Modeling of first-flush reactor for stormwater treatment

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MODELING OF FIRST-FLUSH REACTOR FOR STORMWATER TREATMENT

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirement for the degree of
Master of Science in Civil Engineering
in
The Department of Civil and Environmental Engineering

by
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August 2011
This thesis is dedicated

To my father Fangqing Sun
To my mother Jianti Li
And
To my family and friends
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ...................................................................................................................... iii

LIST OF TABLES ...................................................................................................................................... vi

LIST OF FIGURES .................................................................................................................................. vii

ABSTRACT .............................................................................................................................................. ix

CHAPTER 1. INTRODUCTION ........................................................................................................ 1
  1.1 Background ........................................................................................................................................ 1
  1.2 Goal and Objectives .............................................................................................................................. 2

CHAPTER 2. LITERATURE REVIEW OF NONPOINT SOURCE (NPS) POLLUTION ...... 4
  2.1 Introduction .......................................................................................................................................... 4
  2.2 Major Sources of Nonpoint Source Pollution ..................................................................................... 4
    2.2.1 Pollution from Urban Stormwater ................................................................................................. 4
    2.2.2 Pollution from Highway Stormwater .............................................................................................. 7
    2.2.3 Pollution from Agricultural Runoff ................................................................................................ 9
    2.2.4 Pollution from Atmospheric Deposition ....................................................................................... 10
  2.3 Modeling and Estimation of NPS Pollution ......................................................................................... 13
    2.3.1 Assessment and Application of NPS Pollution Models .................................................................. 13
    2.3.2 Total Maximum Daily Load (TMDL) Calculations ..................................................................... 17
  2.4 NPS Pollution Management ............................................................................................................... 21
    2.4.1 Low–Impact Development (LID)/Best Management Practices (BMPs)
        Implementation ................................................................................................................................. 21
  2.5 Socioeconomic Analysis of NPS Pollution Control ........................................................................... 29
  2.6 Conclusions ....................................................................................................................................... 31

CHAPTER 3. COLUMN EXPERIMENT ON NITROGEN REMOVAL .......... 32
  3.1 Introduction ........................................................................................................................................ 32
  3.2 Laboratory Experiments Using Natural Stormwater ....................................................................... 32
    3.2.1 Gathering of Stormwater Samples ............................................................................................... 32
    3.2.2 Selection of Filter Media ............................................................................................................... 34
    3.2.3 Introduction to Stormwater Column Experiments ...................................................................... 36
    3.2.4 Data from Stormwater Column Experiments ............................................................................. 37
  3.3 Laboratory Experiments Using Secondary Wastewater ................................................................... 39
    3.3.1 Introduction to Wastewater Column Experiments ................................................................... 39
    3.3.2 Data from Wastewater Column Experiments ........................................................................... 41
  3.4 Conclusions ...................................................................................................................................... 42

CHAPTER 4. NUMERICAL MODELING OF DENITRIFICATION PROCESS IN FIRST-
  FLUSH REACTOR ................................................................................................................................. 43
  4.1 Introduction ........................................................................................................................................ 43
4.2 First-Flush Reactor and VART Model ................................................................. 43
   4.2.1 First-Flush Reactor ......................................................................................... 43
   4.2.2 VART Model ................................................................................................. 44
4.3 Conceptual Model for First-Flush Reactor ...................................................... 46
4.4 Numerical Model for First-Flush Reactor: VART-DN Model ......................... 48
   4.4.1 VART-DN Model for Simulation of Denitrification Process ......................... 48
   4.4.2 Modeling of Bacterial Growth ...................................................................... 49
   4.4.3 Modeling of Dissolved Oxygen Consumption .............................................. 50
   4.4.4 Estimation of Dissolved Organic Carbon Consumption Rate ...................... 50
4.5 Sensitivity Analysis ......................................................................................... 51
4.6 Numerical Solution Procedure for VART-DN Model ....................................... 53
4.7 Summary and Conclusions .............................................................................. 58

CHAPTER 5. TESTING OF VART-DN MODEL ............................................................. 60
  5.1 Introduction ........................................................................................................ 60
  5.2 Testing of VART-DN Model ............................................................................. 60
     5.2.1 Testing of VART-DN Model with Stormwater Data .................................... 60
     5.2.2 Testing of VART-DN Model with Wastewater Data .................................... 61
  5.3 Summary and Conclusions ............................................................................. 63

CHAPTER 6. SUMMARY AND CONCLUSIONS ............................................................ 65

REFERENCES .......................................................................................................... 67

VITA ......................................................................................................................... 77
LIST OF TABLES

Table 3-1 Sampling dates and conditions................................................................. 36
Table 3-2 Multi-layer Combination of Filter Media Used in Test 1................................ 37
Table 3-3 Multi-layer Combination of Filter Media Used in Tests 3, 4, and 5............... 38
Table 3-4 Results of Column Experiments using Highway Stormwater....................... 38
Table 3-5 Effluent data from laboratory experiments conducted using secondary wastewater ... 41
Table 3-6 Influent data from laboratory experiments conducted using secondary wastewater .... 41
Table 4-1 Model input parameters................................................................................. 51
Table 4-2 Results of sensitivity analysis...................................................................... 52
Table 5-1 Simulated and observed effluent concentrations in the natural stormwater samples... 61
Table 5-2 Values of parameters in the model for stormwater and wastewater data.............. 62
LIST OF FIGURES

Figure 2-1 Air pollution and contaminant source ................................................................. 12
Figure 2-2 Constructed wetland ......................................................................................... 24
Figure 2-3 Structure of constructed wetland .............................................................. 24
Figure 2-4 Bioretention cell .............................................................................................. 25
Figure 2-5 Structure of bioretention cell ....................................................................... 25
Figure 2-6 Structure of green roofs ............................................................................... 26
Figure 2-7 Green roofs ...................................................................................................... 26
Figure 3-1 Stormwater sampling site at the I-10 roadway section at City Park Lake ........ 33
Figure 3-2 Plan view of experimental site (not to scale) .................................................. 33
Figure 3-3 Column experiments setup for the first-flush reactor .................................. 34
Figure 3-4 Filter material: smart sponge .......................................................................... 35
Figure 3-5 Filter material: hydra CX2 ............................................................................. 35
Figure 3-6 Filter material: wood chip .............................................................................. 35
Figure 3-7 Filter material: mulch ..................................................................................... 35
Figure 3-8 Filter material: sawdust .................................................................................. 35
Figure 3-9 Filter material: zeolite .................................................................................. 35
Figure 3-10 Filter material: sands .................................................................................... 35
Figure 3-11 Filter material: gravel ................................................................................... 35
Figure 3-12 Setup of column experiments with wastewater ......................................... 40
Figure 3-13 Measured and simulated nitrate-nitrogen concentrations for wastewater influent ... 40
Figure 4-1 Conceptual structure of first-flush reactor ..................................................... 44
Figure 4-2 Conceptual phases in first-flush reactor ......................................................... 47
Figure 4-3 Conceptual reactions in first-flush reactor .................................................... 47
Figure 4-4 Flow chart for numerical solution of VART-DN model.................................................. 53

Figure 5-1 Comparison between VART-DN simulated and observed nitrate-nitrogen concentrations in the effluent against the influent concentration of the secondary wastewater ... 63
ABSTRACT

Stormwater runoff is one of the most common sources of non-point source water pollution to lakes, rivers and estuaries. Nitrate-nitrogen in stormwater runoff is an important limiting factor to the eutrophication phenomenon. While most pollutants and nutrients, including nitrate-nitrogen, in stormwater are discharged into receiving waters during the first-flush period, no existing Best Management Practices (BMPs) are specifically designed to capture and treat the first-flush portion of urban stormwater runoff. In addition, nitrate-nitrogen removal rates of most existing BMPs are relatively low. This thesis presents results from both laboratory experiments and numerical modeling of nitrate-nitrogen removal in a designed first-flush reactor.

A new numerical tool, called VART-DN model, for simulation of denitrification process in the designed first-flush reactor was developed using the Variable Residence Time (VART) model. The new model is capable of simulating various processes and mechanisms responsible for denitrification in the first-flush reactor, including (1) dispersion and transport, (2) mass exchange, (3) oxygen variation, (4) bacterial growth, and (5) nitrate-nitrogen consumption. The VART-DN model is intended to investigate the influence of oxygen, biomass, dissolved carbon, and temperature on denitrification process. The data used in the development of the VART-DN model were from laboratory experiments conducted using both highway stormwater and secondary wastewater.

Based on sensitivity analysis results of model parameters, the dispersion coefficient, maximum nitrate utilization rate in mobile phase, biomass concentration, oxygen inhibition constant, biomass inhibition constant, temperature and temperature coefficient for denitrification have significant influence on the denitrification process, with percent change in root mean square error (RMSE) being 16.9%, 15.8%, -13.1%, -11.5%, 14.5%, -9.2% and -29.7%, respectively,
when values of the parameters increase by 10%. The average removal rate of nitrate-nitrogen in natural stormwater was 92.05%. The average influent and effluent concentrations in the column experiment with wastewater were 1.189 mg/L and 0.260 mg/L, respectively, with a removal rate of 78.1% for nitrate-nitrogen.

The VART-DN model results for the denitrification process of natural stormwater showed good agreements with observed data; the simulation error was lower than 9.0%. The RMSE for simulating denitrification process of wastewater was 0.8157, demonstrating the efficacy of the VART-DN model.
CHAPTER 1. INTRODUCTION

1.1 Background

Urbanization has produced increasing NPS pollution to water environment (Thurston, 1999; Ngabe et al., 2000). It increased impervious surface and decreased infiltration capacity, causing high peak flow rates and significant first-flush phenomenon. In addition, vehicle emissions and oil leaks produce heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) pollution, especially in parking lots (Mahler et al., 2005). It was reported that urban stormwater runoff alone ranked as the second most common source of water pollution to lakes and estuaries and the third to rivers in the United States (USEPA, 1995; Walker et al., 1999). According to the U.S. Environmental Protection Agency (EPA)’s Nationwide Urban Runoff Program (NURP), heavy metals, especially copper, lead, and zinc, are the most common priority pollutants in urban runoff (Banas, et al., 2010; Bourcier and Hindin, 1979; Chowdhury and Chandra, 1987; Davis and Matthew, 1999; Hoang et al., 2008; Hurley et al., 1995; Krocova et al., 2000; Lawson et al., 2001; Muthanna et al. 2007; Sipos et al., 2008). PAHs and other organic pollutants are also found in stormwater runoff (Asheley and Baler, 1999; Barrick and Prahl, 1987; Gonzalez et al., 2000; Hunter et al., 1979; Krein and Schorer, 2000; Smith et al., 2000; Takada et al., 1990; Van Metre et al., 2000). This phenomenon is called the first-flush (Saget et al., 1996), which is characterized by substantially higher concentrations of pollutants in the initial period of stormwater runoff than later periods (Deletic and Maksumovic, 1998; Gupta and Saul, 1996). The first-flush portion of stormwater runoff contributes a significant amount of pollutants compared with overall stormwater runoff (Lee et al. 2002; Saget et al. 1996; Bertrand-Krajewski et al. 1998; Deletic 1998). If we can treat first-flush portion of stormwater effectively before it reaches a water body, it will definitely decrease pollution to our environment. Water Quality Act
of 1948 and the Clean Water Act (CWA) of 1972 set pollutant disposal requirements in order to protect water. In 1987 the U.S. EPA amended the CWA in order to control certain stormwater discharges under the National Pollutant Discharge Elimination System.

If nutrients, such as nitrogen and phosphorus, are discharged into natural water bodies without treatments, they will definitely increase concentrations of nutrients in the water, which may cause eutrophication and even damage ecological balance. Nitrogen in stormwater is mainly from the atmosphere and particulate organic nitrogen. Evidence showed that production of nitrogen oxides (NO\textsubscript{x}) associated with the transportation sector accounted for nearly 30% of the N input to a desert metropolitan region (Baker et al., 2001). High concentration of dissolved inorganic nitrogen in water bodies may lead to eutrophication, hypoxia, and loss of biodiversity and habitat.

Nitrate-nitrogen is an important limiting factor to eutrophication. If the concentration of nitrate-nitrogen can be reduced to a low level, the phenomenon of eutrophication can be reduced significantly. However, most existing BMPs do not perform well in nitrate-nitrogen removal (Dreelin et al., 2006; Hunt et al., 2007). Moreover, few BMPs are specifically designed for treatment of first-flush portion of stormwater. Consequently, more effective and practical BMPs for first-flush treatment and for removing nitrate-nitrogen are needed.

1.2 Goal and Objectives

The overall goal of this thesis is to present a modeling framework for simulating nutrient removal processes in a first-flush reactor with emphasis on denitrification process. Specific objectives of this thesis are:

1. To provide a comprehensive literature review of urban stormwater management;
2. To collect experimental data for the first-flush reactor;

3. To develop a numerical model for simulating denitrification process in the first-flush reactor; and

4. To test the model using laboratory data.
CHAPTER 2. LITERATURE REVIEW OF NONPOINT SOURCE (NPS) POLLUTION

2.1 Introduction

The chapter presents a comprehensive review of research advances on NPS water pollution caused by urban stormwater, highway stormwater, agricultural runoff, and atmospheric deposition. Modeling progresses and TMDL calculations for NPS pollution are also reviewed. Various low impact development technologies and BMPs for mitigating NPS pollution and their socioeconomic impacts are assessed.

2.2 Major Sources of Nonpoint Source Pollution

Major contributors to nonpoint source pollution include urban stormwater, highway stormwater, agricultural runoff, and atmospheric deposition.

2.2.1 Pollution from Urban Stormwater

Urban stormwater contains a broad spectrum of contaminants ranging from suspended solids to nutrients, heavy metals, and pathogenic bacteria. Stormwater transports the contaminants into rivers, lakes, estuaries, and coastal waters, causing significant pollution of receiving water bodies.

Kang et al. (2009a) investigated characteristics of wet and dry weather heavy metal discharges in the Yeongsan Watershed, Gwangju City, Korea. They found that wet weather flow was a significant contributor to the annual dissolved metal loads, accounting for 44–93% of the annual load depending on the metal species with the exception of Cr (9%) and Cd (27%). Mn, Al, and Fe were the three most abundant metal species in the study area, followed by Zn, Ni, and Cu. Eckley and Branfireum (2009) simulated rain events to investigate the dynamics of mercury
mobilization in stormwater runoff. Results showed that Hg concentrations were highest at the beginning of the hydrograph and were predominately particulate bound. On average, almost 50% of the total Hg (THg) load was transported during the first minutes of runoff, underscoring the importance of first-flush on load calculations. Hg loads accumulated on the road surface during dry periods lead to the Hg runoff load increasing with antecedent dry days.

