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Buildup/Washoff Model for Dissolved Iron in Stormwater Runoff

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LIST OF ABREVIATIONS

@	at
a, b	Parameter
amu	Atomic Mass Units
APHA	American Public Health Association
BAT	Best Available Technology
BCT	Pollutant Control Technology
BMP	Best Management Practice
BOD	Biochemical Oxygen Demand
BPJ	Best Professional Judgment
C	Pollutants Buildup Rate
C°	Degrees Celsius
COD	Chemical Oxygen Demand
CSO	Combined Sewer Overflow
CWA	The Clean Water Act
ELGs	Effluent Limitations Guidelines
EPA	Environmental Protection Agency
F°	Fahrenheit
Fe	Iron
ICP	Inductively Coupled Plasma
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
K°	Kelvin
K_i	Coefficient
$M_{i,1}$	Mass of Pollutant Available on the Surface at the Start of the Storm Event
MS4s	Municipal Separate Storm Sewer Systems
NPDES	National Pollutant Discharge Elimination System
NPS	Non-Point Source
P	Mass of Pollutants Accumulation on the Surface
P_0	Pollutant Remaining on the Highway Surface After the Last Storm
pH	Pondus Hydrogenii
$P_{i,T}$	Mass of Pollutant Washed Off during T
P_L	Limiting (Asymptotic) Surface Load
POTW	Publicly Owned Treatment Works
QA/QC	Quality Assurance / Quality Control
R_v	Total Volume of Runoff of the Storm Event
SSO	Sanitary Sewer Overflow
t	Time since Last Storm
T	Duration of a Storm Event
TDS	Total Dissolved Solids
TMDL	Total Maximum Daily Load
T_s	Time Period between the Midpoints of the Successive Storms
t_s	Time Period from End of the Last Storm to the Beginning of the Next Storm
UNO	University of New Orleans
V	Runoff Volume

VSS	Volatile Suspended Solids
WLA	Waste Load Allocation
Y	Wash Load
Φ	Parameter

ABSTRACT

This research focused on the calibration of the Buildup and Washoff for dissolved iron.

The test site located at the intersection of the Interstate-10 and Interstate-610, New Orleans, Louisiana. Storm water runoff from the examined elevated roadway section was analyzed for 14 storm events.

The model used a linear function of antecedent dry time for the buildup model. The rating curve assumption was selected to estimate the pollutant transport capacity. In a further step the two were combined.

The derived Buildup/Washoff model was calibrated for the collected data and precipitation data of the International Airport of New Orleans.

The obtained power function for pollutant transport capacity is $Y = 0.1028 * V^{0.8212}$, where the transport capacity Y [μg/l] and the total runoff volume V [l]. For the Buildup/Washoff model the 2 year interval gave the most reliable. The value of 12.13 mg/day was obtained for the Buildup Rate C.

CHAPTER 1

INTRODUCTION

In water quality management of streams and planning of remediation the identification and classification of both point and non- point sources assumes an important role. Most of the cases the contribution from non- point sources originating over a large urban areas are more difficult to asses and to control.

Urban runoff was reported as the second most frequent cause of pollution of surface waters, after agriculture. [1] Because urban watersheds characterize higher impervious areas, more frequent human activities and more complex waste load sources, urban runoff transports much more pollutants. This is not only in terms of quantity but also in types. [2] Pollutants discharged from impervious urban areas can significantly affect the environment especially the quality of life in the receiving water bodies. Therefore in the past 30 years the effort to control the pollutant discharge increased continuously. One of the most important tools to asses the impact of storm water runoff, are mathematical models to predict as well as to describe this water quality phenomena.

In the last decades the Environmental Protection Agency (EPA) set regulation of non-point sources in urban areas, but also increased its effort to develop models of urban storm water quality and to realize their importance as analysis and management tools. The developed models may be used to simulate the long and/or short term behavior of urban runoff quality and to evaluate the impact of land use changes in the watersheds under Best Management Practice (BMP) strategies, so that the cost/benefit evaluation of specific measures can be realized more accurately.

Generally, models may be used to address many of the objectives of urban runoff analysis, including:

- Characterize the urban runoff
- Provide input to receiving water analysis
- Determine effects, sizes and combinations of control options
- Perform frequency analyses on quality parameters
- Provide input to cost / benefit analyses. [3]

According to the mentioned study objectives, there are three distinct levels of urban runoff analysis: planning, design/analysis, and operation. [4] Planning models are characterized by their long simulation times, low mathematical complexity and minimum data requirements. Models used in the design and analysis process focus more on detail simulation of single storm events. Their main use is to predict flows and concentrations anywhere in the rainfall / runoff system and can illustrate the detail and exact manner in which abatement procedures or design options affect them. They are typified by short simulation times. Data requirements may be very extensive. Operational models are used to produce actual control decisions during a storm event. They are frequently developed from stochastic design models and applied to a particular system. [5]

CHAPTER 2

SCOPE AND OBJECTIVES

This research focused on storm water runoff from highways. These runoffs represent a considerable contaminant source for the surrounding receiving waters. During this study, three storm events were observed and multiple storm water runoff samples were collected from each storm event and analyzed for many different parameters. The results have been added to the existing data from eleven previous storm events.

The EPA recommends that state water quality standards should be based on dissolved heavy metal concentrations because the dissolved fraction is a better representation of the biologically active portion of the metal in water than is the total or total recoverable fraction. [6]

This document will focus on dissolved heavy metals and will present the Buildup/Washoff behavior for dissolved iron in the storm water runoff from the studied elevated highway. There are circumstances that affect this research. The wet climate of southeast Louisiana presumes that pollutants are washed off completely by frequent storms. Also the limited data that is available for the calibration of the model does not represent in a complete manner the traffic flow patterns and climate for the period of time under consideration.

Based on this premises, this research focused on three primary objectives:

Objective 1: The first objective of this research was to compare the selected model to other models for runoff quality and to calibrate the used Buildup/Washoff model using the data for the observed highway section.

Objective 2: The second objective was to compare the results and adequacy of the model with respect to its use for other urban areas.

Objective 3: The third objective was to apply the developed model for dissolved iron over a past period of time using precipitations records from the nearby meteorological station at the International Airport of New Orleans and review the pollutant Buildup/Washoff over time for elevated highways.

CHAPTER 3

LITERATURE REVIEW

3.1 The Clean Water Act (CWA)

In December 1970, as an outgrowth of the administration's environmental interests, a new independent body, the EPA, was created. This organization assumed the functions of several existing agencies relative to matters of environmental management. It brought together under one roof all of the pollution control programs related to water, air, solid wastes, pesticides, and radiation. The EPA was seen by the administration as the most effective way of recognizing that the environment must be looked on as a single, interrelated system. It is noteworthy, however, that the creation of the EPA made even more pronounced the separation of water quality programs from other water programs.

Even with the enactment of EPA, it was clear that a comprehensive response to water pollution issues was still lacking. It became evident during Congressional hearings in 1971 that relative to the construction grants program, the program was under-funded. To rectify this situation, Congress passed the Water Pollution Control Act Amendments of 1972. Responding to public demand for cleaner water, the law ended two years of intense debate, negotiation, and compromise and resulted in the most assertive step taken in the history of national water pollution control activities, the CWA.

The act departed in several ways from previous water pollution control legislation. It expanded the federal role in water pollution control, increased the level of federal funding for construction of publicly owned treatment works, elevated planning to a new level of significance, opened new avenues for public participation, and created a regulatory mechanism requiring uniform technology-based effluent standards, together with a national permit system for all point-source dischargers as the means of enforcement. As pollution control measures for industrial process wastewater and municipal sewage were implemented and refined, it became increasingly evident that more diffuse sources of water pollution were also significant causes of water quality impairment. Specifically, storm water runoff draining from large surface areas, such as urban land, was found to be a major cause of water quality impairment, including the non-attainment of designated beneficial uses. [7]

The CWA is the cornerstone of surface water quality protection in the United States. The Act does not deal directly with ground water or with water quantity issues. The statute employs a variety of regulatory and non-regulatory tools to sharply reduce direct pollutant discharges into waterways, finance municipal wastewater treatment facilities, and manage polluted runoff. These tools are employed to achieve the broader goal of restoring and maintaining the chemical, physical, and biological integrity of the nation's waters.

For many years following the passage of CWA in 1972, the EPA and different states focused mainly on the chemical aspects of the integrity goal. During the last decade, however, more attention has been given to physical and biological integrity. Also, in the early decades of the Act's implementation, efforts focused on regulating discharges from traditional point source facilities, such as municipal sewage plants and industrial facilities, with little attention paid to runoff from streets, construction sites, farms, and other wet-weather sources.

Starting in the late 1980s, efforts to address polluted runoff have increased significantly. For non point runoff, voluntary programs, including cost-sharing with landowners are the key tool. For wet weather point sources like urban storm sewer systems and construction sites, a regulatory approach is being employed. Evolution of CWA programs over the last decade has also included something of a shift from a program-by-program, source-by-source, and pollutant-by-pollutant approach to more holistic watershed-based strategies. [8]

3.2 Development of the NPDES Storm Water Program

The National Pollutant Discharge Elimination System (NPDES) Storm Water Program has been established with the intention to regulate storm water runoff from point sources through permits. To accomplish these regulations a two phase program was induced. These two different phases will be discussed in the following sections.

3.2.1. Phase I NPDES Storm Water Program

In response to the need for comprehensive NPDES requirements for discharges of storm water, Congress amended the CWA in 1987 to require the EPA to establish phased NPDES regulations for storm water discharges.

Phase I of the U.S. Environmental Protection Agency's (EPA) storm water program was promulgated in 1990 under the CWA. The Phase I program addressed sources of storm water runoff that had the greatest potential to negatively impact water quality. Phase I relies on NPDES permit coverage to address storm water runoff from:

- "medium" and "large" municipal separate storm sewer systems (MS4s) generally serving populations of 100,000 or greater
- construction activity disturbing 5 acres of land or greater
- ten categories of industrial activity.

Operators of the facilities, systems, and construction sites regulated under the Phase I NPDES Storm Water Program can obtain permit coverage under an individually tailored NPDES permit or a general NPDES permit. The first permit was developed for MS4 and some industrial facilities, whereas the second permit was used by most operators of industrial facilities and construction sites. [9]

3.2.2. Phase II NPDES Storm Water Program

The Storm Water Phase II Final Rule is the next step in EPA's effort to preserve, protect, and improve the Nation's water resources from polluted storm water runoff. On August 7, 1995, EPA promulgated application regulations for Phase II of the NPDES Storm Water Program. The Phase II program expands the Phase I program by requiring additional operators of MS4s in urbanized areas and operators of small construction sites, through the use of NPDES permits, to implement programs and practices to control polluted storm water runoff. Phase II is intended to further reduce adverse impacts to water quality and aquatic habitat by instituting the use of controls on the unregulated sources of storm water discharges that have the greatest likelihood of causing continued environmental degradation.

The Phase II regulations established a sequential application process for all Phase II storm water discharges, which included all discharges, composed entirely of storm water, except those specifically classified as Phase I discharges. Such discharges included storm water from small municipal separate storm sewer systems, and commercial and institutional facilities. The application regulations included two tiers. The first tier was for Phase II dischargers, that the NPDES permitting authority determined were contributing to water quality impairment or were a significant contributor of pollutants to waters of the United States. Dischargers that have been designated by the permitting authority were required to obtain a permit and had to submit a permit application within 180 days of notification that an application was required. The second tier of the Phase II storm water application regulations required all remaining Phase II sources (i.e., all Phase II sources not designated by the permitting authority) to submit a permit application by August 7, 2001, but only if the Phase II regulatory Program in place at that time required permits.

Three new classes of facilities were designated for automatic coverage on a nationwide basis:

- Operators of small municipal separate storm sewer systems (MS4s) serving population centers (or equivalents) of at least 10,000 and satellite areas with a population density of 1,000 people per square mile. (about 3500 municipalities)
- Construction activity disturbing between 1 and 5 acres of land, such as small construction activities.
- All highways and streets discharging to MS4s

In addition to expanding the NPDES Storm Water Program, the Phase II Final Rule revises the "no exposure" exclusion and the temporary exemption for certain industrial facilities under Phase I of the NPDES Storm Water Program. [10]

3.2.3. Wet Weather Discharges

"Wet weather discharges" refers collectively to point source discharges that result from precipitation events, such as rainfall and snowmelt. Wet weather discharges include storm water runoff, combined sewer overflows (CSOs), and wet weather sanitary sewer overflows (SSOs). Storm water runoff accumulates contaminants such as oil and grease, chemicals, nutrients, metals, and bacteria as it travels across land. CSOs and wet weather SSOs contain a mixture of raw sewage, industrial wastewater and storm water, and have resulted in beach closings, shellfish bed closings, and aesthetic problems. Under the NPDES permit program, there are the following three program areas: storm water runoff, CSOs and SSOs. Those address each of the wet weather discharges described above. EPA believes that wet weather discharges should be addressed in a coordinated and comprehensive fashion to reduce the threat to water quality, reduce redundant contamination control costs, and provide State and local governments with greater flexibility to solve wet weather discharge problems.

To identify and address cross-cutting issues and promote coordination, EPA established the Urban Wet Weather Flows Federal Advisory Committee in 1995. [11]

3.3 Contaminant Sources and their Effects

In the following section selected information on storm water runoff from highways are presented. Also definitions and explanations for important terms of storm water runoff from elevated highways will we provided.

3.3.1. Distinction between Non-Point and Point Sources

Point Sources

Point sources of contamination are discrete conveyances, such as pipes or man made ditches that discharge pollutants into waters of the United States. This includes not only discharges from municipal sewage plants and industrial facilities, but also collected storm drainage from larger urban areas, certain animal feedlots and fish farms, some types of ships, tank trucks, offshore oil platforms, and collected runoff from many construction sites. [12]

Non-point sources

Non-point source (NPS) pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is caused by rainfall or snowmelt moving over and through the ground. As the runoff moves, it picks up and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, and even our underground sources of drinking water. Loadings of pollutants from NPS enter water-bodies via sheet flow, rather than through a pipe, ditch or other conveyance.

