EFFECTS OF USING CLAY NANOPARTICLES AS A SOIL AMENDMENT TO REMOVE NITRATE
FROM STORMWATER

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Megan Abutin
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COMMITTEE MEMBERSHIP

TITLE: Effects of Using Clay Nanoparticles as a Soil
Amendment to Remove Nitrate from
Stormwater

AUTHOR: Megan Abutin

DATE SUBMITTED: June 2018

COMMITTEE CHAIR: Rebekah Oulton, Ph.D.
Assistant Professor of Civil and Environmental
Engineering

COMMITTEE MEMBER: Amro El Badawy, Ph.D.
Lecturer of Civil and Environmental
Engineering

COMMITTEE MEMBER: Bwalya Malama, Ph.D.
Assistant Professor of Natural Resources
Management and Environmental Science

ABSTRACT
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Megan Abutin

Development of urban areas continues to increase, disrupting the natural ecosystem and the pathways for water to drain into downstream water bodies. As the amount of impervious area increases, pollutants can accumulate on the surface and enter the water cycle by stormwater. In most cities, the stormwater flows into a storm drain that is discharged into a water body. Low Impact Development technology has been developed to treat stormwater prior to discharge downstream. A bioretention cell is used to treat stormwater pollutants such as nitrate, phosphorus, total suspended solids, and metals. Past research has indicated that the removal efficiency of nitrate by bioretention cells greatly varies from a 75% reduction in nitrate concentration to the addition of nitrate in the effluent from leaching of the bioretention cell. It is important to remove nitrate from water because it can cause negative environmental and human effects. Excess nitrate in the environment can lead to eutrophication, resulting in the death of fish. If ingested by infants, nitrate can cause “blue baby syndrome” leading to death. One area of study that focuses on the removal of nitrate from stormwater is maximizing the efficiency of the designed soil media. The addition of a clay amendment could lead to higher removal efficiencies. The use of clay nanoparticles, or nanoclays, can maximize the amount of surface area available for adsorbance potentially increasing the amount of nitrate removed from water. The goal of this study was to identify a nanoclay with high adsorbance by testing its nitrate removal efficiency and then determining if it would be feasible to add to a bioretention cell by calculating the hydraulic conductivity to compare to industry design values. This study analyzed a montmorillonite clay, a bentonite nanoclay, and a pre-modified trimethyl stearyl ammonium nanoclay as a 1% w/w added amendment to a Nevada sand to determine the number of pore volumes required until the system reached breakthrough. The pre-modified nanoclay required the highest amount of water, 19 pore volumes, until breakthrough was reached. The fraction of nanoclay was increased to 2% w/w and breakthrough was not seen in the volume of water that was filtered through the system. The hydraulic conductivity for this nanoclay/sand mixture was 14 in/hr, greater than most minimum design values. Since the results so far indicated that this mixture would efficiently remove nitrate and still meet the minimum hydraulic conductivity, a synthetic stormwater solution was filtered through the column to test the nitrate removal when it is competing with other pollutant ions. This resulted in a projected breakthrough of 27 pore volumes and a 9 in/hr associated hydraulic conductivity. Future research can be completed to assess the best methodology to homogeneously mix the nanoclay particles with the sand to prevent leaching of the nanoclays. The next step in optimizing a bioretention cell for water quality treatment would be to focus research on how plants affect the system. If plants are able to remove nitrate from the system entirely, the lifetime of the bioretention cell could increase.

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Chapter 1: Introduction & Literature Review

Urbanization continues to increase in both developed and developing countries. Natural ecosystems are being transformed into areas of high impervious surfaces such as streets, sidewalks, and parking lots, decreasing the amount of infiltration to the groundwater table. In climates with seasons where there is little to no precipitation, pollutants such as nitrogen, phosphorous, petroleum hydrocarbons, metals, synthetic organics, and accumulated sediment and soil can build up on these impervious surfaces. When the first rain events occur, excess runoff that flows along these surfaces accumulates these pollutants ("Preliminary Data Summary"). When this runoff is discharged to the storm drain system, it can carry that pollutant load with it, ultimately affecting urban landscaping and water bodies downstream. For many cities, the storm drain system collects the water and releases it into these local water bodies such as rivers and lakes with minimal to no treatment for those types of dissolved or suspended pollutants ("Stormwater Discharges"). This pollutant load can negatively affect the water quality of these surface sources and can lead to contamination of recreational water bodies and potential drinking water sources (Hatt et al.).

Stormwater contamination due to nitrate occurs in areas where agriculture and urban landscaping are common. As a result of excess fertilizers, nitrates can build up on the top layer of soil. After being flushed by stormwater, these nitrates can flow into the storm drain system, then into receiving waters. High concentrations of nitrate in the environment can disrupt ecosystems; an increase in nitrates in lakes and streams can

cause excess algal growth and subsequently result in eutrophication of the water body (Gaffield et al.).

Nitrate can also cause negative health effects on humans such as methemoglobinemia or “blue baby syndrome” in infants which can result in death. In adults, nitrates can cause shortness of breath and an increase in miscarriage in women (Gaffield et al.). Human exposure to nitrate runoff can occur in rivers and lakes that allow recreation as well as any public lands such as parks that are downstream of the nitrate source. Treating stormwater runoff prior to entry into these types of surface waters could minimize the negative health impacts associated with nitrates and other pollutants.

In addition, nitrate can leach from agricultural fields into the underlying groundwater aquifers below. The United States Geological Study (USGS) estimated as of 2010 that groundwater accounts for 25% of freshwater use in the United States (Perlman). According to the EPA, the Maximum Contaminant Level (MCL) for nitrate as nitrogen (NO_3^- -N) that will not result in adverse human health effects is 10 mg/L (“National Primary”). Groundwater aquifers that underly agricultural areas have been found to have nitrate concentrations that are more than double the standard of 10 mg/L (Bouchard et al). There is difficulty in regulating the agricultural industry and the amount of fertilizers used by farmers. An increased removal efficiency in nitrate by downstream technology could help remedy the contamination of aquifers and receiving water bodies without requiring farmers to decrease their crop yield by decreasing their fertilizer use.

Poor and McDonnell conducted a study on the seasonality of nitrate runoff on three land use types: agricultural, residential, and forest. The study showed that agriculture as a land use type was positively correlated to higher concentrations of nitrate in runoff to water bodies compared to residential and forest land use types. The study did not find a correlation between the varying intensity of storm events and nitrate levels downstream of an agricultural land use (Poor and McDonnell). The results indicated that runoff from agricultural land showed the highest nitrate concentrations right after the first storm event due to build up from the summer months. The study estimated that the excess nitrate build-up on the top soil of the fields in the study was approximately 6 mg/L (Poor and McDonnell). As the rainy season continued, the concentration of nitrate decreased until it reached a steady concentration.

The study also showed that the peak nitrate concentration in the river downstream from the residential land use was due to relatively high flow rates and not high nitrate concentrations. High flow rates in residential land use can be attributed to larger areas of impervious surfaces. Normal fertilizer application on landscaped areas will result in increased nitrate loading to receiving waters because of the increased runoff (Poor and McDonnell).

Low Impact Development (LID) technologies have been used to improve the water quality of stormwater runoff and reduce flooding in urban cities to meet the predevelopment conditions of the site ("Urban Runoff"). The technology can be integrated into the city

landscape to reduce the percentage of impervious surfaces. When the natural watershed characteristics are known, LIDs attempt to maintain the hydrology of the predeveloped site. One approach to managing stormwater employed by these technologies is to recreate the natural ecosystem to reduce flooding and protect water quality of the local ecosystem by trying to mimic natural processes such as infiltration and evapotranspiration ("Urban Runoff"). LID technologies commonly used to treat water quality include bioswales, permeable pavement, and rain gardens. One of the most common technologies used is a bioretention cell (BRC), which protects water quality by using vegetation and a design soil mixture to treat water as it flows through the cell (Figure 1). LIDs can also be implemented at the location of outflow for agricultural fields to treat the excess nitrate in the stormwater runoff.

Figure 1: Schematic of a bioretention cell (Winston et al.)

Bioretention cells are commonly used because they are known to treat stormwater contaminants such as Total Suspended Solids (TSS), phosphorous, and other metals with

greater efficiency than other LID technologies (Hunt et al). A breakdown of the media typically used in a bioretention cell is shown in Table 1.

Table 1: Common bioretention cell soil media design (Hunt et al.)

Type of soil	Percentage (%)
Sand	85-88
Silt and Clay	8-12
Organic Matter	3-5

Compared to other studied pollutants that BRC's are known to treat, nitrate is shown to have the lowest removal efficiency by most LID technologies (Hsieh and Davis). Most studies conducted also show a lot of inconsistency with the removal efficiency of nitrate, ranging from 200% additional nitrate in the BRC effluent to 77% removal (Shrestha et al.). The nitrate removal efficiency values vary depending on the size of the storm. For larger storms, greater than an inch in rainfall depth, negative nitrate removal is shown indicating that the bioretention cell was unable to treat nitrate and likely leached nitrate into the effluent water. The study concluded that an increase in nitrate was most likely due to nutrient export from the compost added to the BRC soil media. By reducing the amount of compost, the amount of nitrate leached from the bioretention cell can be reduced.

Hunt et al. recommends choosing a higher percentage of clay in the range shown in Table 1 when the main contaminant of concern is nitrate. Clay particles can remove nitrate

without the addition of surface modification. Clays swelling capacity and high specific area have resulted in numerous studies being conducted to determine the effects of their addition in bioretention cell design soil media. These clay particles can participate in ion exchange and adsorption in their natural states. Clay is known to have a high specific surface area and can treat water more effectively through adsorbance (Liu and Zhang).

While soil mixtures with high clay content achieve the highest pollutant removal, they also decrease the velocity of infiltration which can subsequently lead to flooding (Hsieh and Davis). Optimization of the clay-to-sand ratio can allow for higher removal efficiencies of pollutants. Selecting a clay with high adsorbent properties may further increase the removal efficiency of nitrate without needing to increase the amount of clay needed, thereby minimizing infiltration rate impacts.

The natural properties of clay depend on the soil mineral that is most dominant. The dominant mineral changes based on how the clay was formed. Some common mineral types that have been identified as adsorbent materials are allophane, montmorillonite, illite, bentonite, and kaolin. In a study completed by Liu and Zhang, it was determined that montmorillonite-based clays (Figure 2) had the highest absorption efficiencies due to the weak bonds between layers that allows water to enter.