Some organic matters were also detected from urban stormwater. Bjorklund et al. (2009) studied phthalates and nonylphenols (NPs) in urban runoff. A modified Quantitative Water Air Sediment Interaction (QWASI) model was applied to investigate substance distribution in road runoff passing through a sedimentation facility. The results showed that aqueous concentrations of pollutants varied considerably; branched NPs were detected up to 1.2 μg·L⁻¹, whereas Di(2-Ethylhexyl) Phthalate (DEHP), Di-Isodecyl Phthalate (DIDP), and Di-Isomethyl Phthalate (DINP) were up to 5.0, 17, and 85 μg·L⁻¹, respectively. Zushi and Masunaga (2009) analyzed first-flush loads of perfluorinated compounds (PFCs) in stormwater runoff from Hayabuchi River basin. Perfluorocarboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs) with different chain lengths were monitored in the study. Concentrations of short-to medium-chain-length PFCAs showed no marked increase with the storm-runoff event. However, concentrations of PFDA (Perfluorodecanoic acid) and PFUnA (Perfluoroundecanoic acid) increased 3.4 (1.5–5.0 ng·L⁻¹) and 2.0 (3.3–6.7 ng·L⁻¹)–fold, respectively. This study demonstrated that large loads of long-chain-length PFCAs were discharged to the Hayabuchi River during the first-flush after the rain event.

Obermann et al. (2009) investigated characteristics of first-flush in a mediterranean catchment. Nutrient export was evaluated in terms of normalized cumulative loads (NCL) and three rating indices. FF25 (first-flush based on the load delivered by the first 25% of runoff
volume) values for ammonium, total suspended soils (TSS), and volatile suspended solids (VSS) were 0.79, 0.72 and 0.70, respectively. Passeport and Hunt (2009) analyzed nutrient characteristics of asphalt parking lot runoff for eight sites in North Carolina. Event mean concentrations (EMCs) and loads were measured from eight asphalt parking lots in North Carolina using automated flow meters and rain gauges. The number of water quality samples collected varied from 11 to 26 per site. Concentrations of total nitrogen (TN), total Kjeldahl nitrogen (TKN), ammonia–nitrogen (NH$_4^+$–N), nitrate–nitrogen (NO$_3^-$–N), total phosphorus (TP), and ortho–phosphate were 1.57, 1.19, 0.32, 0.36, 0.19, and 0.07 mg·L$^{-1}$, respectively.

Particles of dust washed off streets by stormwater are an important pathway of PAHs into urban streams. Zhao et al. (2009) analyzed size distributions and diffuse pollution impacts of PAHs in street dust in urban streams in the Yangtze River Delta. The content of total PAHs ranged from 1629 to 8986 μg·kg$^{-1}$ in street dust particles. The PAHs quantities increased from 2.41 to 46.86 μg·m$^{-2}$ in the sequence of new residential, rising through main roads, old town residential, commercial and industrial areas.

Stormwater runoff is an important contributor to the transport of indicator bacteria from urbanized watersheds to nearby receiving waters. Hathaway et al. (2009) analyzed indicator bacteria removal in stormwater best management practices (BMPs) in Charlotte, North Carolina. Among nine BMPs, only a wet pond, two wetlands, a bioretention area, and a proprietary device removed fecal coliforms with efficiency higher than 50% and one of the wetlands and the bioretention area had removal efficiency greater than 50% for *Escherichia coli* (*E. coli*). Results indicated that wet, nutrient–rich environments in many stormwater BMPs might contribute to the bacterial persistence in the BMP systems.
Wong et al. (2009) evaluated public health risks at recreational beaches in Lake Michigan. They found that Lake Michigan recreational beaches were being adversely impacted by human fecal pollution. Culturable viruses were detected by cell culture in 16 of the 30 (53%) water samples collected from Silver Beach in St. Joseph, Michigan and 9 of the 28 (32%) water samples collected from Washington Park Beach, Michigan City, Indiana. Most probable number estimation of viruses ranged from <0.6 MPN/100mL to 4.33 MPN/100mL at Silver Beach with an average of 0.85 MPN/100mL. The range was between <0.5 MPN/100mL and 5.70 MPN/100mL at Washington Park Beach with an average of 1.0 MPN/100mL.

2.2.2 Pollution from Highway Stormwater

Aryal and Lee (2009) investigated characteristics of suspended solids and micropollutants in first–flush runoff in Winterthur, Switzerland. Particle–bound micropollutants, such as PAHs, phthalate esters, and heavy metals (Cr, Ni, Cu, Zn, Pb), were investigated and detected. Among the three types of micropollutants, the concentration of PAHs showed similar behavior to suspended soils (SS). Lau et al. (2009) analyzed characteristics of highway stormwater runoff in Los Angeles. Strong correlations were observed among the heavy metals and between heavy metals and total PAHs. Total suspended solids were well correlated with most heavy metals according to datasets collected from 62 storm events. This study also revealed that approximately 30 to 35% of the mass being discharged in the first 20% of the runoff volume. Kalainesan et al. (2009) studied the performance of sedimentation basins (SBs) at highway construction sites. The data showed peak concentrations of TSS, total aluminum, total manganese, total iron, and total phosphate were closely correlated to localized rainfall peaks. High dissolved concentrations of metals (Fe, Mn, Mg and Ca), sulfate, and phosphate were observed to be drained into the SBs.
Lancaster et al. (2009) evaluated performance of roadside infiltration in managing stormwater runoff in semiarid eastern Washington. Particulates Cu, Zn, and Pb were monitored and levels of Cu, Zn, and Pb in the aqueous phase of runoff ranged from 10–200 \( \mu g \cdot L^{-1} \), while levels in sediments ranged from 20–75 mg \( \cdot kg^{-1} \) (dry weight). McKenzie et al. (2009) investigated metals associated with stormwater–relevant brake and tire samples. Representative tire and brake samples were collected from privately owned vehicles and aqueous extracts were analyzed for twenty–eight elements. Principal components analysis (PCA) revealed that tires were most influenced by Zn, Pb, and Cu, while brakes were best characterized by Na and Fe followed by Ba, Cu, Mg, Mn, and K; the latter three might be due to roadside soil contributions. Notably elevated Cd contributions were also found in several brake samples. Yun et al. (2009) investigated PAHs removal from road runoff in an urban nonpoint source pollutant reducing treatment system. The system was designed to treat the first-flush of stormwater from road. Under the operating condition with 0.55h hydraulic retention time and maximum road runoff of 9.5 \( m^3 \cdot h^{-1} \), the mean residual PAHs were 0.699 to 1.339 g \( \cdot L^{-1} \) and the percentage mean removal efficiency was 61.4 to 69.7%.

Murakami et al. (2009) carried out an experiment to evaluate sorption behavior of heavy metal species. They applied soakaway sediment receiving urban road runoff from residential and heavily trafficked areas by sequential batch tests. They found that the soakaway sediment adsorbed Ni in road runoff, whereas Zn was desorbed from the soakaway sediment in sorption tests. Ni, Cu, Zn, and dissolved organic carbon concentrations were higher in soakaway sediment leachates, obtained from sorption tests using heavily trafficked road dust leachates, than those using residential road dust leachates. Ni and Cu dominantly existed as stable complexes.
Dissolved organic matter in road runoff possibly enhances the release of Zn from soakaway sediments.

### 2.2.3 Pollution from Agricultural Runoff

Packett et al. (2009) investigated pollutant sources of the southern Great Barrier Reef lagoon. Results indicated that maximum pollutant concentrations at basin and sub-catchment scales were closely related to the percentage area of croplands receiving heavy rains. However, grazing lands contributed the majority of the long-term average annual load of most common pollutants. They also suggested that improved land management targets, rather than water quality targets, should be implemented to reduce the Great Barrier Reef (GBR) pollution.

Kato et al. (2009) studied runoff characteristics of nutrients from an agricultural watershed with intensive livestock production. On the basis of one year’s data, the mean concentrations of TP, TN, NO$_3^-$–N, and NH$_4^+$–N of drainage water were 2–6 times higher than those of the receiving river flowing through the watershed with low livestock density. The results suggested that the transport of the particulate materials and of TN, dissolved nitrogen (DN), and NO$_3^-$–N were mainly influenced by direct runoff (DR) and base-flow (BF), respectively. The results also revealed that the transport pathway of dissolved phosphorus (DP) and NH$_4^+$–N was similar to that of particulate materials and was affected by desorption from soil particles.

Zhang et al. (2009a) studied nutrient runoff induced by Hurricane Katrina from an agricultural area to coastal waters in Biscayne Bay, Florida. Nutrient concentrations before Katrina ranged from 0.06–24.2 μM (mean 3.3 μM) for nitrate and 0.01–0.18 μM (mean 0.1 μM) for soluble reactive phosphate. Five days after Katrina, nitrate concentrations ranged from 0.87–80.0 μM (mean 17.0 μM), with a bay-wide mean increase of 5.2–fold over pre-hurricane levels. Soluble reactive phosphate concentrations ranged from 0.07–0.62 μM (mean 0.2 μM), with a
bay–wide mean increase of 2–fold over pre–hurricane levels. The increases mostly occurred in an agricultural area in the southern Biscayne Bay watershed near Homestead.

Chua et al. (2009) investigated nutrients and suspended solids in dry weather and storm flows from a tropical catchment with various proportions of rural and urban land use. The EMCs of nutrients and TSS from sampling stations which had agricultural land use activities upstream were found to be higher. Comparison of Site EMCs (SMCs) with published data showed that the SMCs of the nutrients and TSS were generally higher than SMCs reported for forested areas but lower than published SMCs for urban areas. Positive correlations (p<5%) were found between loading and peak flow at locations impacted by urbanization or agricultural activities. Chen et al. (2009a) estimated the critical nutrient amounts (CNA) based on input–output analysis in the ChangLe watershed, an agriculture–dominated area in eastern China. Annual TN applied or generated amount (AGA) exceeded CNA by 53.2–61.3% and 46.0–55.2% according to the reach–end and whole–reach control methods, respectively. In contrast, TP AGA values were 90.3–95.9% and 68.3–73.2% below CNA values according to reach–end and whole–reach control methods, respectively.

Simon and Makarewicz (2009) studied stormwater events in Graywood Gully, a small agricultural watershed of Conesus Lake, New York, USA. The study revealed that levels of total coliforms, *E. coli*, *Enterococci*, and total heterotrophic bacteria were elevated in stormwater relative to nonevent flow. The median level of *E. coli* in nonevents was 200 CFU/100 mL whereas the median level during events was 3660 CFU/100 ml. Storm events accounted for 92% of all *E. coli* loading from Graywood Gully.

### 2.2.4 Pollution from Atmospheric Deposition

Huston et al. (2009) investigated the characterization of atmospheric deposition as a
source of contaminants in urban rainwater tanks in Brisbane, Queensland, Australia. Results indicated that flux of total solids mass correlates with average daily rainfall ($R^2 = 0.49$), indicating the dominance of the wet deposition contribution to total solids mass. On average 97% of the total mass of analyzed components was accounted for by $\text{Cl}^-$ (25.0%), $\text{Na}^+$ (22.6%), organic carbon (OC) (20.5%), $\text{NO}_3^-$ (10.5%), $\text{SO}_4^{2-}$ (9.8%), inorganic carbon (5.7%), $\text{PO}_4^{3-}$ (1.6%), and $\text{NO}_2^-$ (1.5%). For other minor elements the average flux from highest to lowest was in the order of Fe > Al > Zn > Mn > Sr > Pb > Ba > Cu > Se.

Pineda Rojas and Venegas (2009) carried out a study on atmospheric deposition of nitrogen emitted in the metropolitan area of Buenos Aires (MABA) to coastal waters of de la Plata River in Argentina. Results showed that mean annual deposition was 69,728 kg–N·year$^{-1}$ over 2,339 km$^2$ of the river. Dry deposition contributions of N–NO$_2$, N–HNO$_3$ and N–NO$_3^-$ to the mean annual deposition were 44%, 22%, and 20%, respectively. Wet deposition of HNO$_3$ and N–NO$_3^-$ represents 3% and 11% of total annual value, respectively. Dolislager et al. (2009) summarized the Lake Tahoe Atmospheric Deposition Study (LTADS). LTADS estimated that approximately 185, 3, and 755 metric tons respectively of N, P, and particulate matter (PM) directly deposited to the lake from the atmosphere. The data indicated that ammonia contributed the bulk of the N loading. Aerosols with diameters greater than 2.5 mm contribute the bulk of the P and PM mass loadings. The emission sources of P and PM appear to be primarily local and associated with motor vehicles.

Figure 2-1 (http://connecticutwatertrails.com) shows air pollution and contaminant source from atmospheric deposition.

Organic pollutants also were found in atmospheric deposition. Kang et al. (2009b) investigated several persistent organic pollutants to the East Rongbuk Glacier in the Himalayas.
from atmospheric deposition. The most abundant compounds detected in the snow samples were γ–hexachlorocyclohexane (γ–HCH) and α–HCH with mean concentrations of 123 pg·L⁻¹ and 92 pg·L⁻¹, respectively.

Zhang et al. (2009b) reviewed dry deposition of atmospheric mercury. Elemental gaseous mercury (Hg⁰), reactive gaseous mercury (RGM), and particulate mercury (Hgₚ) were studied. Typical dry deposition velocities (V_d) of Hg⁰ were in the range of 0.1–0.4 cm·s⁻¹ over vegetated surfaces and wetlands, but substantially smaller over non–vegetated surfaces and soils below canopies. RGM could deposit very quickly onto any type of surface, with its V_d ranging from 0.5–6 cm·s⁻¹. The very limited data for Hgₚ suggested that its V_d values were in the range of 0.02–2 cm·s⁻¹. Wan et al. (2009) investigated concentrations of RGM and Hgₚ in ambient air from a remote site at Changbai Mountain area in northeastern China. Results showed that mean concentrations of RGM and Hgₚ were 65 and 77 pg·m⁻³. THg concentrations ranged from 11.5 to
15.9 ng·L⁻¹ in rainwater samples and 14.9–18.6 ng·L⁻¹ in throughfall samples. Wet depositional flux in Changbai area was calculated to be 8.4 μg·m⁻²·a⁻¹, and dry deposition flux was estimated to be 16.5 μg·m⁻²·a⁻¹ according to a throughfall method and 20.2 μgm⁻²·a⁻¹ using a modeling method.

