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Physicochemical Treatment of Combined Sewer Overflow using Natural Polymers

by

Omotola Ajao

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Windsor, Ontario, Canada

Physicochemical Treatment of Combined Sewer Overflow using Natural Polymers

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ABSTRACT

The hazard posed by combined sewer overflow (CSO) to receiving water cannot be overemphasized due to its significant contribution of pollutants. Ontario's Procedure F-5-5 stipulates a minimum treatment limit of 50% reduction in suspended solids (SS) and 30% reduction in the 5-day biochemical oxygen demand (BOD_5) for CSOs discharged in Ontario. The City of Windsor, Ontario, currently uses a synthetic polymer (Zetag 7873) for CSO treatment at its retention treatment basin (RTB) utilizing a physicochemical treatment method. Environmental persistence and potential toxicity are common concerns associated with synthetic polymers. These concerns may be limited when plant or animal based natural polymers are utilized.

The effectiveness of commercially available natural polymers were evaluated for Windsor CSO treatment. The results show that Tanfloc SG was able to surpass the target of Procedure F-5-5 up to removal efficiencies of 91% and 56% for SS and BOD_5 respectively for polymer dosages ranging between 5 mg/L – 30 mg/L.

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LIST OF ABBREVIATIONS

AOC	Area of Concern
BMP	Best Management Practice
BOD_5	5-day Biochemical Oxygen Demand
CEPT	Chemically Enhanced Primary Treatment
CSO	Combined Sewer Overflow
CSS	Combined Sewer System
DPS	Dual Polymer System
DRP	Dissolved Reactive Phosphorus
GLWQA	Great Lakes Water Quality Agreement
IJC	International Joint Commission
MDL	Method Detection Limit
RE	Removal Efficiency
RTB	Retention Treatment Basin
SCADA	Supervisory Control and Data Acquisition
SS	Suspended Solids
TDP	Total Dissolved Phosphorus
TP	Total Phosphorus
TRP	Total Reactive Phosphorus
WWTP	Wastewater Treatment Plant

1 INTRODUCTION

1.1 Background

Several years back, sewer systems were designed to adequately convey sanitary and pretreated industrial wastewater as well as stormwater runoff to a treatment plant in a single pipe system. This type of systems are now referred to as a combined sewer systems (CSS). Wastewater treatment plants (WWTP) were also designed to adequately treat wastewater during dry weather and wet weather events based on the assumption that over time, there would be minimal fluctuations and a long-term trends in hydrological variables (Denault, et al., 2006). Over the years, however, population growth has triggered an increase in wastewater production as well, increasing trends in precipitation have increased stormwater water flow (He, et al., 2011; Denault, et al., 2006; Semadeni-Davies, et al., 2008), ageing pipes and pipe fittings also enabled the infiltration of groundwater into sewer systems. Therefore, depending on the magnitude of a storm event and the extent of snowmelt, CSS and WWTP may exceed their design capacity during wet weather conditions, which may consequently result in manhole and outfall surcharges. Therefore, to prevent basements and streets flooding as a result of these surcharges as well as to prevent wastewater treatment plants from receiving an excessive hydraulic loads for which it was not designed, the WWTP is bypassed and untreated wastewater is discharged directly into a receiving surface water body. This untreated water is referred to as combined sewer overflow (CSO) and it contains pathogens, organic compounds, solids, metals, and other pollutants that are harmful to the aquatic environment.

Results of various studies have highlighted the significance of CSO pollutant loadings to the environment. For example, based on the study carried out by LaFontaine, Cowie, Buratto and Associates Limited in 1994, CSOs contribute less than 5% of the Detroit River's volumetric load, this contributes approximately 27% of the total annual solid load and 14% of the total annual 5-day biochemical oxygen demand (BOD_5) (Li, et al., 2003). These loadings are relatively high when compared to other major sources of pollution in the Detroit River (Ahmed, et al., 2008). In addition, CSOs have been identified as a significant contributor of bacteria to the Detroit River as compared to wastewater treatment plants' contributions in Michigan and Ontario (Ahmed, et al., 2008). As reported in numerous Remedial Action Plans for Great Lakes Areas of Concern, CSOs are a possible cause of deterioration in the Great Lakes (Irvine, et al., 2005). CSOs have also been linked to the recent algae blooms in Lake Erie due to its substantial contribution of phosphorus load to the Lake Erie Basin, with CSOs in Ohio alone contributing 90.4 million tonnes of phosphorus annually (IJC, 2014).