These pollutants include:

- Excess fertilizers, herbicides, and insecticides from agricultural lands and residential areas;
- Oil, grease, and toxic chemicals from urban runoff and energy production;
- Sediment from improperly managed construction sites, crop and forest lands, and eroding stream-banks;
- Salt from irrigation practices and acid drainage from abandoned mines;
- Bacteria and nutrients from livestock, pet wastes, and faulty septic systems;

Atmospheric deposition and hydro-modification are also sources of nonpoint source pollution.

States report that non-point source pollution is the leading remaining cause of water quality problems. The effects of non-point source pollutants on specific waters vary and may not always be fully assessed. However, we know that these pollutants have harmful effects on drinking water supplies, recreation, fisheries, and wildlife.

Other impacts coming along with urbanization are the increasing amount of storm water runoff, contribution to stream bank erosion and possibility of downstream flooding. Impervious concrete and asphalt surfaces of new roadways prevent storm water from soaking into the ground, where it was once absorbed. This increases the total volume of storm water runoff. It also increases the value of the peak storm water discharge, and decreases the time it takes to reach this peak. Increased runoff volumes and peak discharge levels result in increased levels of flooding risk.

Collecting runoff water from non-point sources, such as roadway shoulders, is difficult, thus in this research project, storm water runoff from an elevated highway has been analyzed. Samples were collected from the drainage pipe of this elevated highway, which collects water from a known impervious area. Consequently, calculating the volume of the storm water runoff and addressing the contaminant loading to this known area was possible. [13]

3.3.2. Factors affecting runoff quality

Sources

One of the major contaminant sources of storm water runoff is traffic. All means of transportation directly and indirectly contribute much to the contamination found in highway runoff. Vehicles are a source of metals, oil, grease, lead, asbestos, and rubber. Sometimes de-icing chemicals such as salts or other materials deposited on highways are also indirectly contributed to vehicles. Other major sources of contaminants in the runoff include dust that settles on the road and shoulders and dissolved constituents, such as acids and particulate matter from atmospheric fallout. Urban construction sites contribute sediment, plant debris, and asphalt. Storm water runoff also contains refuse such as street litter. A number of common highway maintenance practices, such as salting, also may adversely affect water quality. The nature of the materials, methods used, and the proximity of the maintenance activity to a body of water increase the likelihood of adverse effects. [14]

Highway Runoff Quality

Numerous factors may affect the quality of highway runoff including traffic volume, precipitation characteristics, roadway surface type, and the nature of the contaminants themselves. Research continues into the relationship between these factors and the concentration of contaminants in highway runoff because of the complexity and importance of this topic. The precipitation characteristics that may impact the water quality of highway runoff include the number of dry days preceding the event, the intensity of the actual and preceding storm event, and their durations. Intensity of the actual storm event has a significant impact because many of the contaminants are associated with particulate matter, such as dust, which are more easily mobilized in high intensity storms. Constituents in storm water runoff showing a strong correlation with suspended solids include metals, organic compounds, total organic carbon, and biochemical oxygen demand.

Higher concentrations of contaminants are often observed in the first runoff from a storm, a phenomenon referred to as first flush effect. This is especially true for dissolved components including nutrients, organic lead, and ionic constituents.

In general, concentrations of particle-associated contaminants show a more complex temporal variation related to rainfall intensity and the flushing of sediment through the drainage system.

The effect of highway paving material (asphalt versus concrete) on the quality of highway runoff appears to be minimal. Most studies have found that highway surface type was relatively unimportant compared to such factors as surrounding land use. It has also been reported that the type of collection and conveyance system for highway runoff, such as storm sewer, grassy swale has a greater effect on runoff quality than pavement type. [15]

Contaminants in Runoff Pollution

Runoff pollution is that associated with rainwater or melting snow that washes off roads, bridges, parking lots, rooftops, and other impermeable surfaces. As it flows over these surfaces, the water picks up dirt and dust, rubber and metal deposits from tire wear, antifreeze and engine oil that has dripped onto the pavement, pesticides and fertilizers, and discarded cups, plastic bags, cigarette butts, pet waste, and other litter. These contaminants are carried into our lakes, rivers, streams, and oceans.

Contaminants in runoff pollution from roads, highways, and bridges include:

Sediment: Sediment is produced when soil particles are eroded from the land and transported to surface waters. Natural erosion usually occurs gradually because vegetation protects the ground. When land is cleared or disturbed to build a road or bridge, however, the rate of erosion increases. The vegetation is removed and the soil is left exposed, to be quickly washed away in the next rain. Erosion around bridge structures, road pavements, and drainage ditches can damage and weaken these structures.

Soil particles settle out of the water in a lake, stream, or bay onto aquatic plants, rocks, and the bottom. This sediment prevents sunlight from reaching aquatic plants, clogs fish gills, chokes other organisms, and can smother fish spawning and nursery areas.

Other pollutants such as heavy metals and pesticides adhere to sediment and are transported with it by wind and water. These pollutants degrade water quality and can harm aquatic life by interfering with photosynthesis, respiration, growth, and reproduction.

Oils and Grease: Oils and grease are leaked onto road surfaces from car and truck engines, spilled at fueling stations, and discarded directly onto pavement or into storm sewers instead of being taken to recycling stations. Rain and snowmelt transport these pollutants directly to surface waters.

Heavy Metals: Heavy metals come from some "natural" sources such as minerals in rocks, vegetation, sand, and salt. But they also come from car and truck exhaust, worn tires and engine parts, brake linings, weathered paint, and rust. Heavy metals are toxic to aquatic life and can potentially contaminate ground water.

Debris: Grass and shrub clippings, pet waste, food containers, and other household wastes and litter can lead to unsightly and polluted waters. Pet waste from urban areas can add enough nutrients to estuaries to cause premature aging, or "Eutrophication."

Road Salts: In the Snow Belt, road salts can be a major pollutant in both urban and rural areas. Snow runoff containing salt can produce high sodium and chloride concentrations in ponds, lakes, and bays. This can cause unnecessary fish kills and changes to water chemistry.

Fertilizers, Pesticides, and Herbicides: If these are applied excessively or improperly, fertilizers, pesticides, and herbicides can be carried by rain waters from the green parts of public rights-of-way. In rivers, streams, lakes, and bays, fertilizers contribute to algal blooms and excessive plant growth, and can lead to eutrophication. Pesticides and herbicides can be harmful to human and aquatic life. [16]

Effects of Highway Runoff

The type and size of the receiving body, the potential for dispersion, the size of the catchment's area, the relative amount of highway runoff, and the biological diversity of the receiving water ecosystem are just some of the factors that determine the extent and importance of highway runoff effects. Concentrations of contaminants in the water columns of receiving waters generally show small changes due to highway runoff. This may be the result of dilution of the highway runoff by flow from the rest of the watershed. However, stream and lake sediments have been found to have high concentrations of heavy metals and are the primary source for the bioconcentration of metals in aquatic biota.

Bioassay tests of organisms from streams and lakes receiving highway runoff generally have not demonstrated acute toxicity, although very high traffic volumes or other site-specific conditions may produce a toxic response. Chronic toxicity resulting from bioaccumulation of contaminants in highway runoff has not been thoroughly investigated, although studies have documented higher concentrations of metals in fish and other aquatic biota living near highways.

Highways can have an impact on groundwater, including changes in water quality in surface and shallow aquifers. Highway runoff that infiltrates into the ground may result in the contamination of groundwater with contaminants including metals, nitrogen, and organic compounds. The effects of highway runoff on groundwater are highly variable depending on depth to the water table, hydrological conditions, and soil characteristics. Soils can prevent or reduce the amount of some contaminants reaching groundwater through retention, modification, decomposition, or adsorption. Therefore, groundwater contamination is a particular concern where the aquifer is shallow (less than 4 feet). [15]

3.4. NPDES Effluent Limits

When developing effluent limits for a NPDES permit, a permit writer must consider limits based on both the technology available to treat the pollutants (i.e., technology-based effluent limits), and limits that are protective of the water quality standards of the receiving water (i.e., water quality-based effluent limits). [17]

3.4.1. Quality-based Effluent Limits

On August 26, 1996, the EPA published in the Federal Register a policy outlining an interim approach for incorporating water quality-based effluent limitations into NPDES storm water permits. The policy was developed to address the variable nature In response to recent questions regarding the type of water quality based effluent limitations that are most appropriate for NPDES storm water permits, the Environmental Protection Agency (EPA) is adopting an interim permitting approach for regulating wet weather storm water discharges. Due to the nature of storm water discharges, and the typical lack of information on which to base numeric water quality-based effluent limitations (expressed as concentration and mass), EPA will use an interim permitting approach for NPDES storm water permits. The interim permitting approach uses best management practices (BMPs) in first-round storm water permits, and expanded or better-tailored BMPs in subsequent permits, where necessary, to provide for the attainment of water quality standards. In cases where adequate information exists to develop more specific conditions or limitations to meet water quality standards, these conditions or limitations are to be incorporated into storm water permits, as necessary and appropriate. This interim permitting approach is not intended to affect those storm water permits that already include appropriately derived numeric water quality-based effluent limitations. Since the policy only applies to water quality based effluent limitations, it is not intended to affect technology-based limitations, such as those based on effluent guidelines or the permit writer's best professional judgment, that are incorporated into storm water permits. [18]

Each storm water permit should include a coordinated and cost-effective monitoring program to gather necessary information to determine the extent to which the permit provides for attainment of applicable water quality standards and to determine the appropriate conditions or limitations for subsequent permits. Such a monitoring program may include ambient monitoring, receiving water assessment, discharge monitoring (as needed), or a combination of monitoring procedures designed to gather necessary information.

This interim permitting approach applies only to EPA; however, EPA also encourages authorized States and Tribes to adopt similar policies for storm water permits. This interim permitting approach provides time to more fully assess the range of issues and possible options for the control of storm water discharges for the protection of water quality. This interim permitting approach may be modified as a result of the ongoing Urban Wet Weather Flows Federal Advisory Committee policy dialogue on this subject. [19]

3.4.2. Technology-based Effluent Limits

There are two general approaches for developing technology-based effluent limits for industrial facilities:

1. Using national effluent limitations guidelines (ELGs) and
2. Using Best Professional Judgment (BPJ) on a case-by-case basis (in the absence of ELGs).

National Effluent Limitation Guideline (ELGs)

Technology-based effluent limits for Publicly Owned Treatment Works (POTWs) are derived from secondary treatment standards (Table 1). The intent of a technology-based effluent limitation is to require a minimum level of treatment for industrial/municipal point sources based on currently available treatment technologies while allowing the discharger to use any available control technique to meet the limitations. For industrial sources, the national ELGs are developed based on the demonstrated performance of a reasonable level of treatment that is within the economic means of specific categories of industrial facilities. Where national ELGs have not been developed, the same performance-based approach is applied to a specific industrial facility based on the permit writer's BPJ. In some cases, effluent limits based on ELGs and BPJ (as well as water quality considerations) may be included in a single permit. When developing technology-based effluent limitations for non-municipal dischargers, the permit writer must consider all applicable standards and requirements for all pollutants discharged. As indicated above, applicable technology-based requirements may include national standards and requirements applicable to all facilities in specified industrial categories, or facility-specific technology-based requirements based on the permit writer's BPJ. It is important, therefore, that permit writers understand the basis of the national standards and the differences between the various required levels of treatment performance. [17]

An important aspect of municipal wastewater is that it is amenable to biological treatment. The biological treatment component of a municipal treatment plant is termed secondary treatment and is usually preceded by simple settling (primary treatment). In response to the CWA requirements, EPA evaluated performance data for POTWs practicing secondary treatment and established performance standards based on its evaluation. Secondary treatment standards, therefore, are defined by the limitations provided in Table 1.

Parameter	30-Day Average	7-Day Average
5-Day BOD	30mg/l	45mg/l
TSS	30mg/l	45mg/l
pH	6 – 9 s.u. (instantaneous)	---
Removal	85% BOD_5 and TSS	---

Table 1: Secondary Treatment Standards

Contaminants	Unit	Concentration		
		Weak	Medium	Strong
TSS	[mg/L]	100	220	350
VSS	[mg/L]	80	165	275
TDS	[mg/L]	250	500	850
VDS	[mg/L]	105	200	325
COD	[mg/L]	250	500	1000
Alkalinity	[mg/L]	50	100	200

Table 2: Typical Components in Untreated Domestic Wastewater [20]

Effluent limitations guidelines and performance standards are established by EPA for different industrial categories since the best control technology for one industry is not necessarily the best for another. These guidelines are developed based on the degree of pollutant reduction attainable by an industrial category through the application of control technologies, irrespective of the facility location. Using these factors, similar facilities are regulated in the same manner. In theory, for example, a pulp and paper mill on the west coast of the United States would be required to meet the same technology-based limitations as an identical plant located on the east coast (unless there were special site-specific concerns that had to be addressed). To date, EPA has established guidelines and standards for more than 50 different industrial categories (e.g., metal finishing facilities, steam electric power plants, iron and steel manufacturing facilities). [18]

Best Professional Judgment (BPJ) Limits

Best Professional Judgment limits (BPJ-based limits) are technology-based limits derived on a case-by-case basis for non-municipal (industrial) facilities. BPJ limits are established in cases where ELGs are not available for, or do not regulate, a particular pollutant of concern. BPJ is defined as the highest quality technical opinion developed by a permit writer after consideration of all reasonably available and pertinent data or information that forms the basis for the terms and conditions of a NPDES permit. The authority for BPJ is contained in Section 402(a)(1) of the CWA, which authorizes the EPA Administrator to issue a permit containing "such conditions as the Administrator determines are necessary to carry out the provisions of this Act", prior to taking the necessary implementing actions, such as the establishment of ELGs.