Figure 2: Structural figure of montmorillonite clay (Uddin)

Montmorillonite clay is arranged in octahedral layers composed of aluminum and oxygen that is sandwiched by tetrahedral layers composed of silicon and oxygen atoms (Smith). In between the sheets, positive exchangeable cations such as magnesium, potassium, or sodium create a net positive charge and are available for ion exchange (Smith). The larger cations that reside in this layer lead to a greater swelling capacity of the clay when they become hydrated creating more room in the particle and increasing the surface area. The expanding crystal lattice and plastic properties of the montmorillonite clays allow this expansion in the particles that results in efficient adsorbents.

Montmorillonite clay participates in several mechanisms in the uptake of contaminants: adsorption, ion exchange, ligand exchange, partition, surface precipitation, and structural incorporation (Figure 3).

Figure 3: Montmorillonite clay can participate in these 6 mechanisms (Zhu et al.).

Zhu et al. conducted a study focused on the different mechanisms of adsorption and measured which ones occurred in different scenarios. Each of the mechanisms is described below including those thought to be involved in the uptake of nitrate. Surface adsorption can be physical or chemical and involves overcoming London-van der Waals forces or the formation of chemical bonds. Ion exchange is more effective for holding sorbed ions, and it occurs when ionic contaminants are exchanged with existing ions on the montmorillonite clay. Most of the pre-existing ions on montmorillonite are cations which result in a high cation exchange capacity. Ligand exchange is similar ion exchange except a ligand, which can be an ion or a molecule, are exchanged in the process. Partition is the distribution of a contaminant between two phases meaning that the contaminant can enter into the structure of the clay rather than just adsorb to the surface. This

mechanism occurs when hydrophobic organic contaminants are being treated by soil and will not occur for nitrate. Surface precipitation is the formation of precipitates on the surface of the montmorillonite clay. The concentration of nitrate in stormwater is typically low enough that precipitates will not form. Structural incorporation involves the contaminant ions adsorbing into the structure of the clay (Zhu et al.). The main mechanisms involved in the removal of nitrate from stormwater are surface adsorption and ion or ligand exchange. Montmorillonite clay can participate in these mechanisms because of the structure described above, and results from previous studies indicate that it would be a good clay to use in the design of bioretention cell soil media (Zhu et al.).

The existing properties of montmorillonite clay have shown that it can be an effective adsorbent. If sorption is the dominant mechanism used to remove nitrate from water, it is crucial to have a high specific surface area to have more binding sites for the nitrate to adsorb onto the particle. This factor has introduced an opportunity for research into clay nanoparticles, or nanoclays, that have an increased amount of surface area because the particles are so small. Most of the previous research focuses on using nanoclays as a building block for nanocomposites that can be modified for a specific application (Morgan).

Nanoparticle research has increased as more beneficial properties are being discovered. Among the abilities being researched is the use of nanoparticles for increased absorbance in the treatment of water due to their increased surface area. With a larger surface area

available, there may be an increase in the quantity of adsorbents that can attach to sites on the clay particles. With more adsorbent sites available, there will be a reduced quantity of nanoparticles that are required in the sand mixture of the BRC which could in turn reduce the impact from the addition of clay on the hydraulic conductivity, allowing water to flow through the bioretention cell quicker.

Past studies on the use of nanoparticles to treat water typically use a metal base such as nanoscale zero-valent iron to remove pollutants through a chemical transformation (Li et al). This nanoparticle is typically modified with nickel, copper or lead. Nanoscale zero-valent iron has been shown to generate metallic ions and ammonia as a byproduct of removing nitrate (Li et al). This additional pollution would need to be treated as well to prevent the release of these ions into the hydrologic system after water flows through the BRC. Removal rates of nitrate using this nanoparticle tend to be fairly high; however, it can be expensive to modify nanoscale zero-valent iron. Clay nanoparticles, or nanoclays, have preliminarily been researched because of their potential to be more environmentally friendly. Clay is a readily available adsorbent material that can be found in natural deposits or ordered from a manufacturer. Using clay as the main adsorbent material as opposed to a metal particle eliminates the possibility for the addition of another toxic contaminant to the ecosystem (Li et al). In addition, clay is cost effective compared to other adsorbents.

A study conducted by Siddiqi used several different nanoclays as soil amendments to test the removal efficiency of nitrate. Siddiqi conducted batch isotherm experiments to analyze the ability of the nanoclays to remove nitrate from water. Column experiments were conducted using sand/nanoclay mixtures to determine the resulting hydraulic conductivity and the number of pore volumes required for breakthrough. The study concluded that pre-modified trimethyl stearyl ammonium nanoclay was the most effective adsorbent and maintained a hydraulic conductivity of 12.6 in/hr through the soil column at 1% nanoclay (Siddiqi).

1.1 Purpose

This study will build on the research gaps identified in the literature review, and specifically experiments conducted by Siddiqi. This study will look to confirm the results from her study and expand the exploration on the most promising soil amendment.

Specifically, this study proposes to address the following tasks:

- The first task will be to determine the amount of nitrate leached from the various clays and nanoclays. An additional variable addressed in this task is to determine if different ratios of nanoclay to sand affect the leached nitrate concentration.
- The second task of this study is to observe the nitrate removal efficiency of different nanoclays and differing ratios of nanoclays to sand when a simple nitrate solution flows through a column. This will be measured in the amount of pore volumes that are required for the mixture to reach breakthrough. A pore volume

is the ratio of the volume of pore space in the soil to the total volume; a pore volume of effluent is the volume of solution equal to the volume of pore space in the cell. For the sand type being used in this experiment, one pore volume was found to be 96.5 mL (Siddiqi).

- The third task incorporates a synthetic stormwater solution in place of the nitrate solution to see how the system reacts when other pollutants can compete with nitrate as it adsorbs to the clay. Again, pore volumes of solution that pass through the soil column before nitrate breakthrough occurs will indicate efficacy of nitrate removal.
- The fourth task of this study is to analyze the feasibility of using the different mixtures when designing a bioretention cell. The hydraulic conductivity values through the soil column under different conditions can be compared to the minimum hydraulic conductivity required of bioretention cells to determine if viability of each mixture for larger-scale application.

Chapter 2: Materials & Methods

In order to address these goals, a series of experiments was developed as described in this section. These experiments were developed to address the specific research tasks identified above.

2.1 Materials

Several chemicals were used to prepare the nitrate solution and the synthetic stormwater solution (Table 2). All chemicals used in this experiment were purchased from Fisher Scientific.

Table 2: Chemicals required to prepare nitrate solution and synthetic stormwater solution

Chemical Name	Chemical Formula	CAS Number
Sodium nitrate	NaNO_3	7631-99-4
Glycine	$\text{NH}_2\text{CH}_2\text{COOH}$	56-40-6
Dibasic sodium phosphate	Na_2HPO_4	7558-79-4
Cupric sulfate	CuSO_4	7758-98-7
Lead chloride	PbCl_2	7758-95-4
Zinc chloride	ZnCl_2	7646-85-7
Calcium chloride	CaCl_2	10043-52-4

Because this study is building on previous research, the clays chosen were determined partly based on the results from that experiment (Siddiqi). The Nevada sand was purchased from the Gordon Sand Company and was used as the base sand, similar to the previous study. The sand has a mean grain diameter of 0.15 mm and was found to have a specific gravity of 1.8 (Siddiqi). A montmorillonite clay purchased from Sigma Aldrich was used as a control to compare the differences of the removal efficiency and hydraulic conductivity between clay and nanoclay. The montmorillonite clay was purchased in larger granules ranging from 0.5-1.25 mm according to the specifics provided by the supplier.

Two nanoclays were chosen to verify the results from the study conducted by Siddiqi. The unmodified hydrophilic bentonite clay and a nanoclay treated with 25-30 wt. % trimethyl stearyl ammonium were chosen because both clays contain montmorillonite as their base clays and were the best performing clays of the previous study. The purpose of the pretreatment was to add a positively-charged coating to the clays by the amine groups that are often associated with the hydrogen atoms that would be able to attract anions like nitrate ("Nitrate CRD 943"). The pre-modified nanoclay was the best performing clay in terms of its effectiveness to remove nitrate in Siddiqi's study. The nanoclays were purchased from Sigma Aldrich. The unmodified hydrophilic bentonite clay has an average particle diameter size ≤ 25 microns. The pre-modified nanoclay has an average particle diameter size ≤ 20 microns. The unmodified hydrophilic bentonite nanoclay was chosen as a control nanoclay for comparison to the pre-modified nanoclay.

2.2 Methods

The experimental methods employed in this study are based on the previous studies discussed above.

2.2.1 Calculating hydraulic conductivity

The falling head permeameter test shown in Figure 4 was used to test the hydraulic conductivity. A column with a diameter of 2.43 inches and a height of 2.98 inches was used. The diameter of the falling head standpipe was 0.787 inches. A total of 344.2 grams of dry sand filled the column (Siddiqi).

The nanoparticles were added to the sand using a bath sonicator, Branson 2800. The appropriate amount of sand and nanoclay was weighed out and added to a jar. 50 mL of water was added to the jar to create a wet slurry. The jar was inverted and shaken to pre-mix the nanoparticles, sand, and water prior to use of the bath sonicator. To prevent aggregation of the nanoparticles, the slurry mixture was put in a bath sonicator for 2 hours to completely mix the nanoclay into the sand. Mixing via sonication is an important step in the procedure to maintain the properties of the nanoclay. This methodology prevents the nanoclays from aggregating during mixing with the base sand.

*Figure 4: A schematic of the falling head test used to calculate hydraulic conductivity
(Bahmani et al.)*

After the mixture was sonicated, the slurry was added to the column. The valve at the bottom of the column was opened to allow the excess water in the column to drain out, and the remaining soil was leveled with the top of the column before conducting the falling head test. Next, the valve was closed, and one pore volume of water was filled into the standpipe. To conduct the test, valve was opened and at the same time, a timer was started to record the amount of time required to filter the required pore volume of water through the column. As water was filtered through the column, the change in head and the time required for a pore volume of water to move through the column was recorded. A pore volume is the ratio of the volume of pore space in the soil to the total volume. For the sand type being used in this experiment, one pore volume was equivalent to 96.5 mL (Siddiqi). The change in head and change in time was used to calculate hydraulic conductivity using Equation 1.

$$K = 2.3 \frac{aL}{At} \log_{10} \frac{h_1}{h_2} \quad (\text{Equation 1})$$

Where a= cross sectional area of the standpipe (cm²)

L= length of the column (cm)

A= cross sectional area of the column (cm²)

t= change in time for one pore volume to filter through the column (seconds)

h₁= initial height of water in the standpipe (cm)

h₂= final height of water in the standpipe (cm)

All variables in the equation are defined in Figure 4 and 2.3 is a conversion factor. Resulting values were compared to values used for typical hydraulic conductivities through bioretention cells.

