

ABSTRACT

Title of Document: Management of ammoniacal nitrogen in stormwater runoff in filtration-based stormwater control measures.

Golnaz Khorsha, Doctorate of Philosophy, 2016

Directed By: Professor Allen P. Davis, Ph.D., P.E.
Department of Civil and Environmental
Engineering

Nitrogen in stormwater runoff plays a dominant role in the eutrophication of receiving waters. The challenge in treating nitrogen lies in its diverse speciation and biological cycling. This work aimed to improve removal of influent and mineralized ammonium through the use of sorption media and nitrification in preparation for subsequent denitrification. Two media, clinoptilolite (ZT) and hydrous-aluminosilicate (CA), were characterized in a series of batch and sorption column experiments, which indicated superior performance of ZT because of its higher capacity (206 months life-expectancy) and faster kinetics (60 min). Competition with Ca^{2+} and K^{+} resulted in smaller and slower sorption for both media. Removed ammonium in ZT was highly extractable, signifying its potential bioavailability. Sorption columns exhibited high removal during influent NH_4^{+} increases, desorption with influent concentration drops, and lower ammonium removal upon rewetting/saturating. Nitrification in bio-active sorptive media enhanced removal efficiency, particularly for alternating wet/saturated-dry/unsaturated conditions, with smaller desorption occurring. ZT application in filtration-based stormwater control measures is recommended.

Management of Ammoniacal Nitrogen in Stormwater Runoff using filtration-based
Stormwater Control Measures

By

Golnaz Khorsha

Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
[Doctoral of Philosophy]
[2016]

Advisory Committee:

Professor Allen Davis, Chair

Professor Alba Torrents

Assistant Professor Birthe Kjellerup

Professor Kaye L. Brubaker

Professor John Lea-Cox

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Dedication

I thank my mother for all her love, patience, and care, without which this work could not have been completed. My gratitude to the rest of my family, especially my brother.

For my mother whom:

“

برای ما، یک شب
سجود سبز محبت را
چنان صریح ادا کرد
که ما به عاطفه سطح خاک دست کشیدیم
و مثل لهجه یک سطل آب تازه شدیم.

”

Sepehri, Sohrab. Poem: Friend (Doost), lines 23 – 27.

Acknowledgements

I wish to express my sincere gratitude to Dr. Allen Davis of the University of Maryland, College Park for his continued support and advice during the course of my thesis and stay at the University of Maryland. I thank the Maryland State Highway Administration under the direction of Christie Minami for funding this project.

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1. Introduction

Today more than 50 percent of the world population resides in urban areas, and this number is projected to rise to 66 percent by 2050 (World Urbanization Prospects, 2014). This increase is followed by further urbanization of lands as caused by development of cities, and to allow for transport of goods from rural to urban areas. One of the impacts of urbanization is the increase in the impervious areas, which affects the water cycle in the environment, causing reduction of infiltration of water into the soil and an increase in flooding frequencies in urbanized areas. The runoff originating from these land areas carries with it many pollutants, such as suspended solids, organic compounds, heavy metals, excess nutrients, including nitrogen, and contributes a significant amount of pollutants to the receiving water bodies. The impairment caused by urban runoff is substantial, and can be attributed to approximately 5,000 square miles of estuaries, 1.4 million acres of lakes, and 30,000 miles of rivers (EPA, 2006). With a need for more highly urbanized areas, the need to address this problem posed by urban runoff is paramount.

Rainfall is stochastic and event-based in nature, and so are the pollutants that are carried by urban runoff. Pollutant variability can exist within an event; that is to say that varying concentrations of specific pollutants during a storm are likely to take place. During the initial stages of rainfall, the runoff flowing on the surface of urban areas will wash the urban areas and will mobilize the higher concentrations and hence mass of pollutants. This phenomenon is commonly known as first flush, where higher concentrations of pollutants are transported in the initial period of a runoff event (Hvutved-Jacobsen et al., 2010).

One way to characterize wet/saturated weather pollution is through introducing a temporal definition to relate the intermittent pollutant discharge and the environmental effects it produces. Pollutants in stormwater runoff can be categorized into pollutants with acute or cumulative effects.

Pollutants with acute effects are those corresponding to a single or specific extreme event. On the other hand, for certain pollutants, a single event does not have a significant effect on the environmental conditions, but rather the cumulative contribution of rainfall events corresponding to a series of events that have taken place for a season or other specific period of time. Excess nutrients, including nitrogen, tend to fall in the second category (Hvutved-Jacobsen et al., 2010). Figure 1 demonstrates the time and spatial effects of pollutant loading in the receiving water. As illustrated, the general time-scale for observation of impact of an inflow of excess nitrogen in the receiving water body is on the order of week/s, as highlighted in the algal bloom in Figure 1, but continuous influx of nutrients to lakes and other water bodies as a result of runoff can cause longer lasting impacts, particularly during the wet/saturated seasons.

New management technologies, such as bioretention and sand filters, are emerging to address urban runoff challenges, and treatment of urban runoff has come a long way from the traditional approach of conveying water downstream from where it falls. These practices typically employ the use of porous media in excavated basins that receive runoff. Particles can be removed from the runoff via filtration, while the removal of dissolved pollutants can take place through chemical and biological processes. Since nitrogen is one of the primary causes of eutrophication, previous research studies have focused on the treatment of stormwater runoff with respect to nitrogen. While removal of heavy metals and phosphorous has been successfully observed using vegetation, soils, mulch, compost, and other media, poor nitrate reduction, and at times nitrate production has been observed (Davis et al., 2006). Therefore, removing nitrogen from urban runoff remains to be one of the challenges of treating urban runoff.

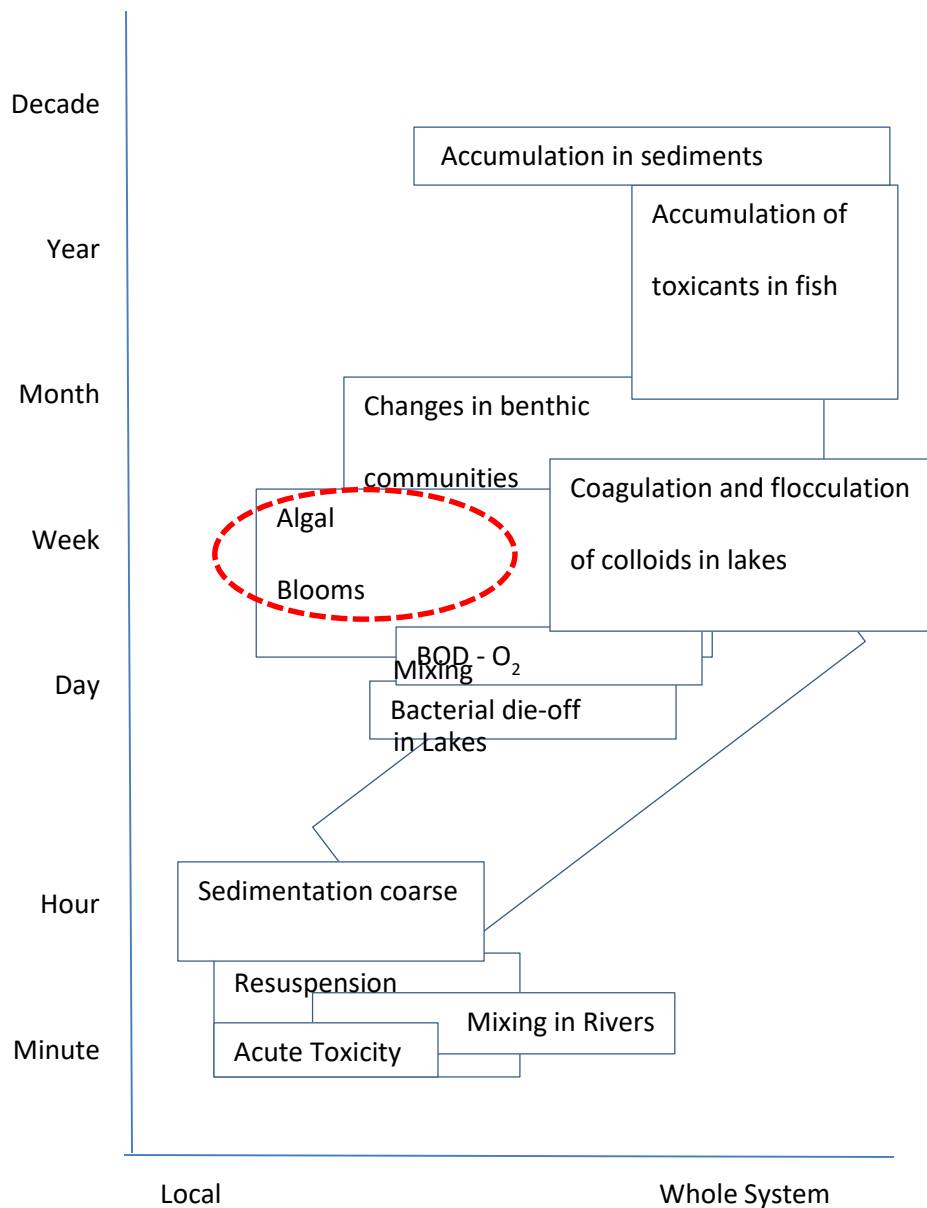


Figure 1. Schematic on temporal and spatial impacts of stormwater runoff on the receiving water bodies – Reproduced from Figure 1.3 of *Urban and Stormwater Pollution: Concepts and Engineering* (Hvitved-Jacobsen et al., 2010). Algal bloom can be attributed to excess nutrients, including nitrogen, as circled in the Figure.

Nitrogen and its Fate in Urban Runoff

The challenge in treating nitrogen in urban runoff lies in its complexity of biochemical characteristics (Li and Davis 2014). The first is diverse speciation of nitrogen existing in runoff, which is highly variable, and the changing performance of the bioretention cell with site, seasons,

and is influenced by the dry/unsaturated period in between rain events (Taylor et al., 2005, Kayhanian et al., 2007, Collins et al., 2010, Hvitved-Jacobsen et al., 2010, Li and Davis, 2014). For example, the available nitrogen in the runoff from an agricultural area differs from that of industrial land. In urban areas, the source of organic nitrogen is likely to be the decomposition of leaves, plant material, and petroleum-based molecules; vegetation, animal dropping, and fertilizers are other commonly contributing sources (Taylor et al., 2005). Figure 2 provides a schematic on the fate of nitrogen found in a bioretention cell (Li and Davis, 2014), where the green arrows show infiltration, and the red arrows denote portion of nitrogen found in the effluent.

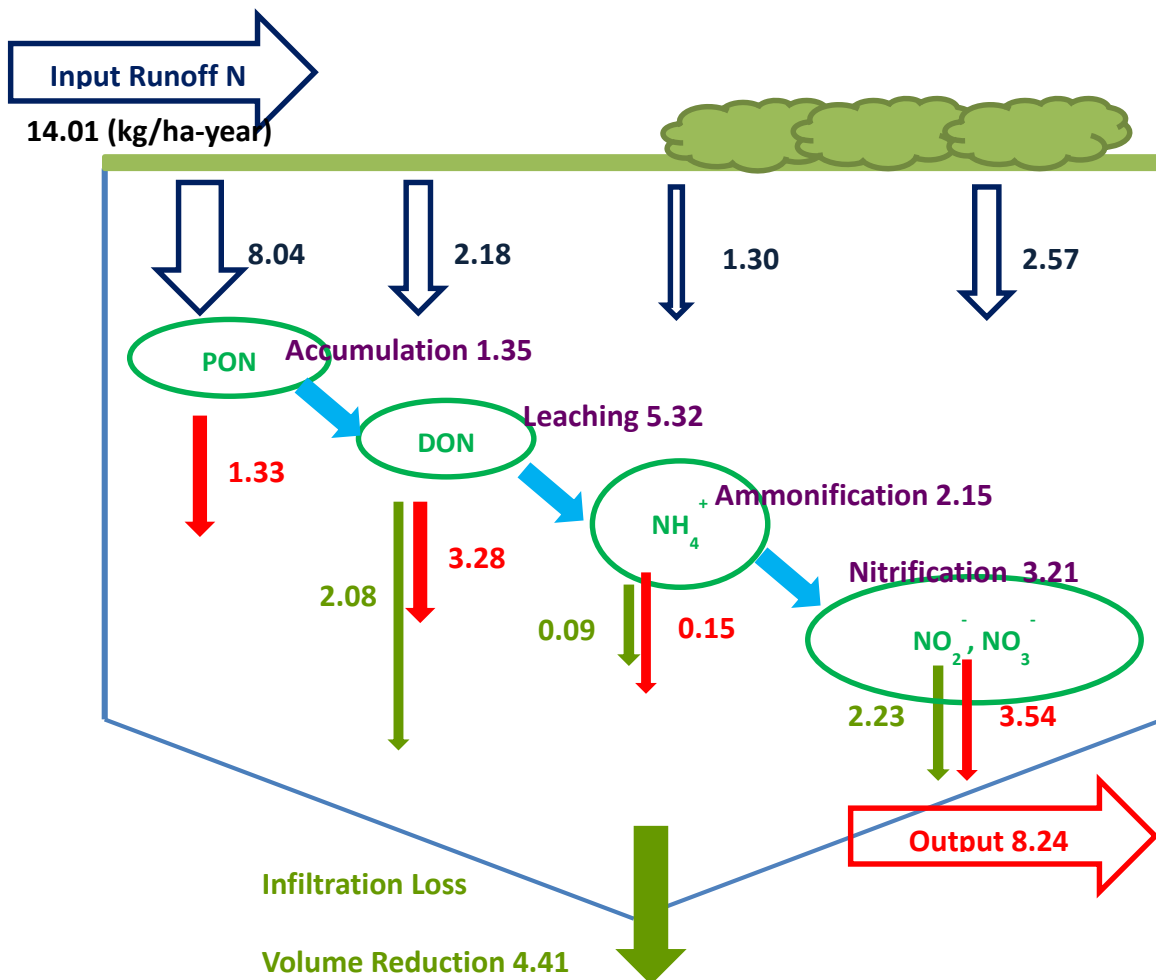
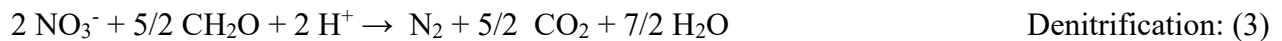


Figure 2. Fate of Nitrogen in a bioretention cell, Figure reproduced from Li and Davis, 2014. The red marks on the graph account for effluent/output, and the green markings demonstrate infiltration loss.

Overall, nitrogen is characterized as (organic N, ammonium), nitrate (NO_3^-), and nitrite (NO_2^-). Each of these forms has different characteristics, such as mobility in the environment, oxidation state, and charge, and hence requires its own unique removal mechanism. For example, filtration of particulate form of nitrogen can occur in a sand filter, while chemical removal of dissolved organic nitrogen (DON found in form of amino acids and sugars from degradation of organic matter), and ammonium can occur via chemical processes such as partitioning or sorption. Because of its high solubility, attenuation of nitrate, on the other hand, is low (Kim et al., 2003).

Another complexity posed in removal of nitrogen is the nitrogen cycle. Reactions 1 – 3 give a more detailed overview of the chemical changes taking place in the nitrogen cycle. In natural conditions, nitrogen fixation (i.e., conversion of nitrogen gas to ammonia) occurs through abiotic pathways (sunlight) and biosynthesis. Fixation of nitrogen through biosynthesis often leads to the formation of proteins and nucleotides ($-\text{NH}_2$), making the most reduced form of nitrogen its predominant organic form, such as amino acids and amino sugars. Once decomposed, free ammonium/a will be released. Fate of nitrogen is also highly dependent on the operating conditions and design of the respective bioretention cell, and leaching of dissolved organic nitrogen (DON) as well as nitrate has been observed (Li and Davis, 2014).



Organic Nitrogen

The biodegradation/decomposition of organic nitrogen is very complex. Several models can be used to describe the turnover of organic matter in agricultural soils, where ON is found in high concentrations. Biodegradation of ON has been shown to be highly dependent on the microorganism responsible for biosynthesis and the amino acid chains involved, and tends to be slower than that of non-nitrogenous organic compounds, particularly in systems where the concentration of ON is scarce (Jenkinson, 1990; Jones, 1999). The mean half-life of organic-N is highly dependent on the soil type, and an average half-life for 10 top soil samples collected from two agroecological zones within northwest England and North Wales at high concentrations of amino acid mixtures (5 mM in soil solution) at 18°C was found to be 1.7 ± 0.6 h (Jones, 1998). Another study suggested that ammonification (equation 1) was dependent on the soil horizons, and for top soil enriched in organic matter (i.e., Ah horizon), the half-life was found to be 13.9 ± 0.7 h (Jones and Kiellhad, 2002, Soil Horizons and Other Layers). With this decomposition of larger organic molecules, smaller and lighter ON molecules are formed. These molecules are more water soluble, which leads to an increase in the activity (concentration) of ON in stormwater (Thorkild, et al., 2010).

Nitrification

As can be seen from equation 2, ammonium undergoes nitrification, a two-step process, which takes place under oxic conditions and in the presence of autotrophic bacteria. In the first step, ammonium is oxidized to nitrite. This is an energy-yielding reaction, with $\Delta G_r^\circ = -45.79$ kJ/e⁻ equivalent (Rittman and McCarty, 2001). The most common bacteria that are responsible for this step include *Nitrosomonas*, *Nitrosococcus*, *Nitrosopira*, *Nitrosovibrio*, and *Nitrosolobus*. The second step of nitrification is the conversion of nitrite to nitrate with $\Delta G_r^\circ = -37.07$ kJ/e⁻

equivalent, and is predominantly carried out by *Nitrobacters* and *Nitrospira*. All of these bacterial genres are obligate aerobes, and require the use of oxygen in the presence of limited organic carbon. Nitrification has been indicated in bioretention cells (Davis et al., 2001).

Denitrification

The final step in the nitrogen cycle is denitrification, or the reduction of nitrate to nitrogen gas (equation 3). Denitrification involves the step-by-step electron reduction of nitrate (NO_3^-) to NO_2^- , NO, N_2O , and finally N_2 . Since the oxygen concentration controls whether the facultative aerobes can respire nitrate, anoxic conditions and the presence of organic carbon or other electron donors are needed for denitrification to take place.

The kinetics of nitrification and denitrification are of great importance; at low temperatures, both nitrification and denitrification will slow and for temperatures less than 4°C, both processes will reduce significantly, although denitrification at 8 and 4°C in soil systems has been found to persist (Thompson, 1989). The nitrification rate at higher temperatures corresponds to a first order reaction with respect to ammonium, while the reaction order of denitrification varies with its concentration (Reddy, et al., 1977, Smith, 1978).

In previous research on bioretention, nitrification of ammonium has been indicated, and since nitrate and nitrite readily dissolve in water, the completion of the nitrogen cycle through denitrification is the only effective way for reducing the discharge of nitrogen to the receiving water bodies (Davis et al., 2001). To do this, the decomposition of organic nitrogen and its transformation to ammonium has to take place. The available ammonium will then have to undergo nitrification, so that an anoxic zone rich in organic matter could efficiently reduce the nitrate and ensure the return of nitrogen gas to the atmosphere. Therefore, to achieve both nitrification and denitrification, sorption and biological processes should be incorporated into a

stormwater treatment system, and different conditions (i.e., oxic and low organic matter and anoxic and high dissolved organic matter concentration) are needed to complete the nitrogen cycle.

2. Research Goals

The overall objective of this work is to produce effective removal of excess nitrogen in urban runoff. It was hypothesized that by prolonging the retention time of nitrogen within the SCM, more effective removal can be achieved first by capturing and retaining the nitrogen species within a specific layer until they have been transformed according to expected nitrogen cycling. Because of the diverse speciation of nitrogen, and species susceptibility to different treatment and biological transformation, a step-wise approach was employed, where each of the nitrogen species was targeted differently. Effective removal was hypothesized to be achieved by enhancing two different parameters in any stormwater control measure (SCM), and in particular the sand filter. To achieve the increased retention time within the SCM, selective media were used to enhance the uptake of influent nitrogen by the filtering media. The second was through harnessing the nitrogen cycle beyond the oxic zone (i.e., the eventual transformation of nitrogen to nitrate in oxic zones), which can be addressed by creating an anoxic zone for denitrification.

Nevertheless, the efficiency of this design is contingent on complete nitrification of ammonium, either as the influent ammonium or as ammonium newly released from decomposition of organic nitrogen, prior to reaching the anoxic zone. In order to complete nitrification of ammonium in the second zone, increased retention time of this compound in the filter should be, such that ammonium that is not nitrified is captured by the media. Figure 3 shows the proposed design for treating nitrogen in urban runoff. The SCM or filter, should then be divided into three zones:

1. In order to prevent leaching of DON, an ammonification zone should be constructed within the filter, which would capture organic nitrogen through filtration and sorption until DON is ammonified.
2. A nitrification zone should then follow the ammonification zone. Here, all ammonium should be captured and held until nitrification is complete.
3. Finally, an anoxic zone should be constructed in the filter to allow for denitrification of nitrate.

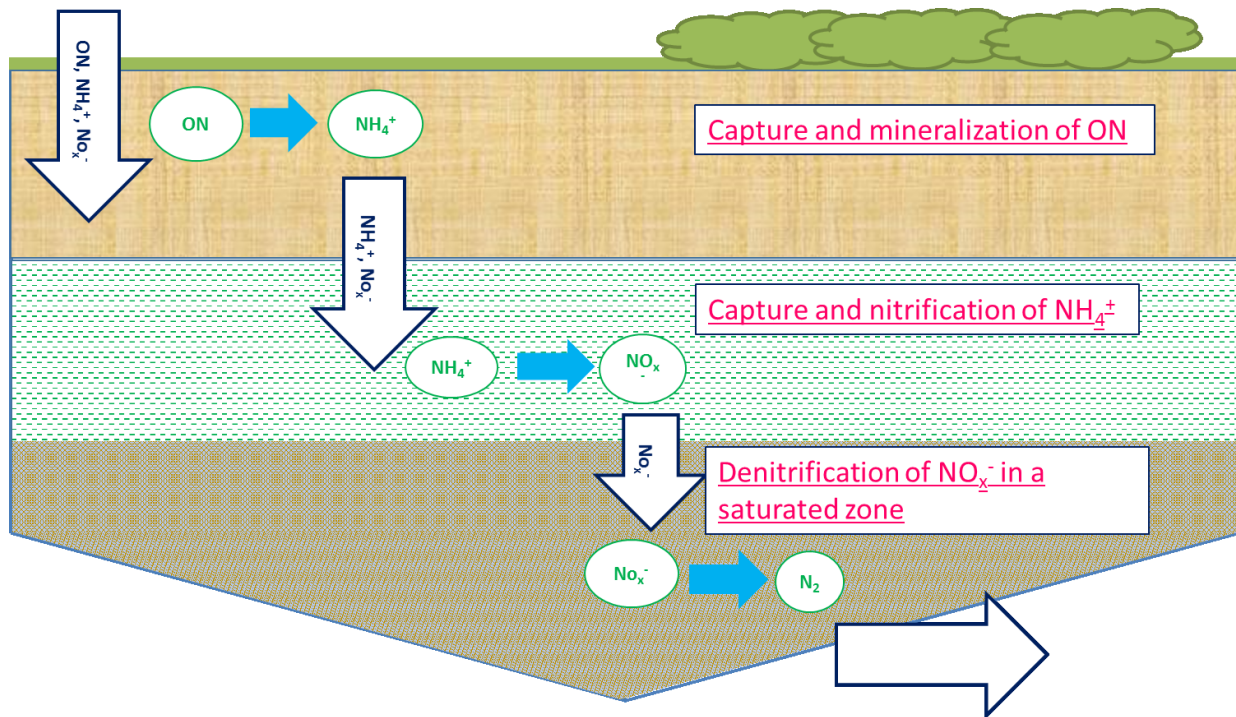


Figure 3. Modified Design of Sand Filter for removal of nitrogen in highway runoff through filtration and nitrification/denitrification processes

3. Research Objectives:

The objective of this work is improving nitrogen removal, with respect to ammonium (both as influent and mineralized form from ON) in a filtration-based SCMs treating stormwater runoff. One of the challenges of removal of excess nitrogen in stormwater is the transformation of ammonium to nitrate. To address this issue, changes to the design of a SCM need to be made, which include segregating the filter into zones to allow each part of the nitrogen cycle to be carried out in its specific section for optimal removal. For enhancing ammonium removal in the SCM, the filter should encapsulate the following characteristics:

- Increasing the retention time of stormwater pollutants within the filter
- Capture of different species of nitrogen in different sections of the filter for sequential capture and transformations of nitrogen, as illustrated in Figure 3 (i.e., capture of ammonium in an oxic layer).
- Combination of sorption and nitrification to complement the two processes, and enhance ammonium uptake and transformation.

The retention time of ammonium within the filter needs to be increased through the use of sorptive media in order to retard the transport of ammonium from the filter prior to nitrification.

This work is divided into two parts of biotic and abiotic. In the abiotic part, media selection and characterization is accomplished to determine sorption capacity of commonly found sorbents for removal of ammonium. Once the adsorbents are selected, column studies are conducted to determine the breakthrough of each sorbent in biotic and abiotic settings. Objectives 1 – 5 appear below to allow for selection of the appropriate media.

Objective 1: Selection of a media that possess high capacity for removal of ammonium.
(Abiotic Phase)

Objective 2: Selection of media that allows for rapid capture of ammonium (Abiotic Phase)

Objective 3: Understanding the reversibility/extractability of ammonium uptake by the media, and selection of media that allows for the captured ammonium to be

bioavailable such that nitrifying bacteria would be able to utilize this ammonium for nitrification. (Abiotic Phase)

Objective 4: Testing the media to monitor ammonium removal in flow-based systems in conditions similar to those found in the field (Abiotic Phase), including simulating different wet/saturated and dry/unsaturated conditions, and different flow and concentration loads.

Objective 5: Monitor the performance of the selected media in sorption and nitrification systems through comparing the performance of biotic and abiotic columns for selected media. (Biotic Phase)

Prior to the initiation of testing, tasks were defined for each of the objectives, and their combination will allow for effective understanding and hence design of sand filters and other SCMs for effective reduction of excess ammonium (either as influent in the stormwater or degraded from ON) via a modified sand filter or other bioremediation cells.

To effectively implement and optimize the design of a sand filter/bioretention cell for removal of ammonium, this work has been divided into three parts. The first part of this work focused on selection and characterization of effective media in a series of batch experiments. The next part focused on further testing to examine media performance in flow-based systems under different environmental conditions. Finally, combination of sorption and nitrification in flow-based systems was tested to understand the performance and role of different processes in conditions expected in filtration-based SCMs.

Each of these objectives is investigated and discussed in the following chapters.

4. Methods and Materials.

The materials and methods used for studies addressing different objectives are presented in three parts for clarity.

I. Batch Studies

This section provides a description of the procedures of batch-scale experimentation for media selection and characterization. These studies were designed to address objectives 1 – 3.

Reagents and Media

All chemicals were reagent grade and obtained from Fisher Scientific or Sigma Aldridge. NH_4Cl was prepared from 500 mg/L $\text{NH}_4\text{Cl-N}$ stock solution, and NaCl , KCl , and CaCl_2 were prepared from 0.6 M, 0.3 M, and 0.1 M stock solutions, respectively. Deionized water was used throughout experimentation.

After completion of preliminary tests on a wide range of materials, including clay agglomerates (Montmorillonite, Attapulgite, and hydroaluminosilicate), activated carbon, recycled materials (such as coconut shells and crushed brick), and clinoptilolite zeolite, hydroaluminosilicate (CA) and Clinoptilolite zeolite (ZT) were chosen for further testing because of higher capacity, durability, and more favorable pH range (i.e., 7.5 – 8). CA was obtained from AGSORB (Taft, CA); Table 1 provides the chemical composition of this material. ZT, with a chemical formula of $(\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]_{24}\text{H}_2\text{O})$, with $0.34 \text{ cm}^3 \text{ liq/cm}^3$ crystal intracrystalline pore volume was also obtained for testing from Bear-River Minerals (Preston, ID).

Prior to testing, each medium was washed in deionized water until the washing solution was clear. This step was followed by a NaCl wash (0.25 M), at 32 oscillations/min for a

minimum of 8 hours. Subsequently, the media were rinsed and shaken in deionized water at the same frequency for an additional 5 hours, with the rinsing solution replaced a minimum of 4 times. Each medium was dried at 105°C until reaching a steady mass, after which they were sieved through No. 10 (2 mm) and 20 (0.841 mm), and the coarse and the fine materials were discarded.

Table 1. Chemical Composition of California Aluminosilicate (CA). Oildri.com

Characteristics	Hydrous Aluminosilicate
SiO ₂	80%
Al ₂ O ₃	9%
CaO	1%
MgO	2%
Na ₂ O	<u>≤ 2%</u>
H ₂ O	8%
Liquid Holding Capacity (% by weight)	27
pH	8
Attrition	75-85

Sorption Isotherms

0.5 g of each medium was placed in 50 mL centrifuge tubes, and 50 mL of solution was added to establish isotherms. To test the potential competition of other commonly encountered cations (i.e., Na⁺, K⁺, and Ca²⁺) with NH₄⁺, three binary systems (i.e., CaCl₂ – NH₄⁺, KCl – NH₄⁺, and CaCl₂ – NH₄⁺) and an additional Mixed Background – NH₄⁺ system were prepared. The mixed background consisted of 0.0034 M CaCl₂, 0.01 M KCl, and 0.01 M NaCl. All studies were carried out at I = 0.03 M, pH = [6.7 – 7.5], and T = 22 ± 2 °C. This ionic strength was selected for testing as the median value between seawater and freshwater, with consideration of [Cl⁻] reported in stormwater between 22 – 2100 mg/L, with road salt concentrations dominated by Na⁺ and Ca²⁺ (Granato and Smith, 1999, Gardner and Royer, 2010). K⁺ was also tested

because of its application in fertilizers (Wang et al., 2013). The pH of samples was adjusted via addition of 1 M HCl, and the concentration of $[\text{NH}_4^+\text{-N}]$ was varied from 1 – 20 mg/L (0.07 to 1.43 meq $\text{NH}_4^+\text{-N/L}$) in 1 mg $\text{NH}_4^+\text{-N/L}$ increments. The samples were mixed for 24 hours, and the concentrations of ammonium and the background cations were determined. All experimentation was conducted in duplicate.

Kinetics of uptake

A 2 L sample of 2.5 mg $\text{NH}_4\text{Cl} - \text{N} / \text{L}$ was added to 20 g of neutralized media (pH = 6.8). Four different samples, each containing different ratios of 0.03 M NaCl and 0.03 M Mixed Background were constructed. The pH of the samples was adjusted to 6 – 7.2. Samples were then mixed in an automatic shaker at 32 oscillations/ min for a specific amount of time [5, 15, 30, 60, 180, 300, 480, 1440 min]. A 15-mL aliquot of sample was collected at each of the specified time intervals, and the solution and solid phase was immediately separated and filtered for further analysis.

