in green roofs than the control plot, R.

Similar to pH and nitrate concentration, soil type is most influential on sulfate concentration. Topsoil runoff was much higher in sulfate than hydroponic runoff. This could be due to a mineral composition of the topsoil high in sulfates or sulfides such as gypsum or pyrite.

Expanded clay appeared to have been affected by soil depth; the two clay plots with 3cm depth had the lowest sulfate levels. However, no variation from drainage type or plant presence was detected.

Perlite and vermiculite plots are similar in that they have no differences created by the tested variables. For both soil types, average concentrations were respectively similar except for plots with aggregate drainage and 9cm soil depths. These plots had slightly higher sulfate concentrations than other plots in their soil groups.

Topsoil runoff showed a difference between plots with and without vegetation. Sulfate concentration in the plot with vegetation was approximately 42% higher than the plot without. Drainage type and soil depth had no apparent difference on concentrations.

Ion concentration in conventional roof runoff was again unexpectedly higher than that in bulk precipitation. Noguchi et al. (1995) attribute greater sulfate concentration in precipitation to the presence of asphalt, which also explains the discrepancy in the green roof data. A correlation matrix for nitrate concentration of all plots is shown below in Figure 5.5.

It is unclear whether sulfate was absorbed by soil in this experiment. However, it was found that sulfate concentration in runoff was not reduced by green roofs, as originally proposed. Furthermore, topsoil plots carried a much greater amount of sulfate in their runoff than hydroponic plots and thus should be avoided if attempting to reduce sulfate concentration in runoff.

	C1	C2	C3	C4	C5	P1	P2	P3	P4	P5	V1	V2	V3	V4	V5	T1	T2	T3	T4	T5	R	CR	Volume (L)	pH
pH																								1.00
Precip. Volume (L)																							1.00	0.90
CR																						1.00	-0.77	-0.77
R																					1.00	0.91	-0.85	-0.88
T5																				1.00	0.16	0.07	-0.21	0.11
T4																			1.00	0.51	-0.33	-0.39	0.50	0.67
T3																		1.00	0.68	0.70	-0.34	-0.21	0.27	0.62
T2																	1.00	0.75	0.93	0.36	-0.52	-0.48	0.60	0.81
T1																1.00	0.65	0.14	0.69	0.18	-0.16	-0.29	0.19	0.35
V5															1.00	-0.51	-0.08	0.55	-0.07	0.67	0.06	0.11	-0.17	0.03
V4														1.00	0.80	-0.23	-0.49	-0.02	-0.61	-0.23	-0.49	-0.52	0.15	0.24
V3													1.00	0.58	0.97	-0.35	0.08	0.64	0.14	0.79	0.02	0.04	-0.07	0.14
V2												1.00	0.93	0.59	0.98	-0.47	-0.03	0.60	-0.06	0.64	-0.06	0.03	-0.10	0.13
V1											1.00	0.33	0.36	-0.21	0.40	-0.34	0.05	0.36	0.12	0.55	0.42	0.27	-0.50	-0.29
P5										1.00	0.39	0.88	0.90	0.91	0.92	-0.36	-0.07	0.54	-0.08	0.71	0.05	0.05	-0.29	-0.04
P4									1.00	0.90	0.30	0.94	0.97	0.73	0.97	-0.33	0.02	0.58	0.05	0.73	0.02	0.06	-0.11	0.12
P3								1.00	0.81	0.69	0.26	0.70	0.76	0.82	0.69	0.16	0.54	0.85	0.48	0.70	-0.27	-0.23	0.21	0.52
P2							1.00	0.91	0.98	0.93	0.34	0.99	0.97	0.64	0.99	-0.77	0.16	0.95	0.04	0.82	-0.09	0.03	-0.07	0.32
P1						1.00	0.57	0.81	0.37	0.19	-0.14	0.30	0.29	0.48	0.21	0.52	0.79	0.74	0.65	0.37	-0.54	-0.44	0.52	0.80
C5					1.00	0.25	0.95	0.72	0.92	0.86	0.58	0.92	0.95	0.58	0.96	-0.43	0.07	0.67	0.10	0.75	0.14	0.19	-0.17	0.05
C4				1.00	0.95	0.39	0.97	0.73	0.90	0.74	0.47	0.94	0.89	0.18	0.92	-0.42	0.12	0.68	0.11	0.64	-0.01	0.10	-0.01	0.21
C3			1.00	0.97	0.94	0.31	0.95	0.69	0.88	0.70	0.52	0.90	0.89	0.21	0.91	-0.49	0.10	0.64	0.11	0.58	-0.02	0.06	0.08	0.22
C2		1.00	0.85	0.93	0.83	0.59	0.87	0.78	0.80	0.60	0.46	0.83	0.76	0.01	0.77	-0.11	0.30	0.74	0.28	0.67	-0.02	0.08	-0.01	0.30
C1	1.00	0.63	0.25	0.38	0.23	0.92	0.54	0.67	0.27	0.11	-0.12	0.26	0.22	-0.08	0.14	0.54	0.80	0.76	0.67	0.40	-0.43	-0.26	0.38	0.71

FIGURE 5.5. Correlation matrix for sulfate concentration of all plots. Significance exists when the r-value is greater than or equal to the critical value (±0.66). This value was calculated by applying degrees of freedom (df = n-2) to a sample set of 9 (df =7) and a 95% confidence interval (p = 0.05) to the table of critical values for Pearson correlation in a two-tailed test.

Chapter Six: Conclusions

Overall, the green roof study was successful. Though the negative impact of green roofs on sulfate ion concentration was unanticipated, it was found that green roofs did in fact reduce nitrate ion concentrations and acidity of runoff.

In terms of reducing harmful affects of acid rain on the environment, the best green roof choice would be constructed with vegetation present, modular drainage and a hydroponic soil at a 3cm depth. Though expanded clay and perlite both produced excellent runoff samples in terms of nitrate concentration and pH, perlite would be a better soil choice due to its light weight and moderate grain size. The larger grain size characteristic of expanded clay caused undesired settling, as the peat shifted and gathered below the robust but lightweight clay pebbles. This left less for the shallow root system of the sedum plant to hold onto. In addition to this, the perlite used in this study was 75% less expensive than the expanded clay.

The suggested soil depth could vary by plant type. The *sedum acre* used in this study had a root system that extended approximately 2-3cm into the soil. During and after precipitation events, the modular drainage held water in place just below the soil layer and allowed the roots to remove its nutrients (such as nitrate). Shallow-rooted plants sitting in 9cm soils could not remove as many nutrients as those in 3cm soils, in which the roots were much closer to the water. However, 9cm soils would be more tolerant of erosion and with larger plants, could remove greater quantities of nutrients from precipitation. More conclusive results would be obtained from a larger, replicative study.

Of course, the main goal for green roof implementation is water retention. As expected, topsoil and sod plots retained the greatest volume of precipitation. This, along with the fact that they too significantly neutralized acid precipitation, qualify topsoil and sod to be a good green roof choice despite their lack of sulfate and nitrate removal. As with most environmental remediation, techniques are dependent on situation, location and financial freedom.

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Appendix I: Five Ion Standards

Explanation

Each ion chromatography analysis included two aliquots of a five ion standard solution and two laboratory fortified matrices, both created in the laboratory to measure precision and accuracy. The solution contains sodium, potassium, chloride, nitrate and sulfate ions. Units are in milliequivalents per liter (meq/L). Definitions of table labels are as follows:

"P5-labdup": The laboratory duplicate of sample P5.

"Mean": Average concentration of P5 and P5-labdup.

"LFM": Laboratory fortified matrix. The LFM is used to determine contamination by spiking a sample with a known concentration. The LFM contained sample P5, five-ion standard and deionized water in a ratio of 1:1:8.

"5 ion STD conc.": Measured concentrations of each ion in the five ion standard.

"% Recovery": Percent of ions in standards measured by ion chromatographer. Calculated by dividing difference of LFM and mean by the 5 ion STD conc. and multiplying by 100.