During the first round of NPDES permits in the early-to-mid-1970s, a majority of permits were based on the authority of Section 402(a) (1) of the CWA. These first round so-called best engineering judgment permits were drafted because effluent guidelines were not available for many industries. As effluent guidelines began to be promulgated, permit writers had to rely less on their best engineering judgment and could apply the ELGs in permits. As the implementation of the age of toxic pollutant control continues, the use of BPJ conditions in permits has again become more common. However, the statutory deadline for compliance with technology-based effluent limits (including BPJ-based pollutant limits) was March 31, 1989. Therefore, compliance schedules cannot be placed in permits to allow for extensions in meeting BPJ pollutant limits. BPJ has proven to be a valuable tool for NPDES permit writers over the years. Because it is so broad in scope, BPJ allows the permit writer considerable flexibility in establishing permit terms and conditions. Inherent in this flexibility, however, is the burden on the permit writer to show that the BPJ is reasonable and based on sound engineering analysis. If this evaluation of reasonableness does not exist, the BPJ condition is vulnerable to a challenge by the permittee. Therefore, the need for and derivation of the permit condition, and the basis for its establishment, should be clearly defined and documented. References used to determine the BPJ condition should be identified. In short, the rationale for a BPJ permit must be carefully drafted to withstand the scrutiny of not only the permittee, but also the public and, ultimately, an administrative law judge. [17]

Establishment of BPJ Permit Limits

The NPDES regulations state that permits developed on a case-by-case basis of the CWA must consider

- the appropriate technology for the category class of point sources of which the applicant is a member, based on all available information, and
- Any unique factors relating to the applicant.

To set BPJ limits, a permit writer must first determine a need for additional controls beyond existing ELGs. The need for additional controls may be the result of the facility not falling under any of the categories for which ELGs exist (e.g., barrel reclaimers, transportation equipment cleaning facilities, or industrial laundries) or discharging pollutants of concern that are not directly or indirectly addressed by the development of the ELGs (e.g., a pharmaceutical manufacturer or a petroleum refiner may discharge elevated levels of organic solvents for which category-specific guidelines do not exist). It should be noted that prior to establishing BPJ-based limits for a pollutant not regulated in an effluent guideline, the permit writer should ensure that the pollutant was not considered by EPA while developing the ELGs (i.e., BPJ based effluent limits are not required for pollutants that were considered by EPA for regulation under the effluent guidelines, but for which EPA determined that no ELG was necessary).

In setting BPJ limitations, the permit writer must consider several specific factors as they appear in 40 CFR §125.3(d). These factors, which are enumerated below, are the same factors required to be considered by EPA in the development of ELGs and, therefore, are often referred to as the Section 304(b) factors:

- For best practicable control technology (BPT) requirements:
  - The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application
  - The age of equipment and facilities involved
  - The process employed
  - The engineering aspects of the application of various types of control techniques
  - Process changes*
  - Non-water quality environmental impact including energy requirements*
- For best conventional pollutant control technology (BCT) requirements:
  - All items in the (BPT) requirements indicated by an asterisk (*) above
  - The reasonableness of the relationship between the costs of attaining a reduction in effluent and the effluent reduction benefits derived
  - The comparison of the cost and level of reduction of such pollutants from the discharge of POTWs to the cost and level of reduction of such pollutants from a class or category of industrial sources
- For best available technology (BAT) requirements:
  - All items in the BPT requirements indicated by an asterisk (*) above
  - The cost of achieving such effluent reduction.

A permit writer must consider each of these factors in establishing BPJ-based conditions in permits. Since BPJ contains an element of judgment or educated opinion, a permit writer with the proper tools should be able to establish BPJ conditions in permits that are both technically sound and reasonable. A technically sound and reasonable permit is not likely to be successfully challenged by the permittee or a third party. In this context, "technically sound permit conditions" means that the conditions are achievable with existing technology. "Reasonable" means that the conditions are achievable at a cost that the facility can afford. Historically, some of the other factors, such as age, process employed and non-water quality impacts have assumed lesser importance than the technical and economic feasibility evaluations. [17]

3.5. Best Management Practice

Best Management Practices (BMP) can be either structural or non-structural practices that are implemented to minimize the impacts of anthropogenic constituents generated by urban and traffic activities on water quality. The term was first used in the USA in the 1970s to refer to practices that could be used to mitigate both urban runoff quantity and quality. Common in-situ BMPs include detention/retention basins filters, vegetated swales, infiltration/exfiltration trenches and porous pavement. Less common, but innovative BMPs include a variety of infiltration systems that passively incorporate adsorption and filtration. No single BMP can address all storm water problems. Each type has certain limitations based on drainage area served, available land space, cost, pollutant removal efficiency, as well as a variety of site-specific factors such as soil types, slopes, depth of groundwater table, etc. Careful consideration of these factors is necessary in order to select the appropriate BMP or group of BMPs for a particular location. [21]

3.5.1. Types of Storm Water BMPs

There is a variety of storm water BMPs available for managing urban runoff. Regardless of the type, storm water BMPs are most effective when implemented as part of a comprehensive storm water management program that includes proper selection, design, construction, inspection and maintenance. Storm water BMPs can be grouped into two broad categories: structural and non-structural. Structural BMPs are used to treat the storm water at either the point of generation or the point of discharge to either the storm sewer system or to receiving waters. Non-structural BMPs include a range of pollution prevention, education, institutional, management and development practices designed to limit the conversion of rainfall to runoff and to prevent pollutants from entering runoff at the source of runoff generation. [22]

3.5.2. BMP Selection

BMP selection is a complex process. There are a number of competing factors that need to be addressed when selecting the appropriate BMP or suite of BMPs for an area. It should be stressed that BMPs should be incorporated into a comprehensive storm water management program. Without proper BMP selection, design, construction and maintenance, BMPs will not be effective in managing urban runoff. BMP selection can be tailored to address the various sources of runoff produced from urbanized areas. For example, a particular suite of BMPs may be developed for use on construction sites and new land development, where opportunities exist for incorporating BMPs that are focused on runoff prevention, reducing impervious surfaces and maintaining natural drainage patterns. In established urban communities, a different suite of BMPs may be more appropriate due to space constraints. In these areas, BMPs may be selected to focus on pollution prevention practices along with retrofit of the established storm drain system with regional BMPs. Site suitability for selecting a particular BMP strategy is key to successful performance. Most BMPs have limitations for their applicability, and therefore cannot be applied nationwide. [22]

3.6. Model Development

3.6.1 Two Types of Models for Runoff Quality:

Deterministic or Physically Based Models:

This kind of models nowadays is used very widespread and well documented in the professional literature. They try to simulate the variation in runoff quantity and quality by describing pollutant generation, accumulation, wash- off and transport. However this process requires detailed input data which rarely is available. If obtainable the data acquisitions are expensive, time consuming and require complex computation.

Statistically or stochastically based Models:

There are less data requirements for stochastic models, but because they are not as common their development is not as well documented as is the case for deterministic models. In addition to the data requirements their main advantages lies in their less intense computations and therefore they allow simulations for long time periods. Furthermore they express results in a probabilistic framework and thus allows for risk assessment to be done directly and easily. This strategy also leads to an easy comparison of success probabilities versus associated implementation costs of any abatement plan. [2]

3.6.2 The Stochastic Model

Although there are two modeling methods, deterministic and statistical/stochastic, and each has its own advantages, the division between them is really not well defined. For example, deterministic models use design storms as their inputs and parameters of deterministic model can be fitted to data using statistical techniques. [23] On the other hand, statistically-based relationships could be checked by physically-based analysis to test their physical reliability. Moreover, both deterministic and stochastic approaches could be used in the same model as shown in [24] and [25]. Statistical models are usually developed by establishing regression equations between runoff quality parameters and their explanatory variables which have the greatest influence on the quality parameters. Because of data limits, some important explanatory parameters like land use and antecedent dry time are not always statistically significant. [23]

3.6.3 Pollutant Buildup Model

The U.S. Geology Survey developed a general regression model for long term load estimation, based on rainfall data. The regression model was between storm runoff loads and physical, and climatic characteristics. [26]

It was found that the most accurate models were those for the more arid western United States and the least accurate models were those for wetter areas. Therefore, an important conclusion of this study was that in urban areas subject to small mean annual rainfall, the pollutants accumulated never washed off completely during any storm. In areas that have larger mean annual rainfall, the pollutants accumulation can be washed off completely by more frequent storms. As a result, the succeeding storm may produce the same quantity of rainfall as the preceding storm, but may produce considerable smaller storm-runoff loads. The Survey suggested that in this case, it be better to consider another variable, storm antecedent dry time. [2]

Several Pollutant Buildup Functions

Storm antecedent dry time is usually taken under consideration in the form of pollutants buildup functions. "Buildup" refers to all of the complex processes of dry weather that occur between storms, including deposition, wind erosion, street cleaning, etc. The idea is that all such processes lead to a net accumulation of pollutants, which are then "washed off" during storm events. [3] Buildup formulations cover a range of linear and nonlinear functions of dry days prior to a storm event, and different models accept different options. It has been summarized [27] that buildup relationships generally fall into one of four functional forms: Linear function, power function, exponential function, and Michaelis- Menton function:

Linear: $P = C * t$

Where P = mass of pollutants accumulation on the surface;

t = time since last storm;

C = coefficient of pollutants Buildup Rate

Power: $P = C * t^{b}$

Where b = exponent

Exponential: $P = P_L (1 - e^{-bt})$

Where P_L = limiting (asymptotic) surface load

Michaelis- Menton: $P = P_L * t / (C+t)$ [5].

3.6.4 Pollutant Washoff Model

Washoff is the process of erosion or solution of pollutants from a subcatchment surface during a period of runoff. From theoretic standpoint, sediment transport theory may describe this process, but in practice, it is difficult even unrealistic to use the theory, because of lack of data for parameter evaluation and other difficulties. Thus, almost all modeling activities for washoff focus on empirical formulations.

The results from research done by the U.S. Geology Survey [26] implied that total storm rainfall and total drainage area were the most significant variables in the runoff quality regression model described previously. Obviously, storm runoff volume has very close relationship to all the significant explanatory variables in the runoff loads models. Moreover, the Survey established regression models for runoff volume, and it was found that the models have the same significant explanatory variables as runoff loads models. [2] The bases for many of the empirical formulations of washoff are the results of Sartor and Boyd. [28] The results are remarkable in that there is an unmistakable tendency toward an exponential or first order decay washoff process. Nakamura [28] shows similar experimental results in his plots showing linear relationships between the log of a remaining mass of pollutant on the surface versus cumulative runoff volumes. [2]

Two Washoff Models

The exponential Washoff model in the form of

$$P_{i,T} = M_{i,1} [1- \exp (-K_i * R_v)]$$

is widely used in most deterministic quality models, such as SWMM and STORM [29], where

T = duration of a storm event;

$P_{i,T}$ = mass of pollutant i washed off during T;

$M_{i,1}$ = mass of pollutant i available on the surface at the start of the storm event;

K_i = coefficient;

R_v = total volume of runoff of the storm event. [2]

Besides the exponential Washoff model, rating curves are also often used as a convenient formulation for washoff prediction. They usually take the form of a power function. Although they are purely empirical, several studies outlined below show that power functions give good estimates for runoff quality in many cases. V.P. Singh and V.J. Chen

[30] found from their investigation that for wash load and runoff volume were linearly related on logarithmic paper. In other words, the relationship between Y and V could be modeled by

$$Y = a * V^b \quad \text{or}$$

$$\text{Log } Y = \text{Log } a + b * \text{Log } V$$

where, a, b, = parameter;

Y = wash load;

V = runoff volume.

In [31] the author compounded various models based on prediction sum of squares. He suggested that storm runoff was the most significant independent variable for runoff quality models and that power functions demonstrated superior performance over other models. In addition, the investigation by Diniz [32] showed that the pollutant washoff model could be of the form of a power function. [2]

3.7. Heavy Metals

Heavy metals are elements having atomic weights between 63.546 and 200.590, and a specific gravity greater than 4.0. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Excessive levels of essential metals, however, can be detrimental to the organism.

All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low. The colloidal and particulate metal may be found in

1) Hydroxides, oxides, silicates, or sulfides; or

2) Adsorbed to clay, silica, or organic matter.

The soluble forms are generally ions or unionized organometallic chelates or complexes. The solubility of trace metals in surface waters is predominately controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system.

The behavior of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. Sediment composed of fine sand and silt will generally have higher levels of adsorbed metal than will quartz, feldspar, and detrital carbonate-rich sediment. Metals also have a high affinity for humid acids, organo-clays, and oxides coated with organic matter. [33]

The water chemistry of the system controls the rate of adsorption and desorbtion of metals to and from sediment. Adsorption removes the metal from the water column and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. Metals may be desorbed from the sediment if the water experiences increases in salinity, decreases in redox potential, or decreases in pH.

1. Salinity increase: Elevated salt concentrations create increased competition between cations and metals for binding sites. Often, metals will be driven off into the overlying water.
2. Redox Potential decrease: A decreased redox potential, as is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metal ions into the overlying water.
3. pH decrease: A lower pH increases the competition between metal and hydrogen ions for binding sites. A decrease in pH may also dissolve metal-carbonate complexes, releasing free metal ions into the water column (Connell et al., 1984).

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to humans and to the environment. [33]

3.7.1 **Iron**

Basic Information

Symbol: Fe

Atomic Number: 26

Atomic Mass: 55.845 amu

Melting Point: 1535.0 °C (1808.15 °K, 2795.0 °F)

Boiling Point: 2750.0 °C (3023.15 °K, 4982.0 °F)

Number of Protons/Electrons: 26

Number of Neutrons: 30

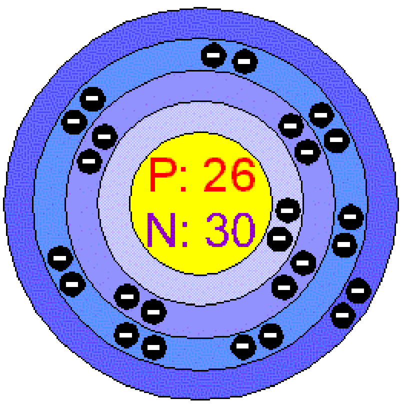
Classification: Transition Metal

Crystal Structure: Cubic

Density @ 293 K: 7.86 g/cm^3

Color: Silvery

Atomic Structure



Number of Energy Levels: **4**

First Energy Level: **2**

Second Energy Level: **8**

Third Energy Level: **14**

Fourth Energy Level: **2**

Figure 1: Atomic Structure of Iron

Facts

Date of Discovery: Known to the ancients

Discoverer: Unknown

Name Origin: Latin

Symbol Origin: From the Latin word *ferrum* (iron)

Uses: steel, hemoglobin (carries oxygen in blood)

[34]

Iron is the most abundant element in the core of the earth and one of the most abundant in the earth's crust. Besides aluminum, it is the most important metallic element in the terrestrial environment. With regard to its biological activity, iron is also the most versatile of al the elements. Life without iron is, in all likelihood, impossible since the enormous quantities of this metal in the earth's core resulted and still result in the formation of an effective shield that deflects various forms of solar and cosmic radiation. The unique properties of iron undoubtedly also led to its key role in the catalysis of metabolic processes. Because of the myriad number of important reactions in which iron participates, all organisms require a mechanism for its assimilation so as to avoid the ill effects that result from iron deficiency, which afflicts hundreds of millions of people in the world, particularly children and menstruating women. As well as being extremely useful, iron can also be highly toxic to cellular constituents when present in excess, but the problem of toxic iron overload is virtually limited to man and is far less frequent than iron deficiency. [35]

3.7.2 Dissolved Metals

The toxicity of heavy metals to biota in urban catchments has been regarded as a very important non-point source pollution issue. Numerous studies on heavy metal pollution in urban receiving waters have found that metal transport by surface runoff is closely correlated to the partitioning of the metal forms between dissolved and particulate phases. [36]

The U.S. EPA issued a policy memorandum on October 1, 1993, which was entitled "Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Metals Policy" and stated:

"It is now the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bio-available fraction of metal in the water column than total recoverable metal" does.