White et al. (2009a) measured mercury from wet deposition in Steubenville, Ohio. For a three month period of study, volume–weighted mean Hg concentrations observed at the eight sites ranged from 10.2 to 22.3 ng·L⁻¹. Samples collected at sites less than 1 km from coal–fired utility stacks exhibited up to 72% enhancement in Hg concentrations over regionally representative samples on an event basis and it was estimated that during summertime precipitation, 42% of Hg concentration in near–field samples could be attributed to the adjacent coal–fired utility source. The study conducted by Pandey and Pandey (2009) revealed that concentrations of heavy metals in cultivated soil horizon and in edible parts of open field grown vegetables increased over time and were significantly higher than those recorded in organic farming in glasshouse plots. Multiple regression analysis indicated that the major contribution of most heavy metals to vegetable leaves were from atmosphere. The study also suggested that if the present trend of atmospheric deposition was allowed to continue, it would lead to a destabilizing effect on this sustainable agricultural practice and would increase the dietary intake of toxic metals.

2.3 Modeling and Estimation of NPS Pollution

2.3.1 Assessment and Application of NPS Pollution Models

Park et al. (2009) compared assumptions, methodologies, and predictions of six independent models using the literature and local data for the Upper Ballona Creek Watershed in
Los Angeles, CA. Differences in land used definitions among the six studies produced up to 14% differences in average load predictions for TSS. Differences in runoff coefficient and EMC assumptions produced -70 to 124% differences in average TSS load. The combined effects of all assumptions produced differences in the estimated TSS mass loads by -68 to 118%.

In the study of Lin et al. (2009), an integrated watershed management model (IWMM) was applied for simulating the water quality and evaluating NPS pollutant loads to the I–Liao Creek in Taiwan. Simulated results indicated that NPS pollution had significant contributions to the nutrient loads to the I–Liao Creek during the wet season. Results also revealed that NPS pollution played an important role in the deterioration of downstream water quality and caused significant increase in nutrient loads into the basin’s water bodies. Chang et al. (2009) applied Windows version of the Virginia Stormwater (WinVAST) model to predict watershed responses to BMP implementation. It was found that the peak suspended solid concentration at the outlet of the watershed without any BMP and with one BMP, two BMPs, and three BMPs were 120, 90, 77 and 65 mg·L\(^{-1}\), respectively. Taking into account of all factors, the optimal number of BMPs should be four.

White et al. (2009b) applied the Soil Water Assessment Tool (SWAT) model to investigate quantitative pasture phosphorus management. This tool had been extensively applied in the Lake Eucha/Spavinaw Basin in northeastern Oklahoma and northwestern Arkansas. Results demonstrated the applicability of existing water quality models in the development of user friendly P management tools. Yang et al. (2009) also applied the SWAT model to assess the efficacy of flow diversion terrace (FDT) systems on maintaining surface water quality at the watershed level in the Black Brook Watershed (BBW) in northwestern New Brunswick. SWAT model was calibrated with three years of data (1992–1994) and found that SWAT performed
well in predicting the seasonal variation of water yield ($R^2 = 0.91$) and moderately well for sediment yield ($R^2 = 0.5$). Annual water yield reduction was 20% and annual sediment yield reduction was 56%.

Mishra et al. (2009) applied Hydrologic Simulation Program–Fortran (HSPF) model to investigate nonpoint source pollutant losses from a small watershed in the Damodar Valley Corporation, Hazaribagh, India. The model calibration and validation results revealed that the seasonal trend of HSPF simulated runoff, sediment yield, and NPS pollutants compared reasonably with their measured counterparts. Although nutrient concentrations were generally over–predicted for NO$_3^-$–N and under–predicted for NH$_4^+$–N and water–soluble P in the month of June when fertilizers releasing NH$_4^+$–N and P were applied in rice fields, the differences in the mean concentration were not significantly different at a 95% level of confidence. These results indicated that the HSPF model could be used as a tool for simulating runoff and sediment associated NPS pollution losses from the study area. Easton et al. (2009) applied the variable source loading function (VSLF) model to investigate dissolved phosphorus (DP) mobility based on data from 1996 to 2001. The percent of total DP loss of baseflow, nonmanured soil, manure/manured soil and barnyard were 19.5%, 4.8%, 72.3%, and 3.2%, respectively.

Krouse et al. (2009) applied a model named Battery Litter Mass Loading (BLML) to evaluate heavy metal mass release from urban battery litter. Ag, Cd, Cr, Cu, Hg, Li, Mn, Ni, Pd, Ti, Zn were detected in stormwater runoff. Model results indicated that at some urban sites zinc released from battery litter could be the largest source of zinc in urban pavement runoff. He and Davis (2009) applied a two dimensional Variable Saturated Flow and Transport Model to investigate stormwater flow and pollutant sorption in a bioretention cell. Model results indicated that the outflow volume was less than the inflow due to the storage and the extent of initial
unsaturation in the media. The outflow volume from loamsy sand media was larger than that from sandy loam media. The flow peak was reduced. Concentrations of naphthalene (NP) and pyrene (PY) in runoff vary with depth and most NP and PY (> 90%) were removed within about 3 cm media depth.

Pandey et al. (2009) evaluated the effective management plan for an agricultural watershed using ArcView Soil Water Assessment Tool (AVSWAT) model, remote sensing, and GIS from Banikdih watershed in Eastern India. Mean simulated values of runoff and sediment yield were 104.86 mm and 0.59 t·ha\(^{-1}\), while observed values were 96.12 mm and 0.53 t·ha\(^{-1}\); mean simulated nutrient losses of NO\(_3^–\)-N, Organic N (ON), SP and Organic P (OP) were 0.046, 0.091, 0.030, 0.009 kg·ha\(^{-1}\), while observed values were 0.042, 0.080, 0.026, 0.010 kg·ha\(^{-1}\), respectively, which proved that the model’s ability to simulate different processes and its link with ArcView GIS had a great potential as a tool for predicting the runoff and sediment yield.

Guber et al. (2009) evaluated coliform bacterial removal from vegetated filter strip (VFS) under overland flow condition. The kinematic wave overland flow model and the convective–dispersive overland transport model were applied. The VFS efficiency was found to be <95% in 25%, <75% in 23%, and <25% in 20% of cases. They revealed that relatively long high–intensity rainfalls, low hydraulic conductivities, low net capillary drive of soil, and high soil moisture contents before rainfalls caused the partial failure of VFS to retain coliforms from the infiltration excess runoff.

Coulliette et al. (2009) developed a hydrologic–driven mean trend model to predict levels of \textit{E. coli} in the Newport River Estuary (NPRE), which is a high–priority shellfish harvesting area in eastern North Carolina. This mean trend model was integrated in a Bayesian Maximum Entropy (BME) framework to produce informative space/time(S/T) maps depicting fecal
contamination across the NPREG during winter and summer months. These maps showed that
during dry winter months, predicted EC concentrations were below the shellfish harvesting
standard (14 MPN/100 mL). However, after substantial rainfall of 3.81 cm, the NPREG did not
appear to meet this requirement. Warmer months resulted in the predicted EC concentrations
exceeding the threshold for the NPREG.

Palla et al. (2009) applied the SWMS–2D model, based on Richards’ law and the Van
Genuchten–Mualem functions, to investigate subsurface water flow in the coarse–grained porous
matrix of a green roof. The model adequately reproduced hydrographs, as demonstrated by the
limited relative percentage deviations obtained for the total discharged volume, the peak flow
and the hydrograph centroid. Furthermore, the predicted water content closely matches the
observed one at various depths along the vertical profile where measurements were available,
thus confirming that the model correctly describes the variably saturated flow field within the
green roof.

2.3.2 Total Maximum Daily Load (TMDL) Calculations

Mishra and Deng (2009) presented sediment TMDL for the Amite River, Louisiana, US.
The TMDL development consisted of four components: (1) development of a new 1–D model
for cohesive sediment transport, (2) estimation of sediment loads (sources) due to watershed
erosion, (3) river flow computation, and (4) determination of sediment TMDL for the Amite
River. Sediment erosion in the Amite River Basin was calculated by combining the USLE
(Universal Soil Loss Equation) model with GIS and the digital elevation model of the Amite
River Basin. The calculated average annual rate of soil erosion in the Amite River Basin was
13.368 tons per ha, producing a nonpoint sediment load of 103 mg/L to the Amite River. The
flow computation was performed using the HEC–RAS software. The computed sediment
concentration in the Amite River varied in the range of 3–114 mg/L and sediment TMDL was 281.219 tons/day. The reduction necessary to support beneficial uses of the river was 55% or 275.946 tons/day. Results indicated that the combined application of the new 1–D sediment transport model, GIS, USLE model, and HEC–RAS was an efficient and effective approach to sediment TMDL development. Etemad–Shahidi et al. (2009) calculated TMDL for Total Dissolved Solids (TDS) for the Karkheh Dam Reservoir in Iran. A laterally averaged 2D model called CE–QUAL–W2 was used for the TMDL calculation. Modeling results revealed that a 50% reduction in the TDS load was required for a 40% reduction in TDS at the reservoir outlet.

Stringfellow et al. (2009) investigated the influence of river eutrophication on dissolved oxygen (DO) TMDL. A mass balance model was developed using Watershed Analysis Risk Management Framework (WARMF). Results demonstrated that phytoplankton biomass accumulates rapidly in the 88 km–long reach where plankton from small, slow moving tributaries were diluted and combined with fresh nutrient inputs in faster moving water. Model results also suggested that modest reductions in nutrients alone would not limit algal biomass accumulation, but that combined strategies of nutrient reduction and algal control in tributaries might have benefit. Todd et al. (2009) studied effects of high sediment oxygen demand within an in–stream swamp in Southern Georgia on DO TMDL in coastal blackwater streams. Results indicated that sediment oxygen demand (SOD) rates for in–stream swamps averaged 5.37 gO₂·m⁻²·day⁻¹ and ranged from 0.491 to 14.189 gO₂·m⁻²·day⁻¹, up to 18 times higher than values reported for southeastern sandy–bottomed streams. SOD rates were significantly correlated with a number of sediment parameters, with SOC and TOC in the 0–5 cm depth fraction (the best predictors of SOD rate within the in–stream swamp system), both explaining 35% of the variation. Results also demonstrated that in–stream swamps in blackwater streams played a
principal role in determining the oxygen balance of the watershed as a whole due to areas of intense oxygen demand.

Petersen et al. (2009) employed bacteria loading estimator spreadsheet tool (BLEST) to investigate spatial *E. coli* loads to the Buffalo Bayou watershed in Houston, Texas. Results showed that the dry weather *E. coli* load in Buffalo Bayou was estimated to be 244 billion MPN/day and would require an overall 48% reduction to meet the contact recreation standard, while wet weather loads would need to be reduced by 99.7% by BLEST. Schoen et al. (2009) employed the Bayesian load duration curve to estimate bacterial TMDL in urban streams. Using the best estimate 90th percentile in–stream loads, the Bayesian method predicted indicator bacterial load reductions ranging between 68% for low flows and 99.9% for high flows. The pre–implementation distribution of in–stream indicator bacterial concentration demonstrated that the stream exceeded the standard of 235 cfu/100mL for *E. coli* in 76.1% of the time during the recreational season with a 95% credible interval.

Tiefenthaler et al. (2009) investigated fecal indicator bacteria (FIB) in reference streams during dry weather from Southern California. *E. coli*, *enterococci* and total coliforms were measured from 15 unimpaired streams in 11 southern California watersheds weekly for one full year. Results revealed that nearly 82% of the time, samples did not exceed daily and monthly bacterial indicator thresholds. *E. coli* had the lowest daily percent exceedance (1.5%) compared with *enterococci* (13.7%). Results also demonstrated that indicator bacteria levels fluctuated seasonally with an average of 79% of both *enterococci* and total coliforms exceedances occurring during summer months.

Nicole et al. (2009) estimated mercury loads to San Francisco Bay, California, USA. Results revealed that unfiltered THg concentrations ranged from 3.2 to 75 ng·L⁻¹ and showed a
strong correlation \( R^2 = 0.8, \ p < 0.001, \ n = 78 \) to suspended sediment concentrations (SSC). Daily THg loads varied from below the limit of detection to 35 kg during 2002 to 2006 and from 20.1 to 57 kg during 1995 to 2001. During high flows, THg loads were greatest. According to the 12-year record, 5, 10, 20, 50, and 90% of the THg load occurred in just 0.1, 0.2, 0.6, 4.3, and 42% of the days, respectively. Estimated annual THg loads ranged from 61 ± 21 kg in 2002 to 470 ± 170 kg in 2006 during the period of THg observations. Based on these calculations, the average annual THg load passing into San Francisco Bay through the cross section at Mallard Island from 1995 to 2006 was 260 ± 94 kg.

Schilling and Wolter (2009) applied SWAT model to investigate nitrate–nitrogen load reduction strategies. The SWAT model comprised 173 subbasins and 2,516 hydrologic response units and included point and nonpoint nitrogen sources. Modeling results revealed that nonpoint sources accounted for 95% of the total nitrate export. The reduction in fertilizer applications from 170 to 50 kg·ha\(^{-1}\) would be sufficient to achieve the 34.4% reduction in nitrate loads required in the TMDL. Results also indicated that greatest load reduction for the area of land treated was associated with reducing loads from 55 subbasins with the highest nitrate loads, a 14% reduction in nitrate loads was achieved by reducing applications on 30% of the land area.

Wang et al. (2009) investigated water quality management of an agriculturally dominated watershed, Kansas, USA. Annualized Agricultural Nonpoint Source (AnnAGNPS) simulation indicated that point source dischargers contributed 8% of TN and 24% of TP loadings to the Marmaton River, agricultural nonpoint contributed 55% of TN and 49% of TP loading. 3% of the watershed area (3,244 ha) needed to be targeted to control TN loading whereas 1% of the total area (1,319 ha) was required for TP reduction management based on TMDL analysis and model simulation. Managing the TN areas alone could achieve a 57% reduction in the TP load
required for the TMDL, whereas managing the targeted TP areas could only provide 30% of the required TN reduction. Areas required both TN and TP management comprised 469 ha. Targeting these areas could achieve approximately 22% of the required TN reduction and 29% of the required TP reduction. Overall, 4,094 ha would require management to achieve TMDL reduction goals.

2.4 NPS Pollution Management

2.4.1 Low–Impact Development (LID)/Best Management Practices (BMPs) Implementation

Lai and Lam (2009) investigated characteristics of phosphorus sorption by sediments in a subtropical constructed wetland in Hong Kong Wetland Park (HKWP). They found that sediments had very low equilibrium phosphorus concentration values between 4.6 and 23.6 µg·L⁻¹, suggesting that soluble P would be readily adsorbed under moderate to high P loadings. The adsorption kinetic curves of HKWP sediments rose sharply during the first hour of incubation. The first stage of P sorption was completed within 20 minutes for both phragmites reedbeds and freshwater marsh sediments, with the highest first–order adsorption rate constants being 1.01–2.11 h⁻¹. The second stage of P sorption took for 1.6–6.1 h, with the first–order rate constant between 0.06–0.14 h⁻¹. The third adsorption stage commenced after 1.8–6.4 h of incubation, with the first–order rate constants being 0.003 to 0.007 h⁻¹.