The evident effect of CSO in the environment has led to a new design approach for sewer systems. Sewer systems in relatively newly built communities are designed such that stormwater sewers are separated from sewage sewers. In older communities, however, separating the already existing CSS may not be a feasible option, although it should be noted that when a CSS reaches the end of its service life, it is usually replaced by separate sewers. Hence, regulations are being implemented by authorities of various communities with CSS to reduce the impact of CSOs on receiving waters (Zhu, et al., 2007). In a similar light, the Ministry of the Environment and Climate Change, Ontario specifies that CSOs should be eliminated during dry weather and treated to a certain limit during wet weather flow, as documented in the Procedure F-5-5 (MOE, 2014), before discharging into surface water. Procedure F-5-5 specifies that 90% of wet weather flow should be captured and treated such that 50% of total suspended solids (TSS) and 30% of BOD_5 are removed. In addition, for more than 50% of the time when there is a CSO, the TSS concentration must be less than 90 mg/L.

1.2 CSO Control Strategy

A number of control strategies have been employed to curtail the threat caused by CSO. In-line or off-line storage in tunnels or detention basins are the most commonly used approach (USEPA, 1999). They are used to contain the flow upstream of the WWTP during peak flow and then return it to the sewer system for treatment at the WWTP after the storm event. Storage over time can also facilitate the removal of SS after which the supernatant is discharged directly into the receiving water. Since major pollutants often adhere to solids (Berndtsson, 2014; Wakida, et al., 2014; Aryal, et al., 2010; Boyd, 1988), the removal of solids as a result of sedimentation in the storage facility results in a significant removal of the pollutants that bind to them (Stanley, 1996; Booker, et al., 1996). Pollutant removal can also be achieved through the use of green infrastructure such as a bio-retention basins or a constructed wetlands. However, when these conventional control strategies are employed, ample storage or detention time as well as space for construction of the facility is required for substantial pollutant removal. Thus, due to the cost and the limited availability of land required for construction, especially in an urban setting, it may not be feasible to construct such a large facility. Therefore, the use of a physical-chemical treatment processes is often employed to augment settling in smaller storage basins. This entails the real-time addition of a chemical coagulant and/or flocculant during the storm event to primarily increase particle sizes and increase settling efficiency. An example of such a treatment process is found in the City of Windsor's Retention Treatment Basin (RTB).

1.3 Chemicals used for CSO Treatment

Generally, chemicals commonly used for the physicochemical treatment process are synthetic organic polymers as well as inorganic salts of aluminum and iron such as aluminum chloride (alum), ferric sulfate, and ferric chloride. Although these commonly used chemicals are efficient for pollutants removal, they have a number of drawbacks. For example, the effectiveness of inorganic salts are pH dependent; their use results in the production of voluminous sludge that contains metal ions thereby increasing the cost of dewatering (Ammary & Cleasby, 2004). In addition, metal residue in the effluent may be toxic to the receiving water.

Synthetic polymers on the other hand require lower dosages, and therefore they produce less volume of sludge that may reduce the sludge treatment cost. However, there are some other factors that should be considered and these include: the high cost of purchase, negative impact of the polymer residue in the effluent on the aquatic environment (Kerr, et al., 2014); potential toxicity of their monomers; and long-term adverse health effects to the public (Wu, et al., 2007; Graham, et al., 2008; Yin, 2010; S, et al., 2012). As such, health concerns of synthetic polymers have led to the imposition of strict regulations on their use for potable water treatment in many countries including Switzerland and Japan (Graham, et al., 2008).

To address some of the drawbacks of commonly used chemicals, natural polymers, which are plant or animal based, are becoming popular for reasons related to cost and toxicity (Graham, et al., 2008).

1.4 Objectives

This study is aimed at examining the following:

1. Determining the characteristics of Windsor CSO.
2. Evaluating the effectiveness of natural polymers for the treatment of Windsor CSO.
3. Comparing the effectiveness of a selected natural polymer with existing practise.

1.5 Scope

1. Windsor CSO characterisation
    - Collect and analyse multiple flow proportional discrete samples for SS, BOD and three species of phosphorus.
2. Natural polymer evaluation
    - Evaluate three natural polymers for the treatment of CSOs based on their potential to meet the requirements of Procedure F-5-5.
    - Select one of the natural polymers for further evaluation.
3. Comparison
    - Compare the cost of the selected natural polymer against the present practise.

2 LITERATURE REVIEW

2.1 Impact of Combined Sewer Overflow

During wet weather, untreated CSO can be a significant non-point source of contamination to receiving waters. Its effects on receiving water include reduced oxygen levels, increased pathogens and excess nutrients that could result in eutrophication (Anderson, et al., 2002). Pollutant loading is also influenced by debris washed from land surfaces. In addition, manmade activities, which include contamination from vehicles and atmospheric deposition due to industrialization, also contribute to the overall loading (Gutteridge, Haskins and Davey Pty Ltd, 1981). The volume of CSO impacted by stormwater flow is however more prominent in urban regions due to increased imperviousness (Berndtsson, 2014).

The threat posed by CSO to water quality cannot be overemphasized. In the Great Lakes Region for example, the Detroit River was listed as one of the 43 Areas of Concern (AOCs) by the International Joint Commission (IJC) based on the significant influence of CSO (Green, et al., 2010). A report to the United States' congress indicated that of the 733 water segments within a kilometer downstream of a CSO outfall that were analysed for water quality, 75% were impaired, with a high percentage of these impairments associated with CSOs (USEPA, 2004).