Extraction Studies

To address the third objective of the study, extraction studies were carried out to determine the fraction of captured ammonium that could be released back to the solution via a series of extractions with 1 M KCl. The release of these cations can be used as an indication of bioavailability as it has been suggested that nutrient uptake is more common from soil solution (i.e., release of nutrients from the soil/media particles to the aqueous phase) (Lahav and Green, 1998, Comerford, 2005). First, 7 g of each of the selected media were exposed to 35 mL of 1, 5, 10, 15, and 20 mg $\text{NH}_4^+\text{-N} / \text{L}$ solution at $I = 0.03 \text{ M}$ using NaCl or CaCl_2 . The samples were mixed for 24 hours, the ammonium concentrations of the solution were determined, and sorption density (i.e., q) values obtained, and reported as q_{tot} . At this point solid and solution phases were

separated, and the extraction of exchangeable ammonium at neutral pH was determined according to the Chapman method (Ross, 1995). The solid phase was filtered and dried using 95% ethanol, and washed in eight steps, each using a 25-mL 1 M KCl solution. The results are reported as the percentage of ammonium initially removed from solution and that recovered from the cumulative extraction. Additionally, the data obtained from ammonium extraction were used to establish an isotherm relationship for sorbed ammonium that is KCl extractable (q_{ext}).

Analytical Methods

Ammonium concentration was determined via Standard Method 4500F (Eaton and Franson, 2005) within 24 hours of completion of tests. The samples were also analyzed using a Dionex ICS-1100 ion chromatograph, using CSRS 4 mm suppressor and columns and an eluent flow rate of 1.0 mL/min as prescribed by Dionex, Inc to determine the concentrations of Ca^{2+} , K^+ , Mg^{2+} , and Na^+ and to monitor production of any nitrite (NO_2^-) or nitrate (NO_3^-) (Eaton and Franson, 2005). The tested concentrations were all in the instrument range of 0.001 – 2 mM for Ca^{2+} , K^+ , and Mg^{2+} , 0.04 – 43 mM for Na^+ , and 0.003 – 1.6 mM for NO_3^- .

Data Analysis

Sorption isotherms for ammonium

Langmuir and the Freundlich isotherms were both examined to quantify the sorption characteristics of the media. Based on the goodness of fit, however, the results for the Freundlich isotherm are presented here. The Freundlich isotherm (equation 4) is an empirical relationship between the concentration of ammonium at equilibrium (C_e) and the concentration of ammonium on the surface of the adsorbent (q [mg $\text{NH}_4^+\text{-N/g}$ media]). All measurements for the equilibrium concentrations were taken after 24 hours.

$$q = k_f C_e^{1/n} \quad (4)$$

The concentrations of other available cations are also reported as $q_c = (C_i - C_e)V/M$, where C_i and C_e are the initial and equilibrium concentrations of each cation, V is the volume of the solution, and M is the mass of adsorbent used. If the cation present was not initially added to the sample, $C_i = 0$, and negative values for q are reported, which denote release or leaching of the cation from the media. A graphical presentation of the data was used to illustrate the net uptake and net release of cations.

Rate of ammonium uptake

Rates of sorption were quantified using the pseudo-second order rate model (equation 5) (Azizian, 2004). Other models, such as the Lagergren's (pseudo-first order), and the parabolic diffusion model were also investigated to quantify the kinetics of ammonium uptake by the media. Nevertheless, because the pseudo-second order model resulted in the strongest correlation, this model was used for quantification of kinetics of ammonium uptake by CA and ZT. This model has previously been used to quantify the uptake of Cr (VI) onto activated carbon (Sharma and Forster, 1996), pesticide phosphamidon onto antimony (VI) cation exchanger (Varshney et al., 1996), Cu^{2+} and Ni^{2+} on peat (Ho et al., 1996) and Hg^{2+} on soil (Yin et al., 1997). Other works focusing on sorption of ammonium from aqueous solution also indicate that the pseudo-second order model can describe well the kinetics of ammonium sorption onto different media, including zeolites, with $R^2 > 0.990$ (Karadag et al., 2006, Halim et al., 2010, Huang et al., 2008). The pseudo-second order model describes ammonium uptake from the solution to the solid phase based on the concentration of ammonium in the solid phase (q), where q and q_e represent the solute sorbed per gram of sorbent at time t and at equilibrium, respectively.

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (5)$$

Solving this differential equation, equation 6 is derived (Ho and McKay, 2000, Azizian, 2004, Ho, 2006).

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

The equilibrium time is defined, as the point for which $\frac{q_t}{q_{24}} \geq 0.95$. The 95% confidence interval for the collected data was calculated. The measured data, pseudo-second order model, and the corresponding confidence interval (95%) are presented graphically, and the model parameters are also reported. Values of q_e used in the data set are predicted by the model.

II. Abiotic Column Studies

This section provides the description of experiments conducted to address objective 4. Testing described here were completed to assess performance of CA and ZT in flow-based systems, with the focus of ammonium removal via sorption/ion exchange pathways in different environmental conditions typical of SCMs.

Reagents and Media

All chemicals were reagent grade and obtained from Fisher Scientific or Sigma Aldridge. NH_4Cl was prepared from 500 mg/L $\text{NH}_4\text{Cl-N}$ stock solution, and NaCl , KCl , and CaCl_2 were prepared from 0.6 M, 0.3 M, and 0.1 M stock solutions, respectively. Deionized water was used throughout experimentation.

Two different media were selected for testing based on results obtained from batch experimentation (Chapter 5). First is Clinoptilolite zeolite (ZT), with a chemical formula of $(\text{Na}_3\text{K}_3)[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$ and intracrystalline pore volume of $0.34 \text{ cm}^3 \text{ liq/cm}^3$,

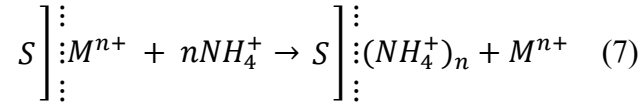
purchased from Bear-River Minerals (Preston, ID). Hydroaluminosilicate agglomerates were obtained from AGSORB (Taft, CA). Two media pretreatment methods were employed. The first pretreatment was used for determination of the capacity of the media in columns (section 2.2), which included rinsing with DI water until a clear supernatant was observed, followed by washing the media with 0.25 M HCl, followed by an additional wash with 0.25 M NaOH, for 8 hours each. This was followed by rinsing with DI water, and slight addition of acid if needed to neutralize the media. The second method was employed for all other column studies, in which the two-step 0.25 M HCl and NaOH wash was replaced with a two-step 0.25 NaCl wash for a minimum of 8 hours. All testing equipment were also washed with 1 N HCl. All media went through a final DI rinse until a clear solution was obtained; the pH was neutralized with addition of HCl as needed.

Determination of Capacity in Column Studies

Three glass columns of 2.7 cm diameter and height of 50 cm were selected to test the capacity of the media for ammonium sorption for CA, ZT, and 50:50 Sand:ZT (v/v). A 42 cm media layer was constructed in the columns, with an additional 5 cm and 3 cm coarse sand (particle diameter (d_p) of 2 mm) layer placed on the bottom and top of the column, respectively. A thin layer of glass wool was also placed at the two ends of the columns. Columns were filled and packed with media by first filling the column with DI, and adding sand and media, while using a long spatula to rid the media of trapped air bubbles. The columns were subsequently washed with DI water for 24 hours at the testing velocity.

A synthetic stormwater consisting of 2.5 mg $\text{NH}_4\text{Cl-N/L}$ was applied through the column until media exhaustion. Ammonium removal via these media can be described by equation 7,

where S denotes the surface of the media, and M^{n+} a cation bound to the surface, with n constituting its charge.



An ionic strength of 0.03 M was chosen for testing as the median value between freshwater and seawater and also based on $[Cl^-]$ values reported in the urban runoff between 21 – 2200 mg/L, with road salt concentrations dominated by Na^+ and Ca^{2+} (Granato and Smith, 1999, Gardner and Royer, 2010); two different background electrolytes were selected. The first was composed entirely of NaCl, while the second consisted of 0.01 M NaCl, 0.01 M KCl, and 0.0034 M $CaCl_2$, and is referred to Mixed Background. The capacity of the media was then determined through applying the synthetic stormwater through the columns continuously at a flow rate of 0.8 mL/min ($U = 8.3$ cm/h). The experiment was continued until NH_4^+ -N exhaustion of the media (i.e., bed volume $(\frac{\text{Cumulative volume of synthetic stormwater treated}}{\text{Volume of media in the column}} \text{ for which } [NH_4^+-N]_{out}/[NH_4^+-N]_{in} \geq 1)$). All testing was conducted at neutral pH of 6.5 ± 0.3 and room temperature ($T = 22 \pm 2^\circ C$).

After exhaustion of the ZT and 50:50 Sand: ZT, the media were regenerated through rinsing with 0.1 M HCl at $U = 8.3$ cm/h for a total of 50 bed volumes, at which point the concentration of ammonium in the effluent was undetected ($NH_4^+-N < 0.05$ mg/L). This is consistent with findings in the literature, suggesting successful regeneration of clinoptilolite, as well as its higher resistance to degradation by acidic solutions (Du et al., 2005). The media were then neutralized via an additional wash with 0.01 M NaOH for an average of 2 days, followed by a subsequent DI wash, and the effluent pH after 40 hours was determined to be 6.5 ± 0.3 . NH_4^+ /NaCl synthetic stormwater was then applied to all media. Regeneration of CA resulted in

discoloration of the media, and hence a new identical CA column was constructed as previously described.

Effect of Wet/saturatedWet/saturated – Dry/unsaturated conditions on media performance

For both CA and ZT, shorter columns with $L = 23.8$ cm and $D = 2.7$ cm were chosen for analysis. The shorter length was used to save material and shorten the contact time ($t_c = \text{Pore volume/volumetric flow rate}$) These columns were packed as above, but with a 17 cm media height. Synthetic stormwater of 0.03 M NaCl and 2.5 mg NH_4^+ -N/L was added under both continuous and intermittent settings. A dry/unsaturated period of 3 days was used, which consisted of pumping air through the column. It should be noted that the term dry/unsaturated does not indicate that the media is free of any pore and/or residual water, but rather infers that the column is not receiving any influent synthetic stormwater. A 24 hour wet/saturated period for $U = 8.3$ cm/h followed the dry/unsaturated period. Frequent sampling was conducted, particularly immediately after the column restart, to map a performance comparison between the wet/saturated and dry/unsaturated columns. The experiments were continued until exhaustion of the media.

Effect of velocity/contact time on Media Performance

To test the effect of velocity on media performance, identical CA and ZT columns were tested in NH_4^+ - NaCl systems and velocities of $U = 8.3$ and 42.0 cm/h were continued until exhaustion. For ZT, an additional superficial velocity of 26.8 cm/h was also investigated because of the noted superior performance of ZT.

Effect of influent concentration Step changes on media performance

The effect of variable influent ammonium concentration was investigated at 0.03 M NaCl for a media layer of 17 cm and $U = 8.3$ cm/h. The experiment was initiated with an influent ammonium concentration of 2.5 mg/L continuously fed to the column for 3 consecutive days, after which the influent ammonium concentration was increased to 5 mg NH_4^+ -N/L, and subsequently 1 mg NH_4^+ -N/L. Each of the concentrations were applied to the column for three consecutive days prior to introducing a step change. This experiment continued until exhaustion of the media.

Analytical Methods

All analytical testing conducted and their corresponding detection limits are listed in Table 2. Tests were performed as described in the previous section of this chapter for NH_4^+ -N, Ca^{2+} , K^+ , Mg^{2+} , and Na^+ . Production of NO_2^- -N and NO_3^- -N were monitored using ion chromatography Dionex ICS-1100 (Eaton and Franson, 2005) to detect any possible biological activity in the columns.

Table 2. Analytical Method and corresponding detection limits for analysis (Eaton and Franson, 2005).

	Analytical Method	Detection Limit	
Ca^{2+}	ICS-1100	0.001 - 2	mM
K^+	ICS-1100	0.001 - 2	mM
Na^+	ICS-1100	0.04 - 43	mM
Mg^{2+}	ICS-1101	0.001 - 2	mM
NH_4^+ -N	4500F	0.05 - 1	mg/L
NO_2^- -N	ICS-1100	0.306 - 30.6	mg/L
NO_3^- -N	ICS-1100	0.226 - 22.6	mg/L
H_2PO_4^- -P	ICS-1100	0.2 - 10	mg/L
SO_4^{2-}	ICS-1100	0.1 - 20	mg/L

Data Analysis

Performance of the media was analyzed using the cumulative $\text{NH}_4^+\text{-N}$ sorbed [mg], calculated according to equation 8, where Q is the volumetric flow rate, t_B is the exhaustion time, and C_{in} is the influent ammonium concentration. C_i and C_{i+1} correspond to the effluent ammonium concentrations at t_i and t_{i+1} .

$$[\text{NH}_4^+ - \text{N}]_{\text{sorbed}} = Qt_B C_{in} - Q * \sum_0^{t_B} \left((t_{i+1} - t_i) * \frac{C_{i+1} - C_i}{2} \right) \quad (8)$$

The sorption capacity (q) obtained was then calculated by dividing $[\text{NH}_4^+ - \text{N}]_{\text{sorbed}}$ by the mass of media used in the columns. The q reported in this study corresponds to the average q values obtained at the breakthrough time and those immediately preceding and following the breakthrough for which q was found to asymptote to a maximum value.

The collected data were used to estimate the effective life-span of the media in a field situation. An average annual rainfall of 113 cm for the city of College Park, MD was used. An SCM-to-drainage area of 5% (Design Manual for Bioretention in Stormwater Treatment, 1993, Research News and Current Facts, 2013) and a $\text{NH}_4\text{-N}$ -removal media depth of 0.4 m (H_B) was assumed. An average runoff ammonium concentration of 1.02 mg $\text{NH}_4^+ - \text{N/L}$ was used (Collins et al., 2010). The average annual ammonium nitrogen mass loading (M_{field}) is calculated by multiplying the average $\text{NH}_4^+\text{-N}$ concentration (C) by the drainage area (A_D) and the average rainfall depth (H) (i.e., $H * A_D * C$). The estimated capacity of media in a bioretention (M_B) is calculated from equation 9.

$$M_B = M_C / V_C * V_B = M_C / V_C * H_B * 0.05 * A_D \quad (9)$$

In equation 9, M_C corresponds to the total mass of $\text{NH}_4^+\text{-N}$ removed by the column, V_C and V_B refer to the volume of media in the column and in the SCM. The ratio of M_B (mg N) and

the annual M_{field} (mg N /year) provides an estimate for the lifespan of media used in the filtration SCM (t_{field}).

III. Ammonium removal from synthetic stormwater in bio-active sorption ZT columns.

The procedures described in this section refer to experimentation conducted to address objective 5 in monitoring ammonium removal in bio-active sorption ZT columns in typical SCM conditions.

Reagents and Media

All chemicals were reagent grade and obtained from Fisher Scientific or Sigma Aldridge. NH_4^+ -N and NaCl were prepared from 500 mg/L and 0.6 M stock solutions, respectively, and deionized water was used throughout experimentation.

Mined clinoptilolite zeolite (ZT), with a chemical composition of $(\text{Na, K, Ca})_{23}\text{Al}_3(\text{Al, Si})_2\text{Si}_{13}\text{O}_{38}\cdot 12\text{H}_2\text{O}$, surface area of 24.9 m^2/g , and intracrystalline pore volume of 0.34 $\text{cm}^3 \text{ liq}/\text{cm}^3$, was purchased from Bear-River Minerals (Preston, ID). Mineral identification of this media using x-ray diffraction, performed in University of Maryland, College Park Soil Laboratory, indicated the dominant presence of clinoptilolite, with a small fraction of the rock occupied by quartz. The cation exchange capacity of ZT was determined to be 1.2 meq/g ZT as NH_4^+ -N (Chapman, 1965). Pretreatment of the media was carried out by rinsing a solid to liquid ratio of 0.05 V/V with DI water until a clear solution was obtained, followed by two 0.25 M NaCl washes for 12 hours each. A final rinsing with DI water was subsequently carried out, after which the media was dried at 104°C until reaching a steady weight.

Continuous Columns

Two continuous columns were packed with ZT as prescribed in section II of Methods and Materials. The influent solution for both column consisted of 0.03 M NaCl background electrolyte. The synthetic stormwater for column (C) contained 2.5 mg $\text{NH}_4^+\text{-N/L}$. This concentration was maintained until it was observed that nitrate production had reached steady state (deviation ≤ 0.2 mg $\text{NO}_3^- \text{- N/L}$), after which, the influent ammonium concentration was increased from 2.5 mg $\text{NH}_4^+\text{-N}$ to 5 mg $\text{NH}_4^+\text{-N}$ to observe the effect of $\text{NH}_4^+\text{-N}$ concentrations on $\text{NO}_{2/3}^-$ production.

The higher concentration feed of 5 mg $\text{NH}_4^+\text{-N}$ was constantly stirred and aerated, using an air diffuser at 0.1 mL/min. The influent concentration of ammonium was checked frequently to ensure no loss of ammonium. The chemistry of synthetic stormwater was changed on 4070 BV (390 days) to include, 1 mg/L of Ca^{2+} as CaCl_2 , 3 mg/L Mg^{2+} as MgSO_4 , 1 mg/L K^+ as KH_2PO_4 , and 2 mg/L NaHCO_3 . The NaCl content of the stormwater was reduced to maintain I = 0.03 M, and the pH of solution was maintained at 6.9.

Effect of Wet/saturated - Dry/unsaturated conditions on media performance

The column was packed as above, with influent $\text{NH}_4^+\text{-N} = 2.5$ mg/L at 0.03 M NaCl, and superficial velocity $U = 8.3$ cm/h. The experiments were conducted by simulating a dry/unsaturated period of 2 – 21 days, followed by a simulated wet/saturated period, which lasted 24 – 48 hours, during which frequent sampling took place. TOC, TN, $\text{NH}_4^+\text{-N}$, $\text{NO}_{2/3}^- \text{- N}$, pH, and DO were measured in the effluent samples.

Effect of step changes of influent $\text{NH}_4^+\text{-N}$ on media performance

Different influent stormwater ammonium (i.e., 0.03 M NaCl, and 1, 2.5, and 5 mg $\text{NH}_4^+\text{-N/L}$) concentrations were evaluated by lowering the influent NH_4^+ (C_{in}) from 5 to 2.5, 5 to 1, or 2.5 to 1 mg $\text{NH}_4^+\text{-N/L}$. The stormwater velocity was 8.3 cm/h, with each influent concentration being fed to the column for a minimum of 3 days. After progression of the experiment, this duration was increased to up to 7 days or until nitrate production was seen to reach a steady value, with fluctuations ≤ 0.2 mg $\text{NO}_3^- \text{-N/L}$. The influent was aerated at 0.1 mL/min. TOC, TN, $\text{NH}_4^+\text{-N}$, and $\text{NO}_{2/3}^- \text{-N}$, pH, and DO were measured in the effluent samples.

Characterization of exhausted media

Upon completion of the column experiments, the media from each column was transferred to a clean beaker. The moisture content of ZT was determined by heating the samples at 105 °C until reaching a steady mass in quadruple samples from each column. The total carbon (TC) and inorganic carbon (IC) content of ZT from the columns as well as that of virgin ZT was determined using Shimadzu Total Organic Carbon Analyzer (TOC-L). The organic carbon content of the samples was then determined by subtracting IC from TC for each sample, and reported as % TC, % IC, and % OC. The inorganic nitrogen content ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) of the exhausted and virgin ZT was also determined through 2 M KCl extractions at 1:10 solid to liquid ratio (Maynard and Kalra, 1993). Testing was done for duplicate samples, and the $\text{NH}_4^+\text{-N}$ was used for calculating adsorbed ammonium, q .

Analytical testing

A list of analytical tests conducted, as well as the corresponding detection limits are summarized in Table 2. The $\text{NO}_{2/3}^- \text{-N}$, sulfate, and phosphate were monitored using ion

chromatography (Dionex ICS-1100), with an anion pack suppressor, column, and guard column at 1.2 mL/min and 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃.

A Shimadzu TOC-L TOC Analyzer was used to determine the total nitrogen and total organic carbon of the effluent and influent samples. The pH of the effluent was measured using an Orion pH meter. An Orion DO probe was also used for measurements of the dissolved oxygen content of samples. Organic nitrogen was calculated by subtracting the effluent ammonium, nitrite, and nitrate species, from the ammonium concentrations.

Data Analysis

The cumulative mass output of each of the nitrogen species from the columns was obtained using the trapezoidal rule integration; the cumulative nitrogen mass retained by ZT (ZT – NH₄⁺) was obtained by subtracting the total effluent nitrogen from the cumulative nitrogen loaded for each column. The sorption capacity (*q*) was then calculated by taking the ratio of ZT – NH₄⁺ to the total mass of ZT used for each column.

The period for which the column operated at steady state with respect to both ammonium and nitrate was chosen for characterizing nitrification. For all columns this phase occurred after media exhaustion, and it was found that the net effluent nitrogen (NH₄⁺-N + NO₃⁻-N) was equal to the input, and consequently, corresponding to a constant *q*. Hence, it was assumed that nitrification was responsible for the disappearance/loss of ammonium in the column, and rate of sorption (*r*_{sorp}) equals rate of desorption (*r*_{des}). Mass balance equations for ammonium and nitrate for steady state conditions appear in equations 10 – 12.

$$\frac{dA}{dt} \cdot dV = QA - Q(A - dA) - r_{sor} \cdot dV + r_{des} \cdot dV - r_{nit} \cdot dV = 0 = QdA - r_{nit} \cdot dV \quad (10)$$

$$\frac{dN}{dt} \cdot dV = QN - Q(N + dN) + r_{nit} \cdot dV = 0 = QdN - r_{nit} \cdot dV \quad (11)$$

$$[A]_{in} = [N]_{out} + [A]_{out} \quad (12)$$

; where A and N denote ammonium and nitrate concentrations in the solution, respectively, Q is the volumetric flow rate [mL/min], dV is the differential volume element, V is the pore volume of ZT for each column [mL], $r_{\text{sor.}}$, $r_{\text{des.}}$, and r_{nit} correspond to the rate of sorption, desorption, and nitrification in the columns. The obtained expressions for ammonium and nitrate for first and zero order nitrification under the conditions assumed appears in equations 13-14 for first order, and 1-16 for zero order rates.

$$[NH_4^+ - N] = [NH_4^+ - N]_o e^{-k_1 t_r} \quad (13)$$

$$[NO_3^- - N] = [NH_4^+ - N]_o (1 - e^{-k_1 t_r}) \quad (14)$$

$$[NH_4^+ - N] = [NH_4^+ - N]_o - k_0 t_r \quad (15)$$

$$[NO_3^- - N] = k_0 t_r \quad (16)$$

5. Characterizing Clinoptilolite Zeolite and Hydroaluminosilicate Aggregates for Ammonium Removal from Stormwater Runoff

(Chapter accepted for publication by the *Journal of Environmental Engineering*).

Introduction

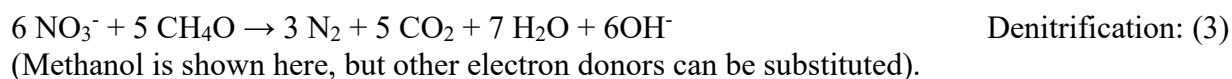
With increased urbanization, polluted stormwater has become a major cause of degradation of natural waters. According to the U.S.EPA, the impairment caused by urban runoff is substantial, and is accountable for degradation of approximately 5,000 square miles of estuaries, 1.4 million acres of lakes, and 30,000 miles of rivers (U.S.EPA, 2009). With more land being continuously developed, the need to address the environmental problems posed by urban runoff is paramount.

New management technologies, such as bioretention and sand filters, are evolving to address complex urban runoff challenges. Filtration-based stormwater control measures (SCMs) are promising, and have been shown to reduce volume, and remove specific pollutants, such as suspended solids, heavy metals, phosphorous, and fecal coliform (Davis et al., 2001, Davis et al., 2006, Hunt et al., 2006, Sun et al., 2007, Davis et al., 2009, Hatt and Fletcher, 2009). Nitrogen removal, nonetheless, remains challenging. The fate of nitrogen in stormwater runoff has been dominated by variable TN and NO_3^- removal, and even export of nitrate and dissolved organic nitrogen (DON) has been observed in field-scale bioretention studies (Hunt et al., 2006, Hatt and Fletcher, 2009, Passport et al., 2009, Rosenzweig et al., 2011, Li and Davis, 2014). The challenge in treating nitrogen in stormwater runoff lies in its biochemical complexity. Nitrogen has a diverse speciation, and its fate is heavily influenced by the nitrogen cycle, causing the

eventual transport of nitrogen species with lower mobility (i.e., ON and NH_4^+) to biologically transform to NO_3^- , which is highly mobile in the environment (Li and Davis, 2014). The following is a more in-depth summary of the fate of nitrogen in SCMs.

Nitrogen has a diverse speciation in urban runoff, and its speciation and concentration varies with site and season. Runoff nitrogen can be characterized as organic N (both particulate and dissolved), ammonium, nitrate (NO_3^-), and nitrite (NO_2^-) (Duncan, 1999, Tiefenthaler et al., 2000, Taylor et al., 2005, Kayhanian et al., 2007, Collins et al., 2010, Hvitved-Jacobsen et al., 2010, Davis and Li, 2014). While filtration of particulate nitrogen and retention of dissolved organic nitrogen and ammonium can occur via chemical processes such as partitioning or sorption, because of high solubility, attenuation of nitrate is low (Davis et al., 2001, Kim et al., 2003, Dietz and Clausen, 2005). The average TN values in stormwater reported for different urban land uses are between 1.3 to 3.2 mg N/L (Collins et al., 2010).

Transformation of nitrogen via mineralization, nitrification, and denitrification can occur in SCMs. Equations 1 – 3 from chapter 1 provide an overview of the chemical changes driving the nitrogen cycle.



In mineralization (equation 1), R-NH₂ represents an organic nitrogen species, which is biologically converted into ammonium. This process is carried out in an energy-releasing multi-step process, which can eventually convert a large fraction of organic nitrogen (up to 100%) into ammonia/um (Kadlec and Knight, 1996). Eventual transformation of organic nitrogen to nitrate

has been noted in SCMs, and in a recent study conducted on a bioretention cell in Maryland, 32.2 % of the organic nitrogen, corresponding to 2.15 kg / ha-year was found to ammonify (Li and Davis, 2014), which will contribute to the ammonium loading.

Previous works have focused on evaluation of overall performance of bioretention cells with respect to nitrogen species (Li and Davis, 2014, Davis et al., 2001 and 2006), and a systematic approach to the nitrogen problem is needed, whereby step-wise capture and biotransformation of different nitrogen species is investigated. Implementation of an anoxic zone in stormwater SCMs has been recommended and has been found to enhance nitrogen removal (Dietz and Clausen, 2005, 2006, Davis et al., 2006). While a biologically-mediated nitrification/denitrification system is a potential solution for nitrogen removal, biological processes should be complemented with chemical pathways for increased efficiency, particularly in cold temperatures or during times of shock loads/ first flush phenomena. Therefore, the abiotic capture of ammonium, either present in the influent or produced in the SCM mineralization step, is required to assist in complete denitrification of all stormwater N within a potential anoxic zone. Few works have looked at abiotic removal of ammonium in stormwater settings. Most of the previous ammonium research has focused on the removal of ammonium from wastewaters (i.e., 5– 880 mg $\text{NH}_4^+ \text{-N}$ / L in wastewater (Klieve and Semmens, 1979, Haralambous et al., 1992, Weatherley and Miladinovic, 2004, Sprynskyy et al., 2005, Wen et al., 2005, Wang et al., 2006, Guo et al., 2008)), with most concentrating on ammonium-N concentrations of 40 mg/L or higher, vis-à-vis an average median ammonium and total Kjeldahl nitrogen of 0.18 – 1.07 and 1.3 – 3.2 mg N/L in urban runoff, respectively (Taylor et al., 2005, Kayhanian et al., 2007, Collins et al., 2010). Because of the many differences between wastewater and stormwater conditions, there is a need to investigate and characterize ammonium uptake under stormwater SCM

conditions. This work aims to address this problem by selection of optimum treatment media for ammonium removal in SCMs. The optimum media should exhibit the following characteristics:

1. The media should have high durability and capacity with respect to ammonium in the presence of other competing cations present in urban stormwater.
2. The media should allow for rapid capture of ammonium during infiltration rates above 5 cm/hr.
3. Removed ammonium should be bioavailable to support nitrification.

The information derived from this study will lead to design recommendations for effective removal of ammonium in sand filter/bioretention SCMs.

Materials and Methods

The materials and methods for this phase of study are provided in chapter 4, section I.

Results and Discussion

The mechanism of ammonium removal is likely a mixture of adsorption and ion exchange, as to be discussed. For simplicity, *sorption* is used throughout this manuscript.

Sorption Isotherms

Figure 4 displays the experimental data and the Freundlich isotherm model fits for both CA and ZT. ZT has a higher capacity for uptake of ammonium for all the selected background electrolytes (Figure 4b). As shown in Figures 4a and b, the uptake of ammonium for the tested concentrations corresponds to a maximum $q_{ZT} = 1.4 \text{ mg NH}_4^+\text{-N / g}$ for ZT but only $q_{CA} = 0.5 \text{ mg NH}_4^+\text{-N / g}$ for CA. In CA, the highest ammonium removal was found to occur in 0.03 M NaCl, followed by 0.01 M CaCl₂. Convergence of the isotherms occurs for 0.03 M NaCl and 0.01 M CaCl₂ for higher ammonium loadings for CA (i.e., $C_e \geq 9.1 \text{ mg NH}_4^+\text{-N/L}$). Similarly in ZT, convergence of the NaCl and CaCl₂ curves occurs, but for $C_e \geq 4.9 \text{ mg NH}_4^+\text{-N/L}$, indicating

the stronger affinity of ZT for ammonium uptake than that of CA for NH_4^+ - CaCl_2 systems. Therefore, at higher ammonium concentrations, the difference in competition for Na^+ and Ca^{2+} with NH_4^+ becomes less significant. Since in stormwater, the $\text{NH}_4\text{-N}$ concentration is small (compared to other cations, i.e., average of 0.29 -1.2 mg $\text{NH}_4\text{-N/L}$), competition of the cations is expected to persist in this range (Taylor et al., 2005, Kayhanian et al., 2007, Collins, 2009).

For mixed background, where a combination of cations was present, and for 0.03 M KCl, lower ammonium removal compared to that of NaCl and CaCl_2 was observed. These two isotherm curves intersect for CA at C_e of 10 mg NH_4^+ - N /L and $q_{CA} = 0.2$ mg $\text{NH}_4^+\text{-N} / \text{g CA}$; for $C_e \leq 10$ mg $\text{NH}_4^+\text{-N/L}$, the mixed background shows a higher ammonium uptake than that KCl. Additionally, in ZT for lower ammonium loadings (i.e., $C_e \leq 2.3$ mg $\text{NH}_4^+\text{-N/L}$), ammonium uptake for 0.03 M KCl is higher than that of 0.01 M CaCl_2 . This low range (i.e., $C_e \leq 2.3$ mg $\text{NH}_4^+\text{-N/L}$) is more typical of stormwater (Taylor et al., 2005, Kayhanian et al., 2007, Collins et al., 2010). The findings here for both CA and ZT show the greatest ammonium uptake for 0.03 M NaCl, followed by CaCl_2 , Mixed Background, and KCl. Sorption of ammonium for both media was found to be represented well by the Freundlich isotherm, and the results are displayed in Table 3. The coefficient of determination is greater than 0.70 for all cases, with the exception of 0.03 M Mixed Background for CA where $r^2 = 0.65$.