	Sodium (meq/L)	**Potassium meq/L)**	**Chloride meq/L)**	**Nitrate meq/L)**	**Sulfate meq/L)**
Standard Conc.					
7/23/2008					
P5	0.4285	0.3357	0.3982	0.0333	0.138
P5-labdup	0.424	0.3302	0.3671	0.026	0.1384
Mean	0.4263	0.3329	0.3827	0.0297	0.1382
LFM	5.7004	2.8233	6.6204	0.2697	2.157
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00

% Recovery	98.62	93.39	109.16	74.41	100.94
CR	0.0282	0.1615	0.1858	0.0798	0.087
CR-labdup	0.028	0.1527	0.1821	0.0722	0.0792
Mean	0.0281	0.1571	0.1839	0.076	0.0831
LFM	5.4453	2.7121	6.8061	0.3649	2.2116
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	101.3	95.81	115.89	89.56	106.43
8/7/2008					
P5	0.1903	0.0138	0.019	0.0212	0.0396
P5-labdup	0.1919	0.0148	0.0146	0.0158	0.0356
Mean	0.1911	0.0143	0.0168	0.0185	0.0376
LFM	5.3593	2.4491	6.4815	0.2743	2.1297
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	96.64	91.31	113.13	79.32	104.6
CR	0.0177	0.0056	0.0151	0.0488	0.049
CR-labdup	0.0232	0.0069	0.0167	0.0585	0.0523
Mean	0.0205	0.0062	0.0159	0.0537	0.0506
LFM	5.206	2.4504	6.5793	0.2897	2.2011
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	96.96	91.66	114.86	73.16	107.52
9/7/2008					
P5	0.366	0.0204	0.1167	0.0513	0.0631
P5-labdup	0.3669	0.0236	0.1111	0.023	0.0743
Mean	0.3664	0.022	0.1139	0.0372	0.0687
LFM	5.1912	2.2879	6.6908	0.2905	2.1716
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	90.22	84.97	115.1	78.55	105.14
CR	0.0253	0.004	0.0252	0.1572	0.0154
CR-labdup	0.0403	0.0107	0.0336	0.2287	0.0318
Mean	0.0328	0.0074	0.0294	0.1929	0.0236
LFM	4.9522	2.3414	6.7861	0.3712	2.1993
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	91.99	87.53	118.24	55.27	108.79
9/9/2008					
P5	0.264	0.2141	0.3115	0.0096	0.0427
P5-labdup	0.2702	0.2204	0.3087	0.0084	0.0422
Mean	0.2671	0.2172	0.3101	0.009	0.0424
LFM	5.2967	2.5762	7.1751	0.2086	2.2485
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	94.05	88.46	120.14	61.87	110.3
CR	0.0148	0.2939	0.352	0.0349	0.0406
CR-labdup	0.013	0.2855	0.3446	0.0207	0.0419
Mean	0.0139	0.2897	0.3483	0.0278	0.0413
LFM	5.116	2.6692	7.3584	0.3025	2.2751
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	95.4	89.23	122.68	85.16	111.69
9/13/2008					

P5	0.275	0.279	0.3713	0.0541	0.0403
P5-labdup	0.296	0.2775	0.373	0.0463	0.0575
Mean	0.2855	0.2783	0.3721	0.0502	0.0489
LFM	4.9313	2.4673	6.8067	0.2508	2.1583
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	86.87	82.09	112.61	62.18	105.47
CR	0.0215	0.1408	0.147	0.0473	0.1209
CR-labdup	0.0192	0.108	0.1526	0.0835	0.1152
Mean	0.0203	0.1244	0.1498	0.0654	0.118
LFM	4.8743	2.4157	6.8577	0.3008	2.314
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	90.76	85.92	117.39	72.96	109.8
9/14/2008					
P5	0.2762	0.6168	0.8016	0.0605	0.0509
P5-labdup	0.2695	0.6041	0.7337	0.02	0.048
Mean	0.2728	0.6105	0.7677	0.0403	0.0494
LFM	5.0828	2.8831	7.4801	0.2589	2.2157
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	89.94	85.23	117.47	67.78	108.31
CR	0.0237	0.0818	0.0875	0.0451	0.0834
CR-labdup	0.0133	0.0702	0.0892	0.0413	0.087
Mean	0.0185	0.076	0.0884	0.0432	0.0852
LFM	5.1849	2.524	6.728	0.3183	2.2702
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	96.61	91.8	116.19	85.29	109.25
9/29/2008					
P5	0.2287	0.0824	0.1179	n.a.	0.0775
P5-labdup	0.2649	0.0957	0.1363	n.a.	0.0814
Mean	0.2468	0.0891	0.1271	n.a.	0.0795
LFM	4.1808	1.9353	5.004	0.1936	1.7018
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	73.56	69.23	85.35	n.a.	81.12
CR	0.0176	0.0263	0.0224	0.0121	0.0208
CR-labdup	0.0175	0.013	0.0232	0.0142	0.0262
Mean	0.0175	0.0196	0.0228	0.0131	0.0235
LFM	3.6978	1.7404	4.5534	0.1966	1.572
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	68.82	64.53	79.28	56.88	77.43
10/1/2008					
P5	0.2456	0.1463	0.1688	n.a.	0.0821
P5-labdup	0.2388	0.1436	0.1655	n.a.	0.0736
Mean	0.2422	0.1449	0.1672	n.a.	0.0779
LFM	5.6356	2.6668	7.0436	0.2487	2.3187
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	100.85	94.57	120.34	n.a.	112.04
CR	0.0142	0.2601	0.2826	0.0403	0.0564
CR-labdup	0.0191	0.2586	0.2828	0.0463	0.0567

Mean	0.0167	0.2593	0.2827	0.0433	0.0566
LFM	5.2874	2.758	7.0616	0.2871	2.2784
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	98.56	93.7	118.63	75.56	111.09
10/9/2008					
P5	0.24	0.1894	0.2409	0.0052	0.0715
P5-labdup	0.2327	0.1823	0.2232	0.0062	0.063
Mean	0.2364	0.1859	0.232	0.0057	0.0673
LFM	5.7073	2.7539	7.1213	0.2643	2.3504
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	102.3	96.3	120.56	80.16	114.16
CR	0.0103	0.2538	0.2777	0.0711	0.0731
CR-labdup	0.0583	0.2462	0.2743	0.1061	0.0916
Mean	0.0343	0.25	0.276	0.0886	0.0823
LFM	5.3903	2.7595	7.2093	0.3056	2.3478
5 ion STD conc.	5.35	2.67	5.71	0.32	2.00
% Recovery	100.15	94.11	121.33	67.26	113.27

Appendix II: Recovery of Standards

Explanation

Percent recovery by the ion chromatographer of ions in six-cation and five-anion standard solutions is measured to determine precision and accuracy of the analysis. Units are in parts per million (ppm). Definitions of table labels are as follows:

"From Dionex": Concentrations supplied by the manufacturer for the six-cation and five-anion Dionex solutions.

"Measured Standards": Concentrations of Dionex standard solutions measured by ion chromatography at the start of each analysis.

"Recovery %": Percent of ions in standards measured by ion chromatographer. Calculated by dividing measured concentration over supplied concentration and multiplying by 100.

"Mean Recovery %": The mean of all calculated recoveries for each ion.

	Fluoride (ppm)	Chloride (ppm)	Nitrate (ppm)	Phosphate (ppm)	Sulfate (ppm)	Lithium (ppm)	Sodium (ppm)	Ammonium (ppm)	Potassium (ppm)	Magnesium (ppm)	Calcium (ppm)
From Dionex:	**19.7**	**30.2**	**100**	**150**	**150**	**50**	**199**	**249**	**496**	**248**	**498**
Measured Standards:											
7/23/2008											
6 cation std						50.11	198.45	242.31	486.43	245.87	495.22
5 anion std	19.46	43.63	114.74	139.65	147.05						
Recovery (%)	98.77	144.46	114.74	93.10	98.04	100.22	99.72	97.31	98.07	99.14	99.44
8/7/2008											
6 cation std						47.74	189.34	232.57	465.23	234.54	472.22
5 anion std	19.24	33.38	95.74	145.61	147.28						

Recovery (%)	97.65	110.53	95.74	97.08	98.19	95.48	95.14	93.40	93.80	94.57	94.82
9/7/2008											
6 cation std						43.00	171.54	233.21	428.50	214.38	429.63
5 anion std	20.50	47.21	102.60	151.40	154.57						
Recovery (%)	104.06	156.31	102.60	100.93	103.05	85.99	86.20	93.66	86.39	86.44	86.27
9/9/2008											
6 cation std						44.83	178.15	238.06	442.15	222.33	444.33
5 anion std	20.64	41.06	101.51	158.30	157.44						
Recovery (%)	104.78	135.95	101.51	105.53	104.96	89.66	89.52	95.60	89.14	89.65	89.22
9/13/2008											
6 cation std						46.62	184.49	242.92	456.51	231.00	461.43
5 anion std	n.a.	39.11	106.68	163.53	162.10						
Recovery (%)	n.a.	129.49	106.68	109.02	108.06	93.24	92.71	97.56	92.04	93.15	92.66
9/14/2008											
6 cation std						41.71	167.84	247.26	424.99	213.44	431.73
5 anion std	20.77	58.32	102.87	159.45	157.37						
Recovery (%)	105.43	193.13	102.87	106.30	104.92	83.42	84.34	99.30	85.68	86.06	86.69
9/29/2008											
6 cation std						49.58	196.18	263.20	484.69	246.87	493.65
5 anion std	20.76	49.22	101.75	161.01	157.45						
Recovery (%)	105.38	162.97	101.75	107.34	104.97	99.16	98.58	105.70	97.72	99.55	99.13
10/1/2008											
6 cation std						52.34	207.04	285.79	509.03	259.93	519.39
5 anion std	21.43	34.96	105.66	162.85	163.03						
Recovery (%)	108.77	115.76	105.66	108.57	108.69	104.69	104.04	114.78	102.63	104.81	104.30
10/9/2008											
6 cation std						49.98	198.73	279.60	499.32	250.69	503.51
5 anion std	21.58	35.49	106.20	161.22	163.45						
Recovery (%)	109.55	117.52	106.20	107.48	108.97	99.97	99.86	112.29	100.67	101.09	101.11

Appendix III: All Ion Concentrations and Percent Errors

Explanation

This table contains all ion concentrations obtained by ion chromatography. Units are in milliequivalents per liter (meq/L) and kilograms (kg). Definitions of table labels are as follows:

"% Error": Percent error determines accuracy and precision by calculating the difference between cation and anion concentrations, which should ideally by zero. This calculation is done by using the formula: $\left|\frac{\text{cations-anions}}{\text{cations+anions}}\text{x100}\right|$

"Precip. Weight (kg)": Mass of runoff or precipitation measured in each bottle for each sample.