2.2.2 Calculating removal efficiency of nitrate

A solution of known nitrate concentration typical of influent stormwater was prepared using sodium nitrate (NaNO₃). A nitrate concentration of approximately 1.7 mg/L was used, with the actual concentration of each trial verified with Ion Chromatography (IC). This nitrate solution was filtered through the column and collected at the outfall after each pore volume. The solution was filtered using a 0.22 µm nitrocellulose membrane to remove any sand or nanoparticles that were also released from the column. After filtration, the effluent nitrate concentration was determined using the IC. Breakthrough curves were created that illustrate how much water could flow through the column before the capacity of the mixture to remove nitrate had been exhausted. Breakthrough

is termed as the number of pore volumes required until the same or higher concentration of nitrate is measured in the effluent. This indicates that nitrate is no longer being removed by the sand and nanoclay mixture.

2.2.3 Addition of Synthetic Stormwater

From previous studies, a synthetic stormwater solution was made and filtered through the column (Table 3). As mentioned above, this experiment was conducted to determine the effect on nitrate removal efficiency in more realistic water systems with ions competing with nitrate to adsorb to the clay.

Table 3: Synthetic Stormwater solution (Davis et al.)

Pollutant	Chemical	Concentration (mg/L)
Nitrate	Sodium nitrate (NaNO_3)	2
Organic nitrogen	Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$)	4
Phosphorus	Dibasic sodium phosphate (Na_2HPO_4)	0.6
Copper	Cupric sulfate (CuSO_4)	0.08
Lead	Lead chloride (PbCl_2)	0.08
Zinc	Zinc chloride (ZnCl_2)	0.6
Dissolved solids	Calcium chloride (CaCl_2)	120

The same procedure was followed from the nitrate solution using the 2% w/w nanoclay treated with 25-30 wt. % trimethyl stearyl ammonium. This pre-modified nanoclay was

the best performing nanoclay, discussed in the results, in terms of nitrate removal efficiency while maintaining appropriate hydraulic conductivity. Although other ions were present in the effluent because they were introduced in the synthetic stormwater, they were not analyzed. Nitrate removal efficiency was then calculated and compared to the results from the same nanoclay mixture using only a nitrate solution.

2.3 Analytical Methods

An Ion Chromatography (IC) system from Thermo Fisher Scientific was used to analyze the concentration of nitrate in the samples from the falling head test. The model used was a Dionex ICS-1600 with an autosampler Dionex model AS-DV. To test for nitrate, a Dionex IonPac AS7 IC column was used in the IC. This specific column is used for separation for multiple polyvalent anions ("Dionex"). The column can test for the concentration of different anions that corresponds to a specific retention time. The system produces a curve and the area under the curve for each anion at their respective retention times that represents the concentration of that ion. A calibration curve of area versus known concentration from the data was used to calculate the nitrate concentration of the unknown samples. Knowing the retention time of nitrate from the calibration curve, the nitrate peak can be identified in the unknown samples. The lower detection limit of the IC can be determined from an estimation using the mean, standard deviation, and a specific confidence factor. Any other peaks that occurred were ignored in this study. Prior to using the IC, the samples were filtered using a 0.22 μm nitrocellulose membrane filter to prevent clogging of the column and back pressure in the IC.

2.4 Real-World Application Analysis

For each sand/nanoclay mixture, a breakthrough volume was determined that is discussed in the results. The number of pore volumes can be translated into a total volume of water that flowed through the column before breakthrough occurred. This total volume is the amount of water that the mixture can handle before it reaches its nitrate removal capacity. The volume can be used to find the total depth in inches that would result using Equation 2.

$$P = \frac{V_T}{A} \quad (\text{Equation 2})$$

Where P = the depth in inches

V_T = the total volume of water in in³

A = the area of the cross section of the column in in²

The depth of water can be used to compare to the depth of water from a rain event. Most LID technologies whose main purpose is to treat stormwater quality are designed to treat volumes from smaller storm events, with a controlled overflow catchment in place for larger events.

2.5 Quality Assurance/Quality Control

QA/QC measures described below that were used for this experiment were based on those outlined from the previous study (Siddiqi). To act as a control, DI water was run through the falling head test column to determine the concentration of nitrate that was

leached from the sand. This process was completed for all the sand and nanoclay mixtures tested to determine the effluent concentration of nitrate leached from the clays themselves. The resulting background concentrations of nitrate were subtracted from the concentrations measured after each pore volume. Prior to conducting the falling head test for each sample with the nitrate solution, DI water was run through and collected after one pore volume and after four pore volumes. This accounted for any fluctuations in background nitrate concentrations leaching from the sand or nanoclay in each mixture.

In addition, the nitrate solution was filtered through a sand only sample to test the adsorption of sand by itself. The percent of improvement of removal efficiency for the nanoclays was compared to the sand only sample to determine the increase of efficiency by adding nanoclays to the traditional bioretention cell soil mixture.

Each batch of samples was run through the IC using specific QA/QC measures to ensure the machine was working correctly. Known concentrations of 1,5,10, and 20 mg/L of nitrate were prepared and included in each batch to create a calibration curve. For each pore volume, a split sample was run identical to the original sample to check that the machine was measuring the concentration of nitrate with precision. A control verification standard (CVS) of 20 mg/L was included in the middle and end of each batch of samples to test that the IC was operating correctly during the entire run.

A target influent nitrate concentration of 1.72 mg/L ($\text{NO}_3\text{-N}$) was selected to match environmentally relevant concentrations. Actual influent nitrate solution concentration was verified for each sample using the IC. The original nitrate concentration fluctuated among samples, so it was the measured concentration that was used when calculating percent removal.

For each sand/nanoclay mixture, background nitrate concentrations were tested in duplicate. Triplicates were taken if the two data samples did not agree with each other. When testing the nitrate removal efficiency, duplicates or triplicates of each different sand/nanoclay mixture were run, and outliers were excluded from the final data sets.

Chapter 3: Results & Analysis

A series of experiments was conducted to test the ability to remove nitrate from water using different nanoclay to sand mixtures. The hydraulic conductivity of each mixture was calculated to determine the feasibility of using the mixture in a real world bioretention cell. The results from this experiment that were found by replicating the methods from the study conducted by Siddiqi are compared to the results from that study. Data from each experiment was collected and displayed in an appropriate figure or table with analysis accompanied for each data set.

3.1 Background Nitrate Concentrations

The background concentration for sand was established to determine the amount of nitrate that was leached from sand. The background nitrate concentrations from each of the sand/clay mixtures was found by running ten pore volumes of DI water through the column and sampling every pore volume. Ten pore volumes were chosen as the initial amount based on results from the study conducted by Siddiqi. Most of the nanoclay mixtures had reached breakthrough before ten pore volumes of water was filtered through the column. A graph showing the nitrate concentration versus the number of pore volumes indicated how much nitrate was leaching each additional pore volume of water (Figure 5).

Figure 5: Background nitrate concentration for sand was determined by flowing DI water through the column (n = 3)

For each sample, regardless of the nanoclay that was added, the soil mixture leached the highest amount of nitrate in the first one or two pore volumes then remained relatively constant for the duration of the test. The average background nitrate concentration leached from the sand only mixture was 0.39 mg/L. This concentration was subtracted out from the concentration of nitrate recorded in the background trials for each nanoclay so that the concentration of nitrate leached specifically from each nanoclay could be determined. Adjusted results are summarized in Table 4.

Table 4: Background nitrate concentrations of each different nanoclay mixture

Sand Description	Background Nitrate Concentration (mg/L)	Percent of initial nitrate solution
1% montmorillonite clay	0.41	23.8%
1% bentonite nanoclay	0.73	42.4%
1% pre-modified nanoclay	0.38	22.1%
2% pre-modified nanoclay	0.28	16.3%

An environmentally relevant nitrate concentration of 1.72 mg/L was determined for use in the nitrate breakthrough tests (discussed below). The “percent of initial nitrate solution” calculation in Table 4 indicates the concentration of nitrate leached from the clay additive compared to this environmentally-relevant concentration. Because the environmentally-relevant nitrate concentration is so low, the amount of nitrate that is leached is a large percentage of what is introduced to the system. If the nanoclay leaches more nitrate into the water, the number of pore volumes required for breakthrough will be less than the actual number. When designing a bioretention cell for a real-world situation, the extra nitrate that is being introduced to the system from the nanoclay would need to be accounted for to determine the volume of water that could be filtered through the cell. The potential nitrate contribution inherent to the nanoclay is an important characteristic to take into consideration when deciding what nanoclay to use.

The montmorillonite clay leached 0.41 mg/L or 24% of the total amount of nitrate that was introduced to the system. This was a significant amount because it exceeded the

background concentration of nitrate produced by the 2% pre-modified nanoclay. The montmorillonite clay added to the mixture was half the amount of the pre-modified nanoclay but had a higher background nitrate concentration. Bentonite nanoclay had the highest concentration of nitrate leached as a result of flowing DI water through the soil column with 0.73 mg/L of nitrate resulting in 42% of the total concentration. This could indicate that bentonite particles were leached from the soil column. If the bentonite nanoparticles themselves were removed from the column and contained high levels of nitrate inherent to the clay, the measured concentration of nitrate in the effluent could be higher than through the nitrate leaching mechanisms discussed above. This result indicates that all the nitrate introduced to the system from the nanoclay was leached into the effluent rather than a small percentage remaining in the column adsorbed to the nanoclay if the mixture had been homogeneously mixed.