A CSO jeopardizes the quality of receiving water due to factors such as the high flow rate of discharge, which often causes erosion of the water bank and destabilization of its receiving water's ecology. The aesthetics of such a water body is adversely affected when debris, accumulated as a result of surface runoff, is deposited on the water surface. Most importantly, CSOs contribute immensely to the pollutant loading of receiving waters in the form of settleable and nonsettleable solids, pathogens, organic matter, nutrients, metals, polyaromatic hydrocarbons and other important pollutants.

Despite the varying concentration of pollutants in a CSO during a storm, there are instances when instantaneous pollutant concentrations may become so high that the water quality standards are violated (USEPA, 2008). Although there have been reports in the literature that the concentration of some pollutants are less in CSOs as compared to sanitary sewage, studies have shown that the mass loading of these pollutants is significant due to the volume of stormwater runoff (Gutteridge, Haskins and Davey Pty Ltd, 1981; Droste & Hartt, 1975).

The uniqueness of CSO, lies in the variability of its pollutant load from one storm event to the other, from region to region, by land use, weather, seasons as well as physical structures and maintenance (Berndtsson, 2014; Droste & Hartt, 1975). In a similar light, variability within an event cannot be overlooked and it is often explained by the first flush phenomenon.

The first flush phenomenon is described by the initial high pollutant concentration immediately after a storm begins that later diminishes as the storm event proceeds. This may be because easily removable pollutants are washed off as soon as the storm commences or as a result of resuspension of sediments that were in the drainage channel before the storm event (Gutteridge, Haskins and Davey Pty Ltd, 1981). The first flush effect may also depend on the size and slope of the piping system as well as the time interval between successive storms (Shu, 2004). Compared to sanitary sewage, the SS concentration in a CSO is typically higher due to resuspension of sediments, but the lower concentration of pollutants such as phosphorus, nitrogen, COD and BOD_5 in CSO may be due to dilution by the constituent stormwater (Shu, 2004; Metcalf & Eddy, Inc., 2003).

2.2 CSO Management

The environmental impact of CSOs mainly lies in the hydrological and pollution shock load. The need to eliminate or otherwise reduce the risk of pollution from CSO has given rise to structural and non-structural best management practises (BMPs) (IJC, 2014). A suitable combination of structural and non-structural BMPs has achieved an 85% reduction in TSS and 50% reduction in total phosphorus (TP) (Pennsylvania DEP, 2006).

Non-structural BMPs, as the term implies, have fewer structural attributes. They are focused rather on policy changes, educational campaigns, planning and implementation. This approach can be as simple as street sweeping, water conservation, basing fertilizer application on soil tests as opposed to generalised practise, downspout disconnection as well as better management of grass clippings and pet waste (Pennsylvania DEP, 2006; IJC, 2014). For example, composted manure used as a source of fertilizer can significantly reduce TP loading to a receiving water as compared to inorganic fertilizer (IJC, 2014). Non-structural BMPs can also involve a more technical approach through low impact development. In such a case, reduced imperviousness gives room for stormwater infiltration.

On the other hand, structural BMPs are designed and engineered to reduce runoff volumes and/or reduce pollutants in the event of an overflow. An example of this is found in the City of Windsor’s RTB; others include bioretention basins, detention and retention basins, storage tunnels and constructed wetlands. Although bioretention systems may not be entirely reliable for the removal of nitrogen, it has been reported to have efficiently removed dissolved phosphorus when the media is adjusted with iron-enhanced sand (LeFevre, et al., 2014).

2.2.1 City of Windsor's Retention Treatment Basin

Based on the requirements of the Great Lakes Water Quality Agreement (GLWQA), efforts to restore the Detroit River's beneficial uses and to delist it as an AOC started in 1985 with a remedial action plan (RAP). According to the stage 1 report of the RAP (MDNR and MOE, 1991), the City of Windsor's storm and combined sewer overflow were identified as a significant non-point source of pollutants to the Detroit River. This, initiated the upgrade made to the City of Windsor's Lou Romano Water Reclamation (LRWRP) to include secondary treatment and the construction of the RTB along the Riverfront (Green, et al., 2010).

The RTB was adopted for the city's CSO treatment based on the recommendation of a Windsor CSO characterisation and treatability study (Stantec, 2001). The study reported that chemical addition reduces the size requirement of the RTB to about 15% the size of a conventional settling facility, while also meeting the requirements of Ontario's Procedure F-5-5.