Yates and Prasher (2009) investigated phosphorus reduction from agricultural runoff in a pilot–scale surface–flow constructed wetland (CW). Tanks were flooded continuously with an artificial agricultural runoff solution containing 0.3 mg·L⁻¹ dissolved reactive P. The six treatment tanks retained 0.9–1.6 gP·m⁻², which corresponded to an average removal efficiency of 41%. There was no significant difference in the P retention by the two soil types. A bromide
tracer test revealed a mean hydraulic retention time of 2.2 days for all tanks. However, the active volume of the sand tanks was greater. This investigation suggested that a sandy soil might be less prone to reducing conditions in a surface–flow CW and therefore maintained its role as a P sink for a longer time than the sandy clay loam.

Gregoire et al. (2009) investigated the role of artificial wetland (AW) ecosystems in mitigating agricultural nonpoint–source pesticide pollution. Results revealed that the control of the hydraulic design and the use of adsorbing materials could be useful to increasing the pesticide’s residence time and the contact between pesticides and biocatalyzers. Pesticide fluxes could be reduced by 50–80% when hydraulic pathways in AWs were optimized by increasing ten times the retention time, by recirculation of water, and by deceleration of the flow. A bioremediation method should lead to an almost complete disappearance of pesticide pollution.

Chen et al. (2009b) carried out an experiment on nitrogen and phosphorous removal by ornamental and wetland plants. Canna, iris, calla lily and dwarf papyrus were compared with arrow arum, pickerelweed and bulltongue arrowhead. Results showed that N and P removed from the nutrient recirculation system (NRS) units planted with canna (98.7% N and 91.8% P) were higher than those planted with iris and arrow arum (31.6% and 31.5% N, and 38.5% and 26.3% P, respectively). Results also suggested that canna was a promising ornamental species for stormwater pollutant mitigation, and harvesting the aboveground biomass of canna could effectively remove N and P from the treatment system.

Figure 2-2 (http://www.gocolumbiamo.com/PublicWorks/Sewer/wwtppg_4.php) and Figure 2-3 (https://engineering.purdue.edu/~frankenb/NU-prowd/images9.htm) show practical a constructed wetland and a structural diagram of constructed wetland, respectively.
Zgajnar–Gotvajn and Zagorc–Koncan (2009) carried out a study on bioremediation of highway stormwater runoff. A biological activator Micropan Petrol (Eurovix, s.r.l., Italy) was used. The activator was a mixture of enzymes, bacteria and nutrients which was intended to be used for activation and improvement of biodegradability of hydrocarbons in crude oil. It contained natural microorganisms with optimal capacity for degradation of complex hydrocarbons. The application of activators increased degradation of organic pollution (up to 60%), but it should be added only once in a low concentration. The application of activator was necessary only in the case of heavier pollution. It would increase pollution in the case of low polluted stormwater runoff.

Diblasi et al. (2009) evaluated the removal effectiveness of PAHs in a bioretention cell. It was an infiltration/filtration practice containing a mixed layer of about 90 cm of soil, sand, and organic matter, planted with appropriate vegetation. Results indicated that the PAHs EMC reduction ranged from 31 to 99%, with a mean discharge EMC of 0.22 μg·L⁻¹. The mass load decreased from a mean value of 0.0180 kg·ha⁻¹·yr⁻¹ to 0.0025 kg·ha⁻¹·yr⁻¹, suggesting an average PAHs mass load reduction of 87% to the discharging watershed. PAHs removal positively correlated with TSS removal.

Passeport et al. (2009) studied performance of grassed bioretention cells in reducing stormwater runoff pollution in central North Carolina. Results showed that EMCs and loads of effluent nitrogen species except for NO₂⁻–N and NO₃⁻–N were significantly (α = 0.05) lower than those of the inflow, and nitrogen species load reductions ranged from 47 to 88%. TP and OPO₄⁻–P EMCs were significantly lower than those at the inlet. Reductions were 58% and 63% for TP, and 78% and 74% for OPO₄⁻–P for two bioretention cells, respectively. Considering effluent concentrations in addition to removal rates, the grassed cells showed promising results for fecal
coliform (FC) and nutrient pollution abatement when compared to conventionally vegetated bioretention (trees, shrubs, and mulch) previously studied.

Figure 2-2 Constructed wetland

Figure 2-3 Structure of constructed wetland

Figure 2-4 (http://ian.umces.edu/imagelibrary/displayimage-87-132.html) and Figure 2-5 (http://www.epa.gov/oaintrnt/stormwater/cells_infiltration.htm) show practical bioretention cell and structure diagram of bioretention cell, respectively.
Characteristics of Two–layered porous landscaping detention basin were investigated by Guo et al. (2009). Results revealed that the ratio of design infiltration rate to sand–mix hydraulic conductivity was very important to selecting the thickness of sand–mix layer underneath a porous bed and the total filtering thickness for both sand–mix and gravel layers was found to be related to the drain time and infiltration rate. Diebel et al. (2009) analyzed the effectiveness of landscape planning for agricultural nonpoint source pollution reduction. Results indicated that in most watersheds, a large proportion (approximately 70%) of pollutants could be eliminated from streams with buffers. Cumulative frequency distributions of load reduction potential indicated that targeting pollution reduction in the highest 10% of Wisconsin watersheds would reduce TP and sediment loads in the entire state by approximately 20%.

Figure 2-6 (http://walmart-enviro.pbworks.com/w/page/12579507/Green-Roof) and Figure 2-7 (http://www.pacwestroofinginc.com/Rooftypes-Vancouver/Green-Roofing-ancouver.html) show structure diagram of green roofs and practical green roofs, respectively.
Teemusk and Mander (2009) analyzed the temperature regime of a light weight aggregates (LWA)–based greenroof in comparison with a modified bituminous membrane roof. Results showed that in Estonian climatic conditions, an extensive greenroof was sufficiently capable of protecting the roof membrane from extreme temperatures. Measurements also showed that the surface of the LWA media in the greenroof heats and cools more than the surface of the bituminous roof. Berndtsson et al. (2009) investigated runoff water quality from intensive and extensive vegetated roofs. Results indicated that both extensive and intensive vegetated roofs were a sink of NO₃⁻–N and NH₄⁺–N with similar performance. The intensive vegetated roof was also a sink of TN in contrast to the extensive roof. Phosphorus release was observed from the extensive vegetated roof but not from the intensive vegetated roof. Release of DOC and potassium was observed from both roofs. Getter et al. (2009) analyzed carbon storage of different plants of green roofs. Results showed greens roofs composed primarily of Sedum species in Michigan and Maryland stored 162 g·C·m⁻². Storage of greens roofs also composed primarily of Sedum species in East Lansing, MI ranged from 64 g·C·m⁻² to 239 g·C·m⁻².
Blecken et al. (2009a) evaluated the influence of a submerged zone and a carbon source on heavy metal removal in stormwater biofilters. A submerged (anoxic) zone (SZ) and a cellulose based carbon source (C) were used because they could enhance denitrification. The results showed that SZ and C had a significant impact on metal treatment especially for Cu and the best metal treatment was achieved with 450 and 600mm SZ.

Characteristics of phosphorus adsorption on aluminum oxide media was investigated by Sansalone and Ma (2009). Results indicated that adsorption increased with decreasing aluminum oxide coated media (AOCM) size and decreasing pH; Ca$^{2+}$ enhanced P adsorption by forming ternary complexes; SO$_4^{2-}$ inhibited P adsorption by competing for available adsorption sites. Ionic strength and NO$_3^-$ had minor to negligible effects on adsorption equilibrium, respectively. The equilibrium adsorption capacity for P by AOCM was strongly dependent on pH and P adsorption (mg of P·g$^{-1}$ of media) increased with decreasing AOCM size.

Wild and Davis (2009) simulated the performance of vegetated storage–infiltration BMP based on historic Maryland rainfall data. The model BMP was effective in attenuating volume (42% total volume reduction) and peak flow (median peak output to peak input flow ratio was 0.058). The simulated mean effluent pollutant event mean concentration was much less than the influent (0.284 compared with 1.51 mg·L$^{-1}$) and the overall mass load reduction was 92%. However, the results also suggested a need to incorporate into BMP performance guidelines the impact of the variable influent hydrologic and pollutant concentration characteristics. Emphasis should be placed on discharge water quality and statistical distributions rather than on single–percent removal values.

Blecken et al. (2009b) evaluated the influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters in laboratory. They revealed that the
biofilters receiving regular stormwater input were capable of removing over 95% metals. The highest metal accumulation occurs in the top layer of the filter media. However, after antecedent drying before a storm event exceeding 3–4 weeks, the filters performed significantly worse, although metal removal still remained relatively high.

Syring et al. (2009) introduced the attenuation of roadway–derived heavy metals by wood chips. They used oak and maple chips with particle sizes ranged from 0.9–20 mm. Results indicated that the highest dissolved copper concentration in the effluent was 3%–25% of input, but with little retention of the total copper mass. The wood chips aged up to 9 months had the most effective treatment; the wood chip had capacity of 0.16 g SS per g wood. However, some kinds of heavy metal released from the wood chips in the runoff. Applications of wood chips in treating roadway runoff would not provide a significant decrease in TMDL contributions.

Hatt et al. (2009) summarized the hydrologic and pollutant removal performance of stormwater biofiltration system at the field scale. Results showed that biofilters could effectively attenuate peak runoff flow rates by at least 80% and reduced runoff volumes by 33%. Load reduction of suspended solids and heavy metals could reach 90% but nitrogen was difficult to remove. They suggested that reconfiguration of biofilter design to manage the deleterious effects of drying on biological activity was necessary to ensure long term nitrogen removal.

Faucette et al. (2009) investigated stormwater pollutant removal performance of compost filter socks (FS). FS had high removal efficiency to pollutants, 65% of clay (<0.002 mm), 66% of silt (0.002–0.05 mm), 17% of NH$_4^+$–N, 11% of NO$_3^-$–N, 74% of total coliform (TC), 75% of E. coli, 37–72% of Cd, Cr, Cu, Ni, Pb, and Zn. However, removal efficiency increased to 87 and 99% for TC and 89 and 99% for E. coli, respectively when BactoLoxx was added; 47–74% for heavy metal when MetalLoxx was added; 27% for NH$_4^+$–N when NitroLoxx was added.
Liu et al. (2009) examined the hydraulic and chemical response of a volumetric clarifying filter (VCF) system to 1,088 m² concrete–paved watershed loadings in Baton Rouge, Louisiana, for fully captured events. VCF deployment incorporated aluminum oxide–coated media for phosphorus adsorption after it was demonstrated that common media (perlite and sand) were ineffective for adsorption. Results indicated that while interevent runoff retention was a common practice, the coupled hydrochemical behavior and fate of runoff chemicals subject to storage must be integrated into such unit operations and best management practices require more frequent maintenance and sludge removal.

2.5 Socioeconomic Analysis of NPS Pollution Control

Davis and Birch (2009) investigated the cost–effectiveness of stormwater remediation measures in urban areas. The article revealed that priority pollutants were predominantly (79–87%) derived from runoff from residential property and roads as disseminated urban surfaces. The apportionment of funding in better accordance with the maximum potential effectiveness of stormwater treatment modes and the pollutant–export characteristics of urban catchments could thus be expected to achieve a more cost–effective result from such funding initiatives.

Williams and Wise (2009) analyzed economic impacts of alternative approaches to stormwater management and land development. Results showed that reduction in lot size to preserve open–space and conversion from a curb and gutter stormwater drainage system to a swale–based system would both result in a lower sale price per lot. Estimated construction costs indicated that this same combination of site planning and stormwater system design would result in the lowest per lot construction cost. The ratio of revenue (sale price) to construction cost showed that a development incorporating lot size reductions for open–space preservation and a
swale–based stormwater management system was the preferred option over the first half of the study period, but was not in the second half.

Houdeshel et al. (2009) evaluated the life–cycle costs of LIDs. Vegetative roofs, rainwater catchment systems, and bioretention facilities could be estimated using cost tools recommended by the Water Environment Research Federation (WERF). These tools provided a detailed framework to facilitate cost estimation for capital costs, operation and maintenance costs, and life–cycle net present value. The tools could serve as a format for cost reporting for past, current and future projects, and also provided users with planning–level cost estimates. The use of the cost tools would enable consistent reporting of cost data on LIDs. Users would be able to determine the cost of each component of the project, both in materials and in planning and design.

Marengo et al. (2009) developed green streets prototypes to reduce combined sewer overflows for Cincinnati. Green streets program included porous pavements, subsurface infiltration, infiltration trench, bioretention, and vegetated planter box, vegetated roof. CH2M HILL’s Low Impact Feasibility and Evaluation (LIFE) model was applied to evaluate each of the BMP concepts in terms of runoff reductions resulting from the planned level of storage, infiltration into the subsurface soils, and evapotranspiration. Cost estimates were developed to assess runoff reduction efficiency. For vegetated curb extensions, infiltration under parking, tree trenches, porous sidewalk prototype, percent of volume reduction was 33% and unit runoff reduction cost was $0.23–0.33 gallon$^{-1}$; for vegetated curb extensions, infiltration under parking prototype were 97% and $1.48–1.72$ gallon$^{-1}$; for bioretention were 42% and $0.33$ gallon$^{-1}$; for porous pavement were 100% and $0.71–0.96$ gallon$^{-1}$; for vegetated roofs were 56% and $0.21$ gallon$^{-1}$. 
2.6 Conclusions

This chapter presents a comprehensive review of latest research advances in nonpoint source water pollution. Modeling progresses in total maximum daily load calculations for nonpoint source pollution are also reviewed. Various low impact development technologies and BMPs for mitigating nonpoint source pollution and their socioeconomic impacts are assessed.

Due to the first-flush phenomenon of nonpoint source pollution, more effective BMPs for treatment of first-flush portion of stormwater runoff should be developed and applied. Modeling tools for simulation of contaminant removal in BMPs are also needed.
CHAPTER 3. COLUMN EXPERIMENT ON NITROGEN REMOVAL

3.1 Introduction

This chapter introduces two sets of columns experiments on nitrogen removal; one set of laboratory experiments was conducted with natural stormwater, and the other set of laboratory experiments was conducted with secondary wastewater. Both of them are used in this study to simulate nitrate-nitrogen removal in the first-flush reactor.

3.2 Laboratory Experiments Using Natural Stormwater

3.2.1 Gathering of Stormwater Samples

The column experiment data listed in the report by Deng (2009) were used for investigating denitrification process in the first-flush reactor. A series of stormwater samples were collected from the I-10 elevated roadway section over City Park Lake in urban Baton Rouge. Figure 3-1 (Deng, 2009) shows stormwater sampling site at the I-10 roadway, where the average annual daily traffic (ADT) volume for the eastbound I-10 lanes is 70,400 vehicles, and the mean annual precipitation at the site is about 1460 mm/year.