The primary mechanism for toxicity to organisms that live in the water column is by adsorption to or uptake across the gills; this physiological process requires metal to be in a dissolved form. This is not to say that particulate metal is nontoxic, only that particulate metal appears to exhibit substantially less toxicity than does dissolved metal. On October 1, 1993, in recognition that the dissolved fraction is a better representation of the biologically active portion of the metal than is the total or total recoverable fraction, the Office of Water recommended that dissolved metal concentrations be used for the application of metals aquatic life criteria and that State water quality standards for the protection of aquatic life (with the exception of chronic mercury criterion) be based of dissolved metals. Consequently, with a few exceptions, each metal's total recoverable-based criterion must be multiplied by a conversion factor to obtain a dissolved criterion that should not be exceeded in the water column. The Waste Load Allocation (WLA) of Total Maximum Daily Loads (TMDLs) must then be translated into a total recoverable metals permit limit.

Dissolved metal is operationally defined as that which passes through a 0.45 μm filter and particulate metal is operationally defined as total recoverable metal minus dissolved metal. Even at that, a part of what is measured as dissolved is particulate metal that is small enough to pass through the filter, or that is adsorbed to or complexed with organic colloids and ligands. Some or all of this may be unavailable biologically. [37]

3.7.3 Analytical Methods for Heavy Metals

There are a number of analytical methods available in principle for the determination of trace metals. In fact, however, there are only a few instrumental methods with sufficiently high detection power currently applied in routine analysis. In these methods one can distinguish between single element and multi-element methods that can reach detection limits close to or even below typical metal levels in environmental and biological materials. Therefore, in many cases, provided that sampling and sample preparation do not introduce significant bias, these methods, if properly applied, promise fairly accurate results. The methods most frequently used at present in routine and reference tasks are various modes of the multi-element method of plasma induced atomic emission spectrometry and plasma source mass spectrometry with impressive detection power. [38]

The Inductively Coupled Plasma Source

An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field. This field is inductively coupled to ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP, subjecting the constituent atoms to temperatures of about 6000 to 8000 degrees Kelvin. Because this results in almost complete dissociation of molecules, significant reduction in chemical interferences is achieved. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra. The ICP provides an optically “thin” source that is not subject to self-absorption except at very high concentration. Thus linear dynamic ranges of four to six orders of magnitude are observed for many elements. The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multi-element determination of metals. [39]

CHAPTER 4

METHODOLOGY

In the following section the various methods used to complete this research effort will be explained. This included the development and identification of a test site as well as the collection and analyses of highway storm water runoff samples of 14 different storm events. Following to that the laboratory analyses will be shortly described and at the end a brief introduction to the calibration of the stochastic model will be given.

4.1. Experimental Site Characteristics / Highway Runoff

In order to characterize the highway runoff water quality, a spectrum of storm events has been sampled at the experimental site. A maximum of fifteen fully labeled samples (date, sample number and time at which it was collected) have been collected for each storm, from the time of the start of observable rainfall. Samples were collected every 2 minutes until peak flow has been reached and then every 4 minutes thereafter. All the data recorded, measurements taken and samples collected have been logged on apposite data sheets alongside the time at which they have been taken.

The initial task of the research consisted of finding the right location for the experimental site. The site was located on the intersection of the I-10 and I-610 highways direction Baton Rouge beneath the eastbound lane of the I-610. This part of the highway was ideal for the research work because of the fast and easy access by car from the University-campus even during rush hours. This was from significant importance because samples had to be taken from the very first runoff flowing out of the pipe. Because weather forecast is not always reliable and rainfall not easy to predict the fast access of the test site by car was very important. Moreover part of the highway courses over a bridge where the drainage of the runoff can be determined easily. In this case it can be assumed that all storm water will run off each drainage-section of the bridge and can easily be collected. Therefore, it is easier to determine the area drained and the amount of storm-water runoff for each section. Last but not least, the site was located in a safe neighborhood, which made the work safe even during night hours.

The sampling location was constructed beneath the Interstate-610 eastbound lane. (Figure 2). The I-610 elevated roadway has three eastbound lanes of Portland cement concrete. This highway carries an average daily traffic load of 40,000 vehicles per day. The mean annual precipitation at the experimental site is 62 in/yr (1572 mm/yr), with the highest monthly rainfalls, 6.2 in/month (156 mm/month), during the months of July and August. The specific drainage area of the elevated roadway section drains to two storm drains on the leading edge of the outside lane (Figure 2). This specific drainage area from which the storm water runoff had to be characterized is 6,288 ft^2 large (Figure 3).

The storm water runoff is discharged without treatment directly into the 17^{th} Street Canal. This is representative of the heavily traveled elevated sections of major arterial highways that are typical of south Louisiana's elevated infrastructure. [38]

The area beneath the elevated highway was made ready for the establishment of the experimentation station. This involved the cleaning of a sufficient large area for the construction of the experiment station, installation of all necessary equipment for the performance of the measurements, lighting and finally making the facility secure by the installation of a fence off area. The process of site preparation also included the construction of a small concrete dam around the manhole where samples were collected from the two outflow pipes in order to prevent infiltration of surface runoff water from the surrounding environment to the runoff from the elevated highway section.

Figure 2: View of the Experimental Site and Manhole.

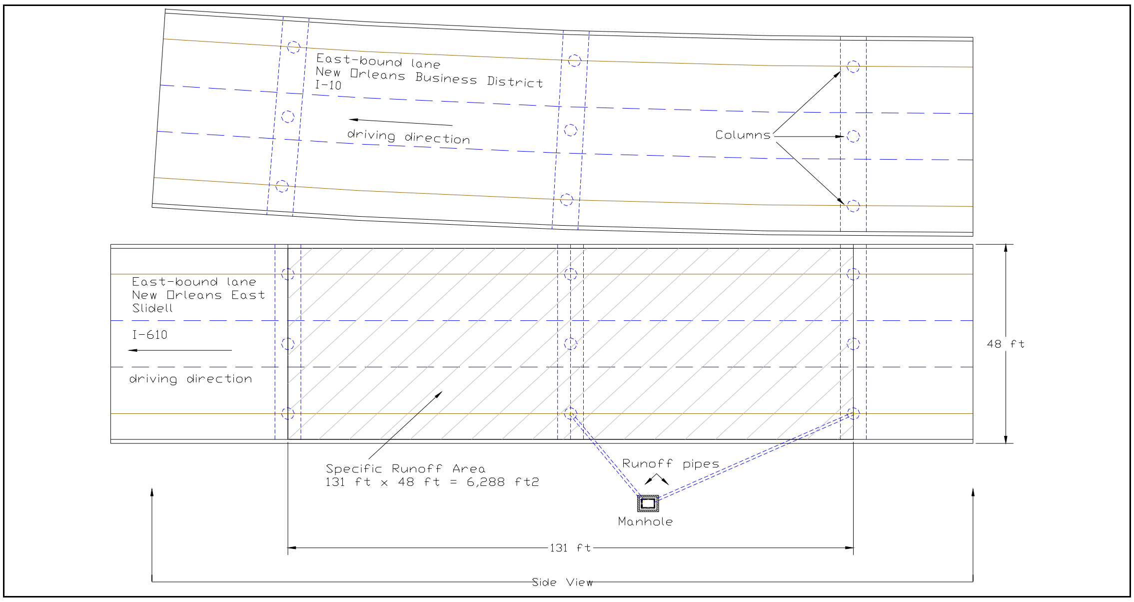


Figure 3: Plan View of the Specific Drainage Area (6,288 ft2) of the Selected Highway Section of Interstate- 610 in Orleans Parish, New Orleans, Louisiana.

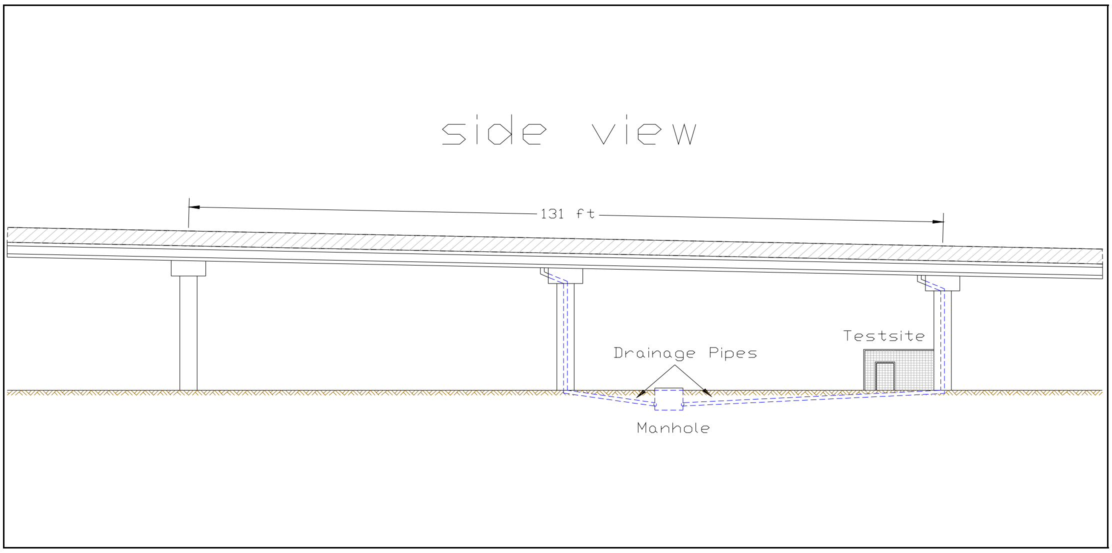


Figure 4: Side View of Section through the Selected I-610 Highway Section at the Experimental Site. [38]

Figure 5: The Experimental Site beneath the East-Bound Lane of the Interstate-610.

Figure 6: Drainpipes in Manhole from which the Highway Runoff is Collected.

4.2. Meteorological Information and Traffic Counts

Meteorological information was a crucial component in this study in order to facilitate the collection of the highway storm water runoff samples at the very beginning of rainfall events. Vehicles potentially represent a major pollutant source in the highway storm water runoff and for that reason traffic counts were performed.

4.3. Sources of Meteorological Information

The sources used to gather meteorological information were local weather forecasts for long-term predictions, the local DOPPLER radar and traffic cams along the interstate I-10 to track the location and progression of the storm events. The latter two were accessible online in the World Wide Web and could be used to track the storms at any desired time with good precision.

The used links are shown below:

http://www.weather.com/weather/local/70122?whatprefs=

http://nola.com/traffic/cams/

http://www.accuweather.com

Since the first flush of every storm event was very important for the research, this meteorological information was of fundamental significance. [38]

4.4. Traffic Counts

Traffic flow characteristics and hydrology are two of the principle variables that significantly affect pollutant loading. Consequently, vehicular counts were performed every 15 minutes, starting immediately upon arrival at the experimental site. The duration of each count was 2 to 4 minutes. In addition to these recordings, another traffic count was carried out, where counts where done hourly for 4 days (2 week days and 2 weekend days), in order to obtain a reasonable average value for the number of vehicles passing this specific highway section. [38]

4.5. Storm Water Runoff Sampling and Flow Measurements

Highway storm water runoff was collected in the storm sewer manhole displayed in Figure 5. Storm water runoff from the highway section was transported to the manhole through 2 drainage pipes. Flow intensity measurements and sampling collection was performed in the above mentioned manhole for both pipes. [38]

4.6. Flow Measurements

The collection of runoff samples was carried out using two 5-gallon-buckets; one for each drainpipe. Both buckets were marked with a liter scale in order to obtain the collection volume and were rinsed out with clean water before every collection. In addition, the collection time was recorded to be able to determine the runoff flow rate. Subsequently, the collected highway runoff from both drainpipes was mixed together for each sample and poured into clean polypropylene sample bottles. Fully labeled 1-liter samples (date, sample number and time at which it was collected) were collected from the time of the first flow of storm water runoff coming out of the drainpipes at the manhole (defined as time 0) to the collection of 10 to 15 runoff samples, or the end of the particular storm event, which ever came first. Depending on the intensity of the storm and the associated runoff flow, samples were collected every two to five minutes. In event periods of very low runoff flows, the collection intervals were increased to obtain sufficient quantities of storm water runoff to perform all planned wet chemistry analyses.

Since flow measurements are essential to calculate mass loading contributions, recordings were carried out throughout the sampling duration of the storm, from the moment of first runoff flow generation (first runoff reaching the manhole through the drainpipes) until the completion of the particular rainfall runoff sample amount (usually between 10 – 15 samples). Volumetric flow rates were noted down with every collected sample by measuring the amount of collected water and the collection time. Storm water runoff from the elevated roadway section was sampled for fourteen storm events throughout the course of the study from which hydrologic and water quality data were collected. [38] However, only samples from 13 runoff events were analyzed for dissolved heavy metals.