Hence, the high-rate RTB is designed for a 7.85 m^3/s peak flow using polymer flocculation to aid rapid settling. Based on the CSO treatability study, Zetag 7873, which is a liquid cationic polymer, was recommended for treatment at a polymer dose of 5 mg/g of the influent TSS (Li, et al., 2003),. Polymer dosing is controlled automatically to respond to varying influent TSS concentrations as the storm events progress (Stantec, 2014). During an overflow event, CSO and the pre-mixed polymer are simultaneously added to the influent of the RTB. The mixture is henceforth stored in the RTB before it is conveyed back to the sewer system for treatment at the LRWRP. However, if the flow exceeds the storage capacity of the RTB before the end of the storm event, treated effluent is discharged directly into the Detroit River.

2.3 Physicochemical Treatment Method

Total solids in a wastewater stream consists of settleable, suspended, and dissolved solids. The dissolved solids are described by their ability to pass through a filter with a pore diameter less than or equal to 2 µm while suspended solids on the other hand will not pass through a 2 µm filter pore size (USEPA, 2012). The settleable portion of the solids is able to settle under gravity alone within a short period of time. However, suspended solids may or may not settle under their own weight depending on the characteristics of the particles and the design of the sedimentation unit (Metcalf & Eddy, Inc., 2003). Colloids, for example, are stable suspensions and are unable to settle out solely with gravitational force.

The primary stage of water treatment entails the physicochemical clarification process that involves the coagulation and flocculation of colloidal particles and other suspended solids. Coagulation and flocculation reduce the force that binds the respective particles, this improves their rate of settling and aids efficient removal. Depending on the complexity of the problem, the clarification process may incorporate any or all of coagulation, flocculation, flotation, sedimentation (Tacchi & Churchill, 1977), and filtration. In a similar light, Mhaisalkar, et al. (1991) described coagulation-flocculation and then sedimentation as the most extensively used process for the removal of suspended particles during water treatment.

2.3.1 Coagulation and Flocculation Mechanism

Typically, the net charge of particles of colloids in wastewater is negative and they are kept in suspension by Brownian motion, under stable conditions. Coagulation, which entails the rapid and vigorous mixing of chemical coagulants with the raw wastewater, is done to reduce their surface charge of colloid particles. The dispersed colloidal particles are thereafter kept in suspension through a constant but reduced mixing to facilitate the collision and hence agglomeration of the dispersed particles. The increased particle size improves the settling rate of the particles in the sedimentation unit.It also improves the quality of the filtrate in the situation where the particles are filtered out. Coagulation-flocculation mechanisms can be summarized by a combination of any of the following methods (Miller, et al., 2008; Menezes, et al., 1996):

Adsorption and charge neutralization: When inorganic salts of iron and aluminum are added as coagulants to the coagulation unit, the hydrolysis products of their metals are formed. Colloidal particles therefore adsorb oppositely charged ions of the hydrolysis products to form a metal hydroxide precipitate. In the case where polymers are used as primary coagulants, cationic polymers are adsorbed to wastewater particles causing the charges to be neutralised. The precipitates formed in both cases are enlarged during flocculation to floc particles size that are readily settleable.

Adsorption and interparticle bridging: There can be an attraction between a long polymer chain and the surface of a suspended particle. Particles are therefore adsorbed to several of the attachment points on the polymer chains. Polymer chains are bridges between colloid particles that enable the forming of flocs (Figure 2.1), when there is room for attachment to its segment (Bolto & Gregory, 2007). Flocs are formed as a result of a significant number of loops extending from the polymer (Ghosh, et al., 1985). The bridging ability of the polymer depends on the length and structure of the polymer chain and these in turn depend on the mixing intensity (Young, et al., 2000).

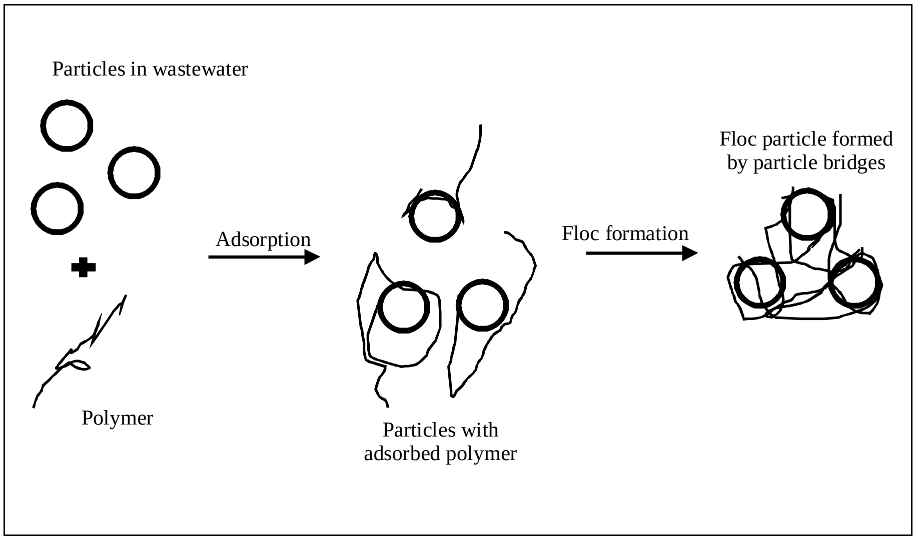


Figure 2.1: Interparticle bridging with polymers

Adapted from Metcalf & Eddy, Inc., (2003)

Sweep flocculation: Settling floc particles sweep through wastewater and entrap particles in suspension, forming larger flocs while they settle. This mechanism is common with particles that are removed through sedimentation (Metcalf & Eddy, Inc., 2003). A combination of sweep flocculation and adsorption mechanisms occur when the turbidity and coagulant doses are high (Rossini, et al., 1999).