Twice as much nanoclay was added to the soil column for the 2% pre-modified clay, however, the background nitrate concentration leached from the column did not increase. The 1% pre-modified clay had a background nitrate concentration of 0.38 mg/L or 22% of the total nitrate. In the study conducted by Siddiqi, the background nitrate levels were measured after one pore volume and four pore volumes averaging to 0.57 mg/L. The results from this study are 33% lower than the background nitrate concentration in the previous study. One of the biggest distinctions between studies is the methodology used to mix the nanoclays with the sand. This difference could be the reason why the results from the previous study were so high. If the nanoclays were not

mixed well with the sand, it could lead to leaching of more nanoclays, therefore a higher background nitrate concentration.

The nitrate concentration measured in the 2% mixture was 0.1 mg/L lower than the amount measured for the 1% mixture. This result could suggest that when only 1% of pre-modified clay was mixed in sand, some of the nanoclay was leached resulting in a higher concentration of nitrate in the effluent. When 2% of the nanoclay was mixed with sand, a smaller background concentration of nitrate could have resulted for two reasons. The first reason is that the 2% of nanoclay had a slower hydraulic conductivity, discussed in Section 3.7, resulting in fewer losses. Secondly, since there were more nanoclays in the mixture, they could have adsorbed the nitrate that was leaching from the sand or other nanoparticles vertically higher in the column, thereby reducing the total concentration of nitrate leached from the mixture.

3.2 Nitrate removal efficiency of sand

The nitrate removal efficiency of sand was used to determine how effective sand by itself was at removing nitrate from water. The background nitrate associated with the sand mixture itself was subtracted from the concentration measured using the IC. Breakthrough occurred between 3 and 4 pore volumes. Figure 6 below illustrates the breakthrough curve for the sand.

Figure 6: Nitrate breakthrough curve for sand only ($n = 2$)

The results from this test modified the methodology used for the other mixtures. Since breakthrough for the other mixtures would not be reached before the sand only mixture, the number of pore volumes that was filtered through the other mixtures was increased if breakthrough still was not reached. In addition, before the nitrate solution was added to the standpipe, DI water was run through the column and a sample was taken after one pore volume and after four pore volumes to analyze the background concentration of nitrate to compare to the sand only results. This was done to analyze the initial nitrate leached from the column and the background nitrate that was leached after the sand reached breakthrough and could not adsorb more nitrate. The Nevada sand is a good option as a base sand but would still need a soil amendment to effectively remove nitrate.

3.3 Nitrate removal efficiency of montmorillonite clay

A regular-scale montmorillonite clay was mixed with sand and tested for breakthrough. This mixture is more typical of the soil media that is used in the design of bioretention cells in the industry today. The regular clay/sand mixture breakthrough curve shown in Figure 7 occurred at 5 pore volumes. When the mixture reached breakthrough, only 70% of the total amount of influent nitrate was measured in the effluent. At this point, the mixture was still adsorbing some of the nitrate from the water but could not adsorb 100%. Future research should increase the volume of water filtered through the column to see if the mixture reaches a point where nitrate can no longer be sorbed to the clay and 100% of the influent nitrate is measured in the effluent. This breakthrough rate was used as the control for comparison with the other nanoclay/sand mixtures. By using this mixture as a control, the nitrate removal efficiency results of the nanoclay will indicate how much improvement can be made from the practices that are used in the industry today.

Figure 7: Nitrate breakthrough curve for 1% montmorillonite clay/sand mixture ($n=2$)

Montmorillonite clay did not show significant improvement in nitrate removal compared to sand by itself. This result is not favorable because the addition of the clay particles decreased the hydraulic conductivity by almost 50% but did not show much improvement in the volume of stormwater that could be filtered through the column. The addition of the montmorillonite clay to the sand mixture was expected to increase the surface area resulting in an increase of adsorbance. The results show an increase of 1-2 pore volumes compared to the sand only mixture. In the study conducted by Siddiqi, 1% w/w of a kaolin clay was added to sand and breakthrough was reached after 7 pore volumes (Siddiqi). Typically, montmorillonite clay is known to have stronger adsorbent properties than kaolin clay, so this result is not what was expected. This may be due to the larger diameter of clay particle that was used for the montmorillonite clay. Smaller diameter particles have larger surface areas and higher adsorbance rates. This clay may perform better if it was purchased with a smaller grain size diameter.

3.4 Nitrate removal efficiency of bentonite nanoclay

Bentonite nanoclay was used to compare how different nanoclays compared with each other when tested for nitrate removal. A calibration curve was created with each batch of samples that was tested to calculate the concentration of nitrate using known concentrations. The amount of nitrate that is leached due to the nanoclay was subtracted from the measured concentration of nitrate for each pore volume. The bentonite nanoclay/sand mixture resulted in a breakthrough volume of about 5 pore volumes (Figure 8), similar to the control clay.

Figure 8: Nitrate breakthrough curve for 1% w/w bentonite nanoclay/sand mixture
(n = 3)

The breakthrough volume of bentonite was about twice the breakthrough pore volume of sand. There was little if no improvement over the removal of nitrate from using the montmorillonite clay with sand. It was expected that there would be a bigger increase in the number of binding sites and surface area of the nanoclay that would result in an increase of the adsorption of nitrate to the nanoclay. Bentonite clay consists mostly of montmorillonite which is typically a good adsorbent. In this study, bentonite was used in its purchased form without any surface modifications. This result could indicate that bentonite is not a good adsorbent for nitrate in its natural state. These results indicate that this specific bentonite clay is not a good soil amendment to add to a bioretention cell for the purpose of removing nitrate from stormwater.

The nitrate removal efficiency results support the speculation from the concentration of leached nitrate from the background nitrate tests. The breakthrough results are lower than what would be expected if the bentonite particles were mixed or retained more successfully with the sand. Visual findings first indicated that nanoparticles or sand particles were washed out of the soil column while the falling head test was being conducted. The effluent water leaving the valve from the column was very opaque and the color matched the color of the mixture in the column. For all the trials that were run using bentonite nanoclay, regardless of whether DI water or nitrate was run through the column, the first pore volume was the darkest in color. With each additional pore volume that flowed through the column, the opaqueness of the effluent water decreased. If this nanoclay was used in a full scale bioretention cell, the excess nitrate that is still leached would need to be considered if there is an effluent concentration limit that is trying to be reached. Adding more bentonite nanoclay could increase the volume of water required for breakthrough without decreasing the hydraulic conductivity drastically because some of the nanoclay is being leached.

3.5 Nitrate removal efficiency of pre-modified nanoclay

The pre-modified nanoclay was the best performing from the experiment conducted by Siddiqi seen in Figure 9. The 1% w/w of this pre-modified nanoclay was chosen to replicate the results from the previous experiment.

Figure 9: Breakthrough curves for clay amended Nevada sand (Siddiqi)

Due to time constraints of the previous study, only ten pore volumes of a simple nitrate solution were run through the column and tested for nitrate concentration. The results showed that breakthrough was not reached within the first ten pore volumes. It was estimated for the 1% pre-modified nanoclay that breakthrough would occur around 17 pore volumes using a polynomial behavior trend (Siddiqi).

An increased number of pore volumes were run through the soil column to test the projected breakthrough from the previous study. The 1% pre-modified nanoclay may have reached breakthrough around 19 pore volumes (Figure 10).

*Figure 10: Nitrate breakthrough curve for 1% w/w pre-modified nanoclay/sand mixture
($n = 3$)*

For the first ten pore volumes, there is little change in the amount of nitrate in the effluent. At this point, it is likely that most of the nitrate is being adsorbed to the sand and nanoclay. There is a steady increase in the concentration of nitrate as additional pore volumes of water flow through the column until breakthrough may occur between 19 and 20 pore volumes. During 17,18, and 19 pore volumes, the trend looks like it may be reaching breakthrough. However, after 20 pore volumes of water, an upward trend continues that may indicate breakthrough was not yet reached. If the mixture had reached breakthrough between 19 and 20 pore volumes, the sand/nanoclay mixture had reached its capacity for the amount of nitrate that could be adsorbed. This is four times the amount of water that could be handled from a typical clay and sand mixture used in industry (represented by the control mixture). This additional nitrate retention capacity

would allow bioretention cells to handle larger storms or decrease the size of the area of the bioretention cell required to treat the design storm specified by the city or county.

The hydraulic conductivity, discussed in more detail in Section 3.7, of the pre-modified nanoclay for 1% w/w was 24 in/hr. The minimum design value for hydraulic conductivity used in industry is 5 in/hr (“Post Construction Requirements”). Since the experimental value is still greater than what is needed for a bioretention cell, the amount of nanoclay added was increased to 2% w/w. The hydraulic conductivity values discussed in Section 3.7 indicate that the hydraulic conductivity associated with this weight percentage would still be higher than the minimum required for design.

The nitrate removal efficiency is predicted to increase with an increase in surface area from more available nanoparticle adsorbent binding sites. However, adding more nanoclays could result in a decrease of the hydraulic conductivity below the required value. The test was performed on the 2% w/w pre-modified nanoclay/sand mixture and the falling head test results were analyzed after the trial was completed to determine if the weight percentage would be in the allowable range. The results of the breakthrough experiment can be seen in Figure 11.

Figure 11: Nitrate breakthrough curve for 2% w/w of pre-modified nanoclay/sand mixture ($n = 2$)

Twenty pore volumes of water were run through the column to compare to the previous trial. For the entire volume of water that flowed through the column, the removal percent remained constant at 24% and only differed by 1%. Most of the nitrate that was being introduced to the system from the nitrate solution was being adsorbed onto the nanoclay and sand mixture. Breakthrough was not seen in the number of pore volumes that was tested. Since there was no change in nitrate concentration for the duration of the test, predicting breakthrough via polynomial analysis was also not possible. Findings indicate that the additional nanoclay may offer significant improvements in nitrate removal while keeping hydraulic conductivity within an acceptable range. The results confirm the expected hypothesis of increased nitrate removal efficiency. Increased nitrate removal could also be due to a slower hydraulic conductivity from the addition of more nanoclays. The slower flow could increase the time that nitrate comes in contact with the nanoclay

particles, therefore increasing adsorbance. It is hard to determine if adding twice the amount of nanoclays leads to twice the amount of pore volumes required for breakthrough. Additional trials should be run increasing the volume of water until breakthrough is reached.

