

2012-09-13

Synthesis and Evaluation of Nutrient Leaching From an Oleophilic Fertilizer Biofilter Soil Amendment

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Wilkins, J. (2012). Synthesis and Evaluation of Nutrient Leaching From an Oleophilic Fertilizer Biofilter Soil Amendment (Master's thesis, University of Calgary, Calgary, Canada). Retrieved from <https://prism.ucalgary.ca>. doi:10.11575/PRISM/27952

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Synthesis and Evaluation of Nutrient Leaching From an Oleophilic Fertilizer Biofilter Soil
Amendment

by

JASON WILKINS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

CALGARY, ALBERTA

SEPTEMBER, 2012

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Abstract

Laboratory column studies were used to quantify the nitrogen and phosphorus leaching dynamics from a biofilter soil, fertilizer amendments, and experimental controls throughout four years of simulated runoff application.

The results showed that the biofilter soil starting materials were a significant source of nutrients, particularly for nitrogen. Compost was identified as the ideal nitrogen amendment, leaching only 7% of the mass initially added to the test column. This minimal washout response was attributed to the slow mineralization of humic materials. Lecithin and Nitroform[®] leached the lowest amount of phosphorus amongst the tested soil amendments, whereas the inclusion of polymerized tung oil with these nutrient sources (oleophilic fertilizer) only expedited phosphorus release. In contrast, the oleophilic fertilizer demonstrated a more controlled nitrogen release than the Lecithin and Nitroform[®] and this inconsistency was attributed to greater microbial nitrogen immobilization over phosphorus upon carbon based biostimulation.

Acknowledgements

I would like to thank the following for their contribution to this project;

Dr. Angus Chu

Mr. Bert van Duin, M.Sc., P.Eng.

Mr. Daniel Larson

Mr. Mirsad Berbic

Dr. Abimbola Abiola

Dr. Patrick Hettiaratchi

Mr. Usman Khan, M.Sc.

Dr. Michael Collins

Westhoff Engineering Resources, Inc.

Agrium, Inc.

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Chapter One: Introduction

Anthropogenic eutrophication of receiving water bodies is perhaps one of the most important challenges facing water resources managers today and phosphorus is the major element contributing to this problem (Tofflemire and Chen, 1977). Increased phosphorus loads may lead to eutrophication and algal blooms in aquatic environments that may result in the depletion of dissolved oxygen and high turbidity in aquatic ecosystems (Hsieh *et al.*, 2007). These deleterious conditions can lead to poor water quality and the loss of aquatic biodiversity in water bodies. With increasing stricter restrictions on nutrient loads into watercourses many watershed groups, regulators, designers and municipalities have embraced Low Impact Development (LID) as a promising approach to improve on watershed protection.

From a stormwater perspective, LID entails a paradigm shift with an increased preference for source control practices over end-of-pipe solutions for hydrologic restoration. Curbs, gutters and storm ponds are losing popularity to a suite of source control practices that aim to treat water quality and quantity at the source. Stormwater biofilters, also known as rain gardens or bioretention areas, have emerged as one of the preferential source controls as of late.

Stormwater biofilters are an excavated basin under which perforated drain pipes maybe laid and covered with a gravel envelope. A sand based soil media is often placed over the gravel and plants and mulch are added to the surface. Runoff is directed to the area, infiltrates, and exits the cell via drain pipe outflow, exfiltration, or evapotranspiration. Bypasses are generally installed to circumvent flows in excess of the design event for the facility. The intent using biofilters to promote infiltration is to affect better stormwater quality and quantity treatment

when compared to conventional practices. The overarching concerns with biofilters may be attributed to their allegedly short lifespan, the need for increased maintenance as compared with a pipe based system, and the propensity to develop into a nutrient source rather than a sink. The bulk of these concerns can be addressed, or mitigated through, sensible design, engineering and construction diligence. The soil media is a key component in determining the water quality performance and lifespan of the biofilter and as such, refining the soil composition for the local climate to ensure long-term functioning and environmental protection is a primary focus of many designers.

Sandy soils are often recommended for use in stormwater biofilters which receive runoff and are thus intermittently flushed with substantial quantities of water. However, sandy soils with a high infiltration rate typically have a lower nutrient holding capacity than most well structured clay and loam based soils, and may require a degree of fertilization to facilitate plant establishment (Li *et al.*, 2000; Lehmann and Schroth, 2003; Jaber *et al.*, 2005; Yang *et al.*, 2008). Herein lays the balance between distinguishing a soil media with adequate hydraulic conductivity to support long-term functioning of the infrastructure, while concurrently retaining enough nutrients and available water to facilitate plant establishment and growth. Many biofilter media specifications include compost in their composition to improve soil structure and supply nutrients however; nominal amounts literature has assessed its effect on stormwater quality. Alternately, the development of a nutrient delivery system that can regulate the release of nutrients in soil based filter systems flushed with substantial quantities of water can help reduce the pollution inherent in any fertilizer application and the adverse effects of nutrient leaching into the ecosystem.

The overarching goals and objectives of this experiment are as follows;

- Gain a better understanding of nutrient leaching from a biofilter soil amended with compost.
- Develop an alternate nutrient delivery system in the form of an oleophilic fertilizer for use in a biofilter soil media to support plant growth and minimize nutrient export from the system.
- Evaluates nutrient leaching from the oleophilic fertilizer when compared to experimental controls and compost as one of the more commonly specified soil amendments.

The intent of utilizing an oleophilic fertilizer in biofilter media is to ensure acceptable long-term water quality while supporting plant establishment and growth. Oleophilic fertilizer use in biofilters could potentially allow for a greater facility lifespan due to the ability to use a soil media with higher conductivity without nutrient limitations. In addition, there is excellent potential for hydrocarbon bioremediation although this was not evaluated as part of this study. Economically, any reduction in fertilizer loss is a potential cost saving measure with respect to the product as well as the operational costs of subsequent fertilization.

Chapter 2 of this report entails a literature review, which is necessary to provide a better understanding of the various aspects of this multidisciplinary experiment whereas Chapters 3 and 4 discuss the experimental methods and results, respectively. Key findings and recommendations for future studies are presented in Chapters 5.

Chapter Two: Multidisciplinary Review

The following subsections provide insight into the water quality concerns with nutrients in the watershed as well as the current regulatory environment. Biofilter nutrient removal performance and current soil media specifications have been summarized and an introduction to bioremediation and oleophilic fertilizers is provided. A discussion on soil nutrient flux and bioavailability is followed by pertinent background information on the nutrient and oil precursors considered for the fabrication of the oleophilic fertilizer.

2.1 Water Quality Review

2.1.1 Nutrient Leaching and Water Quality Concerns

Nutrient leaching is the downward movement or exfiltration of dissolved nutrients in the soil with percolating water (Lehmann and Schroth, 2003; Camberato, 2001). The potential advantages of controlling nutrient leaching from soils can be considered within an economic or environmental context. From an environmental perspective, much of excess applied nitrogen may be leached or removed from the root zone into surface or ground water supplies, which in turn can lead to increased risk of methemoglobinemia, gastric cancer and other health and environmental concerns (Shaviv, 2001). Generally, there is little risk of impact on groundwater quality from residential stormwater infiltration apart from chlorides, which may pose a risk in northern climates where road salting is prevalent (Pitt *et al.*, 2002). From a nutrient perspective, nitrate has a low to moderate potential of groundwater contamination; however, if the infiltrating water holds high concentrations of nitrate, or nitrate precursors, then it follows that the risk level to groundwater would be comparatively high (Pitt *et al.*, 2002).

There are three forms of nitrogen that are commonly measured in surface water bodies: ammonia (NH_3), nitrates (NO_3^-) and nitrites (NO_2^-). Nitrate and ammonium (NH_4^+) are the typical forms of nitrogen available to plants, and under normal aerobic soil conditions nitrate is the more prevailing form. Nitrate is easily leached from soils as there is little interaction with the negatively charged soil particles or hydroxides; it does not form precipitates and is thus easily transported in the soil (Lehmann and Schroth, 2003). This study focuses on Total Nitrogen (TN) as the reporting measure for nitrogen as per the recommendations by Barton *et al.* (2006) who found that a significant portion of nitrogen leached from sandy soils was in the organic form. TN is the sum of Total Kjeldahl Nitrogen (organic, ammonia, ammonium) and nitrate/nitrite (NO_x). Utilizing TN as the reporting measure gives the 'end picture' perspective that accounts for the ultimate fate of the different nitrogen species. For example, organics may have yet to decompose and mineralize (ammonification) to inorganic forms. The disadvantage of using totals as the study reporting measure is a loss of experimental resolution that can help better delineate biogeochemical processes in the results.

While significant nitrate transport can be expected given its solubility, most phosphorus is found only in minute amounts dissolved in water that percolates through soil (Cooke and Williams, 1973). The majority of inorganic phosphorus is bound to iron and aluminum hydroxides, soil colloids or calcium precipitates. Organic phosphorus is mostly associated with living organisms and consists of easily decomposable phosphorus compounds such as nucleic acids and phospholipids. This study focuses on Total Phosphorus (TP) as the reporting measure for phosphorus. TP Phosphorus can be classified as the dissolved forms (orthophosphates), inorganic forms (acid hydrolyzable phosphate) and organically bound forms. No significant

ecological export pathway exists for phosphorus as is the case with nitrogen where it may be converted to a gaseous form upon denitrification. The soil water regime with respect to nutrient flux shall be further elaborated on in later in this chapter.

Phosphorus is thought to control the level of primary productivity in western Canadian lakes despite many of the lentic and lotic systems in Alberta being already naturally eutrophic (Howard *et al.*, 1999). Because phosphorus is the limiting nutrient in Alberta freshwater systems, the aquatic environment is particularly sensitive to further phosphorus enrichment. Increased primary productivity can lead to decreased dissolved oxygen levels, and can be detrimental to aquatic ecosystems resulting in fish kills (Howard *et al.*, 1999). Major phosphorus inputs into the watercourse can be a result of both point source and non point source pollutants. Industrial wastes, organic manure, wastewater sludge, agricultural runoff and detergents all may contribute to phosphorus loadings (Minton, 2005).

2.1.2 Existing Regional Water Quality Guidelines Summary

At the time of writing, the City of Calgary (City) maintains no municipal stormwater regulation that defines water quality targets for nitrogen or phosphorus despite the elevated nutrient levels and mesotrophic conditions observed immediately downstream of the City (AENV, 2007). The City does have an obligation to limit nutrient loading to the Bow River as specified in it's wastewater and stormwater Environmental Protection and Enhancement Act (EPEA) approval authorized by Alberta Environment (AENV). The terms and conditions outlined in the approval stipulate that the City shall maintain a Total Loading Management Plan and limit the TP load to 340 kg/day as an annual average. The 340 kg/day loading objective adopted for TP is predicated on maintaining the surface water quality guideline of 5.0 mg/L dissolved

oxygen to support aquatic health (City of Calgary, 2008). The loading limit was derived from water quality modeling efforts that incorporated phosphorus loads from both stormwater and wastewater which is typical in EPEA reporting and approvals. As such, there is an allowance for stormwater phosphorus loading in the approval although it may be somewhat coupled with wastewater regulation.

The Western Irrigation District, both a water supplier to agricultural and municipal users as well as a stormwater services provider, has stipulated outright TP stormwater limits. The district wide draft guideline stipulates a maximum permissible TP concentration in stormwater of 0.03 mg/L (MPE Engineering Ltd., 2007).

Provincial water quality guidelines for the protection of freshwater aquatic life have also been identified by Alberta Environment (1999) as per the Surface Water Quality Guidelines for Use in Alberta. The guidelines set chronic (continuous) targets for TP and TN of 0.05 mg/L and 1.0 mg/L, respectively.

From a watershed perspective, the Bow River Basin Council has prepared water quality guidance as outlined in the Bow Basin Watershed Management Plan: Phase One – Water Quality (BBWMP). Therein, physical, chemical and biological parameters and subsequent water quality objectives or thresholds have been identified for specific reaches of the river. The Bow River Central Reach, which encompasses the Calgary region, outlines specific water quality objectives for total and dissolved phosphorus as well as a number of nitrogen species. Water quality objectives from the BBWMP relevant to this study are summarized in Table 1.

Table 1 Bow River Basin Water Quality Objectives (Central Reach)

Parameter	Water Quality Objective
Nitrate (nitrate+nitrite as N)	1.5 mg/L
Total Ammonia (NH ₃)	The lower of 0.2 mg/L during the growing season or US EPA (1999)
Total Dissolved Phosphorus	0.015 mg/L during the growing season for aquatic plants. Provisional 0.054 mg/L objective for the winter season.
Total Phosphorus	0.028 mg/L. Provisional 0.075 mg/L objective for the winter season.

The 2010 State of the Environment Report by the City of Calgary provides some insight on the condition of the Bow and Elbow Rivers with respect to the current nutrient concentrations in the water bodies. Since monitoring began in 2004, the TP concentrations downstream of the City are frequently higher than the BBWMP water quality objective of 0.028 mg/L, although they are typically below the 0.05 mg/L limit as per the provincial Surface Water Quality Guidelines (City of Calgary, 2011). TP concentrations are found to decay significantly with further distance downstream (City of Calgary, 2011).

Water quality monitoring in the Bow River demonstrated TN concentrations well above the provincial guidelines. Similar to phosphorus, concentrations decrease with increasing distance downstream. It is important to note that the baseline conditions - which refer to nitrogen and phosphorus concentrations upstream of the City - are significantly lower and within water quality objective limits. This anthropogenic increase in nutrient loads yields a trophic shift from the naturally occurring oligotrophic to mesotrophic conditions in the Bow River south of Calgary (AENV, 2007).

2.1.3 Stormwater Biofilter Nutrient Removal Performance Review

A number of studies have evaluated biofilter water quality performance with a comprehensive review thereof prepared by Roy-Poirier *et al.* (2010). The intent of this section is to provide an overview of nitrogen and phosphorus removal, with an emphasis on studies that specifically identify organic amendments in their biofilter soil composition.

It can be difficult to make generalizations on water quality performance when significant variation exists amongst biofilter engineering design and the experimental methods designed to ascertain performance data. While biofilters have typically demonstrated consistent removal of principal stormwater contaminants such as Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD), and metals (copper, lead, zinc), their performance record with respect to nutrient removal is both varied and complex. Furthermore, a variety of reporting methods only adds to the inability to distil 'one size fits all' guidelines for biofilter soil media specifications. For instance, performance removal measures are typically reported as a concentration decreases or mass reductions; both of which are ultimately subject to the chemical properties of the influent (Roy-Poirier *et al.*, 2010). Physical biofilter design characteristics such as, soil depth, soil type and drainage configurations can also be adjusted to meet the performance objectives of the filter. The characteristics of the soil composition is of particular interest as classification, organic matter content, available phosphorus content (PO_4^-) and the Cation Exchange Capacity (CEC) are directly related to biofilter nutrient removal performance (Hsieh and Davis, 2005a).

2.1.4 Nitrogen and Phosphorus Performance

Despite variable results from field and laboratory experiments, some generalities may be derived from the existing literature. With respect to nitrogen, removal in biofilters is consistently found as moderate to good for ammonium (Davis *et al.*, 2001; Davis *et al.*, 2006; Dietz and Clausen, 2005; Bratieres *et al.*, 2008) and organic nitrogen. Removal of these nitrogen species is often attributed to sorption or filtration unit processes. Transformation, or more specifically nitrification, is considered another principal ammonium removal pathway. Nitrogen reductions are often reported from a mass removal basis that accounts for water balance losses despite actual effluent concentration increases (Hunt *et al.*, 2006).

The depth of biofilter soil is an important property in that the filter should sorb any soluble ions as runoff percolates downwards through the media as the exchange capacity of the soil is diminished (Hatt *et al.*, 2007). Hatt *et al.* (2007) and Hatt *et al.* (2008) found that while physical straining and filtration of particulate bound and organic nitrogen species occurred in the upper few centimetres of the soil column, the removal was ultimately masked due to leaching from the lower sections of the filter, resulting in a net export of TN. This contrasts with findings from Davis *et al.* (2001) that found better nitrogen and phosphorus removal with increasing soil depth.

Over time, previously filtered nitrogen species may decompose and mineralize, ultimately leading to the leaching of their solubilised forms (Hatt *et al.*, 2008). Biofilter NO_x production is well established (Davis *et al.*, 2001; Davis *et al.*, 2006; Hsieh and Davis, 2005b; Bratieres *et al.*, 2008, Hatt *et al.*, 2007; Hatt *et al.*, 2008) and reductions, if any, are often found to be poor (Davis *et al.*, 2001; Hsieh and Davis, 2005b; Dietz and Clausen, 2005). Increases in

readily soluble nitrate ultimately lead to elevated TN concentrations when used as the experimental reporting measure.

Two principal long-term removal pathways exist for soil nitrogen; that is, di-nitrogen off-gassing via denitrification and immobilization by plant uptake and sequestration. The role of vegetation should not be underestimated. Henderson *et al.* (2007) established that vegetated biofilter mesocosms provided significantly greater ($\approx 200\%$) nitrogen removal in when compared to non-vegetated columns. The vegetated mesocosm constructed with sandy loam soil was perhaps the most representative of a conventional biofilter soil media, and the mass removals reported from this mesocosm were 90% and 77% for TP and TN respectively. The vegetated treatments removed most of the NO_x from the synthetic stormwater whereas non-vegetated mesocosms either removed no influent NO_x or discharged effluent at higher NO_x concentrations than the influent (inferring nitrification). Furthermore, Bratieres *et al.* (2008) found that the presence and type of vegetation is the main influence on biofilter nitrogen removal. Vegetated columns affected greater nitrogen removal on a whole however, the type of vegetation was found to be critical. *Carex appresssa* and *Melaleuca ericifolia* species provided NO_x reductions whereas the other three species tested demonstrated NO_x production.

Biofilters are generally regarded as a phosphorus sink with reported reductions in TP effluent concentrations or more often, mass reductions (Davis *et al.*, 2001; Davis *et al.*, 2006; Hsieh and Davis, 2005a; Hsieh *et al.*, 2007; Bratieres *et al.*, 2008; Sansalone *et al.*, 2010; Henderson *et al.*, 2007). However, some experiments yielded variable results (Hunt *et al.*, 2006; Hsieh and Davis, 2005a) or conversely, demonstrated a net TP leaching (Dietz and Clausen, 2005; Hatt *et al.*, 2007; Hatt *et al.*, 2008). As with nitrogen, particulate bound or organic

phosphorus is removed by physical filtration whereas the dissolved fractions are removed by sorption to hydroxides and biochemical immobilization unit processes. Biofilters have been shown to be less effective in controlling dissolved phosphorus compared to the filtration of particulate bound or organic forms although the latter types may eventually mineralize into dissolved species (Sansalone *et al.*, 2010).

The BMP Database (www.bmpdatabase.org) was developed to provide scientifically defensible set of data on Best Management Practices (BMPs) and their water quality performance. The database is to be updated annually albeit as of the time of writing (July 2011) statistical performance summaries offered by the BMP Database were under revision and not available for download. As such, the following results are based on the 2008 statistical summaries by Geosyntec Consultants and Wright Water Engineers Inc. Data from 57 biofilters are included in the summaries for which the following performance data, which outlines the percent change between influent and effluent concentrations, was provided.

- Total Phosphorus – 36% increase
- Dissolved Phosphorus – 489% increase
- Total Nitrogen – 17% decrease
- Nitrate – 2% increase
- TKN – 19% decrease

Please see Appendix A for full details of the BMP Database statistical summaries.

2.1.5 Organic Amendments and Nutrient Leaching

A number of benefits may be attributed to the addition of compost to biofilter media. Compost can increase or maintain the hydraulic conductivity; increase soil water retention,

increase ion exchange, porosity and provide many of the nutrients necessary for successful plant establishment. However, not all composts are created equal, and the source materials and composting methodology can yield composts of significant variability. While most varieties of organic matter can be used in compost fabrication, other constituents need to be considered as residual nitrates and orthophosphates can impair water quality (Lenhart, 2009). For example, naturally fallen deciduous leaves contain less nitrogen and phosphorus than manures as nutrients in the foliage are translocated to the roots upon winter senescence. Despite the nutrient content of the starting material, the maturity of the compost has a greater effect on leaching as immature composts are subject to further decomposition. Nonetheless, residual nitrogen and phosphorus will almost always be associated with composted organic matter and are expected to be leached until a steady state is achieved (Hsieh and Davis, 2005a; Hsieh *et al.*, 2007; Bratieres *et al.*, 2008; Lenhart, 2009).

Interestingly, only a few studies have purposefully examined nutrient leaching from organic biofilter soil amendments although inferences can be made from the general biofilter literature. The following is a review of studies that identify organic amendments in the biofilter soil composition.

Hatt *et al.* (2008) filled 6 columns with soil types that ranged from fine sand to a sandy loam, compost and mulch blend. The columns were doused with a semi-synthetic spiked runoff, that replicated typical stormwater pollutant concentrations, and the application volume loosely simulated the precipitation climate in Melbourne Australia (653 mm/yr). With the exception of the sand column, all of the soil mixtures tested demonstrated increased TP leaching from 150% to 400% over the influent concentration. Similar water quality results were found for nitrogen.

Table 2 illustrates the mean changes in load reductions throughout the duration of the experiments; however, mass increases are overestimated from what would be experienced at a field site where infiltration would account for some of the pollutant mass reduction.

Table 2 Pollutant Removal Efficiency of Six Filter Media Types (Hatt *et al.* 2008)

	TSS	TP	TN	TOC	Cu	Mn	Pb	Zn
	29	0.08	0.45	1	0.06	0.01	0.15	0.22
	Event mean hydraulic loading (g/m ²)							
	Load Reduction (%)							
S	99 ± 1	97 ± 1	38 ± 1	59 ± 8	97 ± 1	94 ± 1	99 ± 1	99 ± 1
SL	93 ± 4	-65 ± 16	-18 ± 15	-103 ± 17	97 ± 1	-32 ± 54	99 ± 1	99 ± 1
SLH	92 ± 3	-143 ± 17	-37 ± 4	-146 ± 19	96 ± 1	-71 ± 19	99 ± 1	98 ± 1
SLVP	90 ± 3	-73 ± 15	-23 ± 12	-129 ± 22	94 ± 2	-26 ± 52	95 ± 2	96 ± 4
SLCM	92 ± 4	-409 ± 40	-111 ± 41	-178 ± 13	94 ± 1	-152 ± 100	97 ± 1	96 ± 1
SLCMCH	96 ± 1	-437 ± 50	-164 ± 14	-165 ± 5	93 ± 1	-178 ± 189	97 ± 1	96 ± 1

Load reductions are reported as the mean of three replicates ± standard deviation. Note: a negative load reduction indicates leaching of previously retained pollutants and/or native material.

(S) sand, (SL) sandy loam, (SLH) 8:2 sandy loam/hydrocell ameliorant, (SLVP) 8:1:1 sandy loam / vermiculite/perlite, (SLCM) 6:2:2 sandy loam/compost/mulch, (SLCM) 6:2:2 sandy loam/compost/ mulch on charcoal drainage layer

Hatt *et al.* (2008) found that the TP losses, attributed to filtration occurring in the upper portion of the column, were substantially outweighed by leaching from native soil materials at lower depth. The phosphorus in the effluent was almost entirely in the dissolved form which increased with increasing soil column depth. The effects of compost addition to the soil are most apparent upon comparison the SLCM (sandy loam, compost, mulch) and SLCMCH (sandy loam, compost, mulch, charcoal) columns that contained 10% and 20% compost respectively. Comparing water quality results between the compost amended and non amended soils, it is evident that the inclusion of compost may increase nutrient export 400-500% for both TN and TP.

The TP concentration increases followed largely a linear relationship with filter depth demonstrating that leaching is directly proportional to the hydraulic retention time or the

depth of media through which the water is flushed (Hatt *et al.*, 2008). This finding has particular biofilter design implications and highlights the importance of approximately equivalent retention times and compaction between the soil columns in this study.