Double layer compression: Colloidal particles are primarily surrounded by the stern layer and diffuse layer and are referred to as the double layer. The stability of the colloidal particles depends on the thickness of the double layer, which in turn depends on the zeta potential of the particle. The zeta potential, which is a measure of the ionic strength of the particle, reduces as aqueous ion concentration increases due to the presence of an inorganic coagulant. As such, the compressed double layer reduces due to reduced repulsive forces and consequently, the particles are destabilised.

2.3.2 Mixing

Rigorous mixing is often applicable where the effective blending of two or more substances is required. In wastewater treatment, mixing is applied in the blending of chemicals in the coagulation and flocculation basins. It is also applicable during aeration, equalization, and neutralization during pH control. In addition, mixing is done where it is important to keep the content of a reactor in suspension, such as in suspended growth treatment process, aerobic and anaerobic conditioning of bio-solids and sludge. (Metcalf & Eddy, Inc., 2003).

The unit process of the wastewater treatment dictates the intensity and time of mixing. For example, aluminium hydroxide, which is as hydrolysis product required for adsorption and charge neutralization in the coagulation unit, takes about 7 seconds to be formed (Rossini, et al., 1999). More time is thus required for the sweep flocculation mechanism that enables larger flocs to be formed. Hence, it is of great importance to rapidly disperse the coagulant in the fluid bulk and thereafter, reduce the intensity of mixing to prevent the flocs formed from shearing.

Mixing of fluid is made possible through natural or forced disturbance of particles suspended in the fluid. A natural disturbance occurs as a result of the collision between the molecules of the fluid, known as Brownian motion. A forced disturbance, on the other hand, can be achieved through the vibration of the fluid stream by pumping a stream of fluids into a similar larger fluid body (Rushton, 1952), otherwise known as a hydraulic jump, or by passing the fluid through a baffled channel. In addition, mechanical and pneumatic vibrators can also be used to achieve forced disturbances. For effective mixing it is important to account for the rate of material transfer. This can be simulated through a pilot plant scale model study and thereafter scaled up for the operating parameters of the plant scale using a fluid mechanic principle known as similitude (Rushton, 1952).

2.3.3 Jar Testing

The coagulation, flocculation, and sedimentation of the water treatment process can be simulated on a lab scale using the jar testing apparatus. This is done to evaluate treatment parameters such as: the performance of various coagulants and coagulant aids and their corresponding optimum dosage (Li, et al., 2003; Ebeling, et al., 2003; Exall & Jiri, 2013), mixing intensity (Lai, et al., 1975; Cornwell & Bishop, 1983; Mhaisalkar, et al., 1991); rapid mixing time (Kan, et al., 2002; Aktas, et al., 2013); and optimum settling time, as well as the sequence of addition in situations where dual coagulants are used (Ammary & Cleasby, 2004). A jar test also enable the visual evaluation of variables such as the time the first floc was formed, floc size and quality as well as the settling rate of the floc. It may also be conducted to determine the effect of plant operating conditions such as the temperature variation during the winter and summer (Gilcreas, 1965).

A conventional jar test is conducted using a jar testing machine that is equipped with jars for holding the samples and a stirring device that operates at a variable speed. In runs containing more than one jar, the experiment is handled such that there is minimal variation in protocol in all the jars. This is so because a slight difference may affect the result of the jar test.

The jar test process primarily consists of three stages: the flash or rapid mix stage which represents coagulation; the slow mix representing the flocculation stage; and the settling time, which represents the activity in the sedimentation basin. The data obtained from the jar test experiment can be used for a pilot plant design. This can then be scaled up for the actual plant design.

The detention time in the jar and the treatment plant basin may vary as a result of the difference in energy transfer between water molecules in the jar and that of the water in the treatment plant (Gilcreas, 1965). Rapid mix design is difficult because it is influenced by several factors that include raw water characteristics, type and dose of coagulants as well as the intensity and duration of mixing (Mhaisalkar, et al., 1991). In fluid mechanics the principle of similitude is used to relate performance at one operation size to the performance at a different operating size.

To duplicate the desired mixing efficiency achieved on a smaller scale, it is important to replicate the dynamic conditions (Rushton, 1952). This entails keeping the direction of flow and the ratio of forces at corresponding positions the same (Rushton, 1952) by maintaining a geometrically similar system as well as keeping the power input per unit volume constant (Metcalf & Eddy, Inc., 2003). Hence, the jar test is scaled up using the product of mixing intensity (G) and time (t), as the scaling factor.