3.6 Nitrate removal efficiency from synthetic stormwater

A synthetic stormwater was run through the column using the recipe described in the materials and methods section. Twenty pore volumes of the solution were run through the column with the 2% w/w pre-modified nanoclay/sand mixture to determine nitrate removal in a more realistic model water. This mixture was chosen because it produced the highest number of pore volumes required for breakthrough. The breakthrough curve shown in Figure 12 indicates that breakthrough was not observed during the twenty pore volumes that was run through the column. A comparison of the efficiency of nitrate removal for the 2% pre-modified nanoclay using the nitrate solution and the synthetic stormwater can be seen in Figure 12.

Figure 12: A comparison of representative nitrate breakthrough curves for 2% w/w of pre-modified nanoclay/sand mixture (n = 1)

For the first 8 pore volumes, the 2% pre-modified nitrate removal efficiency behaved similarly to when the nitrate solution was run through the column. For the remaining volume of synthetic stormwater that is added to the column, less nitrate is adsorbed to the nanoclay/sand mixture and the concentration of nitrate in the effluent is increased at a steady rate. The concentration does not level off in the volume of water that is used. Using a polynomial analysis, breakthrough is estimated to be around 27 pore volumes. The 2% w/w pre-modified nanoclay/sand mixture required fewer pore volumes to reach breakthrough for the synthetic stormwater compared to the nitrate solution.

These results indicate that there is some competition between nitrate and the other ions that are present in the synthetic stormwater. A study indicated that montmorillonite

nanoclay showed selectivity of anions similar to the Hofmeister series of anions based on free energy of hydration (Chitrakar et al.). The series from highest to lowest selectivity is $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{HPO}_4^{2-}$. Montmorillonite has a high affinity for nitrate, however, stormwater with perchlorate ions will be able to compete with nitrate. When perchlorate adsorbs to the clay, the binding sites available for nitrate is reduced which will reduce the amount of stormwater required for breakthrough. The 2% w/w pre-modified nanoclay/sand mixture was less efficient at removing nitrate when it was competing with other ions from the stormwater. However, the mixture still performed better than any of the other mixtures that only used the simple nitrate solution. The results indicate the using 2% w/w of this nanoclay would be effective to remove nitrate from stormwater.

3.7 Hydraulic Conductivity

The falling head test was performed using a method that can be compared to the constant head test, ASTM D 2434-68. The hydraulic conductivity was calculated for each of the samples while DI water, nitrate, or synthetic stormwater were run through the column. A summary of the hydraulic conductivity can be seen in Table 5. A synthetic stormwater solution was only passed through the sand mixed with 2% w/w pre-modified nanoclay because it had the best nitrate removal results using the nitrate solution.

Table 5: Summary of Hydraulic Conductivity

Soil Mixture Description	Hydraulic Conductivity (in/hour)		
	DI water	Nitrate solution	Stormwater
Sand only	50	51	n/a
Sand w/ 1% montmorillonite clay	18	35	n/a
Sand w/ 1% bentonite nanoclay	45	38	n/a
Sand w/ 1% pre-modified nanoclay	35	24	n/a
Sand w/ 2% pre-modified nanoclay	13	14	9

The sand only column had a very fast hydraulic conductivity (approximately 50 in/hr) that did not vary based on the type of solution that was passed through the column. For the sand mixed with 1% w/w of montmorillonite clay, there was a 50% difference from when the DI water was run through the column compared to the nitrate solution. The sample with only DI water had a hydraulic conductivity of 18 in/hr compared to 35 in/hr for the nitrate solution.

For both columns with 1% nanoclay mixtures, the hydraulic conductivity is faster when DI water flows through the column compared to nitrate flowing through the column. This decrease in velocity could be attributed to increased adsorbance of nitrate and other ions to the clay particles. As more nitrate binds to the nanoclay, it further decreases the void spaces which decreases the velocity of flow through the column. Dissolved sodium ions in the nitrate solution could also be occupying the pore space causing the hydraulic

conductivity to decrease. This observation was not seen for the sand with 2% w/w of pre-modified nanoclay but note that the hydraulic conductivity of the 2% nanoclay column is significantly slower in all cases. It is likely that the additional clay shows a greater effect at retarding flow than the sorptive effect seen in the columns with a lower clay percentage.

By visual observation, some of the bentonite nanoclay or sand leached out of the column during the first few pore volumes that passed through the column. The initial effluent collected was very opaque in color and was more difficult to filter out the solids. Some property of the bentonite clay, possibly as the net surface charge, prevented it from mixing with the sand during the sonication step of mixing. Since the sand and nanoclay did not mix together very well, the nanoclay was able to leach out of the column. Without the nanoclay in the mixture, the hydraulic conductivity was not much slower than the sand only mixture. This conclusion that bentonite leached out of the soil is supported by the nitrate removal efficiency results discussed in Section 3.4.

One of the main design parameters of a bioretention cell is the hydraulic conductivity. For sand, the hydraulic conductivity is generally faster compared to other soil types such as silt and clay because the size of the particles is bigger, allowing the water to flow in the void spaces between sand particles. Typical values for the hydraulic conductivity of sand can range greatly from 10 in/hr to 1000 in/hr ("Natural Resources"). These values depend on the origin of sedimentary rock material. Clay particles tend to have much slower

hydraulic conductivities because the particles are a lot smaller. Introducing clay nanoparticles to the sand will fill some of the void spaces, decreasing the hydraulic conductivity. Different weight percentages of nanoclay to sand will be tested to determine the amount of nanoclay particles that can be added while still maintaining the acceptable range of hydraulic conductivity for a bioretention cell. Hydraulic conductivity requirements vary by region, but a typical minimum value found in California is 5 in/hr (“Post Construction Requirements”). This design parameter is important to prevent flooding around the area of the BRC.

The 2% pre-modified nanoclay had the slowest hydraulic conductivity for the nitrate solution of 14 in/hr which is still well above the minimum flow. When the synthetic stormwater solution was run through the 2% pre-modified mixture, the hydraulic conductivity decreased by 36% from the nitrate solution to 9 in/hr. A factor of safety of 2 or 3 should be used when designing because the hydraulic conductivity of the bioretention cell can change based on the construction of the technology. The addition of more nanoclay could decrease the velocity of flow through the cell below the minimum design value. Bioretention cells are used both to treat the water quality of stormwater runoff, and to allow for infiltration or storage of stormwater. The bioretention cell must be able to filter or store a certain storm or have supplemental LID technology surrounding it that can handle the overflow. It would be more cost effective to design the bioretention cell to handle the entire storm than to design two different LID technologies to treat water

quality and volume of runoff. Consequently, no tests with higher percentages of nanoclays were conducted.

Chapter 4: Conclusions

Several conclusions can be made from the results discussed in the previous section and applied to a more practical application. DI water was filtered through each specific mixture to find the background nitrate concentration leached. This concentration was subtracted from the concentration of nitrate in the effluent when a nitrate solution was filtered through the column to get a more accurate concentration of nitrate adsorbed. After selecting the top performing nanoclay, a synthetic stormwater solution was filtered through the column to determine how competing ions affect the ability of the nanoclay to adsorb nitrate. For each different solute that was used, the hydraulic conductivity was measured to determine if the nanoclay/sand mixture could be used in a real world bioretention cell.

4.1 Nitrate Removal

Each sand and clay or nanoclay mixture behaved differently in the amount of nitrate it was able to adsorb until it reached its capacity. The 1% w/w montmorillonite clay amendment had the fewest number of pore volumes, indicating the least capacity for nitrate removal, followed by the 1% w/w of bentonite nanoclay, 1% w/w pre-modified nanoclay, and 2% w/w pre-modified nanoclay. Previous studies indicated that the pre-modified nanoclay possessed a high affinity for nitrate adsorbance, and this result was confirmed in this experiment (Siddiqi).

4.2 Hydraulic Conductivity

The hydraulic conductivity is one of the main design parameters when designing Low Impact Development technology and therefore was one of the main parameters of this study. The 2% pre-modified nanoclay and sand mixture that had the strongest nitrate removal response in for both nitrate solution and synthetic stormwater was still able to maintain a hydraulic conductivity that was above the typical design value. Other pollutants in the synthetic stormwater solution may compete with the nitrate for adsorbent sites and could be the reason for the additional decrease in hydraulic conductivity seen with synthetic stormwater compared to the nitrate/DI solution.

4.3 Potential Stormwater Capacity

Each sand mixture is associated with a different volume of water that it can treat. These results can be used to apply these bench scale results to full-scale systems. For example, the analysis below considers the capacity of these model BRC to treat a storm in San Luis Obispo, since that is the location of where research took place. The weather is temperate with generally around 20 inches of rain per year (“Temperature”). This is much lower than the average rainfall of the United States which is around 40 inches (“Temperature”).

Depending on the location, the National Oceanic and Atmospheric Administration (NOAA) produces precipitation frequency estimates with 90% confidence as illustrated by Table 6 for the San Luis Obispo region.

Table 6: Precipitation frequency estimates with 90% confidence intervals (US

Department of Commerce et al.)