Figure 3-2 (Deng, 2009) shows a plan view of the site. Stormwater runoff is generated from a 544m$^2$ section of Portland Cement Concrete (PCC) pavement and collected from the lower expansion joint. The pavement catchment area in the site is 12.2m wide by 44.6m long, with a tangential slope of 2.02%. Arrows in Figure 3-2 indicate the direction of flow. All flow was captured from the downspout connected to the lower expansion joint, as shown in Figure 3-1 and Figure 3-2.
Figure 3-1 Stormwater sampling site at the I-10 roadway section at City Park Lake

Figure 3-2 Plan view of experimental site (not to scale)
3.2.2 Selection of Filter Media

Figure 3-3 shows three columns with different combinations of filtering material layers for laboratory experiments.

![Figure 3-3 Column experiments setup for the first-flush reactor](image)

Filters medium used in laboratory experiment include: (a) a mixture of Smart Sponge and Hydra CX2, (b) wood chip, (c) mulch, (d) zeolite, (e) sand, (f) sawdust, and finally, (g) gravel.

Smart Sponge (Figure 3-4) (http://www.abtechindustries.com/index.asp?mid2=169) is an innovative polymer that is chemically selective to hydrocarbons and can destroy bacteria. Smart Sponge can fully encapsulate recovered oil, and prevent absorbed oil from leaching.

Hydra CX2 (Figure 3-5) (http://www.wateronline.com/article.mvc/North-American-Green-Introduces-HydraCX2-Cott-0001) is a high-performance hydraulic mulch, which is used to reduce sediment loss or filters loss.
Figure 3-4 Filter material: smart sponge

Figure 3-5 Filter material: hydra CX2

Figure 3-6 Filter material: wood chip

Figure 3-7 Filter material: mulch

Figure 3-8 Filter material: sawdust

Figure 3-9 Filter material: zeolite

Figure 3-10 Filter material: sands

Figure 3-11 Filter material: gravel
Wood chip (Figure 3-6), mulch (Figure 3-7) and sawdust (Figure 3-8) provide dissolved carbon sources as well as carriers for bacteria.

Zeolite (Figure 3-9) has a porous structure that can accommodate a wide variety of cations, which can remove some heavy metals in stormwater.

Sands (Figure 3-10) and gravel (Figure 3-11) provide surface area for bacteria and prevent the reactive media from clogging the effluent piping.

3.2.3 Introduction to Stormwater Column Experiments

Ten gallons of natural stormwater samples were collected using two coolers on September 14, 2008, December 9, 2008, January 24, 2009, March 16, 2009, respectively, from the I-10 elevated roadway section over City Park Lake in urban Baton Rouge. Table 3-1 shows experimental sample dates and rainfall precipitation.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Sampling date and rainfall</th>
<th>Antecedent rainfall date and amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>09/14/2009; 0.44 inch</td>
<td>09/11/2009; 0.41 inch</td>
</tr>
<tr>
<td>Test 3</td>
<td>12/09/2009; 0.57 inch</td>
<td>12/04/2009; 0.94 inch</td>
</tr>
<tr>
<td>Test 4</td>
<td>01/24/2009; 0.05 inch</td>
<td>01/18/2009; 0.04 inch</td>
</tr>
<tr>
<td>Test 5</td>
<td>03/16/2009; 0.76 inch</td>
<td>03/15/2009; 1.43 inch</td>
</tr>
</tbody>
</table>

Influent and effluent samples were analyzed for conventional water quality parameters in the Water Quality Laboratory in the Department of Civil and Environmental Engineering at LSU by standard methods. The influent was continuously pumped into the columns using a micropump. The effluent was controlled through a valve. In order to achieve a minimum
residence time of 24 hours, the effluent flow rates varied in the range of 400–600 ml/hour. Actual residence time of the stormwater in columns ranged from 25 to 31 hours. The diameter of the column is 15.2 cm, the height of woodchips/mulch/sawdust media layer is 0.28 m, the flow velocity is 0.0000109 m/s, and the Hydraulic Residence Time (HRT) is 30 hours.

The intermittent periods for the tests #4 and #5 were 45 days and 50 days, respectively. The columns were kept dry during the intermittent periods to mimic the potential natural scenario to occur in the first-flush reactor and to investigate the effect of dormant periods on contaminant removal efficiency of the columns. The tests #4 and #5 were intended to examine the durability of the first-flush reactor and the long term variability of contaminant removal efficiency of the reactor. Therefore, experiment conditions including the filter media and flow rates were not changed for the last three runs.

### 3.2.4 Data from Stormwater Column Experiments

Table 3-2 and Table 3-3 show filter layer combinations used in the 4 tests.

Table 3-4 presents results from the column experiments conducted by Deng (2009) using highway stormwater, which contain 4 different tests.

**Table 3-2 Multi-layer Combination of Filter Media Used in Test 1**

<table>
<thead>
<tr>
<th>Layer/ scenario</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wood Chip</td>
<td>Spanish Moss</td>
<td>Mulch</td>
</tr>
<tr>
<td>2</td>
<td>Sand</td>
<td>Sand</td>
<td>Sand</td>
</tr>
<tr>
<td>3</td>
<td>Sawdust</td>
<td>Sawdust</td>
<td>Sawdust</td>
</tr>
<tr>
<td>4</td>
<td>Gravel</td>
<td>Gravel</td>
<td>Gravel</td>
</tr>
</tbody>
</table>
Table 3-3 Multi-layer Combination of Filter Media Used in Tests 3, 4, and 5

<table>
<thead>
<tr>
<th>Layer/ scenario</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sponge/Hydra CX2</td>
<td>Hydra CX2</td>
<td>Mulch</td>
</tr>
<tr>
<td>2</td>
<td>Sand</td>
<td>Sand</td>
<td>Sand</td>
</tr>
<tr>
<td>3</td>
<td>Sawdust</td>
<td>Sawdust</td>
<td>Sawdust</td>
</tr>
<tr>
<td>4</td>
<td>Gravel</td>
<td>Gravel</td>
<td>Gravel</td>
</tr>
</tbody>
</table>

Table 3-4 Results of Column Experiments using Highway Stormwater

<table>
<thead>
<tr>
<th>Test No. /Sampling date</th>
<th>Column</th>
<th>TSS</th>
<th>TN</th>
<th>NO\textsubscript{2} as N</th>
<th>NO\textsubscript{3} as N</th>
<th>TKN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>09/14/08</td>
<td>1-0*</td>
<td>72</td>
<td>2.16</td>
<td>0.52</td>
<td>1.64</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td></td>
<td>1-A</td>
<td>50</td>
<td>2.0</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1-B</td>
<td>62</td>
<td>1.35</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>1-C</td>
<td>56</td>
<td>2.45</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>2.45</td>
</tr>
<tr>
<td>09/15/08</td>
<td>3-0</td>
<td>1029</td>
<td>11.59</td>
<td>0.27</td>
<td>2.71</td>
<td>8.61</td>
</tr>
<tr>
<td></td>
<td>3-A</td>
<td>20</td>
<td>3.6</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>3-B</td>
<td>97</td>
<td>23.9</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>23.90</td>
</tr>
<tr>
<td></td>
<td>3-C</td>
<td>18</td>
<td>2.10</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>1.51</td>
</tr>
<tr>
<td>Test 3</td>
<td>4-0</td>
<td>239</td>
<td>10.40</td>
<td>0.41</td>
<td>4.74</td>
<td>5.25</td>
</tr>
<tr>
<td>12/09/08</td>
<td>4-B</td>
<td>42</td>
<td>10.60</td>
<td>n.a.</td>
<td>0.78</td>
<td>9.82</td>
</tr>
<tr>
<td></td>
<td>4-C</td>
<td>37</td>
<td>5.00</td>
<td>n.a.</td>
<td>0.78</td>
<td>4.22</td>
</tr>
<tr>
<td>12/10/08</td>
<td>5-0</td>
<td>54</td>
<td>2.00</td>
<td>0.07</td>
<td>0.16</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>5-A</td>
<td>8</td>
<td>1.50</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>5-B</td>
<td>103</td>
<td>6.20</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>6.20</td>
</tr>
<tr>
<td></td>
<td>5-C</td>
<td>61</td>
<td>1.60</td>
<td>n.a.</td>
<td>&lt;0.02</td>
<td>1.60</td>
</tr>
</tbody>
</table>

*1-0, 3-0, 4-0, and 5-0 are influent concentrations.
3.3 Laboratory Experiments Using Secondary Wastewater

3.3.1 Introduction to Wastewater Column Experiments

Data from laboratory experiments conducted by Eljamal et al. (2009), Eljamal et al. (2008), and Eljamal et al. (2006) were also used. The column experiments were carried out using resin columns of 45 cm height and 10 cm internal diameter. The wire mesh (0.1 mm) and the filter paper (ADVATEC no. 6) were placed at the bottom of each column. The top and the bottom of the column were closed using glass transparent resin plates with tubes (20 mm Diameter) inserted for the flow inlet and flow outlet. Columns were packed to a height of 30 cm with soil and sawdust. The column was packed with a mixture of sawdust (50%) and soil (50%). The secondary wastewater was constantly supplied at the top of the two columns for 56 days and the average temperature was measured at 22°C. The wastewater level was maintained at 30 cm depth above the soil sawdust surface throughout the experiment. The average flow rate was 0.011 cm$^3$/s.

Influent and effluent samples were collected daily in glass bottles and then chemical concentration was determined. The cation concentration was measured by the atomic absorption device (PerkinElmer Japan, 3100 model), while anion concentration was measured by the ion chromatography (Yoko Analytical Systems model). Electric conductivity, oxidation–reduction potential, dissolved oxygen and pH were measured by electrode (DKK-TOA). Hydraulic heads were measured using piezometers located 0, 5, 10, 20, 30 cm below the sand–sawdust surface. The values of piezometers were used for calculation of permeability. The permeability of the columns was calculated from the flux and pore water head using Darcy’s law. Flux was measured by the discharge rate of effluent from the outlet. Secondary treated municipal
wastewater was supplied from Wajiro wastewater treatment plant, the soil was collected from actual paddy field and the sawdust was collected from a local wood factory in Fukuoka City, Japan.

Figure 3-12 Setup of column experiments with wastewater (Eljamal et al. 2009)

Figure 3-13 Measured and simulated nitrate-nitrogen concentrations for wastewater influent (Eljamal et al. 2009)
Figure 3-12 (Eljamal et al. 2009) shows column experiment setup, and Figure 3-13 (Eljamal et al. 2009) shows measured and simulated nitrate-nitrogen concentration for the two columns.

### 3.3.2 Data from Wastewater Column Experiments

Table 3-5 Effluent data from laboratory experiments conducted using secondary wastewater

<table>
<thead>
<tr>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.2857</td>
<td>10.0</td>
<td>0.3571</td>
<td>24.0</td>
<td>0.2886</td>
<td>36.0</td>
<td>0.2486</td>
</tr>
<tr>
<td>1.9</td>
<td>0.3229</td>
<td>11.1</td>
<td>0.3914</td>
<td>25.0</td>
<td>0.2486</td>
<td>38.0</td>
<td>0.1771</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1429</td>
<td>14.0</td>
<td>0.3914</td>
<td>27.9</td>
<td>0.2486</td>
<td>39.1</td>
<td>0.1086</td>
</tr>
<tr>
<td>4.0</td>
<td>0.3229</td>
<td>14.9</td>
<td>0.3571</td>
<td>29.0</td>
<td>0.1771</td>
<td>42.1</td>
<td>0.1086</td>
</tr>
<tr>
<td>5.9</td>
<td>0.3571</td>
<td>16.0</td>
<td>0.3229</td>
<td>30.0</td>
<td>0.1771</td>
<td>44.0</td>
<td>0.1457</td>
</tr>
<tr>
<td>7.1</td>
<td>0.18</td>
<td>17.1</td>
<td>0.2886</td>
<td>30.9</td>
<td>0.3229</td>
<td>46.0</td>
<td>0.1086</td>
</tr>
<tr>
<td>7.9</td>
<td>0.4629</td>
<td>20.9</td>
<td>0.2857</td>
<td>32.0</td>
<td>0.2486</td>
<td>52.0</td>
<td>0.1086</td>
</tr>
<tr>
<td>9.0</td>
<td>0.3571</td>
<td>23.0</td>
<td>0.4629</td>
<td>35.0</td>
<td>0.18</td>
<td>55.9</td>
<td>0.1429</td>
</tr>
</tbody>
</table>

Table 3-6 Influent data from laboratory experiments conducted using secondary wastewater

<table>
<thead>
<tr>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
<th>Time (t(day))</th>
<th>NO$_3$-N (C(mg/L))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.425714</td>
<td>17.1</td>
<td>1.142857</td>
<td>30.0</td>
<td>1.425714</td>
<td>42.0</td>
<td>0.785714</td>
</tr>
<tr>
<td>8.0</td>
<td>1.245714</td>
<td>20.9</td>
<td>1.145714</td>
<td>31.0</td>
<td>1.108571</td>
<td>52.1</td>
<td>1.142857</td>
</tr>
<tr>
<td>11.1</td>
<td>1.245714</td>
<td>23.1</td>
<td>1.285714</td>
<td>32.0</td>
<td>1.322857</td>
<td>55.9</td>
<td>0.642857</td>
</tr>
<tr>
<td>14.0</td>
<td>1.322857</td>
<td>24.0</td>
<td>1.322857</td>
<td>35.1</td>
<td>0.894286</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>1.322857</td>
<td>25.0</td>
<td>1.288571</td>
<td>39.0</td>
<td>1.322857</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-5 and Table 3-6 show effluent and influent data of laboratory experiments conducted with secondary wastewater, respectively.
3.4 Conclusions

Data from two laboratory experiments were collected. Both of them contain nitrate-nitrogen concentrations of influent and effluent, different kinds of filter materials, water flow velocities, and reactor sizes. The data can be used to modify VART model and investigate denitrification process in the first-flush reactor.
CHAPTER 4. NUMERICAL MODELING OF DENITRIFICATION PROCESS IN FIRST-FLUSH REACTOR

4.1 Introduction

The objective of this chapter is to present a new mathematical model for simulation of denitrification process in the first-flush reactor. To that end, a conceptual model for description of various processes and mechanisms responsible for denitrification process will be presented first. Then, the VART model presented by Deng and Jung (2009) will be modified to incorporate the denitrification-associated reaction terms into the VART model, forming a new model: VART-Denitrification (VART-DN) model. The VART-DN model will then be calibrated using the data collected in chapter 3. A sensitivity analysis will be conducted to investigate the sensitivity of the VART-DN model to the variation of model input parameters.