2.4 Coagulation/Flocculation Treatment Chemicals

2.4.1 Inorganic Salts

Inorganic salts of aluminum and iron such as aluminium chloride, ferric chloride and ferric sulphate are generally termed as coagulants in the wastewater treatment context. Polyaluminum chloride and polyiron chloride are prehydrolysed metals salts used for the coagulation purpose as well. The hydrolysis products formed when these salts are added to the wastewater stream are responsible for particle aggregation.

Although inorganic salts are generally known for efficient pollutant removal, their performances is not always consistent owing to the sensitivity of these salts to changing raw wastewater pH. Hence, the need for pH adjustment may lead to additional chemical costs. The inorganic salts pose a toxicity risk to receiving water due to the presence of metal ions in their residue. Also, their use results in the production of voluminous sludge that is expensive to dewater.

2.4.2 Polymers

Polymers are organic compounds that are composed of smaller molecules known as monomers. The vast majority of polymers used in wastewater treatment processes originate from synthetic materials and are broadly referred to as synthetic polymers. However, some polymers are sourced from natural materials.

With respect to their ionic charge, polymers can be characterised as cationic, anionic and non-ionic. The cationic polymers, being positively charged polymers are either used as a coagulants or as a coagulant aids. Anionic polymers are negatively charged and they are used mainly as a coagulant aid. The non-ionic polymers have neutral charges and can be used as either coagulants or coagulant aids. The molecular weights of polymers, that range from $<10^5$, $10^5 – 10^6$, and $>10^6$ for low, medium and high weights respectively, significantly influences the efficiency of a polymer when used as a coagulant aid (Bolto & Gregory, 2007). However, their high molecular weight and equivalent charge density distinguish polymer from the conventional inorganic coagulants and flocculants (Tacchi & Churchill, 1977; Chang, et al., 2005).

Compared to inorganic coagulants, polymers are less pH dependent; the concentration of dissolved ion in the effluent is reduced; and polymers may be more effective for the removal of natural organic matter (Chang, et al., 2005). The use of polymers as coagulant aids also comes with various advantages that include: reduced chemical dosage requirement; increased floc size and strength; reduced sludge volume; and an increase in the rate of solid-water phase separation (Bolto & Gregory, 2007; Ghosh, et al., 1985), which enhances the ease of sludge dewatering.

2.4.2.1 Synthetic Polymer

In as much as synthetic polymers have been reported to be highly efficient and help address the major drawbacks of inorganic coagulants, they come with a number of shortcomings. They are often expensive and are less biodegradable (Graham, et al., 2008). The ecology of the receiving water body is endangered as the residual polymer in discharged effluent poses a toxicity risk. In addition, the build-up of the residual polymer on gills of fishes compromises their O_2 intake and may eventually lead to death (Kerr, et al., 2014). Similarly, residual monomers from the manufacture of certain polymers may also have negative impacts on the environment. As such, chlorinated by-products like toluene, 1,4-dichlorobenze, and chloroform have been observed in the effluent of drinking water purification processes as a result of polymer usage (Lee, et al., 1998).

Although the effects of residual synthetic polymers on the ecosystems have been reported, their long-term health effects on humans still remain unknown (Kawamura, 1991). This has, therefore, led to the imposition of stringent regulations in their monomer content as well as their use for drinking water treatment in some countries such Switzerland and Japan (Graham, et al., 2008; Kawamura, 1991).

2.4.2.2 Natural Polymers

Similar to synthetic polymers, natural polymers also address the limitations of inorganic coagulants. In addition, they may also help address some of the limitations of synthetic polymers such as cost, biodegradability, and toxicity. They were used several years ago in developing countries, mainly because of cost considerations (Kawamura, 1991). In recent times, however, there has been increasing interest in their use due to health concerns posed by conventional coagulants and flocculants (Graham, et al., 2008; Renault, et al., 2009; Hsu, et al., 2009).

Natural polymers are generally extracted directly or modified from natural materials. Examples of natural polymers are polysaccharides, such as starch and hydroxyethyl cellulose, chitosan, tannins as well as sodium alginate. Chitosan is produced from the deacetylation of chitin. Chitins are generally extracted from shells of crustaceans. Tannins are polyphenols extracted from the bark of trees while sodium alginate is an anionic polymer extracted from brown seaweed. In addition to being used as coagulants, chitosan and sodium alginate have a variety of applications in the biomedical industry, which include their use as additives in food.