Duration	Average recurrence interval (years)									
	1	2	5	10	25	50	100	200	500	1000
5-min	0.173 (0.152-0.199)	0.210 (0.184-0.242)	0.259 (0.226-0.300)	0.299 (0.258-0.350)	0.353 (0.291-0.432)	0.394 (0.316-0.496)	0.436 (0.339-0.567)	0.479 (0.359-0.647)	0.538 (0.381-0.767)	0.584 (0.396-0.871)
10-min	0.247 (0.217-0.285)	0.301 (0.264-0.347)	0.371 (0.324-0.430)	0.428 (0.370-0.501)	0.506 (0.417-0.619)	0.565 (0.453-0.712)	0.625 (0.485-0.813)	0.687 (0.514-0.928)	0.772 (0.547-1.10)	0.837 (0.568-1.25)
15-min	0.299 (0.263-0.344)	0.364 (0.319-0.420)	0.449 (0.392-0.520)	0.518 (0.447-0.606)	0.612 (0.505-0.749)	0.683 (0.548-0.860)	0.756 (0.587-0.984)	0.831 (0.622-1.12)	0.933 (0.661-1.33)	1.01 (0.686-1.51)
30-min	0.413 (0.362-0.475)	0.503 (0.440-0.579)	0.620 (0.541-0.717)	0.715 (0.617-0.837)	0.844 (0.696-1.03)	0.943 (0.756-1.19)	1.04 (0.810-1.36)	1.15 (0.858-1.55)	1.29 (0.912-1.84)	1.40 (0.947-2.08)
60-min	0.597 (0.524-0.687)	0.727 (0.637-0.838)	0.896 (0.782-1.04)	1.03 (0.892-1.21)	1.22 (1.01-1.49)	1.36 (1.09-1.72)	1.51 (1.17-1.96)	1.66 (1.24-2.24)	1.86 (1.32-2.65)	2.02 (1.37-3.01)
2-hr	0.892 (0.782-1.03)	1.10 (0.966-1.27)	1.37 (1.20-1.59)	1.59 (1.37-1.86)	1.87 (1.55-2.29)	2.09 (1.68-2.63)	2.31 (1.79-3.00)	2.53 (1.89-3.41)	2.82 (2.00-4.02)	3.05 (2.06-4.54)
3-hr	1.14 (0.996-1.31)	1.42 (1.24-1.64)	1.78 (1.55-2.06)	2.06 (1.78-2.41)	2.44 (2.01-2.99)	2.72 (2.18-3.43)	3.00 (2.33-3.91)	3.29 (2.46-4.43)	3.66 (2.60-5.22)	3.95 (2.68-5.89)
6-hr	1.56 (1.37-1.80)	1.99 (1.75-2.30)	2.53 (2.21-2.93)	2.96 (2.56-3.46)	3.52 (2.91-4.31)	3.94 (3.16-4.96)	4.35 (3.38-5.66)	4.76 (3.56-6.43)	5.31 (3.76-7.56)	5.72 (3.88-8.52)
12-hr	1.97 (1.73-2.27)	2.57 (2.26-2.97)	3.34 (2.91-3.86)	3.94 (3.40-4.61)	4.73 (3.90-5.79)	5.31 (4.26-6.69)	5.89 (4.57-7.66)	6.47 (4.84-8.73)	7.22 (5.12-10.3)	7.80 (5.28-11.6)
24-hr	2.44 (2.23-2.73)	3.28 (2.99-3.67)	4.34 (3.94-4.87)	5.18 (4.66-5.88)	6.29 (5.45-7.42)	7.12 (6.01-8.60)	7.94 (6.52-9.86)	8.77 (6.97-11.2)	9.86 (7.48-13.3)	10.7 (7.79-14.9)
2-day	3.03 (2.76-3.39)	4.15 (3.78-4.64)	5.58 (5.07-6.27)	6.73 (6.06-7.64)	8.27 (7.16-9.75)	9.43 (7.97-11.4)	10.6 (8.70-13.2)	11.8 (9.37-15.1)	13.4 (10.1-18.0)	14.6 (10.6-20.4)
3-day	3.40 (3.11-3.80)	4.70 (4.28-5.26)	6.38 (5.79-7.16)	7.73 (6.96-8.77)	9.56 (8.28-11.3)	11.0 (9.26-13.2)	12.4 (10.2-15.4)	13.8 (11.0-17.7)	15.8 (12.0-21.2)	17.3 (12.6-24.2)
4-day	3.69 (3.37-4.13)	5.11 (4.66-5.73)	6.97 (6.33-7.83)	8.48 (7.63-9.62)	10.5 (9.12-12.4)	12.1 (10.2-14.6)	13.7 (11.3-17.0)	15.4 (12.2-19.7)	17.6 (13.4-23.7)	19.3 (14.1-27.1)
7-day	4.43 (4.04-4.95)	6.10 (5.56-6.83)	8.32 (7.56-9.34)	10.2 (9.13-11.5)	12.7 (11.0-15.0)	14.7 (12.4-17.7)	16.7 (13.7-20.8)	18.8 (15.0-24.2)	21.8 (16.5-29.3)	24.1 (17.6-33.8)
10-day	4.93 (4.50-5.52)	6.77 (6.17-7.58)	9.23 (8.38-10.4)	11.3 (10.1-12.8)	14.1 (12.2-16.6)	16.4 (13.8-19.8)	18.7 (15.4-23.2)	21.2 (16.8-27.2)	24.6 (18.7-33.1)	27.3 (19.9-38.2)
20-day	6.30 (5.75-7.04)	8.61 (7.85-9.64)	11.7 (10.7-13.2)	14.3 (12.9-16.3)	18.0 (15.6-21.2)	20.9 (17.6-25.2)	23.9 (19.6-29.7)	27.1 (21.5-34.7)	31.5 (23.9-42.4)	35.1 (25.6-49.1)
30-day	7.63 (6.96-8.53)	10.4 (9.46-11.6)	14.1 (12.8-15.8)	17.2 (15.4-19.5)	21.5 (18.6-25.3)	24.9 (21.0-30.0)	28.4 (23.4-35.3)	32.2 (25.6-41.3)	37.5 (28.4-50.4)	41.7 (30.4-58.3)
45-day	9.42 (8.60-10.5)	12.7 (11.6-14.2)	17.1 (15.5-19.2)	20.7 (18.6-23.5)	25.7 (22.3-30.3)	29.7 (25.1-35.9)	33.8 (27.8-42.0)	38.2 (30.4-48.9)	44.2 (33.5-59.4)	49.0 (35.7-68.6)
60-day	11.1 (10.1-12.4)	14.8 (13.5-16.6)	19.7 (17.9-22.2)	23.8 (21.4-27.0)	29.4 (25.4-34.6)	33.8 (28.5-40.8)	38.3 (31.4-47.5)	43.0 (34.2-55.2)	49.5 (37.6-66.6)	54.7 (39.9-76.6)

The precipitation depth is dependent on the duration of the rainfall and the average recurrence interval in years. Using the breakthrough volume of each mixture, the capacity for the total number of storms by rainfall depth is shown in Table 7.

Table 7: Number of storms allowed based on the allowable volume in inches

	Storm size					
Sand mixture description	Volume	1 yr-24 hr	2 yr-24 hr	5 yr-24 hr	10 yr-24 hr	25 yr-24 hr
Sand only	4.4	1.9	1.4	1.1	0.9	0.7
Sand+1% montmorillonite clay	6.4	2.7	2.0	1.5	1.3	1.0
Sand+1% bentonite nanoclay	7.6	3.3	2.4	1.8	1.5	1.3
Sand+1% tri nanoclay	24.8	10.6	7.9	5.9	5.0	4.1
Sand+2% tri nanoclay	25.4	10.9	8.1	6.1	5.1	4.2

Looking specifically at designing a BRC in San Luis Obispo County, the San Luis Obispo Low Impact Development Handbook outlines the amount of rainfall to design for. Since the central coast of California does not receive a large amount of rainfall, it is not as important to design LIDs for volume reduction. LID design can focus on removing pollutants from stormwater and increasing the quality of the water downstream. To adhere to the water quality treatment performance requirement, a low Impact technology must be able to retain stormwater runoff that is equivalent to the volume of runoff generated by the 85th percentile 24-hour storm event (“Post Construction Requirements”). The design storm is in the 85th percentile in terms of size for all storms that occur in the county; therefore, it is greater in size than all but 15% of the storms that occur. Looking at the map of San Luis Obispo County, this storm event would produce 1.2 inches of precipitation. Table 8 summarizes the results of each sand/nanoclay mixture and how many storms each mixture can treat until its limit is reached. Note that this table shows only the number of

85th percentile storms; a BRC could handle several smaller storms that may eventually add up in volume to one of these larger storms.

Table 8: Number of storms allowed based on the SLO design storm

Sand mixture description	# of storms
Sand only	3.7
Sand+1% montmorillonite clay	5.3
Sand+1% bentonite nanoclay	6.4
Sand+1% tri nanoclay	20.6
Sand+2% tri nanoclay	21.2

By itself, sand can remove nitrate from almost four storms in San Luis Obispo before it has reached its nitrate removal capacity and can no longer treat the stormwater that flows through it. The bentonite nanoclay in sand can remove nitrate from about six and a half storms. The best performing pre-modified nanoclay with 1% w/w can handle just over twenty storms. A design rainfall depth of 1.2 inches for a 24-hour storm falls between the recurrence interval of two and five years. Using a conservative statistical analysis and assuming the recurrence interval is closer to two years, a BRC with 1% pre-modified nanoclay with sand mixture could effectively address nitrate removal for almost 40 years, assuming the climate remains relatively unchanged, before breakthrough occurred

Chapter 5: Future Research/Recommendations

After completion of the experiment that was conducted to complete this thesis, some recommendations for future research and experiments has been identified.

5.1 Prevent leaching of bentonite nanoclay

Additional research into the removal of nitrate is needed to confirm the most effective design soil. When testing the addition of bentonite nanoparticles, the full potential of their adsorbent properties could not be reached since it was observed that some of the nanoparticles were leached out of the column. An improvement in the methodology of mixing the nanoparticles with the sand could possibly eliminate this issue. This could include a longer sonication period, an increased amount of water in the slurry, or the addition of an acid to help the clay mix with the sand. Bentonite nanoclay leaching could also be prevented by adding a nylon or mesh filter to the bottom of the column to prevent sand and nanoclay particles from being removed.

Bentonite is part of the montmorillonite clay type which typically has the greatest potential for adsorbance. If the methodology could be improved, the nitrate removal efficiency of this nanoclay type could increase. An advantage to using this specific bentonite nanoclay is that it does not need to be modified and can be more inexpensive than a pre-treated clay. Bentonite could also have higher a higher affinity for adsorption and remove nitrates from water better than the pre-modified nanoclay that was used for this experiment. In addition, the results from the hydraulic conductivity test may not

accurately represent the real values if the nanoparticles did not leach out. Additional falling head tests should be conducted with a different methodology to mix the nanoclay with the sand to determine what the measured hydraulic conductivity would be if the nanoclay did not leach out.

5.2 Additional volume of water

One problem associated with adsorption is that the nitrates never get fully removed from the system. There is the possibility that once they get adsorbed to the clay, over time they can leach back into the water that will eventually flow through the column. An additional experiment using an increased number of pore volumes of nitrate solution should be conducted to determine if the nitrate gets released from the clay. This release would be indicated in a breakthrough curve where the effluent concentration exceeds the influent nitrate concentration, showing that previously-sorbed nitrate is being desorbed.

In a real BRC implementation, this release of nitrate would mean that the bioretention cell could remove nitrate from stormwater but would later release that nitrate back into the environment after a large storm or several smaller storms. This study could also determine the lifetime of the soil media and how often maintenance would need to be provided. After a certain amount of volume passed through the bioretention cell, the soil mixture would have to be removed and a new mixture put in to replace it.