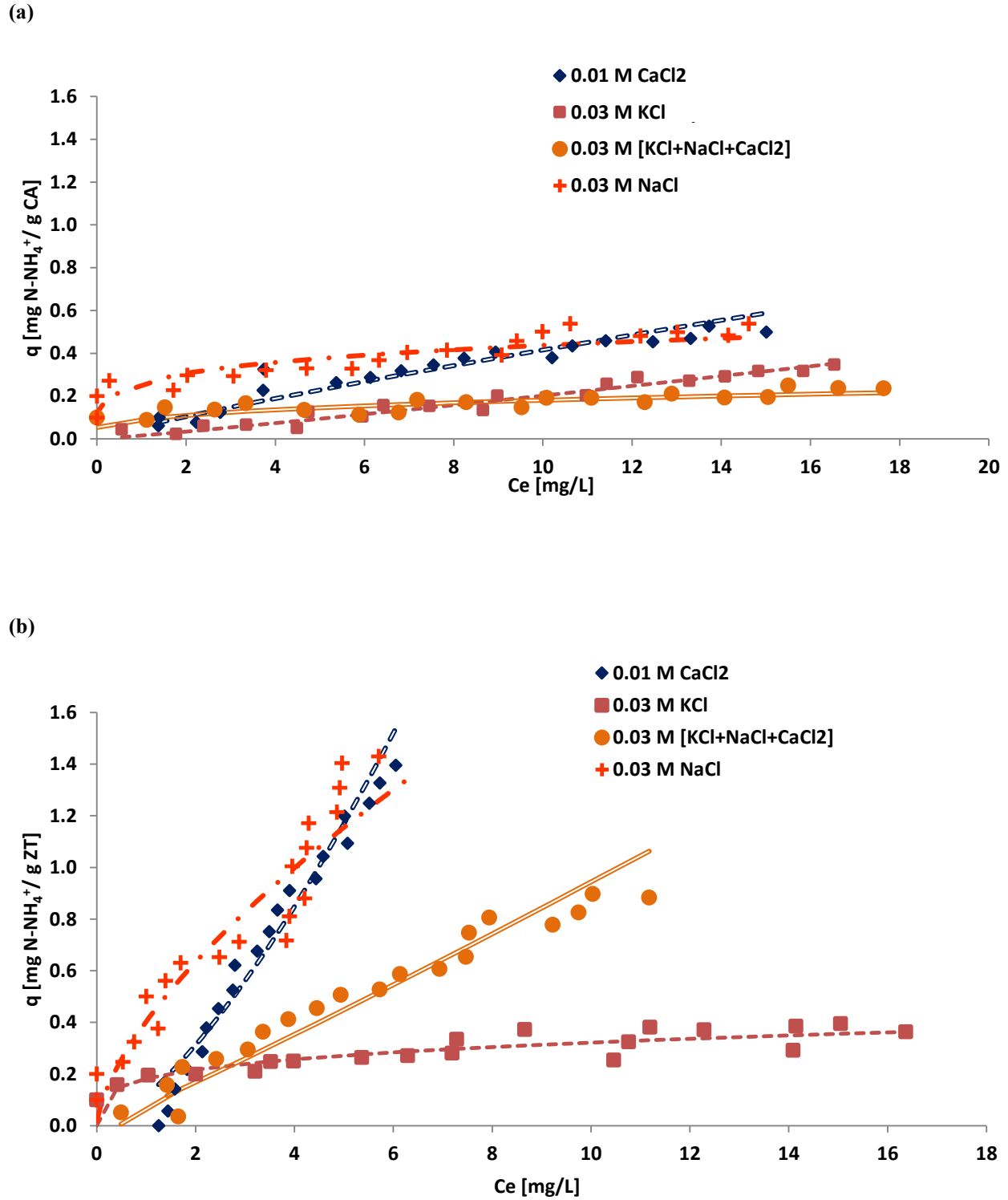


Figure 4. Sorption of Ammonium and the fitted Freundlich isotherms for different electrolyte backgrounds of 0.01 M CaCl_2 , 0.03 M KCl , 0.03 M NaCl , 0.03 M Mixed Background, containing 0.01 M NaCl , 0.01 M KCl , 0.0034 M CaCl_2 at neutral pH range of [6 – 7.2] and $T = 25 \pm 1^\circ \text{C}$, for (a) California aluminosilicate clay agglomerates (CA) and (b) Clinoptilolite Zeolite (ZT).

Table 3. NH₄-N Freundlich sorption isotherm parameters for California Aluminosilicate aggregates and Clinoptilolite Zeolite for different electrolytes backgrounds at Ionic Strength of 0.03 M constructed from 0.01 M CaCl₂, 0.03 M KCl, 0.03 M NaCl, and Mixed Background, containing 0.01 M NaCl, 0.01 M KCl, and 0.0034 CaCl₂, at neutral pH [6 - 7.2] and T = 22 ± 1 ° C.

Background Electrolyte	CA			ZT		
	K _f	1/n	r ²	K _f	1/n	r ²
0.01 M CaCl ₂	0.06	0.86	0.92	0.12	1.44	0.96
0.03 M KCl	0.02	1.10	0.95	0.18	0.25	0.80
0.03 M NaCl	0.26	0.22	0.78	0.40	0.65	0.87
Mixed Background	0.09	0.31	0.70	0.08	1.07	0.96

The discrepancies in the published data can be attributed to the differences in the ZT structure obtained from different regions, pretreatment differences, and the range of ammonium concentrations and background electrolytes studied. Concentrations of ammonium in stormwater (0.18 – 1.1 mg NH₄⁺-N/L) are much lower than those the wastewater studies discussed (i.e., 5 – 880 mg/L NH₄⁺ /L), such that the available ammonium exists in concentrations much lower than the background salts. In wastewaters, however, because of higher ammonium concentrations, competition of background cations and ammonium becomes more dominant. Moreover, ZT is a tectosilicate, and sorption capacity is dependent on the exchange cations and differences in the type and concentration of these cations can alter sorption characteristics of the media (Kithome et al., 1998).

The concentrations of background cations were also analyzed in these experiments. Because the background cation concentrations were fixed at higher levels, they did not vary significantly, and the average values are presented in Figure 5 on a meq basis. Here, a positive sign for q indicates sorption, while negative q values indicate the release of cations. It should be noted that the average q values for certain cations were too small to be clearly displayed in Figure 5, such as Ca²⁺ in Figure 5a, and NH₄⁺ and Na⁺ in Figure 5c.

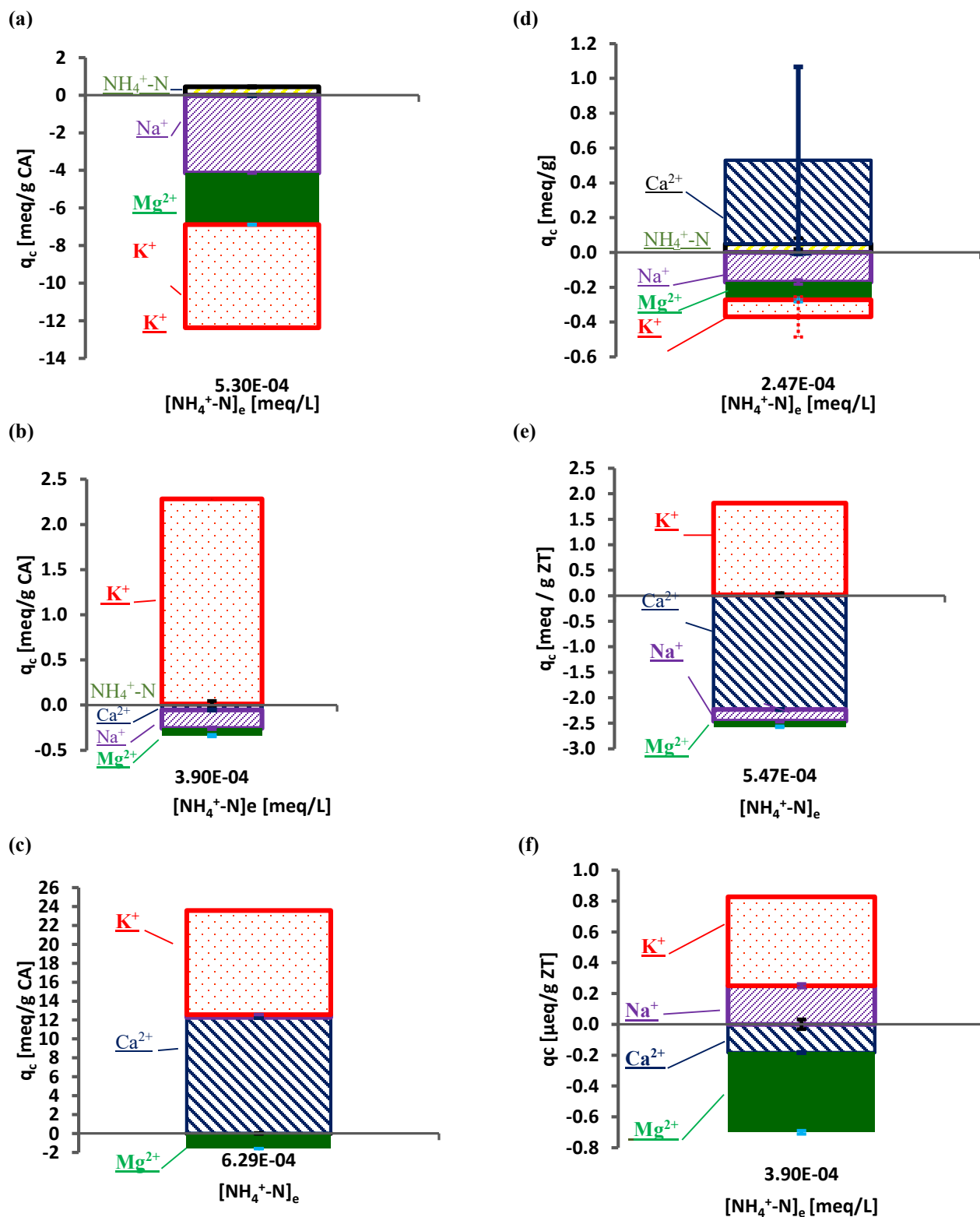


Figure 5. Mean uptake for ammonium and other cations during ammonium sorption studies. Positive values indicate sorption/uptake while negative values indicate release of the cation from the media. Results for 0.01 M $CaCl_2$ for CA (a) and ZT (d), 0.03 M KCl for CA (b) and ZT (d), and 0.03 M Mixed Background for CA (c) and ZT (f) at pH = 6.5 – 7.2 and T = 22 \pm 2 $^\circ$ C

Overall, the dominant cation (i.e., the cation(s) used in the makeup of the background electrolyte) has the highest uptake, with the exception of NH_4^+ - CaCl_2 for CA (i.e., $q_{CA} = -0.04 \pm 0.09$ meq/g CA, Figure 5a). Moreover, in the NH_4^+ - CaCl_2 systems, calcium uptake shows the highest variability, with an average calcium release of $q_{CA} = -0.04 \pm 0.09$ meq/g for CA (Figure 5a – this value is too small, and thus not visible in this figure) and $q_{ZT} = 0.48 \pm 0.54$ meq Ca^{2+} /g ZT (Figure 5d). In NH_4^+ - CaCl_2 systems, for CA the uptake of ammonium occurs as displayed in the sorption isotherms, while Na^+ ($q_{CA} = -4.10 \pm 0.30$ meq / g CA), Mg^{2+} ($q_{CA} = -2.70 \pm 0.54$ meq / g), and K^+ ($q_{CA} = -5.49 \pm 0.87$ meq / g) were released from the media. For ZT (in NH_4^+ - CaCl_2 systems), on the other hand, uptake of NH_4^+ and Ca^{2+} ($q_{ZT} = 0.48 \pm 0.54$ meq/g) occur (Figure 5d), while Na^+ ($q_{ZT} = -0.17 \pm 0.01$ meq/g), Mg^{2+} ($q_{ZT} = -0.10 \pm 0.01$ meq/g), and K^+ ($q_{ZT} = -0.10 \pm 0.01$ meq / g) were released.

For NH_4^+ - KCl mixtures, ammonium removal was lowest, and is dominated by the high uptake of potassium by both media (i.e., $q_{CA} = 2.27 \pm 0.73$ meq/ g (Figure 5b) and $q_{ZT} = 1.80 \pm 0.05$ meq/g (Figure 5e)), and release of Ca^{2+} ($q_{CA} = -0.05 \pm 0.01$ meq / g and $q_{ZT} = -2.23 \pm 0.01$ meq / g), Mg^{2+} ($q_{CA} = -0.08 \pm 0.00$ meq / g and $q_{ZT} = -0.11 \pm 0.01$ meq/g), and Na^+ ($q_{CA} = -0.25 \pm 0.02$ meq/g and $q_{ZT} = -0.23 \pm 0.01$ meq/g) was observed.

Finally, in NH_4^+ - mixed background mixtures (Figures 5c and 5f), CA showed removal of Ca^{2+} , while small release of Ca^{2+} from ZT was observed ($q_{CA} = 12.3 \pm 0.2$ meq /g CA and $q_{ZT} = -0.179 \pm 0.062$ meq / g ZT). In both media, uptake of K^+ ($q_{CA} = 11.0 \pm 1.9$ meq /g CA and $q_{ZT} = 0.58 \pm 0.06$ meq / g ZT), was coupled with release of Mg^{2+} ($q_{CA} = -1.60 \pm 0.00$ meq /g CA and $q_{ZT} = -0.52 \pm 0.83$ meq / g ZT). Na^+ shows minimal removal by CA ($q_{CA} = 0.29 \pm 0.01$ meq / g CA) and ZT ($q_{ZT} = -0.25 \pm 0.03$ meq / g ZT).

In CA, a balance between the cations removed ($\sum(nM^{n+})_{removed}$) and those released ($\sum(nM^{n+})_{released}$) is not observed for any of the background electrolytes, whereas for ZT these differences between the sum of cations removed and released approaches zero (i.e., $(\sum(nM^{n+})_{removed} - \sum(nM^{n+})_{released}) = 0.2 \pm 0.5 \frac{meq}{g ZT}$, $-0.8 \pm 1.8 \frac{meq}{g ZT}$, and $0.16 \pm 0.5 \frac{meq}{g ZT}$ for NH_4^+ - $CaCl_2$, NH_4^+ - KCl , and NH_4^+ - Mixed Background, respectively). These observations suggest an ion exchange mechanism for ZT.

Overall, for lower ammonium loadings reflective of stormwater conditions (i.e., $C_e = 1.07 \pm 1.39$ mg NH_4 -N/L) (Collins et al., 2010), both media show high removal of ammonium from solution, with ZT removal being the greatest. Although stormwater may have a lower ammonium concentrations than these evaluated, ammonium release from organic matter will increase concentrations over that of incoming stormwater. Furthermore, the efficiency of ammonium removal is dependent on the chemistry of the stormwater, and it was found for both media that the presence of K^+ reduced ammonium removal. Ca^{2+} was also found to compete with NH_4^+ cations but to a lesser extent. The lowest ammonium removal for both media was found in the presence of K^+ and Mixed Background. Displacement of Ca^{2+} by K^+ also appears to take place for ZT at 0.03 M KCl as the uptake of K^+ was coupled with release/leaching of Ca^{2+} . CA was found to have a lower affinity for Ca^{2+} uptake, which makes the material feasible for use in calcareous regions.

Kinetics of Sorption

Infiltration rate and the resulting contact time are important aspects of stormwater sand filter and bioretention performance. Therefore, the rates of sorption of ammonium to CA and ZT were studied, and the effects of different background cations, namely Ca^{2+} and K^+ on the

sorption kinetics were also investigated. The results appear in Figure 6. The pseudo-second order rate model was employed to quantify the kinetics of sorption of ammonium for the different background electrolytes for both media, and Table 4 summarizes the equilibrium times, k_2 (Equation 6), and the coefficient of determination of the pseudo-second order rate model. This model described the data well, with $r^2 \geq 0.88$ for CA and $r^2 \geq 0.86$ for ZT for all the kinetics studies for all systems. The q_e was predicted by the pseudo-second order model.

Throughout the testing it was observed that the degree of ammonium sorption increases with time. In all data sets, the q value at 24 hours was selected as the equilibrium time as it was observed that q values asymptote towards this value. To identify the equilibrium point, deviation from q at $t = 24$ hr was calculated $\left(\frac{q_t - q_{24}}{q_{24}}\right)$, where q_t and q_{24} correspond to the q value obtained at time t and at $t = 24$ hours. The equilibrium time was then defined as the time at which q is within 5% of q_{24} . Moreover, the rate of change of ammonium sorption (i.e., $\Delta q / \Delta t$) was calculated for each of the measurements, and these values were also used as an indication of equilibrium time. It was found that for the time at which sorption was within 5% of q_{24} , $\frac{\Delta q}{\Delta t} \leq 10^{-5} \frac{\text{mg NH}_4\text{-N}}{\text{g.min}}$. The confidence intervals for each of the background electrolytes is also demonstrated in Figure 6. As can be seen, the 95% confidence interval, reported as error bars in Figure 6, reduces with increasing concentration of Mixed Background. This is due to smaller extent of uptake with increasing Ca^{2+} and K^+ . Overall, the confidence interval for the models was found to be 7 – 12% of the q_e ($\frac{q_t}{q_{24}} \geq 0.95$) observed.

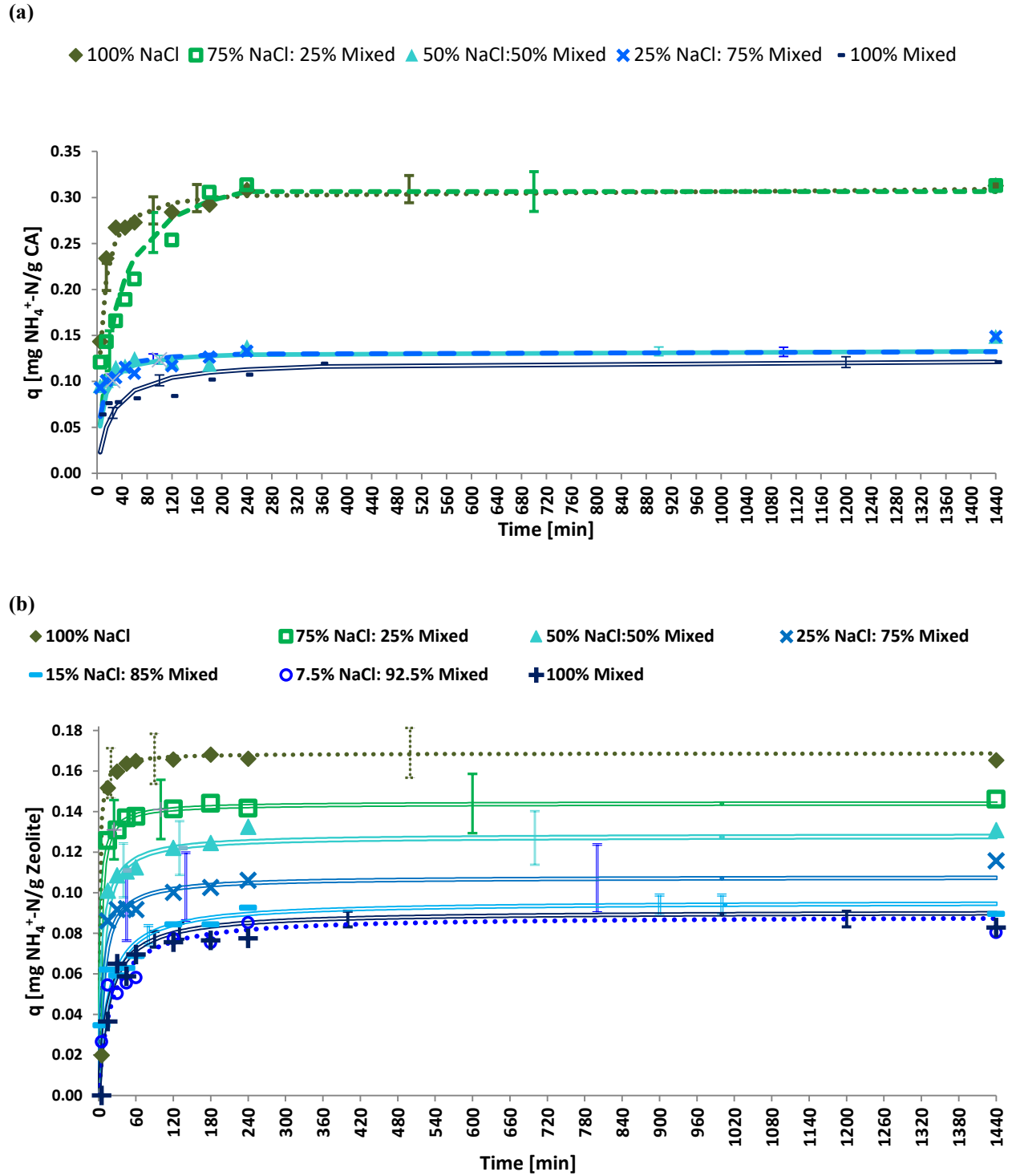


Figure 6. Kinetics of sorption of 2.5 mg $\text{NH}_4^+\text{-N/L}$ onto (a) CA and (b) ZT at different mixtures of 0.03 M NaCl and 0.03 M Mixed Background (0.01 M NaCl, 0.01 M KCl, and 0.0034 M CaCl_2) at neutral pH [6.5 – 7.2] and $T = 22 \pm 2^\circ\text{C}$. The concentration of each specific cation for a specific mixture appears in Table 4. The data points and confidence intervals represent the experimental results and the fitted lines correspond to their respective pseudo-second order model.

Table 4. Equilibrium time (t_e), rate constants, and the coefficient of determination for the pseudo-second order model k_2 for Clinoptilolite Zeolite (ZT) and California Aluminosilicate (CA) at $I = 0.03$ M, containing different ratios of 0.03 M NaCl and 0.03 M mixed background containing 0.01 M NaCl, 0.01 M KCl, and 0.0034 M $CaCl_2$ at neutral pH range of [6.5 - 7.2] and $T = 22 \pm 1^\circ C$

Clinoptilolite Zeolite						
% NaCl	[Na ⁺] M	[Ca ²⁺] M	[K ⁺] M	t_e [min]	k_2 [g.mg ⁻¹ .min ⁻¹]	r^2
100%	0.030	0.000	0.000	30	4.74	1.00
75%	0.025	0.003	0.001	120	2.67	0.91
50%	0.020	0.005	0.002	180	1.29	1.00
25%	0.015	0.008	0.003	240	1.31	0.86
15%	0.013	0.009	0.003	240	0.64	1.00
7.5%	0.012	0.009	0.003	240	0.57	1.00
0%	0.010	0.010	0.003	240	0.68	1.00

California Aluminosilicate						
% NaCl	[Na ⁺] M	[Ca ²⁺] M	[K ⁺] M	t_e [min]	k_2 [g.mg ⁻¹ .min ⁻¹]	r^2
100%	0.03	0.00	0.00	> 240	0.47	0.88
75%	0.025	0.003	0.001	> 240	0.11	1.00
50%	0.02	0.005	0.002	> 240	0.93	1.00
25%	0.015	0.008	0.003	> 240	1.30	0.98
0%	0.01	0.01	0.003	> 240	0.37	0.95

The data observed for CA (Figure 6a) show the extent of ammonium removal is reduced from 0.31 to 0.12 mg NH_4^+-N / g CA with the increase in Mixed Background content (less Na^+ in electrolyte). All the samples from 0.03 M NaCl to 0.03 M Mixed Background show an equilibrium time equal to or greater than 240 minutes. At $t = 240$ minutes, the samples containing 100% and 75% NaCl are close to equilibrium (i.e., $\frac{q_{t=240 \text{ min}}}{q_{24}} = 0.98$), and this ratio becomes smaller (0.98 to 0.88) with the increase in the mixed background content. Based on deviations of q at 240 min to q_{24} , it appears that the increase in the mixed background content retards the approach to equilibrium. As displayed in Figure 6b, the fastest and greatest extent of uptake of ammonium for ZT corresponds to 0.03 M NaCl. It was also found that for ZT as the mixed background content increases from 0% to 100%, not only is a decrease in the extent of removal of ammonium observed (i.e., from $q = 0.17$ to 0.08 mg NH_4^+-N /g at 0.03 M NaCl and

0.03 M Mixed Background, respectively), but also the equilibrium time was found to increase from 45 minutes to 240 minutes at 0.03 M NaCl and mixed background, respectively.

Other studies investigating the rate of simultaneous and individual sorption of K^+ and NH_4^+ onto ZT showed rates of sorption similar to this study, with samples approaching equilibrium from 30 minutes to 8 hours (Rozic et al., 1998, Guo et al., 2007, Arslan and Veli, 2011). As seen in Table 4, a reduction in k_2 from 4.7 to 0.68 $g.mg^{-1}min^{-1}$ is observed with an increase in the mixed background fraction of the solutions for ZT. Previous findings suggest that lower rates occur with increase in the valence of the exchangeable cation(s) (Sparks, 2003). Nevertheless, ions such as K^+ and NH_4^+ tend to have slower rates compared to that of Ca^{2+} or Mg^{2+} . This can be explained by the smaller hydrated radius of K^+ and NH_4^+ , which can cause partial or total collapse of the interlayer spaces found in clay minerals, and retard the kinetics of sorption (Sparks, 2003). The smallest hydrated radius corresponds to K^+ (3.31 Å) = NH_4^+ (3.31 Å) < Na^+ (3.58 Å) < Ca^{2+} (4.12 Å) (Conway, 1981). In clays, sorption of ammonium can change based on the presence of other cations. For example, it was suggested that the presence of monovalent cations can increase the rate and capacity of sorption of ammonium (Weatherley and Miladinovic, 2004). Furthermore, the clay structure plays an important role in the process. The actual sorption of NH_4^+ and K^+ onto micas and vermiculites is in the order of milliseconds, while sorption of ammonium onto kaolinite is slower than that of Ca^{2+} and Mg^{2+} (Sparks, 2003). Sorption of ammonium onto colloidal-state clays was found to be more rapid than that of ZT, and equilibrium was established after 5 minutes (Rozic, et al., 1998). Nevertheless, the clay agglomerate used in this study exhibit a small fraction of 1:2 layer structure, and has an average particle diameter of 2 mm. The kinetics of uptake of ammonium by CA is hence slower than that

of ZT, and if employed in SCMs, long contact times need to be ensured for satisfactory ammonium removal.

ZT has the more rapid rate of ammonium removal, which is most favorable in stormwater treatment where rapid drainage is desirable to treat high volumes of runoff. Furthermore, the chemistry of stormwater affects the rate of sorption. In areas where high concentrations of competing cations, such as Ca^{2+} , are found, higher retention time in the SCM media is necessary to allow for optimum removal of ammonium. Since in stormwater, the presence of a mixture of cations is expected, the rate of sorption may be likely similar to the rate at mixed background electrolyte, although Na^+ is estimated to account for 98% of all road salt (Sanzo and Hencar, 2006).

Moreover, other constituents can also affect the availability of other cations in the solution. For example, hydroxyapatite has a very low solubility ($K_{sp} = 7.35 \times 10^{-60}$), and for $\text{I} = 0.03$ M, $\text{pH} = 6.5$, and P as orthophosphate of 0.6 mg/L, precipitation begins for $\text{Ca}^{2+} \geq 0.0012$ M. Precipitation reduces the soluble calcium content that is competing with NH_4^+ , possibly lowering the degree of competition between NH_4^+ and Ca^{2+} . Since the cations used in this analysis are present at higher concentrations than that of NH_4^+ , even with their possible precipitation, competition is thought to persist. The presence of other ligands, such as SO_4^{2-} and Cl^- as well as other cations can result in reduced precipitation of calcium and phosphate.

Based on these previous observations ZT is recommended for use, and from batch experiments, it is recommended that the stormwater filtration SCMs allow for up to 30 – 120 minutes of contact time to reach maximum capacity, based on the chemistry of stormwater runoff being treated.

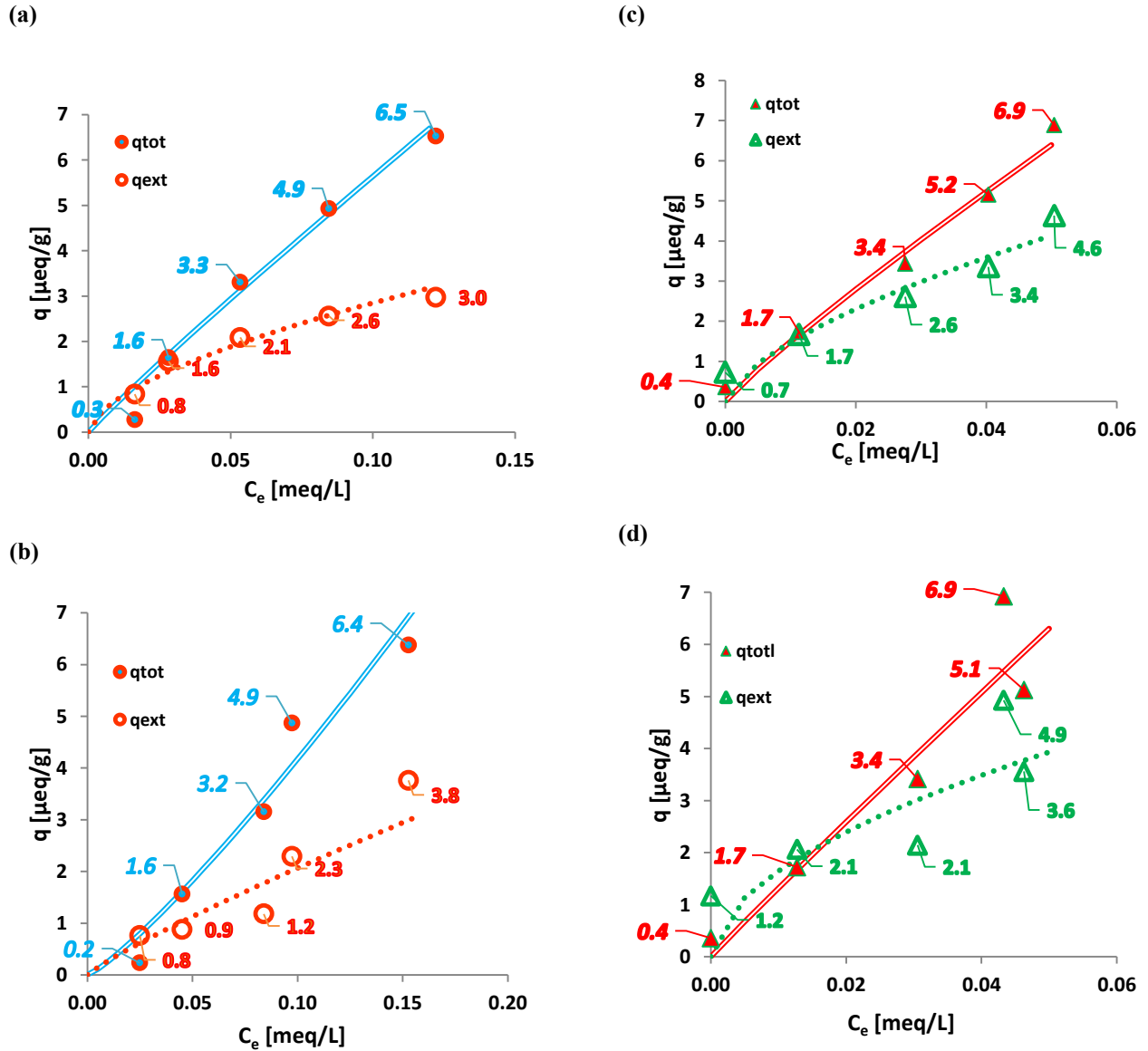
Ammonium Extraction

Extractability and cation exchange characteristics of sorbed ammonium by the media are important and can determine the long-term performance of the media for use in stormwater SCMs. Since the desired adsorbate should allow for the bioavailability of captured ammonium, the extractability of ammonium from the surface can be used as an indication of the media that best allows for availability of nutrients for the nitrifying bacteria needed for completion of the nitrification process within the SCMs.