Although unable to effectively remove colloidal matter (Hu, et al., 2013; Kawamura, 1991), the effectiveness of chitosan for the removal of other suspended solids has been reported under a wide concentration range (Kawamura, 1991; Chung, et al., 2013). Hence, its use has been suggested with polyaluminum chloride (PACl) for higher turbidity removal efficiency (RE) (Hsu, et al., 2009). A tannin based polymers have also been reported to be efficient for the treatment of municipal wastewater as well as for the clarification of surface water (Beltran-Heredia, et al., 2011). The effectiveness of

Moringa oleifera seeds for pollutant removal has also been reported in various studies (Muyibi & Evison, 1995; Ndabigengesere & Narasiah, 1996; Muthuraman & Sasikala, 2013),

2.5 Phosphorus

Nutrients such as phosphorus are important for life. Phosphorus aids the growth of terrestrial and aquatic plants, which are essential to the ecosystem. However, as important phosphorus is, it is can be detrimental to the environment when present in excessive amounts. Being an important factor that causes eutrophication in surface water, it aids the growth of phytoplankton such as algae. Phytoplankton competes with aquatic life for oxygen, therefore resulting in the killing of fish and loss of biodiversity, when in excessive amount. Eutrophication may become a nuisance as a result of its green colouration, as well as leading to public beach closures. Hence, a balance of phosphorus is important.

Phosphorus generally enters surface water bodies through point and non-point sources. Point sources can be as a result of the direct discharge of municipal and industrial wastewater while non-point sources can be the result of stormwater runoff, CSO, phosphorus from polluted air, and from weathered rocks. Phosphorus in stormwater and CSO results from sources like organic and inorganic fertilizers from cultivated land, automobile exhaust detergents, food residue, decaying plants as well as animal excreta (Liu & Davis, 2013; Erickson, et al., 2007).

2.5.1 Phosphorus Speciation

Phosphorus occurs broadly in dissolved or particulate form as phosphates, in surface water; organisms; as well as in soils and sediments. Filtration through 0.45 µm filters distinguishes the dissolved from the particulate fraction, although this type of assumption should be made with caution because it is generally accepted that there are smaller particles in water and wastewater samples (Spivakov, et al., 1999). In both dissolved and particulate states, phosphate is introduced into the environment in different chemical forms such as orthophosphate (reactive phosphorus), condensed phosphate (acid hydrolyzable phosphorus) and organically bound phosphorus.

Unlike acid-hydrolysable and organic phosphorus, reactive phosphorus readily responds to chemical reactions processes in water. As such, it does not require prior hydrolysis, oxidation or digestion processes before quantification (Spivakov, et al., 1999). However, acid-hydrolysable and organic phosphorus are first converted to orthophosphates before they are quantified by various techniques.

The summation of these three forms amounts to the total phosphorus content in both the dissolved and the particulate states while the sum of the total dissolved phosphorus and total particulate phosphorus yields the overall count of total phosphorus present. The significant fractions of phosphorus in the environment are summarised in Table 2.1. However, each form may change between their dissolved and particulate states (Spivakov, et al., 1999). With approximately 90% of dissolved reactive phosphorus (DRP) being readily available for biomass uptake as compared to approximately 30% of particulate phosphorus (IJC, 2014), DRP is sometimes referred to as bioavailable phosphorus.

Table 2.1: Phosphorus Species

	Particulate Phosphorus	**Dissolved Phosphorus**
Total Phosphorus	Total suspended phosphorus	Total dissolved phosphorus
Total Reactive Phosphorus	Suspended reactive phosphorus	Dissolved reactive phosphorus
Total Acid-hydrolysable Phosphorus	Suspended acid-hydrolysable phosphorus	Dissolved acid-hydrolysable phosphorus
Total Organic Phosphorus	Suspended organic phosphorus	Dissolved organic phosphorus

2.5.2 Phosphorus and Eutrophication in the Great Lakes Region

In the 1960s, eutrophication was a huge water quality issue in the Great Lakes as a result of excessive phosphorus input (Environment Canada, 2013). This led to enormous algae growth throughout the Great Lakes. To address the issue, the Great Lakes Water Quality Agreement (GLWQA) established a total phosphorus (TP) loading target with the aid predictive models (Chapra & Dolan, 2012). As such, limits were set for the use of phosphorus in detergent and wastewater treatment plants were upgraded. The 1972 GLWQA successfully led to a decline in phosphorus levels in the Great Lakes (Environment Canada, 2013).

However, there was a re-emergence of excessive algae growth in the Great Lakes in the mid-1990s. Although phosphorus is still the main influencing factor for the eutrophication, this re-emergence is now perceived to be more complex than in past decades (Environment Canada, 2013). It has been hypothesized that the recent resurgence is due to invasive aquatic species such as zebra and quagga mussels that established themselves in Lake Ontario in the early 1990s (Chapra & Dolan, 2012). These Dresseinid mussels constantly capture and excrete nutrients in areas close to the shore, and therefore increase the assimilation of TP (Chapra & Dolan, 2012; Environment Canada, 2013)

In 2011, Lake Erie experienced its worst algae bloom ever. As in the previous occurrence, phosphorus was identified as a major influencing factor. However, dissolved reactive phosphorus (DRP) is said to be the major cause of the recent water quality decline (IJC, 2014) due to its bioavailability. CSO has thus been identified as a major source of pollution and most importantly a major source of phosphorus in the Great Lakes Region (USEPA, 2015; IJC, 2014). The 2012 GLWQA, stipulates a revised phosphorus reduction target for Lake Erie by February 2016 (USEPA, 2015).