5.3 Effective homogeneous incorporation of nanoclays

The methodology section of this report describes how the nanoclays were mixed in with the sand using a bath sonicator. For this experiment, immediately after they were sonicated, the slurry mixture was transferred into the column for the falling head test. One problem that may affect the homogeneity of the mixture is the potential for reaggregation of nanoparticles after sonication. This was not a parameter tested in this thesis. Further experiments could use the bath sonicator to mix the nanoclays with the sand and then wait for differing periods of time before adding it to the soil column. It could also be useful to test the hydraulic conductivity without any sonication to see how effective the treatment mixes the nanoclays into the sand. Differences in the hydraulic conductivity will indicate whether the amount of time after sonication has ended will have an effect on how well the nanoclays mixed with the sand. The sonication process would have to be performed as part of construction of the bioretention cell. Some alternative method may have to be employed with such a large volume of sand compared to the amount that is used for the column.

5.4 Using plants to completely remove nitrate from the system

An additional area of research could include the addition of plants. Surface vegetation is typically part of BRC design. When plants take water from the void spaces of the soil that contains nitrate, it could be removing it from the ecosystem completely. This could extend the lifetime of the bioretention soil mixture before it needs to be replaced. This

experiment would require a larger-scale column that would support plants, and a longer time scale to utilize their growing season.

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Appendix A: IC nitrate results

The following appendix contains data from the IC's analysis of nitrate for each mixture that was tested. For each concentration, the average was taken at each pore volume of all the trials that were run.

1. Sand only

Concentration (mg/L)	Area			DI water	Nitrate solution
1	0.52		Pore volumes	Concentration (mg/L)	
5	2.20		1	0.79	1.27
10	4.22		2	0.42	1.84
20	9.53		3	0.34	2.67
			4	0.34	2.77
Co (mg/L)	2.80		5	0.31	2.79
			6	0.30	2.78
			7	0.33	2.77
			8	0.34	2.78
			9	0.42	2.77
			10	0.32	2.76

Appendix A: IC nitrate results

2. 1% w/w montmorillonite clay with sand

Concentration (mg/L)	Area			DI water	Nitrate solution
1	0.35		Pore volumes	Concentration (mg/L)	
5	2.04		1	0.80	0.83
10	4.31		2	0.84	1.50
20	9.66		3	0.79	2.43
			4	0.80	2.56
Co (mg/L)	2.69		5	0.83	2.65
			6	0.81	2.61
			7	0.82	2.66
			8	0.76	2.66
			9	0.78	2.65
			10	0.81	2.63

Appendix A: IC nitrate results

3. 1% w/w bentonite nanoclay with sand

Concentration (mg/L)	Area			DI water	Nitrate solution
1	0.29		Pore volumes	Concentration (mg/L)	
5	2.12		1	1.84	0.66
10	4.31		2	1.23	1.36
20	9.12		3	0.93	2.16
			4	0.90	2.10
Co (mg/L)	2.38		5	1.08	2.22
			6	1.09	2.26
			7	1.08	1.83
			8	1.08	2.34
			9	1.05	2.25
			10	0.89	2.28

Appendix A: IC nitrate results

4. 1% pre-modified trimethyl stearyl ammonia nanoclay

A	B	C	D	E	F
Concentration (mg/L)	Area			DI water	Nitrate solution
1	0.34		Pore volumes	Concentration (mg/L)	
5	2.02		1	0.92	0.69
10	4.41		2	0.80	0.68
20	9.55		3	0.74	0.69
			4	0.74	0.69
Co (mg/L)	1.87		5	0.77	0.69
			6	0.75	0.69
			7	0.72	0.69
			8	0.76	0.69
			9	0.73	0.70
			10	0.74	0.74
			11	0.75	0.83
			12	0.73	0.94
			13	0.73	1.08
			14	0.74	1.24
			15	0.71	1.51
			16	0.75	1.82
			17	0.74	2.06
			18	0.71	2.01
			19	0.72	2.12
			20	0.71	2.39

Appendix A: IC nitrate results

5. 2% w/w pre-modified trimethyl stearyl ammonia nanoclay

Concentration (mg/L)	Area			DI water	Nitrate solution	Stormwater
1	0.36		Pore volumes	Concentration (mg/L)		
5	2.09		1	0.77	0.52	0.56
10	4.25		2	0.72	0.52	0.59
20	9.26		3	0.66	0.52	0.65
			4	0.65	0.50	0.65
Co (mg/L)	2.18		5	0.64	0.52	0.64
			6	0.66	0.52	0.63
			7	0.64	0.52	0.64
			8	0.64	0.52	0.64
			9	0.65	0.52	0.68
			10	0.65	0.52	0.76
			11	0.68	0.52	0.87
			12	0.65	0.52	0.95
			13	0.64	0.52	1.04
			14	0.64	0.52	1.11
			15	0.64	0.52	1.57
			16	0.67	0.52	1.27
			17	0.64	0.52	1.28
			18	0.64	0.52	1.38
			19	0.64	0.52	1.49
			20	0.65	0.52	n.a.

Appendix B: Hydraulic Conductivity

The following appendix shows the raw data for the falling head test that was conducted for each mixture. The data is separated depending on the solution that was filtered through the column: DI water, the simples nitrate solution, or the synthetic stormwater.

1. Sand only
 - a. DI water

Column parameters		Hydraulic Conductivity			
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	106	57.4	5.3	0.0178	25.29
2	93	57.4	5.3	0.0203	28.82
3	89	57.4	5.3	0.0212	30.12
4	82	57.4	5.3	0.0231	32.69
5	84	57.4	5.3	0.0225	31.91
6	83	57.4	5.3	0.0228	32.30
7	84	57.4	5.3	0.0225	31.91
8	83	57.4	5.3	0.0228	32.30
9	83	57.4	5.3	0.0228	32.30
10	84	57.4	5.3	0.0225	31.91
				average	30.95
Trial 2					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	54	57.4	5.3	0.0350	49.64
2	45	57.4	5.3	0.0420	58.57
3	41	57.4	5.3	0.0461	63.38
4	36	57.4	5.3	0.0525	72.46
5	36	57.4	5.3	0.0525	72.46
6	37	57.4	5.3	0.0511	70.45
7	36	57.4	5.3	0.0525	72.46
8	35	57.4	5.3	0.0540	74.59
9	35	57.4	5.3	0.0540	74.59
10	36	57.4	5.3	0.0525	72.46
				average	69.80
Notes					
1. Measure height from where water exits apparatus to initial water level in burette and from where it exits to final water level					
2. One pore volume = 96.5 mL					
3. burette: 2 cm diameter, 1 pore volume length = 51.75 cm					

Appendix B: Hydraulic Conductivity

b. Nitrate

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	51	57.4	5.3	0.03708	52.56
2	48	57.4	5.3	0.03940	55.84
3	50	57.4	5.3	0.03782	53.61
4	51	57.4	5.3	0.03708	52.56
5	51	57.4	5.3	0.03708	52.56
6	51	57.4	5.3	0.03708	52.56
7	52	57.4	5.3	0.03637	51.55
8	52	57.4	5.3	0.03637	51.55
9	52	57.4	5.3	0.03637	51.55
10	52	57.4	5.3	0.03637	51.55
				average	52.59
Trial 2					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	54	57.4	5.3	0.03502	49.64
2	53	57.4	5.3	0.03568	50.58
3	54	57.4	5.3	0.03502	49.64
4	55	57.4	5.3	0.03439	48.74
5	55	57.4	5.3	0.03439	48.74
6	55	57.4	5.3	0.03439	48.74
7	54	57.4	5.3	0.03502	49.64
8	52	57.4	5.3	0.03637	51.55
9	52	57.4	5.3	0.03637	51.55
10	53	57.4	5.3	0.03568	50.58
				average	49.94
Notes					
1. Measure height from where water exits apparatus to initial water level in burette and from where it exits to final water level					
2. One pore volume = 96.5 mL					
3. burette: 2 cm diameter, 1 pore volume length = 51.75 cm					

Appendix B: Hydraulic Conductivity

2. 1% w/w montmorillonite clay with sand

a. DI water

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	120	57.4	5.3	0.01576	22.34
2	130	57.4	5.3	0.01455	20.62
3	131	57.4	5.3	0.01444	20.46
4	135	57.4	5.3	0.01401	19.86
5	140	57.4	5.3	0.01351	19.15
6	146	57.4	5.3	0.01295	18.36
7	150	57.4	5.3	0.01261	17.87
8	160	57.4	5.3	0.01182	16.75
9	192	57.4	5.3	0.00985	13.96
				average	18.82
Trial 2					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	116	57.4	5.3	0.01630	23.11
2	121	57.4	5.3	0.01563	22.15
3	123	57.4	5.3	0.01538	21.79
4	132	57.4	5.3	0.01433	20.31
5	166	57.4	5.3	0.01139	16.15
6	166	57.4	5.3	0.01139	16.15
7	175	57.4	5.3	0.01081	15.32
8	187	57.4	5.3	0.01011	14.33
9	192	57.4	5.3	0.00985	13.961
10	193	57.4	5.3	0.00980	13.889
				average	17.716

Appendix B: Hydraulic Conductivity

b. Nitrate

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	72	57.4	5.3	0.02627	37.23
2	66	57.4	5.3	0.02866	40.61
3	76	57.4	5.3	0.02488	35.27
4	77	57.4	5.3	0.02456	34.81
5	79	57.4	5.3	0.02394	33.93
6	80	57.4	5.3	0.02364	33.51
7	82	57.4	5.3	0.02306	32.69
8	83	57.4	5.3	0.02279	32.30
9	84	57.4	5.3	0.02251	31.91
				average	34.69
Trial 2					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	65	57.4	5.3	0.02910	41.24
2	65	57.4	5.3	0.02910	41.24
3	69	57.4	5.3	0.02741	38.85
4	72	57.4	5.3	0.02627	37.23
5	72	57.4	5.3	0.02627	37.23
6	75	57.4	5.3	0.02522	35.74
7	77	57.4	5.3	0.02456	34.81
8	83	57.4	5.3	0.02279	32.30
9	85	57.4	5.3	0.02225	31.535
10	89	57.4	5.3	0.02125	30.118
				average	36.028