4.7. Storm Water Runoff Analyses

Prior to any analytical procedure the collected samples were fully mixed because of the high particulate loadings in almost all runoff samples. This was performed to ensure that measurements taken are representative for the parent samples and to ensure sample homogeneity.

Comprehensive documentation of the recognized Standard Methods, which are referenced as the analytical techniques for each analysis performed, is not restated in this thesis. The author has only listed any deviation from, or specific modifications to the recognized analytical procedures used. The reader is referred to the "APHA Standard Methods for the Examination of Water and Wastewater" if further detailed review of each of these procedures is necessary. [40]

4.7.1. Field Measurements

In addition to the collection of each storm water sample, field data analysis was performed immediately at the experimental site. After the storm water runoff collection, the samples were transported to the environmental engineering laboratory at the University of New Orleans for further analysis. The parameters measured at the test site are listed below:

- Temperature (^{o}C)
- pH (s.u.) (APHA Standard Method 4500- H+B)
- Redox potential (+mv) (APHA Standard Method 2580 B)
- Conductivity (μS/cm) (APHA Standard Method 2510)

All electronic devices were calibrated before and properly cleaned with distillation water after every storm event. A portable Orion 290-A+-meter with a silver/silver chloride (Ag/AgCl) combination electrode was used to measure oxidation/reduction potential, temperature and pH. This silver/silver chloride electrode was used instead of conventional potassium chloride probes because of the interference of heavy metals on measuring Redox potential using conventional combination electrodes.

An YSI Model 85 digital meter was used to measure conductivity and again to measure the temperature to make sure that the values of the two meters were equal in order to have an additional measurement device control. [38]

4.7.2. Laboratory Procedures

This chapter focuses on the different analysis performed in the laboratory after collecting samples. First of all time sensitive analysis will be explained followed by the lab procedure sequence.

4.7.3. Time Sensitiveness and Analysis

After the cessation of the storm water runoff collection and the field analysis, the samples were transported to the environmental engineering laboratory at the University of New Orleans (UNO) for further analysis. Time sensitive data analyses were performed immediately or at most within 12-hours of collection. If it was not possible to perform these analyses immediately, the samples were refrigerated at 5 °C and analyzed within 12 hours of initial sample collection.

All water quality parameters measured were documented in the laboratory notebook. All devices were calibrated prior to determine the samples.

Following analysis are time sensitive and were analyzed as soon as possible.

- Chemical Oxygen Demand (mg/L) (APHA Standard Method 5220-D and Hach Method 8000 (1992))
- Acid preservation of 15-mL aliquot for heavy metal analysis

As soon as the time sensitive laboratory analyses were complete the non-time sensitive laboratory analyses proceeded. These analyses are specifically:

- Total Suspended Solids (mg/L) (APHA Standard Method 2540-D).
- Dissolved heavy metal analysis using an ICP-AES
- Suspended and Dissolved Solids (APHA Standard Methods 2540-D and 2540-E)

All data are logged in analysis specific laboratory notebooks, from which the data was than transferred to electronic files for interpretation. All analyses have been performed in triplicate for statistical verification. A blank and standard has been prepared for each batch of samples. The exact number of blanks will be approximately 5% of the number of samples run as recommended with QA/QC specifications of APHA Standard. Arithmetic means and standard deviations of the triplicates are calculated. [38]

Dissolved Heavy Metal Analysis and Sample Preservation

Metal element portioning between the dissolved and particulate-bonded phases in storm water runoff is a dynamic process. The dissolved phase is defined as metal elements that pass through a 0.45-μm cellulose acetate membrane filter. The dissolved heavy metal analyses were performed partly at the Louisiana State University (LSU) in Baton Rouge. [38] The first step consisted in pre-washing all filters to insure freedom from contamination. The filter device was pre-conditioned by rinsing it with de-ionized water. The dissolved phase filtrate was acid preserved in 15-ml polystyrene flasks to less then pH 2 with trace metal grade HNO_3 in accordance with APHA Standard Methods 3010-B. [40]

Dissolved heavy metal analyses performed in the chemistry department at the University of New Orleans were carried out, using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) - Varian Vista MPX, in accordance with APHA Standard Method 3120-B. [40]

Before starting heavy metal analysis it was necessary to prepare the computer program and to select the elements that had to be analyzed. The task here was to find a wavelength location, where elements had a high energy-intensity and possibly low interference with other elements. Every element was found at a certain wavelength and with certain intensity. Wavelengths for the analyzed heavy metals are shown in Table 3.

Element	Wavelength [nm]	Instrument Detection Limit [mg/L]
Al	396.152	1
As	188.98	3
Cr	267.716	2
Cu	324.754	1
Fe	259.94	1
Mn	257.61	0.4
Ni	231.604	1
Pb	283.305	2
Zn	213.857	1

Table 3: Wavelengths Used for Dissolved Heavy Metal Elements

Subsequently, the instrument had to be calibrated using multi-element standard solutions and a blank to give the device reference conditions. The blank and the standardized concentration were then used to generate a calibration line with energy intensity of the element as a function of its concentration.

After the ICP-OES was calibrated and the elements were selected the argon gas supply and the cooling system were activated. One hour later the test analysis was performed, analyzing samples with known concentrations to verify measuring precision. Furthermore, this test analysis was carried out after every 10 samples to guarantee accuracy of the analyses.

At that point, the instrument was ready for use and samples were analyzed for 10 different metal elements (Al, As, Cu, Cd, Cr, Fe, Mn, Ni, Pb, and Zn). For the dissolved heavy metal analyses, three analyses were performed for every sample and the mean was used as sample concentration to minimize statistical errors. Furthermore, the sample supply tube was rinsed with distilled water after every analysis and a control sample with known concentration was analyzed after every 10 samples. [42]

4.8. Model Developing

This study derived a stochastic water quality model from highways runoff. A linear function of storm antecedent dry time was selected as the pollutant Buildup model. A power function of runoff volume (rating curve) was chosen to simulate storm pollutant transport capacity so that the pollutant washed off by the storms were dependent on pollutant supply and storm transport capacity.

Because the Buildup function depended on storm antecedent dry time which was a random variable and had a storm simulation mechanism, the whole quality model was actually climate-related and a stochastic one although it was based on the concept of deterministic models. It can be seen that the model in this study takes advantage of both deterministic models and statistical models. It includes the important variable storm antecedent dry time which is usually not included in most developed statistical models. It is simple in structure yet easy to calibrate. More importantly, it requires minimum input data. [2] For the sake of simplicity, also due to data limits, a linear Buildup function was chosen in this study. There was no reasonable criterion found to determine which function is the best Buildup formula.

It is easy to see that due to the exponential Washoff model, pollutant accumulation is washed off completely only if runoff approaches infinite. But as described earlier, the US Geology Survey [26] suggested that in areas which had larger mean annual rainfall, the pollutant accumulation may be washed off completely by more frequent storms. On the other hand, in a power formula, pollutant Washoff is only dependent on runoff volumes and independent of pollutant available at the beginning of a storm. Therefore, in this case, there is an infinite supply of pollutant available for Washoff and therefore it only depends on storm sediment transport capacity which is determined by storm runoff volume.

Therefore, the study determined the Washoff as follows:

First, a pollutant transport capacity Y, was computed as a power function of runoff volumes V,

$$Y = a*V^b,$$

where, a, b, = parameter.

Second, pollutant available for Washoff, P, was computed as

$$P = P_0 + C*t,$$

where, P_0 = the pollutant remaining on the highway surface after the last storm,

$C*t$ = the pollutant accumulation during the dry period between storms, computed by the linear buildup model described before.

Last, determine pollutant Washoff:

$$\text{Washoff} = \text{Min}(Y, P),$$

That is to say, if the capacity to transport pollutants was greater than the quantity stored on the surface, all pollutants were removed. Otherwise, the removal was equal to the capacity just computed. [2]

CHAPTER 5.

DISCUSSION OF RESULTS

The goal of this study was to calibrate the selected Washoff and Buildup Model and to try to find out if it could give reasonable results regarding the pollutant transport in storm water runoff from the observed Interstate section. In the following chapter the methods used to develop the models will be explained. This includes the development and calibration of all generated models as well as the comparison of the obtained results. For this research a total of fourteen different storm events were collected and analyzed as described in the Methodology and precipitation records of the last 35 years were used.

5.1. Calibration of the Buildup/Washoff Model

5.1.1. Calculation of Runoff from Rainfall Records

In this study daily rainfall records of the International Airport of New Orleans from 1968 to 2003 were used to calculate runoff and duration of the single storm events. A direct linear relationship between precipitation P and runoff V were assumed. By using linear regression between the values of precipitation and runoff of the collected storms a value of 4024.8 l/in for the parameter Λ was obtained.

The computer program uses the formula $V = \Lambda \cdot P$ to determine the values for the storm events.

5.1.2. Storm Parameters and Runoff Processes

Pollutants are carried by runoff into receiving water bodies. It is known that not all storms produce runoff. Thus, in this study, storm events were defined as those producing runoff. Figure 7 illustrates the transformation of rainfall records into storm events. [2] The upper part shows the measured rainfall over time and the lower part the created single storm events and their distribution over time. Only those events that had intensity higher then the limit value and therefore could produce runoff are considered. Storms are defined by V_s which is computed by the sum of the rain volume and uniformly distributed over the duration of the rainfall, t_s the time since the last storm, which also needs to be greater than the time limit of one day to consider the rainfall a storm event, and the duration of the storm $D_{s.}$

Considering the continuity of pollutants buildup during the runoff phase, this study defined antecedent dry time T_s involved in the buildup model as the time period between the midpoints of the successive storms instead of the time period from the end of the last storm to the beginning of the next storm, t_s. The parameter t_s makes storm separate.

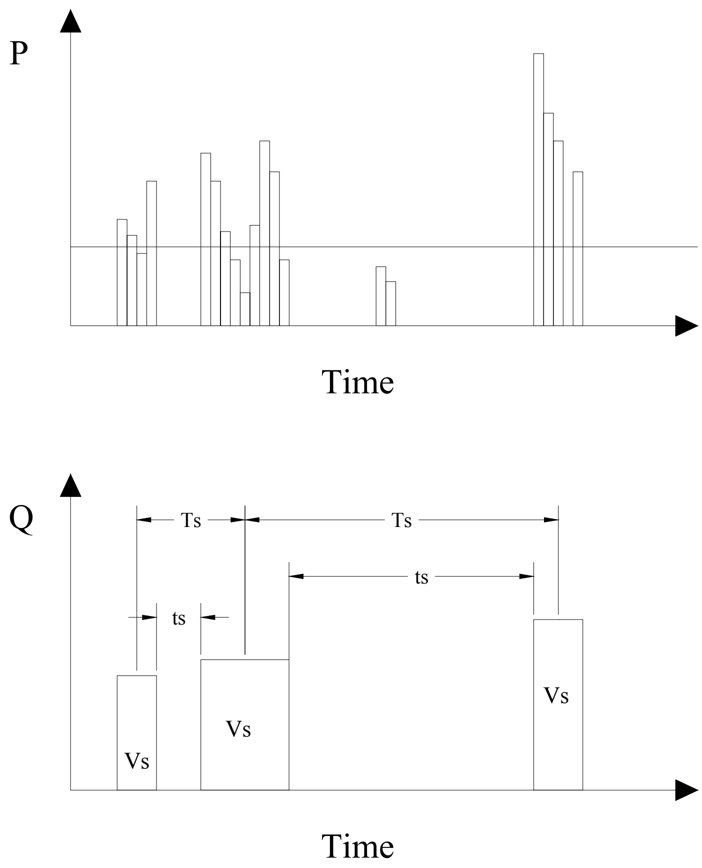


Figure 7: Transformation of Rainfall Records to Storm Events [2]

5.1.3. Estimating Parameters of Pollutant Transport Capacity (Washoff)

As described previously the stochastic Buildup/Washoff model came from deterministic models. So far, all parameters in a deterministic water quality model are calibrated simultaneously by using trial and error methods. [44] [45] Such methods require continuously measured water quality data which is usually not available at the planning level. This study first calibrated the power function of storm pollutant transport capacity, and then estimates the accumulation parameter from the calibrated transport capacity function and runoff events. There are two parameters "a" and "b" in the transport capacity model $Y = a*V^b$. Theoretically, the parameters "a" and "b'' should be estimated by those storms during which pollutant Washoff is equal to their transport capacity. In practice, we should chose those storms whose runoff volumes are much smaller than the average and that have the antecedent dry periods of time much longer than the average. In this study, since the measured data were few, all storms (Table 4) were used to estimate the parameters. Dissolved iron was selected to investigate the adequacy of the Buildup/Washoff Model for elevated highways. Therefore samples of 14 storm events from the last 3 years were collected at the earlier described test site, and used to calibrate the model. Iron gave the most stable results for the Washoff model compared to other metals.

Date of Event	Total Flow V [l]	Fe [mg]
3/25/01	1408	256.94
3/28/01	431	120.84
4/24/01	14240	3214.49
7/2/01	1779	1015.31
7/4/01	4618	1394.84
10/10/01	80	8.69
11/22/01	491	33.16
2/1/02	354	32.17
3/1/02	626	1146.69
4/8/02	9844	6462.89
11/18/03	7527	1986.77
2/10/04	909	266.48
4/6/04	456	120.80

Table 4: Runoff and Dissolved Iron Loading Data from the Colleted Storm Events

Figure 8 demonstrate that there is a good linear relationship between log-transformed measured runoff volumes and dissolved iron Washoff.