Another series of tests, conducted in the Seattle area by Pitt *et al.* (2001), examined the effects of two varieties of compost soil amendments on stormwater soil infiltration and water quality. The composition of the two composts were a yard waste and a sawdust/municipal waste blend mixed at a 3:1 ratio by volume and composted in windrows for a minimum of one year. In general, the compost amended soils were found to have increased infiltration rates, but significantly increased concentrations of nutrients in the runoff (Pitt *et al.*, 2001). Data from the study was interpreted in the context of mass fluxes and all nitrogen and phosphorus subsurface flow mass discharges increased; particularly for ammonia (340% increase), phosphate (200% increase), plus TP, nitrates, and TN (all 50% increase) (Pitt *et al.*, 2001). Table 3 from Pitt *et al.* (2001) summarizes the expected changes in surface runoff and subsurface flow mass pollutant discharges associated with compost amended soils.

Table 3 Changes in Pollutant Discharges from Surface Runoff and Subsurface Flow at New Compost Amended Sites, Compared to Soil Only Sites (Pitt *et al.* 2001)

Constituent	Surface Runoff Discharges (mass), Amended-Soil Compared to Unamended Soil	Subsurface Flow Discharges (mass), Amended-Soil Compared to Unamended Soil
Runoff Volume	0.09	0.29
Phosphate	0.62	3.0
Total phosphorus	0.50	1.5
Ammonium nitrogen	0.56	4.4
Nitrate nitrogen	0.28	1.5
Total nitrogen	0.31	1.5
Chloride	0.25	0.67
Sulfate	0.20	0.73
Calcium	0.14	0.61
Potassium	0.50	2.2
Magnesium	0.13	0.58
Manganese	0.042	0.57
Sodium	0.077	0.40
Sulfur	0.21	1.0
Silica	0.014	0.37
Aluminum	0.006	0.40
Copper	0.33	1.2
Iron	0.023	0.27
Zinc	0.061	0.18

2.1.6 Biofilter Soil Media Specifications

As demonstrated by the experiments highlighted in chapter 2.2, biofilter media, when amended with compost, demonstrates significant increases in subsurface mass discharges particularly for ammonia, phosphate, total phosphorus, nitrates, and total nitrogen. Of the thirteen reviewed stormwater publications authored by various municipalities and agencies across North America, eleven recommended compost additives to their biofilter soil media. It is emphasized that the type, maturity and characteristics of the compost vary amongst the specifications if specification were indeed provided. A brief summary of the publications reviewed for their biofilter media specifications is shown in Table 4.

In light of the previously reviewed studies, it is apparent that the treatment objective of the biofilter must be firmly established in order to affect the type and level of treatment expected from the facility prior to specifying a filter media. Without careful regulation and proper soil composition, biofilters will have a propensity to mobilize nutrients in effect becoming a nutrient source rather than a sink (Pitt *et al.*, 1999; Cooke and Williams, 1973; Hatt *et al.*, 2008).

Table 4 Biofilter Media Specifications Summary

Source	Biofilter Media Specifications			
	Sand	Loam	Compost	Comments
Hydrologic Bioretention Performance and Design Criteria for Cold Climates (Davidson <i>et al</i> 2008)	<i>20-70% construction grade, clean free of deleterious materials, AASHTO M-6 or ASTM C-33 with grain size 0.02" - 0.04"</i>		<i>30-50% organic leaf: Mn/DOT Grade 2</i>	<i>Avoid the use of fine textured soils containing silt or clay particles. They infiltrate slowly increasing their susceptibility to freezing. Ideally 0% clay content.</i>
Calgary Source Control Handbook (Westhoff Engineering Resources 2007)	<i>(0.05-2mm) proportion 50 to 70% dry weight of the mineral fraction.</i>	<i>silt (0.002-0.05mm) 10-30%, clay (<0.002mm) 0-5% proportion of the dry weight mineral fraction.</i>	<i>15-30% compost, mature with 50-60% organic matter</i>	<i>pH 5-6, soluble salts < 500 ppm, mg P and K @ 95 , 275 and 234 kg/ha respectively</i>
Bioretention Design Specification and Criteria (PGC Maryland)	<i>50-60% sand AASHTO M-6 or ASTM C-33 with grain size 0.02" - 0.04"</i>	<i>20-30% topsoil shall have a sandy loam, loamy sand, or loam texture per USDA textural triangle.</i>	<i>20-30% leaf compost</i>	<i>maximum clay content < 5%, PH Range 5.5-6.5, Organic matter 1.5-3.0%</i>
BMPs Guide for Stormwater (GVSD 1999)	<i>35-60% sand by volume</i>	<i>silt 30 -55%, clay 10-25%</i>		
Design of Stormwater Filtering Systems – (Clayton and Schueler 1996)	<i>35-60% sand by volume</i>	<i>silt 30 -55%, clay 10-25%</i>		<i>clay content less than 25% by volume. PH Range 5.2-7, Organic matter 1.5-4.0%, Phosphorus 75 lbs/acre min.</i>

Source	Biofilter Media Specifications			
	Sand	Loam	Compost	Comments
				<i>Potassium 85 lbs/acre min. magnesium 35lbsper acre.</i>
Stormwater Management for Smart Growth – (Davis, A., and McCuen, R., 2005)	<i>50% construction Sand; d₁₀of at least 0.6mm</i>	<i>20-30% Topsoil</i>	<i>20-30% leaf mulch</i>	<i>Clay content less than 10% to maintain high infiltration rates.</i>
Bioretention Performance, Design, Construction and Maintenance – (Hunt. W., and Lord. W., 2006)	<i>85-88% sand, washed medium is sufficient</i>	<i>8-12% fines of clay and silt</i>	<i>3-5% organic matter. Newspaper much, peat moss</i>	
Stormwater Source Control Design Guidelines – (GVSD 2005)	<i>pit run sand (0.075mm-12.5mm) as per section 02226 in MMCD(2000)</i>	<i>As per section 02921 table 2 in MMCD(2000) including organic requirements as noted in compost column.</i>	<i>lawn areas min 8%, planting areas min 15%</i>	<i>treatment soil depth 450mm min, 120mm recommended</i>
Stormwater Biofiltration Systems Adoption Guidelines (FAWB 2009)	<i>Clay & Silt <3% (<0.05mm), very fine sand 5-30% (0.05-0.15mm), fine sand 10-30% (0.15-0.25mm), medium to coarse sand 40-60% (0.25-1.0 mm), coarse sand 7-10% (1-2 mm) fine gravel < 3% (2-3.4mm)</i>	<i>25% sphagnum Peat</i>	<i>organic matter content - less than 5%(w/w)</i>	<i>filter media should be well graded i. pH 5.5-7.5, EC<1.2dS/m,P <1mg/kg</i>

Source	Biofilter Media Specifications			
	Sand	Loam	Compost	Comments
Bioretention – Stormwater Design Specification No. 9, (Virginia DCR 2010)	85-88% sand	8-12% soil Fines	3-5% organic matter in the form of leaf compost	
The Minnesota Stormwater Manual - Soil Mix A (2005)	55-66% construction sand (0.02"-0.04") ASTM C33 clean free of deleterious materials.	10-20% top soil (sandy loam, loamy sand, with less than 5% clay content)	25-35% organic leaf compost	
The Minnesota Stormwater Manual - Soil Mix B (2005)	50-70% construction sand (0.02"-0.04") ASTM C33 clean free of deleterious materials.	10-20% top soil (sandy loam, loamy sand, with less than 5% clay content)	30-50% organic leaf compost	
Urban Storm Drainage Criteria Manual (UDFCD 2010)	85% ASTM C33 Sand		7.5% compost (Vol.) 7.5% shredded Paper (Vol.)	

2.2 Oleophilic Fertilizers and Bioremediation Review

2.2.1 Bioremediation

The vast majority of studies pertaining to oleophilic fertilizers are found in the bioremediation literature. The application of an oleophilic fertilizer in biofiltration media is a novel approach to stormwater management. Insight into the presumed performance and limitations of these fertilizers may be gleaned from studies undertaken to assess them as per their original intent; as biostimulants in the reclamation of oil spills. While hydrocarbon remediation is certainly a considerable benefit when employing oleophilic fertilizers in biofilter media, the focus of this study is to assess nutrient leaching from biofilter media amended with an oleophilic fertilizer. Logical extensions to this study would include a focus on the ability of oleophilic fertilizer soil amendments to treat hydrocarbons in stormwater or support plant growth.

Numerous oleophilic fertilizers have been developed as biostimulants to facilitate the bioremediation of oil spills in marine environments, and much of the underlying philosophy of how an oleophilic fertilizer may function in a biofilter was assembled from this well studied field. Biostimulation refers to the addition of rate limiting nutrients to expedite the biodegradation process, as nutrients are often the limiting factor in oil biodegradation (Zhu *et al.*, 2004). The efficacies of these commercial products have been extensively reviewed in the scientific literature albeit limited field trials have been undertaken as studies are both difficult and expensive.

In order to overcome the rapid washout of soluble nutrients in aqueous environments, oleophilic formulations were devised to enhance hydrocarbon degradation by indigenous

bacteria in nutrient limited environments (Nikolopoulou *et al.*, 2007; Zhu *et al.*, 2004). The basis for oleophilic fertilizers is that oil degradation principally occurs at the oil-fertilizer interface and, given the attraction between the two hydrophobic substrates, enhanced biodegradation should occur without the need to significantly increase nutrient concentrations in the ambient pore water (Nikolopoulou *et al.*, 2007; Zhu *et al.*, 2004). This characteristic of oleophilic fertilizers is of particular importance in high energy aquatic environments such that nutrient losses would be minimized. Further to this notion, nutrient concentrations must be maintained in the environment to support the maximum growth rate of hydrocarbon remediating bacteria. As such, maximizing the residence time of nutrients in the contaminated zone is also one of the principle objectives for bioremediation (Boufadel *et al.*, 1999).

In addition to providing nutrients; many of these products include surfactants to maximize the oil-fertilizer interface thereby creating optimal conditions where bacterial degradation of the oil may transpire. It was originally thought that a commercially available product could be utilized as a plant fertilizer in biofilter media however; upon further review it was decided that an innovative fertilizer design, based on the principles gleaned from bioremediation studies and applications, was the best approach given the limitations of commercial fertilizers to be outlined in Section 2.2.2.

One of the major challenges with any fertilizer application, and those intended for biostimulation in particular, is how to best control the nutrient releases such that optimal nutrient concentrations are maintained in the pore water (Zhu *et al.*, 2004). That is, if nutrients are released too rapidly they can wash away as whereas too slow of a release rate may be limiting for microbial or plant populations to flourish. This fundamental principle of

solubilization holds true for the uptake of nutrients by plant roots. The controlled release of fertilizers should be such that their release is optimal in providing a high use efficiency by the plants in that the release mimics plant consumption kinetics thereby mitigating potential detrimental ecological impacts (Zhu *et al.*, 2001). A low solubility fertilizer will have less potential to leach from the soil, a reduction in foliage burning tendency and availability more in accordance with long season plant demands (Clark *et al.*, 1948).

However, too modest of a release rate, particularly in areas that are prone to high washout, may never achieve optimal concentrations and consequentially, may not support the intended biotic populations. Safferman (1991) suggested that release rates for many oleophilic fertilizers are indeed too modest to support hydrocarbon degrading bacteria. There is no evidence that suggests that this is the necessarily the case for plant bioavailability. While no information was found pertaining to plant uptake of oleophilic nutrients in particular, it is understood that plants have the capacity to uptake of insoluble nutrients through symbiotic assistance.

2.2.2 Commercial Oleophilic Fertilizers Efficacy

Commercially available products were reviewed in light of the study objectives and substantial limitations were identified. These products were either of a proprietary nature with aspects of their composition undisclosed or they are pre-inoculated with various species of bacteria, surfactants and/or emulsifiers that were deemed inappropriate for use in a biofilter fertilizer. For example, all of the reviewed formulations for which data was available lack potassium, a nutrient required to support plant growth. Additionally, some the formulations contained additives such as surfactants with potential human toxicity issues (Nikolopoulou and

Kalogerakis, 2008). Perhaps one of the most prominent limitations to utilizing a commercial fertilizer is the potential to affect the biofilter media's field capacity. Should the oleophilic fertilizer coat the organic fraction of the soil, thus rendering it hydrophobic, significant reductions in the soil's field capacity may be experienced in an already sandy soil type. Assessing the effect of the an oleophilic fertilizer on the soil field capacity was not within the scope of this study however the effect the fertilizer has on this soil property should be investigated in future works.

Historically, one of the most prominent commercial oleophilic fertilizer is Inipol EAP22, which is a micro emulsion composed of urea, sodium laureth phosphate, 2-butoxy-1-ethanol and oleic acid. The US Environmental Protection Agency's (EPA) Emergency Management National Contingency Plan Product Schedule notes that this product is no longer manufactured (www.epa.gov/OEM/content/ncp/product_schedule.htm). The persistence of this product in the environment has been assessed with variable results. That is, while some studies have shown Inipol EAP22 to persist in sandy shorelines, others have found the product to be rapidly washed out (Zhu *et al.*, 2004). Furthermore, concerns exist pertaining to the potential toxicity of the 2-butoxy-1-ethanol surfactant to both humans and wildlife (Nikolopoulou and Kalogerakis, 2008).

F1 is another reviewed bioremediation product that combines a polymerized urea formaldehyde fertilizer with an insoluble phosphorus source that is seeded with a hydrocarbon degrading bacteria culture that exclusively uses the F1 product as its nutrient source. The tenet behind the F1 product is that only the bacterial culture that is pre-inoculated within the product is capable of using the nutrients, whereas indigenous bacterial populations are unable to

capitalize on F1. Rosenberg *et al.* (1996), performed experiments with the intent to determine the percentage of nitrogen that will leach from a beach sand treated with the F1 product. Comparisons were made with two alternate commercial biostimulation products composed of soluble nitrogen sources. The control sand was treated with an ammonium salt. When the treated sands were washed with water it was found that the F1 effluent only leached 3% of the applied nitrogen into the wash water in contrast to the other three preparations which lost from 67% to 81% of the nitrogen mass.

From a non-commercial perspective, Lee *et al.* (1995) conducted experiments in-situ on beach sand comparing the performance of organic (fish bonemeal) and inorganic nutrients (ammonium nitrate and triple phosphate) to enhance hydrocarbon bioremediation and to assess nutrient release kinetics. The study found that the application of inorganic fertilizers rapidly elevated interstitial pore water phosphorus concentrations whereas the organic fertilizer demonstrated a lower release rate and thus, slow release characteristics under the study conditions. Furthermore, the study found that inorganic concentrations quickly decreased in the sand after fertilizer application suggesting rapid physical loss or utilization whereas the sand treated with the organic bone meal fertilizer demonstrated the highest nutrient concentrations.

The effectiveness of oleophilic fertilizers is somewhat dependant on the characteristics of the environment in which they are applied. For instance, water soluble fertilizers may be more cost effective in low energy, fine grained environments whereas oleophilic fertilizers may be more suited to high energy, coarse grained sands or a rocky outcropping setting (Nikolopoulou *et al.*, 2007). This distinction is based on the dynamic washout of nutrients from the action of

tides and waves (Zhu *et al.*, 2004). These findings allude to the applicability of oleophilic nutrients in biofiltration media in that stormwater is passed through a sandy soil often under pressure resulting from ponding above the surface.

2.3 Nutrient Bioavailability Review

Nutrient acquisition by flora and fauna entails robust knowledge of the processes that regulate the bioavailability of nutrients such as decomposition, mineralization and soil biogeochemistry (BassiriRad, 2005). The intent of this section is not to detail each of these mechanisms, rather to gain an appreciation for the major process that will govern the bioavailability of the fertilizer synthesized in this study. The optimal fertilizer nutrient release strategy would be direct uptake of nutrients with limited release into the soil pore water thereby minimizing washout from infiltrating stormwater.

The overwhelming majority of nutrients taken up by plants are in the inorganic form and as such, organics are typically mineralized to an inorganic form prior to uptake (Barber, 1984). Practically all nutrient uptake is from the soil pore water solution, which conveniently allows effective movement to the plant root mycorrhizal system (Comerford, 2005). Thus an understanding of the transport of dissolved compounds in the soil matrix is important when designing nutrient application strategies and formulas.

Complex interactions and competition between plant roots, soil bacteria and chemical reactions all affect the availability of nutrients to the plant (Shaviv, 2001). Nutrient distribution, CEC, pH, temperature, moisture content, cellular respiration, root morphology, symbiosis' and a plethora of biogeochemical processes all influence nutrient uptake. Uptake mechanisms can be complex as the nutrient concentrations at the root are in constant flux as nutrients and water

are taken up at differing rates than what is supplied by the soil. Once in solution, nutrient uptake into the plant roots is governed by ion absorption kinetics; however, it is the supply characteristics of the soil, the soil micro biota and mycorrhizae amongst other factors that affect the soil nutrient flux (Barber, 1984). Furthermore, most transformations that nutrients undergo in the soil are concentration dependant such that the processes which transpire when nutrient availability exceeds plant requirements will typically decrease nutrient concentrations in the soil (Shaviv, 2001).

2.3.1 Solid Phase Nutrient Release

The underlying tenet to nutrient release from the solid phase is the maintenance of pore water nutrient concentrations. The release of nutrients from the solid phase to the soil solution occurs through biochemical (mineralization, immobilization) and physiochemical (sorption, precipitation, dissolution) processes (Comerford, 2005). These processes are contingent on the soil characteristics and may be further regulated by the presence of mycorrhizae. A significant portion of mineralized nutrients may subsequently be immobilized by micro-biota and thus the net rate of mineralization is often much lower than the gross rate (Prescott, 2005). It is foreseeable that release from the solid phase may be somewhat contingent on the decomposition of the oleophilic fertilizer prior to the biogeochemical processes that regulate their concentrations in the soil solution.

2.3.2 Decomposition

Decomposition refers to the physical breakdown of organic materials, typically by biological enzymatic means whereas mineralization refers to the release of inorganic nutrients to the soil solution (Prescott, 2005; Comerford, 2005). Soil organic matter is a complex mixture

of compounds in various states of decay (Barker and Bryson, 2007). Partially decayed matter, or non-humic substances, is the major source of energy for soil micro-biota whereas humic substances are the more stable products of decomposition. Decomposition has generally been studied in the context of vegetative litter and its contribution to nutrient cycling. The decay rate of litter is predominantly dependant on the climatic conditions and the palatability of the substrate to micro-biota (Prescott, 2005). However, it is unclear to what degree litter decomposition mechanisms are applicable to the breakdown of the oleophilic fertilizer fabricated in this study.

Non-humic substances, such as fats, amino acids, proteins and low molecular weight organic acids are readily attacked by micro-organisms and decompose quickly (Barber, 1984). One of the principle ingredients in the oleophilic fertilizer synthesized in this study is tung oil, which is comprised largely of α -eleostearic fatty acids. These fatty acids are of high chemical quality and a rich carbon source that would likely be readily decomposed by soil biota. However, it is unclear how the polymerization of the tung oil may slow the decomposition processes as toughness, or tensile strength, has been shown to slow decomposition in leaf litter (Prescott, 2005). Measuring cellular respiration in a controlled environment would be one option to establish the decay rate of the fertilizer.

2.3.3 Climatic Variables

Climatic variables that effect the soil moisture, oxygen concentration and temperature all have an effect on the soil biological activity responsible for a number of nutrient release and bioremediation functions (Comerford, 2005; Shaviv, 2001). The mineralization of organic matter generally increases with increasing moisture content up to field capacity and then declines

whereas the effects of temperature are more variable (Prescott, 2005). In general, increases in temperature yields an increase in mass loss of plant detritus however it can be difficult to isolate the effect of temperature independent of other factors (Prescott, 2005). As previously noted this is an important property of the study fertilizer as too fast or too slow of a nutrient release may undermine its application as a plant fertilizer.

Field experiments performed by Lee *et al.* (1995) established that in temperatures above 15°C a sulphur coated urea slow release fertilizer was effective in maintaining elevated nutrient concentrations within beach sediments; however, at lower temperatures release rates were suppressed. This observation was attributed to the low temperatures reducing the solubility of the hydrophobic coating on the fertilizer. It is reasonable to expect that similar temperature effects would be applicable for oleophilic fertilizers.

Garcia-Blanco *et al.* (2001) conducted studies on the St. Lawrence River bank on a series of wetland plots treated with oil and various nutrient amendments. The plots were either left vegetated or had the wetland vegetation cut back to suppress the contribution from the vegetation to the remediation process. The study found only minimal remediation (about 35%) across all plots after 21 weeks of evaluation. In fact, slightly better oil removal was experienced in the samples plots where the plants had been removed. The increased bioremediation was attributed to the oxic surface conditions and the lack of competition for nutrients and oxygen between plants and soil micro-organisms. Other wetland studies have derived similar findings whereby biostimulation has also shown to be ineffective at enhancing hydrocarbon degradation due to oxygen limitation (Zhu *et al.*, 2004). This is in part due to the plants being somewhat dependant on the soil micro-biota to transform nutrients into forms that are conducive to plant

uptake. An oxygen limited environment may deprive the soil micro-biota that catalyzes these nutrient transformations consequentially restricting plant nutrient availability.

2.3.4 Phosphorus Soil Flux

As previously noted, mineralization and immobilization refers to the biochemical transformation of nutrients from organic to their inorganic forms by soil micro-biota and organic phosphorus must be hydrolyzed to an inorganic form prior to translocation across plant root membranes (Comerford, 2005). Plants have the ability to uptake phosphorus in multiple formats however the greatest intake is in the orthophosphate forms, HPO_4^{2-} and H_2PO_4^- depending on the pH of the medium (Sanchez, 2007). Mineral forms of phosphorus such as apatite, hydroxylapatite and oxyapatite, which are inherently insoluble can be solubilised under the appropriate conditions and become available for plants and micro-organisms (Rodriguez and Fraga, 1999). Interestingly, it has been shown that organic phosphorus is more readily transported in the soil than inorganic sources (Sanchez, 2007).

The decomposition of organics is performed by numerous saprophytes which affect the release of an inorganic form from the organic substrate. This process is sensitive to the properties of the substrate and the ambient environmental conditions in so much that an alkaline environment favours organic phosphorus mineralization (Rodriguez and Fraga, 1999). With respect to phosphorus substrates, nucleic acids, phospholipids and sugar phosphates are more easily broken down than phytic acid, polyphosphates and phosphonates (Sanchez, 2007). Organic phosphorus found in soils are largely found in the most stable form as inositol phosphate which is synthesized by soil microbes and plants while other common forms include phospho-mono/di/tri-esters, phospholipids and nucleic acids.

Mineralization is typically accomplished by phosphatase enzymes produced by microbial species that are often associated with the plant rhizosphere (Rodriguez and Fraga, 1999; Sanchez, 2007). Bacterial species; *Pseudomonas*, *Bacillus*, *Rhizobium* and a number of others have demonstrated the ability to solubilize insoluble inorganic phosphates and are present in considerable populations in soil and plant rhizospheres (Rodriguez and Fraga, 1999). It is generally accepted that the mineralization of inorganic phosphorus is a consequence of organic acids such as gluconic acid that is synthesized by micro-organisms (Rodriguez and Fraga, 1999). This acidification of the surrounding soil releases phosphorus from mineral forms of phosphate by proton substitution for Ca^{2+} (Rodriguez and Fraga, 1999). Other mechanisms have been considered such as the production of chelating substances, fungi and ATPases. Inorganic forms of phosphorus can be ranked in terms of their bioavailability. From high to low these are; dissolved inorganic, labile inorganic, iron and aluminum bound, calcium and magnesium bound and residual (Reddy and DeLaune, 2008).

While the physiology of phosphate solubilization is still a matter of discussion, it has been found that the presence and concentration of other elements, most notably potassium, are necessary for optimal solubilization rates. Fertilizers that have been coated with hydrophobic material are less sensitive to the aforementioned soil conditions and micro-biota that regulate nutrient release into the soil pore water (Shaviv, 2001).

2.3.4.1 Sorption

Dissolved inorganic phosphorus may be taken up by plants, microorganisms or immobilized by sorption or precipitation reactions. Sorption typically refers to the abiotic retention of inorganic phosphorus in soils. It is the movement of soluble inorganic phosphorus

from the soil solution to the soil surface. Soluble inorganic phosphorus from the soil pore water will bind to the soil mineral surface where it will accumulate without penetrating the surface and maintain equilibrium with the phosphorus concentrations in the soil pore water. Particular soils have a specific capacity for adsorption described by a sorption isotherm demonstrating the equilibrium relationship between the concentrations of adsorbed and dissolved phosphorus at a specific temperature.