	F	Cl	NO_3	SO_4	Li	Na	NH_4	K	Mg	Ca	HCO_3	% Error	pH	Precip. Weight (kg)
07/23/08														
C1	0.0175	0.3718	0.0286	0.1225	0.0169	0.2347	0.0146	0.4342	0.1233	1.6576	4.1	30.3	7.76	2.98
C2	0.1560	0.3396	0.0812	0.2392	0.0268	0.2611	0.1325	0.3783	0.2508	0.8236	1.6	12.7	7.26	2.76
C3	0.0583	0.2885	0.0381	0.3363	0.0342	0.3655	0.0256	0.3857	0.1391	1.6158	4.8	36.5	7.91	0.81
C4	0.0532	0.2368	0.0162	0.3512	0.0413	0.1870	0.0118	0.3250	0.2133	0.8602	1.6	15.9	7.32	1.42
C5	0.0584	0.2623	0.0433	0.3719	0.0399	0.2276	0.0262	0.3644	0.1536	0.7521	0.8	0.9	7.26	3.26
P1	n.a.	0.1701	0.0302	0.0740	n.a.	0.3340	0.0715	0.1625	0.0843	1.5454	2.7	15.0	7.75	3.44
P2	0.0147	0.4002	0.0507	0.1399	n.a.	0.4478	0.0279	0.3040	0.1068	0.5970	1.4	15.0	7.25	1.84
P3	0.0091	0.3074	0.0709	0.1288	0.0006	0.4762	0.0581	0.2615	0.0620	1.3287	2.8	20.5	7.68	2.67
P4	0.0078	0.4869	0.0555	0.1459	0.0011	0.5006	0.0244	0.4133	0.0641	0.4562	1.5	20.1	7.16	3.32
P5	0.0103	0.3982	0.0333	0.1380	0.0013	0.4285	0.0235	0.3357	0.0657	0.4781	1.2	14.4	7.13	3.21
V1	0.0242	0.3101	0.0590	0.1022	0.0057	0.6474	0.0299	0.3608	0.1321	0.9973	3.7	31.8	7.82	0.66
V2	0.0291	0.3163	0.0477	0.1555	0.0098	0.7112	0.0287	0.3403	0.1308	0.5347	2.8	31.2	7.60	2.92
V3	0.1172	0.6066	0.2085	0.3242	0.0079	1.2375	0.3011	0.4625	0.2680	2.4103	5.2	15.9	7.81	3.35
V4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

V5	0.0477	0.5574	0.0528	0.2815	0.0125	1.0119	0.0546	0.3317	0.1456	0.9405	2.6	17.3	7.65	1.37
T1	0.0143	0.4546	0.1318	0.3446	n.a.	0.5787	0.0405	1.4424	0.4819	5.1183	14.5	33.7	7.88	1.98
T2	0.0138	1.0997	0.0515	0.4055	n.a.	0.5172	0.0638	1.5591	0.7292	6.2683	16.4	32.6	7.80	2.83
T3	0.0161	1.4449	0.0540	1.6714	n.a.	1.2880	0.0596	2.0378	0.6602	7.0154	14.8	23.8	8.00	0.97
T4	0.0160	1.3970	0.0305	0.9056	n.a.	1.0063	0.0456	1.8074	0.8552	6.7698	17.1	29.9	7.73	1.64
T5	0.0091	0.1937	0.0592	0.7573	n.a.	0.3432	0.0361	0.9891	0.6656	5.8260	21.3	47.9	7.64	3.33
R	0.0005	0.4076	0.0426	0.0630	n.a.	0.0037	0.0318	0.3493	0.0026	0.0264	0.0	10.7	5.15	0.16
CR	0.0085	0.1858	0.0798	0.0870	n.a.	0.0282	0.0589	0.1615	0.0487	0.4115	0.5	9.7	6.58	3.21
08/07/08														
C1	0.0154	0.0560	0.0318	0.0947	0.0052	0.1378	0.0363	0.0885	0.0976	1.3343	2.1	15.0	7.45	3.78
C2	0.0217	0.0268	0.0061	0.1239	0.0075	0.0363	0.0159	0.0266	0.1681	0.7575	1.0	7.6	7.02	3.86
C3	0.0392	0.0449	0.0187	0.2122	0.0128	0.1759	0.0197	0.1203	0.0956	1.2975	2.1	16.8	7.34	3.71
C4	0.0403	0.0329	0.0237	0.2074	0.0147	0.0692	0.0166	0.0535	0.1950	0.8958	0.9	1.7	6.94	3.84
C5	0.0379	0.0259	0.0023	0.1455	0.0105	0.0718	0.0277	0.0599	0.1154	0.5775	1.1	20.6	6.78	3.85
P1	0.0069	0.0276	0.0321	0.0545	n.a.	0.1939	0.0253	0.0221	0.0597	0.9552	2.0	25.6	7.25	3.71
P2	n.a.	0.0232	0.0023	0.0009	n.a.	0.1669	0.0198	0.0152	0.0585	0.4126	1.1	25.2	7.13	1.03
P3	n.a.	0.0193	0.0277	0.0605	n.a.	0.2551	0.0250	0.0342	0.0359	0.8861	1.9	23.8	7.28	3.71
P4	0.0059	0.0433	0.0824	0.0478	n.a.	0.2205	0.0308	0.0296	0.0356	0.3794	1.1	29.5	6.83	3.71
P5	0.0083	0.0190	0.0212	0.0396	n.a.	0.1903	0.0203	0.0138	0.0434	0.3555	1.0	27.2	6.8	3.55
V1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V2	0.0112	0.0222	0.0177	0.0715	0.0044	0.3821	0.0281	0.0613	0.1052	0.3644	1.7	31.7	6.95	2.41
V3	0.0141	0.0375	0.0358	0.0911	0.0030	0.4138	0.0341	0.0811	0.0882	1.2387	2.8	23.1	7.37	2.87
V4	0.0142	0.0419	0.0193	0.0743	0.0044	0.4611	0.0349	0.0811	0.1011	0.3659	2.0	34.4	7.08	0.97
V5	0.0116	0.0249	0.0146	0.0387	0.0020	0.2194	0.0175	0.0371	0.0601	0.2525	1.5	46.0	7.31	1.57
T1	0.0133	0.2917	0.0655	0.2176	n.a.	0.1686	0.0542	0.5983	0.1895	2.3338	5.0	25.1	7.58	1.07
T2	0.0145	0.0887	0.0618	0.4036	n.a.	0.0578	0.0903	0.7974	0.3079	3.2772	8.1	31.3	7.48	1.86
T3	0.0162	0.0277	0.0164	0.6934	n.a.	0.0658	0.0347	0.4748	0.3621	3.9703	6.3	17.9	7.27	2.83
T4	0.0168	0.2336	0.0314	0.6707	n.a.	0.1542	0.0961	0.8039	0.3784	3.6384	6.6	19.7	7.49	1.46
T5	0.0078	0.1049	0.2583	0.0968	n.a.	0.0818	0.0506	0.4011	0.1668	2.2176	n.a.	n.a.	7.72	0.07
R	0.0149	0.0029	0.0177	0.0009	n.a.	0.0069	0.0038	0.0006	0.0051	0.0152	0.3	82.8	5.93	0.61
CR	0.0054	0.0151	0.0488	0.0490	n.a.	0.0177	0.0243	0.0056	0.0583	0.5188	0.8	19.0	6.45	3.73
09/07/08														
C1	0.0187	0.2102	0.0215	0.2059	0.0065	0.1682	0.0415	0.0727	0.1315	1.8932	2.6	13.8	7.38	n.a.
C2	0.0313	0.1119	0.0200	0.1601	0.0071	0.0631	0.0055	0.0435	0.2376	0.9938	1.1	2.6	6.69	n.a.
C3	0.0388	0.0461	0.0207	0.1697	0.0093	0.1529	0.0083	0.1064	0.1404	1.7545	2.6	13.9	7.54	n.a.
C4	0.0597	0.0558	0.0093	0.1981	0.0115	0.0641	0.0058	0.0436	0.2525	0.9764	1.1	2.5	6.86	n.a.
C5	0.0337	0.2292	0.0190	0.1606	0.0080	0.1412	0.0049	0.0516	0.2204	0.9945	1.0	0.8	6.84	n.a.
P1	n.a.	0.2926	0.0242	0.1351	0.0007	0.3214	0.0074	0.0282	0.1061	1.7168	2.0	5.9	7.3	n.a.
P2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
P3	n.a.	0.0893	n.a.	0.1238	0.0007	0.3627	0.0159	0.0361	0.0609	1.5115	2.3	11.7	7.21	n.a.
P4	n.a.	0.0662	0.0245	0.0615	0.0005	0.3105	0.0177	0.0178	0.0940	0.5501	1.0	7.5	6.69	n.a.
P5	n.a.	0.1167	0.0513	0.0631	0.0006	0.3660	0.0459	0.0204	0.0747	0.5262	1.1	12.6	6.34	n.a.
V1	0.0074	0.0543	0.0135	0.0725	0.0046	0.4889	0.0273	0.1034	0.1270	1.0902	2.8	23.1	7.29	n.a.
V2	0.0086	0.0358	0.0284	0.0674	0.0095	0.7459	0.0380	0.1278	0.1991	0.4944	2.8	29.1	6.73	n.a.
V3	0.1368	0.0972	9.4069	0.1390	0.0058	0.9652	0.1997	0.1304	1.8359	14.2704	4.2	10.9	7.24	n.a.
V4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V5	0.0140	0.0458	0.0845	0.0628	0.0068	0.6867	0.0330	0.1248	0.1765	0.6660	2.3	19.4	6.72	n.a.