Cation exchange analysis, where conducted in two steps. First, ammonium sorption took place. In the second step, the media were washed with concentrated KCl for quantifying q_{ext} from the surface, which was used as an indicator for the extractability characteristics of ammonium, and hence its assumed bioavailability. The total ammonium removed by the media (q_{tot}) and ammonium extraction from the surface via 8 x 1 M KCl (q_{ext}) was quantified using the Freundlich isotherm, and the results are presented in Figure 7. Additionally, the sorption isotherm quantification appears in Table 5, and as can be observed the Freundlich isotherm describes the extractable NH_4^+ (q_{ext}) well for both media and background electrolytes, with a coefficient of determination greater than 0.85 for all samples. Additionally, Table 5 provides the summary of the percentages of ammonium recovered based on ammonium loaded.

For all systems, leaching of ammonium for samples with $C_o = 1 \text{ mg/L}$ was observed; that is the mass of ammonium that was recovered via 8x 1 M KCl extraction was higher than the mass of ammonium that was initially loaded. Leaching was also noted as well for $C_o = 5 \text{ mg/L}$ for ZT – CaCl_2 . For CA – NaCl systems, a gradual increase in the fraction of non-extractable ammonium was observed from 4 to 47% as noted in Table 6. Nevertheless, for CA – CaCl_2 , the

percentage of extractable ammonium does not show a clear trend, although the q_{ext} values show an increase from 0.8 to 3.8 $\mu\text{eq/g}$ CA (Figure 7b).



1

Figure 7. Sorption (q_{tot}) and extractable (q_{ext}) curves for ammonium at equilibrium for CA at 0.03 M NaCl (a), and CA at 0.01 M CaCl₂ (b), ZT at 0.03 M NaCl (c), and ZT at 0.01 M CaCl₂ (d) at neutral pH range of [6.5 – 7.2], $T = 22 \pm 1^\circ\text{C}$.

Table 5. Freundlich Isotherm coefficients K_f and $1/n$ for total sorption and extracted of ammonium of 1, 5, 10, 15, and 20 mg NH_4Cl -N/L for ZT at neutral pH of [6.5 - 7.2] and $T = 22 \pm 2^\circ\text{C}$

Media	Background Electrolyte		K_f	$1/n$	r^2
CA	0.03 M NaCl	Sorption	1.42	0.94	0.94
		Extraction	0.22	0.44	0.88
	0.01 M CaCl_2	Sorption	1.86	1.19	0.94
		Extraction	0.44	0.87	0.94
ZT	0.03 M NaCl	Sorption	3.32	0.97	0.92
		Extraction	4.15	1.16	0.98
	0.01 M CaCl_2	Sorption	27.03	1.63	0.95
		Extraction	17.18	1.60	0.85

Similar observations were made for ZT. In ZT – NaCl mixtures, a gradual increase in the exchangeability of sorbed ammonium was observed from 3.5 to 33% with an increase in ammonium loading (Table 6). For ZT – CaCl_2 , leaching was more prominent (i.e., leaching at $C_e = 0$ [0.011 mg/g ZT]) and $C_e = 0.013$ meq/L [0.005 mg/g ZT]) than ZT - NaCl mixtures (i.e., leaching at $C_e = 0$ mg/L [0.005 mg/g ZT]). Thus, it appears that in NH_4^+ - CaCl_2 mixtures, sorbed ammonium is more exchangeable at lower ammonium loadings (i.e., $C_e = 0.17$ mg/L). For the remaining samples, the fraction of exchangeable ammonium reduces until reaching a constant value (i.e., 65 ± 3 %). It has been previously noted that when the concentration of ammonium in the solution is less than or equal to the exchangeable cations on the surface of the media, cation exchange prevails (Jorgensen, et al., 1976, Spryynsky et al., 2004).

Table 6. Ammonium loadings, ammonium removed from the surface, and the differentiation of percentage of ammonium that is extractable/non-extractable after sorption. Extraction was completed as prescribed by Chapman et al., (1965) in determining soil cation exchange capacity.

	Background I = 0.03 M	Input NH ₄ Cl [mg/L]	% NH ₄ not removed	% Extractable NH ₄ removed (via extraction)	% Non- extractable NH ₄ removed
CA	0.03 M NaCl	1	8.30%	234%	-143%
		5	7.89%	87.4%	4.01%
		10	7.47%	58.5%	26.0%
		15	7.89%	47.8%	42.0%
		20	8.55%	41.6%	46.7%
	0.01 M CaCl ₂	1	34.9%	212%	-147%
		5	12.6%	49.2%	38.2%
		10	11.8%	33.0%	55.3%
		15	9.08%	42.8%	48.1%
		20	10.7%	52.7%	36.7%
ZT	0.03 M NaCl	1	0.00%	202%	-103%
		5	3.16%	93.4%	3.47%
		10	3.86%	73.2%	23.0%
		15	3.76%	62.7%	33.6%
		20	3.53%	64.8%	31.6%
	0.01 M CaCl ₂	1	0.00%	328%	-228%
		5	3.57%	115%	-19.2%
		10	4.28%	60.1%	35.7%
		15	4.32%	66.5%	29.2%
		20	3.03%	69.0%	28.0%

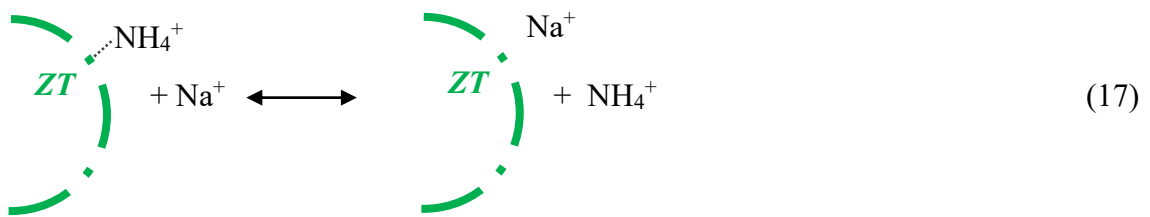
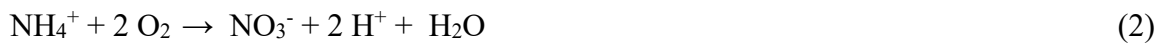
The extraction and sorption curves obtained for ZT at the two different backgrounds are shown in Figure 7c and d; the difference in values obtained for q_{tot} and q_{ext} are small, with a maximum $q_{tot} - q_{ext}$ of 2 $\mu\text{eq NH}_4^+\text{-N / g ZT}$ (i.e., 6.9 – 4.6 for ZT – NaCl and 6.9 – 4.9 for ZT – CaCl₂). The extracted ammonium isotherm for ZT – NaCl shows a near linear relationship ($1/n = 0.97$) (Figure 7c). It is, therefore, concluded that the mechanism involved for removal of ammonium by ZT in the presence of Na⁺ is dominated by cation exchange (Chapman, 1965).

In both media, the differences between q_{tot} and q_{ext} increase with an increase in ammonium loading, but this difference is more prominent in CA (Figure 7a and b). In CA,

particularly CA - NaCl, q_{ext} appears to approach an asymptote at $3 \mu\text{eq} / \text{g CA}$ (Figure 7a), as the changes in q_{ext} become less pronounced for $C_e \geq 0.1 \text{ meq/L}$. Therefore, sorbed ammonium in CA appears to be only partly exchangeable with K^+ , and it is likely that other non-exchangeable sites are responsible for ammonium sorption.

The results obtained from the extraction/cation exchange tests indicate that the mechanism of removal for the two minerals is different. Ammonium removal in ZT is more extractable/exchangeable, and because of this, its higher capacity, and faster kinetics, ZT is more favorable for use in stormwater filtration SCMs than CA.

In a ZT stormwater media, two main reactions are expected to occur between storm-events. Biological transformation of ammonium to nitrate can occur in SCMs (Li and Davis, 2014) as described in equation 2, rewritten below. Nitrification causes a depletion in the ammonium concentration in the pore solution, hence causing a release of sorbed ammonium to the pore solution (equation 17).



With continued transformation of NH_4^+ to NO_3^- through nitrification, the concentration of ammonium in the pore solution will reduce, causing equation 13 to shift to the right, which in turn leads to the release of sorbed NH_4^+ to the solution. As a consequence regeneration of

occupied ZT sites can take place in a ZT media, resulting in higher removal efficiency and greater longevity of media in field applications.

Conclusions and practical considerations

In conclusion, compared to CA, ZT was found to show the highest affinity for removal of ammonium. Ammonium removal was found to be dependent on the background cation/s. Overall, ammonium uptake followed the order: NaCl > CaCl₂ > Mixed Background > KCl, although at higher ammonium loading convergence of curves (NaCl and CaCl₂) or the reversal (KCl and Mixed Background) of curves could be observed. With an increase in the loading of ammonium, ammonium removal was found to be less affected by cation competition. For a stormwater system, however, lower ammonium loadings are commonly observed, and competition between the cations is expected.

Studies showed faster ammonium uptake rates for ZT than CA (t_e between 30-240 minutes for ZT vis-a-vis $t_e \geq 240$ minutes for CA). The kinetics of sorption was well represented by the pseudo second order rate equation. Increase in the concentration of competing cations (Ca²⁺ and K⁺) was seen not only to lower the extent of ammonium removal, but also to slow the kinetics of sorption, particularly for ZT, where t_e shifted from 30 minutes to 240 minutes. The studies indicate a minimum of 240 minutes at $T = 22 \pm 1$ °C for the sorption of ammonium to reach equilibrium when competing cations are present.

Based on the obtained results, the abiotic capture of ammonium cations by the media is partly reversible through 1 M KCl extractions (average 60% for ZT) under the ammonium concentrations studied, although the fraction of ammonium extracted changed with ammonium loading and type of media. The extractability of ammonium from the media was not affected by

the background electrolyte from NaCl to CaCl₂. ZT captured more ammonium from solution, and q_{ext} for ZT was found to be higher than that of CA.

To conclude, clinoptilolite zeolite appears to be highly effective in removal of ammonium in stormwater situations, shows high capacity for ammonium removal, and relatively rapid rates of sorption ($30 \text{ min} \leq t_e \leq 240 \text{ min}$). NH₄⁺ removed by ZT showed high exchangeability tendencies, indicating relative ease of accessibility for nitrifying bacteria, and in doing so regenerating the ZT employed in the SCM.

For a more effective approach for removal of ammonium in stormwater filtration SCMs, chemical processes should be combined with biological nitrification/denitrification, such that all the particulate, dissolved organic, and ammonical nitrogen can be captured via filtration or sorption, and gradually ammonified and nitrified. As discussed, the use of an anoxic zone in SCMs can promote denitrification. Nevertheless, as dictated by microbial processes in the aerobic zone, the efficacy of the system is dependent on mineralization of organic nitrogen to ammonium, and nitrification of all produced (from mineralization) and influent ammonium prior to reaching the anoxic zone in the filter. The design in Figure 8 is recommended for implementation in bioretention cells and sand filters, where application of ZT in the nitrification zone is recommended for enhanced removal of ammonium based on results of this work, indicating high removal efficiency as well as shorter contact times required for optimum ammonium removal. Because of higher removal efficiency, it is expected that mixing ZT with less expensive filtering material such as sand has high potential for stormwater treatment applications. The chemistry of stormwater, which is dependent on the site and season, should be considered during SCM designs for adequate capacity for ammonium removal.

This work will be followed by more field-related experimental testing, including ZT and CA column studies, followed by evaluating the performance of the media in a biologically-active system.

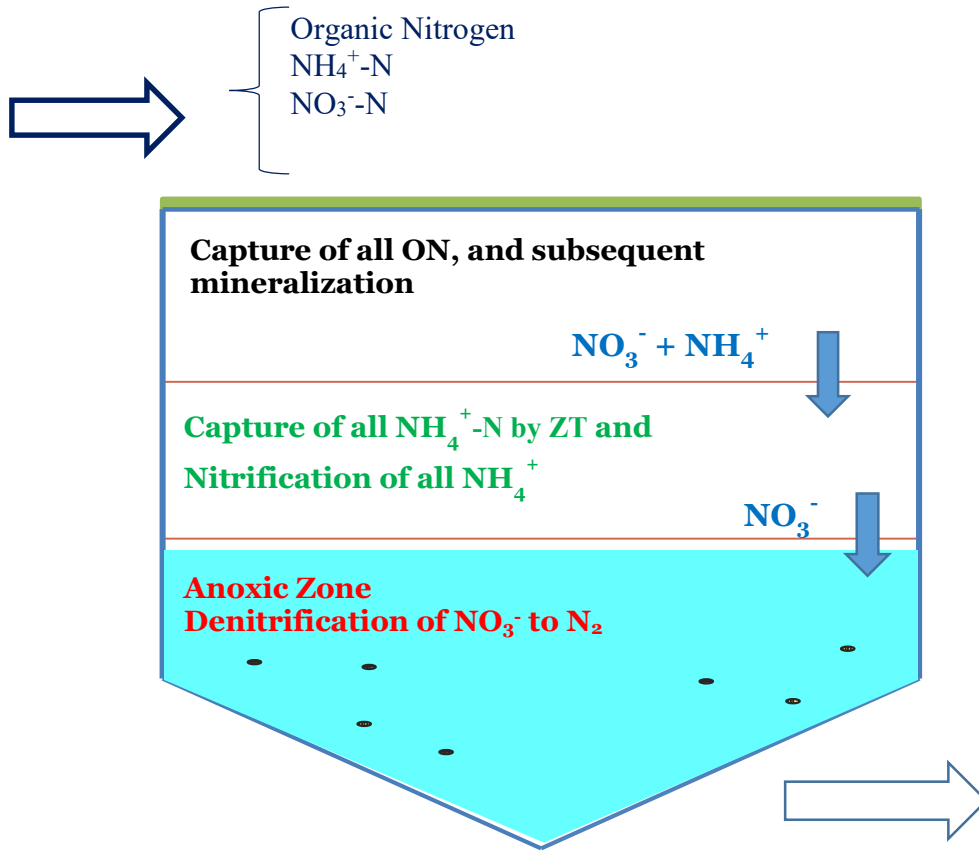


Figure 8. Modified Design of Sand Filter/bioretention cell for removal of nitrogen in runoff.

6. Characterizing Clinoptilolite Zeolite and Hydroaluminosilicate aggregates for ammonium removal in simulated stormwater runoff under column flow conditions

Introduction

The availability of excess nitrogen in aquatic systems can promote the undesirable overgrowth of algae, leading to depleted oxygen levels and jeopardizing the health of aquatic habitats. The blooming algae and microscopic plants can also reduce the transparency of water and compromise the survival of seagrass habitat (USEPA, 2008). In addition to environmental and health problems, the economic losses associated with eutrophication are also significant (Dodds et al., 2009). Urban stormwater runoff has been identified as one of the main sources of eutrophication, with excess nitrogen playing an active role (U.S.EPA, 2009).

To address stormwater pollution, many stormwater control measures (SCMs), such as sand filters and bioretention cells are employed, and although effective in reducing runoff volume, suspended solids loadings, and removal of heavy metals, they have not been highly effective in reducing excess nitrogen. Nitrogen in stormwater has a diverse speciation, often characterized as particulate nitrogen, dissolved organic nitrogen, ammonium, and nitrate (Duncan, 1999, Tiefenthaler et al., 2000, Taylor et al, 2005, Kayhanian et al., 2007, Collins et al., 2010, Li and Davis, 2014). Another influencing factor is the cycling of nitrogen, which results in mineralization of organic nitrogen to ammonium, and nitrification of ammonium. Overall, the fate of nitrogen in SCMs is often associated with poor removal of the incoming nitrogen, and

often the export of organic nitrogen and nitrate production (Hunt et al., 2006, Hatt and Fletcher, 2009, Passport et al., 2009, Rosenzweig et al., 2011, Li and Davis, 2014).

Implementation of a denitrification zone in bioretention is recommended to enhance nitrate reduction (Dietz and Clausen, 2005, 2006, Davis et al., 2006). While a nitrification/denitrification system can be beneficial in enhancing the treatment of nitrogen in urban runoff, it should be combined with other chemical and biological processes, such as sorption and/or ion exchange for effective treatment of excess nitrogen. Sorptive/cation exchange media can be effective in pollutant removal during low temperatures, and shock loads (such as first flush phenomenon in stormwater runoff) and they require smaller land area as well as lower capital cost for operation compared to biological processes (Booker et al., 1996, Miladinovic and Weatherley, 2008). A proposed design for enhancing nitrogen removal involves dividing the SCM into three N treatment layers as demonstrated in Figure 8. This design will allow for capture of organic nitrogen, allowing it to be mineralized into ammonium in the first zone, with the second zone aiming to capture and hold ammonium until its successful nitrification. The 3rd compartment consists of a saturated zone, allowing denitrification to N₂, such that all nitrogen is captured and ultimately transformed to N₂. For this system to be effective, complete capture and transformation of organic nitrogen and ammonium is paramount.

The focus of this work is optimization of ammonium removal in SCMs via chemical (ion exchange/sorption) processes. Ammonium is one of the intermediate nitrogen species between particulate and dissolved organic nitrogen to nitrate. It can enter an SCM in its aqueous form or be produced from the degradation of organic nitrogen (Kadlec and Knight, 1996, Li and Davis, 2014). Median TKN values (organic nitrogen + NH₄⁺-N), although variable in stormwater, are reported to be in the order of 0.73 – 2.5 mg N/L (Kayhanian et al., 2007, Collins et al., 2010, Li

and Davis, 2014). The use of retentive media has the potential to greatly enhance the N operation and performance of media-based SCMs. Overall, research on ammonium removal via cation exchange/sorption suggests that ammonium removal is dependent on the adsorbent type, particle size, flow rate and contact time, pH, and other present competing pollutants, such as competing cations (Jorgensen et al., 1978, Klieve and Semmens, 1978, Booker et al., 1996, Sarioglu, 2005, Sprynskyy et al., 2005, Miladinovic and Weatherley, 2008, Nguyen and Tanner, 2015). However, literature has focused on various wastewaters at typical ammonium concentrations of 5 – 800 mg/L, with most concentrations higher than 10 mg NH_4^+ -N/L. These concentrations are significantly higher than those observed in urban runoff, as discussed in Chapter 5.

Previously, the use of two materials, hydrous-aluminosilicate agglomerates (CA) and clinoptilolite zeolite (ZT), was found to be promising for ammonium removal based on batch-scale experimentation in conditions typical of stormwater runoff (Chapter 5). The findings indicated that ammonium removal by the media was dependent on stormwater chemistry, and the presence of competing cations not only reduced the extent of ammonium removal, but also resulted in slower rates and longer equilibrium times, particularly for ZT (Chapter 5). A wide array of cations can be found in the stormwater environment; of note, Na^+ is expected to be the most dominant in highway runoff, because of its presence in > 98% of road salts used for de-icing (Schneider, 1967, Ramakrishna and Viraraghavan, 2005, Sanzo and Hecnar, 2006). Another commonly encountered road salt is CaCl_2 , and hence the effect of Ca^{2+} on ammonium removal was investigated. Finally, K^+ is known to have the highest inhibitory effect on ammonium removal, and was therefore, used to simulate an environment with high competition posed by cations with ammonium for uptake (Watanabe et al., 2002, Chen et al., 2002, Lei, et al., 2008, Huang et al., 2005, Chapter 5). K^+ is an essential plant nutrient and can be found in

fertilizers. While, findings suggest high performance of these two media based on capacity, kinetic analysis, and potential bioavailability of removed ammonium for application in filtration-based SCMs, the results should be expanded to include flow-based studies for better characterization and optimization of ammonium removal under more realistic conditions.

The objectives of this study are to characterize CA and ZT under flow conditions for implementation in SCMs for ammonium sorption, while simulating field conditions to better understand the fate of ammonium in SCMs. The different scenarios investigated in this work include:

1. Wet/saturated - Dry/unsaturated periods: Rainfall is episodic and typical SCMs experience a wet/saturated period of rainfall, followed by several dry/unsaturated days.
2. Different velocities and Contact times: rainfall intensity and duration are variable, which affect the velocity and retention time of the stormwater runoff within the filtration SCM.
3. Changes in the influent nitrogen concentrations: concentration of pollutants is intra-event, event, and season dependent. For example, in autumn and spring, larger input nitrogen concentrations, particularly organic, are expected because of abscission.

Column studies were evaluated to understand the fate of ammonium removal under each of the discussed conditions. The performance, sorption capacity, and removal efficiency of the media were investigated for each of these conditions.

Materials and Methods

The materials and methods used for examining the performance of CA and ZT are discussed in chapter 4, section II.

Results and Discussion

Capacity of Media

Previous work quantifying ammonium removal in batch settings by ZT and CA suggested that for a contact time of 60 minutes, the ratio of adsorption at time t (q_t) to that of the equilibrium value (q_e) for NH_4^+ in NaCl and NH_4^+ - Mixed Background equaled 80% and 72% respectively for CA, and 100% and 83% respectively for ZT (Chapter 5). Based on the batch data, it appeared that increasing the contact time further could have resulted in more effective ammonium removal, particularly for CA, where an equilibrium time of 4 hours was observed (Chapter 5). Nevertheless, due to pumping limitations and expected field conditions, further increasing the contact time was not done.

In a previous work, removal of ammonium, particularly by ZT, was found to be partly due to cation exchange (Chapter 5). The presence of other cations can affect NH_4^+ removal efficiency and lead to different design parameters for filtration-based SCMs targeting NH_4^+ removal.

The performance of the media for the two different electrolytes, and a comparison with sorption capacity for the same influent concentration of 2.5 mg NH_4^+ -N/L is summarized in Table 7. Figures 9 – 11 also provide a graphical summary of the findings for each of the adsorbents.

Table 7. Summary of sorption capacity (q) obtained for batch (Chapter 5) and column studies, and removal efficiency of media for CA, ZT, and 50% Sand: 50% ZT (v/v) at 0.03 M NaCl and Mixed Background electrolytes for $C_0 = 2.5 \text{ mg NH}_4^+\text{-N/L}$ at neutral pH and $T = 22 \pm 2^\circ\text{C}$

Media	NaCl			Mixed Background		
	q_{Batch} [mg/g]	q_{Column} [mg/g]	$\frac{\sum[\text{NH}_4^+ - \text{N}]_{\text{removed}}}{\sum[\text{NH}_4^+ - \text{N}]_{\text{loaded}}}$	q_{Batch} [mg/g]	q_{Column} [mg/g]	$\frac{\sum[\text{NH}_4^+ - \text{N}]_{\text{removed}}}{\sum[\text{NH}_4^+ - \text{N}]_{\text{loaded}}}$
CA	0.25 ± 0.00	0.33 ± 0.01	0.68 ± 0.01	0.12 ± 0.01	0.13 ± 0.00	0.78 ± 0.02
ZT		0.45 ± 0.03	0.76 ± 0.02		0.15 ± 0.01	0.64 ± 0.05

As illustrated in Figure 9 and Table 7, the presence of other cations resulted in lower $\text{NH}_4^+\text{-N}$ capacity for CA. In the NH_4^+ - Mixed Background, the media exhausted (i.e., $\frac{[\text{NH}_4^+ - \text{N}]_{\text{out}}}{[\text{NH}_4^+ - \text{N}]_{\text{in}}} \geq 1.0$) after 5 days (16 BV), when 1.4 mg $\text{NH}_4^+\text{-N}$ was desorbed from the media. This was unexpected as sorption isotherms observed in batch settings showed high affinity of the media for ammonium removal for NH_4^+ in the Mixed Background system at pH = 6.6 and $T = 22 \pm 2^\circ\text{C}$ (Chapter 5). Competition between the cations in the Mixed Background and ammonium are thought responsible for the poor performance of the column; Ca^{2+} and K^+ in the mixed background electrolyte can compete with NH_4^+ .

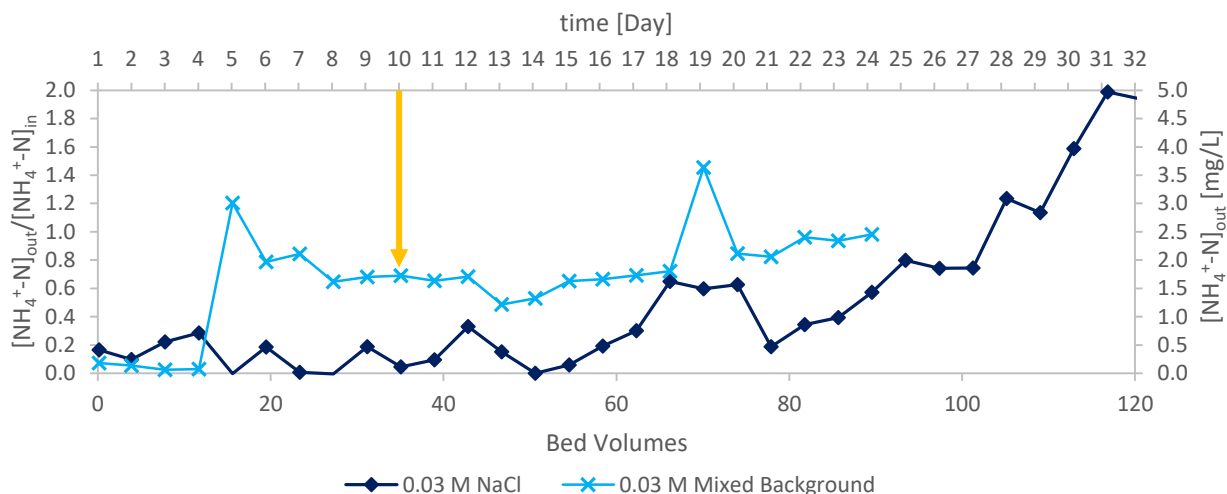


Figure 9. Continuous long column study for California aluminosilicate (CA) for NH_4^+ - Mixed Background and NH_4^+ - NaCl, for $C_{in} = 2.5 \text{ mg NH}_4^+\text{-N/L}$, $\text{pH} = 6 - 7$, $T = 22 \pm 2 \text{ }^\circ\text{C}$, $I = 0.03 \text{ M}$. The concentration of Ca^{2+} in the NH_4^+ - Mixed Background run was reduced from 3 mM to 1 mM on day 10, to investigate the performance of the media at lower concentrations of competing cations. Na^+ was increased from 0.01 to 0.017 to maintain $I = 0.03 \text{ M}$. The concentration of K^+ was not changed.

It has been observed that K^+ can have inhibitory effects on the uptake of ammonium (Guo et al., 2007, Wang et al., 2007, Huang et al., 2010, Chapter 5); nonetheless based on batch-scale studies, uptake of Ca^{2+} was found to be slightly higher than that of K^+ for CA for the concentration range of 1 – 20 mg $\text{NH}_4^+\text{-N/L}$ (Chapter 5). Furthermore, Ca^{2+} is divalent, and release of 1 Ca^{2+} from the media can result in uptake of 2 NH_4^+ , and its reduction in the influent can increase ammonium uptake by CA. Therefore, $[\text{Ca}^{2+}]$ was reduced from 0.0034 to 0.001 M on day 9 to investigate whether ammonium removal by CA can increase by lowering the concentration of Ca^{2+} in the influent. Simultaneously $[\text{Na}^+]$ was increased to 0.017 M to maintain a constant $I = 0.03 \text{ M}$.

The results (Figure 9) indicate a reduction in the concentration of effluent $\text{NH}_4^+\text{-N}$ from 1.7 ($[\text{NH}_4^+\text{-N}]_{out}/[\text{NH}_4^+\text{-N}]_{in} = 0.7$) to 1.2 mg $\text{NH}_4^+\text{-N/L}$ ($[\text{NH}_4^+\text{-N}]_{out}/[\text{NH}_4^+\text{-N}]_{in} = 0.5$) after a few days. This decreasing trend did not persist, however, and the effluent ammonium concentration increased back to 1.7 mg $\text{NH}_4^+\text{-N/L}$ by day 14, and the column exhausted for a second time on day 18. It is hypothesized that, as the active sites on the surface of CA react with

the cations in the influent (NH_4^+ , Na^+ , Ca^{2+} , and K^+), displacement of ammonium ions by more favorable cations occurred, as observed on day 5 (Pontius, 1990).

CA showed greater removal efficiency in the NH_4^+ - NaCl mixture, where exhaustion was observed on day 28 of the experiment after a cumulative nitrogen loading of 63.2 mg. Comparing the performance of CA at two different background electrolytes indicates that competition of cations can lower ammonium removal by CA ($q = 0.33 \text{ mg NH}_4^+\text{-N in NaCl vis-à-vis } 0.13 \text{ mg NH}_4^+\text{-N/L for Mixed background}$) where combination of cations is present.

ZT showed a higher removal capacity of NH_4^+ than CA, as displayed in Table 7 and Figure 10, which is consistent with observations made in batch-scale experiments (Chapter 5). The Mixed Background exhausted after 17 days, and treating 66 bed volumes, equal to 39.8 $\text{NH}_4^+\text{-N mg}$. The media treating $\text{NH}_4^+\text{-N in NaCl}$ showed significantly higher removal, and exhaustion was achieved after 73 days of operation, and treating 551 bed volumes, equal to a cumulative ammoniacal nitrogen loading of 331 mg. The capacity of the media at neutral pH [6.5 – 7], $T = 22 \pm 2 \text{ }^\circ\text{C}$ for an influent of $2.5 \text{ mg NH}_4^+\text{-N/L}$ was determined to be 0.15 mg and 0.45 $\text{mg NH}_4^+\text{-N/g ZT}$ for Mixed Background and NaCl, respectively.

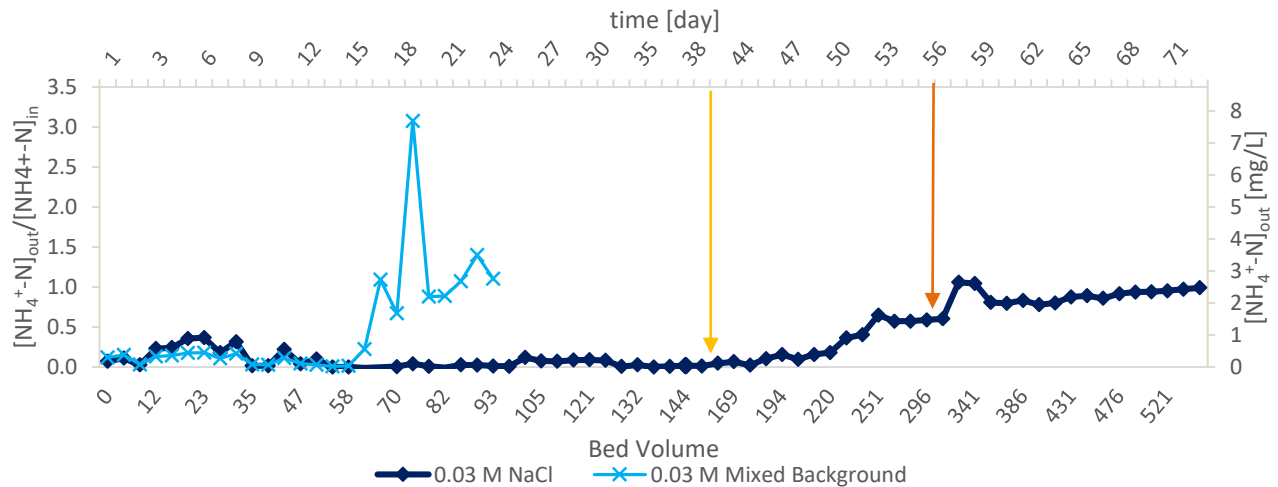


Figure 10. Continuous long column study for Clinoptilolite (ZT) for NH_4^+ – Mixed Background and NH_4^+ - NaCl, $C_{in} = 2.5 \text{ mg NH}_4^+\text{-N/L}$ pH = 6 – 7, $T = 22 \pm 2 \text{ }^\circ\text{C}$. The superficial velocity of the NH_4^+ – NaCl run was increased from 6.8 cm/h to 14.7 cm/h on day 40, and again from 14.7 to 26.3 cm/hr on day 56 to promote breakthrough.