Sorption is typically described as a two step process (Kadlec and Wallace, 2009; Barow, 1978; Hsieh *et al.*, 2007). That is;

- phosphorus rapidly exchanges between the soil pore water and the solid (adsorption)
- phosphorus slowly penetrates into the solid phase (absorption)

The capacity of soil to adsorb phosphorus increases with greater soil clay content or minerals in equilibrium with the phosphorus in the soil pore water (Reddy and DeLaune, 2008). This increase in soil capacity may be attributed to the large amount of surface area that a high clay content can provide in soil. Phosphorus sorbs to clays most predominately in the pH range of 6 to 7 (Minton, 2005). In acidic soil, inorganic phosphorus in soil solution becomes adsorbed to surfaces of iron and aluminum oxide and clay minerals while sorption with calcium is common under alkaline conditions (Sanchez, 2007). It is often found that the sorption of phosphate by soils is decreased if the pH is raised however the effects only become large at high values of pH (Barrow, 1983). The two principal mechanisms regulating adsorption are ion exchange and ligand exchange.

2.3.4.2 Desorption

Desorption or dissolution describes the solubilization of previously sorbed phosphate back into the pore water. This occurs when the phosphorus pore water concentrations drops below that of the adsorbed phosphorus. A portion of the inorganic phosphorus adsorbed on minerals such as calcium carbonate, iron or aluminum oxides and clay surfaces can desorb to buffer decreases in pore water phosphorus concentrations. Unfortunately, few studies address desorption and even fewer investigate the effect of desorption on soil solution concentrations (Comerford, 2005). As previously mentioned, the driving factor in nutrient bioavailability is the maintenance of pore water nutrient concentrations and desorption may be described as an equilibrium reaction derived from isotherms.

The partition coefficient is defined as the ratio of the nutrient concentration associated with the solid to the nutrient concentration in the surrounding soil pore water when the system is at equilibrium. It is a key soil property that inherently describes a variety of complexes that dictate the movement of nutrients in the soil. The partition coefficient, derived from sorption isotherms, is a useful property to assess desorption and is given by;

$$K_d = dC_s / dC_l$$

Where;

K_d = *partition coefficient* - the rate of change of the labile fraction between the two phases,

C_s = concentration of labile nutrients on the solid phase and,

C_l = the nutrient concentration in the pore water.

Both the rate of sorption and desorption are increased with increases in temperature although phosphate once sorbed, is not easily desorbed albeit the amount desorbed typically increases

over time (Barrow, 1983). Graphs of phosphate desorbed vs. phosphate concentration in solution do not coincide with plots of sorption against concentration albeit this is a bit of an oversimplification. Furthermore, the rate of desorption decreases as the period of prior sorption increases suggesting sufficient time has transpired to absorb the phosphate (Barrow, 1983).

2.3.5 Nitrogen Soil Flux

The nitrogen soil flux is distinctly different than that of phosphorus. In soils, nitrogen exists as various inorganic or organic compounds as well as within living organisms – some of which have the capacity to fix nitrogen from the atmosphere. Given the solubility of nitrate and its relative inability to participate in physiochemical reactions within the negatively charged soil matrix, it is readily leached from permeable soils. This is not the case for ammonium as sorption mechanisms factor in controlling its soil solution concentration. Because soils have little capacity to retain nitrate, and given that ammonium accumulation is minimal, the majority of soil nitrogen is associated with organic matter and the release thereof is slow and unpredictable (Barber and Bryson, 2007).

Inorganic nitrogen can be mineralized from non-humic substances or conversely, immobilized into humus by soil micro-biota. Nitrogen immobilized in humus contributes little to the soil nitrogen balance and the majority of mineralized nitrogen is obtained from the vegetative cover or crop (Camberato, 2001). Mineralization of non-humic nitrogen sources is a two part process. The first part, aminization is the breaks down of large nitrogenous molecules and is followed by the conversion to ammonium by the process of ammonification. Ammonium is either in a dissolved state and available for plant uptake, or chemically absorbed to clay

particles as fixed ammonium. In soils, ammonium is rapidly oxidized to nitrate, and because this transformation proceeds rapidly, it is often mineralization that regulates pore water nitrogen concentrations (Comerford, 2005). In light of the reaction kinetics and the greater mobility of nitrate through the soil matrix, nitrate is more often the form of nitrogen readily available for plant uptake. Well aerated soils promote mineralization of nitrogenous organics so as soil water content rise above field capacity organic matter breakdown is slowed (Camberato, 2001).

The ionic forms of nitrogen - nitrate and ammonium - are typically used for plant nutrition and their uptake may be influenced by the soil pH, temperature, and the presence of other ions in the soil solution. While plant sequestration is the main process by which inorganic nitrogen is removed from soil, leaching, denitrification, ammonia volatilization and immobilization also contribute to nitrogen losses (Barker and Bryson, 2007). Denitrification is also a major long-term removal pathway for soil bound nitrogen. The process entails the bacteria facilitated reduction of nitrate to nitrogen gas (N_2) in an anaerobic environment.

The oleophilic fertilizer synthesized in this study uses a slow release type of urea as the nitrogen source. Urea is a ubiquitously applied, water soluble fertilizer that is very reactive in mineral soils after application. Urea hydrolysis is an enzymatically driven conversion of urea to ammonia (NH_3) or ammonium. If urea is not immediately incorporated into the soil by water application, it may react with urease to produce ammonia and carbon dioxide with carbamic acid as a reaction intermediate (Hauck, 1968; Barker and Bryson, 2007). Upon further hydrolysis, the carbonate releases a hydroxyl ion which increases the pH of the immediate soil environment favouring ammonia formation over ammonium. As the formation of ammonia increases, so does the prospect of volatilization which is the loss of nitrogen to the atmosphere

as ammonia gas. A soil's capacity to restrict increases in pH (buffering capacity/CEC) upon urea hydrolysis is important for mitigating ammonia volatilization. Sandy soils typically have a low buffering capacity and thus, pH increases and subsequent ammonia volatilization may be significant (Camberato, 2001). Because stormwater guidelines specify sand based biofilter soils, and given that the oleophilic fertilizer includes a form of urea as the nitrogen source, distributing the oleophilic fertilizer throughout the soil may help minimize potential ammonia volatilization losses.

2.3.6 Soil Nutrient Movement

Nutrients travel through the soil to the roots in solution. Their movement through the soil solution is regulated by mass flow and diffusion but the movement is heavily dependent on the aforementioned soil characteristics that dictate flux. All nutrients can be conveyed by either of the aforementioned means however nitrate, given its solubility, is considered to move via mass flow whereas phosphate is often considered to move by diffusion due to its high sorptive capacity with the soil matrix (Comerford, 2005). Again, both nitrates and phosphates may, and do, utilize both transport means to move through the soil.

Mass flow is the movement of nutrients with the pore water due to a hydraulic gradient, typically between the root and the soil. Mass flow itself is subject to the moisture content of the soil and the physical properties of the soil which determines its hydraulic conductivity. When mass flow cannot keep up with plant nutrient demand, the concentration of nutrients in the rhizosphere is reduced relative to the soil pore water (Comerford, 2005). This condition results in a concentration gradient that drives nutrient movement through the soil solution via diffusion.

Plants that are experiencing nutrient deficiency have the ability to induce a diffusion gradient and the soil water regime plays an integral role in its regulation. The water content in the soil influences the cross-sectional area available for water flow, matric forces and the soil impedance factor which is a measure of the direct path of nutrient movement to the actual path (Comerford, 2005). Diffusive flux is explained by Fick's second law given by Comerford (2005);

$$Q_D = \left[(D_l \theta f(\theta)) / b \right] dC_l / dx$$

Where; Q_D = diffusive flux

D_l = diffusion coefficient of the nutrient in solution

θ = volumetric water content

f = soil *impedance* factor

b = soil buffer power

C_l = nutrient concentration in the soil solution

The selection of soil media is an integral part of the functioning of stormwater infiltration infrastructure. An optimal media is one that demonstrates adequate soil moisture retention capabilities and concurrently, a high level of conductivity. Maintaining a satisfactory level of conductivity has proven difficult as reductions in infiltrative capacity due to clogging have been demonstrated in numerous studies (Le Coustumer *et al.*, 2007; Habec and Christians, 2000; and Hatt *et al.*, 2008). Over time, organic matter accumulates in the soil as vegetative roots grow and die, ultimately leading to variations in water holding capacity and water movement throughout the soil. These long-term processes have been shown to help restore a soil's hydraulic conductivity (FWAB, 2009).

2.3.7 Plant Nutrient Uptake

The assimilation of mineral and organic nutrients by plants transpires at varying rates subject to the composition and disposition of the required nutrients, as well as the composition of the bacteria associated with the root system. One of the most important symbiotic bacteria that facilitate plant growth are known as *rhizobacteria* and their effects has been demonstrated in numerous laboratory and field experiments (Rodriguez and Fraga, 1999). *Rhizobacteria* perform nitrogen fixation to assist in meeting plant demands as well as facilitating the solubilization of inorganic phosphates and the mineralization of organic phosphates thereby rendering it available for root uptake.

Evidence suggests that the adsorption of soil nutrients in many ecosystems is primarily a function of mycorrhizal association and not necessarily exclusive uptake by plant roots (Finlay, 2005; Mullette *et al.*, 1974; Bolan, 1991). Mycorrhiza augments the root system which provides additional surface area and a more finely distributed interface by which nutrients can be translocated (Finlay, 2005). Mycorrhizal hyphae growth effectively short-circuit the distance necessary for diffusion and thereby increase nutrient uptake (Bolan, 1991).

Mycorrhizal fungi have demonstrated the ability to utilize a variety of substrates and are typically found foraging for nutrients in organic residues where the depletion of nitrogen, phosphorus and potassium has been documented through their action (Finlay, 2005). Plants which form mycorrhizal symbiosis have shown to increase the uptake of poorly soluble phosphorus sources such as iron and aluminum phosphate (Bolan, 1991). Substrates intensively colonized by miccorhizzal fungi have demonstrated increased levels of nutrient mobilizing enzymes such as protease, polyphenol oxidase and phosphomonoesterase. Furthermore,

mycorrhiza actively weather minerals and rock yielding bioavailable nutrients through the production of citric and oxalic acid. Acid production has been attributed to solubilizing inorganic nutrient sources and perpetuating biogeochemical nutrient cycling (Finlay, 2005).

Mycorrhizae facilitated weathering of the oleophilic fertilizer developed for this study would be the most optimal nutrient release mechanism in that solubilization and uptake would be localized, thereby minimizing release into the pore water.

In solution, nutrient ion absorption by plant roots may be characterized by either active or passive mechanisms that penetrate the plasma membrane inside cell walls. With respect to active transport, ion uptake generally increases in proportion to equilibrium concentrations and often a maximum rate is experienced at higher concentrations in a manner that may be defined by the Michaelis-Menten equation (Barber, 1984). With respect to nitrogen, specific root transporters have been identified that can influx nitrate, nitrite, ammonium, urea and amino acids (Glass, 2005).

2.3.7.1 Soil Fertilizer Distribution

The distribution of nutrients in the soil is an important aspect of fertilization, particularly for biofilter media. The oleophilic fertilizer synthesized in this study was used to enrich sand which was subsequently blended with the residual biofilter soil media constituents. The importance of nutrient placement increases with decreasing fertilizer application rates and placement often influences the nutrient recovered by plants; particularly in soils that have a high propensity to fix nutrients. In general, root growth is enhanced where the plant has access to pore water phosphorus and root phosphorus influx is closely correlated with root development and the distribution of dissolved phosphorus in the soil solution (Barber, 1984).

However, the effect of phosphorus placement in the soil is somewhat more complex. Plant nutrient uptake is actually increased as the volume of soil fertilized with phosphorus is decreased (Barber, 1984). This finding is attributed to increased uptake by roots with access to the fertilized soil fraction as well as stimulated root growth, which has a greater net effect than the expected reduction of uptake due to supplying a smaller soil fraction with phosphorus (Anghinoni and Barber, 1980). The optimal percent of soil fertilized in order to maximize phosphorus uptake by the plant was found to be in the order of 12.5%. In light of these findings it may be prudent to enrich only a fraction of the sand used in the biofilter media with the oleophilic fertilizer in future field trials to maximize plant uptake and stimulate root development.

2.4 Oleophilic Fertilizer Precursors Review

The ideal properties of the nutrient precursors considered for the synthesis of the study oleophilic fertilizer would be to;

- contain a high nitrogen and phosphorus to carbon ratio in order to minimize biochemical oxygen demand,
- to hold intrinsic hydrophobicity and lipophilicity,
- to have a low water solubility,
- to be biodegradable,
- to have low toxicity,
- to be readily available and,
- be of low cost.

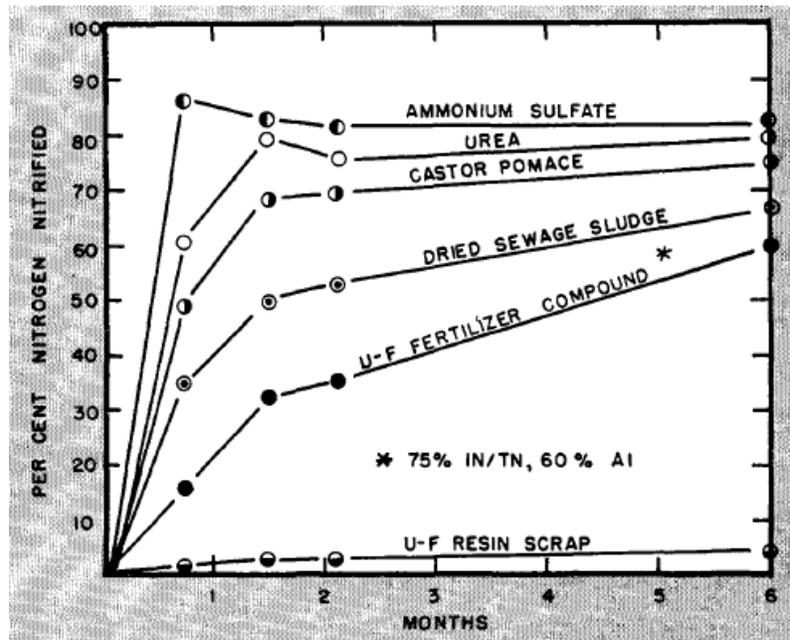
Lipophilicity is considered to be a measure of a substance's ability to dissolve in fats or other polar compounds. This is an important property as the nutrient precursors will need to dissolve in the tung oil fraction of the fertilizer. Various nutrient sources ranging from common agricultural chemicals to compounds that have been utilized in bioremediation studies were reviewed for applicability in the synthesis of the study fertilizer with the aforementioned properties as the basis for their screening.

2.4.1 Nitrogen

A number of potential nitrogen precursors were investigated in the development of the study oleophilic fertilizer. The availability index is a key fertilizer property that is a common measure used to distinguish the agronomic availability of the cold water-insoluble nitrogen fraction. A faster rate of nitrification results in a higher value for the availability index.

The nitrification rate of various nitrogen based fertilizers are shown in Figure 1 which illustrates that urea formaldehyde compounds (noted in the Figure as U-F) are some of the most resistant to nitrification and as such, hold the greatest slow release characteristics of all the products shown. The rate in which these products nitrify is affected by a number of variables of which soil type was found to be the most governing (Kralovec and Morgan, 1954).

Figure 1 Nitrification Rates of Nitrogenous Fertilizers (Kralovec and Morgan, 1954)



The availability index, performance data ascertained from previous studies, and the lipophilic properties of the nitrogen source were all used to screen for potential fertilizer precursors. The following nitrogen sources were considered in this study;

2.4.1.1 Urea or Uric Acid (46% N)

Urea is converted to ammonium after soil application and is either fixed or converted to nitrate via the processes noted in Section 2.3.5. Volatilization losses can be substantial if applied in surface applications (Barker and Bryson, 2007). Urea is readily soluble in water albeit some studies have shown that uric acid is capable of binding to crude oil and as such, is not readily diluted into the ambient water (Nikolopoulou *et al.*, 2007; Koren *et al.*, 2003). This finding may be indicative of the ability of uric acid to dissolve in the drying oil fraction of the oleophilic fertilizer developed for this study. Uric Acids are of natural origin being a waste product of many species and have low solubility in water (Koren *et al.*, 2003).

2.4.1.2 Urea Formaldehyde (38% N)

The condensation of urea with formaldehyde is perhaps the most common nitrogen compound employed in slow release fertilizers. Urea formaldehyde (ureaform) fertilizers are formed by the acid catalyzed reaction of urea with formaldehyde wherein a product is formed that usually contains 36-38% nitrogen with at least 60% of the TN present as cold-water-insoluble. Thus, ureaform is much less soluble than most other chemical nitrogen fertilizers (Clark *et al.*, 1948). Subject to the reaction conditions, the reactants produce methylene urea polymer chains of varying lengths and in turn, the chain length affects the release characteristics of the fertilizer. That is, the longer the methylene urea polymer chain the longer it takes for the nitrogen to become available (Long and Windsor, 1960).

Urea formaldehyde type fertilizers range from highly condensed, polymeric urea formaldehyde resins to products containing a high percentage of short chain, water soluble molecules and un-reacted urea which readily release available nitrogen. In general, ureaform fertilizers exhibit 55- 60% nitrification of the water insoluble nitrogen in six months in an average soil (Kralovec and Morgan, 1954). However; the decomposition of urea formaldehyde fertilizers is chiefly due to microbial activity and as such, nitrogen release is also dependent upon the environmental conditions that regulate microbial activity such as soil moisture, pH, and temperature (Shaviv, 2001; Comerford, 2005). Experiments by Long and Windsor (1960) found that the shorter chain ureaform, methylene-diurea, was mineralized too quickly (90% in two weeks) to be used as a slow release fertilizer whereas the long chain, trimethylene-tetraurea, was much more slow acting releasing 85% nitrogen in 26 weeks.

One example of a commercially available ureaform is Nitroform[®] produced by Agrium Inc. The product guaranteed minimum analysis specifies that powdered Nitroform[®] contains 38% TN, 5% urea (readily available), 8% slowly available water soluble and 25% water insoluble nitrogen.

2.4.1.3 Isobutylidene Diurea IBDU (32% N)

IBDU is similar to urea formaldehyde although it contains only about 32% nitrogen of which 90% is water insoluble (Shaviv, 2001). The utilization of IBDU is less dependent of microbial activity than urea formaldehyde. Rather, the release rate is due to hydrolysis in water and as such, the rate of mineralization is heavily dependent on the soil moisture content (Shaviv, 2001; Barker and Bryson, 2007). Because there is little emphasis on microbial degradation, degradation of IBDU occurs readily in cold environments albeit hydrolysis is accelerated with higher temperatures and pH.

2.4.2 Phosphorus

A number of potential phosphorus sources were investigated as part of the development of the oleophilic fertilizer. Again, one of the key selection characteristics was to identify a lipophilic phosphorus source that would be ideal in a saturated high energy environment. Most phosphorus fertilizers are obtained from mined phosphate rock which, in some unique production situations, can be used as a direct phosphorus source if the soils are distinctly acidic. However, most crops require a readily available water soluble source such as superphosphate or di/mono-ammonium phosphate.

2.4.3 Bioremediation Specific Nitrogen and Phosphorus Sources

A number of nutrient sources that have been identified and tested for application in bioremediation scenarios may be suitable for use as an oleophilic biofilter fertilizer. Olivieri *et al.* (1978) tested a variety of different nitrogen and phosphorus sources and their capacity to degrade a crude oil. Two of the more promising nitrogen compounds identified in the study were ethyl allophanate (21.2% N) and phenyl hydantoin (15.9% N) which are characterised as lipophilic nitrogen sources. The former compound was thought to be a more promising nutrient source as it could be easily synthesized from cheap chemicals and contained more nitrogen than the latter. With respect to phosphorus, soybean lecithin was identified as the most promising bioremediation nutrient of all the sources tested. The full results of this study are shown in Figure 2.

Figure 2 Effect of Various Nutrient Sources on the Biodegradation of Crude Oil (Olivieri *et al.*, 1978)

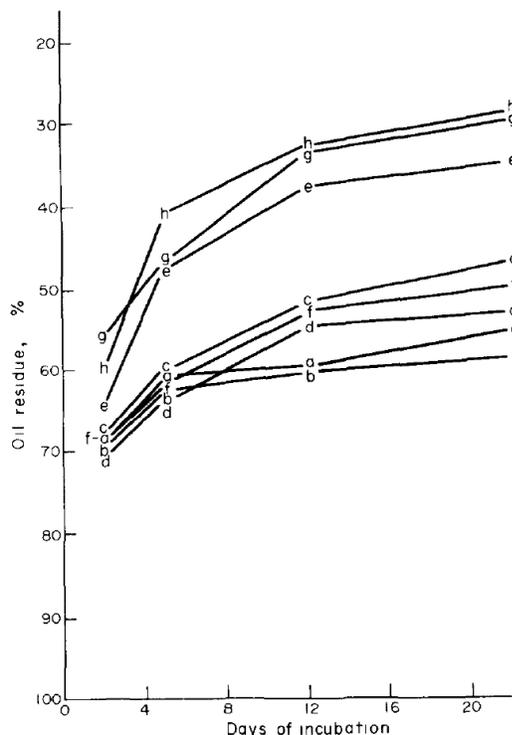


Fig 1 Effect of different sources of phosphorus in the biodegradation rate of Basra crude oil *Phosphorus sources*, (a) Flasks without addition of nutrients, (b) flasks poisoned by $HgCl_2$, (c) octyl phosphonate, (d) dibutyloctyl phosphonate, (e) decyl phosphonate, (f) tributyl phosphate, (g) K_2HPO_4 , (h) lecithin

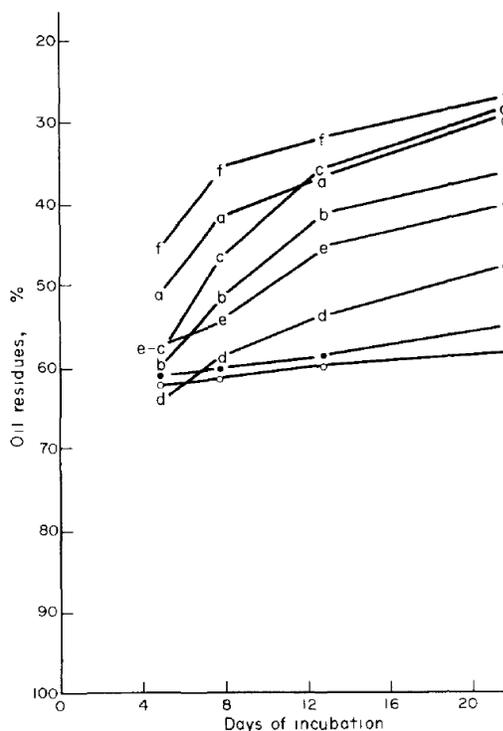
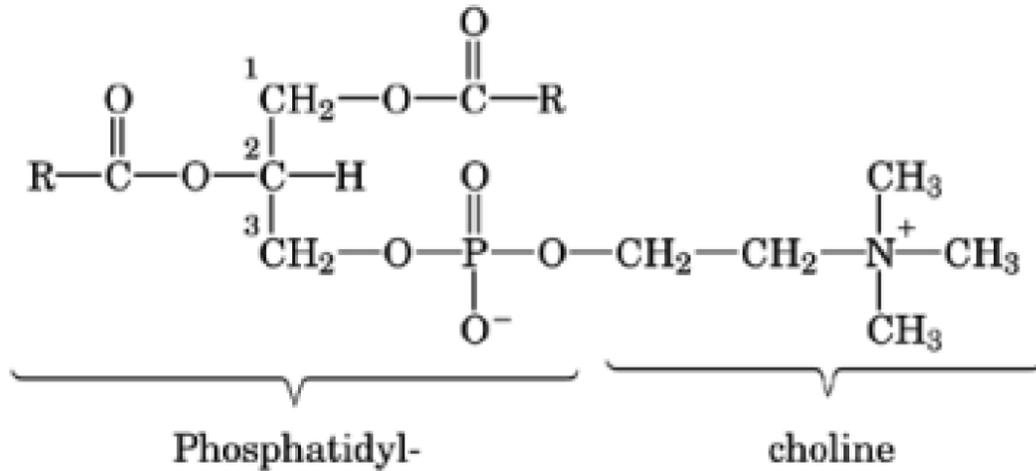


Fig 2 Effect of different sources of nitrogen in the biodegradation rate of Basra crude oil *Nitrogen sources* (a) phenyl hydantoin, (b) butyl hydantoinate, (c) ethyl allophanate, (d) dodecyl urea, (e) phenylacetyl urea, (f) NH_4Cl , (●) flasks without addition of nutrients, (○) flasks poisoned by $HgCl_2$

Soybean lecithin, also known as L-a-phosphatidylcholine is a natural mixture of glycerophospholipids that are non-toxic and a fat soluble natural source of phosphorus (Olivieri *et al.*, 1978). Soybean lecithin contains a cationic choline head and as such, nitrogen is a product of its hydrolysis as inferred by its structure shown in Figure 3.