Appendix B: Hydraulic Conductivity

3. 1% w/w bentonite nanoclay with sand

a. DI water

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	133	57.4	5.3	0.01422	20.15
2	89	57.4	5.3	0.02125	30.12
3	75	57.4	5.3	0.02522	35.74
4	72	57.4	5.3	0.02627	37.23
5	67	57.4	5.3	0.02823	40.01
6	63	57.4	5.3	0.03002	42.55
7	59	57.4	5.3	0.03205	45.43
8	58	57.4	5.3	0.03261	46.22
9	57	57.4	5.3	0.03318	47.03
10	55	57.4	5.3	0.03439	48.74
				average	39.32
Trial 2					
Pore volumes	time, sec	h ₀ (initial height), cm	h ₁ (final height), cm	k, cm/sec	k, in/hr
1	80	57.4	5.3	0.02364	33.51
2	53	57.4	5.3	0.03568	50.58
3	52	57.4	5.3	0.03637	51.55
4	52	57.4	5.3	0.03637	51.55
5	53	57.4	5.3	0.03568	50.58
6	51	57.4	5.3	0.03708	52.56
7	51	57.4	5.3	0.03708	52.56
8	50	57.4	5.3	0.03782	53.61
9	50	57.4	5.3	0.03782	53.61
10	50	57.4	5.3	0.03782	53.61
				average	50.37

Appendix B: Hydraulic Conductivity

b. Nitrate

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	149	57.4	5.3	0.01269	17.99
2	128	57.4	5.3	0.01478	20.94
3	108	57.4	5.3	0.01751	24.82
4	100	57.4	5.3	0.01891	26.80
5	94	57.4	5.3	0.02012	28.52
6	91	57.4	5.3	0.02078	29.46
7	91	57.4	5.3	0.02078	29.46
8	87	57.4	5.3	0.02174	30.81
9	86	57.4	5.3	0.02199	31.17
10	84	57.4	5.3	0.02251	31.91
				average	27.19
Trial 2					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	50	57.4	5.3	0.03782	53.61
2	52	57.4	5.3	0.03637	51.55
3	53	57.4	5.3	0.03568	50.58
4	54	57.4	5.3	0.03502	49.64
5	53	57.4	5.3	0.03568	50.58
6	54	57.4	5.3	0.03502	49.64
7	53	57.4	5.3	0.03568	50.58
8	53	57.4	5.3	0.03568	50.58
9	53	57.4	5.3	0.03568	50.58
10	51	51.4	5.3	0.03536	50.12
				average	50.74

Appendix B: Hydraulic Conductivity

4. 1% pre-modified trimethyl stearyl ammonia

a. DI water

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	104	57.4	5.3	0.01818	25.77
2	86	57.4	5.3	0.02199	31.17
3	67	57.4	5.3	0.02823	40.01
4	70	57.4	5.3	0.02702	38.29
5	69	57.4	5.3	0.02741	38.85
6	70	57.4	5.3	0.02702	38.29
7	73	57.4	5.3	0.02591	36.72
8	72	57.4	5.3	0.02627	37.23
9	79	57.4	5.3	0.02394	33.93
10	78	57.4	5.3	0.02425	34.37
				average	35.46
Trial 2					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	95	57.4	5.3	0.01991	28.22
2	90	57.4	5.3	0.02101	29.78
3	89	57.4	5.3	0.02125	30.12
4	75	57.4	5.3	0.02522	35.74
5	74	57.4	5.3	0.02556	36.22
6	73	57.4	5.3	0.02591	36.72
7	75	57.4	5.3	0.02522	35.74
8	72	57.4	5.3	0.02627	37.23
9	71	57.4	5.3	0.02664	37.75
10	72	57.4	5.3	0.02627	37.23
				average	34.47

Appendix B: Hydraulic Conductivity

b. Nitrate

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	161	57.4	5.3	0.01175	16.65
2	157	57.4	5.3	0.01205	17.07
3	150	57.4	5.3	0.01261	17.87
4	149	57.4	5.3	0.01269	17.99
5	144	57.4	5.3	0.01313	18.61
6	139	57.4	5.3	0.01361	19.28
7	137	57.4	5.3	0.01380	19.57
8	133	57.4	5.3	0.01422	20.15
9	130	57.4	5.3	0.01455	20.62
10	128	57.4	5.3	0.01478	20.94
				average	18.88
Trial 2					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	88	57.4	5.3	0.02149	30.46
2	89	57.4	5.3	0.02125	30.12
3	89	57.4	5.3	0.02125	30.12
4	90	57.4	5.3	0.02101	29.78
5	90	57.4	5.3	0.02101	29.78
6	90	57.4	5.3	0.02101	29.78
7	91	57.4	5.3	0.02078	29.46
8	90	57.4	5.3	0.02101	29.78
9	92	57.4	5.3	0.02056	29.14
10	91	57.4	5.3	0.02078	29.46
11	91	57.4	5.3	0.02078	29.46
12	91	57.4	5.3	0.02078	29.46
13	92	57.4	5.3	0.02056	29.14
14	92	57.4	5.3	0.02056	29.14
15	92	57.4	5.3	0.02056	29.14
16	92	57.4	5.3	0.02056	29.14
17	92	57.4	5.3	0.02056	29.14
18	94	57.4	5.3	0.02012	28.52
19	93	57.4	5.3	0.02034	28.82
20	94	57.4	5.3	0.02012	28.52
				average	29.42
Trial 3					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	106	57.4	5.3	0.01784	25.29
2	109	57.4	5.3	0.01735	24.59
3	110	57.4	5.3	0.01719	24.37
4	110	57.4	5.3	0.01719	24.37
5	110	57.4	5.3	0.01719	24.37
6	110	57.4	5.3	0.01719	24.37
7	111	57.4	5.3	0.01704	24.15
8	110	57.4	5.3	0.01719	24.37
9	110	57.4	5.3	0.01719	24.37
10	110	57.4	5.3	0.01719	24.37
11	112	57.4	5.3	0.01689	23.93
12	113	57.4	5.3	0.01674	23.72
13	109	57.4	5.3	0.01735	24.59
14	110	57.4	5.3	0.01719	24.37
15	111	57.4	5.3	0.01704	24.15
16	111	57.4	5.3	0.01704	24.15
17	111	57.4	5.3	0.01704	24.15
18	110	57.4	5.3	0.01719	24.37
19	110	57.4	5.3	0.01719	24.37
20	110	57.4	5.3	0.01719	24.37
				average	24.34

Appendix B: Hydraulic Conductivity

5. 2% pre-modified trimethyl stearyl ammonia nanoclay
 - a. DI water

Column parameters		Hydraulic conductivity			
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	192	57.4	5.3	0.00985	13.96
2	192	57.4	5.3	0.00985	13.96
3	196	57.4	5.3	0.00965	13.68
4	198	57.4	5.3	0.00955	13.54
5	199	57.4	5.3	0.00950	13.47
6	198	57.4	5.3	0.00955	13.54
7	200	57.4	5.3	0.00946	13.40
8	199	57.4	5.3	0.00950	13.47
9	201	57.4	5.3	0.00941	13.34
10		57.4	5.3		
11	206	57.4	5.3	0.00918	13.01
12	206	57.4	5.3	0.00918	13.01
13	204	57.4	5.3	0.00927	13.14
14	203	57.4	5.3	0.00932	13.20
15	205	57.4	5.3	0.00923	13.08
16	206	57.4	5.3	0.00918	13.01
17	208	57.4	5.3	0.00909	12.89
18	207	57.4	5.3	0.00914	12.95
19	207	57.4	5.3	0.00914	12.95
20	207	57.4	5.3	0.00914	12.95
				average	13.29

Appendix B: Hydraulic Conductivity

b. Nitrate

Hydraulic Conductivity					
Column parameter					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	188	57.4	5.3	0.01006	14.26
2	188	57.4	5.3	0.01006	14.26
3	186	57.4	5.3	0.01017	14.41
4	190	57.4	5.3	0.00995	14.11
5	187	57.4	5.3	0.01011	14.33
6	186	57.4	5.3	0.01017	14.41
7	185	57.4	5.3	0.01022	14.49
8	184	57.4	5.3	0.01028	14.57
9	187	57.4	5.3	0.01011	14.33
10	191	57.4	5.3	0.00990	14.03
11	183	57.4	5.3	0.01033	14.65
12	181	57.4	5.3	0.01045	14.81
13	184	57.4	5.3	0.01028	14.57
14	184	57.4	5.3	0.01028	14.57
15	184	57.4	5.3	0.01028	14.57
16	184	57.4	5.3	0.01028	14.57
17	183	57.4	5.3	0.01033	14.65
18	183	57.4	5.3	0.01033	14.65
19	182	57.4	5.3	0.01039	14.73
20	185	57.4	5.3	0.01022	14.49
				average	14.47

Appendix B: Hydraulic Conductivity

c. Synthetic stormwater

Hydraulic Conductivity					
Column parameters					
Diameter of column, d (cm)	6.17				
Length of column, L (cm)	7.57				
Area of column cross section, A (cm ²)	29.92				
Area of burette cross section, a (cm ²)	3.14				
Trial 1					
Pore volumes	time, sec	h0 (initial height), cm	h1 (final height), cm	k, cm/sec	k, in/hr
1	315	57.4	5.3	0.00600	8.51
2	311	57.4	5.3	0.00608	8.62
3	308	57.4	5.3	0.00614	8.70
4	312	57.4	5.3	0.00606	8.59
5	302	57.4	5.3	0.00626	8.88
6	311	57.4	5.3	0.00608	8.62
7	302	57.4	5.3	0.00626	8.88
8	311	57.4	5.3	0.00608	8.62
9	295	57.4	5.3	0.00641	9.09
10	306	57.4	5.3	0.00618	8.76
11	296	57.4	5.3	0.00639	9.06
12	297	57.4	5.3	0.00637	9.03
13	292	57.4	5.3	0.00648	9.18
14	309	57.4	5.3	0.00612	8.67
15	316	57.4	5.3	0.00598	8.48
16	309	57.4	5.3	0.00612	8.67
17	315	57.4	5.3	0.00600	8.51
18	309	57.4	5.3	0.00612	8.67
19	312	57.4	5.3	0.00606	8.59
20	313	57.4	5.3	0.00604	8.56
				average	8.73