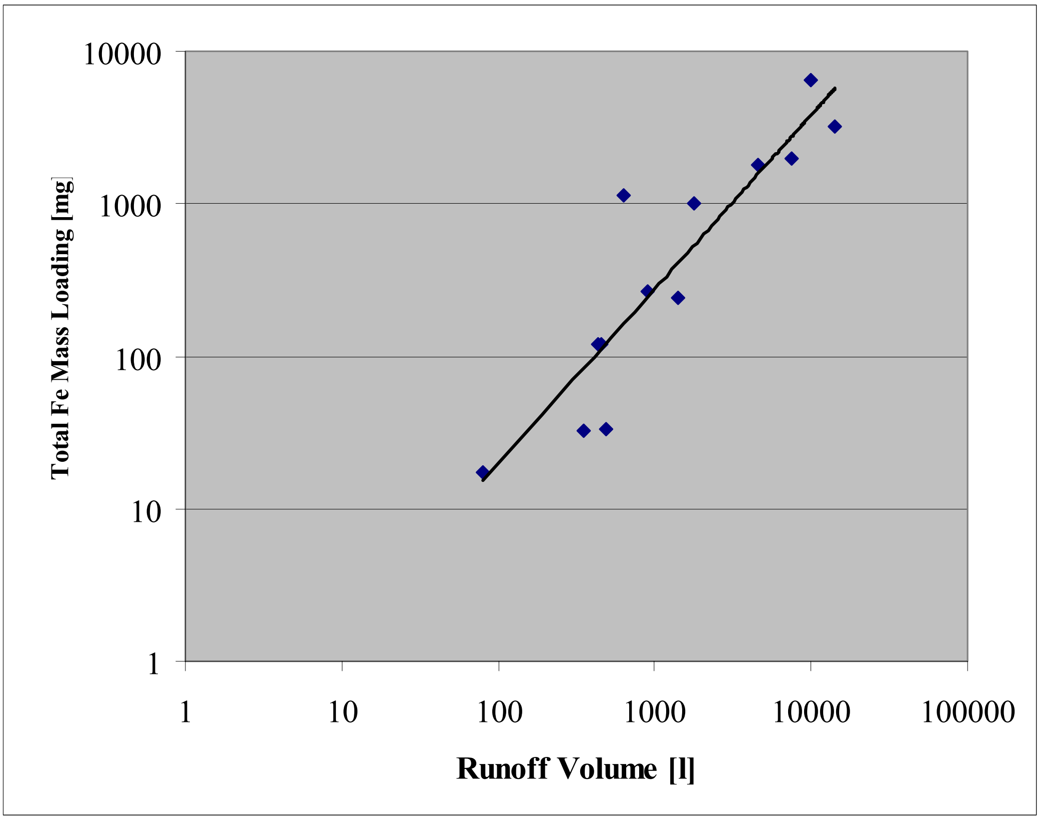


Figure 8: Relationship between Runoff Quantity and Quality

The obtained calibration values for the Washoff model are listed in Table 5

a	0.1028
b	0.8212

Table 5: Parameters for the Washoff Model

This gave a final Washoff model of

$$Y \quad = 0.1028 * V^{0.8212}$$

5.1.4. Calibration of the Buildup Model

The parameter "C", the Buildup coefficient or Buildup Rate, in the model may be estimated by selecting those storm events whose last previous storm has runoff much larger than the average and that have an antecedent dry period of time much shorter than the average. But in practice it is difficult to get sufficient measured data to meet such requirements. Nevertheless, we could estimate the Buildup Rate by means of the calibrated Washoff function, which is described below.

First of all, to estimate the Buildup coefficient, the assumption is made that there exists an interval, in the time domain on which the pollutant Buildup equals the pollutant Washoff. It is assumed that the excess buildup on the surface after the last storm event of the time interval is equal to the amount after the first storm. Then, after a Buildup Rate (maximum Buildup Rate) is assumed, the Buildup function and storm transport capacity model are applied simultaneously to each storm within the interval to determine and sum the amount of the pollutant washed off by the storm. Last, since it is assumed that pollutant Washoff equals to buildup, the summed Washoff is apportioned over the entire interval to obtain a new buildup coefficient. This iterative process is continued until the buildup coefficient remains unchanged before and after iteration.

The initial buildup coefficient was obtained by determining the maximum amount of pollutant that could be washed off in the interval. This amount was computed by applying the washoff function to each storm occurring in the interval, assuming that the Washoff was not limited by pollutant supply for any of the storms. The sum of the pollutant washed off by all the storms within the interval was then linearly apportioned on the interval. [2]

The above assumption implicates that there are two cases. In case 1 the excess pollutant Buildup after the first storm is zero in case 2 the excess is not equal. Previously done studies [2] lead to the observation that only the second case provides reasonable results and in addition for the first case the trial and error iteration process could be unstable, because during the calculation the pollutant amount on the surface can be computed to be negative, and therefore no result can be obtained. The maximum Buildup coefficient was used in the first iteration. In the second step the excess Buildup at the end of the first iteration was used, and so on for the next iterations, until the variation of pollutant excess Buildup at the beginning and the end was less then 0.0001 μg/day.

5.1.5. <u>Buildup Rate C</u>

The procedure to determine the buildup coefficient or Buildup Rate C was used for different time intervals. The total data record was divided into intervals of one calendar year, one seasonal year (from May to April), two years, and five years. The results are listed in Table 6.

Time Interval	No. of Divisions	Estimated Buildup Rate C [μg/d] (Average)	Standard Deviation of C
5 Years	7	15.05	2.07
2 Years	18	12.13	3.06
1 Year	36	11.40	3.41
Seasonal Year	36	12.13	4.94

Table 6: Buildup Rate Based on Different Time Intervals

In this study, the averaged Buildup Rates determined using the interval of two calendar years were selected as the final estimates of the Buildup Rate of dissolved iron in storm water runoff. The results of the calibration are summarized in Table 7.

Parameter	Value	
Λ	4024.8	[l/in]
a	0.1028	[ ]
b	0.8212	[ ]
C	12.13	μg/d

Table 7: Estimated Parameters of the Stochastic Model

In the following Figures 9 to 12 the development of the Buildup Rate over time for the different time intervals are shown. No linear regression relationship between C and time could be observed.