T1	0.0107	3.5900	0.3171	1.5638	0.0008	0.4708	0.0165	1.6786	1.0551	10.0819	12.4	14.7	7.17	n.a.
T2	0.0095	2.2920	1.4883	1.4142	n.a.	0.1919	0.3370	1.7242	1.1235	10.4829	13.1	13.8	7.29	n.a.
T3	0.0081	0.4364	0.1589	1.9015	n.a.	0.1451	0.0554	0.8204	1.0064	9.8693	17.8	26.1	7.45	n.a.
T4	0.0172	5.2230	0.9868	1.7630	n.a.	0.3124	0.2213	2.0575	1.6361	13.6830	15.4	13.3	7.35	n.a.
T5	0.0090	1.2465	1.2465	0.6935	0.0007	0.2323	0.1210	1.2431	0.7452	7.1346	9.2	13.3	7.43	n.a.
R	n.a.	0.0095	0.0106	0.0087	n.a.	0.0070	0.0056	0.0011	0.0059	0.0793	0.3	53.8	6.85	n.a.
CR	n.a.	0.0252	0.1572	0.0154	n.a.	0.0253	0.0199	0.0040	0.0672	0.6854	0.4	14.6	6.71	n.a.
09/09/08														
C1	0.0159	0.2180	0.0101	0.0761	0.0043	0.1284	0.0074	0.1885	0.1191	1.7435	2.7	15.9	8.00	2.55
C2	0.0210	0.2241	0.0023	0.0870	0.0046	0.0438	0.0018	0.1814	0.1912	0.8689	0.9	2.3	7.18	0.64
C3	0.0321	0.4205	0.0056	0.1183	0.0073	0.1220	0.0111	0.4149	0.1247	1.5626	2.1	8.8	7.51	1.80
C4	0.0397	0.3089	0.0072	0.1196	0.0078	0.0512	0.0017	0.2720	0.1963	0.8262	1.0	4.2	7.14	3.71
C5	0.0280	0.2975	0.0070	0.0990	0.0053	0.0687	0.0065	0.2465	0.1425	0.7215	0.7	2.6	7.05	3.69
P1	n.a.	0.2430	0.0071	0.0405	n.a.	0.2121	0.0038	0.1644	0.1010	1.5290	2.8	21.2	7.94	2.62
P2	n.a.	0.3195	0.0043	0.0336	n.a.	0.1635	0.0071	0.2617	0.0944	0.5475	0.7	0.8	7.20	2.77
P3	n.a.	0.2365	0.0151	0.0568	n.a.	0.2970	0.0148	0.1819	0.0522	1.2865	1.8	7.0	7.73	3.68
P4	n.a.	0.2798	0.0190	0.0349	n.a.	0.2175	0.0059	0.2348	0.0752	0.5086	0.8	4.2	6.73	3.68
P5	n.a.	0.3115	0.0096	0.0427	n.a.	0.2640	0.0038	0.2141	0.0414	0.4319	1.0	17.6	6.72	3.72
V1	n.a.	0.2326	0.0095	0.0750	0.0031	0.3894	0.0115	0.2607	0.1666	0.7943	2.3	23.4	7.21	0.89
V2	0.0046	0.3809	0.0139	0.0390	0.0057	0.4412	0.0127	0.3662	0.1240	0.5318	1.5	13.4	7.26	2.77
V3	0.0104	0.4429	0.0023	0.0874	0.0035	0.4817	0.0038	0.4265	0.0929	1.4475	3.0	18.1	7.65	3.65
V4	0.0092	0.2065	0.0226	0.0524	0.0045	0.4520	0.0279	0.2273	0.1052	0.3681	1.5	20.4	7.16	2.07
V5	0.0109	0.0295	0.0109	0.0227	0.0047	0.4533	0.0138	0.0831	0.1029	0.3782	1.3	14.0	7.29	3.60
T1	0.0087	2.7846	0.2742	1.1940	n.a.	0.4587	0.0038	1.6308	0.8532	8.0713	11.1	16.5	7.84	2.36
T2	0.0131	0.9842	0.3828	0.5559	n.a.	0.1587	0.0129	1.2868	0.6586	6.3697	12.0	24.3	8.17	0.30
T3	0.0115	0.3713	0.0112	0.4677	n.a.	0.1122	0.0026	0.8476	0.6684	6.5106	15.4	33.3	7.76	3.43
T4	0.0126	3.6168	0.3963	1.2950	n.a.	0.2446	0.0056	1.9440	1.2029	10.0888	13.1	15.5	7.73	2.54
T5	0.0052	1.1614	1.8207	0.6188	0.0007	0.2525	0.0083	1.3492	0.7101	6.9644	7.6	9.4	7.86	0.60
R	n.a.	0.1531	0.0157	0.0467	n.a.	0.0015	0.0186	0.1241	0.0047	0.0448	0.0	5.3	5.29	0.37
CR	0.0175	0.3520	0.0349	0.0406	n.a.	0.0148	0.0344	0.2939	0.0221	0.3189	0.2	2.9	6.30	3.46
09/13/08														
C1	n.a.	0.1500	0.0158	0.1122	0.0042	0.1235	0.0091	0.1304	0.1403	2.1497	3.5	19.3	7.23	1.87
C2	n.a.	0.2522	0.0066	0.1136	0.0042	0.0368	0.0075	0.1842	0.2084	0.8983	1.8	23.7	7.23	1.26
C3	n.a.	0.1894	0.0128	0.1266	0.0058	0.1117	0.0063	0.2112	0.1484	1.7805	2.6	12.8	7.61	0.25
C4	n.a.	0.1845	0.0142	0.1486	0.0073	0.0478	0.0102	0.1606	0.2448	1.0125	0.9	8.6	6.85	1.61
C5	n.a.	0.2469	0.0137	0.1084	0.0056	0.0643	0.0084	0.1903	0.1709	0.8705	0.9	1.6	6.85	1.92
P1	n.a.	0.2849	0.0360	0.0537	n.a.	0.2272	0.0310	0.2154	0.1083	1.9182	3.5	21.6	7.43	1.49
P2	n.a.	0.3162	0.0131	0.0418	n.a.	0.1587	0.0158	0.2591	0.0852	0.4701	0.8	8.4	7.53	0.68
P3	n.a.	0.2141	0.0077	0.0624	n.a.	0.2812	0.0093	0.1711	0.0637	1.6057	2.8	18.3	7.65	1.37
P4	n.a.	0.2111	0.0190	0.0469	n.a.	0.2173	0.0567	0.1752	0.0935	0.7887	1.1	1.7	6.86	1.65
P5	n.a.	0.3713	0.0541	0.0403	n.a.	0.2750	0.0401	0.2790	0.0593	0.4601	0.5	7.1	6.69	0.92
V1	n.a.	1.0337	0.0313	0.0475	0.0025	0.3054	0.0422	0.8884	0.1246	0.6582	n.a.	n.a.	7.36	0.07
V2	n.a.	0.2598	0.0450	0.0447	0.0050	0.4320	0.0310	0.2637	0.1450	0.4751	2.1	28.9	7.23	1.92
V3	n.a.	0.1608	0.0246	0.0836	0.0039	0.5466	0.0538	0.1951	0.1340	2.1507	4.7	23.4	7.60	1.54
V4	n.a.	0.2055	0.0527	0.0443	0.0042	0.4766	0.0492	0.2215	0.1058	0.3980	1.9	27.4	7.26	0.27
V5	n.a.	0.1526	0.0331	0.0236	0.0036	0.3701	0.0451	0.1706	0.1041	0.4651	2.1	33.2	7.10	1.27
T1	n.a.	1.9372	0.0794	0.9908	n.a.	0.4347	0.0359	1.5252	0.7311	7.1652	12.2	21.2	7.91	0.62