Figure 3 Soybean Lecithin Structure (Wendal, 2000)



In a similar study designed to distinguish the optimal oleophilic nutrients to support oil biodegradation, Atlas and Bartha (1973) found that paraffinized urea demonstrated the best performance of all the nitrogen fertilizers tested. With respect to phosphorus, the same study found that octyl-phosphate and iso-octyl-phosphate supported the most rapid oil degradation of all the sources investigated.

It is important to emphasize that the nutrients that demonstrated the most effective bioremediation results in the preceding reviewed studies by no means implies that they are well suited for application in a biofilter media. However, because the nitrogen and phosphorus sources stimulated hydrocarbon degrading bacteria there is potential that these nutrients would also be palatable to the soil micro-biota that play an important role in soil biogeochemical dynamics.

2.4.4 Soluble and Slow Release Fertilizers Review

Commonly used water-soluble nutrient products include mineral nutrient salts (e.g. KNO_3 , NaNO_3 , NH_4NO_3 , K_2HPO_4 , MgNH_4PO_4), and numerous commercial inorganic fertilizers.

They are typically applied in the field through the spraying of nutrient solutions or spreading of dry granules. These compounds have a high water solubility which ultimately reduces their effectiveness in open systems as they are rapidly diluted and exfiltrated from the system (Zhu *et al.*, 2004). Furthermore, the addition of salts increases the mobile nitrogen and phosphorus in the soil exacerbating nutrient transport in the soil (Rosenberg *et al.*, 1996). When ammonium salts of strong acids are used to grow biomass, the pH of the medium typically decreases with increased growth (Rosenberg and Ron, 1996). Upon decreasing pH, hydrogen ions can compete for select sorptive sites thereby facilitating the leaching process. As previously mentioned, soils with a high sand content have a lower nutrient holding capacity than most clay and loam based soils, emphasizing the need for a controlled release fertilizer in biofilter applications.

Slow release or controlled release fertilizers are readily available nutrient products normally in solid forms that consist of either relatively insoluble nutrients or water-soluble nutrients coated with hydrophobic materials such as paraffin or vegetable oils. Slow release fertilizers are those from which nutrient release into the environment occurs in more or less of in a controlled fashion. These slow release nutrients have potential for application in biofilter media however, it is difficult to control their release rate pattern and duration such that optimal nutrient concentrations are maintained in the interstitial pore water over prolonged periods (Nikolopoulou *et al.*, 2007; Zhu *et al.*, 2001; Shaviv, 2001). The principal mechanisms affecting the control of nutrient release in these fertilizers include the continuity and thickness of the hydrophobic coat, as well as ambient conditions such as moisture content, water temperature, wetting and drying, freeze thaw cycling and biological activity rather than the actual plant needs (Shaviv, 2001; Olivieri *et al.*, 1978).

2.5 Drying Oils Review

The polymerization, or curing, of the oleophilic fertilizer to the sand fraction of the soil media has potential implications that may undermine its suitability in biofiltration media. Ideally, applying the hydrophobic coating exclusively to the sand fraction of the biofilter media will only have a minimal effect on the soil's water retention properties. Sands inherently have poor water retention properties demonstrating high saturated hydraulic conductivity and low field capacity. However, if the fertilizer does not sufficiently harden on the sand prior to blending with the other soil constituents, the potential exists for the fertilizer to transfer onto the organic fraction of the media reducing the soil's water retention capacity. This loss would be beyond that expected from the water holding capacity of the sand fraction alone. While some decline in water retention is to be expected, significant reductions may undermine the use of hydrophobic fertilizers in biofilter soil which already have minimal plant available water. Should sufficient polymerization of the nutrient enriched oil not occur under natural circumstances alone, additional processes may need be explored such as chemical amendments and heating in order to increase the rate of polymerization to the sand.

As previously mentioned, one of the primary concerns with using an oleophilic fertilizer in a soil medium is the rapid biodegradation of the oil due to its fatty acid composition, and high content of organic carbon. It is unclear what affect the autooxidation or curing of the oil fraction of the fertilizer will have on slowing the decomposition process.

The literature review identified only one experiment that was similar in nature to the methods undertaken in this study. Suri and Datta (1995) synthesized a N:P:K ammeline by heating a mixture of urea, superphosphate and muriate of potash in addition to preparing a

urea fertilizer coated with linseed oil. The study compared the effect of the two synthesised fertilizers on the biomass yield of maize when compared to a control and urea fertilization alone. The linseed oil coated urea was prepared in 2:1 proportions respectively and left to dry for 45 days. The resultant mixture was brown, lumpy and sticky and demonstrated a nitrogen release rate of 19.4% in 7 days at 30.3°C in water. The results of the experiment showed that urea coated with linseed oil fertilizer had the highest significant increase in dry matter yield over the control at 116%; whereas the maize treated with urea alone increased the yield by only 50.6%. Furthermore, the linseed coated urea illustrated a 15.7% decrease in soil nitrogen loss when compared to a urea control thereby further illustrating the slow release nature of the fertilizer and greater resistance to nitrification.

2.5.1 Tung Oil and Linseed Oil

Two drying oils were considered in the fabrication of the study fertilizer. Tung oil - also known as China Wood oil - is prepared by removing and pressing the seeds of several species of Aleurites trees and has been used for centuries in China as a coating for wood objects. The second oil, linseed oil, is perhaps one of the most widely used and studied drying oils. It is derived from flax seeds and is comprised of linoleic and linolenic fatty acids with the former as the main constituent (Poth, 2002). Both linseed and tung oils retain a number of properties that make them desirable as a base for the oleophilic fertilizer. Foremost, they are categorized as drying oils which are able to form a stable thin hydrophobic film by reaction with atmospheric oxygen. They also have high solubility in a variety of solvents, are of low cost and are physiologically safe (Poth, 2002).

In order to distinguish the most optimal base for the study fertilizer, insight into the drying reaction with respect to the type of oil was required. The hardening of drying oils is well studied given their extensive use in paints since the 15th century; yet the reactions are complex and not yet completely understood (Lazzari and Chiantore, 1999; Poth, 2002).

These oils have common traits in that they are generally triglycerides with fatty acid esters that contain two or more double bonds. After undergoing alcoholysis, the remaining unsaturated fatty acid esters dictate the drying properties of the oil (Wheeler, 1950).

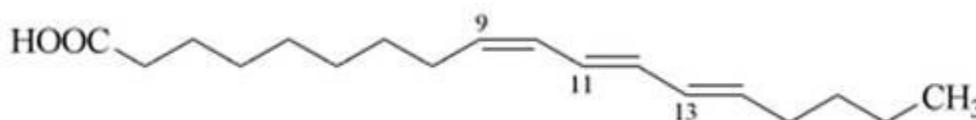
Alcoholysis refers to the transesterification between an alcohol and the fatty acids of triglycerides; a reaction that may be catalyzed with the help of enzymes such as lipases.

Unsaturated fatty acids may vary in two important respects that influence their ability to auto-oxidize; that is the number of double bonds present and their conformation with respect to each other - also referred to as the degree of conjugation (Wheeler, 1950). Oils can be defined based on their iodine value, which refers to the grams of iodine required to saturate the double bonds of 100 g of oil. The iodine value is often used to determine the degree of unsaturation within a fatty acid. The higher the iodine value the higher the degree of unsaturation or double bonds in the molecule. Generally, compounds with an iodine value greater than 140 are considered as drying oils, although such demarcations have been assigned somewhat arbitrarily (Shahidi, 2005). The polymerizing reactions of drying oils can be influenced by the presence of inhibitors and catalysts which shall be discussed at greater length in the following section.

The primary component of tung oil is α -eleostearic acid, a conjugated triple bonded cis, trans, trans-9,11,13-octadecatrienate. The molecular structure of α -eleostearic acid shown in Figure 4; however, pure drying oils may contain mixed esters of α -eleostearic, linoleic and

linolenic acids that all differ slightly in the drying process (Wexler, 1964; Wheeler, 1950). Tung oil contains about 80% α -eleostearic, 4% linoleic, 3% linolenic, 8% oleic, 1% stearic, and 4 % palmitic acid (Thomas, 2000). Two geometrical isomers of α -eleostearic acid occur naturally and all three are readily converted to a higher melting all trans isomer known as β -eleostearic acid (Gunstone, 1967).

Figure 4 α -Eleostearic acid (cis, trans, trans-9,11,13-octadecatrienate)



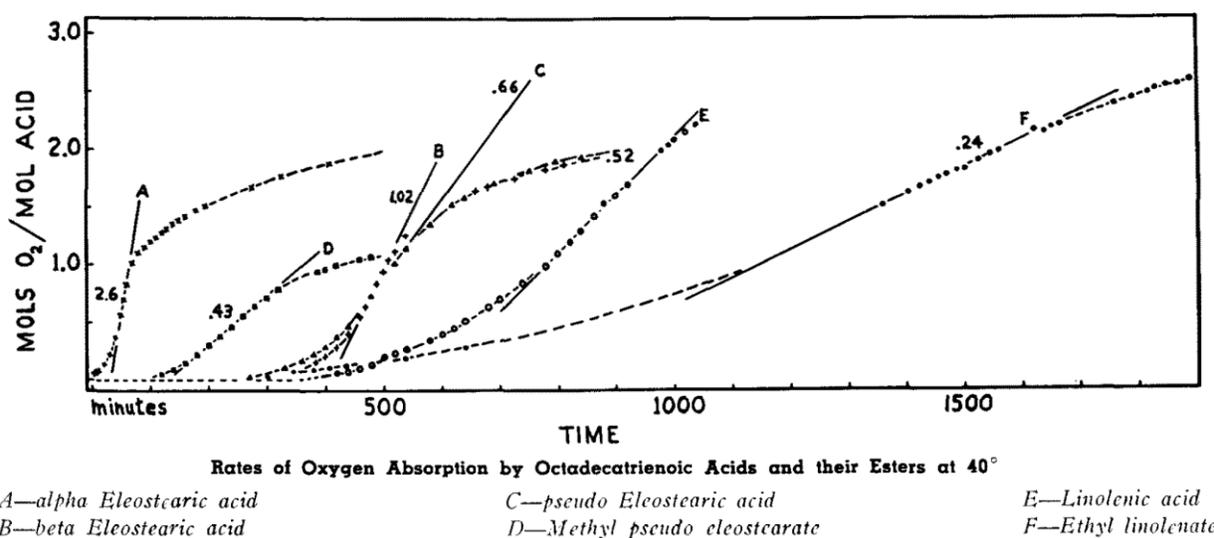
α -Eleostearic acid, a poly unsaturated fatty acid, has three double bonds that are partly or fully conjugated which results in a more reactive or rapid drying than that of an unconjugated systems such as linoleic and linolenic acids; the principal esters found in linseed oil. As such, the oxygen uptake necessary to dry α -Eleostearic acid is lower than that of linseed oil at 12 wt% to 16 wt% absorbed respectively (Poth, 2002; Wheeler,1950). Thus, tung oil quickly forms a skin on the surface at only 5 wt% oxygen absorption and because less oxygen is absorbed, the viscosity of the oil increases at a faster rate (Shahidi, 2005).

2.5.2 Autooxidation

Film formation of drying oils is a complex reaction sequence that is directly related to the chemical reactivity of the double bonds within the fatty acids that absorb oxygen, produce free radicals and subsequently cross link with adjacent fatty acids to couple radicals and form a polymeric network (Lazzari and Chiantore, 1999). The spontaneous reaction between oxygen and the fatty acids - referred to as autooxidation - occurs with unsaturated fatty acids with more than two double bonds in the molecular structure (Poth, 2002). The rate of oxygen

absorption for various drying oils is presented in Figure 5. The main reactions involved in the drying process differs slightly subject to the fatty acid ester but typically includes the formation of hydroperoxides or cyclic peroxides followed by their degradation and ultimately their cross linking (Wexler, 1964). The overall process is complex as both reactions have many intermediates that transpire simultaneously (Privett, 1959).

Figure 5 Octadecatrienoic acids oxygen absorption with time (Myers *et al.*, 1941)

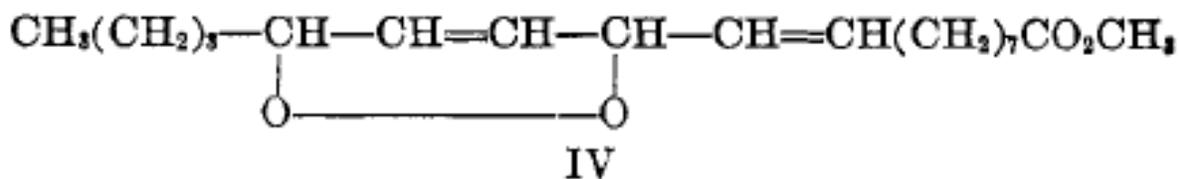


Initially, an induction period (time required prior to initial oxygen uptake) must transpire whereby oxygen uptake increases over time in order to overcome the presence of natural antioxidants such as tocopherols (Lazzari and Chiantore, 1999; Poth, 2002). In certain cases, the induction period may not result exclusively from the presence of inhibitors but rather may be observed as an inherent energy barrier in the chemical reaction leading to peroxide formation (Wexler, 1964). It is important to note that the reaction mechanism differs between conjugated and non-conjugated systems with the former not forming hydroperoxides to the extent of the later (Wheeler, 1950; Poth, 2002; Wexler, 1964).

An understanding of the autooxidation process has been derived from simpler compounds such as methyl oleate. The primary reaction is known to involve the hydroperoxidation of the methylene group adjacent to the olefinic center and occurs via a free radical chain reaction (Gunstone, 1967). The initiation of the oxidative chain reaction involves attack by oxygen on double bond system resulting in the formation of a peroxidized compound corresponding to the formula R1-O-O-R2 and the peroxides, in turn, can oxidize another substance (Poth, 2002; Swern, 1961). Throughout oxidation the double bonds remains intact albeit they have been shown to be displaced from their original location (Wexler, 1964). Furthermore, a conformational change from cis to the more stable trans conformation transpires.

Similar to methyl oleate, the autooxidation of α -eleostearic acid forms what is believed to be predominantly cyclic peroxides albeit non-cyclic peroxides have also been suggested as a reaction intermediate (Wexler, 1964; Shahidi, 2005). Evidence exists that the cyclic peroxide formation is by 1,4 or 1,2 or 1,6 addition of oxygen to the conjugated double bond as shown in Figure 6 which depicts the 1,4 addition. The isomerisation that occurs is uncertain but is thought to involve the displacement of the conjugated system (Brod *et al.*, 1939).

Figure 6 1, 4 Addition to Methyl Elosterate (Wexler, 1964)



Succeeding formation, peroxide degradation occurs albeit the mechanism is far from settled (Privett, 1959). Reactions that have been established are contingent on the reaction

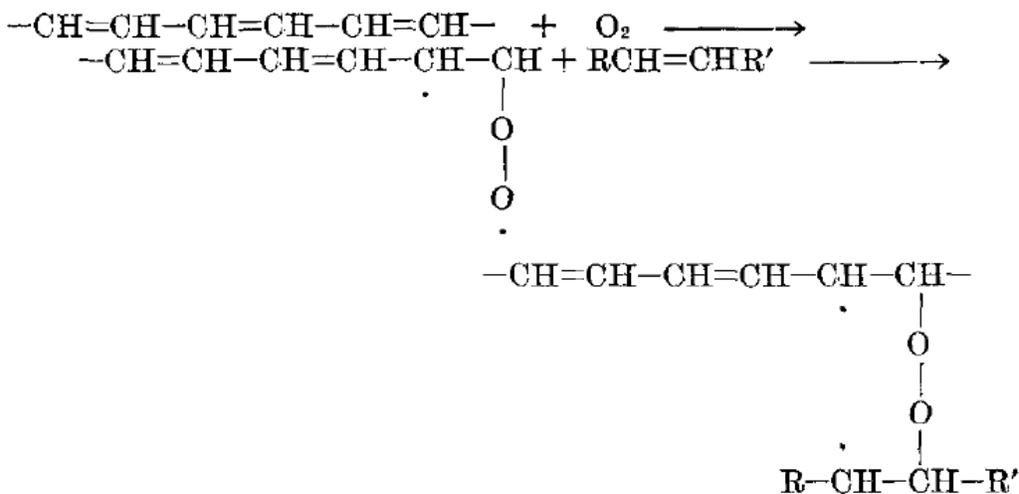
conditions however, peroxide decomposition is understood to be one of the most important polymer forming reactions in oxidative polymerization (Privett, 1959).

The decomposition rate of methyl linoleate hydroperoxides have been demonstrated to follow a first order reaction. That is, the log of the peroxide value yields a linear function over time upon decomposition at 80°C (Wexler, 1964). Furthermore, the thermal decomposition reaction rate of methyl linoleate hydroperoxide is also subject to the initial hydroperoxide concentration in that the rate of decomposition increases with increasing peroxide concentration (Wexler, 1964). This latter property is indicative of the autocatalytic nature of the reaction. While the formation of peroxides occurs readily, decomposition of the peroxides eventually exceeds the rate of formation such that a maximum peroxide value is attained and declines (Gunstone, 1967).

The peroxides react with allylic methylene groups or thermally dissociate to give radicals, initiating a radical chain reaction mechanism, forming polymers via carbon-carbon or carbon-oxygen bonds. Due to the easy 1, 4 addition of radicals to conjugated double bonds, formation of the carbon-carbon bridges is preferred (Poth, 2002). However, upon comparison of conjugated and non-conjugated isomers of 10,12 linoleate oxidation of the conjugated isomer demonstrated no increase in peroxide and the disappearance of the double bonds was proportional to the oxygen absorbed suggesting carbon-oxygen linkages (Swern, 1961). It is at the double bond centers where the cross linking occurs between molecules and the coupling of radicals formed during the decomposition of unstable peroxides leads to the formation of cross links between molecules (Lazzari and Chiantore, 1999). The polymers formed are

predominately dimers although molecules as large as tetramers have been identified (Wexler, 1964).

Figure 7 Possible Mechanism for the Oxidation of Methyl Eleostearate



2.5.2.1 Temperature and Drying Kinetics

The effect of temperature on reaction kinetics is complex and differs contingent on the starting reactants. In general, when the peroxide decomposition is performed under relatively low temperatures, cross-linkages are demonstrated to be predominantly formed from carbon oxygen links (Wexler, 1964). In the case of methyl eleostearate, carbon carbon bonds have been demonstrated to form at temperatures as low as 37°C. Conversely, reactions carried out at relatively high temperatures (100°C) in an inert nitrogen based atmosphere, yielded products that demonstrated carbon-carbon bonds, or less likely, oxygen-carbon bonds (Wexler, 1964). At conditions slightly higher than room temperatures it is suggested that the drying reactions are not appreciably modified and simply transpire at an accelerated rate (Lazzari and Chiantore, 1999).

2.5.2.2 Drying Catalysts

The rate at which oil dries may be increased with the aid of driers, or catalysts, that increase the rate of formation and decomposition of hydroperoxides. Catalysts can be classified into two groups. The first group of metal driers include compounds such as cobalt lead and manganese which increase the rate at which oils dry. Other metals, not as active as the aforementioned, include copper; chromium, iron and tin amongst others. This group may be defined as being susceptible to oxidation from hydroperoxides formed from the initial drying reactions and participate in the drying reactions (Wexler, 1964). The second class of driers include compounds such as calcium and zinc that do not have defined mechanisms (Wexler, 1964). It is believed that these metals hold a participatory role that is physical or mechanical in nature such as facilitating the mobility or solubility of the driers (Wexler, 1964).

With respect to the first class of metal catalysts, the mechanism of action is uncertain but one possibility is that the metals facilitate the oxygen transfer and reactivity (Wexler, 1964). For instance, the association of the unfilled metal orbitals with the oxygen molecule can enhance its activity during the attack on an activated methylene group (Wexler, 1964). Alternately, the metal ion could react directly with the double bond of the fatty acid to form a radical which subsequently may form a hydroperoxide that initiates autooxidation. Irrespective of the mechanism, kinetic studies have demonstrated a decrease in induction period for methyl linoleate when catalyzed by manganese or cobalt. Driers have also demonstrated participation in the decomposition of peroxides through various mechanisms that are also temperature dependant.

Chapter Three: Methods and Materials

The research undertaken for this study was limited to laboratory experiments whereas future efforts may entail field level investigations. The experimental design is discussed in the following sections.

3.1 Oleophilic Fertilizer Ingredients

As discussed in Section 2.2.2, commercially available oleophilic fertilizers were scrutinized for potential applicability in this study; however, a number of shortcomings were identified. These products were either of a proprietary nature with aspects of their composition undisclosed; they were pre-inoculated with bacteria or they contained various surfactants and/or emulsifiers that were deemed inappropriate for use as a biofilter soil amendment. Upon evaluation of the background review, and accounting for practicalities such as cost and availability, the oleophilic fertilizer synthesized was comprised of: tung oil as the curing and oleophilic fraction, soybean lecithin as the lipophilic phosphorus source and Nitroform® as a slow release nitrogen source. While potassium is required as a macronutrient to support plant growth it has been omitted from the fertilizer composition at this time as it is of little concern from a surface water quality perspective.

3.1.1 Phosphorus Source

Soybean lecithin ($C_{12}H_{24}NO_7P$) is a natural mixture of phospholipids consisting phosphatidyl-choline, phosphatidyl-ethanolamine, and phosphatidyl-inositol that is used for a wide variety of applications. Soybean lecithin is a natural lipophilic source of phosphorus that is insoluble in water and soluble in fatty acids. Soybean lecithin with the oil removed was purchased from VWR International, LLC. The weight percent of phosphorus in soybean lecithin

is 9.52% as shown in Table 5. Soybean lecithin was selected as the oleophilic fertilizer's phosphorus source due to its lipophilic characteristics and the favourable results established in the bioremediation studies by Olivieri *et al.* (1978) discussed previously. Furthermore, soybean lecithin is an inexpensive and widely available product.

Table 5 Soybean Lecithin Molar Mass

Element	Mass	Molar Mass	Weight Percent
C ₁₂	12.01	144.12 g	44.30%
H ₂₄	1.01	24.19 g	7.44%
N	14.01	14.01 g	4.31%
O ₇	16.00	122.00 g	34.43%
P	30.97	30.97 g	9.52%
<i>Sum</i>		<i>325.30 g</i>	<i>100%</i>

3.1.2 Nitrogen Source

A proprietary type of urea formaldehyde, Nitroform[®] was provided by Agrium Inc. for use in this study. Nitroform[®] was selected for the fertilizer synthesis due to its slow release characteristics, low cost and easy availability. Nitroform[®] is a slow release nitrogen fertilizer composed of 38% TN of which 5% is urea nitrogen, 8% is slowly available water soluble nitrogen and 25% water insoluble nitrogen. The 8% slowly available water soluble nitrogen is composed of methylene-diurea (C₃H₈N₄O₂) and dimethylene-triurea. Nitroform[®] is designed to elicit nitrogen availability for up to 22 weeks at 26.7°C. Ethyl allophanate was also considered as the oleophilic fertilizer's nitrogen source however, a reliable supplier of the compound could not be found.