4.2 First-Flush Reactor and VART Model

4.2.1 First-Flush Reactor

A conceptual design of the first-flush reactor is shown in Figure 4-1 (Deng, 2009). The first-flush reactor primarily consists of a first-flush diverter and reactive filter media in a reactor container with influent and effluent pipes. A first-flush diverter is designed to capture the first-flush and diverting subsequent runoff to downspout or stormwater drain by a floating ball. When the water level rises, the ball in reactor will rise with water level, and once the reactor is full, the ball rests on a seat inside the diverter chamber preventing any further water from entering the ponding zone of the reactor. The subsequent flow of water is then automatically directed to the stormwater drain.
Multilayer reactive filter media consists of at least 4 layers: (1) a ponding zone for allowing sediments to settle, (2) filtration layers for removing particulate-bound contaminants, (3) reaction layers for removing dissolved heavy metals, nutrients, and other contaminants, and (4) a bottom layer for preventing the reactive media from clogging the effluent piping. The underdrain is designed to hold reactive filter media and the first-flush portion of stormwater runoff. The first-flush runoff is stored in the reactor for a designed residence time to allow reactions to proceed and thereby to achieve required contaminant removal efficiency.

![Figure 4-1 Conceptual structure of first-flush reactor](image)

### 4.2.2 VART Model

The VART model is developed for longitudinal dispersion and transport of solutes in natural streams by Deng and Jung (Deng et al., 2005; Deng et al., 2009; Deng et al., 2010; Jung
The following equations Eq. (4-1)-Eq. (4-5) are main equations for the VART model.

\[
\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} = K_s \frac{\partial^2 C}{\partial x^2} + \frac{A_{adv} + A_{dif}}{A} \frac{1}{T_v} (\lambda C_s - C) + \frac{q_s}{A} C_s
\]  

\[4-1\]

\[
\frac{\partial C_s}{\partial t} = \frac{1}{T_v} (C_s - C) - \frac{q_h}{A_{adv} + A_{dif}} C_s
\]  

\[4-2\]

\[A_{dif} = 4\pi D_s t_s\]  

\[4-3\]

\[T_v = \begin{cases} \frac{T_{min}}{t} & \text{for } t \leq T_{min} \\ \frac{T_{min}}{T} & \text{for } t > T_{min} \end{cases} \quad (T_{min} \geq 0)\]  

\[4-4\]

\[t_s = \begin{cases} \frac{0}{t - T_{min}} & \text{for } t \leq T_{min} \\ \frac{T_{min}}{t} & \text{for } t > T_{min} \end{cases}\]  

\[4-5\]

where \(C\) = solute concentration [M/L^3] in main flow (mobile phase); \(C_s\) = solute concentration [M/L^3] in storage zones or matrix/immobile phase; \(T_v\) = the actual varying residence time [T] of solute; \(t_s\) = the time [T] since the solute release from the immobile phase to mobile phase; \(T_{min}\) = the minimum mean residence time [T] for solute to travel through the advection-dominated storage zone \(A_{adv}\); \(K_s\) = longitudinal Fickian dispersion coefficient excluding the transient storage effect [L^2/T]; \(A\) = cross-sectional flow area of main flow (mobile phase) [L^2]; and \(A_s\) = cross-sectional area of storage zones or immobile phase [L^2]; \(A_{adv}\) = area of advection-dominated transient storage zone with a uniform concentration \(C_s\) [L^2]; \(A_{dif}\) = area of diffusion-dominated transient storage zone [L^2]; \(D_s\) = the effective diffusion coefficient [L^2/T] in matrix/immobile phase and it varies commonly in the range of \(1.0 \times 10^{-5}\) m^2/s – \(1.0 \times 10^{-10}\) m^2/s, \(\lambda\) = the subsurface hyporheic exchange-induced water gain (\(\lambda > 1\)) or loss (\(\lambda < 1\)). It should be noted that the VART model was originally developed for simulation of solute exchange between river flow and hyporheic flow in bottom sediment. The application of VART model in this work is based on the
analogy between the hyporheic exchange in rivers and the exchange of solute between mobile and immobile phases in filter media.

4.3 Conceptual Model for First-Flush Reactor

In order to simulate nitrate removal in first-flush reactor, the VART model is extended in this study to incorporate the reaction processes responsible for denitrification (DN). The extended model is called VART-DN model.

The VART-DN model simulates nitrate-nitrogen removal in two different phases: mobile pore water phase and immobile bio-phase. Denitrification process may be affected by concentrations of nitrate, oxygen, dissolved carbon, and biomass, and HRT, temperature, and mass exchange rate between the two phases. The factors are involved in various reactions leading to the denitrification process: Eq. (4-6) - Eq. (4-8) are main equations of denitrification process.

\[ CH_2O + O_2 \rightarrow CO_2 + H_2O \] (4-6)

\[ NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \] (4-7)

\[ CH_2O + NO_3^- + 4\,S\,H^+ \rightarrow CO_2 + 2\,S\,N_2 + 7\,S\,H_2O \] (4-8)

When the first-flush stormwater runoff flows into the reactor, aerobic heterotroph will use oxygen to consume dissolved carbon Eq. (4-6). At the same time, ammonia will be oxidized into nitrate Eq. (4-7) and then the concentration of oxygen reduces to a low level, providing anoxic condition for denitrification Eq. (4-8). Denitrifying bacteria will utilize dissolved carbon to reduce nitrate to nitrogen, achieving denitrification process (Lee et al., 2006).
Figure 4-2 and Figure 4-3 show conceptual model for different phases, and conceptual reactions in first-flush reactor, respectively.

![Conceptual model for different phases](image1)

**Figure 4-2 Conceptual phases in first-flush reactor**

![Conceptual reactions in first-flush reactor](image2)

**Figure 4-3 Conceptual reactions in first-flush reactor**
4.4 Numerical Model for First-Flush Reactor: VART-DN Model

4.4.1 VART-DN Model for Simulation of Denitrification Process

The VART-DN model consists of the following Equations (4-9) - (4-15) for simulation of the denitrification process:

\[
\frac{\partial N_{\text{Mob}}}{\partial t} + U \frac{\partial N_{\text{Mob}}}{\partial x} = K_S \frac{\partial^2 N_{\text{Mob}}}{\partial x^2} + \frac{A_{\text{Mob}} + A_{\text{Bio}}}{AT_V} (N_{\text{Bio}} - N_{\text{Mob}}) - K_{R1} N_{\text{Mob}}
\]  
(4-9)

\[
\frac{\partial N_{\text{Bio}}}{\partial t} = \frac{1}{T_V} (N_{\text{Mob}} - N_{\text{Bio}}) - K_{R1} N_{\text{Bio}}
\]  
(4-10)

\[
K_{R1} = K_{\text{Max}} \left[ \frac{X}{K_b + X} \right] \left[ \frac{K_{O2}}{K_{O2} + C_{O2-M}} \right] \left[ \frac{C_{\text{Car-M}}}{K_{\text{Car-M}} + C_{\text{Car-M}}} \right] b^{(T-20)}
\]  
(4-11)

\[
K_r = K_{\text{Max}} \left[ \frac{X}{K_b + X} \right] \left[ \frac{K_{O2}}{K_{O2} + C_{O2-B}} \right] \left[ \frac{C_{\text{Car-B}}}{K_{\text{Car-B}} + C_{\text{Car-B}}} \right] b^{(T-20)}
\]  
(4-12)

\[
\frac{\partial X}{\partial t} = \left( v_{\text{max}} \frac{K_{N-Bio} + N_{\text{Bio}}}{K_{N-Bio} + N_{\text{Bio}}} \frac{C_{\text{Car-B}}}{K_{\text{Car-B}} + C_{\text{Car-B}}} - v_{\text{dec}} \right) \cdot X
\]  
(4-13)

\[
\frac{\partial C_{O2-B}}{\partial t} = \frac{1}{T_V} (C_{O2-M} - C_{O2-B}) - K_{R-O2} C_{O2-B}
\]  
(4-14)

\[
\frac{\partial C_{O2-M}}{\partial x} = -K_1 C_{\text{Car-B}} e^{-K_{Vx}} + K_{S-O2} (C_{O2-B} - C_{O2-M})
\]  
(4-15)

where \(N_{\text{Mob}}\) is nitrate concentration (mg/L) in mobile phase; \(N_{\text{Bio}}\) is nitrate concentration (mg/L) in biomass phase; \(U\) is cross-sectionally averaged flow velocity (m/s) in the flow \(x\) (m) direction; \(T_V\) is actual varying residence time (s) of solute; \(A\) is cross-sectional flow area (m\(^2\)); \(A_{\text{mob}}\) is area (m\(^2\)) of mobile phase; \(A_{\text{bio}}\) is area (m\(^2\)) of biomass phase; \(K_S\) is longitudinal dispersion coefficient.
(m²/s); \( K_{R1} \) is the decay rate (1/s) of nitrate-nitrogen in mobile phase; \( K_{R} \) is the decay rate (1/s) of nitrate-nitrogen in biomass phase; \( K_{max1} \) is the maximum nitrate-nitrogen decay rate (1/s) in mobile phase; \( K_{max} \) is the maximum nitrate-nitrogen decay rate (1/s) in biomass phase; \( X \) is denitrifying bacteria concentration (mg/L); \( K_{b} \) is biomass inhibition constant (mg/L); \( K_{O2} \) is half-saturation constant of dissolved oxygen (mg/L); \( C_{O2-M} \) is dissolved oxygen concentration in mobile phase (mg/L); \( C_{O2-B} \) is dissolved oxygen concentration in biomass phase (mg/L); \( C_{Car-B} \) is dissolved carbon concentration in biomass phase (mg/L); \( K_{Car-M} \) is half-saturation constant of dissolved carbon in mobile phase (mg/L); \( K_{Car-B} \) is half-saturation constant of dissolved carbon in biomass phase (mg/L); \( b \) is constant of temperature influence on denitrification; and \( T \) is temperature (°C); \( K_{1} \) is oxygen consuming rate by dissolved carbon in biomass phase (1/day); \( K_{S-O2} \) is reaeration rate constant (1/day).

### 4.4.2 Modeling of Bacterial Growth

In the thesis, it is assumed that bacterial growth only occurs in the biomass phase. The model for bacterial population net growth is the combination of double Monod kinetic equation (Rittmann and McCarty, 2001) Eq.(4-16) and a first order decay equation Eq. (4-17).

\[
\frac{\partial X_{growth}}{\partial t} = v_{max} \frac{C_1}{K_{s1} + C_1} \cdot \frac{C_2}{K_{s2} + C_2} \cdot X_{growth}
\]  (4-16)

\[
\frac{\partial X_{decay}}{\partial t} = -v_{dec} \cdot X_{decay}
\]  (4-17)

where \( X_{growth} \) is the increase in biomass concentration (mg/L), \( v_{max} \) is the maximum growth rate (1/day), \( C_1 \) is the electron donor concentration (mg/L) in bio-phase, \( C_2 \) is the electron acceptor concentration (mg/L) in bio-phase, \( K_{s1} \) is the electron donor half-saturation constant (mg/L), \( K_{s2} \)
is the electron acceptor half-saturation constant (mg/L), $X_{\text{decay}}$ is the decrease in biomass concentration (mg/L), $v_{\text{dec}}$ is a constant decay rate (1/day).

In the process of denitrification, denitrifying bacteria use nitrate as electron donor and dissolved carbon as electron acceptor. The equation for denitrifying bacteria net growth is the combination of growth equation and decay equation, which is shown in Eq. (4-18); and the net biomass concentration change is presented in Eq. (4-13).

$$\frac{\partial X}{\partial t} = \frac{\partial X_{\text{growth}}}{\partial t} + \frac{\partial X_{\text{decay}}}{\partial t}$$  \hspace{1cm} (4-18)

### 4.4.3 Modeling of Dissolved Oxygen Consumption

Dissolved oxygen concentration in the biomass phase is determined by the residence time, dissolved oxygen concentration in mobile phase, and dissolved oxygen consumption rate. Based on DO Sag equation (Streeter and Phelps, 1925; Doddi and Xie, 2008; Adrian et al., 1998; Adrian et al., 1999; Adrian et al., 2004; Roider et al., 2008; Mamedoy, 2006; Widdowson et al., 1988) and the similarity between streams and reactors of oxygen concentration change, the dissolved oxygen concentration in mobile phase can be determined by Eq. (4-15); and the dissolved oxygen concentration in biomass phase can be determined by Eq. (4-14).

### 4.4.4 Estimation of Dissolved Organic Carbon Consumption Rate

In the thesis, the dissolved organic carbon in biomass phase is released from filters of woodchips/mulch/sawdust, which is relatively stable. Thus, in order to simplify the VART-DN
model, it is assumed that the concentration of dissolved organic carbon is constant, with COD being 10 mg/L.