T2	n.a.	0.5249	0.0828	0.3117	n.a.	0.1067	0.0712	1.0046	0.5153	5.0727	11.4	29.1	7.79	0.35
T3	n.a.	0.2396	0.0446	0.4052	n.a.	0.1071	0.1127	0.6959	0.7071	7.2486	16.0	30.6	7.87	0.83
T4	n.a.	2.0818	0.0596	0.7997	n.a.	0.1955	0.0474	1.5940	0.9353	7.9240	14.5	24.0	7.93	0.65
T5	n.a.	0.6832	1.8448	0.4351	n.a.	0.1898	0.0419	1.2403	0.6566	6.4259	7.9	11.9	7.72	0.27
R	n.a.	0.2693	0.0219	0.0825	n.a.	0.0056	0.0090	0.2043	0.0107	0.0854	0.0	8.5	4.68	0.19
CR	n.a.	0.1470	0.0473	0.1209	n.a.	0.0215	0.0405	0.1408	0.0642	0.7324	0.3	23.8	5.87	3.7
09/14/08														
C1	0.0124	0.0966	0.0277	0.1130	0.2098	0.1096	0.0544	0.0950	0.1332	2.0607	3.3	14.3	7.58	2.36
C2	0.0185	0.1739	0.0188	0.1517	0.0041	0.0407	0.0741	0.1262	0.2023	1.0557	1.3	5.0	7.20	1.89
C3	0.0341	0.4348	0.0245	0.1598	0.0067	0.1341	0.0200	0.4253	0.1387	1.7736	2.5	11.6	7.72	0.33
C4	0.0412	0.1762	0.0214	0.1876	0.0072	0.0511	0.0896	0.1588	0.2770	1.4774	1.4	6.0	7.53	2.32
C5	0.0317	0.3456	0.0097	0.1375	0.0053	0.0587	0.0198	0.2901	0.1606	0.8510	0.3	25.4	7.57	1.63
P1	n.a.	0.1762	0.0314	0.0685	n.a.	0.2454	0.0538	0.1375	0.1118	1.9588	3.0	13.3	7.57	1.57
P2	n.a.	0.1483	0.0267	0.0509	n.a.	0.1521	0.0816	0.1065	0.1058	0.8247	1.1	2.1	7.14	1.49
P3	n.a.	0.2251	0.0122	0.0766	n.a.	0.2853	0.0266	0.1864	0.0602	1.5594	2.3	10.5	7.62	2.15
P4	n.a.	0.3924	0.1117	0.0876	n.a.	0.2697	0.1933	0.3525	0.0822	0.6248	0.5	16.5	7.18	2.39
P5	n.a.	0.8016	0.0605	0.0509	n.a.	0.2762	0.0943	0.6168	0.0749	0.4590	1.0	11.4	7.06	2.50
V1	n.a.	0.1566	0.0282	0.0918	0.0030	0.3783	0.0276	0.1991	0.1528	0.7540	1.8	15.6	7.48	1.69
V2	0.0077	0.1738	0.0685	0.0631	0.0064	0.5325	0.0380	0.1956	0.1607	0.4351	3.0	41.5	7.44	2.13
V3	0.0080	0.1688	0.0470	0.0742	0.0045	0.6077	0.0196	0.2389	0.1465	2.3208	5.6	27.7	7.60	2.52
V4	0.0074	0.1590	0.1139	0.0804	0.0052	0.5605	0.0384	0.1959	0.1644	0.5847	1.8	16.5	7.57	0.87
V5	0.0122	0.1441	0.0365	0.0619	0.0065	0.6713	0.0538	0.2254	0.1790	0.5582	3.1	32.9	7.27	2.20
T1	0.0118	1.7713	0.0751	0.9507	n.a.	0.4333	0.0691	1.6987	0.7293	7.0838	14.8	27.5	8.10	0.27
T2	0.0087	0.5837	0.1379	0.2709	n.a.	0.0755	0.0422	1.0472	0.4781	4.7618	14.3	41.0	7.87	0.95
T3	0.0097	0.3986	0.0367	0.3996	n.a.	0.1223	0.0654	1.0185	0.9226	9.1096	22.8	35.6	7.65	2.22
T4	0.0103	1.5845	0.0465	0.6178	n.a.	0.2001	0.0759	1.7215	0.9748	8.2903	17.3	26.9	7.95	0.77
T5	0.0116	0.7528	1.6170	0.3764	n.a.	0.1692	0.0668	1.4343	0.6313	6.1607	8.4	13.7	7.90	0.25
R	n.a.	0.1578	0.0196	0.0698	n.a.	0.0045	0.0165	0.1260	0.0049	0.0467	0.0	10.9	4.72	0.12
CR	n.a.	0.0875	0.0451	0.0834	n.a.	0.0237	0.0616	0.0818	0.0497	0.5201	0.7	10.8	5.87	3.10
09/29/08														
C1	0.0173	0.0574	0.0091	0.1403	0.0039	0.1123	0.0050	0.0614	0.1446	2.2320	2.9	9.9	7.20	3.78
C2	0.0295	0.2022	0.0083	0.1461	0.0045	0.0444	0.0099	0.1636	0.2234	0.8957	1.3	11.4	6.93	3.67
C3	0.0424	0.0472	0.0099	0.1746	0.0068	0.1265	0.0173	0.0950	0.1652	2.0452	2.8	11.2	7.28	2.23
C4	0.0510	0.1047	0.0023	0.2031	0.0074	0.0488	0.0124	0.0888	0.2836	1.1799	1.6	9.5	6.65	3.82
C5	0.0414	0.0389	0.0080	0.1623	0.0063	0.0619	0.0059	0.0456	0.2226	1.1106	0.5	31.9	6.23	3.86
P1	n.a.	0.0396	0.0100	0.0969	n.a.	0.2195	0.0071	0.0242	0.1061	2.0340	2.6	6.9	7.26	3.69
P2	n.a.	0.1236	0.0083	0.0803	n.a.	0.1740	0.0143	0.0863	0.1111	0.6040	1.0	10.1	6.50	3.42
P3	n.a.	0.0521	0.0071	0.0994	n.a.	0.2932	0.0075	0.0434	0.0689	1.7447	2.6	12.2	6.66	3.70
P4	n.a.	0.1865	0.0053	0.0871	n.a.	0.2280	0.0278	0.1527	0.1259	0.7350	1.0	0.4	6.60	3.63
P5	n.a.	0.1179	0.0050	0.0775	n.a.	0.2287	0.0082	0.0824	0.0721	0.5430	1.1	16.4	6.50	3.72
V1	n.a.	0.1416	0.0105	0.0274	0.0027	0.3407	0.0064	0.1794	0.1524	0.7683	1.8	15.4	7.49	2.45
V2	n.a.	0.0327	0.0080	0.0965	0.0063	0.5705	0.0054	0.0995	0.1682	0.4809	2.2	27.4	6.63	3.80
V3	0.0062	0.1934	0.0049	0.1284	0.0038	0.5456	0.0059	0.2592	0.1268	2.1656	4.1	17.6	7.61	3.86
V4	0.0088	0.0454	0.0062	0.1379	0.0056	0.6439	0.0124	0.1288	0.1866	0.5867	2.6	28.3	6.95	1.12
V5	0.0081	0.0905	0.0059	0.1147	0.0059	0.5838	0.0159	0.1580	0.1688	0.5251	1.9	18.5	6.89	3.80
T1	0.0113	0.8402	0.2327	0.9767	n.a.	0.4031	0.0246	1.3531	0.6905	7.0020	12.3	20.5	7.58	3.07
T2	0.0066	0.1988	0.1603	0.3922	n.a.	0.0820	0.0197	1.0562	0.5830	5.7918	11.6	24.3	7.43	2.55