3.1.3 Fertilizer Base / Drying Oil

Of the drying oils evaluated tung oil was deemed as the best suited for the fertilizer synthesis. Due its high degree of conjugation tung oil is one of the fastest drying and heat polymerizing oils with an iodine value ranging from 160-180 (Wheeler, 1950; Poth, 2002). The tung oil will give the study fertilizer its oleophilic properties as well as cure the fertilizer to the sand fraction of the soil media. 100% pure tung oil was purchased from Lee Valley Tools in Calgary, Alberta. As with the Nitroform® and soybean lecithin fertilizer constituents, tung oil is also readily available, low cost and is non-toxic.

3.2 Oleophilic Fertilizer Recipe

A number of typical landscape fertilizers were reviewed in order to establish common nitrogen to phosphorus fertilizer ratios. Starter fertilizers tend to demonstrate higher phosphorus content than regular fertilizers with nitrogen to phosphorus ratios in the order of 10:20 or 20:30. The phosphorus and potassium content reflected in the fertilizer ratio are typically expressed as the amount of oxide in the form of P_2O_5 (phosphorus oxide) and K_2O (potassium oxide) rather than the quantity of nutrient in its elemental form (Shaviv, 2001). Nitrogen is the exception in that it is commonly expressed as its mass equivalent. Because phosphorus is expressed in the form of P_2O_5 , the actual mass percent of elemental phosphorus is 43.6% of the noted ratio. For example, a fertilizer with a 10:20 nitrogen to phosphorus ratio is actually an 10:8.6 elemental nitrogen and phosphorus ratio. While there are synergistic effects when applying multiple nutrient types in concert and at particular ratios, the study fertilizer was designed with approximate 1:1 nitrogen to phosphorus elemental ratio for ease of data interpretation throughout the experiments.

A 7:1 lecithin to Nitroform[®] ratio is required to produce a fertilizer with a 1:1 nitrogen to phosphorus ratio, given the elemental composition of the compounds. More specifically, soybean lecithin = 9.52% phosphorus and 4.31% nitrogen, and Nitroform[®] = 38% nitrogen, therefore a 1:7 ratio of the two compounds yields a 68.2 to 66.6 molar nitrogen to phosphorus ratio, or approximately 1:1.

A fertilizer application rate of 5 lbs/1000ft² (24.41 g/m²) was applied to the experimental soil columns to represent a relatively high degree of fertilization. This application rate is slightly greater than the 3.5 lbs phosphorus per 1000 ft² application rate recommended by the City of Calgary Standard Specifications for Landscape Construction (2011b). While the City guidelines make no recommendation for biofilters specifically, 5 lbs/1000ft² phosphorus was also generally identified as a high phosphorus application rate for various Albertan agricultural practices and crop types.

The soil columns employed in the experimental apparatus have a 50.8mm inner diameter with a corresponding area of 0.002 m². A 50.8 mm column diameter was based on a column sized 50 times greater than the largest soil particle (1.2mm). Pursuant to a 5 lbs/1000ft² soil application, the total nitrogen and phosphorus required per column is 24.41 g/m² × 0.002 m² = 0.0488 g. Enough oleophilic fertilizer was fabricated to produce five columns albeit only two replicates were actually employed in the study. Thus, a total of 0.0488 g/column × 5 columns = 0.244 g of nitrogen and phosphorus was required. This amounts to a phosphorus fertilization of 43 mg/Kg which is well below the 100 mg/Kg maximum soil phosphorus content recommended by FWAB 2008. As previously established a 1:7 Nitroform[®] to soybean lecithin ratio is required to maintain an approximate 1:1 elemental nitrogen to phosphorus ratio therefore;

Soybean Lecithin

Phosphorus Content

$$\begin{aligned} &0.244 \text{ g phosphorus required} \div 9.5\% \text{ (mass \% phosphorus in lecithin)} \\ &= 2.563 \text{ g lecithin} \end{aligned}$$

Nitrogen Content

$$\begin{aligned} &2.563 \text{ g lecithin} \times 4.3\% \text{ (mass \% nitrogen in lecithin)} \\ &= 0.111 \text{ g} \end{aligned}$$

Nitroform[®]

$$\begin{aligned} &0.244 \text{ g nitrogen required} - 0.111 \text{ g N in the lecithin fraction} \\ &= 0.133 \text{ g additional nitrogen required} \\ &0.133 \text{ g additional nitrogen required} \div 0.38 \text{ (mass \% nitrogen in Nitroform[®])} \\ &= 0.351 \text{ g of Nitroform[®]} \end{aligned}$$

Therefore, the theoretical required masses to add to the tung oil base are 2.563 g soybean lecithin and 0.351 g of Nitroform[®] to achieve a fertilizer application rate of 5 lbs nitrogen and phosphorus per 1000 ft² per column.

In addition to being representative of recommended fertilizer application rates, it is prudent to confirm that the masses of nitrogen and phosphorus are indeed sufficient enough to elicit a nutrient leaching response that is anticipated to fall within the detection limits of the analytical methods. The lower limit of the phosphorus analytical method used in this study is 0.02mg/L. Assuming the fertilizer provides a response over 2 years period, and based on an approximate contributing stormwater runoff volume of 16.4 L, which shall be discussed at greater length in the forthcoming sections, the initial mass of fertilizer required to be added to the columns is given by $0.02 \text{ mg/L} \times 16.4\text{L} = 0.32 \text{ mg}$ phosphorus. The amount of phosphorus added to the oleophilic fertilizer test columns far exceeds 0.32 mg and the average nutrient concentration of column effluent should be adequate enough to provide a detectable response.

3.3 Oil to Sand Polymerization

In order to establish the optimal quantity of oil to apply to the sand fraction of the soil media, multiple independent batches of sand and tung oil were constructed with varying volumetric ratios. The objective of the batch tests was to find the least amount of oil that would fully coat the sand whilst leaving very little residual superfluous oil; thus mitigating unnecessary carbon input (BOD) into the soil media. The bulk of the biofilter soil was composed of 20/40 filter sand obtained from Target Products Ltd. in Calgary. The physiochemical properties of this product are shown in Table 6 and Table 7 as distinguished by the supplier.

Table 6 Typical 20/40 Filter Sand Sieve Analysis – Percent Passing

Sieve Opening Size		Cumulative % Passing
ASTM	Metric	
No. 16	1.18mm	100
No. 20	0.85mm	90-100
No. 30	0.60mm	20-45
No. 40	0.42mm	5-10
No. 50	0.30mm	0-1
Effective Size, d_{10} mm		0.45-0.55
Uniformity Coefficient, d_{60}/d_{10}		<1.6

Table 7 **Typical 20/40 Filter Sand Chemical Analysis and Properties**

Chemical Compound		Typical Value, % Weight
Silica	SiO ₂	93.2 -93.6
Alumina	Al ₂ O ₃	3.6 - 4.6
Iron Oxide	Fe ₂ O ₃	0.3 – 0.35
Calcium Oxide	CaO	0.25 – 0.65
Magnesium Oxide	MgO	0.08 – 0.15
Sodium Oxide	Na ₂ O	0.75 – 0.85
Titanium Oxide	TiO ₂	0.1 maximum
Grain Shape		Sub Rounded
Bulk Density		1520-1600 kg/m ³

In order to achieve a more homogenous distribution of the tung oil throughout the sand, two methods were evaluated to decrease the oil’s viscosity prior to blending. The first approach attempted to thin the oil by diluting it with ethanol. Once thinned, the fertilizer precursors would be added to the oil and the mixture blended with the sand fraction of the soil. The sand would then be spread out in a thin layer to allow the ethanol to evaporate. Pure ethanol was purchased from VWR International LLC. and was added in equal proportions to the tung oil. The solution was mixed on high with a magnetic stir bar and after twenty minutes, the solution was still largely heterogeneous and the ethanol approach to thin the oil was abandoned.

The second approach to decrease the oil’s viscosity was to warm it over a hot plate on a low temperature setting. Heating temperatures were kept low in order to minimize the effect on oil polymerization. Shortly after heating, the oil demonstrated an appreciable qualitative

decrease in viscosity. The warmed oil was added to individual petri dishes, each containing a different volumetric oil to sand ratio that ranged from 1:1 to 1:50 and the mixtures were left to dry at room temperature. After two weeks of monitoring, the 1:10 oil to sand mixture was deemed the most appropriate ratio as it completely covered and cured to the sand with little residual oil left in the petri dish. Again, the least amount of oil was selected to minimize surplus carbon input into the soil.

3.4 Oleophilic Fertilizer Fabrication and Sand Enrichment

0.49 L of tung oil was warmed on low with a hot plate for approximately 10 minutes. 2.5618 g and 0.3511 g of Lecithin and Nitroform® were added to the oil respectively, and the solution was stirred with a magnetic stir bar for an additional 20 minutes. 4.9 L of 20/40 filter sand was added to a clean 20 gallon bucket in three lifts with the warmed oleophilic fertilizer added evenly between lifts to facilitate uniform distribution throughout the sand. The pail was sealed and shaken vigorously for 1 hour to ensure thorough mixing. The oleophilic fertilizer enriched sand was removed from the pail and spread about 3 cm thick in foil lined metal trays, covered and then left to dry for a period of 6 weeks. The sand and oil mixture cured into a fairly solid block which was then crushed with a mortar and pestle and passed through an ASTM No. 10 sieve to ensure particle size uniformity. The resulting product was an oleophilic fertilizer enriched sand that was used to blend with the other biofilter soil constituents.

The density of the oleophilic fertilizer enriched sand was substantially lower (68.8%) than the original 20/40 filter sand used in its fabrication. The lower density of the enriched sand may be attributed to the addition of the tung oil with a lower density than the sand and/or the polarity of the fatty acids in the tung oil repelling the sand particles. This change in sand density

had implications on the amount of nitrogen and phosphorus per weight of enriched sand. The mass of nutrients in the enriched sand is given by;

Total Weight of Nutrient Enriched Sand

$$\begin{aligned} 4.9 \text{ L Sand} &= 7645.1 \text{ g} \\ 0.49 \text{ L Tung Oil} &= 460.6 \text{ g} \\ \text{Total Weight} &= 7645.1 \text{ g} + 460.6 \text{ g} = 8105.7 \text{ g} \end{aligned}$$

Phosphorus Content

$$\begin{aligned} 2.562 \text{ g Lecithin} &= 0.244 \text{ g Phosphorus} \\ &= 0.244 \text{ g P} \div 8105.7 \text{ g} \\ &= 3.01 \times 10^{-5} \text{ g P/g Enriched Sand} \end{aligned}$$

Nitrogen Content

$$\begin{aligned} 2.562 \text{ g Lecithin} &= 0.110 \text{ g Nitrogen} \\ 0.351 \text{ g Nitroform}^{\circledR} &= 0.134 \text{ g Nitrogen} \\ &= 0.110 \text{ g} + 0.134 \text{ g} = 0.244 \text{ g Nitrogen} \\ &= 0.244 \text{ g N} \div 8105.7 \text{ g} \\ &= 3.01 \times 10^{-5} \text{ g N/g Enriched Sand} \end{aligned}$$

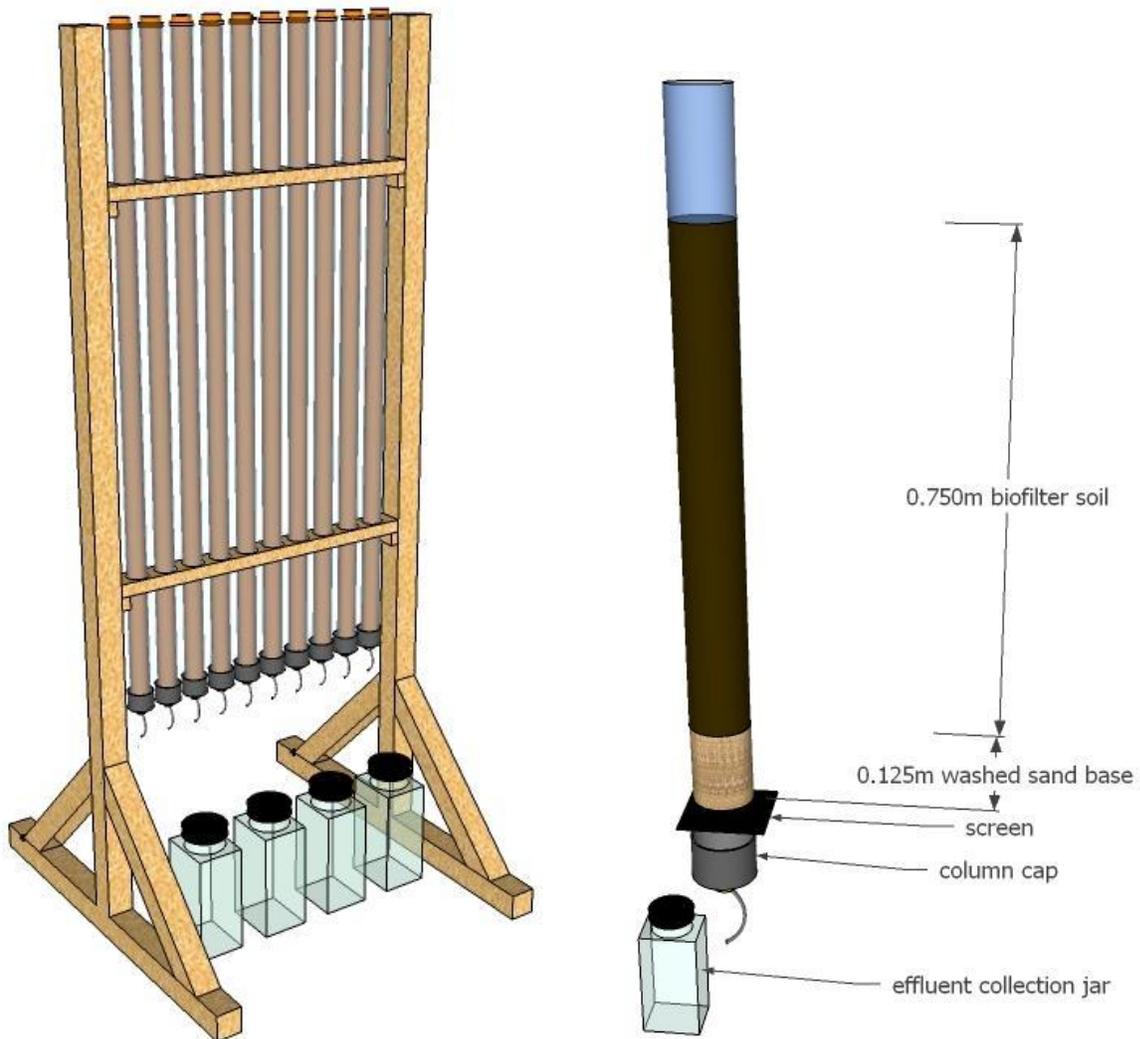
, to follow later in the report, provides full details of the soil media compositions and identifies the change in density between the amended and un-amended sand.

3.5 Description of Experimental Apparatus

The study apparatus – constructed specifically for the experiments - was comprised of 6 acrylic tubes with a 50.8mm internal diameter that were fastened vertically in a customized stand as shown in Figure 8. Each of the acrylic columns was internally coated with sand (adhered by contact cement) to help prevent the dosing water used to flush the columns from preferentially flowing along the column wall rather than infiltrating through the soil media. The column bottoms were fitted with a mesh screen and a 12.5 cm washed sand base to help prevent the soil from washing out of the column. The columns were capped with an ABS pipe

reducer that connected to a short length of vinyl tubing. The pipe reducer created an air gap to ensure unrestricted flow of the effluent prior to collection in glass sample jars via the vinyl tubing. The glass sample jars were acid washed with a weak HCl solution prior to commencing the experiment to prevent contamination from previous uses. Please see Figure 8 for full details of the experimental columns components.

Figure 8 Study Apparatus and Columns Components



The columns were filled to a soil media depth of 0.75 m with a corresponding volume of 1.5 L. A 0.75 m biofilter soil depth is in accordance with the design recommendations given by Westhoff Engineering Resources Inc. (2007) and Hsieh and Davis (2005).

3.6 Biofilter Soil Recipe

The biofilter soil recipe for the majority of the test columns was comprised of 65% washed sand, 25% sphagnum peat and 10% vermiculite by volume. This general baseline soil mix was selected based on review of the biofilter soil specifications presented in Table 4. *No Name* Sphagnum peat, a product of Canada, was purchased from Superstore in Calgary Alberta. Peat is partially decomposed organic material that has been formed from plant detritus in water in the absence of air. The chemical composition of peat is variable and chemically complex but it is highly organic composed of humic and fulvic acids and cellulose (Clark and Pitt, 1999). Schlutz® Vermiculite purchased from Home Depot in Calgary was added to the soil media as the addition of about 10% by volume to the soil media has been shown to help maintain hydraulic conductivity (FAWB, 2009). The proportions of the soil blend were consistent across all the test columns with the exception of the compost column wherein a portion of the peat was substituted with compost. Table 8 provides full details the soil media compositions.

Table 8 Biofilter Soil Media Composition and Amendments

Material	Soil per Column (L)	% of Biofilter Soil	Volume Required (L)	Density (g/L)	Weight (g)
Sand	1.5	65%	0.98	1560.23	1529.02
Oleophilic Fertilizer Enriched Sand	1.5	65% (oleophilic columns only)	0.98	1073.38	1051.92
Peat	1.5	25% (10% in compost column)	0.38	416.88	158.41
Vermiculite	1.5	10%	0.15	97.55	14.63
Compost	1.5	15% (compost column only)	0.23	411.57	94.66

The experimental setup included two columns with their soil media constructed with the oleophilic fertilizer enriched sand whereas the remaining four columns utilized un-amended 20/40 filter sand. Despite the discrepancy in density between the two sands, an equivalent weight (1052 g) was used in all columns whether they were composed of the oleophilic fertilizer enriched sand or the un-amended 20/40 filter sand. In so doing, the un-amended sand columns had a slightly reduced volume with respect to the columns constructed with the oleophilic fertilizer enriched sand.

The mass of sand used to fabricate the oleophilic fertilizer biofilter soil, along with the nutrient concentration outlined in Section 3.4, yields the total mass of nutrients included in each of the test columns. That is, 1052 g of nutrient enriched sand amounts to approximately 31.62 mg of nitrogen and phosphorus within the oleophilic fertilizer test columns. The mass of nutrients included in the other test amendments were prepared in accordance to the mass of

nutrients in the oleophilic fertilizer columns. Due to the decrease in sand density, the fertilizer application rate was less than the previously specified 5 lbs/1000ft².

Five different biofilter column types were analyzed in the experiments with two replicate columns prepared for the oleophilic fertilizer amendment for a total of six study columns. Only two replicates were prepared for the oleophilic fertilizer column due to the limited project budget for materials and analytical reagents. In order to maintain consistency across the columns the biofilter soil media was prepared in independent batches with each of the soil constituents measured by weight and thoroughly mixed by hand prior to loading into the columns. The six columns were prepared as follows, pursuant to the quantities outlined in Table 8.

Negative Control Column – The negative control column was composed of sand, peat and vermiculite.

Positive Control Column – A positive control was included in the study to confirm that the experimental procedure is competent in observing the effect of nutrient leaching from the columns. The positive control column was composed of sand, peat and vermiculite as well as soluble nitrogen and phosphorus sources. Ammonium nitrate (NH₄NO₃) and potassium phosphate (K₂HPO₄) were added to the positive control in accordance with the mass weight of the nutrients in the oleophilic fertilizer columns. The mass percent of elemental nitrogen in ammonium nitrate is 35.00%. Similarly, the elemental phosphorus in potassium phosphate is 17.78%.

The theoretical mass of nutrients to be added to the Positive Control column corresponded to the existing mass of nutrients present in the oleophilic fertilizer columns. That is, to yield 31.64 mg of nitrogen and 31.62 mg phosphorus in the Positive Control column, 90.4mg of ammonium nitrate and 84 mg potassium phosphate is required. 89.19 mg of ammonium nitrate and 177.16 mg of potassium phosphate was added to the sand peat and vermiculite soil blend and mixed by hand prior to loading into the column.

Oleophilic Fertilizer Columns – Two replicate columns were prepared with the nutrient enriched sand, peat and vermiculate pursuant to the quantities outlined in Table 8.

Lecithin & Nitroform[®] - Soybean lecithin and Nitroform[®] were added to a column in order to isolate any possible effects the tung oil fraction in the oleophilic fertilizer may have on nutrient leaching. The lecithin and Nitroform[®] were blended with the sand, peat and vermiculite to yield nitrogen and phosphorus concentrations pursuant to the mass of nutrients in the oleophilic fertilizer columns. That is, 332.14 mg of soybean lecithin and 45.58 mg Nitroform[®] would be required to incorporate 31.62 mg of phosphorus and 31.64 mg of nitrogen. The actual masses of lecithin and Nitroform[®] added to the sand peat and vermiculite soil blend was 331.90 mg and 45.45 mg respectively.

Compost Column – A test column that incorporated compost in its composition was included in the study to loosely represent what is currently specified in a number of stormwater management guidelines for biofilter media as per Table 4. The compost used in this study was Sea Soil which is a composted fish and forest fines soil from Vancouver Island. Sea Soil has a pH of 6.5, is free of heavy metals and contains the following guaranteed minimum analysis of macronutrients: 2.1-.16-.05.

The compost column was composed of 15% compost, 10% peat, 65% sand and 10% vermiculite as per the soil specifications shown in Table 8. As previously noted, the compost column differs in its composition than the other test columns in that only 0.15L (62.53g) of peat was incorporated into the blend.

A complete summary of the total mass of nutrients added to each of the test columns is shown in Table 9.

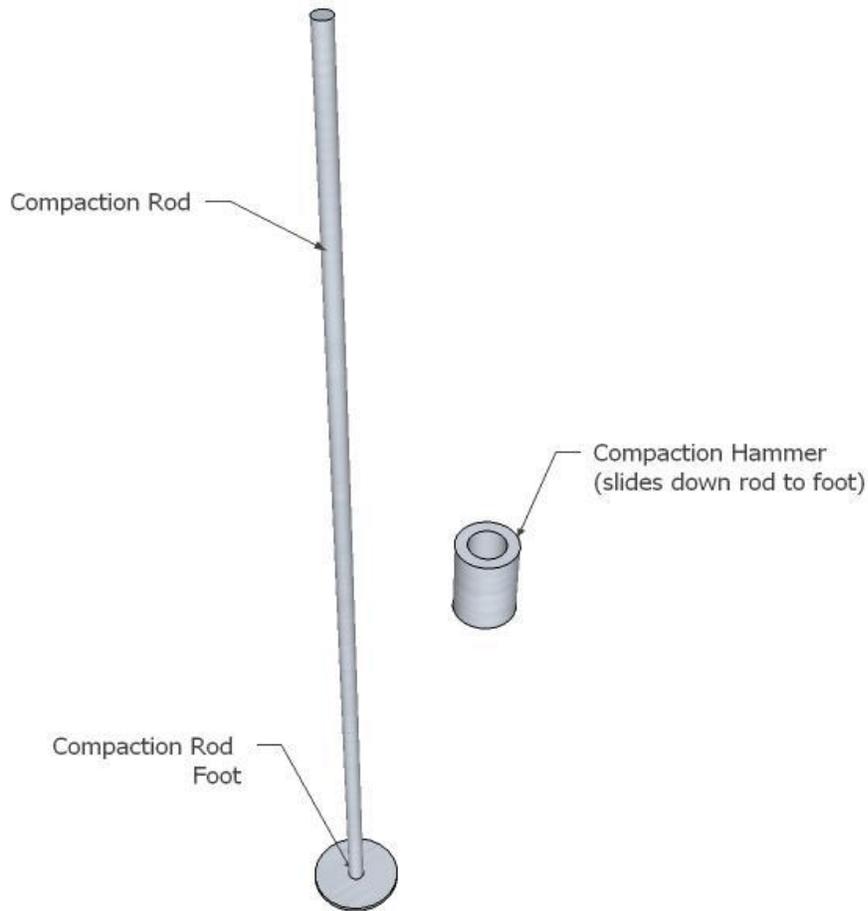
Table 9 Mass of Nitrogen and Phosphorus Added to Test Columns

Column	Phosphorus (mg)	Nitrogen (mg)
Negative Control	0	0
Positive Control	31.50	31.22
Oleophilic Fertilizer (1)	31.62	31.64
Oleophilic Fertilizer (2)	31.62	31.64
Lecithin & Nitroform [®]	31.53	31.55
Compost	37.34	1123.14

3.7 Column Packing

A sub base of 0.25 L of washed 20/40 filter sand was added at the bottom of each column to prevent the soil from washing through the mesh screen. The biofilter soils were added to the test columns in 25 cm (0.5 L) lifts and compacted between each lift with a custom fabricated compacting rod. The rod design had a compaction foot with <2 mm clearance between the foot and the interior column wall and a 460.7 g anvil that was repeatedly dropped 15 times per lift onto the compacting rod's foot from 0.305 m above the top of the soil. A schematic of the compacting rod is shown in Figure 9.