4.5 Sensitivity Analysis

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Functions</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>X axis distance</td>
<td>m</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>U</td>
<td>Flow velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>K_s</td>
<td>Longitudinal dispersion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>R</td>
<td>Ratio of (A_{Bio} + A_{Mob})/A</td>
<td>n.a.</td>
</tr>
<tr>
<td>σx</td>
<td>One calculation circle distance</td>
<td>m</td>
</tr>
<tr>
<td>σt</td>
<td>One calculation circle time</td>
<td>s</td>
</tr>
<tr>
<td>H</td>
<td>Hydraulic conductivity</td>
<td>m/s</td>
</tr>
<tr>
<td>X</td>
<td>density of biomass</td>
<td>mg/L</td>
</tr>
<tr>
<td>T_V</td>
<td>Initial residence time</td>
<td>h</td>
</tr>
<tr>
<td>A_C</td>
<td>Cross sectional area</td>
<td>m²</td>
</tr>
<tr>
<td>K_1</td>
<td>Oxygen consuming rate by dissolved carbon in biomass phase</td>
<td>1/day</td>
</tr>
<tr>
<td>K_{O2}</td>
<td>Oxygen reaeration rate</td>
<td>1/day</td>
</tr>
<tr>
<td>K_{max1}</td>
<td>maximum nitrate utilization rate in mobile phase</td>
<td>1/day</td>
</tr>
<tr>
<td>K_{max}</td>
<td>maximum nitrate utilization rate in biomass phase</td>
<td>1/day</td>
</tr>
<tr>
<td>K_b</td>
<td>biomass inhibition constant</td>
<td>mg/L</td>
</tr>
<tr>
<td>K_{O2}</td>
<td>oxygen inhibition constant</td>
<td>mg/L</td>
</tr>
<tr>
<td>K_{R-O2}</td>
<td>Oxygen consuming rate in biomass phase</td>
<td>day⁻¹</td>
</tr>
<tr>
<td>K_{Car-B}</td>
<td>half-saturation constant of dissolved carbon</td>
<td>mg/L</td>
</tr>
<tr>
<td>C_{Car-B}</td>
<td>Dissolved carbon concentration in biomass phase</td>
<td>mg/L</td>
</tr>
<tr>
<td>K_{N-Bio}</td>
<td>Nitrate-nitrogen half-saturation constant</td>
<td>mg/L</td>
</tr>
<tr>
<td>K_{Car-B}</td>
<td>Dissolved carbon half-saturation constant</td>
<td>mg/L</td>
</tr>
<tr>
<td>C_{O2-M}</td>
<td>Initial oxygen concentration in the mobile phase</td>
<td>mg/L</td>
</tr>
<tr>
<td>C_{O2-B}</td>
<td>Initial oxygen concentration in the biomass phase</td>
<td>mg/L</td>
</tr>
<tr>
<td>T_em</td>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>b</td>
<td>Temperature influence factor</td>
<td>n.a.</td>
</tr>
<tr>
<td>v_{max}</td>
<td>Maximum growth rate of biomass</td>
<td>day⁻¹</td>
</tr>
<tr>
<td>v_{dec}</td>
<td>Constant decay rate of biomass</td>
<td>day⁻¹</td>
</tr>
<tr>
<td>N_{Mob}</td>
<td>Nitrate-nitrogen concentration in mobile phase</td>
<td>mg/L</td>
</tr>
<tr>
<td>N_{Bio}</td>
<td>Nitrate-nitrogen concentration in biomass phase</td>
<td>mg/L</td>
</tr>
<tr>
<td>A_{Bio}</td>
<td>Surface area of biomass phase</td>
<td>m²</td>
</tr>
<tr>
<td>A_{Mob}</td>
<td>Surface area of mobile phase</td>
<td>m²</td>
</tr>
<tr>
<td>A</td>
<td>Surface area of whole system</td>
<td>m²</td>
</tr>
</tbody>
</table>
Table 4-1 presents different parameters used in the VART-DN model. In order to investigate sensitivity of the denitrification process to model input parameters, a sensitivity analysis was carried out by changing each parameter value individually by +10% to investigate changes of root mean square error (RMSE).

Table 4-2 Results of sensitivity analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Values</th>
<th>+10% Values</th>
<th>RMSEs with original data</th>
<th>RMSEs with value +10%</th>
<th>RMSEs Percent change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>m/s</td>
<td>4.24E-6</td>
<td>4.66E-06</td>
<td>0.8157</td>
<td>0.8193</td>
<td>0.441339</td>
</tr>
<tr>
<td>Ks</td>
<td>m²/s</td>
<td>2E-5</td>
<td>2.2E-5</td>
<td>0.8157</td>
<td>0.9537</td>
<td>16.91798</td>
</tr>
<tr>
<td>Kmax1</td>
<td>1/day</td>
<td>2500</td>
<td>2750</td>
<td>0.8157</td>
<td>0.6865</td>
<td>-15.8392</td>
</tr>
<tr>
<td>X</td>
<td>mg/L</td>
<td>20</td>
<td>22</td>
<td>0.8157</td>
<td>0.7079</td>
<td>-13.2156</td>
</tr>
<tr>
<td>K_O2</td>
<td>mg/L</td>
<td>0.77</td>
<td>0.847</td>
<td>0.8157</td>
<td>0.7221</td>
<td>-11.4748</td>
</tr>
<tr>
<td>Kn</td>
<td>mg/L</td>
<td>100</td>
<td>110</td>
<td>0.8157</td>
<td>0.9337</td>
<td>14.4661</td>
</tr>
<tr>
<td>C_Car-B</td>
<td>mg/L</td>
<td>10</td>
<td>11</td>
<td>0.8157</td>
<td>0.8095</td>
<td>-0.76008</td>
</tr>
<tr>
<td>b</td>
<td>n.a.</td>
<td>1.025</td>
<td>1.1275</td>
<td>0.8157</td>
<td>0.5732</td>
<td>-29.7291</td>
</tr>
<tr>
<td>Tem</td>
<td>°C</td>
<td>22</td>
<td>24.2</td>
<td>0.8157</td>
<td>0.7404</td>
<td>-9.23134</td>
</tr>
</tbody>
</table>

Table 4-2 presents results of parameters sensitivity analysis. From results of sensitivity analysis, parameters of dispersion coefficient, maximum nitrate utilization rate in mobile phase, biomass concentration, oxygen inhibition constant, biomass inhibition constant, temperature and temperature coefficient for denitrification have significant influence on the denitrification process, with percent change in RMSE being 16.9%, 15.8%, -13.1%, -11.5%, 14.5%, -9.2% and -29.7%, respectively, when values of the parameters increase by 10%. Other parameters of hydraulic conductivity, maximum growth rate of biomass, constant decay rate of biomass, COD decay rate, cross-sectional area, ratio of (A_Mob + A_Mob)/A, oxygen consuming rate, nitrate half-saturation constant have an insignificant influence on denitrification process.
4.6 Numerical Solution Procedure for VART-DN Model

- Start
- Input initial, boundary conditions, constants and parameters
  - Time and distance calculation of dissolved oxygen concentration in mobile phase
  - Kinetic model calculation of bacterial growth
  - Kinetic model calculation of denitrification reaction process
  - Kinetic model calculation of nitrate-nitrogen concentration in biomass phase
  - Kinetic model calculation of nitrate-nitrogen concentration in mobile phase
  - New concentration calculation of new concentration for all grid points
  - Results formulate and print results of all grid points
  - Next time step

Figure 4-4 Flow chart for numerical solution of VART-DN model
Figure 4-4 shows a flow chart for numerical solution of the VART-DN model. A split-operator method is utilized to split Eq. (4-9) into a pure advection equation and a dispersion equation with the transient storage term. The pure advection process in Eq. (4-10) can be simulated by hyperbolic sub-equation Eq. (4-19):

$$\frac{\partial N}{\partial t} + U \frac{\partial N}{\partial x} = 0, \quad t \in \left(t^{n+1}, t^{n+1/2}\right)$$  \hspace{1cm} (4-19)

where \(n\) represents the time step. Eq. (4-19) can be solved using Semi-Lagrangian approach. The dispersion, transient storage release processes, and denitrification processes in Eq. (4-9) can be simulated by following discretized equation:

$$\frac{N_{Mi}^{n+1} - N_{Mi}^{n+1/2}}{\Delta t / 2} = \frac{K_s}{(\Delta x)^2} \left(N_{Mi+1}^{n+1} - 2N_{Mi}^{n+1} + N_{Mi-1}^{n+1}\right) + \frac{R}{T_v} \left(\frac{N_{Bi}^{n+1} + N_{Bi}^{n+1/2}}{2} - \frac{N_{Mi}^{n+1} + N_{Mi}^{n+1/2}}{2}\right)$$  \hspace{1cm} (4-20)

$$+ K_{R1} \frac{N_{Mi}^{n+1} + N_{Mi}^{n+1/2}}{2}$$

where \(R = (A_{Mob} + A_{Bio}) / A\), the ratio of biomass phase area and mobile phase area to the surface area of reactor.

$$\frac{N_{Bi}^{n+1} - N_{Bi}^{n+1/2}}{\Delta t / 2} = \frac{1}{T_v} \left(\frac{N_{Mi}^{n+1} + N_{Mi}^{n+1/2}}{2} - \frac{N_{Bi}^{n+1} + N_{Bi}^{n+1/2}}{2}\right) - K_R \left(\frac{N_{Bi}^{n+1} + N_{Bi}^{n+1/2}}{2}\right)$$  \hspace{1cm} (4-21)

$$N_{Bi}^{n+1} = \frac{\Delta t \left(N_{Mi}^{n+1} + N_{Mi}^{n+1/2}\right) - (\Delta t + \Delta t K_R - 4T_v)N_{Bi}^{n+1/2}}{4T_v + \Delta t + \Delta t K_R T_v}$$  \hspace{1cm} (4-22)

Denitrification parameter can be presented as:
\[ K_R = K_{Max} \left( \frac{X}{K_b + X} \right) \left( \frac{K_{O2}}{K_{O2} + C_{O2-B}} \right) \left( \frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}} \right) \delta(t-20) \] (4-23)

Eq. (4-23) involves \( K_{Max}, X, K_b, K_{O2}, C_{O2}, C_{Car-B}, K_{Car-B} \), and temperature influence parameter \( b \).

Eq. (4-14) can be discretized as follows:

\[
\frac{C_{n+1}^{O2-Bi} - C_{n+1/2}^{O2-Bi}}{\Delta t/2} = \frac{1}{T_v} \left( \frac{C_{n+1}^{O2-Mi} + C_{n+1/2}^{O2-Mi}}{2} - \frac{C_{n+1}^{O2-Bi} + C_{n+1/2}^{O2-Bi}}{2} \right) - K_{R-O2} \left( \frac{C_{n+1}^{O2-Bi} + C_{n+1/2}^{O2-Bi}}{2} \right) \] (4-24)

\[
C_{n+1}^{O2-Bi} = \frac{\Delta t \left( C_{n+1/2}^{O2-Mi} + C_{n+1/2}^{O2-Mi} \right) - (\Delta t + \Delta t T_v) K_{R-O2} - 4T_v}{4T_v + \Delta t + \Delta t K_b T_v} \] (4-25)

According to Eq. (4-15), combining Eq. (4-15) and \( x=ut \) (\( dx = d(ut) = udt \)) yields,

\[
\frac{dC_{O2-M}(t)}{dt} = -K_s C_{Car-B} e^{-K_{s,t}} + K_s \left( C_{O2s} - C_{O2-M} \right) \] (4-26)

where \( C_{O2-M}(t) \) means: \( C_{O2-M} \) is the function of \( t \).

\[
\frac{dC_{O2-M}(t)}{dt} + uK_s C_{O2-M}(t) = -uK_s C_{Car-B} e^{-K_{s,t}} + uK_s C_{O2s} \] (4-27)

Applying Laplace transform to the above equation gives:

\[
SC_{O2-M}(S) - C_0 + uC_{O2-M}(S) = -uK_s C_{Car-B} \left( \frac{1}{S + K_s} \right) + \frac{uK_s C_{O2s}}{S} \] (4-28)

where \( S \) is the argument of Laplace transform with respect to time \( t \).

\[
C_{O2-M}(S) \ast (S + uK_s) = C_0 - uK_s C_{Car-B} \left( \frac{1}{S + uK_s} \right) + \frac{uK_s C_{O2s}}{S} \] (4-29)

\[
C_{O2-M}(S) = \frac{C_0}{(S + uK_s)} - \frac{uK_s C_{Car-B}}{(S + uK_s)(S + uK_s)} + \frac{uK_s C_{O2s}}{S(S + uK_s)} \] (4-30)
Applying Inverse Laplace transform to Eq. (4-30) gives:

\[ C_{O_2-M}(t) = C_0 e^{-K_{\mu}} - K_1 C_{Car-B} \left( \frac{e^{-K_{\mu}} - e^{-K_{\mu}}}{K_s - K_1} \right) - C_{O_2s} \left( e^{-K_{\mu}} - 1 \right) \]  
Eq. (4-31)

Discretization of \( C_{O2-M} \) equation yields:

\[ C_{O_2-M}^{n+1} + C_{O_2-M}^{n+1/2} = C_0 e^{-K_{\mu(t)}} - K_1 C_{Car-B} \left( \frac{e^{-K_{\mu(t)}} - e^{-K_{\mu(t)}}}{K_s - K_1} \right) + K_s C_{O_2s} \left( \frac{e^{-K_{\mu(t)}} - 1}{K_s} \right) \]
\[ + C_0 e^{-K_{\mu(t)}} - K_1 C_{Car-B} \left( \frac{e^{-K_{\mu(t)}} - e^{-K_{\mu(t)}}}{K_s - K_1} \right) + K_s C_{O_2s} \left( \frac{e^{-K_{\mu(t)}} - 1}{K_s} \right) \]  
Eq. (4-32)

Substitution of Eq. (4-25) into Eq. (4-23) results in:

\[ K_{R}^{n+1} = K_{Max} \left[ \frac{X}{K_b + X} \right] \left[ \frac{K_{O_2}}{K_{O_2} + C_{O_2-M}^{n+1/2}} \right] \left[ \frac{C_{Car-B}}{C_{Car-B} + C_{Car-B}} \right] b^{(T-20)} \]  
Eq. (4-33)

\[ K_{R}^{n+1} = K_{Max} \left[ \frac{X}{K_b + X} \right] \left[ \frac{K_{O_2}}{K_{O_2} + \frac{\Delta t}{4 T_v + \Delta t K_r T_v} (C_{O_2-M}^{n+1} + C_{O_2-M}^{n+1/2}) - (\Delta t + T_v K_{R-M} - 4 T_v) C_{O_2-M}^{n+1/2}} {4 T_v + \Delta t + \Delta t K_r T_v} \right] \]  
Eq. (4-34)

\[ \frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}} \right] b^{(T-20)} \]

\[ \frac{\partial X}{\partial t} = \left( v_{max} \frac{N_{Bio}}{K_{N-Bio} + N_{Bio}} \cdot \frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}} - v_{dec} \right) \cdot X \]  
Eq. (4-35)

\[ \frac{X_{i}^{n+1} - X_{i}^{n+1/2}}{\Delta t / 2} = \left( v_{max} \frac{N_{Bio}}{K_{N-Bio} + N_{Bio}} \cdot \frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}} - v_{dec} \right) \left( X_{i}^{n+1/2} + X_{i}^{n+1/2} \right) \]  
Eq. (4-36)

\[ \mu = \left( v_{max} \frac{N_{Bio}}{K_{N-Bio} + N_{Bio}} \cdot \frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}} - v_{dec} \right) \]  
Eq. (4-37)
\[
\left(\frac{2}{\Delta t} - \mu\right)X_i^{n+1} = \left(\frac{2}{\Delta t} + \mu\right)X_i^{n+1/2}
\] (4-38)

\[
X_i^{n+1} = \left(\frac{2 + \mu}{2 - \mu}\right)X_i^{n+1/2}
\] (4-39)

Substitution of Eq. (4-31) into Eq. (4-26) results in:

\[
K_{Ri}^{n+1} = K_{Max}\frac{\frac{(2 + \mu)}{2 - \mu}X_i^{n+1/2}}{K_b + \frac{(2 + \mu)}{2 - \mu}X_i^{n+1/2}}\left[\frac{C_{Car-B}}{K_{Car-B} + C_{Car-B}}\right]b^{(t-20)}
\] (4-40)