To evaluate a more cost effective design, a mixed media (i.e., 50:50 V/V ZT: Sand) was also tested (Figure 12). The presence of competing cations (Ca^{2+} and K^+) were once again found to reduce the performance of the media, compared to that of the NaCl system. The capacity of the mixed media for NH_4^+ in NaCl was similar to that of pure ZT (0.45 and 0.46 mg NH_4^+ -N/g ZT for ZT and ZT: Sand, respectively). Comparing the results of the mixed and pure ZT columns, the capacity of ZT remained unchanged, despite the reduction in t_m from 175 min to only 50 min.

Other studies for clinoptilolite report higher capacity values ranging from 1.2 to 17.6 mg $\text{NH}_3/\text{NH}_4^+$ -N/g ZT where ammonium concentrations ranged from 10 to 270 mg NH_4^+ -/L, with most studies focusing on NH_4^+ -N \geq 28 mg/L (Booker et al., 1996, Weatherley and Miladinovic, 2004, Farkas et al., 2005, Sprynskyy et al., 2005, Guo et al., 2007, Ashrafzadeh et al., 2008, Hedstrom and Amofah, 2008). The lower influent ammonium concentration in the synthetic stormwater results in reduction of the effective media capacity, following an isotherm-type relationship.

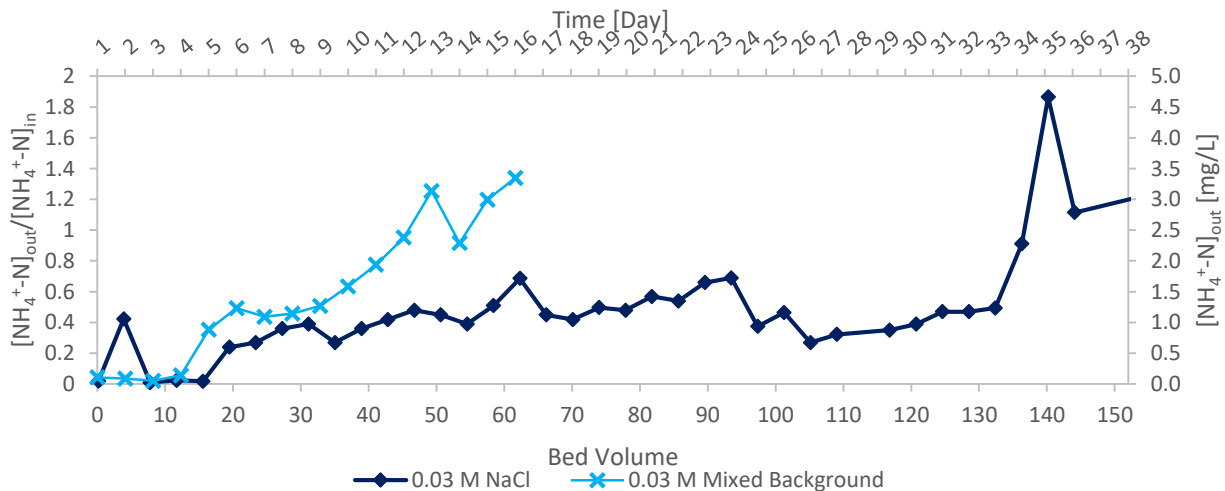


Figure 11. Continuous long column study for a mixed column of Sand and ZT (50:50 v/v) for NH_4^+ - Mixed Background and NH_4^+ - NaCl, $C_{in} = 2.5$ mg NH_4^+ -N/L pH = 6 - 7, and $T = 22 \pm 2$ °C.

Life-span of media in the field

Equation 9 was used to estimate the life span of media, and the results are summarized in Table 8. It is estimated, based on laboratory observations, that the productive life-span of the media in the field would be 10 and 53 months for CA for 0.03 M Mixed background and 0.03 M NaCl, respectively. For ZT, the estimated life span would be 36 and 216 months for 0.03 M Mixed and 0.03 M NaCl, respectively. Finally, a 50% ZT: 50% sand column is calculated to last 20 months under field conditions before breaking through for mixed background, and 44 months for NaCl background. The Mixed background data may be more representative of field conditions since the presence of other cations can interfere with the abiotic uptake of ammonium by the media.

Table 8. Laboratory performance data and the estimated life-span of media for ammonium removal, where U = superficial velocity of simulated runoff through the column, t_b is the breakthrough/exhaustion time, M_c is the mass of ammoniacal nitrogen that was treated by the SCM, M_{Field} is the mass of nitrogen that is calculated to be treated by the media employed in the SCM, t_{Field} is the estimated life-span of media in the field.

	CA		ZT		ZT - Sand	
	Mixed Background	NaCl	Mixed Background	NaCl	MixedBackground	NaCl
U [cm/h]	8.3	6.8	8.3	6.8 → 14.7 → 26.2	8.3	6.8
t_b [Days]	5	27	18	70	13	29
M_c [mg]	11.7	63.2	42.1	257.76	23.4	52.2
M_{Field} = [mg]	1.4×10^6	7.4×10^6	4.9×10^6	3.0×10^6	2.7×10^6	6.1×10^6
t_{Field} = [months]	9.8	52.4	35.4	216	19.6	44

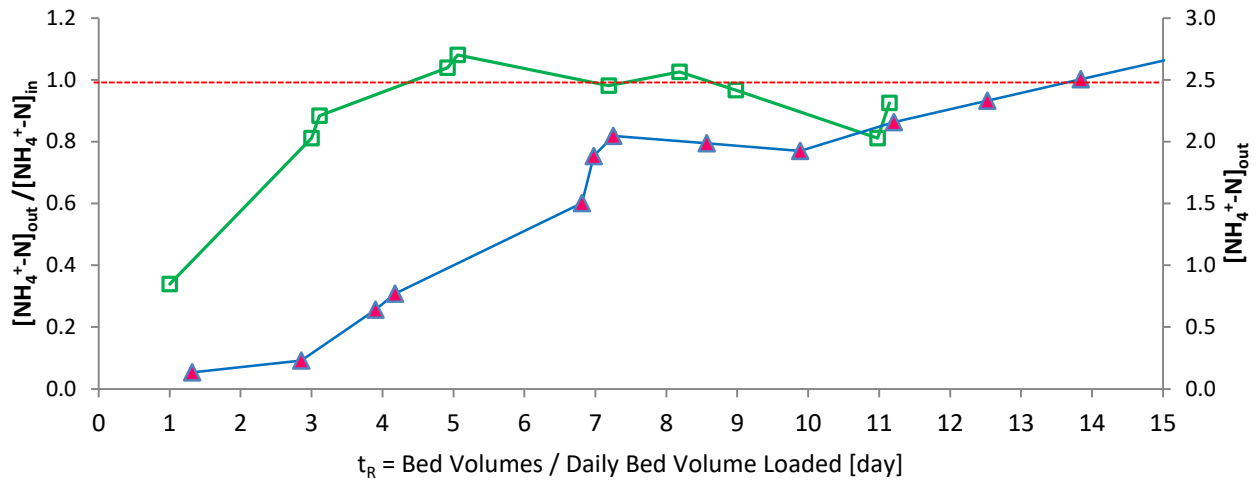
Effect of velocity/contact time on ammonium removal

The efficiency of removal and media capacity for different flow rates and contact times were determined for NH_4^+ -N in NaCl (8.3, 15.1 (ZT only), and 42 cm/h, corresponding to

contact time (t_c) of 47, 26, and 10 minutes). The data are presented with respect to a normalized ammonium loading (i.e., $t_R = \frac{\text{Cumulative Bed Volumes}}{\text{Daily Bed Volume Loaded}}$), with findings illustrated in Figure 13.

For both media, the faster flow rate results in lower removal and faster exhaustion. The performance of CA is poor for faster velocity and slower contact times (i.e., 66% $\text{NH}_4\text{-N}$ removal at $t_R = 1$ day for $U = 42.0$ cm/h vis-a-vis 94.8 % $\text{NH}_4\text{-N}$ removal for $t_R = 1.3$ day and $U = 1.3$ cm/h), and breaks through on the 4th day, corresponding to $t_R = 5$ days, with $C/C_{in} = 1.04$ (Figure 12a). Ammonium mass removal ($\frac{[\text{NH}_4^+ - \text{N}]_{\text{removed}}}{[\text{NH}_4^+ - \text{N}]_{\text{loaded}}}$) for $U = 8.3$ cm/h is equal to 74%, while this value for $U = 42$ cm/h is only 13%. The slower flow rate, corresponding to a longer contact time of 62 minutes, results in better performance by the CA. Furthermore, even within the first day of operation, ammonium removal by the media for the fast velocity rate is reduced, compared to removal at the smaller velocity.

(a)



(b)

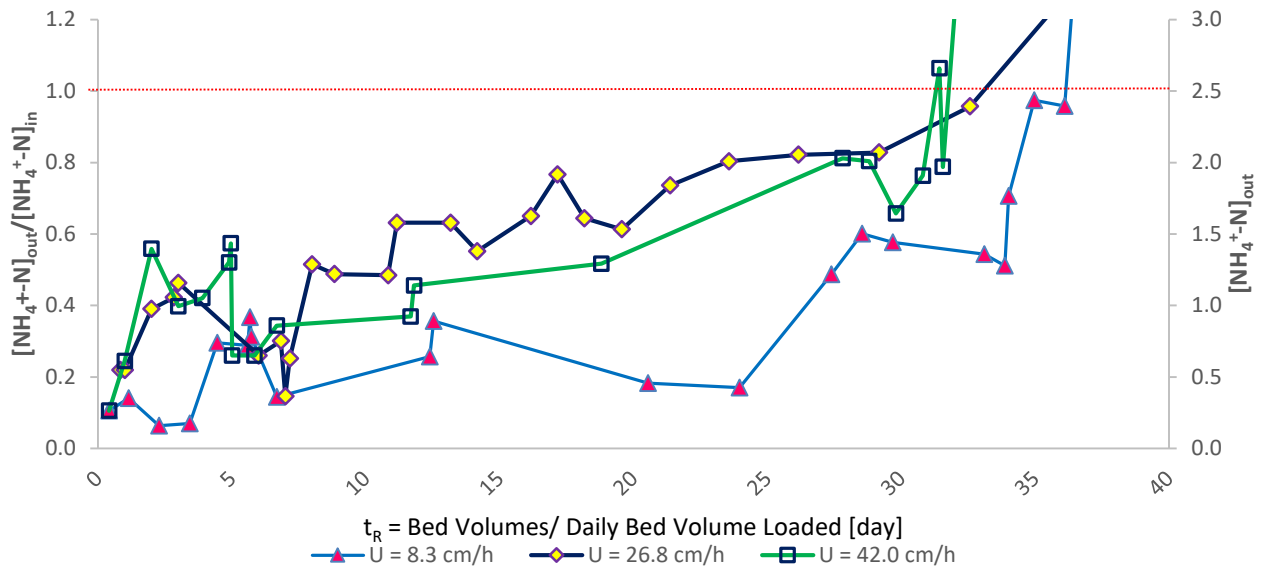


Figure 12. Removal of ammonium at different velocities for (a) CA, and (b) ZT at $T = 22 \pm 2^\circ\text{C}$, for $[\text{NH}_4^+\text{-N}]_{\text{in}} = 2.5$ mg/L, and $I = 0.03$ M NaCl.

The study for ZT also indicates an inverse relationship between velocity and ammonium removal (Figure 12b). The column with a slower velocity of 8.3 cm/h exhausted after 37 days, while the column with velocities of 26 and 42 cm/h exhausted after 31 and 32 days, respectively. The $\text{NH}_4^+\text{-N}$ removal efficiency was found to be 71, 65, and 48% for $U = 8.3, 26,$ and 42 cm/h,

respectively. Moreover, for ZT a net nitrite plus nitrate production of 7 percent was found for $U = 8.3$ cm/h, while for U of 26 and 42 cm/h, this value was found to be 2 percent of the total nitrogen loaded to the columns until media exhaustion. The biological activity of the ZT column will be quantified and discussed in Chapter 7.

The difference in the performance of the fast and slow columns can be attributed to rates of sorption. It is known from the batch experiments (Chapter 5) that at 0.03 M NaCl, 60 minutes is required for 70% overall removal of ammonium by ZT. The slow column had a contact time of 47 minutes, while that for the fast column is only 12 minutes. Although it is noted that column studies result in more efficient ammonium removal (Spryynsky et al., 2004), it can be concluded that longer contact time corresponds to greater removal by ZT. The results observed here are consistent with literature findings, where slower velocities and longer contact times were found to enhance ammonium removal in clinoptilolite and soil columns (Booker et al., 1996, Milan et al., 1997, Spryynsky et al., 2005, Sarioglu et al., 2004, Jellali et al., 2010). Booker et al. (1996) also showed that reducing the velocity could enhance the performance of the media up to a certain limit ($Q < 10$ BV/h). Booker et al. (1996) noted that NH_4^+ -N removal in clinoptilolite is mostly due to pore diffusion, and allowing longer contact times enables the cations to reach the pores within the clinoptilolite structure, and enhance ammonium removal.

Wet/saturated - Dry/unsaturated Conditions

An experiment was performed to mimic the wet/saturated and dry/unsaturated conditions experienced in the field, with a dry/unsaturated interval of 3 days between simulated storm events. The intermittent flow experiment for CA is presented in Figure 13a. The wet/saturated - dry/unsaturated column breaks through after 10 runs, corresponding to an experimental time (wet/saturated + dry/unsaturated) of 50 days. Release of ammonium is commonly observed in

each sample collected immediately after the end of the dry/unsaturated period. The samples showing this release were collected within the first 60 minutes after the dry/unsaturated period. Subsequently, samples collected after 2-4 hours showed a reduction in the effluent ammonium concentration, compared to their previous samples. This leaching is most dominant on the 4th wet/saturated period (increase from 0.35 to 0.49 mg NH₄⁺-N/L), 5th wet/saturated period (0.67 to 0.76 mg NH₄⁺-N/L), 8th wet/saturated period (1.68 to 1.82 mg NH₄⁺-N/L), and finally for the 9th wet/saturated period (1.92 to 2.58 mg NH₄⁺-N). For comparison, the continuous CA run is also displayed in Figure 13a. Both columns show similar trends and removals with 74 and 75 % cumulative ammonium removal for continuous and intermittent columns, respectively, up to the exhaustion of the media. A student's t-test was performed based on bed volumes treated, which indicated less effective ammonium removal in the continuous run compared to that of the intermittent ($P \leq 0.05$).

Figure 13b displays the results for ZT. The continuous column exhausted after 42 days, equivalent to 418 bed volumes. For this run, biological activity was indicated, and an overall 5% and 2% of loaded ammonium was transformed to nitrite and nitrate, respectively, up to the exhaustion of ZT. The nitrification activity began after the first week of operation, although consistent nitrite and nitrate production was not observed until reaching media exhaustion.

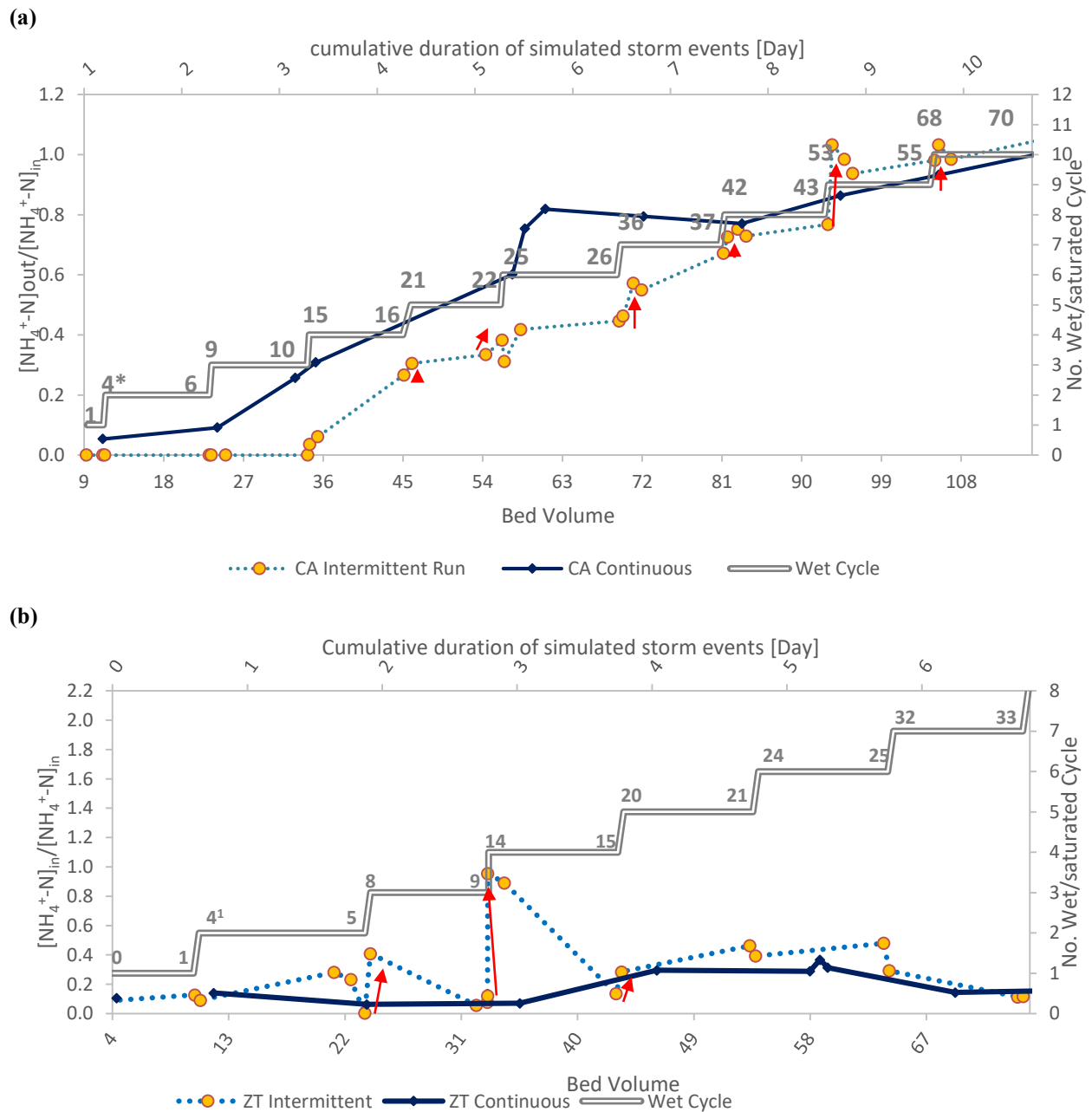


Figure 13. Continuous and intermittent flow conditions of CA (a) and ZT (b) at $C_{\text{in}} = 2.5 \text{ mg NH}_4^+\text{-N/L}$ and $U = 6.8 \text{ cm/h}$ at $I = 0.03 \text{ M}$, $\text{pH} = 6 - 7$, and $T = 22 \pm 2 \text{ }^\circ\text{C}$. The average dry/unsaturated period between two consecutive wet/saturated cycles is 3 days. The secondary x axis denotes the cumulative duration of simulated storm events for both continuous and intermittent columns, while the real-time [day] for the intermittent columns are displayed next to the wet/saturated-dry/unsaturated curve. The changes in the effluent ammonium concentrations immediately after the dry/unsaturated period are displayed with the arrows, where red indicates an increase in the effluent ammonium concentration immediately after the dry/unsaturated period.

¹ Clock time, indicating the duration of the intermittent run [Day].

The clear difference between the continuous and intermittent runs is displacement of ammonium after the dry/unsaturated period. This release of ammonium immediately after the dry/unsaturated period is particularly pronounced for the 4th and 5th wet/saturated periods. The reduction in the effluent ammonium concentration after the initial release illustrates that with further hydration of the media, the ammonium removal performance is enhanced. Furthermore, the release of ammonium regenerates sites that were once occupied, which can cause an immediate increase in the ammonium uptake. This shows that the changes occurring during the dry/unsaturated event are reversible. This initial release causes an overall less efficient ammonium removal compared to that of the continuous run for the initial 8 days. After the 5th run, the removal efficiency of ammonium by the intermittent column increases.

Based on student's t-tests ($P \leq 0.05$), the ZT intermittent (wet/saturated-dry/unsaturated) run does not show a significant difference with that of the continuous. The capacity obtained for the intermittent column after 8 days of operation, equal to 79 BV, corresponds to 0.20 mg NH_4^+ - N/g ZT, vis-à-vis 0.25 mg NH_4^+ - N/g ZT for the continuous run. In a work by Sprynskyy et al. (2005), halting the feed to a ZT column overnight for 12 hours was found to increase its performance. As the feed stops, the ammonium in the pore solution has greater exposure with the surface, and hence higher adsorption can take place, which does not agree with the current work.

Overall, the wet/saturated - dry/unsaturated column differs from the continuous column in several ways. The first is that during the dry/unsaturated events, air is introduced through the media, and as a result air bubbles can get trapped through the pores. These bubbles can change the flow characteristics of the column and reduce the flow path, and hence the contact time in the runs immediately after the dry/unsaturated events. The shorter contact time can result in less ammonium uptake by the media. Another consideration is that dry/unsaturated as the media

becomes less saturated with water a local increase of the ionic strength, and the eventual collapse of the double layer, which reduces the electrostatic interactions between the surface and those of the counter-charged ions (i.e., NH_4^+) (Sparks, 2003). The release of cations held by electrostatic interactions at the surface can thus occur in solution collected before the media is saturated with water again.

In a study by Cho et al. (2009), ammonium removal was found to be enhanced after dry/unsaturated periods in soil columns; this study used vegetation-covered soil media that also allowed for nitrification in-between storm events unlike the data set described in this study. Studies investigating the removal of other polluting cations in stormwater runoff indicate that except for prolonged dry/unsaturated periods (i.e, 3-4 weeks), no significant change in the removal of heavy metals by the media could be observed by vegetation-covered soil columns (Blecken et al., 2009). Hatt et al. (2007) also indicated no adverse effects on the removal of heavy metals by intermittently run soil columns. Nevertheless, their results indicated flushing of dissolved nitrogen species, including NH_4^+ after extended dry/unsaturated periods (Hatt et al., 2007).

Effect of step changes in the influent ammonium concentration on performance

The chemistry of stormwater runoff is site and season dependent (Tiefenthaler et al., 2000), and it is likely that stormwater runoff will exhibit different ammonium concentrations during and for different storm events. ZT has proven to be more effective in ammonium removal than CA. Therefore, an additional experiment investigated the effects of step changes in the influent ammonium concentration on the performance of this medium.

The results obtained in this experiment indicate that the efficiency of removal (C/C_{in}) increases with an increase in the influent ammonium concentration (Figure 14). Release or

desorption of ammonium was observed when C_{in} was reduced to 1 mg NH_4^+ -N/L. From batch experiments, for $C_{in} = 1$ mg NH_4^+ -N/L, $q = 0.2$ mg NH_4^+ -N / g ZT, and 5 mg NH_4^+ -N/L corresponded to 0.3 mg NH_4^+ -N/g ZT (Chapter 5). A drop in the influent ammonium concentration caused desorption/ release of sorbed ammonium from the surface. Desorption of ammonium caused increase from 0.5 to 7.1 mg NH_4^+ -N/L for the initial 2, 4, and 24 hours, was observed for an influent ammonium concentration change of 5 to 1 mg NH_4^+ -N/L.

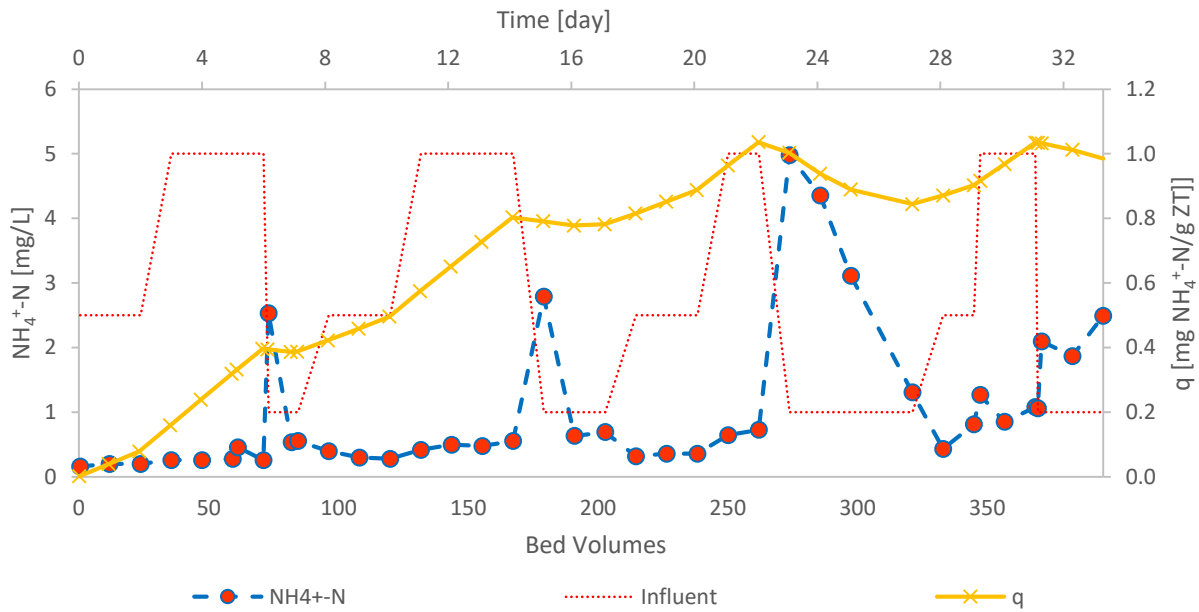


Figure 14. Performance of ZT under varying influent ammonium concentrations from 2.5 mg NH_4^+ -N/L to 5 mg NH_4^+ -N/L and subsequently to 1 mg NH_4^+ -N/L. Testing performed for NH_4^+ - NaCl system at $T = 22 \pm 2^\circ C$

A mass balance was evaluated for ammonium (equation 18), where the cumulative $[NH_4^+ - N]_{in}$, is set equal to cumulative NH_4^+ -N out and NH_4^+ -N removed by the media, assuming no NH_4^+ reaction.

$$[NH_4^+ - N]_{in} = [NH_4^+ - N]_{out} + [NH_4^+ - N]_{sorbed} \quad (18)$$

The duration of desorption (time for which $C/C_{in} > 1.0$) was found to increase from only 4 hours in the first cycle at 73 bed volumes to 96 hours for the 3rd cycle at 273 bed volumes. The change in q before and after the concentration drop increases from 0.01 to 0.19 mg NH_4^+ -N/g

ZT. This is expected as sorption is dependent on the concentration of the adsorbate, and smaller dissolved $\text{NH}_4^+\text{-N}$ corresponds to smaller q values, resulting in desorption of $\text{NH}_4^+\text{-N}$ from the surface. It can be inferred that, with further occupation of sites by NH_4^+ , the amount of N that desorbs in the case of a concentration drop also increases, potentially making the media a source of ammonium in the event of an influent ammonium concentration drop.

Conclusions

The capacity experiments of CA, ZT, and 50:50 Sand: ZT (v/v) suggest a reduction in the ammonium removal capacity with respect to ammonium in the presence of competing cations, namely Ca^{2+} and K^+ . Therefore, the chemistry of stormwater and the surrounding environment should be incorporated into the design considerations of SCMs for nitrogen removal. Based on column observations, ZT has a significantly higher capacity (0.45 mg $\text{NH}_4^+\text{-N/g}$ ZT for NaCl) for ammonium removal than CA (0.33 mg $\text{NH}_4^+\text{-N/g}$ CA) at 2.5 mg/L $\text{NH}_4\text{-H/L}$, and it can be mixed with other less expensive media, such as sand, for more economical field applications. Preliminary field estimates suggest a life-span of 216 months for a media depth of 40 cm for ZT alone.

For CA, no significant difference in the performance of the media under wet/saturated - dry/unsaturated conditions compared to continuous columns could be observed, while the wet/saturated - dry/unsaturated ZT column showed less removal capacity for ammonium (0.20 mg/g ZT for the wet/saturated-dry/unsaturated run vis-à-vis 0.25 mg $\text{NH}_4^+\text{-N/g}$ ZT for continuous run) for 75 treated bed volumes. Increase in the effluent ammonium concentration, in the range of 0.2 to 1.7 mg $\text{NH}_4^+\text{-N/L}$, was observed in the samples collected immediately after the dry/unsaturated period for both media.

Contact time, t_c , was found to play an important role in ammonium removal by both media. Columns operating at higher velocities of 42 cm/h had low removal efficiency (13% for CA and 24% for ZT) compared to those at 8.3 cm/h (74% for CA and 71% for ZT).

Finally, variations in the effluent ammonium concentrations were found to be significant in cases when a reduction in the influent ammonium concentration occurs. The time and extent of desorption was also found to increase from 2 hours to 24 over the course of three weeks. This observation is a shortcoming of sorption/cation exchange media, where a reduction in the influent concentration shifts the approach to equilibrium and results in desorption of ammonium ions.

Despite the release of NH_4^+ -N observed during the variable influent ammonium concentration studies, ZT remains highly effective in ammonium removal because of its higher capacity in the presence and absence of competing cations, and its removal efficiency during the faster infiltration rate of 42 cm/hr.

The use of ZT is recommended for a nitrogen-focused stormwater SCM. The design recommendations for implementing this media within a filtration-based SCM depended on the site and conditions of the SCM, and the chemistry of stormwater. Nevertheless, a contact time of 50 minutes is desired for optimum removal. Reducing this value to 30 minutes, results in lowering ammonium removal efficiency by 20%.

7. Characterizing Laboratory-Scale Clinoptilolite bio-active sorption columns for Removal of Ammoniacal Nitrogen in Simulated Stormwater Runoff.

Introduction

Nitrogen in stormwater runoff has become one of the main causes of impairment of the aquatic habitat (Abal et al., 2001, Galloway et al., 2003, Harris et al., 1996, EPA, 2000, Dodd et al., 2009). Excess nutrients, particularly nitrogen loading to the receiving waters have caused eutrophication, hypoxia, loss of biodiversity, and has depreciated the aesthetic and recreational values of the nation's waters (Gray, 2000, "Chesapeake 2001, Galloway et al., 2003, Dodd et al., 2009). Stormwater control measures (SCMs) have aimed to reduce pollutant loadings associated with stormwater runoff. While SCMs have been effective in reducing certain pollutants, such as heavy metals, and suspended solids, nitrogen removal was found to be variable, and at times export of nitrogen has been observed (Davis et al., 2001, 2003, Hsieh and Davis, 2005, Fletcher et al., 2007, Hunt et al., 2006, Li and Davis, 2014).