Figure 9 Compaction Rod Schematic



The test columns were equally compacted to help standardize the effect on the saturated hydraulic conductivity amongst the columns. The compaction methodology was based largely on ASTM F1815-06 (2010) which is the biofilter soil evaluation standard recommended by FAWB (2009). This method is applicable for sand based soil mixes and defines a compaction technique to exert a total potential energy across the cross sectional area of the soil. A total potential energy of $3.03\text{J}/\text{cm}^2$ exerted across the soil core is said to produce a degree of compaction comparable to severely compacted putting green (ASTM, 2010). This specified level of compaction was used as a barometer to provide an appreciation of the

compaction being applied in the experiment. The compactive effort applied to each of the study columns is given by;

$$\text{Compactive effort} = \frac{\left(\frac{\text{blows}}{\text{lift}}\right) (\text{lifts})(\text{hammer wt.})(\text{gravity})(\text{height})}{\text{area of column}}$$

$$\text{Compactive effort} = \frac{(15)(3)(0.406 \text{ kg})(9.81 \text{ m/s}^2)(0.305\text{m})}{20 \text{ cm}^2}$$

$$\text{Compactive effort} = 2.73 \text{ J/cm}^2$$

The degree of compaction applied to the study columns was less than that specified for a severely compacted putting green. This was not only due to the lower application of energy, but also because the soil moisture content of the soil was not brought to field capacity prior compaction as specified in the ASTM method. It is emphasized that there was no intention to replicate a degree of compaction in the test columns equivalent to a severely compacted putting green. Rather, the underlying tenet was to apply a standardized level of compaction across all of the study columns.

3.8 Dosing and Sampling Regime

The experiments were carried out at the University of Calgary's Civil Engineering Hydraulic Laboratory. The annual dosing volume was based on a biofilter sized to 10% of the contributing catchment area (100% impervious) that receives 420mm of precipitation per year. 420mm is the mean annual precipitation depth for Calgary region. Each column has an area of 0.002m² and the total volume of runoff applied to each column is given as;

$$\frac{0.002 \text{ m}^2}{10\%} \times 0.42 \text{ m} \frac{\text{precipitation}}{\text{year}} = 8.4 \text{ L} \frac{\text{runoff}}{\text{year}}$$

The columns were flushed with tap water a total of eight times over a period of eleven weeks with the volume of each dose being 4.2 L, or equivalent to six months of estimated

runoff. As such, the total dosing volume of 33.6 L is loosely representative of four years of synthetic runoff application in the Calgary region. It would be prudent to evaluate the dosing regimen based on a worst case scenario. In Calgary, June is the heaviest month of precipitation with a mean 79.8 mm of rainfall. Based on the total dosing volume of 33.6 L, this runoff application is representative of 21.4 consecutive months of the heaviest rainfall typically experienced in the Calgary region.

The temporal distribution of the runoff applications were completely random with inter-event periods ranging from 3 days minimum to 20 days maximum. Tap water was used to dose the columns and was left in a large open top container for at least 3 days prior to application. This resting period provided the water time to reach consistent dissolved oxygen levels as well as degrade a small amount of the residual chlorine. For each dosing event, water from the storage container was measured and added directly into the top of each column. The application water initially ponded on the surface of the soil and slowly infiltrated through the media. After the full 4.2L runoff application had infiltrated into the soil, the columns were left for approximately three hours to allow the soil to drain as close to field capacity as practically possible. The entire column effluent was collected in individual glass bottles from which aliquots were taken for further water quality analysis.

3.8.1 Water Quality Sample Analysis

Water quality samples were analyzed from the column effluent for six of the eight synthetic runoff applications. More specifically, the first five events were sampled until the effluent concentrations stabilized. Two more dosing events (one year annual equivalent runoff) were run un-sampled, followed up by the eighth and final event for which water quality analysis

was undertaken. Phosphorus, in the form of TP (SM 4500 P-E, HACH Method 8190 - PhosVer[®] 3 with Acid Persulfate Digestion Method) and nitrogen, in the form of TN (HACH Method 10071 – Persulfate Digestion Method) were analyzed at the University of Calgary Civil Engineering Laboratories. Both the TN and TP samples were analyzed with a HACH D2800 spectrophotometer. HACH Method 8190 converts organic and inorganic forms of phosphates to the reactive orthophosphate form by heating the sample with acid and persulfate. Orthophosphate subsequently reacts with molybdate and ascorbic acid yielding a blue colour measurable by the spectrophotometer (HACH, 1998). HACH Method 10071 converts all forms of nitrogen to nitrate with an alkaline persulfate digestion. Nitrate then reacts with chromotropic acid under acidic conditions to yield a yellow colour quantifiable by spectrophotometer (HACH, 1998).

A standard solution was included with every set of samples and the analysis followed the same procedures as the column effluent samples in order to confirm that the analytical method was indeed adequate for the test samples. Two different standard solutions, 1.00 mg/L and 3.00 mg/L were utilized as the TP quality control, and a 10 mg/L standard solution was used for the TN samples. For each sampling event, replicate effluent samples were analyzed from at least one of the test columns and replicates were often analyzed from multiple columns within the same sample set. In some cases, up to six samples from the same column's effluent or standard solution were analyzed for quality assurance purposes.

3.8.2 Dissolved Oxygen Sample Analysis

Based on the preliminary results from the first few sampling events, it was thought that better experimental resolution may be ascertained from dissolved oxygen measurements.

Dissolved oxygen measurements were collected as a barometer of biomass activity in the columns and commenced after the second sampling event. Dissolved oxygen measurements were taken from the dosing water prior to column application as well as from the column effluent after filtering through the biofilter soil media. Measurements were collected with an YSI 550A dissolved oxygen instrument in accordance with the methods outlined in the operation manual (YSI Environmental 2006). The meter was placed directly in the collection jars that were used to capture the column effluent and was gently oscillated until the reading was relatively stable. The dissolved oxygen probe was washed with ultra-pure water prior to transferring to a different column's collection jar in order to mitigate cross-contamination of the effluent.

Chapter Four: Laboratory Results and Discussion

From the outset it should be noted that the following results, obtained in a controlled laboratory setting, may not be representative of biofilter performance in the field. For example, the synthetic stormwater dosing regimen applied in this study was random and therefore not representative of natural hydrologic conditions; nor is the controlled conditions under which the experiments were conducted representative of the natural environment and all its external influences. Despite the limitations, the information derived this experiment is indeed valuable as it unquestionably improves our understanding of nutrient leaching from a biofilter soil media and various fertilizer amendments.

Data acquired from the experiment was interpreted in the following manner:

- Basic observations were derived from the raw water quality including the four year mean effluent TP and TN concentrations;
- The inter-event variability , reflected in the standard deviation, is indicative of the steady release characteristics of the fertilizer amendments;
- The mass balances and the inter-column variability thereof were used to identify significant differences between the amendments;
- The cumulative mass of nutrients leached as a percent of the mass initially applied to the test column, and;
- The potential effects of the wetting and drying regime on nutrient leaching.

4.1 Raw Water Quality Data

The water quality data presented hereinafter was collected from the experiment as discussed in Section 3.8. In brief, the column experiments were designed to simulate and

evaluate four years of equivalent nutrient leaching from a biofilter soil and estimate the magnitude of effects caused by fertilizer amendments. Eight synthetic stormwater events were applied to the study columns over an eleven week period, of which six were sampled for water quality analysis. The analysis included TP and TN measurements as well as dissolved oxygen measurements.

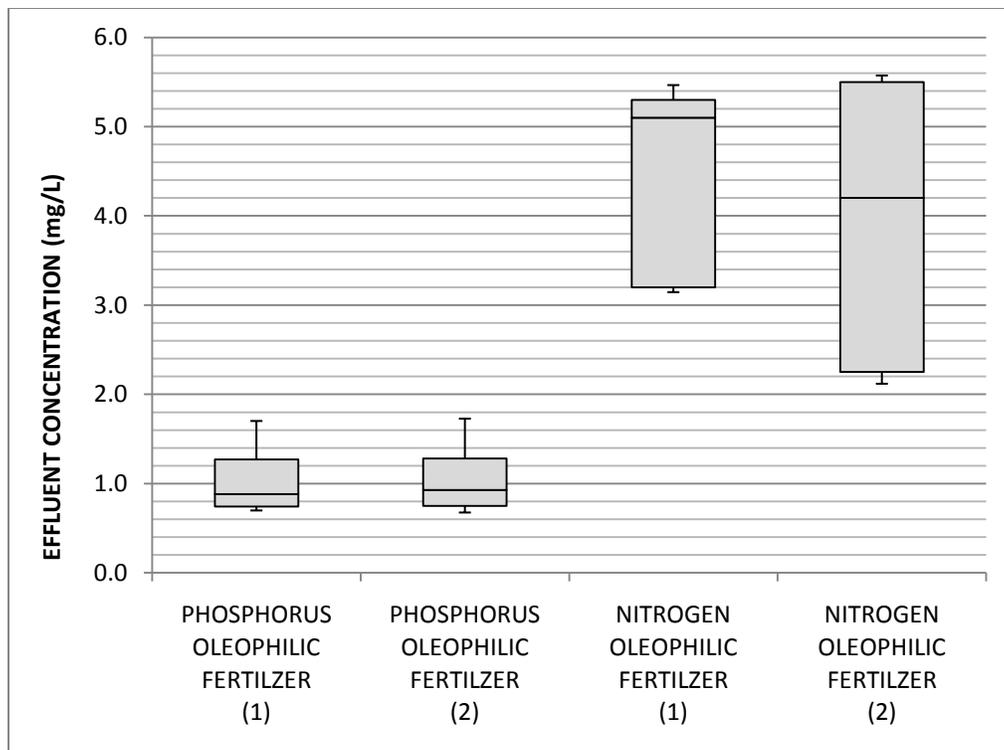
JMP® v.9.0 statistical analysis software by SAS Institute Inc. was utilized to interpret the raw data. The Shapiro-Wilk test for normality was run to confirm that the data was not normal, which was also visually apparent from the histogram distributions of the data. The non-parametric Wilcoxon Rank Sum Test was then used to rank and compare the effluent concentrations between each of the test columns. Non-parametric tests are useful to test whether the means or medians are the same across groups for non-normally distributed data (SAS Institute Inc., 2010). Due the small number of samples taken from each column per event, the statistical analysis demonstrated generally poor powers and the statistical interpretation was largely excluded from the discussion. Similarly, paired responses for each event could not be interpreted due to the small number of samples taken for each event. The full results of the Wilcoxon Rank Sum Test have been included in Appendix B for review.

The statistical difference between the two replicate Oleophilic Fertilizer columns was of particular interest as the results thereof distinguished how best to treat the data from these columns for further interpretation. Furthermore, the performance of the replicate columns alluded to the homogeneity of the fertilizer distribution amongst the sand fraction of the soil as well as the subsequent blending with the other biofilter soil constituents. No statistical difference was found between the replicate Oleophilic Fertilizer amendment columns

($p=0.8967$ and $p=0.9753$ for TP and TN respectively) and as such, the average effluent concentration for the replicates was utilized to represent the Oleophilic Fertilizer amendment effluent concentrations for the particular sampling date. It is noted that the full data set from both replicate columns were used in the statistical interpretation of the data.

A box plot of both the TN and TP effluent concentrations for the replicate Oleophilic Fertilizer columns is shown in Figure 10 for the 4 years of simulated runoff application. The boxes denote the 25th, 50th, and 75th percentiles whereas the whiskers depict the maximum and minimum values.

Figure 10 Oleophilic Fertilizer Effluent Concentration Box Plots



4.1.1 Nitrogen

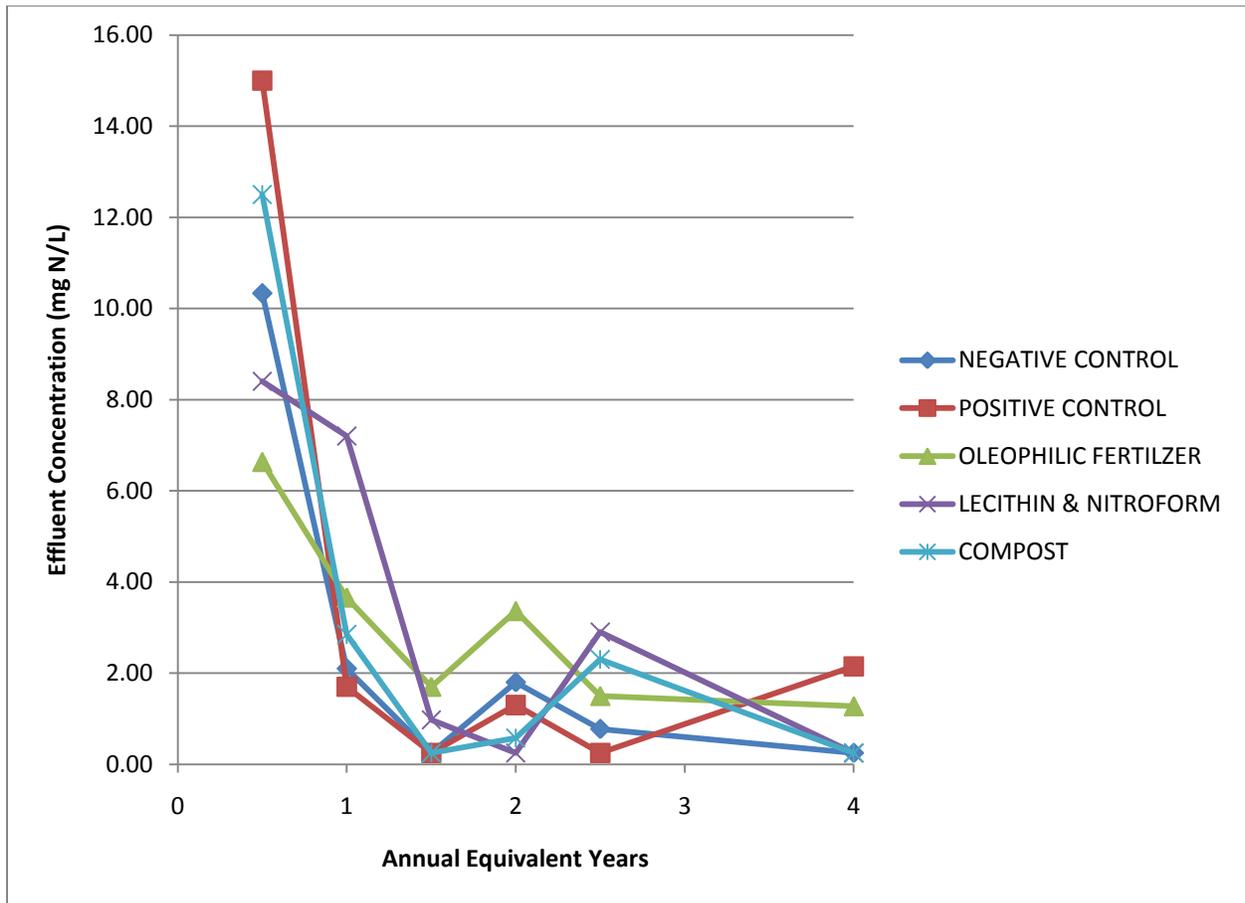
The nitrogen water quality results showed fairly consistent leaching performance and behaviour amongst all the test columns. A summary of the nitrogen raw water quality data

from the six sampled events is presented in Table 10 as well as Figure 11 in which is the graphical representation of the raw data. Some of the TN samples fell below the detection limit for the analytical method (0.5 mg/L) and have been reported as ½ the detection limit (0.25 mg/L) for data interpretation purposes as per the recommendation by Helsel, 1990.

Table 10 Total Nitrogen Effluent Concentrations

Sample Date (Equivalent Years Runoff)	Negative Control (mg/L)	Positive Control (mg/L)	Oleophilic Fertilizer (mg/L)	Lecithin & Nitroform® (mg/L)	Compost (mg/L)
12-Nov-10 (0.5)	10.33	15.00	6.63	8.40	12.50
17-Nov-10 (1)	2.10	1.70	3.66	7.20	2.85
26-Nov-10 (1.5)	0.25	0.25	1.70	0.98	0.25
10-Dec-10 (2)	1.80	1.30	3.36	0.25	0.58
18-Dec-10 (2.5)	0.78	0.25	1.50	2.90	2.30
27-Jan-11 (4)	0.25	2.15	1.28	0.25	0.25
<i>Mean</i>	<i>2.58</i>	<i>3.44</i>	<i>3.02</i>	<i>3.33</i>	<i>3.12</i>
<i>Std. Deviation</i>	<i>3.87</i>	<i>5.71</i>	<i>2.03</i>	<i>3.62</i>	<i>4.73</i>

Figure 11 Total Nitrogen Effluent Concentration Over Annual Equivalent Time



The net release of nitrogen from the study columns is likely due to the significant amount of nitrogen intrinsic to peats as the amount of nitrogen can be considerable. The estimated nitrogen concentration in soils ranges from 0.02% in subsoils to 2.5% for deep peats (Barker and Bryson, 2007). As illustrated in Table 10, the columns amended with the Oleophilic Fertilizer yielded the lowest average TN effluent concentration, and demonstrated the lowest standard deviation of all the fertilizer amendments tested. All other fertilizer amendments leached average TN concentrations higher than the Oleophilic Fertilizer columns in the

following order from lowest to highest; Compost, Lecithin & Nitroform[®] and the Positive Control column.

However, keeping the original starting mass of nitrogen added to the columns in context, the compost column leached substantially less nitrogen than the other fertilizer amendments. That is, the compost amended test column had a starting mass of nitrogen over 350 fold greater than the other test columns and still maintained a comparable average effluent concentration. The initial mass of nutrients added to each of the column amendments are shown in Table 9.

As expected, the Positive Control column, treated with soluble ammonium nitrate, showed the greatest average effluent concentration and leached readily as shown in Figure 11. The Positive Control test column demonstrated the highest initial effluent concentration and dropped to the lowest effluent concentration by the second simulated event. The variability between sampling events, reflected in the high standard deviation, is likely a result of the leachable nature of the ammonium nitrate soil amendment. This implies that the experimental design and methods were indeed adequate to detect the anticipated experimental response.

As shown in Figure 11, all the study columns showed a distinct drop in effluent concentrations after the first simulated runoff event with the Lecithin & Nitroform[®] amendment demonstrating the least substantial drop of all the test columns. While the column effluent TN concentrations initially decreased substantially, they eventually stabilized after 1.5 years of annual equivalent runoff to the end of the testing period. This demonstrates that most nitrogen species do not participate in sorption mechanisms and nitrogen is readily washed from

the growing media. After this initial flush, effluent concentrations may eventually stabilize to levels akin to water quality targets.

While the BBWMP does not have recommended water quality targets for TN specifically, the mean column effluent TN concentrations exceeded the 1.5 mg/L performance objective for nitrate-nitrite in the Central Reach of the Watershed. Despite the early washout, after 1.5 years of equivalent runoff application effluent concentrations appear to have stabilized below the 1.5 mg/L target suggesting that biofilters would indeed be an ideal source control practice to meet nitrogen performance objectives. It is emphasised that the previous statement, and performance data, is predicated on using tap water as the runoff influent.

There are a number of extenuating variables that may affect the release of nitrogen from soil. Hatt *et al.* (2007b) and Hatt *et al.* (2008) found that inter-event time or variable wetting and drying regimes has direct implications on nitrogen release from biofilter soil media. That is, soil drying periods may enhance the aerobic mineralization of organic matter and subsequently release immobilized nitrogen when moisture conditions decrease to a point that induces micro-biota death.

Barton *et al.* (2006) also found that the irrigation regime, both frequency and quantity, had the greatest effect on nitrogen leaching from fertilized coarse textured soils; releasing almost four times more nitrogen under high levels of irrigation. This may be a result of at least some sections of the soil going anaerobic and releasing previously adsorbed nitrogen species (Clark and Pitt, 2001). More specifically, Clark and Pitt (2001) found compost to leach greater amounts of ammonia under anaerobic soil conditions whereas peat was found to release elevated levels of nitrate.

Efforts were made to investigate the antecedent dry days and any correlation to nutrient leaching. Figures were generated from the experimental data that plotted TN concentration from the column effluent vs. the number of drying days between subsequent water applications or antecedent conditions however; no clear trend or relationship was distinguishable. Please refer to Appendix C for full details of the effect of variable antecedent dry days on nitrogen leaching from the study columns.

The experimental columns were designed with an air gap at both the bottom and top and were flushed with oxygen saturated water. As such, it is unlikely that anaerobic conditions developed within the soil column and this was further confirmed with dissolved oxygen measurements taken from the effluent. Furthermore, the columns lacked any vegetation which may help facilitate denitrification due to symbiotic relationships with denitrifying bacteria and biologically active layers that form adjacent to plant roots (Hatt *et al.*, 2007b). In light of the aforementioned circumstances, denitrification was not considered to be a major nitrogen loss pathway and affecting effluent concentrations in the experiment. Ammonia volatilization was also not considered as a significant contributor to nitrogen loss in the study due to the mixing of the fertilizer throughout the soil column with very little surface exposure.

4.1.2 Phosphorus

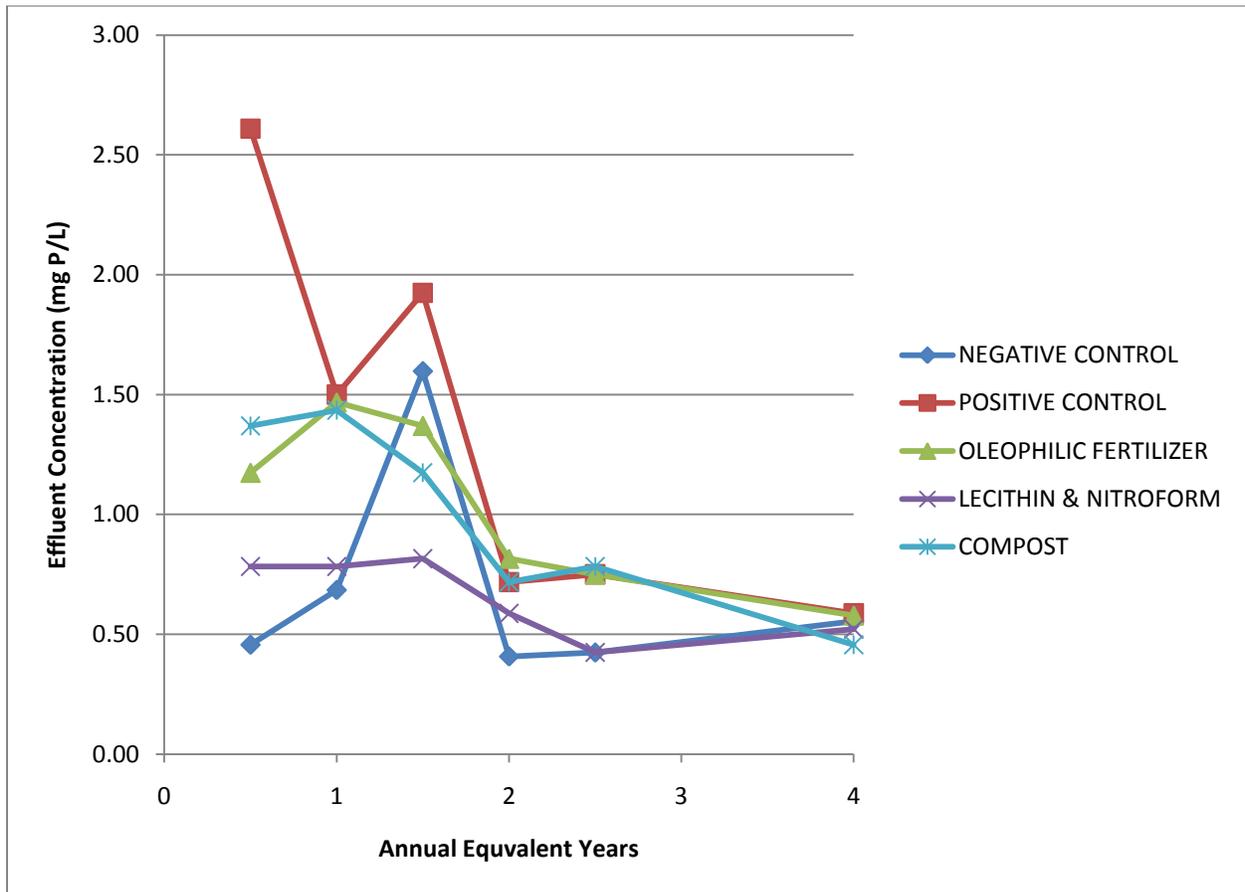
The phosphorus water quality results were moderately different from the nitrogen results. Perhaps the most notable difference was that the TP effluent concentrations were substantially lower than the TN concentrations. Furthermore, the columns demonstrated relatively consistent TP effluent concentrations after each subsequent simulated event, whereas the TN response yielded a large initial flush and concentrations dropped substantially

upon the second runoff application. The consistency of the leaching behaviour is apparent upon comparison between the TP and TN standard deviations from each column. A summary of the phosphorus raw water quality data from the six sampled events is presented in Table 11 as well as in Figure 12 which is the graphical representation of the raw data.