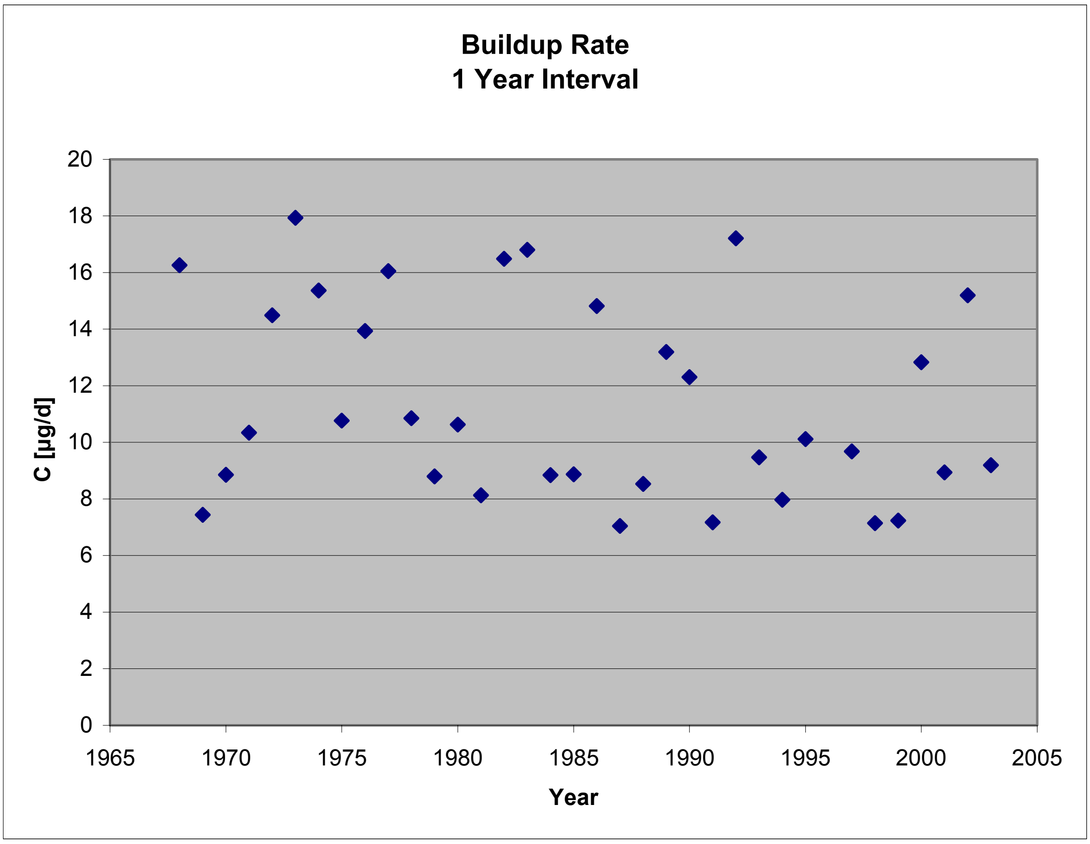


Figure 9: Buildup Rate Based on 1 Calendar Year Time Intervals

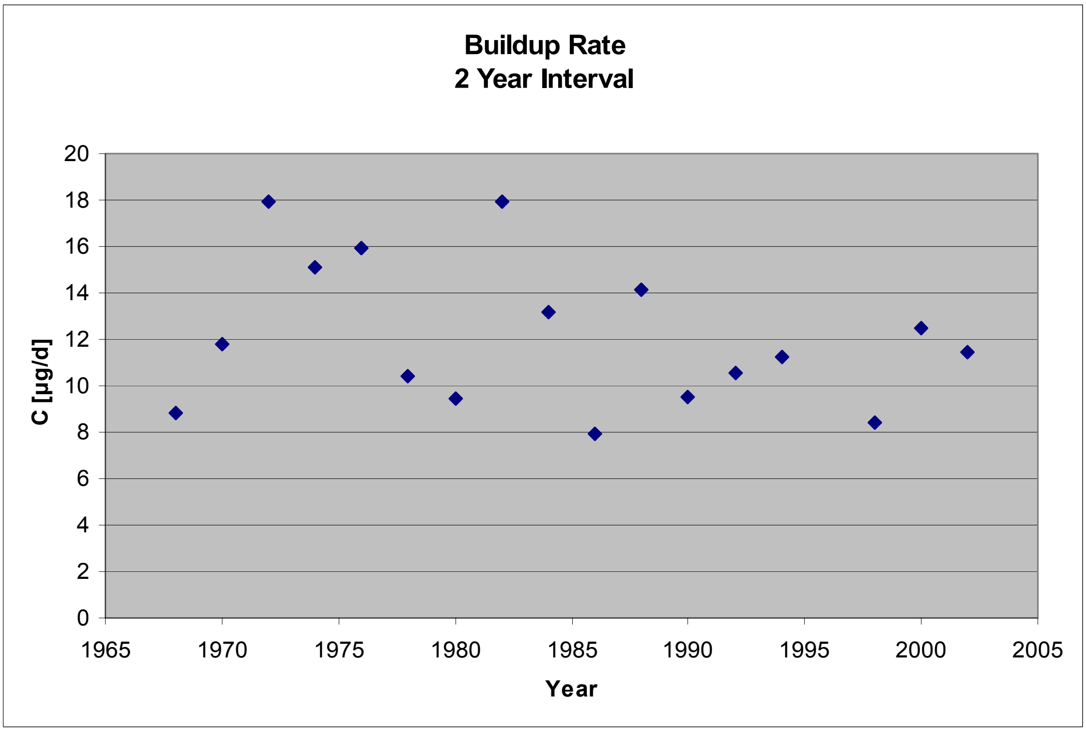


Figure 10: Buildup Rate Based on 2 Years Time Intervals

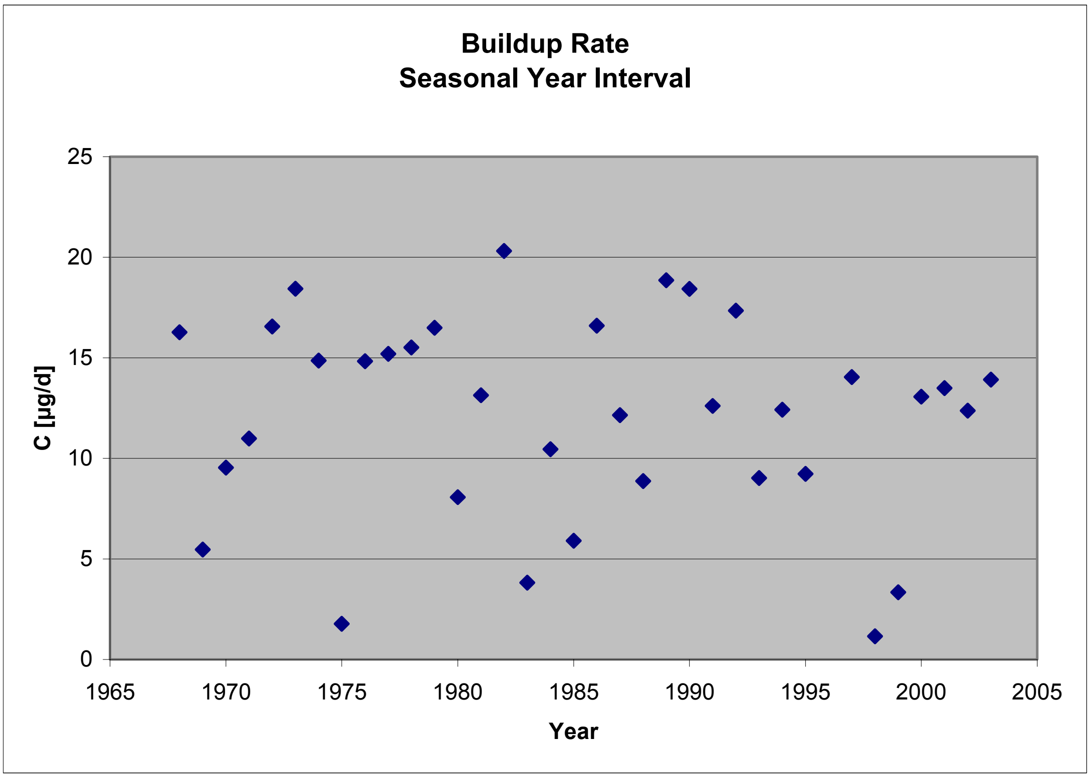


Figure 11: Buildup Rate Based on Seasonal Year Time Intervals

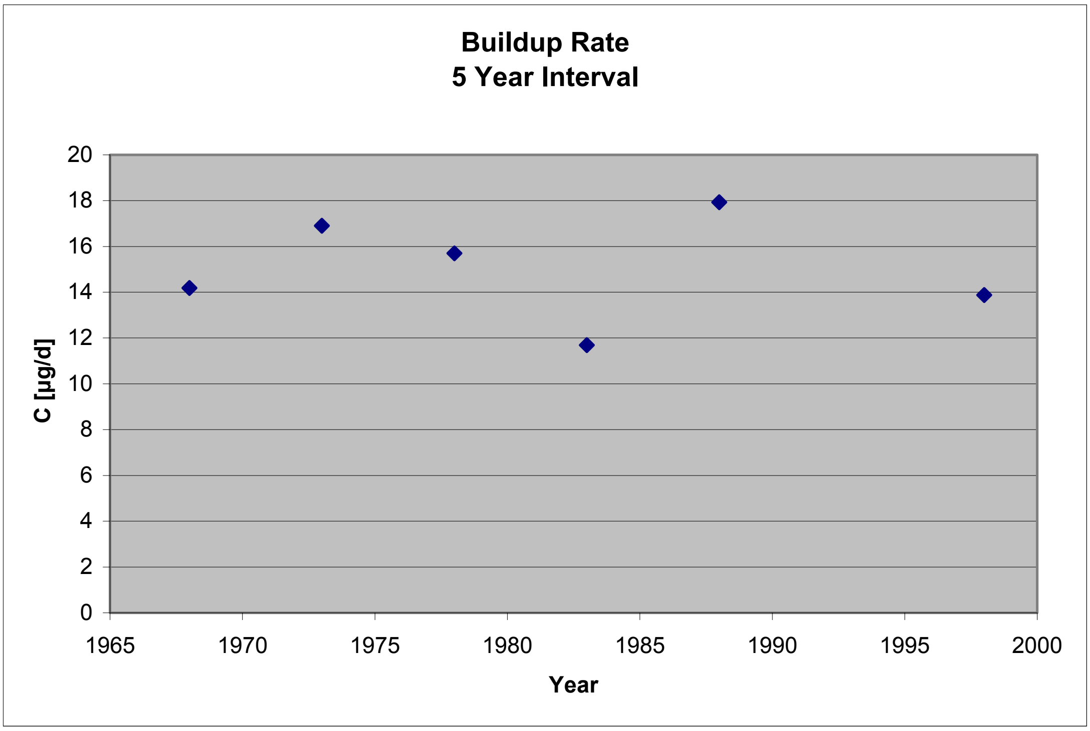


Figure 12: Buildup Rate Based on 5 Years Time Intervals

5.2. Analysis of Results

5.2.1. Characteristics of the Estimated Buildup Rate

Table 7 through 11 and Figures 9 through 12 do not show a significant increase or decrease of the Buildup Rate over time. All results demonstrate that the obtained Buildup Rate C will differ if estimated over different time intervals. If averaged the Buildup Rate over the entire studied time period from1968 to 2003 the results listed in Table 11 are obtained. Table 11 shows that as the length of the interval decreases, the average Buildup Rate for dissolved iron also decreases. It could be found that too short or too long intervals are not suitable for calibrating the buildup model. This is reasonable because of the assumption and of the sensibility of the linear model to outliers of storm antecedent dry time on a calibration time interval.

Therefore, based on the results listed in Table 8 the most appropriated length of the interval is two calendar years with results in 18 divisions of the 36 studied years. The five year calibration interval could not be considered reliable, because only six calibrations could be computed. Compared to the calendar and seasonal year interval the two year interval gave more stable and reliable results and therefore was selected as finally used calibration time period. Considering the heterogeneity of storm distribution in each year, the average of the estimated Buildup Rate C on the optimal time interval could be taken as final result of the model calibration.

C = 12.13 μg/day Buildup Rate for dissolved iron

Looking at the way in which pollutant Buildup Rates were estimated based on non-zero excess Buildup after the first storm on an interval it will be noticed that the maximum Buildup C_0 coefficient was used in the first iteration. It was still assumed that the dissolved iron available after the first storm was zero in the first iteration, and then the excess buildup at the end of the last storm C_1 in the calibration interval was used in the second iteration. Table

8 through 11 shows how the corrections were applied and the final value of C_2 was found. K_1 is the number of storms in the calibration interval that were not supply limited and the Washoff depended only from the transport capacity of the runoff Y. K_2 is the number of storms that were supply limited and therefore a complete Washoff of the accumulated pollutant on the surface took place. In Tables 8 to11 to 10 P_1 expresses the reduction in % from the maximal Buildup Rate C_0 to the final result C_2. It indicates the improved accuracy of the model in relation to the rating curve method. The reduction of the Builup Rate is a consequence of the limited pollutant supply. P_2 expresses the percentage of storms that were supply limited related to the total number of storm events in the calibration interval. Therefore a high value for P_2 is related to a high value for P_1.

Year	C_0 [μg/d]	C_1 [μg/d]	C_2 [μg/d]	K_1 [ ]	K_2 [ ]	P_1 [%] $(C_0-C_2) / C_2$	P_2 [%] $K_2 / (K_1+K_2)$
1968	16.5470	16.2891	16.2613	60	4	1.8	6.3
1969	12.7308	10.9799	7.4403	35	26	71.1	42.6
1970	12.1807	11.6846	8.8520	36	22	37.6	37.9
1971	13.4603	12.6873	10.3363	44	12	30.2	21.4
1972	16.5633	15.2320	14.4931	46	16	14.3	25.8
1973	19.5433	18.8966	17.9307	58	10	9.0	14.7
1974	17.3999	16.9006	15.3661	48	14	13.2	22.6
1975	17.5217	16.4313	10.7666	38	22	62.7	36.7
1976	15.7426	15.0457	13.9345	50	10	13.0	16.7
1977	16.1334	16.0781	16.0526	51	3	0.5	5.6
1978	17.3521	15.3193	10.8510	40	21	59.9	34.4
1979	14.9973	13.3136	8.7968	31	23	70.5	42.6
1980	16.1408	13.4838	10.6298	37	16	51.8	30.2
1981	12.7876	11.4501	8.1294	46	17	57.3	27.0
1982	19.0086	18.0202	16.4864	42	16	15.3	27.6
1983	18.6185	17.3453	16.8049	52	7	10.8	11.9
1984	12.5916	11.5758	8.8402	34	21	42.4	38.2
1985	15.1760	14.4089	8.8708	36	28	71.1	43.8
1986	15.1603	15.0282	14.8164	52	8	2.3	13.3
1987	13.8731	11.4378	7.0446	28	28	96.9	50.0
1988	18.3390	15.0294	8.5331	32	25	114.9	43.9
1989	14.7986	14.7685	13.1918	53	6	12.2	10.2
1990	16.6564	14.3302	12.3067	46	16	35.3	25.8
1991	22.0741	17.9735	7.1754	17	40	207.6	70.2
1992	18.3353	17.4032	17.2097	56	7	6.5	11.1
1993	12.9122	11.4730	9.4661	39	23	36.4	37.1
1994	12.3089	11.1221	7.9730	31	21	54.4	40.4
1995	14.7135	12.4459	10.1121	45	15	45.5	25.0
1997	12.7389	11.4359	9.6793	44	18	31.6	29.0
1998	16.1794	13.9943	7.1478	21	22	126.4	51.2
1999	11.2059	10.4717	7.2369	40	19	54.8	32.2
2000	12.8408	12.8169	12.8282	48	2	0.1	4.0
2001	15.2740	14.2310	8.9365	27	29	70.9	51.8
2002	15.2329	15.2251	15.1997	57	4	0.2	6.6
2003	15.2160	13.9012	9.1922	36	22	65.5	37.9

Table 8: Statistical Results of the Iterating the Buildup Coefficient on Calendar Year Intervals

Year	C_0 [μg/d]	C_1 [μg/d]	C_2 [μg/d]	K_1 [ ]	K_2 [ ]	P_1 [%] $(C_0-C_2) / C_2$	P_2 [%] $K_2 / (K_1+K_2)$
1968	14.6415	13.8331	8.8284	79	46	65.8	36.8
1970	12.8214	12.7000	11.8038	103	11	8.6	9.6
1972	18.0391	17.9375	17.9244	117	13	0.6	10.0
1974	17.4621	17.3370	15.0741	96	26	15.8	21.3
1976	15.9369	15.9046	15.9066	107	7	0.2	6.1
1978	16.1844	14.9306	10.4079	77	38	55.5	33.0
1980	14.4390	12.8971	9.4158	83	33	53.3	28.4
1982	18.8152	18.5231	17.9179	104	13	5.0	11.1
1984	13.8679	13.8399	13.1575	109	10	5.4	8.4
1986	14.5009	13.4227	7.9213	57	59	83.1	50.9
1988	16.5712	15.0204	14.1622	101	15	17.0	12.9
1990	19.3279	18.2134	9.5176	60	59	103.1	49.6
1992	15.6201	14.6449	10.5629	78	47	47.9	37.6
1994	13.5063	12.9791	11.2519	93	19	20.0	17.0
1998	13.7235	11.9354	8.4218	69	33	63.0	32.4
2000	14.1535	14.0191	12.5072	91	15	13.2	14.2
2002	15.2245	14.8956	11.4168	89	30	33.4	25.2

Table 9: Statistical Results of the Iterating the Buildup Coefficient on 2 Years Intervals

Year	C_0 [μg/d]	C_1 [μg/d]	C_2 [μg/d]	K_1 [ ]	K_2 [ ]	P_1 [%] $(C_0-C_2) / C_2$	P_2 [%] $K_2 / (K_1+K_2)$
1968	16.4683	16.3518	16.2698	59	6	1.2	9.2
1969	11.0749	9.6235	5.4635	25	32	102.7	56.1
1970	12.0157	10.8670	9.5388	42	17	26.0	28.8
1971	16.2950	15.9499	10.9903	37	26	48.3	41.3
1972	16.9676	16.5456	16.5521	58	3	2.5	4.9
1973	18.5261	18.4781	18.4367	56	6	0.5	9.7
1974	15.5394	15.1602	14.8613	55	10	4.6	15.4
1975	16.1060	12.5028	1.7740	4	52	807.9	92.9
1976	15.1136	14.8639	14.8283	59	3	1.9	4.8
1977	18.0281	15.8866	15.2002	51	11	18.6	17.7
1978	16.8579	16.6310	15.5136	48	5	8.7	9.4
1979	17.1356	16.5653	16.4945	57	2	3.9	3.4
1980	11.5977	10.7437	8.0745	37	13	43.6	26.0
1981	15.7497	14.3587	13.1387	52	10	19.9	16.1
1982	20.6729	20.4520	20.3163	51	6	1.8	10.5
1983	14.9476	14.3146	3.8219	12	47	291.1	79.7
1984	13.9730	13.1920	10.4554	42	17	33.6	28.8
1985	12.5571	10.9377	5.9013	30	26	112.8	46.4
1986	18.0645	16.9196	16.5943	57	9	8.9	13.6
1987	16.7047	16.5903	12.1468	43	11	37.5	20.4
1988	12.5695	10.4381	8.8769	42	14	41.6	25.0
1989	19.0286	18.9778	18.8553	62	5	0.9	7.5
1990	18.8848	18.4850	18.4283	50	4	2.5	7.4
1991	18.7624	15.8480	12.6106	41	19	48.8	31.7
1992	17.5173	17.4821	17.3445	61	4	1.0	6.2
1993	10.3408	9.4036	9.0230	49	9	14.6	15.5
1994	14.6887	13.3144	12.4148	42	15	18.3	26.3
1995	12.6636	10.1793	9.2340	48	9	37.1	15.8
1997	14.3800	14.3558	14.0444	47	6	2.4	11.3
1998	12.1835	9.6660	1.1495	6	40	959.9	87.0
1999	10.9066	9.0816	3.3478	25	32	225.8	56.1
2000	14.0739	13.2789	13.0691	52	2	7.7	3.7
2001	16.9550	15.1724	13.4956	44	12	25.6	21.4
2002	14.2193	13.5125	12.3721	54	8	14.9	12.9

Table 10: Statistical Results of the Iterating the Buildup Coefficient on Seasonal Year Intervals

Year	C_0 [μg/d]	C_1 [μg/d]	C_2 [μg/d]	K_1 [ ]	K_2 [ ]	P_1 [%] $(C_0-C_2) / C_2$	P_2 [%] $K_2 / (K_1+K_2)$
1968	14.3050	14.2220	14.1852	280	21	0.8	7.0
1973	17.2656	17.1094	16.9019	283	21	2.2	6.9
1978	16.0517	15.8700	15.6980	275	14	2.3	4.8
1983	15.0608	14.8032	11.6841	214	80	28.9	27.2
1988	18.0248	17.9349	17.9302	289	9	0.5	3.0
1998	14.1972	13.9262	13.8802	258	11	2.3	4.1

Table 11: Statistical Results of the Iterating the Buildup Coefficient on 5 Years Intervals

		P1 [%] $(C_0-C_2) / C_2$	P2 [%] $K_2 / (K_1+K_2)$
Annual	Average	45.0	29.0
	Maximum	207.6	70.2
Seasonal	Average	87.6	25.4
	Maximum	959.9	92.9
2 Years	Average	**34.8**	**23.8**
	Maximum	103.1	50.9
5 Years	Average	6.2	8.8
	Maximum	28.9	27.2

Table 12: Statistical Results of the Improved Accuracy by the Stochastic Model

5.2.2. Advantages of the Stochastic Model

As noted in previous sections of this study in many cases, the rating curve method in the form of $Y = a \cdot V^b$ does not estimate the pollutant load washed- off, but it simulates the pollutant transport capacity of the storm water runoff. If it is used to predict pollutant load in wet areas as Southeast Louisiana with frequent storms it certainly overestimates the actual values. The stochastic model in this study uses the concept that combines the build-up and wash-off at the same time. The pollutant load in runoff for each storm is either limited by the transport capacity Y, or the available pollutant previously accumulated during the dry period on the surface of the highway. Compared to the results of the rating curve only (C_0) the used combined method (C_2) the pollutant Buildup Rate decreases significantly. The improved accuracy of the stochastic model in estimating storm water runoff quality is represented in Table 8- 11, where the two parameters C_0 and C_2 are compared and the reduction is expressed in the form of

$$P_1 = (C_0 - C_2) / C_2.$$

P_2 expresses the fraction of storms which are supply limited in relation to the total number of storms and is a parameter for the increased accuracy achieved by the combined method.

$$P_2 = K_2 / (K_1 + K_2).$$

Based on the results of Table 12 the rating curve overestimates the pollutant loads in runoff about 35% for the final result for the calibration interval of two years. Table 12 also shows that those storms accounted for a proportion of total storms of about 24 % on the average over the 35 years. The principal error might come from the parameters "a" and "b" which were estimated by all collected storm events instead of those with the pollutant wash-off really to their transport capacity, which made C_0 and K_2 smaller than their true values. Another error source may be the estimation of runoff volume by using the linear regression model $V = \Lambda \cdot P$. Using this model there is no distinction between summer and winter storms which differ in their characterization: Short and strong precipitation during spring and summer and more continuous but less intense rainfall in fall and winter. This factor of course influences significantly their pollutant transport capacity.