T3	0.0314	0.1967	0.0091	0.7469	n.a.	0.0947	0.0072	0.7819	0.8747	8.7746	18.0	28.6	7.62	3.68
T4	0.0133	1.2007	0.0464	0.7539	n.a.	0.1638	0.0295	1.5528	0.8434	7.2652	13.9	23.5	7.63	1.59
T5	0.0063	0.3736	1.5534	0.4805	n.a.	0.1755	0.0100	1.0444	0.6050	6.2578	7.0	7.5	7.69	0.47
R	n.a.	0.2729	0.0050	0.0075	n.a.	0.0021	0.0062	0.2278	0.0055	0.0698	0.3	30.5	6.12	0.50
CR	n.a.	0.0224	0.0121	0.0208	n.a.	0.0176	0.0060	0.0263	0.0411	0.7522	0.4	29.9	6.52	3.70
10/01/08														
C1	0.0148	0.1191	0.0028	0.0632	0.0027	0.0795	0.0057	0.1401	0.1403	2.1518	3.2	14.9	7.68	2.30
C2	0.0295	0.1107	0.0026	0.0775	0.0036	0.0297	0.0051	0.0965	0.2211	0.9876	1.1	0.9	7.44	0.51
C3	0.0392	0.2424	0.0045	0.1331	0.0056	0.1197	0.0081	0.2805	0.1729	2.1485	2.6	4.9	7.70	0.60
C4	0.0488	0.1356	0.0079	0.1311	0.0063	0.0418	0.0063	0.1288	0.2454	1.0424	1.1	1.6	7.18	2.39
C5	0.0370	0.1074	0.0046	0.1289	0.0050	0.0524	0.0069	0.1037	0.1988	1.0038	0.8	12.0	7.33	2.59
P1	n.a.	0.2534	0.0023	0.0530	n.a.	0.1904	0.0070	0.2374	0.1112	2.0029	3.0	13.0	7.73	0.72
P2	n.a.	0.1132	0.0052	0.0517	n.a.	0.1494	0.0097	0.0934	0.1236	0.6694	0.8	3.7	6.88	1.24
P3	n.a.	0.1324	0.0112	0.0846	n.a.	0.2558	0.0064	0.1311	0.0673	1.7063	2.1	3.6	7.60	2.16
P4	n.a.	0.2431	0.0114	0.0635	n.a.	0.2034	0.0123	0.2147	0.1065	0.6642	0.8	3.6	7.07	1.85
P5	n.a.	0.1688	0.0023	0.0821	n.a.	0.2456	0.0159	0.1463	0.0724	0.5356	0.8	1.8	6.85	2.59
V1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V2	0.0077	0.1626	0.0023	0.0578	0.0058	0.4896	0.0133	0.2197	0.1738	0.4755	1.4	9.6	7.33	2.54
V3	0.0055	0.2350	0.0023	0.1015	0.0042	0.5970	0.0069	0.3035	0.1416	2.4330	5.0	21.0	7.81	2.40
V4	0.0067	0.1498	0.0023	0.1157	0.0052	0.5873	0.0192	0.2206	0.1834	0.5855	2.0	17.4	7.31	0.32
V5	0.0111	0.1314	0.0023	0.0823	0.0058	0.5866	0.0151	0.2143	0.1603	0.4906	2.1	22.5	7.30	2.38
T1	0.0100	0.7854	0.3714	0.6964	n.a.	0.3406	0.0143	1.4946	0.7312	6.9984	13.3	22.6	7.95	1.05
T2	0.0110	0.2215	0.0435	0.2187	n.a.	0.0672	0.0116	1.0171	0.5307	5.1954	11.7	28.3	7.95	0.81
T3	0.0104	0.1640	0.0064	0.3743	n.a.	0.0895	0.0049	0.8076	0.9281	8.9042	19.1	29.4	7.79	2.16
T4	0.0095	0.8893	0.0243	0.5231	n.a.	0.1506	0.0162	1.5169	0.7840	6.7330	15.7	30.2	8.00	0.49
T5	0.0094	0.2998	1.7191	0.3137	n.a.	0.1339	0.0052	1.1216	0.6786	6.4177	7.2	6.6	7.84	0.83
R	n.a.	0.2575	0.0341	0.0440	n.a.	0.0023	0.0157	0.2113	0.0088	0.0714	0.1	16.9	4.97	0.30
CR	n.a.	0.2826	0.0403	0.0564	n.a.	0.0142	0.0350	0.2601	0.0296	0.5109	0.3	11.2	6.34	3.54
10/09/08														
C1	0.0121	0.3634	0.0114	0.0953	0.0033	0.0932	0.0068	0.3573	0.1654	2.4125	3.7	15.8	7.79	0.94
C2	0.0254	0.5033	0.0023	0.0975	0.0034	0.0289	0.0109	0.4363	0.2336	1.0255	1.4	7.7	7.23	0.50
C3	0.0251	0.6443	0.0023	0.0958	0.0043	0.0890	0.0038	0.6225	0.1812	1.9686	3.0	13.5	7.75	0.21
C4	0.0472	0.4237	0.0241	0.1386	0.0055	0.0410	0.0115	0.3695	0.2102	0.8740	0.9	0.7	7.25	1.00
C5	0.0353	0.2309	0.0023	0.1131	0.0041	0.0462	0.0052	0.2128	0.1533	0.7783	0.7	5.2	7.34	0.79
P1	n.a.	0.6856	0.0023	0.0338	n.a.	0.1712	0.0083	0.5783	0.0929	1.9183	2.4	6.0	7.72	0.30
P2	n.a.	0.2512	0.0023	0.0522	n.a.	0.1311	0.0079	0.2229	0.0758	0.4300	0.6	2.1	6.96	0.42
P3	n.a.	0.2355	0.0048	0.0484	n.a.	0.2330	0.0040	0.2216	0.0732	1.7109	3.0	18.9	7.65	0.91
P4	n.a.	0.2190	0.0045	0.0372	n.a.	0.1709	0.0190	0.2013	0.0979	0.5755	1.6	27.2	7.02	0.88
P5	n.a.	0.2409	0.0052	0.0715	n.a.	0.2400	0.0116	0.1894	0.0748	0.5781	0.9	5.4	6.98	0.80
V1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V2	0.0057	0.2984	0.0097	0.0668	0.0047	0.4067	0.0162	0.3296	0.1513	0.5292	2.0	24.7	7.45	0.60
V3	0.0082	0.3548	0.0127	0.0757	0.0035	0.5262	0.0101	0.4135	0.1395	2.3925	5.4	25.3	7.97	0.78
V4	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
V5	0.0078	0.1280	0.0083	0.0573	0.0042	0.4181	0.0086	0.1934	0.1665	0.6603	1.8	15.9	7.16	0.63
T1	0.0135	0.7712	0.0999	0.6759	n.a.	0.3380	0.0062	1.3914	0.6551	6.4594	10.0	13.3	8.15	0.42
T2	0.0088	0.2644	0.0081	0.1786	n.a.	0.0528	0.0055	0.9381	0.4347	4.4465	12.2	36.6	8.05	0.60
T3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

T4	0.0109	0.6974	0.0150	0.3982	n.a.	0.1076	0.0068	1.3313	0.6300	5.5515	13.5	31.4	8.03	0.74
T5	0.0093	0.4261	1.6358	0.3855	n.a.	0.1743	0.0134	1.2984	0.6777	6.5739	9.5	15.6	8.00	1.10
R	0.0014	1.1913	0.0339	0.0448	n.a.	0.0029	0.0052	0.8838	0.0136	0.0903	0.1	15.9	4.72	0.10
CR	n.a.	0.2777	0.0711	0.0731	n.a.	0.0103	0.0485	0.2538	0.0379	0.5375	0.3	10.3	6.11	2.50

Appendix IV: Deionized Blank Concentrations

Explanation

Each ion chromatography analysis included an aliquot of deionized water. Ion concentrations for these samples are in the table below. Units are in milliequivalents per liter (meq/L). Definitions of table labels are as follows:

“Mean”: Average concentration of each ion for all collections.