Substitution of Eq. (4-22) into Eq. (4-20) gives:

\[
\frac{N_{Mi}^{n+1} - N_{Mi}^{n+1/2}}{\Delta t/2} = \frac{K_x}{(\Delta t)^2} \left( N_{Mi}^{n+1} - 2N_{Mi}^{n+1/2} + N_{Mi}^{n+1}\right) +
\]

\[
\frac{R}{T_y} \left\{ \frac{\Delta t (N_{Mi}^{n+1} + N_{Mi}^{n+1/2}) - (\Delta t + \Delta t T_v K - 4T_v)N_{Bi}^{n+1/2}}{4T_v + \Delta t + \Delta t K T_v} + N_{Bi}^{n+1/2} \right\} - \frac{N_{Mi}^{n+1} + N_{Mi}^{n+1/2}}{2}
\] (4-41)

Rearranging Eq. (4-32) produces:
Finally, the numerical solution to VART-DN model can be expressed as:

$$\frac{N_{M1}^{n+1}}{\Delta t/2} - \frac{N_{M1}^{n+1/2}}{\Delta t/2} = \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1/2} - 2 \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1} + \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1}$$

$$+ \frac{R}{T_v} \left( \frac{\Delta t}{2} \frac{N_{M1}^{n+1}}{\Delta t/2} \right) \left( \Delta t + \Delta T_v K_R - 4T_v \right) N_{Bi}^{n+1/2} + \frac{N_{M1}^{n+1/2}}{2} + \frac{N_{M1}^{n+1/2}}{2} \right) + \frac{N_{M1}^{n+1}}{\Delta t/2} - \frac{N_{M1}^{n+1}}{\Delta t/2}$$

$$= \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1} - 2 \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1/2} + \frac{R \Delta t N_{M1}^{n+1}}{2 T_v} \left( 4 T_v + \Delta t + \Delta t K_R T_v \right)$$

$$- \frac{\Delta t + \Delta T_v K_R - 4 T_v}{2 T_v} N_{Bi}^{n+1/2} + \frac{R N_{Bi}^{n+1/2}}{2 T_v} - \frac{R N_{Bi}^{n+1/2}}{2 T_v}$$

$$\frac{N_{M1}^{n+1}}{\Delta t/2} + 2 \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1/2} - \frac{R \Delta t N_{M1}^{n+1}}{2 T_v} \left( 4 T_v + \Delta t + \Delta t K_R T_v \right)$$

$$+ \frac{R N_{M1}^{n+1/2}}{2 T_v} - \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1} - \frac{K_s}{(\Delta x)^2} N_{M1}^{n+1} = \frac{R \Delta t N_{M1}^{n+1/2}}{2 T_v} \left( 4 T_v + \Delta t + \Delta t K_R T_v \right)$$

$$- \frac{\Delta t + \Delta T_v K_R - 4 T_v}{2 T_v} N_{Bi}^{n+1/2} + \frac{R N_{Bi}^{n+1/2}}{2 T_v}$$

4.7 Summary and Conclusions

This chapter presents a numerical model for simulation of denitrification process in the designed first-flush reactor. In addition to physical dispersion and transport processes included in
the VART model, additional denitrification related items are added to the VART model, leading to the VART-DN model. The VART-DN model mainly describes the influence of dissolved oxygen, biomass, dissolved carbon, and temperature on denitrification process. The model for bacterial population net growth is the combination of the double Monod kinetic equation and a first order decay equation; the oxygen change model is based on the first order DO Sag equation. Data used in the VART-DN model were collected from laboratory experiments conducted with natural stormwater and secondary wastewater, respectively.

Based on sensitivity analysis results of model parameters, the dispersion coefficient, maximum nitrate utilization rate in mobile phase, biomass concentration, oxygen inhibition constant, biomass inhibition constant, temperature and temperature coefficient for denitrification have significant influence on the denitrification process, with percent change in the RMSE being 16.9%, 15.8%, -13.1%, -11.5%, 14.5%, -9.2% and -29.7%, respectively, when values of the parameters increase by 10%.
CHAPTER 5. TESTING OF VART-DN MODEL

5.1 Introduction

Although the VART model was tested with a wide variety of tracer release data (Deng and Jung, 2009; Deng et al., 2010), it is important to test the VART-DN model with more data involving denitrification process. To that end, two types of laboratory data were collected: (1) laboratory data from column experiments conducted with natural stormwater and (2) laboratory data from column experiments conducted with secondary wastewater. Testing results are assessed according to the percent error and/or the Root Mean Squared Error (RMSE).

5.2 Testing of VART-DN Model

5.2.1 Testing of VART-DN Model with Stormwater Data

The basic information about the collection of stormwater data was introduced in chapter 3. The stormwater effluent data from different samples are shown in Table 5-1 in terms of observed nitrate-nitrogen concentration. Also listed in this table are simulated concentrations of nitrate-nitrogen in the effluent from the experimental columns. For instance, in case of Test 4-B the effluent concentration simulated using the VART-DN model is 0.71 mg/L while the observed effluent concentration is 0.78 mg/L; the influent nitrate-nitrogen concentration is 4.74 mg/L.

Since observed effluent concentrations for test 1, test 3 and test 5 are undetectable, simulated effluent concentrations for the tests are also very low, indicating that the VART-DN model is capable of simulating nitrate-nitrogen concentration change successfully.

Removal rate of test 1 = (input-observed)/input = (1.64-0.02)/1.64=0.988.

Following the same calculation, removal rates for the four column tests are 98.8%, 99.3%, 82.6%, and 87.5%, respectively. The average removal rate is 92.05%.
Table 5-1 Simulated and observed effluent concentrations in the natural stormwater samples

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Column test</th>
<th>Observed concentration (NO₃ as N)</th>
<th>Simulated concentration (NO₃ as N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test 1</td>
<td>1-A</td>
<td>&lt;0.02</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>1-B</td>
<td>&lt;0.02</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>1-C</td>
<td>&lt;0.02</td>
<td>0.018</td>
</tr>
<tr>
<td>Test 3</td>
<td>3-A</td>
<td>&lt;0.02</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>3-B</td>
<td>&lt;0.02</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>3-C</td>
<td>&lt;0.02</td>
<td>0.019</td>
</tr>
<tr>
<td>Test 4</td>
<td>4-B</td>
<td>0.78</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>4-C</td>
<td>0.78</td>
<td>0.71</td>
</tr>
<tr>
<td>Test 5</td>
<td>5-A</td>
<td>&lt;0.02</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>5-B</td>
<td>&lt;0.02</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>5-C</td>
<td>&lt;0.02</td>
<td>0.009</td>
</tr>
</tbody>
</table>

The simulation error for test 4 = |(Observed– Simulated)|/ Observed ×100% = |0.78-0.71|/0.78=9.0%. The simulation errors for other 3 tests cannot be calculated due to undetectable observed concentrations. However, they also show very low errors.

5.2.2 Testing of VART-DN Model with Wastewater Data

Based on the wastewater data mentioned in chapter 3, values of the model input parameters for natural stormwater and secondary wastewater are determined and listed in Table 5-2. Figure 5-1 shows the simulated and observed effluent concentrations as well as the influent concentration based on the wastewater data. The RMSE of the simulation result with wastewater data is 0.8157, indicating that the fitting of the simulated effluent concentration of nitrate-nitrogen to observed one is reasonable.
Table 5-2 Values of parameters in the model for stormwater and wastewater data

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Functions</th>
<th>Units</th>
<th>Values for wastewater data</th>
<th>Values for stormwater data</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>X axis distance</td>
<td>m</td>
<td>0.3</td>
<td>0.28</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
<td>s</td>
<td>4833256</td>
<td>108000</td>
</tr>
<tr>
<td>U</td>
<td>Flow velocity</td>
<td>m/s</td>
<td>4.24×10^{-6}</td>
<td>1.09×10^{-3}</td>
</tr>
<tr>
<td>K_s</td>
<td>Longitudinal dispersion coefficient</td>
<td>m²/s</td>
<td>0.00002</td>
<td>0.00002</td>
</tr>
<tr>
<td>R</td>
<td>Ratio of (A_{Bio}+A_{MoB})/A</td>
<td>n.a.</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>σx</td>
<td>One calculation circle distance</td>
<td>m</td>
<td>0.03</td>
<td>0.028</td>
</tr>
<tr>
<td>σt</td>
<td>One calculation circle time</td>
<td>s</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>H</td>
<td>Hydraulic conductivity</td>
<td>m/s</td>
<td>5×10^{-11}</td>
<td>5×10^{-11}</td>
</tr>
<tr>
<td>X</td>
<td>density of biomass</td>
<td>mg/L</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>T_v</td>
<td>Initial residence time</td>
<td>h</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>A_c</td>
<td>Cross sectional area</td>
<td>m²</td>
<td>0.007854</td>
<td>0.01815</td>
</tr>
<tr>
<td>K_1</td>
<td>Oxygen consuming rate by dissolved carbon in biomass phase</td>
<td>l/day</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>K_{s-O2}</td>
<td>Oxygen reaeration rate</td>
<td>l/day</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>K_{max1}</td>
<td>maximum nitrate utilization rate in mobile phase</td>
<td>l/day</td>
<td>2500</td>
<td>1000</td>
</tr>
<tr>
<td>K_{max}</td>
<td>maximum nitrate utilization rate in biomass phase</td>
<td>l/day</td>
<td>2000</td>
<td>1000</td>
</tr>
<tr>
<td>K_b</td>
<td>biomass inhibition constant</td>
<td>mg/L</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>K_{O2}</td>
<td>oxygen inhibition constant</td>
<td>mg/L</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>K_{R-O2}</td>
<td>Oxygen consuming rate in biomass phase</td>
<td>day⁻¹</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>K_{Car-B}</td>
<td>half-saturation constant of dissolved carbon</td>
<td>mg/L</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>C_{Car-B}</td>
<td>Dissolved carbon concentration in biomass phase</td>
<td>mg/L</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>K_{N-Bio}</td>
<td>Nitrate-nitrogen half-saturation constant</td>
<td>mg/L</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>K_{Car-B}</td>
<td>Dissolved carbon half-saturation constant</td>
<td>mg/L</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>C_{O2-M}</td>
<td>Initial oxygen concentration in the mobile phase</td>
<td>mg/L</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>C_{O2-B}</td>
<td>Initial oxygen concentration in the biomass phase</td>
<td>mg/L</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Tem</td>
<td>Temperature</td>
<td>℃</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>b</td>
<td>Temperature influence factor</td>
<td></td>
<td>1.025</td>
<td>1.025</td>
</tr>
<tr>
<td>v_{max}</td>
<td>Maximum growth rate of biomass</td>
<td>day⁻¹</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>v_{dec}</td>
<td>Constant decay rate of biomass</td>
<td>day⁻¹</td>
<td>0.15</td>
<td>0.15</td>
</tr>
</tbody>
</table>
According to data collection in chapter 3, the average influent and effluent concentrations in the column experiment with wastewater were 1.189 mg/L and 0.260 mg/L, respectively, with a removal rate of 78.1% for nitrate-nitrogen.

![Graph showing comparison between VART-DN simulated and observed nitrate-nitrogen concentrations in the effluent against the influent concentration of the secondary wastewater](image)

**Figure 5-1** Comparison between VART-DN simulated and observed nitrate-nitrogen concentrations in the effluent against the influent concentration of the secondary wastewater

### 5.3 Summary and Conclusions

The removal rate of nitrate-nitrogen in natural stormwater through the first-flush reactor varied in the range of 99.3% - 87.5%, and the average removal rate for the 4 column tests was 92.05%. The average influent and effluent concentrations in the column experiment with wastewater were 1.189 mg/L and 0.260 mg/L, respectively, with a removal rate of 78.1%.
The VART-DN model is able to simulate the denitrification process of both natural stormwater and secondary wastewater in reactive filter media. Modeling results show good agreements with observed data. The average simulation error for the natural stormwater data is lower than 9.0%. The RMSE of simulation result for the wastewater data is 0.8157. The modeling results demonstrate that the VART-DN model can successfully simulate denitrification process in the first-flush reactor.
CHAPTER 6. SUMMARY AND CONCLUSIONS

The primary contributions of this thesis can be summarized as follows:

1. The thesis presents a comprehensive review of research advances in nonpoint source (NPS) water pollution caused by urban stormwater, highway stormwater, agricultural runoff, and atmospheric deposition. Modeling progresses and total maximum daily load (TMDL) calculations for NPS pollution are also reviewed. Various low impact development technologies and BMPs for mitigating NPS pollution and their socioeconomic impacts are assessed.

2. The first-flush reactor is an effective BMP device for efficient treatment of urban stormwater runoff. The confirmed combination of multilayer reactive filter media for the first-flush reactor consists of at least 4 layers: (1) a ponding zone for allowing sediments to settle, (2) filtration layers for removing particulate-bound contaminants, (3) reaction layers for removing dissolved heavy metals, nutrients and other contaminants, and (4) a bottom layer for preventing the reactive media from clogging the effluent piping.

3. The removal rate of nitrate-nitrogen in natural stormwater through the first-flush reactor varied in the range of 99.3% - 87.5%, with an average removal rate of 92.05%. The average influent and effluent concentrations in the column experiments with wastewater were 1.189 mg/L and 0.260 mg/L, respectively, with a removal rate of 78.1% for nitrate-nitrogen.

4. A new model, called VART-DN model, was developed for simulation of denitrification process in the designed first-flush reactor. The VART-DN model is capable of simulating various processes and mechanisms responsible for the denitrification, including: (1) nitrate-nitrogen dispersion and transport, (2) mass exchange between mobile phase and biomass phase, (3) oxygen decay, and (4) bacterial growth. The model for bacterial population net growth
is the combination of a double Monod kinetic equation and a first order decay equation; the oxygen change model is based on a first order DO sag equation.

5. Based on results of sensitivity analysis of model input parameters, dispersion coefficient, maximum nitrate utilization rate in mobile phase, biomass concentration, oxygen inhibition constant, biomass inhibition constant, temperature and temperature coefficient for denitrification have significant influence on the denitrification process, with percent change in RMSE being 16.9%, 15.8%, -13.2%, -11.5%, 14.5%, -9.2% and -29.7%, respectively, when values of the parameters increase by 10%.

6. The VART-DN model was able to simulate the denitrification process of natural stormwater with a simulation error lower than 9.0% as compared with observed data; the RMSE of the VART-DN model for simulating denitrification process of wastewater is 0.8157, demonstrating the efficacy of the VART-DN model.
REFERENCES


**VITA**

Shaowei Sun was born in May, 1983, in Rizhao, China. He graduated from Yantai University, with a Bachelor of Science degree in environmental engineering in the year 2006 and graduated from Xi’an University of Architecture & Technology, which has one of four national key labs of environmental engineering in China, with a Master of Science degree in environmental engineering in the year of 2009. After graduation, he received graduate research assistantship to begin his study in water resources program in the Civil and Environmental Engineering Department at Louisiana State University, Baton Rouge, United States, in August 2009. He conducted research under the supervision of Dr. Zhi-Qiang Deng.