As mentioned in Chapter 3, statistical models are often developed by establishing regression equations. Because of data limits, some important explanatory parameters, such us antecedent dry time are not always statistically significant. In fact, R. Erlacher [38] compounded various statistical models based on the same measured water quantity and quality data as used in this study in witch the antecedent dry time did not result statistical significant.

CHAPTER 6

CONCLUSION AND RECOMANDATIONS

Models that can predict the pollutant transported by storm water runoff from urban watersheds and especially from highways are important tools of urban storm water quality management, planning and decision processes. The models can be divided in two major groups: deterministic and statistical/stochastic ones. Statistical models consist of equations, which were computed by regression. In many cases, because of data limits, some logical parameters as land use and precedent dry days do not always result statistical significant.

The Buildup/Washoff formulation used in this study is a common method to calibrate a deterministic pollutant discharge model. The linear function of antecedent dry time was selected to simulate the pollutant build up during dry periods between storm events. For the storm pollutant transportation capacity Y the power curve of the total runoff volume was chosen and the parameters "a" and "b" were calculated by regression and the final numeric result for the formula $Y = a \cdot V^b$ was $Y = 0.1028 \cdot V^{0.8212}$. The pollutant Washoff therefore was both dependent on pollutant supply, as well as storm transport capacity and both factors were connected. Storm antecedent dry days in the linear buildup function was a randomly distributed parameter. The model of this study consequently became a climate – related and a stochastic one, even if it was developed on the concept of deterministic models.

The stochastic model was calibrated by using data collected from a highway section situated at the split of I-10 and I-610 west of New Orleans, Louisiana, over the last three year period. A total of fourteen storm events were collected. The precipitation data were obtained from the International Airport of New Orleans. The calibration of the buildup model was based on the assumption that after a certain time period the excess buildup after the last storm event of the interval is equivalent to the pollutant amount at the beginning. The two concepts, the pollutant transport capacity (rating curve) and the linear pollutant buildup were applied simultaneously to each storm within the interval to find the Buildup Rate C. The iteration was continued until the results were stable and the difference between the last both results were less than the predetermined limit of 0.0001. µg/day. The assumption indicated that the excess buildup after the last storm event was equal to that after the first storm, so there were two cases in which the excess may or may not be zero. For this study only the second case was studied. Previously conducted studies concluded that only for this possibility stable results can be obtained. [2] In the first case during the calculation the pollutant amount accumulated on the surface can be computed to be negative, and therefore no reasonable and stable results for the iteration process could be obtained, otherwise the pollutant amount resulted to be negative.

The goal of this study was to calibrate the selected Buildup/Washoff Model and to try to find out if it could give reasonable results regarding the pollutant transport in storm water runoff from the observed Interstate section. There could get stable results for the two years time interval. An average Buildup Rate of 12.13 µg/d of dissolved iron was obtained as final result. Moreover it could be seen that the Buildup Rate C is equal to the Washoff. Although the used model was calibrated by few measured data and based on some simple assumptions, the analysis gave reasonable result. The analysis proved that if only the rating curve only (no pollutant supply limit) was used the estimated pollutant Washoff of the storms would be overestimated by over 30 % on average and for some single calibration intervals of more than 100%.

The model in this study takes advantages of both deterministic and statistical models. It includes some important variables, like storm antecedent dry time, and for other urban watersheds important parameter as land use can be implemented, which is usually not possible in the most statistical models. It is simple in structure and easy to calibrate, furthermore only a minimum on input data is required to obtain reasonable results. This is an important advantage, because for most urban areas only limited data is available on storm water runoff quality and quantity are available.

Therefore the model of this study can be used to understand the long term behavior of pollutant discharge in storm water runoff from highways and its impact on the environment. This improved understanding should become an important tool in the planning process of infrastructures. The impact of various land uses and climate changes and other factors can be evaluated and there impact estimated by varying the parameters a, b, C and Λ. For changed circumstances and planed infrastructures the environmental impact can be simulated, and this simulation can help taking responsible decisions. A climate change can be taking in consideration by using new data and recalculating Λ. New land use and a higher traffic level can be simulated by varying the parameters a and b. Also changes in car technology i.e. new tire materials, different tire construction and new brake disk materials can also be considered by using new storm water runoff quality data.

Furthermore it is possible to improve the accuracy and reliability of the model by using more detailed data for the calibration. For example hourly precipitation records could be used if available, for the Buildup model, and for the calibration of the Washoff model only storms events that are not supply limited, with a high antecedent dry time, should be used. Testing different calibration intervals and testing different minimum time intervals between storm events could also be used to improve the accuracy of the model.

Because of its simple use and relative high reliability it can become more used in the planning of infrastructure and land use in urban areas.

BIBLIOGRAPHY

[1] Anonymous, 1986, Meeting the Challenge of Non- Point Source Control, Journal of Water Pollution Control Federation 58, 730- 740.

[2] Mo, X., 1993, A Stochastic Water Quality Model for Urban Watersheds, Thesis Study, University of New Orleans

[3] Huber, W.C., Dickinson R.E., 1988, Storm Water Management Model, Version 4, EPA, Athens, GA

[4] Marsalek, J., 1991, Pollutant Loads in Urban Stormwater: Review of Methods for Planning- Level Estimate, Water Resources Bulletin, 27, 283- 291

[5] Huber, W.C., 1986, "Deterministic Modeling of Urban Runoff Quality", Proceedings of the NATO Workshop on Urban Runoff Pollution, Springer- Verlag, Heidelberg, FRG,277-304

[6] U.S. EPA, Office of Water, June 1996, "Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion", EPA 823-B-96-007, http://www.epa.gov/ostwater/guidance.pdf, 11.05.2003

[7] Viessman, W, Hammer, M.J., 1998, "Water Supply and Pollution Control", 6th Edition, Addison Wesley Longman Inc., Menlo Park, California, USA.

[8] U.S. EPA, "Introduction to the Clean Water Act", http://www.epa.gov/watertrain/cwa/, 11.05.03

[9] U.S. EPA, December 8, 1999, "NPDES – Regulations for Revision of the Water Pollution Control Program Addressing Storm Water Discharges; Final Rule", Report to Congress on the Phase II Storm Water Regulations, 40 CFR Parts 9, 122, 123, and 124

[10] U.S. EPA, Office of Water, January 2000, “Storm Water Phase II Final Rule”, EPA 833-F-00-001, www.epa.gov/npdes/pubs/fact1-0.pdf, 07.25.2002

[11] U.S. EPA, 1995, “Wet Weather Discharges”, NPDES, http://cfpub.epa.gov/npdes/wetweather.cfm, 11.05.2003

[12] U.S. EPA, “Glossary”, http://www.epa.gov/watertrain/cwa/glossary.htm#wqs 11.13.03

[13] U.S. EPA, “What is Non-Point Source Pollution? Questions and Answers”, NPDES, http://www.epa.gov/owow/nps/qa.html, 07.30.2002

[14] Schöpf, R., August 2002, “BOD – COD Relationship”, Master’s Thesis, University of New Orleans, New Orleans, Louisiana

[15] Department of Environmental Resources, “Guidance for post-construction highway runoff management: Storm water pollution”, North Central Texas Council of Governments, http://www.highwaybmp.dfwinfo.com/Sections/SecII.html. 11.10.03

[16] U.S. EPA, Office of Water, August 1995, “Controlling Non-Point Source Pollution from Roads, Highways and Bridges”, EPA 841-F-95-008a, http://www.epa.gov/owow/nps/roads.html, 12.04.2003

[17] U.S. EPA, April 1996 “Appendix: B: Effluent Guidelines and Standards”, NPDES Permit Writer's Manual, http://www.epa.gov/npdes/pubs/chapt_05.pdf : technology based, 04.23.2002

[18] U.S. EPA, 2003, “Water Quality-Based Permitting”, http://yosemite.epa.gov/R10/water.nsf/ , 11.14.2003

[19] U.S. EPA, 2003, “Interim Permitting Approach for Water Quality-Based Effluent Limitations in Storm Water Permits”, http://www.epa.gov/fedrgstr/EPA-WATER/1996/August/Day-26/pr-21017DIR/pr-21017.html, 11.11.2003

[20] U.S. EPA, 2003, “Water Quality-Based Effluent Limits”, www.epa.gov/npdes/pubs/chapt_06.pdf , 11.11.2003

[21] Chad Cristina, EI , Jarrod Tramonte, EI , John J. Sansalone, Ph.D., P.E. "A GRANULOMETRY-BASED SELECTION METHODOLOGY FOR SEPARATION OFTRAFFIC-GENERATED PARTICLES IN URBAN HIGHWAY SNOWMELT RUNOFF", Louisiana State University Department of Civil and Environmental Engineering

[22] U.S. EPA, 1999, "Description and Performance of Storm Water Best Management Practices", Urban Storm Water BMP Study, EPA-821-R-99-012, Part C, http://www.epa.gov/OST/stormwater, 05.12.2002

[23] Hemain, J. C., 1986, Statistically-Based Modeling of Urban Runoff Quality: State of the Art, Proceedings of the NATO Workshop on Urban Runoff Pollution, Springer-Verlag, Heidelberg, FRG,277-304

[24] Servat, E. 1985, TSS, BOD_5, COD Accumulation and Transport over Urban Catchment Surface: A Modeling Approach, NATO Workshop on Urban Runoff Pollution, Montpellier, August 25-30, France

[25] Van der Heijden R., L. Lijklema, R.H. Aalderink, 1985, A Statistical Methodology for the Assessment of Water Quality Effects of Storm Water Discharges, NATO Workshop on Urban Runoff Pollution, Montpellier, August 25-30, France

[26] Driver, N. E. and B. M. Troutman, 1989, Regression Models for estimating Urban Storm Runoff Quality and Quantity in the United States, Journal of Hydrology, 109, 221- 236

[27] Ammon, D.C.,1979, Urban Stormwater Pollutant Buildup and Washoff Relationships, Master of Engineering Thesis, University of Florida, Gainesville

[28] Nakamura, E., 1984, Factors Affecting the removal Rate of Street Surface Contaminants by Overland Flow, Journal of Research, Public Works Research Institute, Ministry of Construction, Japan

[29] Jewell, T.K., 1982, Improved Techniques for Modeling Stormwater Quality, Second International Conference on Urban Storm Drainage, June 14-19, Urban, Illinois USA, 156-165

[30] Singh, V.P. and V.J. Chen, 1982, On the Relationship between Sediment Yield and Runoff Volume, in Singh, V.P (Ed.), Modeling Components of Hydraulic Cycle, Water Resources Publications, Littleton, CO, 555-579

[31] Wegener, K.R., 1982, Selection of Parametric Stormwater Pollutant Loading Models Using Predictive Reliability Analysis, Thesis, Louisiana State University

[32] Diniz, E.V., 1979, Water Quality Prediction for Urban Runoff – an alternative Approach, Proceedings, SWMM User's Group Meeting, U.S. EPA, Washington, D.C., 112

[33] Water Quality Group, "Heavy Metals in Watersheds", North Carolina State University, http://h2osparc.wq.ncsu.edu/info/hmetals.html, 11.13.2003

[34] Chemical Elements, Yinin Bentor, "An Online, Interactive Periodic Table of the Elements", http://www.chemicalelements.com/index.html, 11.13.2003

[35] Merian, E., 1991, "Metals and Their Compounds in the Environment – Occurrence, Analysis and Biological Relevance", VCH Publishers, Inc., New York

[36] Yuan, Y., Hall, K., Oldham, C., February 2001, "A preliminary model for predicting heavy metal contaminant loading form an urban catchment", The Science of the total Environment, Amsterdam, Elsevier Pub. Co., Vol. 266, pp. 299-307

[37] U.S. EPA, Office of Water, June 1996, "The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit from a Dissolved Criterion", EPA 823-B-96-007, http://www.epa.gov/ostwater/guidance.pdf, 05.07.2002

[38] Erlacher, R., 2004, Regression Analysis of Dissolved heavy Metals in Storm Water Runoff from Elevated Highways, Dissertation Study, University of New Orleans

[39] Institut fuer Mineralogie, "Inductively Coupled Plasma – Atomic Emission Spectrometry", University of Wuerzburg, http://www.uni-wuerzburg.de/mineralogie/links/tools/icp-aes.html

[40] APHA, AWWA, WEF, 1999, "Standard Methods for the Examination of Water and Wastewater", 20th Ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.

[41] Varian Inc., "Inductively Coupled Plasma – Atomic Emission Spectrometry", http://www.varianinc.com/cgibin/nav?varinc/docs/osi/icpaes/atwork/index&cid=885936, 09.02.2002.

[42] Gschnitzer Armin, May 2003, "Characterization and Prediction of Dissolved Heavy Metals Associated with Storm Water Runoff from Elevated Highways", Ph.D. Dissertation, University of New Orleans, New Orleans, Louisiana

[43] Di Toro, D.M. et al, 1979, A statistical Method for the assessment of urban Stormwater, Prepared by Hydroscience, Inc. for the EPA, Office of Water Planning and Standards, Washington, D.C.

[44] Alley, W.M., 1981, Estimation of Impervious-Area Washoff Parameters, Water Resources Research, 17, 1161-1166

[45] Alley, W.M., 1981, Estimation of Accumulation Parameters for Urban Runoff Quality Modeling, Water Resources Research, 17, 1157-1164

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