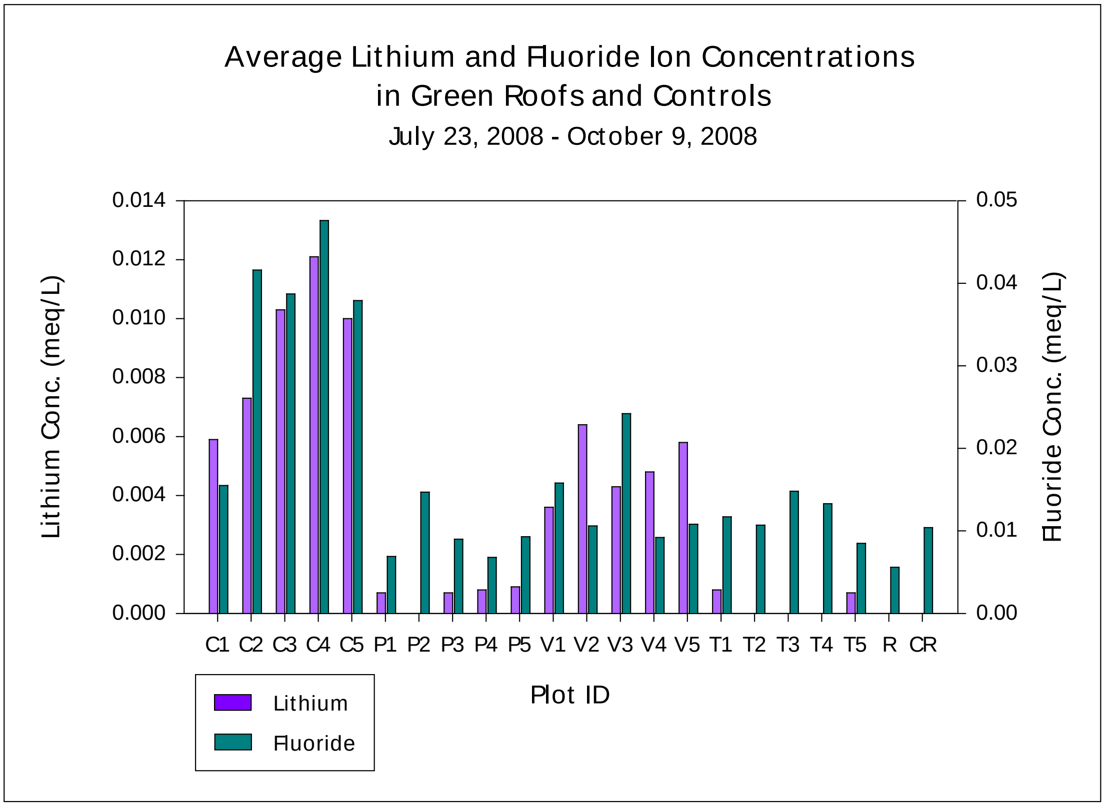
“S.D.”: Standard deviation of the mean.

“MDL”: Minimum detection limit. Calculated by finding the sum of three times the standard deviation and the mean.

	Fluoride (meq/L)	Chloride (meq/L)	Nitrate (meq/L)	Phosphate (meq/L)	Sulfate (meq/L)	Lithium (meq/L)	Sodium (meq/L)	Ammonium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)
7/23/2008	n.a.	0.0017	0.0025	n.a.	0.0012	n.a.	0.0005	0.0015	0.0003	0.0005	0.0054
8/7/2008	n.a.	0.0019	n.a.	n.a.	0.0006	n.a.	0.0010	0.0004	0.0004	0.0005	0.0075
9/7/2008	n.a.	0.0023	0.0031	n.a.	0.0010	n.a.	0.0055	0.0037	0.0011	0.0006	0.0092
9/9/2008	n.a.	0.0013	0.0012	n.a.	n.a.	n.a.	0.0004	0.0019	0.0003	0.0005	0.0087
9/13/2008	n.a.	0.0017	0.0003	n.a.	n.a.	n.a.	0.0007	0.0007	0.0004	0.0004	0.0100
9/14/2008	n.a.	0.0020	0.0015	n.a.	0.0012	n.a.	0.0008	0.0060	0.0005	0.0011	0.0277
9/29/2008	n.a.	0.0017	n.a.	n.a.	0.0009	n.a.	0.0003	0.0002	0.0001	0.0004	0.0079
10/1/2008	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0002	0.0004	0.0001	0.0004	0.0082
10/9/2008	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.0004	0.0003	0.0002	0.0006	0.0105
Mean	n.a.	0.0018	0.0017	n.a.	0.0010	n.a.	0.0011	0.0017	0.0004	0.0006	0.0106
S.D.	n.a.	0.0003	0.0011	n.a.	0.0003	n.a.	0.0017	0.0020	0.0003	0.0002	0.0066
MDL	n.a.	0.0027	0.0050	n.a.	0.0018	n.a.	0.0062	0.0076	0.0013	0.0012	0.0303

Appendix V : Lithium and Fluoride Concentrations

Average lithium and fluoride ion concentrations in runoff from all plots throughout the experiment.



Appendix VI: Precision

Explanation

Each ion chromatography analysis included two laboratory duplicates to measure precision. Units are in milliequivalents per liter (meq/L). Definitions of table labels are as follows:

“P5-labdup”: The laboratory duplicate of sample P5.

“Mean”: Average concentration of P5 and P5-labdup.

“S.D.”: Standard deviation of mean.

“Precision (%)”: Measures replicability of sample and laboratory duplicate. Calculated by dividing the standard deviation by the mean and multiplying by 100.

“Mean Precision (%)”: Average of all precision calculations by ion.

	Fluoride (meq/L)	Chloride (meq/L)	Nitrate (meq/L)	Sulfate (meq/L)	Lithium (meq/L)	Sodium (meq/L)	Ammonium (meq/L)	Potassium (meq/L)	Magnesium (meq/L)	Calcium (meq/L)
7/23/2008										
P5	0.0103	0.3982	0.0333	0.1380	0.0013	0.4285	0.0235	0.3357	0.0657	0.4781
P5-labdup	0.0069	0.3671	0.0260	0.1384	0.0007	0.4240	0.0283	0.3302	0.0700	0.4803
Mean	0.0086	0.3827	0.0297	0.1382	0.0010	0.4263	0.0259	0.3329	0.0679	0.4792
S.D.	0.0024	0.0219	0.0052	0.0002	0.0004	0.0031	0.0034	0.0039	0.0031	0.0016
Precision (%)	27.5337	5.7294	17.5387	0.1650	38.2792	0.7382	13.2895	1.1599	4.4947	0.3251
CR	0.0085	0.1858	0.0798	0.0870	n.a.	0.0282	0.0589	0.1615	0.0487	0.4115
CR-labdup	0.0131	0.1821	0.0722	0.0792	n.a.	0.0280	0.0405	0.1527	0.0513	0.4188
Mean	0.0108	0.1839	0.0760	0.0831	n.a.	0.0281	0.0497	0.1571	0.0500	0.4151
S.D.	0.0033	0.0026	0.0053	0.0055	n.a.	0.0001	0.0130	0.0062	0.0018	0.0052
Precision (%)	30.6827	1.4088	7.0250	6.6154	n.a.	0.4754	26.1859	3.9362	3.6039	1.2506
8/7/2008										
P5	0.0083	0.0190	0.0212	0.0396	n.a.	0.1903	0.0203	0.0138	0.0434	0.3555
P5-labdup	n.a.	0.0146	0.0158	0.0356	n.a.	0.1919	0.0183	0.0148	0.0465	0.3878
Mean	n.a.	0.0168	0.0185	0.0376	n.a.	0.1911	0.0193	0.0143	0.0450	0.3717
S.D.	n.a.	0.0031	0.0038	0.0029	n.a.	0.0012	0.0015	0.0007	0.0022	0.0228
Precision (%)	n.a.	18.3941	20.6559	7.6433	n.a.	0.6139	7.5447	4.9502	4.8435	6.1407
CR	0.0054	0.0151	0.0488	0.0490	n.a.	0.0177	0.0243	0.0056	0.0583	0.5188
CR-labdup	n.a.	0.0167	0.0585	0.0523	n.a.	0.0232	0.0315	0.0069	0.0603	0.5328