The challenge in treating nitrogen lies partly in its diverse speciation and the differences in the corresponding susceptibility of each nitrogen form to treatment methods. Nitrogen can enter runoff as organic nitrogen (ON) in dissolved and particulate forms, ammonium (NH_4^+), and nitrate (NO_3^-) (Duncan, 1999, Tiefenthaler et al., 2000, Taylor et al, 2005, Kayhanian et al., 2007, Collins et al., 2010, Li and Davis, 2014). High ammonium concentrations often occur during anoxic/ reducing conditions, or organic pollution, while high nitrate concentrations are associated with urban areas (Gibb, 2000). The fate of nitrogen in SCMs is directly influenced by

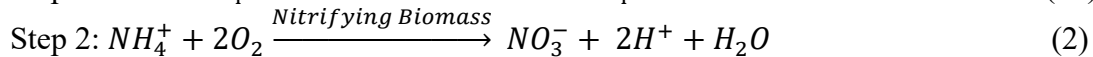
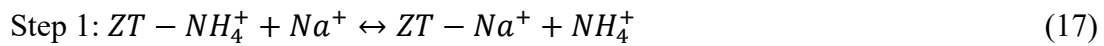
the nitrogen cycle. In short, ON can be degraded and mineralized to produce ammonium, and ammonium is in turn nitrified in aerobic environments (Hunt et al., 2006, Hatt and Fletcher, 2009, Passport et al., 2009, Rosenzweig et al., 2011, Li and Davis, 2014). This cycle ultimately results in the transformation of ON and NH_4^+ -N to NO_3^- . Nitrate has low attenuation in SCMs. Therefore, the treatment of nitrogen requires the capture and mineralization of ON, oxidation of incoming and mineralized ammonium, and finally reduction/denitrification of NO_3^- to N_2 .

As in municipal wastewater treatment, a nitrification-denitrification process can be an effective approach, but the removal efficiency within the SCM is contingent on nitrification of the influent ON and NH_4^+ to nitrate prior to reaching the anoxic zone. Additionally, SCMs are prone to many fluctuations, such as different pollutant and flow loads, and different wet/saturated- dry/unsaturated cycles, which could limit biological processes, including nitrification (Sansalone et al., 2005). Recently, a sorption/biological filtration retrofit was suggested as illustrated by Figure 8 (Chapter 5), where ion exchange/sorption combined with nitrification was proposed to be beneficial, particularly during inhibitory conditions for nitrification, such as low temperature (Water Environment Federation, 1998, Kim et al., 2005), and/or shock loads (Krüner and Rosenthal, 1983, Qui et al., 2010).

Combining the two processes can benefit the performance of the sorptive media as well. Testing done in simulated wet/ saturated- dry/unsaturated conditions and fluctuating influent NH_4^+ indicated that while high removal was obtained during shock/peak ammonium influent concentrations, desorption occurred during drops in the influent NH_4^+ , as well as lower removal immediately after the simulated dry/unsaturated periods in abiotic clinoptilolite zeolite (ZT) columns (Chapter 6). Moreover, sorption/nitrification filters can be advantageous as with nitrification of dissolved ammonium, NH_4^+ can be released from the surface to compensate for

the drop in the ammonium concentration, leading to the regeneration of some of the sites on ZT. This regeneration can greatly benefit the operation efficiency as per previous research 50 – 60% of the cost associated with ion exchange is attributed to the chemical regeneration of media (Koon and Kaufmann, 1971).

This process of biological regeneration of ZT through nitrification has previously been studied in wastewater treatment, where exhaustion of media for NH_4^+ is followed by concurrent biological regeneration (Semmens et al., 1977, Lahav and Green, 1997). Equations 2 and 13 are used to summarize the steps required for biological regeneration (Semmens et al., 1997, Lahav and Green, 1997).



The use of a simultaneous sorption and nitrification column for wastewater treatment has also illustrated enhanced ammonium removal (Miladinovic and Weatherley, 2008). Gisvold et al., (2000) also used zeolite-containing expanded clay aggregates for ammonium removal from wastewater, and demonstrated continuous regeneration of media by nitrification without any changes to the media sorption capacity after 8 months of operation. The predominant focus of ammonium removal using ZT has been on wastewater, with most of the studies using $[\text{NH}_4^+\text{-N}] \geq 20 \text{ mg/L}$ (Semmens et al., 1977, Booker et al., 1996, Lahav and Green, 1997, Gisvold et al., 2000, Miladinovic and Weatherley, 2008), and there is a need to investigate the performance of a combined sorption and nitrification under SCM conditions.

The effectiveness of the combined sorption/nitrification SCMs also depends on the nature of media. Zeolite groups, including clinoptilolite and chabazite are noted to provide excellent framework for the growth of nitrifiers, and the addition of ZT to aerobic/anoxic reactors has resulted in higher ammonium removal rates (Gisvold et al., 2001, He et al., 2007, Wu et al, 2008,

Miladinovic and Weatherley, 2008, Smith, 2011). Recent work in stormwater has illustrated that clinoptilolite exhibits high ammonium removal capacity, rapid removal (within 30 min), and high potential for extractability of sorbed ammonium for potential nitrification (chapter 5 and chapter 6). Nevertheless, these works have focused on batch and column studies in an abiotic setting.

The objective of the current work is to expand on the previous studies of implementing clinoptilolite (ZT) as bioactive sorptive media in SCMs. To assess the performance of ZT in filtration-based SCMs, typical field conditions were used, including simultaneous sorption and nitrification, sorption and nitrification in wet/saturated – dry/unsaturated, and under variable ammonium loadings. Characterization of this media under these conditions was then investigated according to the following:

1. Investigating sorption and nitrification potential in continuous ZT columns, where simultaneous sorption and nitrification of NH_4^+ can take place.
2. Investigating the performance of nitrification-sorption ZT column in wet/saturated-dry/unsaturated conditions and monitoring the changes in the effluent nitrogen concentrations.
3. Monitoring the performance of nitrification-sorption ZT column under fluctuating loadings, for both increase and decrease in the influent ammonium concentrations

Results and Discussion

ZT performance in continuous nitrifying columns

The performance of a bio-active continuous ZT column at $U = 8.3$ cm/h for 2.5 and subsequently 5 mg NH_4^+ -N/L at 0.03 M NaCl is described here.

Performance of ZT for influent concentration of 2.5 mg NH_4^+ -N/L at 0.03 M NaCl.

This section investigated the performance of a sorption-nitrification ZT column under continuous feed of 2.5 mg NH_4^+ -N/L at 0.03 M NaCl (Figure 15). The abiotic portion of this experiment was discussed in a previous chapter for $t = 0 - 37$ days (0 - 387 bed volumes).

Nitrate production was observed immediately prior to the exhaustion of the media (327 bed volumes (BV) and 31 days of operation), where the effluent NO_3^- -N increased from 0.1 – 1.2 mg/L for 327 to 687 BV (31 – 66 days). From 687 – 822 BV (67 – 79 days), the effluent ammonium and nitrate concentrations are comparable and exhibit near constant values, and the column appears to operate at steady state conditions. The average concentration values of ammonium and nitrate are presented in Table 9. While a simultaneous sorption-nitrification column was found to reduce the effluent ammonium concentrations, it did not reduce the net nitrogen output of the column.

Table 9. Nitrification rate constants for two different feed concentrations in continuous setting, Rates obtained after steady state was reached for both concentrations.

C_{in} [mg NH_4^+ -N/L]	$[\text{NH}_4^+$ -N] [mg/L]	$[\text{NO}_3^-$ -N] [mg/L]	ΣN_{out} [mg/L]	k_1 [min^{-1}]	k_0 [$\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$]
2.5	1.3 ± 0.1	1.2 ± 0.1	2.6 ± 0.1	-0.018	-0.032
5	3.5 ± 0.4	1.7 ± 0.3	4.9 ± 0.7	-0.009	-0.039

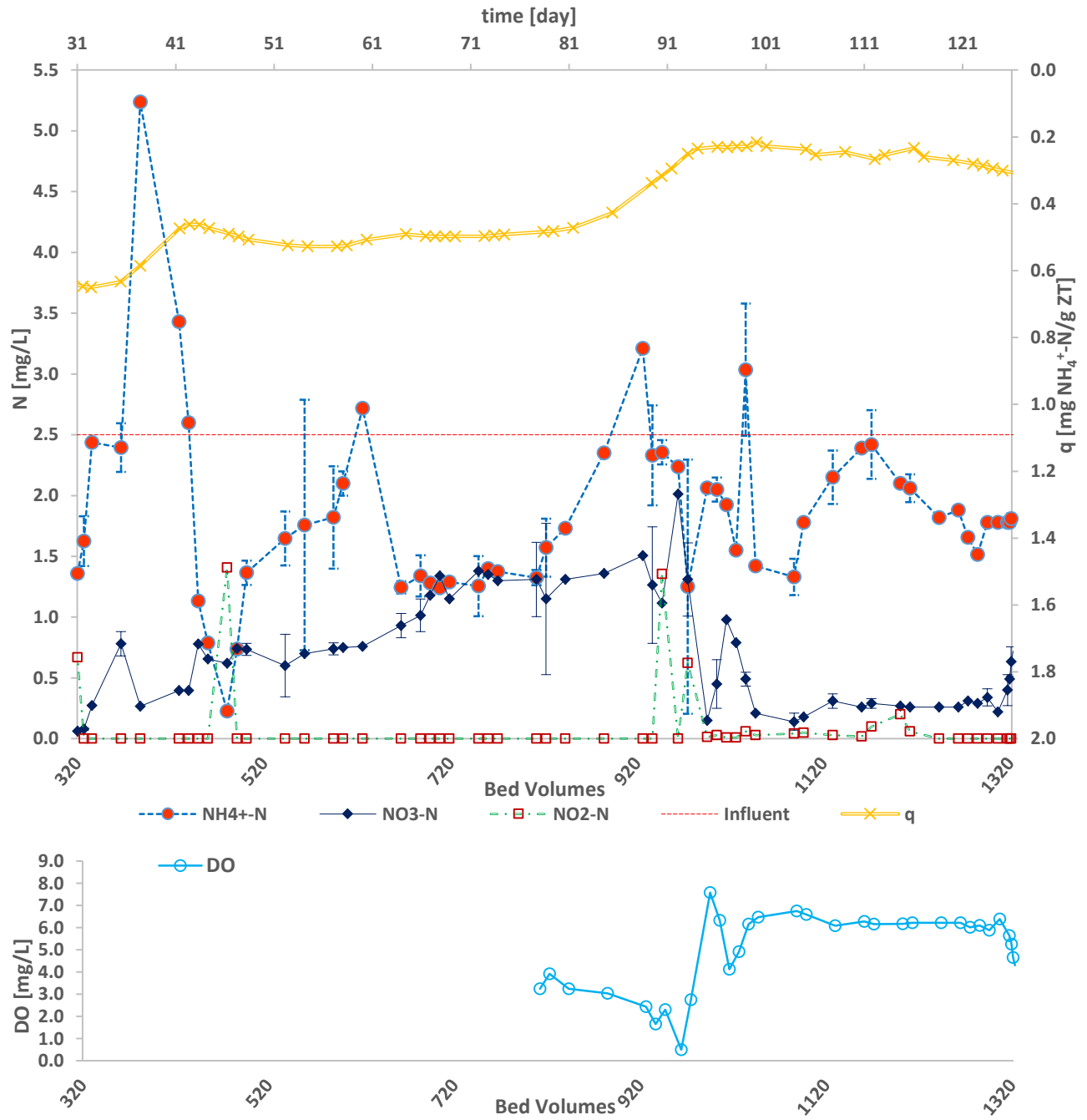


Figure 15. The performance of ZT in continuous setting in 0.03 M NaCl background electrolyte for C_{in} of 2.5 at $T = 22 \pm 4^\circ\text{C}$. The average values and the standard deviations for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ are reported where at least duplicate samples were collected per day.

During the steady state phase, the net effluent nitrogen ($\sum N_{\text{out}} = \text{NH}_4^+ \text{-N} + \text{NO}_3^- \text{-N}$) was nearly equal to the influent ammonium loading, with an average of 2.6 ± 0.1 mg N/L. The q calculated reached an asymptote at 0.49 ± 0.01 mg $\text{NH}_4^+ \text{-N/g ZT}$. On average, 49% of the influent ammonium transformed to nitrate, and based on mass balance considerations, the disappearance of ammonium corresponds well with the production of nitrate in the column. The data set for the 687 – 822 BV were used to quantify rate constants for first (equations 13 – 14) and zero order rate (equations 15 – 16) in Table 9. While a simultaneous sorption-nitrification column was found to reduce the effluent ammonium concentration, it did not reduce the net nitrogen output of the column.

Following a 13 day steady state period, the effluent $\text{NH}_4^+ \text{-N}$ began to increase from 822 to 926 BV, although the $\text{NO}_3^- \text{-N}$ concentration remained at 1.2 mg/L. The net effluent nitrogen was found to be greater than that of the influent, which caused a decrease in the calculated q from 0.48 to 0.25 mg $\text{NH}_4^+ \text{-N/g ZT}$. It is possible that with continued nitrification, some of the ammonium from the surface is desorbed to compensate for the loss of ammonium by nitrification. This has previously been observed by Smith, (2011). The nitrate concentration finally decreased from 995 to 1320 BV, and $\sum N_{\text{out}} \leq 2.5$ mg $\text{NH}_4^+ \text{-N/L}$. This reduction in the effluent nitrate coincided with a pump malfunction at 1279 which resulted in high flow rates ($U > 60$ cm/h). This high flow rate washed a small fraction of media (i.e., < 0.5 g) out of the column, and could have potentially resulted in the washout of biomass from the column.

DO measurements indicated a stoichiometric relationship of 1.68 ± 0.32 moles O_2 consumed/mole $\text{NO}_3^- \text{-N}$. This value is close to the stoichiometric value of 2 moles O_2 consumed/mole $\text{NO}_3^- \text{-N}$ needed for nitrification. It is likely that the consumption of DO was due to nitrate production within the column.

The maximum nitrate concentration observed for this experiment was 2.0 mg NO₃⁻ -N/L. Overall, it appears that with continued nitrification of ammonium, desorption of ammonium from the surface could occur in response to the ammonium loss. A depletion of ammonium ions from the pore solution, can result in the release of ammonium from the surface, which also results in regeneration of ZT sites. However, this phenomena did not result in a reduction in the effluent nitrogen concentrations.

The calculated q (0.63 mg NH₄⁺-N/ g ZT), particularly at the time of exhaustion are significantly higher than those for abiotic batch and column studies (0.21 mg NH₄⁺-N/g ZT). Investigating the effect of the presence of a nitrifying biofilm on ZT capacity, Park et al. (2002) reported that the presence of a biofilm on ZT did not reduce media capacity for ammonium removal, while Wen et al. (2006) reported similar findings for fine (1 – 3.2 mm), whereas in coarser ZT (8.0 – 15 mm), the ion exchange sorption capacity reduced by 22% in batch systems. It is unclear what has caused the increase in the media capacity. It is possible that some of the ammonium is utilized for biomass generation, and the observations made here suggest that nitrification resulted in a higher q value.

Enhanced ammonium removal in combined nitrification/sorption column studies has previously been indicated for ZT (Gisvold et al., 2000, Miladinovic and Weatherley, 2007). It should also be noted that the current study reports the performance of a simultaneous sorption/nitrification column after the media had exhausted. Increasing the concentration can be useful as it enables higher capacity of media for ammonium removal in a sorption/nitrification column prior to media exhaustion.

Performance of ZT for influent concentration of 5 mg NH₄⁺-N/L at 0.03 M NaCl

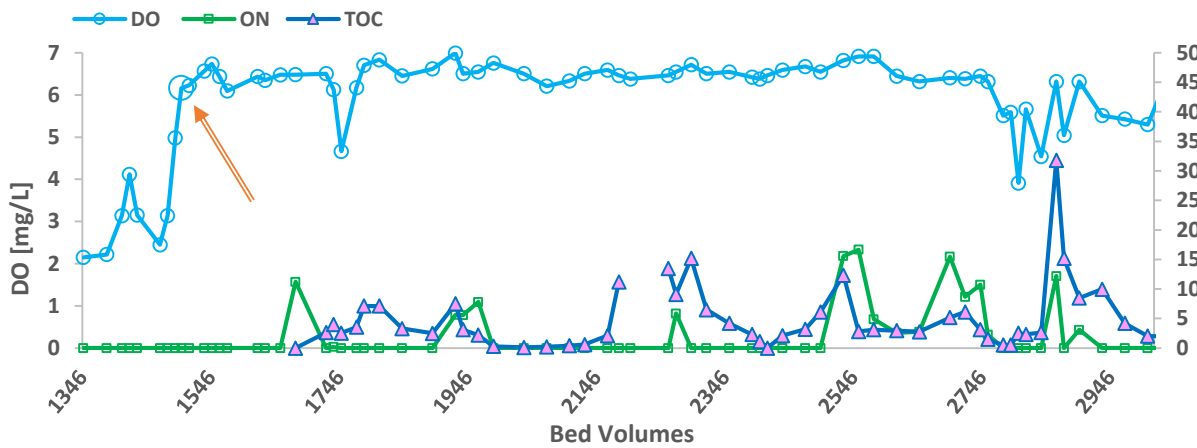
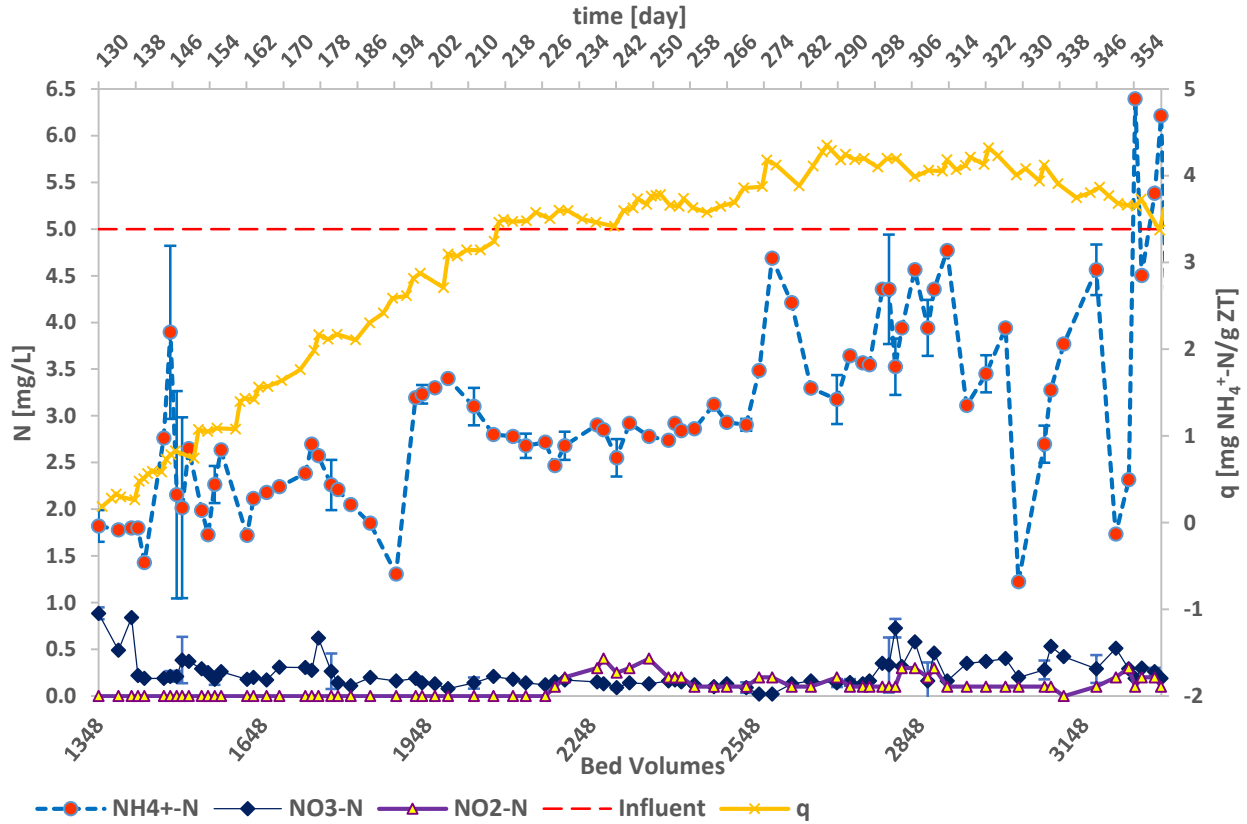
The influent ammonium concentration was increased from 2.5 to 5 mg NH₄⁺-N/L at 1346 bed volumes (128 days). Figure 16a summarizes the performance of the media prior to exhaustion with respect to NH₄⁺-N, while Figure 16b presents the data after media exhaustion. Influent aeration began for this column at 1481 Bed volumes (144 days).

As expected, increasing C_{in} resulted in higher sorption capacity, particularly from 1736 – 3299 BV. Low effluent nitrate concentrations were measured (0.2 ± 0.1 mg NO₃⁻-N/L), with an average NH₄⁺-N of 2.7 ± 0.7 mg/L. Comparing nitrate production for the two different ammonium loadings indicated that smaller nitrate production took place for C_{in} = 5 mg NH₄⁺-N/L, particularly from 1719 – 2569 BV. The low nitrate production could be due to the possible washout of the nitrifiers during the mentioned pump malfunction. The media under higher ammonium loading exhausted at 3003 BV and 287 days, equivalent to treating 1345 BV and 158 days under feeding of 5 mg NH₄⁺-N/L in 0.03 M NaCl. The *q* values are significantly higher than that observed during the batch experiments (1.6 mg NH₄⁺-N/g ZT for combined sorption/nitrification vis-à-vis 0.5 mg NH₄⁺-N/g ZT).

Upon exhaustion of the media, the effluent NH₄⁺-N shows some oscillations, but tends to be close to that of the influent. The effluent nitrate concentration can be described in three parts. From 3004 – 3365 BV, NO₃⁻-N averaged 0.4 ± 0.1 mg NO₃⁻-N/L. From 3366– 4002 BV, the nitrate concentration increased to 1.2 mg NO₃⁻-N/L. At 4013 BV, an increase in the nitrate concentrations is observed, which is likely associated with the higher aeration and an increase in the ambient temperature from 21 to 26°C. The net export of nitrogen from the column after media exhaustion (i.e., N_{out} > 5 mg N/L) occurs for 3427 – 4122 BV. The ammonium

concentration in this range is close to that of the influent ($4.5 \pm 0.9 \text{ mg NH}_4^+\text{-N/L}$), and it seems likely that some of the ammonium from ZT was desorbed in response to nitrification.

(a)



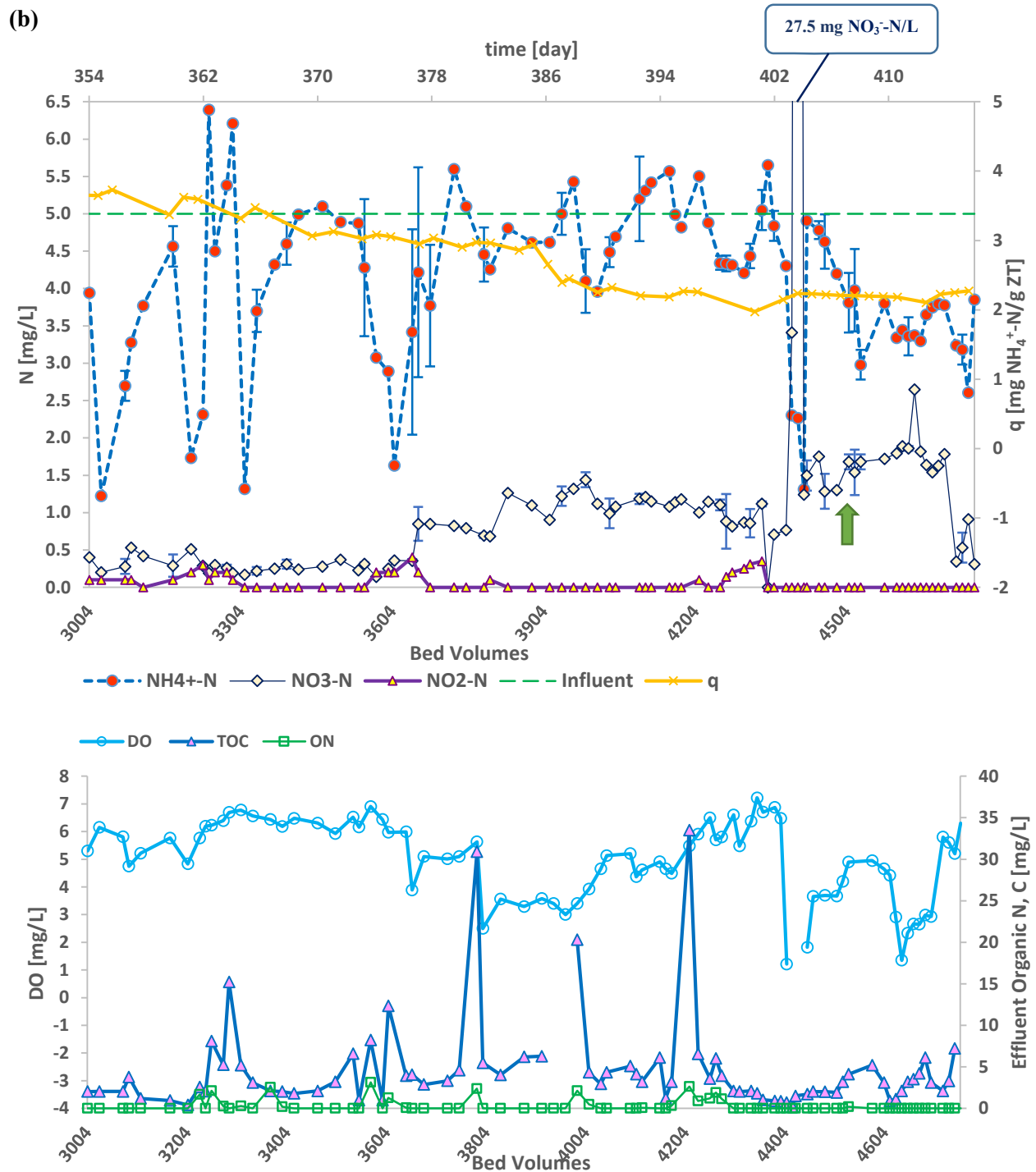


Figure 16. The performance of ZT in continuous setting in 0.03 M NaCl background electrolyte for the increased C_{in} from 2.5 to 5 mg $\text{NH}_4^+\text{-N/L}$ at 1379 bed volume (129 days) at $T = 22 \pm 4^\circ\text{C}$ before (a) and after (b) exhaustion of the media. The average values and the standard deviations for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ are reported where at least duplicate samples were collected per day. The orange arrow at 1482 bed volumes in Figure 16a marks the point of aeration of the influent, and the arrow in Figure 16b marks the start point from which nutrients were added to the column continuously.

Steady state conditions appear for 4059 – 4277 BV, with average concentrations of 3.5 ± 0.4 mg NH_4^+ -N/L, 1.7 ± 0.3 mg NO_3^- -N/L, and a calculated q of 2.63 ± 0.05 mg NH_4^+ -N/g ZT. The average ratio of consumed DO to nitrate was found to be 1.72 ± 0.64 mol O_2 / mol NO_3^- -N, which is close to the stoichiometric value of 2 mol O_2 / mol NO_3^- -N. In Figure 16 a and b, spikes in the effluent TOC can be observed, which could have resulted from possible sloughing and/or lysing of cells; subsequent decomposition of organic carbon also requires oxygen. Comparing the effluent TOC and DO values, in Figure 17b, an increase in the TOC (4.6 to 20.9 mg/L) is immediately followed by a reduction in the DO value from 5.6 to 2.5 mg/L at 3786 BV. The effluent nitrate concentration is also increasing at this point. Examining the change in the effluent DO and nitrate, 2.42 mmol O_2 was consumed per mmol NO_3^- produced, which was greater than the stoichiometric oxygen to nitrate ratio. It thus appears that at specific times, release of TOC could have also caused a reduction in the effluent DO. Nevertheless, since only few such instances are found in the collected data, it appears that the disappearance of DO corresponds strongly with nitrification.

Effluent pH was also measured, with an average pH of 5.1 ± 0.2 , and was found to reduce with increasing nitrate concentrations. During the nitrification process, 2 meq of H^+ is produced for 1 meq NO_3^- -N being formed, hence this inverse relationship could be indicative of produced acidity during nitrification. A direct stoichiometric relationship could not be obtained here because of the ability of the ZT surface to neutralize some of the produced acidity.

The net nitrate production for 2.5 and 5 mg NH_4^+ -N/L did not differ significantly from one another (1.3 ± 0.1 mg NO_3^- -N/L vis-à-vis 1.7 ± 0.3 mg NO_3^- -N/L for 2.5 and 5 mg NH_4^+ -N/L, respectively). First and zero order rate equations were assumed for each of the runs receiving two influent concentrations. The rate coefficients obtained for 2.5 and 5 mg NH_4^+ -N/L

for first order were found to be different, suggesting a smaller rate of nitrification for $C_{in} = 5 \text{ mg NH}_4^+\text{-N/L}$, and k_1 of -0.009 min^{-1} , compared to -0.018 min^{-1} observed for $C_{in} = 2.5 \text{ mg NH}_4^+\text{-N/L}$. Nevertheless, similar zero-order rate constants (k_0 of -0.032 and $-0.039 \text{ mg.L}^{-1}.\text{min}^{-1}$ for $C_{in} = 2.5$ and $5 \text{ mg NH}_4^+\text{-N/L}$, respectively) were observed. It is possible that over the course of the experiment, the nitrification process has changed particularly as a result of pump malfunction and the long duration of experiment. Despite these changes, the zero order renders similar results, and it is likely that nitrification in ZT sorption columns observed in this study is zero order.

For both C_{in} values, an increase in the nitrate production could be observed when the effluent $\text{NH}_4^+\text{-N}$ approached that of the influent. This is particularly evident for $5 \text{ mg NH}_4^+\text{-N/L}$, where effluent ammonium concentrations of 2.7 mg/L resulted in little nitrate concentrations ($< 0.3 \text{ mg NO}_3^-\text{-N/L}$). Semmens et al., (1977) found that the rate of nitrification was independent of the ammonium concentration for $\text{NH}_4^+\text{-N} > 20 \text{ mg/L}$ but was first order for $\text{NH}_4^+\text{-N} \leq 20 \text{ mg N/L}$. The concentrations tested here are much smaller than $20 \text{ mg NH}_4^+\text{-N/L}$; it is possible that as the surface becomes increasingly occupied with ammonium, any loss of ammonium by nitrification in the pore solution is offset by desorption/release of ammonium from the surface, such that the surface acts as a reserve of ammonium by the nitrifiers. Once the surface becomes depleted, the sites are freed and can engage in ammonium sorption, making the simultaneous nitrification/sorption ZT filter an appealing option for bioretention cells.

Effects of Wet/saturated -Dry/unsaturated conditions on Performance of ZT in a sorption-nitrification system

Previous assessments on the performance of a sorption ZT column under wet/saturated -dry/unsaturated conditions indicated higher ammonium in the effluent after the dry/unsaturated

period, for simulated 7 wet/saturated - dry/unsaturated cycles (Chapter 6). With progression of the experiment, nitrate was detected in the effluent from cycle 8, the results of which are discussed in this chapter. Figure 17 and 18 summarize findings of this study for wet/saturated-dry/unsaturated wet/saturated dry/unsaturated cycles 8 to 56, with the data presented per cumulative BV of synthetic stormwater (Figure 17), and as real time (Figure 18). As displayed in Figures 17 and 18, the start of the nitrifying/sorptive experiment is marked by no change in the effluent NH_4^+ after the dry/unsaturated period ($0.3 \text{ mg NH}_4^+\text{-N/L}$), and an increase in the nitrate concentration from 0.0 to $0.8 \text{ mg NO}_3^-\text{-N/L}$. The greatest effluent nitrate (i.e., $\text{NO}_3^-\text{-N} > 4.5 \text{ mg/L}$) and ammonium are observed for cycles 9 and 10, followed by smaller nitrate concentrations. At the end of cycle 10, a malfunction to the pump occurred which could have upset the system. For these two cycles, the net nitrogen export was greater than that of the influent, which resulted in reduction of the q (0.19 to $0.05 \text{ mg NH}_4^+\text{-N/g ZT}$).