Table 11 Total Phosphorus Effluent Concentrations

Sample Date (Equivalent Years Runoff)	Negative Control (mg/L)	Positive Control (mg/L)	Oleophilic Fertilizer (mg/L)	Lecithin & Nitroform® (mg/L)	Compost (mg/L)
12-Nov-10 (0.5)	0.46	2.61	1.17	0.78	1.37
17-Nov-10 (1)	0.68	1.50	1.47	0.78	1.43
26-Nov-10 (1.5)	1.60	1.92	1.37	0.82	1.17
10-Dec-10 (2)	0.41	0.72	0.82	0.59	0.72
18-Dec-10 (2.5)	0.42	0.75	0.75	0.42	0.78
27-Jan-11 (4)	0.55	0.59	0.58	0.52	0.46
<i>Mean</i>	<i>0.69</i>	<i>1.35</i>	<i>1.03</i>	<i>0.65</i>	<i>0.99</i>
<i>Std. Deviation</i>	<i>0.46</i>	<i>0.81</i>	<i>0.36</i>	<i>0.16</i>	<i>0.39</i>

Figure 12 Total Phosphorus Effluent Concentration Over Annual Equivalent Time



The test column amended with Lecithin & Nitroform[®] demonstrated the lowest mean effluent TP concentration and maintained the lowest standard deviation of all the test columns. The mean TP concentration from the Negative Control column was approximately equivalent to the Lecithin & Nitroform[®] column although the standard deviation, or inter-event variability, was substantially greater for the Negative Control. All other column amendments leached average TP concentrations higher than the Lecithin & Nitroform[®] amendment in the following order from lowest to highest; Compost, Oleophilic Fertilizer and the Positive Control. The Compost and Oleophilic Fertilizer amendments demonstrated approximately equivalent mean

TP effluent concentrations with comparable standard deviations; however, the starting mass of phosphorus initially added to the Compost column was slightly higher than that of the Oleophilic Fertilizer columns as shown in Table 9.

In general, all of the fertilizer amendments tested, including the starting media (Negative Control), demonstrated depreciating TP concentrations with subsequent stormwater events. The Positive Control amendment was the only column to exhibit a lower effluent concentration for the second simulated runoff event whereas all other amendments showed an increase. However, TP concentrations spiked in the Positive Control column for the third synthetic runoff application as it did in the Negative Control column. Possible rationale for the spike in concentrations in these particular columns is unclear.

The TP effluent concentrations did not appear to stabilize as quickly, or as distinctively as they did with the nitrogen results; albeit fairly steady levels were achieved after two years of equivalent runoff application. Despite this, after four years of simulated runoff the effluent concentrations from all the columns far exceeded the 0.028 mg/L BBWMP water quality objectives for TP in the Central Reach of the Watershed. This suggests that these biofilters would not be an ideal source control practice to meet TP performance objectives in the Bow River, particularly given that the study results were ascertained with clean tap water as the influent.

Similar to the nitrogen results, figures were generated from the experimental data that plotted TP concentration from the column effluent versus the number of drying days between subsequent water applications, despite that phosphorus has been previously shown to be unsusceptible to leaching due to antecedent moisture variability (Hatt *et al.*, 2007b; Clark and

Pitt, 2001). In theory, any iron bound phosphorus may be predisposed to desorption under anaerobic conditions. If the ambient conditions change to anaerobic, ferric iron (+3) reduces to the more soluble ferrous iron (+2) and sorbed phosphate ions are released back into the pore water (Ann *et al.*, 2000; Mitsch and Gosselink, 2007; Kadlec and Wallace, 2009). The results from this study distinguished no clear relationship between phosphorus leaching and antecedent dry days as per the Figure shown in Appendix C.

4.2 Mass Balances

It has been suggested that significant limitations exist when interpreting BMP effectiveness from a percent removal perspective (Wright Water Engineers and Geosyntec Consultants, 2007). One of the major limitations with reporting water quality enhancement from this perspective is that the results are very much a function of the influent quality (Roy-Poirier *et al.*, 2010). That is, higher influent pollutant concentrations ultimately yield a 'cleaner' effluent or better percent removal between influent and effluent concentrations. Because this study utilizes a clean influent, percent leached is an applicable performance measure, particularly when interpreted from a mass balance perspective.

In this study, mass leaching refers to the increase in the total mass of nutrients between the inlet and outlet runoff streams passing through the study apparatus columns. This approach is further simplified given that the nutrient concentrations in the tap water used as the synthetic runoff are considered to be nil. To assess nutrient mass leaching from the various biofilter soil amendments the nutrient mass in the effluent was calculated as follows;

$$\sum C_e \times V_i$$

Where;

C_e = the mean effluent pollutant concentration (mg/L) for the dosing event,

V_i = the total inflow volume (L)

The sum was taken over the six sampled events to yield the total mass discharge of nutrients per soil amendment. This approach was considered valid as the columns acted effectively as a closed system wherein no appreciable water losses would be experienced. As such, the influent volume would more or less equal the effluent volume for each runoff event. The mass balances reported in this study have not made assumptions, nor included, the nutrients leached from the two unsampled runoff events. This data could be included by interpolating an effluent concentration from the bracketing sampled events. An estimate of the effluent concentrations for the unsampled events can be quickly inferred from Figure 11 and Figure 12. However, because this study is predominantly concerned with the effects of nutrient amendments with respect to each other and the experimental controls, the inclusion of the two interpolated constants across all columns would provide little additional insight.

The total mass discharge for both TN and TP is presented in Table 12 and Table 13, respectively for each of the soil amendments tested. Furthermore, the mass leaching results were also reported as a percentage of the initial nitrogen and phosphorus added to each column. With the exception of the Compost column, all the experimental test columns encompassed a starting soil media composition consistent with the Negative Control. As such, the mass of nutrients leached from the Negative Control column was deducted from each of the other test columns in order to isolate the effect of each particular fertilizer amendment on effluent quality. This approach is predicated on the uniformity of the baseline biofilter soil

across all test columns. The biofilter media composition of the Compost column was different than that of the Negative Control in that a percentage of the peat was replaced with compost as discussed previously in Section 3.6. For this reason, simply abstracting the mass of nutrients in the Negative Control's effluent from the Compost column may not be appropriate.

4.2.1 Nitrogen Mass Balance

As shown in Table 12, all the fertilizer amendments leached a similar mass of TN over the course of the eight synthetic runoff events. The inter-column standard deviation for the total mass of TN leached was 5.5mg, or about $\pm 7\%$ from the mean (82.3mg) across all the biofilter amendments excluding the Negative Control. This measure is representative of the variability between the fertilizers evaluated. As expected, the Negative Control test column leached the lowest mass of TN followed by the Oleophilic Fertilizer, Compost, Lecithin & Nitroform[®] and the Positive Control in an increasing order. Strictly from a mass discharge perspective, the Oleophilic Fertilizer performed the best out of all the fertilizer treatments. However, keeping the starting mass of nitrogen added to each of the study columns in context, the Compost amendment performed best leaching only 7% of the initial mass of nitrogen applied whereas the Oleophilic Fertilizer columns leached an average of 241%.

With the exception of Compost, all the fertilizer amendments leached well over two fold more nitrogen than what was initially added to each test column. The mass discharge of TN from the Negative Control column demonstrated that that the baseline soil media itself was a significant source of TN leachate, independent of the fertilizer amendments. By subtracting the mass of TN leached from the Negative Control column from the other test columns the effect of the fertilizer amendments on nutrient leaching could be isolated. As shown in Table 12, the

Oleophilic Fertilizer columns leached only 35% of the TN present in the Oleophilic Fertilizer treatment when the leachate contributing from the biofilter media starting materials was neglected. This further suggests that the bulk of the nitrogen found in the effluent was actually sourced from the initial biofilter soil constituents (sand/peat/vermiculite), rather than the actual fertilizer amendment. In addition, it may be unreasonable to isolate the effects of the Compost amendment by omitting the mass leached from the Negative Control as the biofilter soil composition in the Compost column contains less peat than all other test columns.

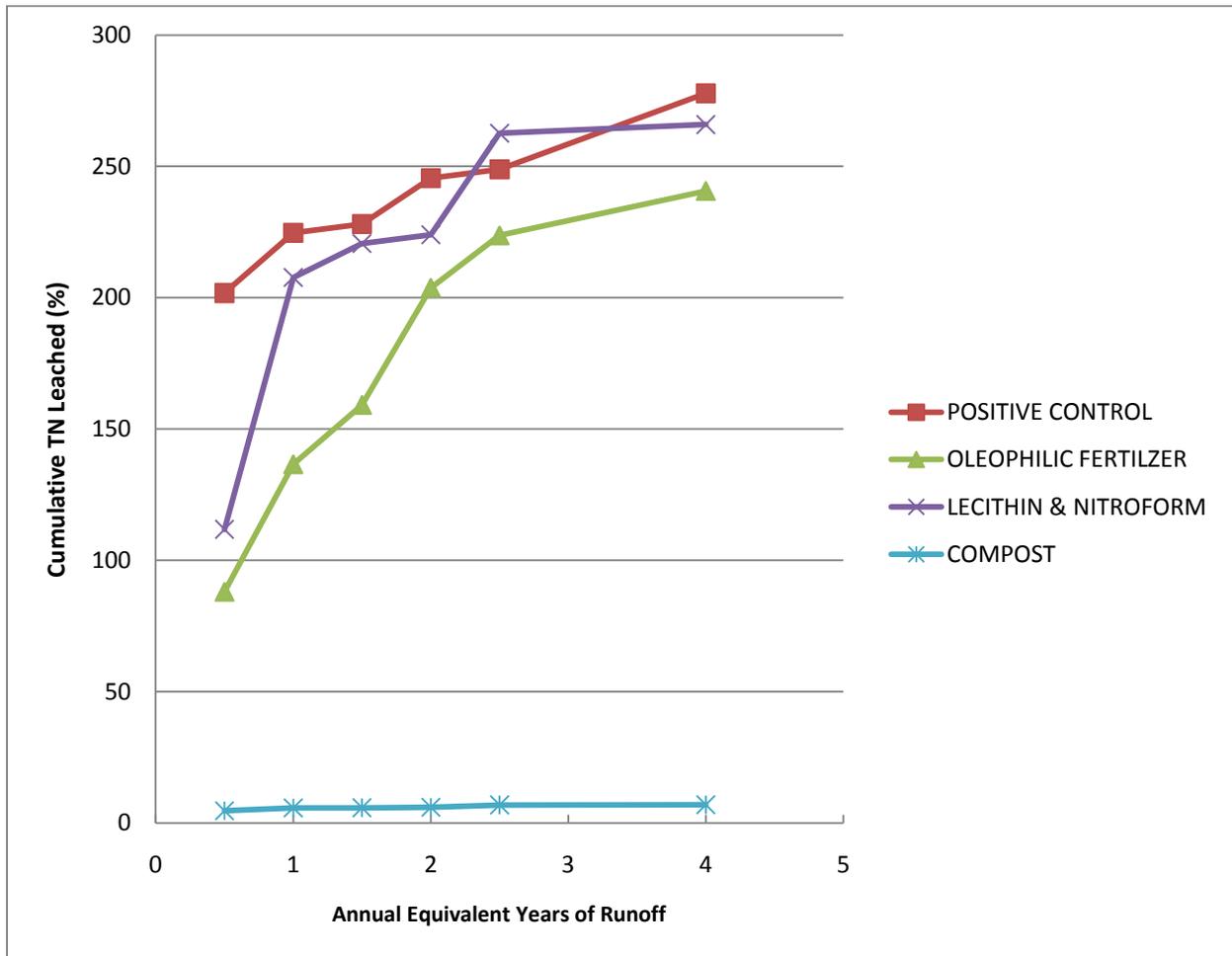
Table 12 Total Nitrogen Mass Balance

	TN Mass Discharge (mg)	TN Mass Discharge as a % of TN Added to Column (%)	TN Mass Discharge (Negative Control Subtracted) (mg)	TN Mass Discharge as a % of TN Added to Column (Negative Control Subtracted) (%)
Negative Control	65.14	-	-	-
Positive Control	86.73	277.8%	21.60	69.2%
Oleophilic Fertilizer	76.14	240.7%	11.01	34.8%
Lecithin & Nitroform®	83.90	265.9%	18.76	59.5%
Compost	78.65	7.0%	13.51	1.2%

As may be inferred from Table 12, the Oleophilic Fertilizer amendment columns leached about 10% less TN than the Lecithin & Nitroform® column. Because the only variation between these two treatment columns was the addition of tung oil, it may be inferred that the polymerized tung oil was indeed effective at controlling or slowing the release of the TN over the duration of the 11 week experiments or 4 years of equivalent runoff. In contrast, the controlled release that may be attributed to the inclusion of the polymerized tung oil was not consistent within the TP results and may undermine this finding. The effectiveness of tung oil on controlling nutrient delivery in the soil shall be discussed further in Section 4.3.

The mass balance results are perhaps best interpreted as the cumulative mass of nutrients leached as a percentage of the initial mass added to the column. It is in this format that the data is most clearly presented and conclusions are most easily identified. Please see Figure 13 for full details of the cumulative mass of TN leached as a percentage of the total mass applied.

Figure 13 Cumulative Nitrogen Leached as a Percent of Initial Mass Applied



The most prominent observation ascertained from the nitrogen results was the distinct difference in leaching from the compost amended column when compared to the other soil

amendments. These results are indicative of the slow release characteristics of nitrogen in soil organic matter and in particular, well humified composts (Lenhart, 2009). Humus fractions such as humin; humic acids, and fluvic acids are the degradation products or microbial residues of organic matter and are more stable than non-humic substances (Barker and Bryson, 2007). Although the mineralization of humus is subject to environmental factors such as moisture content and temperature, mineralization is generally very slow and humic substances contribute little to plant nutrition (Barker and Bryson, 2007; Prescott, 2005; Lenhart, 2009).

There are a number of constraints acknowledged with the experimental design that may have implications for the nitrogen results in particular. The lack of vegetation as part of the overarching biofilter system and the associated biological processes was a significant missing factor as plant assimilation and decay is an important aspect in biofilter nutrient cycling (Davis *et al.*, 2006; Bratieres *et al.*, 2008; Henderson *et al.*, 2007). Because of this, the experimental results are not indicative of nutrient release patterns when vegetation is present which plays an important role in the nitrogen cycle. For instance, biological uptake itself is a long-term removal pathway for nitrogen and plants also facilitate denitrification due to the formation of thin anoxic zone near the roots and by developing symbiosis' with denitrifying bacteria. Another major constraint of the study was working within an experimental time frame. While the results are presented as four years of equivalent runoff data, the experiments were actually conducted over a period of 11 weeks. It is likely that better mineralization, and perhaps greater nitrogen leaching, would be observed after four years of time had passed, particularly from the compost soil amendment.

4.2.2 Phosphorus Mass Balance

As shown in Table 13, the fertilizer amendments leached varying degrees of TP over the course of the eight simulated runoff events. The inter-column standard deviation for the total mass of TP leached was $\pm 7.2\text{mg}$ or about $\pm 28\%$ from the mean (25.3mg) across all the biofilter amendments, excluding the Negative Control. These findings were considerably higher than the inter-column variability demonstrated in the nitrogen results; particularly given that the total mass of TP leached was less than half of that for TN. Overall, the TP mass discharges were significantly less (70%) than the TN leached from the test columns despite the equivalent amount of nitrogen and phosphorus added to each of the fertilizer amendments.

Table 13 Total Phosphorus Mass Balance

	TP Mass Discharge (mg)	TP Mass Discharge as a % of TP Added to Column (%)	TP Mass Discharge (Negative Control Subtracted) (mg)	TP Mass Discharge as a % of TP Added to Column (Negative Control Subtracted) (%)
Negative Control	17.33	-	-	-
Positive Control	33.97	107.8%	16.64	52.8%
Oleophilic Fertilizer	25.85	81.8%	8.53	27.0%
Lecithin & Nitroform [®]	16.44	52.1%	-0.89	-2.8%
Compost	24.93	66.8%	7.60	20.4%

Interestingly, the Lecithin & Nitroform[®] fertilizer amendment demonstrated the lowest TP mass discharge over the six sampled runoff applications and was approximately equivalent to the mass of TP leached from the Negative Control. In an increasing order of TP leached, the Lecithin & Nitroform[®] and Negative Control were followed by the Compost - which had a slightly higher initial mass of phosphorus - and the Oleophilic Fertilizer. As expected, the

Positive Control amendment leached the greatest mass of TP, slightly more than what was initially applied to the column. With the exception of the Positive Control, all the study columns leached less TP than the mass initially added to the fertilizer amendment. These results suggests that the baseline biofilter soil materials were not as significant of a source of TP as they were for TN and reflect the relatively immobile nature of phosphorus in soil (Bolan, 1991).

The Compost amendment leached about 44% more TP than the Negative Control column and it is probable that the compost retained a substantial labile pool of phosphorus that may have been easily desorbed upon flushing. Residual nutrients are almost always associated with composted organic matter (Lenhart, 2009). This is further indicated by the high concentration of TP in the effluent from the first runoff application. These findings are congruent with work by Pitt *et al.* (2001) that found a 50% increase in subsurface flow TP concentrations from a compost amended soil. However, due to the large variability in compost types and experimental design, comparing results between studies can be inherently difficult.

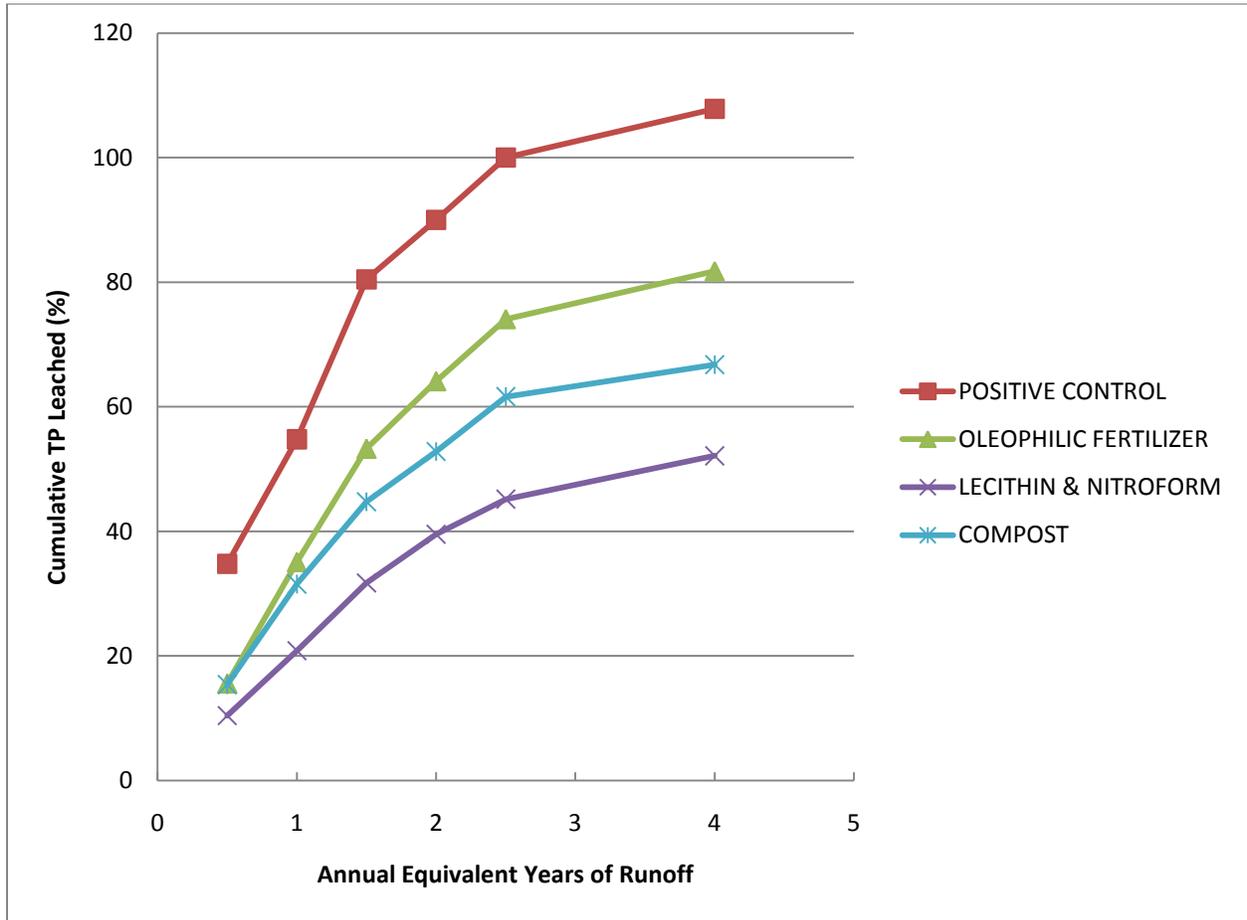
In contrast to the TN results, the Lecithin & Nitroform[®] amendment performed significantly better than the Oleophilic Fertilizer; leaching 30% less TP than what was originally added to the column from a mass balance perspective. This implies that the tung oil was ineffective at controlling TP leaching from the biofilter media and perhaps even expedited its release. A possible explanation for this inconsistency between the nitrogen and phosphorus results shall be discussed in Section 4.3.

Table 13 depicts the mass of TP leached when contributions from the initial starting biofilter media materials are omitted. That is, the Negative Control column was subtracted from the other test columns in order to isolate the effect of the fertilizer amendments on TP leaching

of the initial mass of the amendment when the nutrient contribution from the biofilter starting materials was neglected. As noted previously, the biofilter soil composition in the Compost test column is slightly different than that of the Negative Control and simple omission of the Negative Control TP mass discharge from the from Compost column may not be appropriate; particularly, given that the TN results show the biofilter media starting materials to be a significant source of nitrogen.

The mass balance results are perhaps best reported as the cumulative mass of nutrients leached as a percentage of the initial mass added to the column. It is in this format that the data is most clearly presented and conclusions are most easily identified. Please see Figure 14 for full details of the cumulative mass of phosphorus leached as a percentage of the total mass applied.