Mean	n.a.	0.0159	0.0537	0.0506	n.a.	0.0205	0.0279	0.0062	0.0593	0.5258
S.D.	n.a.	0.0011	0.0069	0.0024	n.a.	0.0039	0.0051	0.0009	0.0014	0.0099
Precision (%)	n.a.	6.7175	12.8211	4.6679	n.a.	18.8820	18.2997	15.1761	2.3220	1.8774
9/7/2008										
P5	n.a.	0.1167	0.0513	0.0631	0.0006	0.3660	0.0459	0.0204	0.0747	0.5262
P5-labdup	n.a.	0.1111	0.0230	0.0743	0.0007	0.3669	0.0073	0.0236	0.0794	0.5300
Mean	n.a.	0.1139	0.0372	0.0687	0.0007	0.3664	0.0266	0.0220	0.0771	0.5281
S.D.	n.a.	0.0039	0.0200	0.0079	0.0000	0.0006	0.0273	0.0023	0.0033	0.0027
Precision (%)	n.a.	3.4373	53.7608	11.5173	3.8444	0.1754	102.8030	10.2564	4.2694	0.5082
CR	n.a.	0.0252	0.1572	0.0154	n.a.	0.0253	0.0199	0.0040	0.0672	0.6854
CR-labdup	0.0047	0.0336	0.2287	0.0318	n.a.	0.0403	0.0252	0.0107	0.0773	0.7464
Mean	n.a.	0.0294	0.1929	0.0236	n.a.	0.0328	0.0225	0.0074	0.0722	0.7159
S.D.	n.a.	0.0060	0.0505	0.0115	n.a.	0.0106	0.0037	0.0048	0.0072	0.0431
Precision (%)	n.a.	20.2361	26.1894	48.9219	n.a.	32.3748	16.5324	64.9529	9.9334	6.0190
9/9/2008										
P5	n.a.	0.3115	0.0096	0.0427	n.a.	0.2640	n.a.	0.2141	0.0414	0.4319
P5-labdup	n.a.	0.3087	0.0084	0.0422	n.a.	0.2702	n.a.	0.2204	0.0554	0.4339
Mean	n.a.	0.3101	0.0090	0.0424	n.a.	0.2671	n.a.	0.2172	0.0484	0.4329
S.D.	n.a.	0.0020	0.0008	0.0003	n.a.	0.0043	n.a.	0.0045	0.0099	0.0014
Precision (%)	n.a.	0.6394	9.2067	0.7148	n.a.	1.6206	n.a.	2.0639	20.5197	0.3218
CR	0.0175	0.3520	0.0349	0.0406	n.a.	0.0148	0.0344	0.2939	0.0221	0.3189
CR-labdup	0.0137	0.3446	0.0207	0.0419	n.a.	0.0130	0.0015	0.2855	0.0215	0.3094
Mean	0.0156	0.3483	0.0278	0.0413	n.a.	0.0139	0.0180	0.2897	0.0218	0.3141
S.D.	0.0027	0.0052	0.0100	0.0009	n.a.	0.0013	0.0233	0.0059	0.0004	0.0067
Precision (%)	17.2830	1.5046	36.1481	2.2073	n.a.	9.1487	129.7306	2.0523	1.8714	2.1394
9/13/2008										
P5	n.a.	0.3713	0.0541	0.0403	n.a.	0.2750	0.0401	0.2790	0.0593	0.4601
P5-labdup	n.a.	0.3730	0.0463	0.0575	n.a.	0.2960	0.0766	0.2775	0.0407	0.3528
Mean	n.a.	0.3721	0.0502	0.0489	n.a.	0.2855	0.0583	0.2783	0.0500	0.4065
S.D.	n.a.	0.0012	0.0055	0.0121	n.a.	0.0149	0.0258	0.0011	0.0131	0.0759
Precision (%)	n.a.	0.3321	10.9060	24.8530	n.a.	5.2079	44.2829	0.3980	26.2411	18.6652
CR	n.a.	0.1470	0.0473	0.1209	n.a.	0.0215	0.0405	0.1408	0.0642	0.7324
CR-labdup	n.a.	0.1526	0.0835	0.1152	n.a.	0.0192	0.0401	0.1080	0.0532	0.5688
Mean	n.a.	0.1498	0.0654	0.1180	n.a.	0.0203	0.0403	0.1244	0.0587	0.6506
S.D.	n.a.	0.0039	0.0256	0.0040	n.a.	0.0016	0.0003	0.0231	0.0078	0.1157
Precision (%)	n.a.	2.6224	39.1357	3.4209	n.a.	8.0633	0.7077	18.6040	13.3119	17.7853
9/14/2008										
P5	n.a.	0.8016	0.0605	0.0509	n.a.	0.2762	0.0943	0.6168	0.0749	0.4590
P5-labdup	n.a.	0.7337	0.0200	0.0480	n.a.	0.2695	0.0366	0.6041	0.0627	0.5228
Mean	n.a.	0.7677	0.0403	0.0494	n.a.	0.2728	0.0654	0.6105	0.0688	0.4909
S.D.	n.a.	0.0480	0.0287	0.0021	n.a.	0.0047	0.0407	0.0089	0.0086	0.0452
Precision (%)	n.a.	6.2505	71.1590	4.2034	n.a.	1.7185	62.2630	1.4655	12.4970	9.1982
CR	n.a.	0.0875	0.0451	0.0834	n.a.	0.0237	0.0616	0.0818	0.0497	0.5201
CR-labdup	n.a.	0.0892	0.0413	0.0870	n.a.	0.0133	0.0333	0.0702	0.0406	0.4524
Mean	n.a.	0.0884	0.0432	0.0852	n.a.	0.0185	0.0475	0.0760	0.0451	0.4862
S.D.	n.a.	0.0012	0.0026	0.0025	n.a.	0.0073	0.0200	0.0082	0.0064	0.0479
Precision (%)	n.a.	1.3564	6.1075	2.9842	n.a.	39.4274	42.0909	10.8131	14.2156	9.8418

9/29/2008										
P5	n.a.	0.1179	0.0050	0.0775	n.a.	0.2287	0.0082	0.0824	0.0721	0.5430
P5-labdup	n.a.	0.1363	0.0049	0.0814	n.a.	0.2649	0.0112	0.0957	0.0779	0.5633
Mean	n.a.	0.1271	0.0050	0.0795	n.a.	0.2468	0.0097	0.0891	0.0750	0.5532
S.D.	n.a.	0.0130	0.0000	0.0027	n.a.	0.0256	0.0021	0.0094	0.0041	0.0143
Precision (%)	n.a.	10.2198	0.7132	3.4419	n.a.	10.3548	21.7762	10.5753	5.5338	2.5936
CR	n.a.	0.0224	0.0121	0.0208	n.a.	0.0176	0.0060	0.0263	0.0411	0.7522
CR-labdup	n.a.	0.0232	0.0142	0.0262	n.a.	0.0175	0.0062	0.0130	0.0428	0.7662
Mean	n.a.	0.0228	0.0131	0.0235	n.a.	0.0175	0.0061	0.0196	0.0420	0.7592
S.D.	n.a.	0.0005	0.0015	0.0038	n.a.	0.0000	0.0001	0.0094	0.0012	0.0099
Precision (%)	n.a.	2.2979	11.2592	16.1619	n.a.	0.1689	2.4153	47.8716	2.7892	1.3068
10/1/2008										
P5	n.a.	0.1688	n.a.	0.0821	n.a.	0.2456	0.0159	0.1463	0.0724	0.5356
P5-labdup	n.a.	0.1655	n.a.	0.0736	n.a.	0.2388	0.0058	0.1436	0.0707	0.5152
Mean	n.a.	0.1672	n.a.	0.0779	n.a.	0.2422	0.0109	0.1449	0.0716	0.5254
S.D.	n.a.	0.0024	n.a.	0.0060	n.a.	0.0047	0.0072	0.0020	0.0012	0.0145
Precision (%)	n.a.	1.4071	n.a.	7.7511	n.a.	1.9604	66.0591	1.3501	1.6539	2.7514
CR	n.a.	0.2826	0.0403	0.0564	n.a.	0.0142	0.0350	0.2601	0.0296	0.5109
CR-labdup	n.a.	0.2828	0.0463	0.0567	n.a.	0.0191	0.0401	0.2586	0.0262	0.4425
Mean	n.a.	0.2827	0.0433	0.0566	n.a.	0.0167	0.0375	0.2593	0.0279	0.4767
S.D.	n.a.	0.0002	0.0042	0.0002	n.a.	0.0034	0.0035	0.0011	0.0024	0.0484
Precision (%)	n.a.	0.0550	9.7381	0.4173	n.a.	20.5349	9.4352	0.4160	8.5382	10.1501
10/9/2008										
P5	n.a.	0.2409	0.0052	0.0715	n.a.	0.2400	0.0116	0.1894	0.0748	0.5781
P5-labdup	n.a.	0.2232	0.0062	0.0630	n.a.	0.2327	0.0155	0.1823	0.0593	0.4799
Mean	n.a.	0.2320	0.0057	0.0673	n.a.	0.2364	0.0135	0.1859	0.0670	0.5290
S.D.	n.a.	0.0125	0.0007	0.0060	n.a.	0.0051	0.0027	0.0050	0.0110	0.0694
Precision (%)	n.a.	5.3775	12.5552	8.9124	n.a.	2.1784	20.2428	2.6678	16.3460	13.1253
CR	n.a.	0.2777	0.0711	0.0731	n.a.	0.0103	0.0485	0.2538	0.0379	0.5375
CR-labdup	n.a.	0.2743	0.1061	0.0916	n.a.	0.0583	0.1302	0.2462	0.0434	0.5405
Mean	n.a.	0.2760	0.0886	0.0823	n.a.	0.0343	0.0893	0.2500	0.0407	0.5390
S.D.	n.a.	0.0023	0.0248	0.0131	n.a.	0.0339	0.0578	0.0054	0.0039	0.0021
Precision (%)	n.a.	0.8499	27.9954	15.8740	n.a.	98.8727	64.6687	2.1520	9.6518	0.3943
MEAN PRECISION (%)	**25.1665**	**4.9353**	**21.9362**	**9.4707**	**21.0618**	**14.0287**	**38.1369**	**11.1590**	**9.0354**	**5.7997**