This period of export is followed by lower ammonium and nitrate concentrations in the subsequent cycles (98 – 107 BV), which could have resulted from adsorption onto freed sites on ZT. This trend is repeated for other cycles where high export ($\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$) was followed by subsequent samples with lower N concentrations, examples of which occur at 158 BV (cycle 16), 325 BV (cycle 32), 476 BV (cycle 42). For the samples collected after the dry/unsaturated period, nitrate concentrations appear to follow an overall inverse trend compared with ammonium, and in regions where high nitrate concentrations are observed, smaller ammonium was detected in the same sample or those subsequently collected. This is particularly evident for 495 – 660 BV.

The column exhausts after treating 457 BVs, equivalent to 48 cumulative wet/saturated days, and 41 simulated wet/saturated events. At the time of exhaustion q was calculated to be

0.69 mg NH_4^+ -N/L, which is within 6% of the continuous run (0.65 mg NH_4^+ -N/g ZT), although the continuous column exhausted after 387 BV. Based on the student t-test for $\alpha=0.05$, the intermittent column had significantly less NH_4^+ -N in the effluent and higher effluent NO_3^- -N. Nitrate production was observed for the 8th simulated wet/saturated-event, which corresponds to 34 days from the start of the experiment, and is comparable to the results observed for the continuous column with nitrate concentrations first appearing after 31 days of operation. The total organic carbon of the samples for 237 – 688 BV were measured, where spikes in the effluent TOC were detected, indicating possible wash-out of biomass following the dry/unsaturated period. In previous studies, Baldwin and Mitchell (2000) and Scholz et al. (2002) suggested that during the dry/unsaturated period, release of NH_4^+ -N bound to cells can occur as a result of death of the bacterial community.

Overall, the performance of ZT under wet/saturated- dry/unsaturated conditions was marked by oscillations in the effluent ammonium and nitrate content, with an overall increase in the export of ammonium for samples with smaller nitrate concentrations. Furthermore, with progression of the experiment, the nitrate concentrations in the effluent increased, while ammonium concentrations decreased.

During the course of the study the samples exhibiting a decrease in the NH_4^+ -N after the dry/unsaturated period tended to correspond to an increase in NO_3^- -N, with the possible implication that with higher nitrate production, a reduction in the effluent ammonium concentration is observed. Moreover, the duration of the dry/unsaturated period did not seem to significantly affect the performance of the column. In a previous study, Cho et al. (2009) reported enhanced removal of ammonium after dry/unsaturated periods in soil columns covered with vegetation, with results indicating nitrification between storm events. Hatt et al. (2007) also

reported spikes in the effluent nitrogen as total nitrogen, NO_x , and NH_4^+ , which increased with the duration of dry/unsaturated period. The effect of dry/unsaturated period leads to more oxic conditions, resulting in mineralization of organic matter and nitrification, thereby releasing NH_4^+ and NO_3^- (McComb and Qui, 1997).

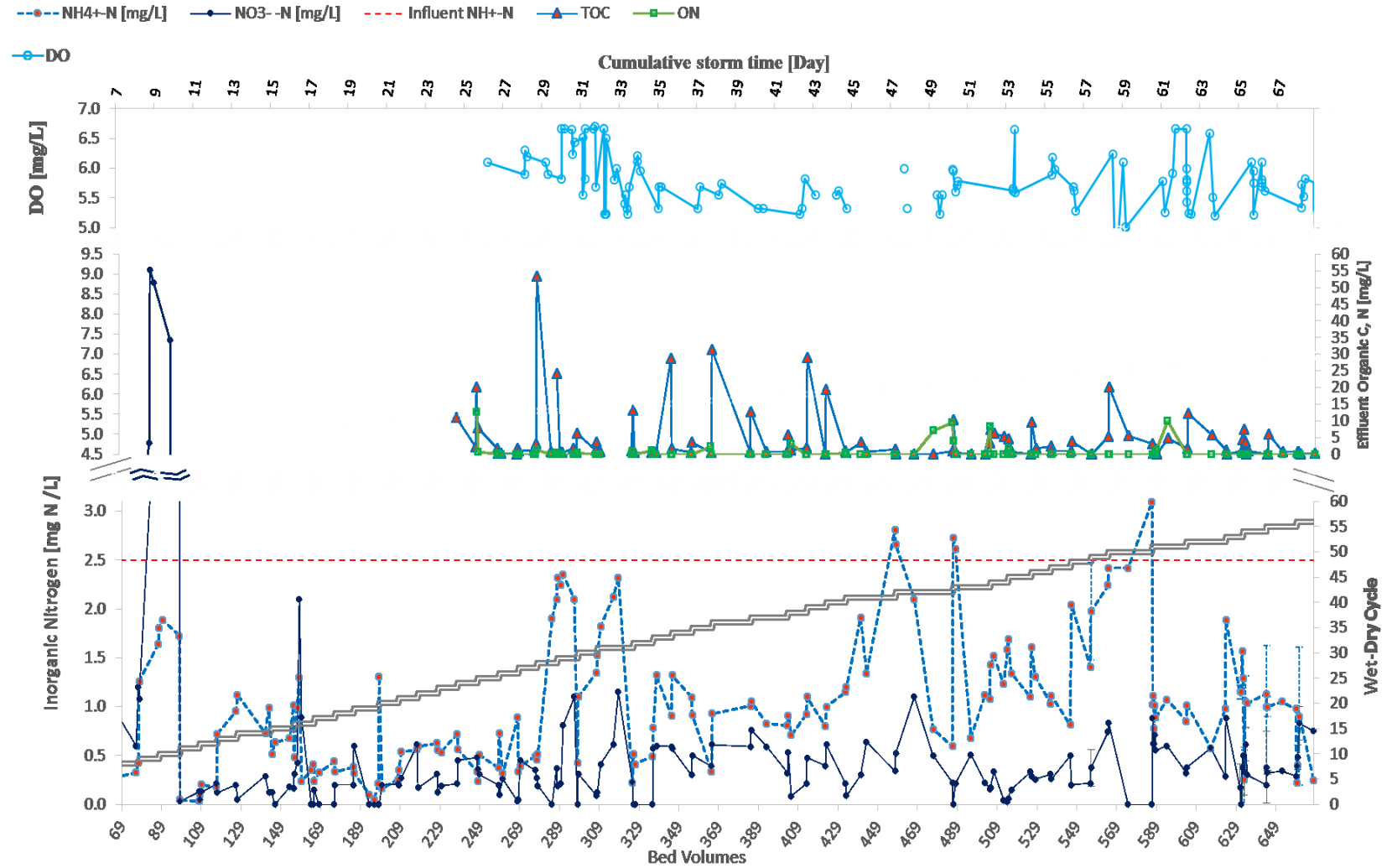


Figure 17. The performance of a sorption-nitrification ZT column under wet/saturated-dry/unsaturated conditions from cycle 8 – 56 for $C_{in} = 2.5 \text{ mg NH}_4^+\text{-N/L}$ at 0.03 M NaCl and $T = 22 \pm 4^\circ\text{C}$ presented based on bed volumes treated from the start of the experiment.

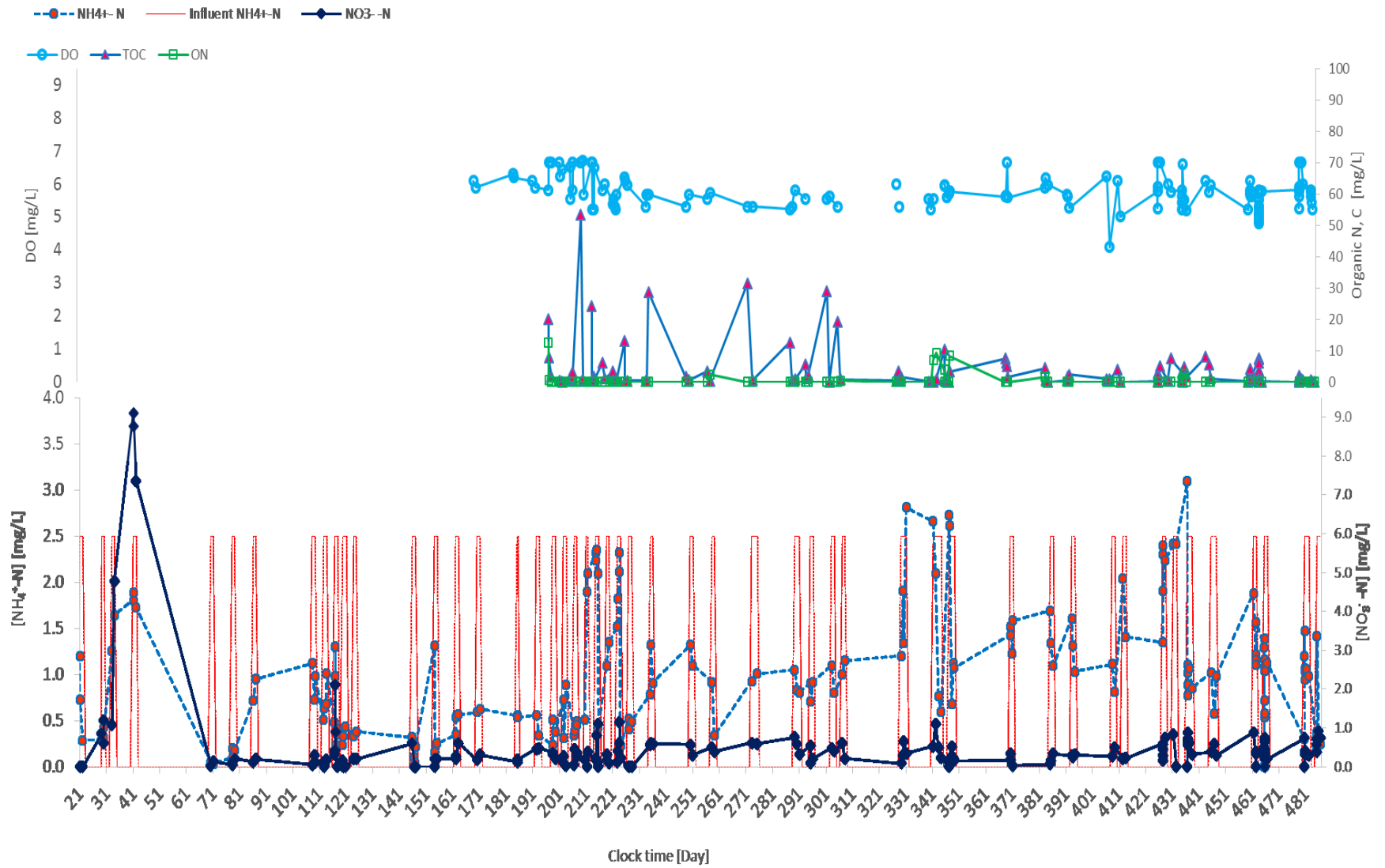


Figure 18. The performance of a sorption-nitrification ZT column under wet/saturated-dry/unsaturated conditions from cycle 8 – 56 for $C_{in} = 2.5 \text{ mg NH}_4^+\text{-N/L}$ at 0.03 M NaCl and $T = 22 \pm 4^\circ\text{C}$ presented based on clock time from the start of the experiment.

Detailed profiles of the effluent concentrations for a typical wet/saturated-dry/unsaturated cycle appear in Figure 19. An increase in the effluent nitrate concentration at time zero, corresponding to the sample collected immediately after the start of the wet/saturated event, is observed. This increase, particularly for Figure 19a (0.2 to 0.7 mg NO₃⁻-N/L) and 19b (0.2 to 0.7 mg NO₃⁻-N/L) is likely caused by nitrification during the dry/unsaturated period, as for both cases a decrease in the ammonium concentration can also be seen, from 3.1 to 1 and 1.1 to 0.3 mg NH₄⁺-N/L for Figure 19a and 19b, respectively. Nevertheless, the nitrate that is being produced is smaller than the reduction in the effluent ammonium concentration. It is possible that via nitrification some of the sites on ZT are regenerated, and some of the ammonium is being adsorbed by the media. Figure 19c, on the other hand, illustrates smaller changes in the effluent concentrations, with gradual increase in the effluent ammonium concentrations. Nitrate concentrations appear to reach steady values after the initial 60 minutes in Figure 19 a and b, which is similar to findings of Hsieh and Davis (2007) indicating wash-off of nitrate produced between storm events.

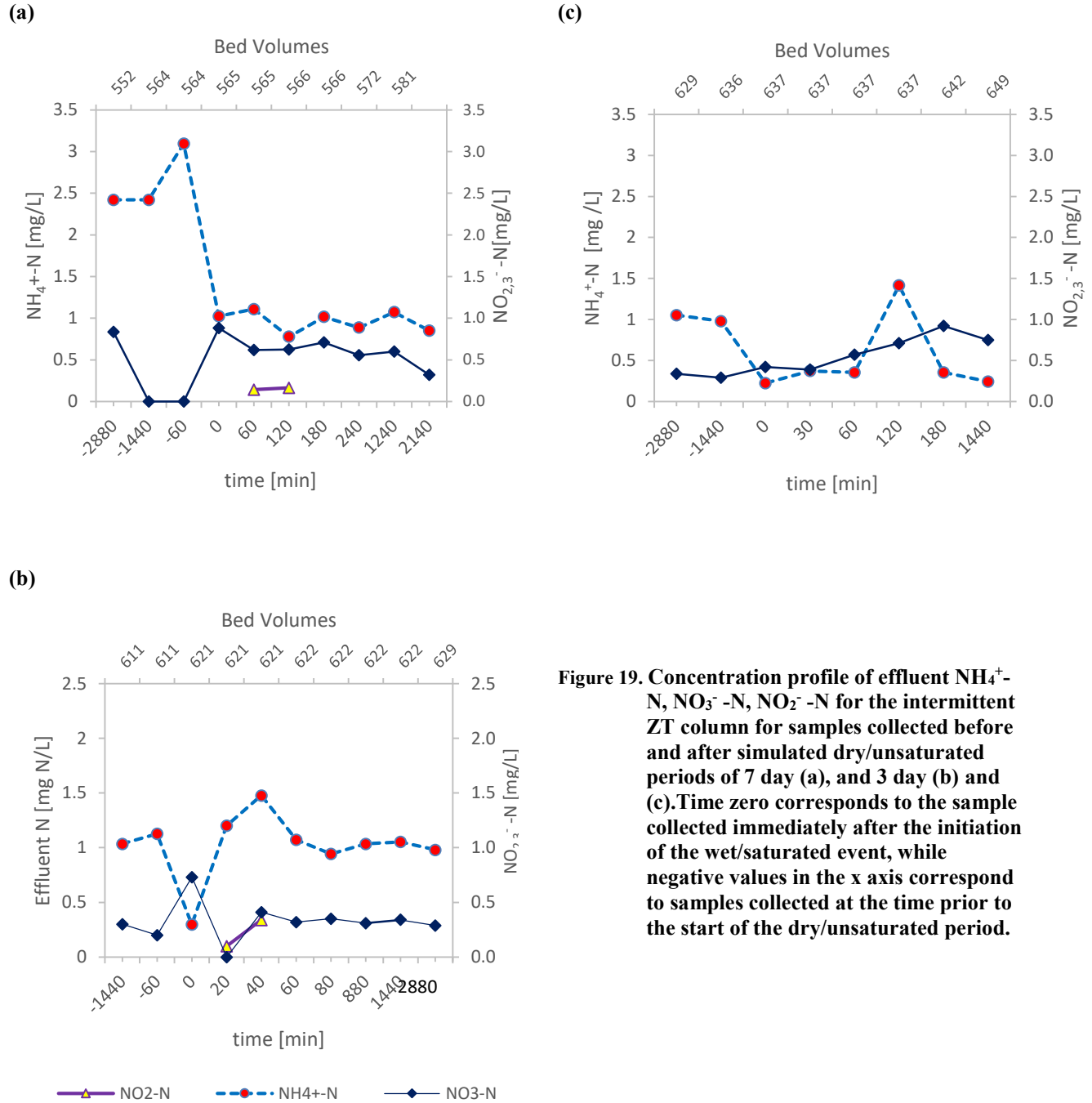


Figure 19. Concentration profile of effluent $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, $\text{NO}_2^-\text{-N}$ for the intermittent ZT column for samples collected before and after simulated dry/unsaturated periods of 7 day (a), and 3 day (b) and (c). Time zero corresponds to the sample collected immediately after the initiation of the wet/saturated event, while negative values in the x axis correspond to samples collected at the time prior to the start of the dry/unsaturated period.

Unlike the continuous run, the wet/saturated-dry/unsaturated column does not appear to reach steady state, or have consistent nitrate production. It is possible that the high concentrations of the TOC observed in this column signify loss of biomass, which could prevent the column from reaching mature nitrification. Nonetheless, only four of the wet/saturated events

exhibited effluent ammonium concentration $> 2.5 \text{ mg NH}_4^+ \text{-N/L}$ in wet/saturated-dry/unsaturated conditions, and it appears that with further nitrification, the performance of the intermittent column improves. The average oxygen consumed in the column was found to be $1.5 \pm 0.3 \text{ mol O}_2/\text{mol NO}_3^- \text{-N}$, which is well within the theoretical range observed for nitrification. The average effluent pH from this column was 5.8 ± 0.3 , and was found to have an inverse relationship with effluent nitrate, which is suggestive of nitrification process within the column.

To prevent disruption to the media and performance, moisture contents were measured at the end of the experiment for 3 and 5 day dry/unsaturated periods. The saturated media at the end of simulated storm event 57 was found to 34.4% moisture by weight. This moisture content of the media collected from the top 3 cm of the column was found to have reduced to 25.7% and 19.8% after 3 and 5 simulated dry/unsaturated days. Although the moisture content had reduced, it appears that during the simulated dry/unsaturated period, the media continues to retain a portion of its water content, which can potentially prevent the death of microorganisms. Reduction of the moisture content can also increase in the ionic strength of the pore solution. It should be noted that during the dry/unsaturated period air is passed through the up-flow column; since the media at the bottom receives fresh air, compared to the media at the top where air is expected to have mixed with the water content of the pores, it is possible that the media at the bottom of the column is less saturated with water compared to the media at the top end of the column.

Effect of step-changes in the influent $\text{NH}_4^+ \text{-N}$ on media performance

Changes in pollutant loading are one of the characteristics of stormwater runoff. A previous study investigating the effect of step-changes in the influent ammonium indicated that reduction in the influent concentration leads to desorption of ammonium, while increasing the

influent concentration resulted in high removal rates (Chapter 6). The data shown in Figure 20 represent the continuation of this study, showing both sorption and nitrification processes. Nitrate production occurred from 394 bed volumes, and smaller ammonium desorption was observed during influent concentration drops, particularly for 490 – 540 BV. From 783 BV, a high effluent TOC concentration of 28.7 mg/L is observed, indicating biomass wash-out at this time. Subsequently, for a concentration drop from 5 to 2.5 mg NO_3^- -N/L the effluent ammonium was found to be greater than that of the influent.

The results obtained in the remainder of the experiment, from 819 – 1249 BV indicate oscillations in the effluent NH_4^+ -N and low NO_3^- -N concentrations (< 0.4 mg NO_3^- -N/L). From 1338 bed volumes, however, higher nitrate concentrations are observed. A rise in the ammonium concentration is followed by a rise in the nitrate concentration. Moreover, when higher nitrate concentrations are observed, the extent of desorption (desorption assumed for $[\text{NH}_4^+\text{-N}]_{\text{out}} - [\text{NH}_4^+\text{-N}]_{\text{in}} > 0$) is smaller compared to desorption observed with no nitrification. The reduction in the influent concentration from 5 to 1 mg NH_4^+ -N at 1638 provides an example of this case, where a stepwise increase in the nitrate concentration from 0.1 to 0.7 mg NO_3^- -N occurs, resulting in the eventual reduction of NH_4^+ -N in the solution. Increasing the ammonium concentration from 1 to 2.5 mg NH_4^+ -N, however, is followed by an increase in the effluent ammonium and reduction of the nitrate concentration. Overall, the highest nitrate concentrations in this study correspond to 1 mg NH_4^+ -N/L influents, where desorption is expected to occur. However, nitrate concentrations and the influent and effluent ammonium concentrations do not strongly correlate.

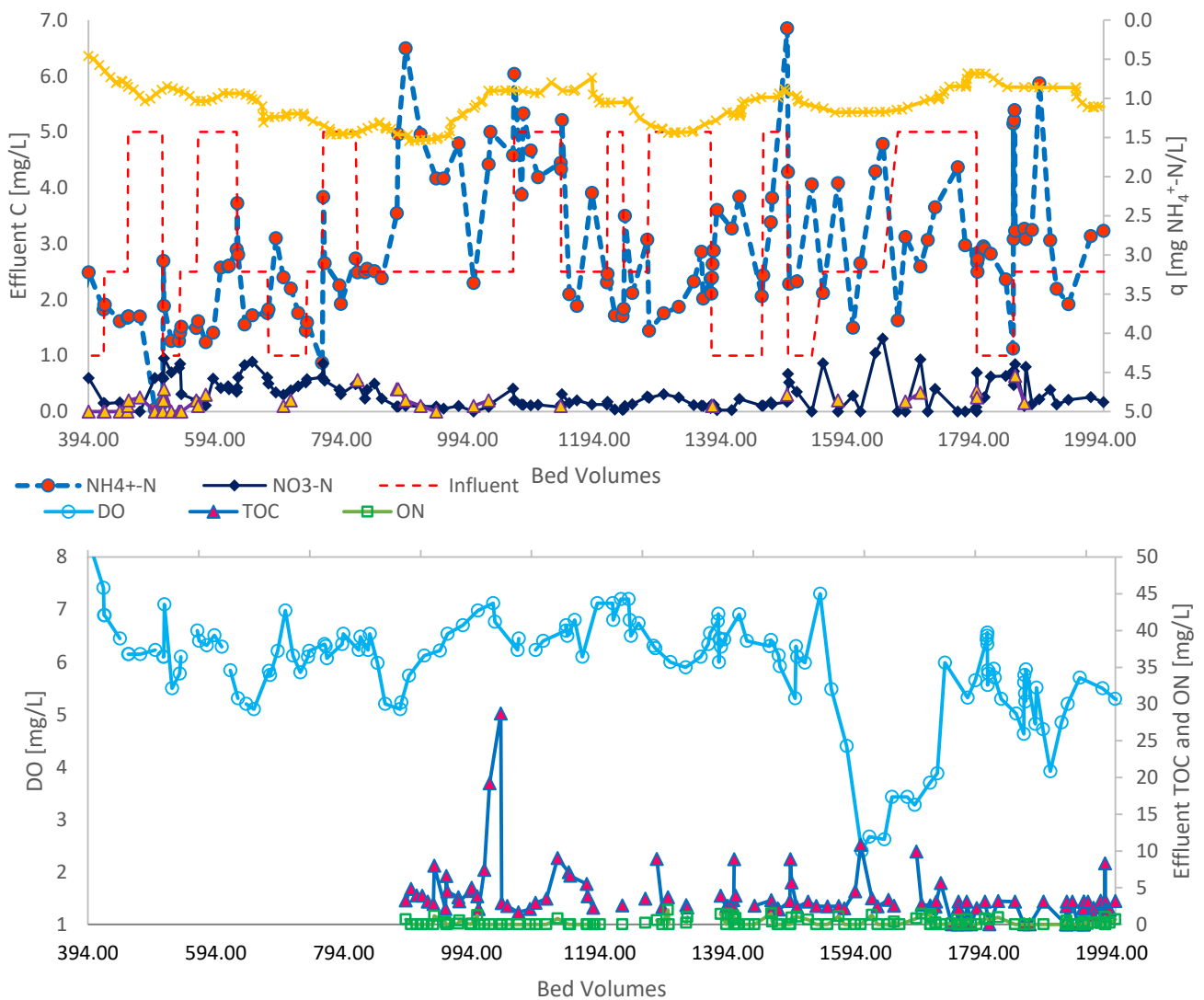


Figure 20. The performance of a sorption-nitrification ZT column under fluctuating ammonium loading of 5, 2.5, and 1 mg NH₄⁺-N/L at 0.03 M NaCl at T = 22 ± 4°C.

Overall this column responded well to high influent ammonium concentrations.

Ammonium removal tends to take place concurrent with sorption in response to an increase in the influent concentration. Previously reduction of the influent concentration in the sorption column was accompanied by release of ammonium sorbed (Chapter 6). However, a drop in the influent concentration for a sorption-nitrification column was accompanied by lower effluent

ammonium, compared to the sorption column, particularly for 394 – 733 BV. For 820 – 1289 BV lower nitrate production could be observed ($\text{NO}_3^- \text{-N} = 0.2 \pm 0.1 \text{ mg/L}$), which corresponded to high effluent ammonium ($[\text{NH}_4^+ \text{-N}]_{\text{out}}/[\text{NH}_4^+ \text{-N}]_{\text{in}} = 1.4 \pm 0.6$) Nevertheless, with further progression of the experiment, higher nitrate concentrations could be observed particularly for 1591 – 2133.

A detailed overview of the last cycle of step change for 1685 – 2185 BV appears in Figure 21. A drop in the influent concentration from 5 to 1 mg $\text{NH}_4^+ \text{-N/L}$ did not produce a pronounced change in the effluent ammonium concentration from 1810 – 1832 (3 days), after which nitrate concentrations begin to increase from 0.3 to 0.6 mg $\text{NO}_3^- \text{-N/L}$; this increase is accompanied by a decrease in the effluent ammonium concentrations, most likely caused by the desorption occurring in the previous days. Increasing the influent concentration from 1 to 2.5 mg $\text{NH}_4^+ \text{-N/L}$ causes increases in the effluent ammonium concentrations. The nitrate concentration averaged $0.75 \pm 0.3 \text{ mg NO}_3^- \text{-N/L}$ with these values decreasing from 1898 to 2101 BV. The results are indicative of nitrate production during periods of desorption. Although nitrification reduced the effluent ammonium concentration, it did not cause the effluent $\text{NH}_4^+ \text{-N}$ to be smaller than that of the influent during influent concentration drops.

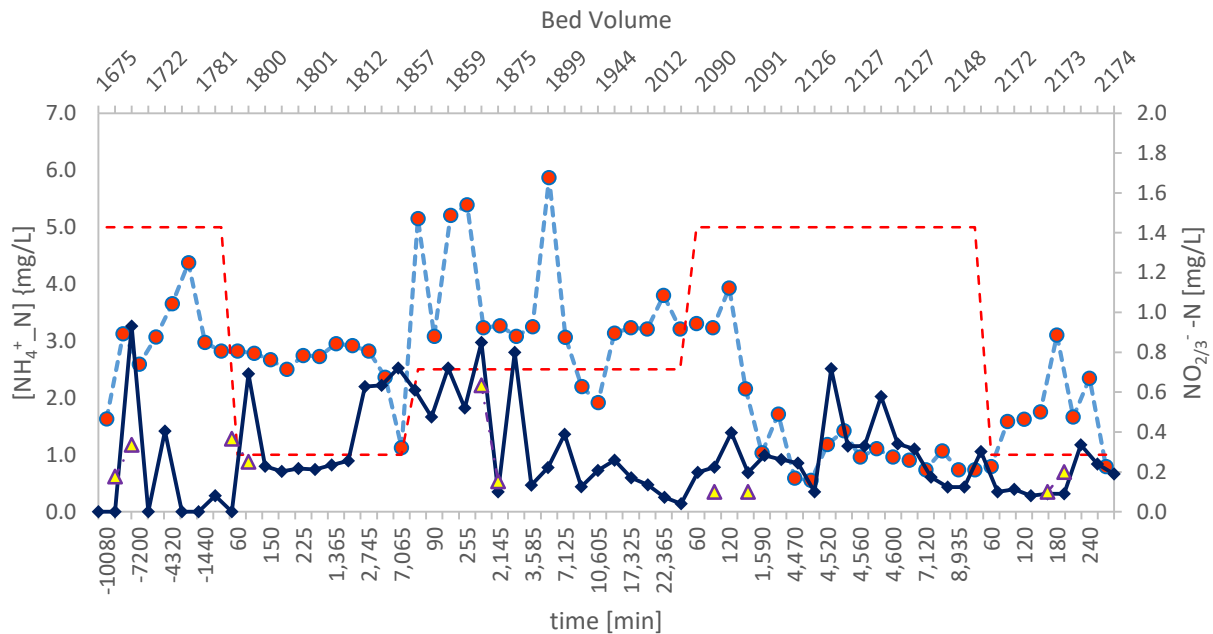


Figure 21. Performance of a nitrification-sorption ZT column under fluctuating ammonium loadings of 5, 2.5, and 1 mg $\text{NH}_4^+\text{-N/L}$ at 0.03 M NaCl at $T = 22 \pm 4^\circ\text{C}$ for the last cycle of step changes in the influent concentration.

In short, reductions the influent $\text{NH}_4^+\text{-N}$ during the course of study desorbed 189 mg $\text{NH}_4^+\text{-N}$ from the media. 61.7% of the total nitrate produced during the course of study occurred during timeframes where desorption was taking place. Although nitrification was not high enough to offset this release of ammonium completely, it appeared to have helped with reducing the effluent ammonium after a reduction in the influent concentrations. The average consumption of oxygen was found to be 1.9 ± 0.4 mol $\text{O}_2/\text{mol NO}_3^- \text{-N}$. No strong correlation between consumed oxygen and TOC is found for the dataset collected, although for 1065 and 1616 BV, sharp spikes in the effluent TOC also coincide with reduction in the effluent DO. Nevertheless, in both cases, an increase in the effluent nitrate is also observed from 0.2 to 0.4 and 0 to 1.3 mg $\text{NO}_3^- \text{-N/L}$. It is not clear whether the effluent TOC of the columns is a result of wash-off of dead or alive biomass. The average effluent pH of the samples was measured and found to be $5.1 \pm$

0.2, and similarly an inverse relationship between pH and nitrate could be observed, where samples with higher nitrate concentrations exhibited lower pH values.

Characterization of exhausted media

At the end of the column experiment, the total and inorganic carbon content of the media were determined. The total inorganic nitrogen (NH_4^+ -N and NO_3^- -N) of the media were also determined. The exhausted and virgin ZT held small amounts of nitrate (i.e., 1.1 – 1.5 $\mu\text{g NO}_3^-$ -N/ g ZT), but were in ammonium as expected (Table 10). The total mass of ammonium that was recovered via 2 M KCl extraction was higher than the calculated q for each of the columns based on the effluent nitrogen concentrations. Part of this could be due to ammonium on the surface of virgin ZT even after the pre-treatment of media before use. Subtracting the NH_4^+ -N value observed for virgin ZT from those of exhausted media, result in values close to one another.