Figure 14 Cumulative Phosphorus Leached as a Percent of Initial Mass Applied



4.3 Tung Oil Additive Results

At the onset of the experiment, it was unclear how the polymerization of the tung oil would improve nutrient delivery in the biofilter soil given the propensity of fats to quickly decompose in the presence of soil microorganisms. The results from the first two synthetic runoff events demonstrated that the Lecithin & Nitroform[®] soil amendment leached substantially less TP than the Oleophilic Fertilizer; whereby the only difference between the two amendments was the inclusion of tung oil. Visual observations made through the opaque acrylic columns showed that the oleophilic fertilizer amended soil had developed a ubiquitous

grey colour when compared to the other soil columns. Based on the two preliminary water quality results and the visual observations, it was hypothesized that the soil micro-biota may be capitalizing on the oil-based fertilizer, proliferating, and subsequently expediting TP release.

In order to gauge the reasonableness of the aforementioned hypothesis, dissolved oxygen measurements were taken from the source water as well as the column effluent in order to provide a barometer of the oxygen demand or cellular respiration transpiring in the columns. As shown in Table 14, the Oleophilic Fertilizer columns demonstrated mean dissolved oxygen levels 44% lower than the Lecithin & Nitroform[®] column which excluded the oil. Furthermore, the Oleophilic Fertilizer dissolved oxygen levels measured in the effluent decreased with subsequent simulated runoff events, which may be representative of increasing micro-biota growth with time.

These results insinuate that despite the polymerization, the presence of carbon rich fatty acids in the Oleophilic Fertilizer effectively stimulated indigenous soil biomass growth that proliferated with time. However, there is no evidence that the increase in soil micro-biota populations induced greater nutrient mineralization or leaching. Nor can it be inferred that this biostimulation resulted in a decline in soil redox conditions, increased denitrification or nitrogen sequestration.

Table 14 **Dissolved Oxygen Concentrations**

Sample Date	Dissolved Oxygen (mg/L)		
	Source Water	Lecithin & Nitroform [®]	Oleophilic Fertilizer
26-Nov-10	6.02	5.09	3.60
10-Dec-10	5.98	2.95	2.34
18-Dec-10	6.85	4.01	1.17
27-Jan-11	7.76	-	1.88
<i>Mean</i>	<i>6.65</i>	<i>4.02</i>	<i>2.25</i>
<i>Std. Deviation</i>	<i>0.84</i>	<i>1.07</i>	<i>1.02</i>

One of the more interesting findings was that the presence of the polymerized tung oil controlled or limited the release of TN whereas TP masses were concurrently increased. Assuming that the carbon rich fatty acids promoted soil biomass growth as per the above discussion, it would be prudent to discern the breakdown of the fertilizer utilization. That is, biogeochemical cycles are tightly coupled in terrestrial systems and observations suggest that “Redfield like” stoichiometric relationships can be applied to soil ecology (Cleveland and Liptzin, 2007). Despite the relative complexity of the soil medium and microbial community structure, a constrained carbon, nitrogen and phosphorus elemental molar ratio of 60:7:1 has been identified for soil micro-biota (Cleveland and Liptzin, 2007). This may have implications on the predicted net mineralization of the nutrients in the biofilter soil amendments. That is, the stimulated growth of soil micro-biota in the tung oil amended column may have mineralized and subsequently immobilized nitrogen and phosphorus pursuant to the 7:1 “Redfield like” N:P ratio. Thus, the net mineralization of nitrogen would be less than that for phosphorus and more TP would be measured from the Oleophilic Column effluent. It has been previously documented that additions of readily available carbon can stimulate microbial activity, and this in turn has

been associated with a net decline in nitrogen availability due to subsequent immobilization (Prescott, 2005). Given the complexity of other physiochemical processes transpiring in the soil media, it is unlikely that this stoichiometric ratio would be observed in the column effluent.

Chapter Five: Conclusions and Recommendations

Increasing emphasis on stormwater quality is propelling regulatory changes and innovative approaches to stormwater nutrient management. Biofilters have emerged as a popular stormwater BMP although their water quality performance with respect to nutrients removal is varied. The primary objectives of this research were to synthesize and evaluate the effect of an oleophilic fertilizer employed in a biofilter media and to gain a better understanding of nutrient leaching from a biofilter soil. Whilst the following section summarises the principal findings of this study, the second section recommends the subsequent steps to further develop the oleophilic fertilizer concept for use in stormwater biofilters.

5.1 Conclusions

The conclusions section is divided into two main parts. The first part outlines the lessons learned from the oleophilic fertilizer fabrication which is followed by the key findings derived from the water quality analysis.

5.1.1 Oleophilic Fertilizer Synthesis

Of particular importance, all of the oleophilic fertilizer precursors were easily sourced at a low cost. The synthesis methods evaluated were simple and successful.

1. A 10:1 volumetric sand to oil ratio was found to be the least amount of oil that would fully coat the sand while leaving very little residual oil to minimize superfluous carbon input.
2. The lack of a statistical difference between the two replicate Oleophilic Fertilizer test columns demonstrates that the fertilizer synthesis methods were effective; yielding a

homogenous distribution of the fertilizer precursors throughout the oil and subsequently, the enriched oil amongst the biofilter media.

3. Warming tung oil over low heat for a short period of time was found to be an adequate method to decrease its viscosity with the intent of distributing the oil evenly amongst the sand. Provided the mixing of the sand and oil were sufficient, it is probable that no thinning would be required, thereby minimizing the amount of effort in the fabrication. This is important for large scale manufacturing and optimization.

5.1.2 Evaluation of Nutrient Leaching

1. Controls:

Negative: The biofilter soil starting materials, sand/peat/vermiculite, were a significant source of nutrients as identified by the substantial TN and TP concentrations in the column's effluent. More specifically, the Negative Control column leached higher concentrations of TN than TP; suggesting that the baseline biofilter media was either a greater source of nitrogen or alternately, the biogeochemical properties of the soil were more adapt at retaining phosphorus. After four years of simulated "clean" runoff, the Negative Control's effluent TP concentrations still exceeded the 0.028mg/L BBWMP water quality target for the Central Reach of the Watershed.

Positive: The high leachability of the Positive Control amended with Ammonium Nitrate (NH_4NO_3) and Potassium Phosphate (K_2HPO_4), in both TN and TP showed that the experimental design and methods were appropriate to evaluate nutrient leaching from the study columns.

2. Total Nitrogen:

Despite the early washout response shown by all the test columns, the rate of TN leaching appears to have stabilized after 1.5 years of equivalent runoff application. These long-term concentrations were akin to BBWMP water quality targets for nitrogen suggesting that biofilters may be an ideal source control practice to meet the nitrogen water quality performance objectives in the Watershed. However, this data was ascertained with tap water and may not be indicative of biofilter performance when influent nitrogen concentrations are increased.

With respect to the fertilizer amendments, the compost column leached the lowest amount of TN at only 7% of the initial added mass after four years of equivalent runoff application. This minimal nitrogen release may be attributed to the stability or slow mineralization of the humic substances that comprise the compost used in this study. Furthermore, The effects of time on mineralization were under represented due to the constraints of working within an experimental timeframe.

The Oleophilic Fertilizer performed the best out of the remaining fertilizer amendments, demonstrating the lowest mass leached and the lowest inter-event variability or steady release characteristics. However, all amendments, with the exception of compost, leached 240% to 280% more TN than what was initially added to columns, rendering their performance almost incomparable with the compost results. These findings suggest that compost is the ideal biofilter nitrogen amendment although supplies may be subject to significant variation in composition. Furthermore, it is unclear if the bioavailability or temporal nutrient delivery of compost is rapid enough to match biofilter plant demands.

3. *Total Phosphorus:*

After four years of simulated runoff application, TP effluent concentrations from all the test columns far exceeded the 0.028mg/L BBWMP TP water quality target for the Central Reach of the Bow River Watershed. This suggests that these particular biofilters would not be an ideal source control practice to meet TP performance objectives.

With respect to the fertilizer amendments, the Lecithin and Nitroform[®] biofilter amendment leached the lowest mass of TP over the study period and demonstrated the lowest inter-event variability or steady release characteristics of all the amendments tested. The Compost amendment was found to be a greater source of TP than it was for TN, leaching 44% more TP than the Negative Control column. This may be attributed to a labile inorganic phosphorus fraction in the compost that was easily desorbed upon dosing as evidenced in the results by the high TP concentration from the first stormwater runoff application.

4. *Effect of Tung Oil:*

Tung oil appeared successful at controlling TN release, leaching about 10% less of the initial mass added to the columns when compared to the Lecithin and Nitroform[®] amendment which excluded the oil. Furthermore, the Oleophilic Fertilizer demonstrated a lower inter-event standard deviation, or a more consistent nutrient release, over the four years annual equivalent runoff application. In contrast, tung oil was shown ineffective at controlling TP leaching as the oil amended columns released greater amounts of phosphorus than the non-amended column. One plausible explanation is that the oil's carbon rich fats stimulated the proliferation soil micro-biota that resulted

in a greater net immobilization of TN over TP. This hypothesis is supported by the 44% lower dissolved oxygen levels observed in the Oleophilic Fertilizer's effluent when compared to the column which excluded the oil. Simultaneously, "Redfield like" stoichiometric relationships for soil ecology favour the immobilization of nitrogen over phosphorus; thus, TP leaching should be more prominent upon carbon induced biostimulation. A similar net decline in nitrogen availability due to soil carbon addition was also established by Prescott (2005).

5. No distinct nutrient leaching trends or effects were identified based on the antecedent dry days between water applications.

5.2 Recommendations for Future Study

In order to further develop the concept of utilizing oleophilic fertilizers in biofiltration media it would be highly informative to pursue the following extensions to this study;

1. The potential for oleophilic fertilizers to enhance hydrocarbon remediation in stormwater biofilters should be investigated.
2. An assessment should be undertaken on the effect of the oleophilic fertilizer on the field capacity or available water content of the soil.
3. Measuring cellular respiration in a controlled environment would be one option to establish biomass kinetics and substrate utilization patterns. This information could be used to distinguish the utilization rate of the fertilizer or evaluate the rigor added due to oil polymerization.
4. Distinguishing nitrogen and phosphorus species in the water quality analysis and taking redox measurements in the soil column would provide better experimental resolution.

5. Dry weight growth studies would confirm that the fertilizer has the potential to promote plant growth.
6. Batch isotherm studies may be beneficial to decipher the controlled release characteristics of the fertilizer minimizing confounding variables.
7. Performing similar research at the field level with the addition of vegetation would provide results that are representative of in-situ conditions.
8. Evaluate the oleophilic fertilizer's potential as a carbon source to facilitate nitrate removal via denitrification.
9. Costing study may be prepared to distinguish the economic viability of this type of fertilizer when compared with more conventional methods of fertilization.
10. A similar study, with more replicates, would provide better statistical power to the results.

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APPENDIX A : MEDIAN OF AVERAGE INFLUENT AND EFFLUENT CONCENTRATIONS OF BMPS

From; Geosyntec Consultants, Wright Water Engineers Inc., 2008

Median of Average Influent and Effluent Concentrations of Best Management Practices

Constituents	Sample Location	Detention Pond (n=25) ¹	Wet Pond (n=46) ¹	Wetland Basin (n=19) ¹	Biofilter (n=57) ¹	Media Filter (n=38) ¹	Hydrodynamic Devices (n=32) ¹	Porous Pavement (n=6) ¹
Suspended Solids (mg/L)	Influent	72.65 (41.70-103.59)	34.13 (19.16-49.10)	37.76 (18.10-53.39)	52.15 (41.41-62.88)	43.27 (27.25-59.58)	39.61 (21.95-76.27)	xx
	Effluent	31.04 (16.07-46.01)	13.37 (7.29-19.45)	17.77 (9.26-26.29)	23.92 (15.07-32.78)	15.86 (9.74-21.98)	37.67 (21.28-54.02)	16.96 (5.90-48.72)
Total Cadmium (µg/L)	Influent	0.71 (0.45-1.28)	0.49 (0.20-0.79)	0.36 (0.11-0.60)	0.54 (0.40-0.67)	0.25 (0.12-0.49)	0.74 (0.37-1.11)	xx
	Effluent	0.47 (0.25-0.87)	0.27 (0.12-0.61)	0.24 (0.11-0.55)	0.30 (0.26-0.35)	0.19 (0.1-0.37)	0.57 (0.25-1.33)	xx
Dissolved Cadmium (µg/L)	Influent	0.24 (0.15-0.33)	0.19 (0.10-0.28)	xx	0.25 (0.21-0.28)	0.16 (0.11-0.21)	0.33 (0.11-0.55)	xx
	Effluent	0.25 (0.17-0.36)	0.11 (0.08-0.15)	xx	0.21 (0.19-0.23)	0.13 (0.10-0.18)	0.31 (0.13-0.71)	xx
Total Copper (µg/L)	Influent	20.14 (8.41-31.79)	8.91 (5.29-12.52)	5.65 (2.67-38.61)	31.93 (25.25-38.61)	14.57 (10.87-18.27)	15.42 (9.20-21.63)	xx
	Effluent	12.10 (5.41-18.80)	6.36 (4.70-8.01)	4.23 (0.62-7.83)	10.66 (7.68-13.68)	10.25 (8.21-12.29)	14.17 (8.33-20.01)	2.78 (0.88-8.78)
Dissolved Copper (µg/L)	Influent	6.66 (0.73-12.59)	7.33 (5.40-9.26)	xx	14.15 (10.14-18.16)	7.75 (4.55-10.96)	13.59 (9.82-17.36)	xx
	Effluent	7.37 (3.28-11.45)	4.37 (3.73-5.73)	xx	8.40 (5.65-11.45)	9.00 (7.28-10.72)	13.92 (4.40-23.44)	xx
Total Chromium (µg/L)	Influent	7.36 (5.49-9.88)	6.00 (3.58-10.08)	xx	5.63 (4.49-7.05)	2.18 (1.66-2.86)	4.07 (2.39-6.91)	xx
	Effluent	3.18 (2.10-4.84)	1.44 (0.79-2.66)	xx	4.64 (3.08-6.98)	1.48 (0.82-2.70)	3.52 (2.14-5.80)	xx
Total Lead (µg/L)	Influent	25.01 (12.06-37.95)	14.36 (8.32-20.40)	4.62 (1.43-11.89)	19.53 (10.11-28.95)	11.32 (6.09-16.55)	18.12 (5.70-30.53)	xx
	Effluent	15.77 (4.67-26.87)	5.32 (1.63-9.01)	3.26 (2.31-4.22)	6.70 (2.81-10.59)	3.76 (1.08-6.44)	10.56 (4.27-16.85)	7.88 (1.64-37.96)
Dissolved Lead (µg/L)	Influent	1.25 (0.33-2.17)	3.40 (1.12-5.68)	0.50 (0.33-0.67)	2.25 (0.77-3.74)	1.44 (1.05-1.82)	1.89 (0.83-2.95)	xx
	Effluent	2.06 (0.93-3.19)	2.48 (0.98-5.36)	0.87 (0.85-0.89)	1.96 (1.26-2.67)	1.18 (0.77-1.60)	3.34 (2.22-4.47)	xx
Total Zinc (µg/L)	Influent	111.56 (51.50-171.63)	60.75 (45.23-76.27)	47.07 (24.47-90.51)	176.71 (128.28-225.15)	92.34 (52.29-132.40)	119.08 (73.50-164.67)	xx
	Effluent	60.20 (20.70-99.70)	29.35 (21.13-37.56)	30.71 (12.80-66.69)	39.83 (28.01-51.56)	37.63 (16.80-58.46)	80.17 (52.72-107.61)	16.60 (5.91-46.64)
Dissolved Zinc (µg/L)	Influent	26.11 (5.20-75.10)	47.46 (37.65-57.27)	xx	58.31 (32.46-79.16)	69.27 (37.97-100.58)	35.93 (4.96-66.90)	xx
	Effluent	25.84 (10.75-40.93)	32.86 (17.70-48.01)	xx	25.40 (18.71-32.09)	51.25 (29.04-73.46)	42.46 (10.38-74.55)	xx
Total Phosphorus (mg/L)	Influent	0.19 (0.17-0.22)	0.21 (0.13-0.29)	0.27 (0.11-0.43)	0.25 (0.22-0.28)	0.20 (0.15-0.26)	0.24 (0.01-0.46)	xx
	Effluent	0.19 (0.12-0.27)	0.12 (0.09-0.16)	0.14 (0.04-0.24)	0.34 (0.26-0.41)	0.14 (0.11-0.16)	0.26 (0.12-0.48)	0.09 (0.05-0.15)
Dissolved Phosphorus (mg/L)	Influent	0.09 (0.06-0.13)	0.09 (0.06-0.13)	0.10 (0.04-0.22)	0.09 (0.07-0.11)	0.09 (0.03-0.14)	0.06 (0.01-0.11)	xx
	Effluent	0.12 (0.07-0.18)	0.08 (0.04-0.11)	0.17 (0.03-0.31)	0.44 (0.21-0.67)	0.09 (0.07-0.11)	0.09 (0.04-0.13)	xx
Total Nitrogen (mg/L)	Influent	1.25 (0.83-1.66)	1.64 (1.39-1.94)	2.12 (1.58-2.66)	0.94 (0.94-1.69)	1.31 (1.19-1.42)	1.25 (0.33-2.16)	xx
	Effluent	2.72 (1.81-3.63)	1.43 (1.17-1.68)	1.15 (0.82-1.62)	0.78 (0.53-1.03)	0.76 (0.62-0.89)	2.01 (1.37-2.65)	xx
Nitrate-Nitrogen (mg/L)	Influent	0.70 (0.35-1.05)	0.36 (0.21-0.51)	0.22 (0.01-0.47)	0.59 (0.44-0.73)	0.41 (0.30-0.51)	0.40 (0.06-0.73)	xx
	Effluent	0.58 (0.25-0.91)	0.23 (0.13-0.37)	0.13 (0.07-0.26)	0.60 (0.41-0.79)	0.82 (0.60-1.05)	0.51 (0.08-1.34)	xx
TKN (mg/L)	Influent	1.45 (0.97-1.94)	1.26 (1.03-1.49)	1.15 (0.81-1.48)	1.80 (1.62-1.99)	1.52 (1.07-1.96)	1.09 (0.52-1.67)	xx
	Effluent	1.89 (1.58-2.19)	1.09 (0.87-1.31)	1.05 (0.82-1.34)	1.51 (1.24-1.78)	1.55 (1.22-1.83)	1.48 (0.87-2.47)	1.23 (0.44-3.44)

¹ Actual number of BMPs reporting a particular constituent may be greater or less than the number reported in this table, which was based

APPENDIX B: JMPV.9.0 -WILCOXON SIGNED RANK TEST RESULTS MATRIXES

TOTAL NITROGEN - WILCOXON RANK TEST

	NEGATIVE CONTROL	POSITIVE CONTROL	OLEOPHILIC FERTILIZER	LECITHIN & NITROFORM®
POSITIVE CONTROL	0.647			
	0.0647			
OLEOPHILIC FERTILIZER	0.0461	0.0808		
	0.3138	0.0832		
LECITHIN & NITROFORM®	0.8419	1	0.3248	
	0.0623	0.0512	0.1472	
COMPOST	1	0.589	0.0191	0.7032
	0.0546	0.0556	0.1984	0.0517

p value
Power

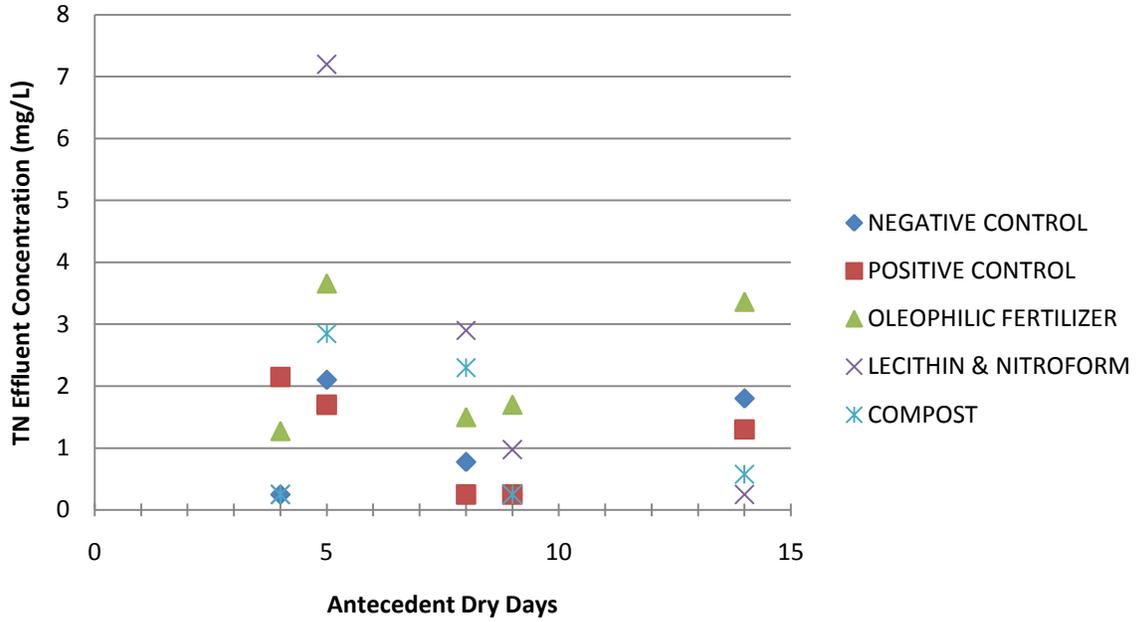
TOTAL PHOSPHORUS - WILCOXON RANK TEST

	NEGATIVE CONTROL	POSITIVE CONTROL	OLEOPHILIC FERTILIZER	LECITHIN & NITROFORM®
POSITIVE CONTROL	0.0266			
	0.4431			
OLEOPHILIC FERTILIZER	0.0167	0.5902		
	0.4695	0.2698		
LECITHIN & NITROFORM®	0.3153	0.1986	0.0825	
	0.0501	0.4619	0.5791	
COMPOST	0.0721	0.4295	0.8515	0.1735
	0.267	0.1814	0.0536	0.4017

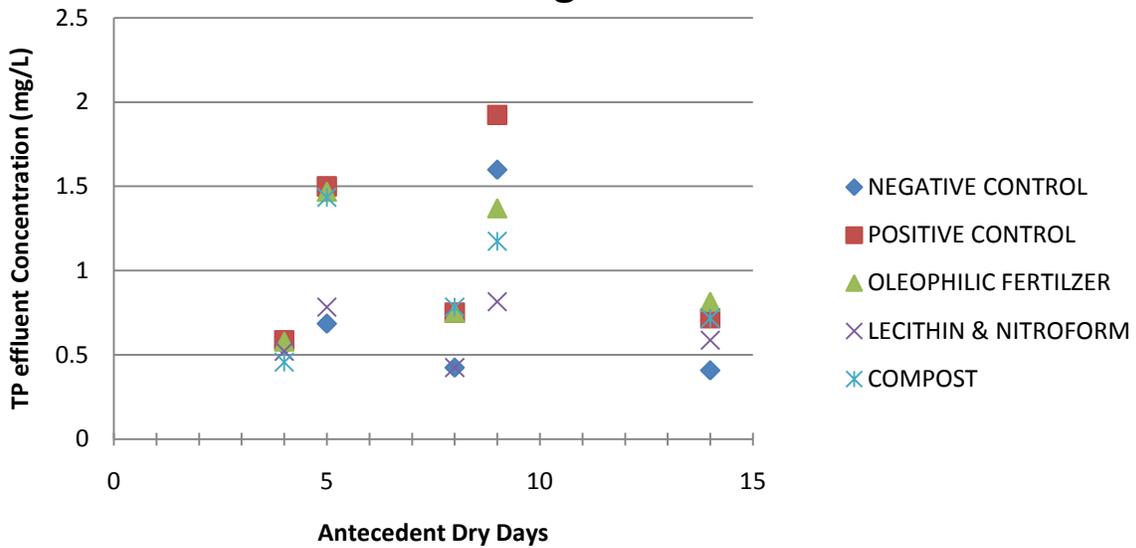
p value
Power

APPENDIX C : INTER-EVENT DRYING TIME VS. EFFLUENT NUTRIENT CONCENTRATIONS

Effect of Inter-Event Drying Time on TN Leaching



Effect of Inter-Event Drying Time on TP Leaching



APPENDIX D : EXPERIMENT PHOTOS



Experimental apparatus with effluent collection jars and source water tan



From left to right; Sand enriched with oleophilic fertilizer, soybean lecithin, Nitroform