Table10. Characterization of inorganic nitrogen for media after completion of the experiment for continuous ZT column (ZTC), ZT under fluctuating influent ammonium concentrations (ZT Δ C), ZT column under wet/saturated-dry/unsaturated conditions (ZT INT), and virgin ZT

Column Media	q [mg NH_4^+ -N/g ZT]			Nitrate [$\mu\text{g NO}_3^-$ -N/g ZT]
	Mehlich Extraction	$[\text{NH}_4\text{-N}]_c - [\text{NH}_4\text{-N}]_v$	calculated	
ZTC	2.8 ± 0.1	2.2 ± 0.2	2.30	1.2 ± 0.3
ZT Δ C	1.8 ± 0.1	1.2 ± 0.2	0.93	1.3 ± 0.1
ZT INT	1.7 ± 0.0	1.1 ± 0.2	0.91	1.5 ± 0.1
Virgin ZT	0.6 ± 0.21			1.3 ± 0.2

Table 11. Characterization of carbon content of exhausted media for continuous ZT column (ZTC), ZT under fluctuating influent ammonium concentration (ZTΔC), ZT under wet/saturated-dry/unsaturated conditions (ZT INT), and virgin ZT

Column Media	Media Carbon Content		
	% Total Carbon	% Inorganic C	% Organic C
ZTC	0.33% ± 0.01%	0.029% ± 0.001%	0.3% ± 0.01%
ZT ΔC	0.25% ± 0.01%	0.031% ± 0.006%	0.23% ± 0.01%
ZT INT	0.23% ± 0.03%	0.032% ± 0.006%	0.19% ± 0.03%
ZT TEST	0.26% ± 0.02%	0.033% ± 0.002%	0.23% ± 0.02%
Virgin ZT	0.60% ± 0.05%	0.544% ± 0.021%	0.056% ± 0.054%

Organic carbon content of the media was determined as a test for the presence of biomass for virgin and exhausted media. The organic carbon was determined by subtracting the total carbon content from the inorganic carbon measurements. Student t-test was used ($\alpha = 0.05$) to compare the carbon content of the exhausted and virgin ZT. The results indicated that the OC of the exhausted media is significantly higher than virgin ZT, while the inorganic carbon content of the exhausted media was found to be significantly lower than that of virgin ZT. It appears that throughout the course of the experiment, the carbon content of the media has changed, with inorganic carbon disappearing and organic carbon becoming more dominant. Total organic carbon content was found to correlate with biomass (Brown et al., 1997), and total organic carbon measurements were used for determination of carbon content of biomass (Figueroa, et al., 2000). Since the influent to the columns did not contain any organic carbon, it is likely that this increase is due to transformation of some of the inorganic carbon of virgin ZT to for synthesis of biomass, as nitrifiers tend to use inorganic carbon as their carbon source (Gerardi, 2002).

Conclusion

This paper reports the findings of three nitrification-sorption ZT columns under conditions typical of stormwater SCMs. The performances of the media in continuous flow at two concentrations of 2.5 and 5 mg NH₄⁺-N/L were tested. The concentration of nitrate did not

change significantly with the increase in the influent ammonium concentration, and the nitrification rate coefficients obtained for the zero order were close to one another (-0.032 vis-à-vis -0.039 mg. L⁻¹.min⁻¹).

It is possible that the ZT media can act as an ammonium reserve for nitrifying bacteria, where local depletion of ammonium in the solution can initiate desorption of the ammonium. This is particularly likely in cases where the net effluent nitrogen was found to be greater than that of the influent nitrogen, making it likely for some of the ammonium from the surface to be utilized for nitrification.

The performance of a sorption-nitrification ZT column under wet/saturated-dry/unsaturated conditions indicated that nitrification was lower than that observed in the continuous columns. This could be due to damage and/or the wash-out of the biomass during and after the dry/unsaturated period. The results indicated that for most simulated wet/saturated events, an increase in the effluent ammonium concentration had occurred after the dry/unsaturated period. Furthermore, for simulated wet/saturated events where an increase in the nitrate concentration had occurred during the dry/unsaturated period, a smaller increase in the ammonium concentration, and at times a decrease in the ammonium concentration could be observed. Therefore, it appears that the combination of both nitrification and sorption can help with the performance of the media for use in SCMs. ZT under wet/saturated-dry/unsaturated conditions showed enhanced overall removal of ammonium compared to that of the continuous feed, with the intermittent ZT treating 18% more synthetic stormwater prior to media exhaustion. The media continued to remove and transform ammonium after exhaustion, suggesting that the wet/saturated-dry/unsaturated conditions lead to enhanced performance of ZT. This has positive

implications for the field, resulting in high ammonium removal during storm events, and their subsequent transformation between storm events.

The performance of a sorption-nitrification ZT column under different influent concentrations showed that smaller desorption takes place in events where a reduction in the influent ammonium took place, although consistent operation in this column could not be observed even after 1999 bed volumes. A combination of sorption and nitrification can result in enhanced performance of ZT under SCM conditions, where nitrification resulted in smaller desorption of ammonium after the dry/unsaturated period and reduction of influent ammonium concentration. Treatment of first-flush is recommended in order to limit desorption. The application of ZT sorption-nitrification SCMs in field-scale is, therefore, recommended.

Based on observations made in this study, it is expected that the performance of ZT will be enhanced during periods where nitrification is occurring. Nitrification, specifically, during the dry/unsaturated period can benefit the operation of the system greatly; an increase in the effluent nitrate corresponded to eventual reduction in the ammonium concentrations. It is expected that a sorption-nitrification filter can perform well under intermittent flow conditions. Nevertheless, during periods when nitrification is not occurring, desorption from the media in the event of influent concentration drops and after the dry/unsaturated period could reduce the overall efficiency of the system.

8. Conclusions and Field Implications

Excess nitrogen in stormwater runoff remains to be a significant source of non-point pollution in the receiving waters. The complexity in treating nitrogen lies in its diverse speciation, and the differences in the susceptibility of each nitrogen form to different treatments. To provide an overview, influent ON (particulate and dissolved) and ammonium can be immobilized via filtration and sorption/ion exchange, while nitrate has low attenuation in the environment. Furthermore, nitrogen species undergo transformations according to the nitrogen cycle. In short, ON is often mineralized to produce ammonium, and ammonium is thereby nitrified. Creating anoxic conditions can result in advantageous nitrogen removal because of denitrification of nitrate.

This work began with the broader goal of enhancing nitrogen removal from stormwater control measures. Although, implementing anoxic conditions within a saturated zone of SCMs has been recommended to promote denitrification, effective reduction of influent nitrogen is contingent on transformation of incoming nitrogen to nitrate prior to reaching this anoxic zone. To achieve this goal, a systematic approach for filtration-based SCMs was proposed whereby stepwise capture and transformation of different nitrogen species would occur. Different layers within the SCMs can be catered to enhance removal and transformation of organic nitrogen to ammonium, and ammonium to nitrate. This work focuses on enhancing ammonium removal within a filtration-based SCM. Five different objectives were defined to achieve this goal, through which optimum media selection and characterization in flow-based systems of sorption and sorption-nitrification would occur. The findings and conclusions obtained in this work are presented for each of the objectives.

Selection of media with high capacity for ammonium removal

Objective 1 focused on selection of media with high capacity for ammonium removal. Testing began by examining sorption behavior of 9 different media, including 2 montmorillonite clay aggregates, attapulgite, hydrous aluminosilicate, clinoptilolite zeolite, crushed brick, pool sand, activated carbon, and coconut shells, out of which hydrous aluminosilicate (CA) and clinoptilolite (ZT) were selected for further characterization because of higher capacity, optimum pH, and durability during testing. It was speculated that the presence of other cations in stormwater pose the greatest degree of competition with ammonium for removal, with the highest concentration of cations for Na^+ , Ca^{2+} , and K^+ (Goebel et al., 2007). The make-up of the background electrolytes tested reflected these cations, which were tested either as a single background electrolyte, or a multi-component background electrolyte (Mixed Background).

The sorption isotherms suggested that ZT holds superior ammonium sorption capacity, compared to CA. Results obtained for both media suggest the highest removal of ammonium for 0.03 M NaCl, followed by 0.01 M CaCl_2 . The order of ammonium removal in different background electrolytes, from high to low was found to be: 0.03 M NaCl > CaCl_2 > Mixed background consisting of Na^+ , Ca^{2+} , and K^+ > KCl, although at higher ammonium concentrations, convergence of the isotherms for at NaCl and CaCl_2 , and their reversal in KCl and Mixed Background could be observed. Compared to a Na^+ system, the sorption capacity for a concentration of 2 mg $\text{NH}_4^+\text{-N/L}$ was found to have reduced by 83.8% and 74.5%, for CA and ZT, respectively. It is expected that in stormwater runoff, with the lower range of ammonium concentration, competition between cations is expected to occur, particularly between NH_4^+ and K^+ . The results are consistent with literature, showing competition between Ca^{2+} and K^+ with ammonium for removal. The concentration of background electrolytes were also measured, and

the results suggested high uptake of K^+ and Ca^{2+} for both media, Furthermore, the net uptake of cations was comparable to the displacement/desorption of cation from the surface for ZT, particularly for KCl and Mixed Background electrolytes.

Selection of media that allows rapid capture of ammonium from stormwater

In the occurrence of storms, the corresponding runoff spends a limited amount of time within the stormwater. Since sorption/ion exchange are processes responsible for removal of ammonium from runoff, the rate of ammonium uptake by the media was quantified. The results indicated shorter contact times were required for ammonium sorption by ZT, with equilibrium times (t_e) of 30 – 240 minutes, compared to $t_e > 240$ minutes for CA. Moreover, the extent and rate of ammonium sorption was found to be dependent on the background electrolytes.

Increasing the concentrations of Ca^{2+} and K^+ resulted in slower uptake of ammonium by both ZT and CA. The kinetics of sorption for both media was represented well using the pseudo-second order model. The chemistry of stormwater is thereby an important parameter that can affect the rate and extent of ammonium removal by the media. In regions and seasons when more dominant presence of these competing cations are expected, the contact time required for optimum ammonium removal is prolonged.

Understanding the reversibility/extractability of ammonium uptake by the media

The next objective focused on assessing the extractability/reversibility of sorbed ammonium from the surface. This was important as nitrification has been shown to depend on

the concentration of ammonium in the pore solution (Lahav and Green, 1998, Comerford, 2005). Therefore, for captured ammonium to be nitrified, it should be available for nitrification. The results obtained rendered that ammonium removed by ZT showed a higher degree of extractability. For lower ammonium loadings (i.e., $[\text{NH}_4^+\text{-N}] \leq 5 \text{ mg/L}$), particularly for ZT, the sorbed ammonium was completely recovered during the extraction step, although the fraction of ammonium that was not extractable increased for both media with the increase in ammonium loading. For ZT 87% of the captured ammonium could be recovered (i.e., $q_{\text{tot}} = 6.9 \text{ meq NH}_4^+\text{-N/g ZT}$ and $q_{\text{ext}} = 4.6 \text{ meq NH}_4^+\text{-N/g ZT}$) while this recovery was only 46% for CA (i.e., $q_{\text{tot}} = 6.5 \text{ meq NH}_4^+\text{-N/g CA}$ and $q_{\text{ext}} = 3.0 \text{ meq NH}_4^+\text{-N/g CA}$) for a background electrolyte of NaCl. The change in the background electrolyte from NaCl to CaCl_2 did not seem to affect the reversibility/extractability of ammonium for either of the media. Based on the results obtained, it is speculated that ammonium that is extractable and hence potentially bioavailable for nitrification is higher in ZT than CA. Furthermore, the high extractability of ammonium and its displacement by K^+ , also suggests an ion exchange mechanism for ZT, which is supported by literature.

Summary of Batch Experiments

In short, based on the results obtained from batch-scale experiments, it appears that ZT is more favorable for ammonium removal because of higher capacity, faster rates, and ammonium sorption. The next phase of the experimentation included flow-based testing for better characterization of these media for use in filtration-based SCMs.

Testing the media to monitor ammonium removal in flow-based sorptive systems simulating SCM conditions

Next, flow-based experiments were conducted to better understand and characterize CA and ZT for applications in filtration-based SCMs. Testing conducted in this phase consisted of several modes of operation.

The first mode of operation was obtaining capacity of media and removal efficiency for sorption-columns for both media in continuous setting. Once this was achieved, testing was done to monitor and characterize the media for use in different environmental conditions expected in typical SCMs, including wet/saturated-dry/unsaturated conditions, variable velocity and contact times, and variable ammonium loadings.

Media Performance in continuous setting

The performance of media under continuous flow-based testing ($C_{in} = 25 \text{ mg NH}_4^+ \text{-N/L}$ and $U = 8.3 \text{ cm/h}$ in long columns) indicated superior capacity of ZT for ammonium removal. The presence of other cations as observed in Mixed Background electrolyte indicated reduction of media capacity compared to that for a NaCl background by 60.6% and 66.6% for CA and ZT, respectively. Furthermore, the capacity calculated for both media at 0.03 M NaCl rendered higher values compared to those observed in previous batch studies. For a more cost-effective design, the performance of a mixed media, consisting of 50:50 pool sand-ZT (V/V) was also tested. The capacities obtained at the end of experiment were comparable to the findings for the pure ZT column. Observations made here were used to predict the life-span of media in the field for a SCM/Drainage area = 5% and 40 cm media depth estimated a life-span of 216 months for ZT for a NaCl system, and 35.4 months for Mixed Background system. The pure ZT column

showed the best performance amongst the three columns of CA, ZT, and sand and ZT mixture columns. It is expected that during colder months, when road salts are applied, a higher competition and thus lower media capacity be observed for all the media tested, while in conditions when Na^+ is the predominant cation higher ammonium removal capacity be realized by the media.

Media performance under continuous and wet/saturated-dry/unsaturated conditions

Two short columns (media depth of 23 cm) were constructed. No significant difference in media capacity under wet/saturated-dry/unsaturated and continuous feed could be observed for CA. ZT, however, demonstrated less removal capacity for ammonium for the continuous run. For both media, increase in effluent ammonium concentrations immediately after the dry/unsaturated period could be observed, in the range of 0.2 to 1.7 mg NH_4^+ -N/L ($C_{\text{in}} = 2.5$ mg NH_4^+ -N/L). For ZT the effluent concentration of both media appear to converge storm events 6 and 7th (31 days of operation). Nitrate production was observed beyond storm event 7th before exhaustion of the media.

Media performance under different stormwater velocities and contact times

The effect of contact time on removal was found to play an important role in the removal efficiency of both CA and ZT. Removal of ammonium for both CA and ZT was found to have an inverse relationship with contact time. Testing on NH_4^+ - Mixed Background columns illustrated that for samples collected after 24 hours, higher effluent concentrations were observed for shorter contact times, particularly for a contact time of 9 min, with $[\text{NH}_4^+-\text{N}]_{\text{out}}/[\text{NH}_4^+-\text{N}]_{\text{in}} = 0.95$ and 0.88 for CA and ZT, respectively.

Columns receiving NH_4^+ - NaCl influent under continuous regime until exhaustion also demonstrated similar findings. The effect of shorter contact time was more evident in CA, where the column operated at 42 cm/h exhausted only after 5 days of operation, with the faster column showing 13% removal until exhaustion, compared to 74% observed for $U = 8.3$ cm/h.

Similar findings were observed for ZT, which were tested under three different velocities of 42, 26.5, and 8.3 cm/h, with the column operated at 8.3 showing better removal efficiency (average $[\text{NH}_4^+ - \text{N}]_{\text{out}}/[\text{NH}_4^+ - \text{N}]_{\text{in}} = 0.82 \pm 0.07$). Furthermore, nitrate production was observed for the slower flow rate, whereas a smaller fraction of nitrogen loading was transformed into $\text{NO}_{2,3}^- - \text{N}$ (9% and 2% for $U = 8.3$ and 42 cm/h, respectively), although the cumulative $\text{NO}_{2,3}^- - \text{N}$ produced in the faster column was higher (7 mg $\text{NO}_{2,3}^- - \text{N}$ vis-à-vis 11.3 mg $\text{NO}_{2,3}^- - \text{N}$). The operation of this column was continued, but nitrate production was found to subside after media exhaustion, which could have been caused by the higher stormwater velocity and wash-out of the microorganisms.

In short, the faster flow rates appear to result in higher effluent ammonium concentrations, although from a cumulative mg N reduction, they did not differ significantly from the slower flow rates. Furthermore, lower concentrations of nitrate were also observed for ZT at 8.3 and 42 cm/h. It appears thus, that while at slower flow rates, lower effluent ammonium can be obtained, it is likely that within the storm-event duration, the media can remove ammonium from the incoming stormwater successfully prior to media exhaustion.

Media Performance under variable influent ammonium loading

The chemistry of stormwater is site and season dependent. Since ZT had proven more effective in reduction of ammonium loading, it was chosen for further analysis. Fluctuations in the influent ammonium concentration for $I = 0.03$ M NaCl indicated highest ammonium removal

to be achieved for the higher influent concentration (i.e., 5 mg NH₄⁺-N/L). Increases in the influent ammonium concentrations resulted in higher media capacity and removals. Nonetheless, reducing the influent concentration resulted in desorption of antecedent ammonium removed by the media. During the abiotic phase, where no nitrate activity could be observed, the degree of desorption was found to increase with further progression of the experiment. Desorption time was found to increase from 4 hours to 24 hours for three simulated reductions in the influent from 5 to 1 mg NH₄⁺-N/L. The calculated q value reduced for each influent reduction, with the highest reduction observed from 1.37 to 1.1 mg NH₄⁺-N/g ZT for the 3rd cycle at 273 BV. The decrease in q value did not continue until reaching a constant steady value. For example, for the first cycle where C_{in} was reduced from 5 to 1 mg/L, the change in q from 0.53 to 0.51 occurred, while for the second reduction in the influent ammonium concentration from 5 to 1 mg/L, the q was subsequently found to reduce from 1.05 to 1.03 mg NH₄⁺-N/g ZT.

Summary of Sorption Column Experiments

The overall results obtained from the sorption column experiments suggest high ammonium removal capacity for ZT. Furthermore, in sorption wet/saturated-dry/unsaturated columns, an increase in the influent ammonium concentrations was observed to take place for CA, and for ZT (storm events 3 – 5). Finally, reducing the flow rates correspond to lower effluent ammonium concentrations. The biggest weakness of the system observed corresponds to cases where a reduction in the influent ammonium concentration occurs. This triggers desorption of ammonium from the surface. Because of superior performance of ZT thus far, further testing was continued for this material.

Testing the media to monitor ammonium removal in flow-based sorption - nitrification ZT columns simulating SCM conditions

Nitrification in continuous ZT column

Nitrate production was observed for ZT close to the time of media exhaustion for 2.5 mg NH_4^+ -N/L at 0.03 M NaCl for $U = 8.3$ cm/h. With continued testing, higher nitrate concentrations could be observed, until reaching a steady concentration of 1.2 ± 0.1 mg NO_3^- -N/L, and effluent NH_4^+ -N of 1.3 ± 0.1 mg N/L. During this phase, it appeared that loss of ammonium corresponded with the amount of nitrate being produced. Nevertheless, with further progression of the experiment, particularly for 822 – 964 BV, the effluent nitrogen surpassed that of the influent, marking possible desorption of ammonium from the surface. Although nitrate production is observed, only during the steady state can consistent reduction in the effluent ammonium be observed. In short, after media breakthrough, although desorption did appear to take place, it did not cause a consistent reduction in the effluent ammonium concentrations.

Increasing the concentration from 2.5 to 5 mg NH_4^+ -N/L resulted in higher ammonium removal but substantial nitrate (ie.. NO_3^- -N > 0.4 mg NO_3^- -N/L) could be observed for periods close to media exhaustion, where effluent ammonium was close to that of the influent, and less sorption occurred. The low nitrate concentrations could have also resulted from higher flow rates caused by a malfunction to the pump. Further progression of the experiment, beyond media exhaustion resulted in higher effluent ammonium concentrations. Nevertheless, a consistent reduction in the effluent ammonium occurred for the last two weeks of the experiment (4419 – 4757 BV), where the net effluent (NH_4^+ -N + NO_3^- -N) approached the influent concentration, with average values of 1.7 ± 0.3 NO_3^- -N/L and 3.5 ± 0.4 mg NH_4^+ -N/L. The q values observed for the columns, demonstrating sorption and nitrification were considerably higher than the

values observed for the sorption columns. It is possible that some of the ammonium is being utilized by the micro-organisms. Another possible explanation is potential denitrification in certain zones showing high biological activity, although the system was rigorously aerated, with effluent DO values > 3 mg/L.

Performance of a nitrification – sorption ZT column under wet/saturated-dry/unsaturated conditions

Nitrate production was observed for ZT from storm event 7. Nitrate production in this column often intersected or was followed by samples demonstrating lower effluent ammonium, indicating possible regeneration of some of ZT via nitrification, and an overall enhancement in the performance of the column in a nitrification-sorption column. This column exhausted after 457 BV, with capacity similar to that obtained in a continuous abiotic column (0.67 mg NH₄⁺-N/L). High effluent TOC could be observed in samples collected immediately after the dry/unsaturated period, indicating possible loss of biomass. The concentrations of nitrate in this column were lower than those observed in the continuous column; nevertheless, it appears that the dry/unsaturated period in combination with nitrification can result in higher performance of ZT, even after exhaustion of media.

The results obtained for storm events 8 – 56 demonstrated an increase in the nitrate concentration during and between storm events. Except for 5 collected samples, equal to 3 storm events, the effluent ammonium concentrations were lower than that of the influent, with an average $[\text{NH}_4^+\text{-N}]_{\text{out}}/[\text{NH}_4^+\text{-N}]_{\text{in}}$ of 0.4 ± 0.2 . Thus successful ammonium removal in wet/saturated-dry/unsaturated conditions via both sorption and nitrification was achieved. The average number of annual wet/saturated-events in Maryland is 116 days, with most storm events lasting from 20 min to 24 hours. The results discussed here shows treatment of influent

ammonium for 57 events, with the column demonstrating nitrification and sorption of ammonium at the end of the experiment. It is expected that ZT will demonstrate high ammonium removal and nitrification in wet/saturated-dry/unsaturated SCMs.

Performance of sorption-nitrification ZT column under fluctuating influent ammonium concentrations

The results obtained in this test suggest smaller desorption of ammonium for periods where nitrification is occurring. Reducing the influent concentration took place as 5 to 1, 5 to 2.5, and 2.5 to 1 mg NH₄⁺-N/L, for which nitrate production also showed an increasing trend. Nitrate and ammonium content of the effluent samples were found to often show the same trend.

Summary of Sorption-Nitrification Columns

In short, nitrification was found to enhance ammonium removal in the ZT columns, particularly for intermittent setting. The extent of nitrification did not show a significant change with increasing influent ammonium concentration. Nitrification in all continuous columns was achieved close to media exhaustion. For the intermittent columns, however, nitrification could be observed prior to media exhaustion, which retarded exhaustion of media by 10 BV compared to the continuous run.

Conclusions

In conclusion, application of ZT in filtration-based SCMS is recommended. This media has superior capacity for uptake of ammonium, as well as rapid removal rates. Furthermore, ZT successful sorption and nitrification observed in wet/saturated-dry/unsaturated conditions could be observed. The only shortcoming observed for this media is desorption of ammonium in the

event of concentration drops. Combination of nitrification and sorption appears to help the performance of the column.

Recommendations and field applications

Based on observations made to date, zeolite is an effective media for removal of ammonium from stormwater solution. Many different environmental conditions are expected to occur, which were tested in different batch and column-scale testing. Figure 22 represents the findings and expectations of the performance of media in the field for a 40 cm layer of ZT (particle size of 2 mm) in a filtration-based SCMs. The observations made in lab were translated to different environmental conditions expected in the field in order to predict the performance of ZT in the field.

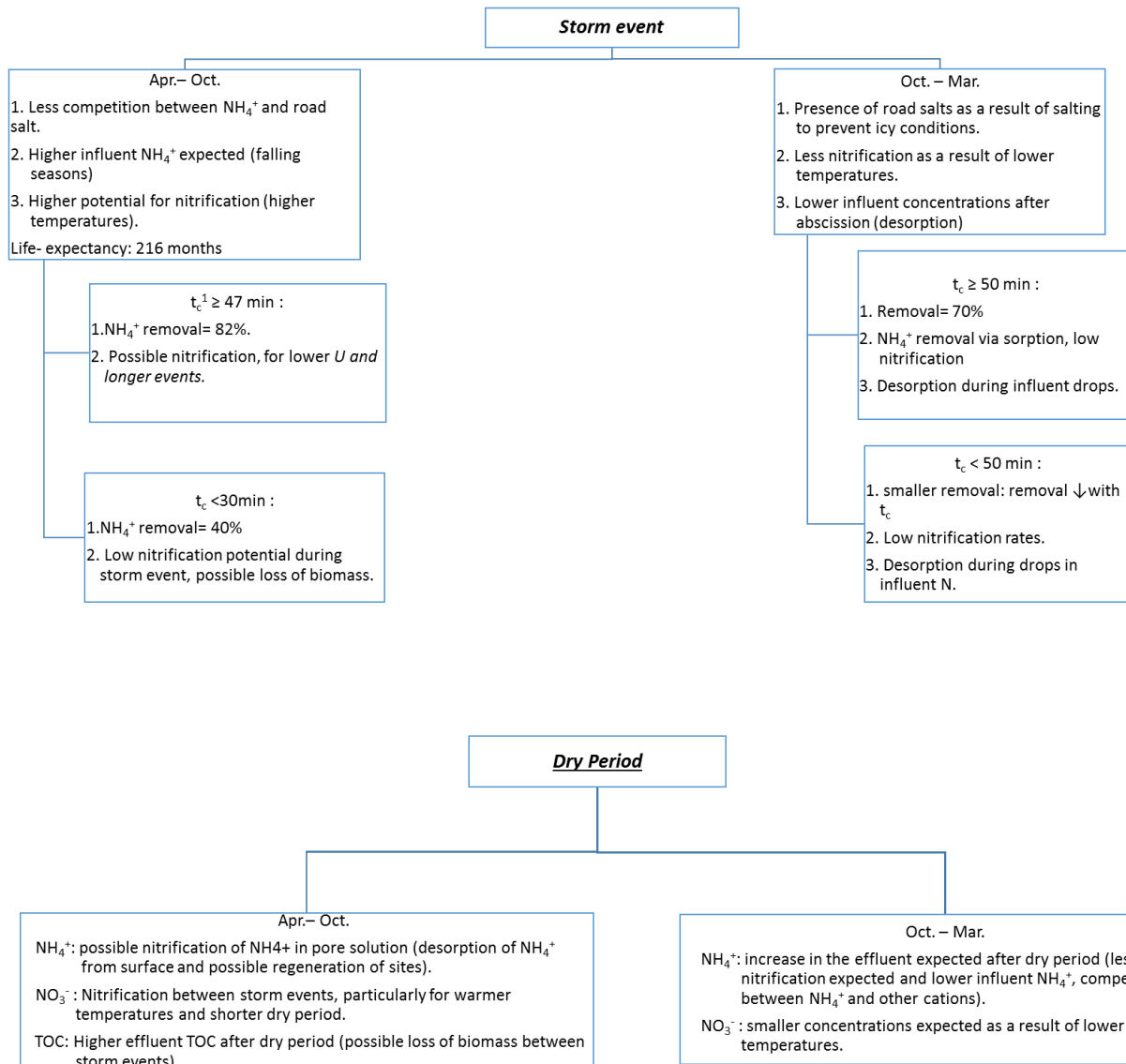


Figure 22. Predicted performance of ZT in filtration-based SCMs.

¹ t_c or contact time is dependent on the ratio of ZT and other media mixed within the nitrification layer. t_c was estimated using $t_c = \frac{L \cdot \emptyset}{\text{infiltration rate } (2-10''/h)}$, where L is the depth of media used in the bioretention cell, and \emptyset is media porosity.

Different time categories were defined to outline the expected performance of ZT in the field. The first important time-frame is the storm-event itself, during which the SCM will receive

the first-flush. Throughout the SCM, each ZT particle is expected to be in contact with the first flush for a short time, which will determine the extent of ammonium uptake, particularly for systems rich in other cations, such as Ca^{2+} and K^+ . Furthermore, for longer or subsequent storm events, lower influent ammonium concentrations are expected, which can result in desorption of some ammonium from ZT, although this desorption can occur to a smaller degree with nitrification. To achieve a contact time of 47 min for an average infiltration rate of 6 in/h, a media depth of 43 cm is required in the field for 100% ZT, with porosity of 0.28.

The next important time frame is the dry/unsaturated period, which occurs between different storm events. This research used 5 different dry/unsaturated periods of 3, 5, 7, 14, and 21 days in determining the effluent concentrations. The effluent ammonium concentration after the dry/unsaturated period, particularly for the abiotic phase, was found to increase. With progression of the experiment, nitrification occurred, and nitrate concentrations were also likely to increase after the dry/unsaturated period, particularly for the 335 – 668 BV.

Finally, seasonal changes can result in different influent concentrations, ambient temperature, and storm event intensity and duration. During abscission/falling season (spring and autumn), higher nitrogen loading is expected. Higher temperatures can promote nitrification. It is hence expected that during the warmer months of April – October, the performance of the ZT SCMs will be enhanced as higher ammonium loadings result in higher media capacity for uptake. Higher temperatures can also promote mineralization of influent ON, resulting in an increase in the influent ammonium, as well as nitrification. Nitrification is expected to take place during the dry/unsaturated period, resulting in possible regeneration of ZT sites, and better removal efficiency of ammonium from the influent.

For the colder months of October – March, however, ZT is expected to have a comparably poor performance. Higher concentrations of road salts, in combination with smaller influent nitrogen concentrations, and expected lower nitrification rates at lower temperatures results in competition of cations, desorption of sorbed ammonium, and smaller nitrification. Treating a small and concentrated volume of stormwater, as expected in first flush conditions, is recommended within the SCMs to promote higher media capacity.

This work has focused on investigating different environmental effects on the performance of ZT in filtration-based SCMs. Out of the media selected, ZT is expected to have the highest ammonium removal efficiency, and is hence recommended for use in the field. Pilot scale studies, where real-time stormwater is infiltrated through a ZT layer can provide more data.

Throughout this research synthetic stormwater containing different cations was used. It is possible that with prolonged exposure to other constituents, including organic matter. some of the charged organic matter could interact with the surface and affect ammonium uptake; this could occur particularly during colder months because of the expected higher concentrations of other cations, salting out of organic matter from the solution phase could occur. Although the course of the experiment, clogs and blockages could not be observed for ZT columns, potential clogging of media in the field could also occur. Furthermore, synthetic stormwater was pumped through the columns, while natural infiltration depending on different stormwater intensities is better representative of field conditions. Additionally, wet/saturated-dry/unsaturated cycles play an important role in urban runoff. The moisture content of the soil is expected to affect the flow characteristics, nitrification potential, and sorption of ammonium. Using pilot SCMs in combination with real stormwater, and moisture content of media can provide a better insight on ZT performance in filtration-based SCMs.

Another important consideration is the role of plants in nutrient removal. Previously vegetation selection was found to be a critical factor for nitrogen removal as well as maintenance of media porosity (Brateries et al., 2008). Furthermore, Hatt et al (2007) and Henderson et al. (2007) also reported similar findings, suggesting that without vegetation, the soil-based media may export nitrogen. Application of ZT in a vegetated biofilter can hence result in enhanced removal of ZT, with possible utilization of nitrogen from ZT by the plants, regeneration of occupied sites is possible. Uptake of NO_3^- by the plants can also help in reducing the net nitrogen export from the SCMs. Nevertheless, plants can also return the nutrient to the SCM, which could potentially result in plant debris and fallen leaves as a source of nitrogen to the SCMs.

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