3 MATERIALS AND METHODS

In order to determine the characteristics of the Windsor CSO, influent into the City of Windsor's RTB was sampled. These samples were analysed for suspended solids, biochemical oxygen demand, total phosphorus (TP), total reactive phosphorus (TRP) and dissolved reactive phosphorus (DRP).

Jar test experiments were also carried out in order to determine the removal efficiencies of commercially available natural polymers. The treatment efficiencies of the natural polymers were compared to those of conventional treatment chemicals such as alum and Zetag 7873. Alum is a widely used chemical for water and wastewater treatment and Zetag 7873 is presently being utilised for Windsor CSO treatment at the RTB.

Experiments were carried out in the wastewater lab of the University of Windsor as well as the pollution control laboratory of LRWRP.

3.1 Sampling Methods

3.1.1 Combined Sewer Overflow

One of the long term control plans for the abatement of CSO recommended by the US Environmental Protection Agency, includes the characterisation of the quality and quantity of the CSO (Irvine, et al., 2005). Stormwater characterisation is based on determining site mean concentrations and their uncertainties as well as the treatability of stormwater by monitoring specific pollutant concentration levels.

The flow proportional sampling method was used to estimate the characteristics of the Windsor CSO. The flow proportional sampling method gives a reliable estimate of the wastewater characteristics (Henze, et al., 2008) and it is done by collecting samples of wastewater over, time based on a specified volume of wastewater flow. For this study, multiple flow proportional discrete samples were collected at the inlet of the Windsor Riverfront RTB with the aid of an automatic Supervisory Control and Data Acquisition (SCADA) system. The collecting carousel is shown in Figure 3.1. The logic controller of the automatic sampler was programmed such that one sample was collected for every 500 m^3 of flow into the RTB. A maximum of 24 samples were collected per storm event.

A composite CSO sample was captured once for polymer evaluation using the jar test procedure.

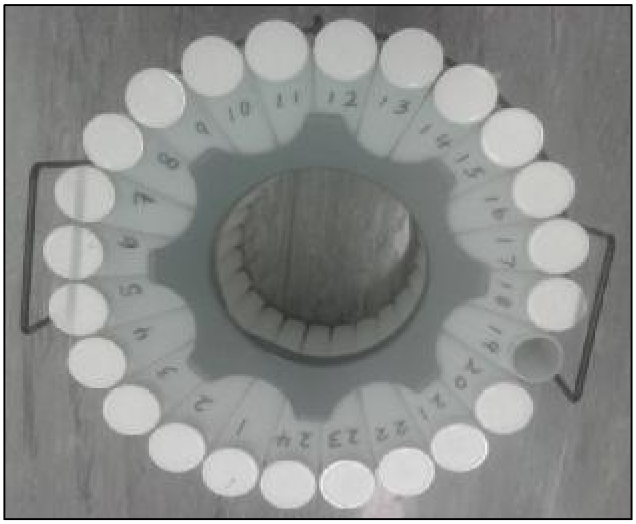


Figure 3.1: Sampling carousel

Samples collected at the end of each storm event were transported to the laboratory of the LRWRP and were transferred into clear wide-mouth sampling glass bottles. They were analysed as soon as possible. Where necessary, samples were preserved and stored according to the guidelines specified in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005) and the analyses were carried out as soon as possible.

3.1.2 Municipal Wastewater

This study is fundamentally aimed at the treatment of CSO, but since CSO is a seasonal event, limited to when there is rainfall, there may be limitations as regarding the time to get samples to be used for a jar test experiment. In order to address this limitation, municipal wastewater was used for the jar test experiment during the polymer selection process since CSO typically consists of municipal wastewater that has been diluted by stormwater. Wet weather flow to the LRWRP has previously been used as a surrogate for Windsor CSO during Windsor CSO treatability study (Li, et al., 2003).

This enabled experiments to be carried out all year round irrespective of the weather condition. Thus, grab samples of municipal wastewater used were collected at the grit chamber of the LRWRP. The selected polymer was further evaluated with CSO.

3.2 Materials

3.2.1 Tanfloc SG and Tanfloc SH

Tanfloc SG and Tanfloc SH samples were supplied by TANAC SA (Montenegro, Brazil). The Tanfloc products are tannin based (Graham, et al., 2008) cationic polymers that were extracted from black wattle (Acacia mearnsi) tree bark. According to the product material safety data sheet (MSDS), tannin extraction is achieved through a reaction with ammonium chloride and formaldehyde.

The Tanfloc SG and Tanfloc SH came as orange and brown powders, respectively, as shown in Figure 3.2. According to the research and development manager of TANAC SA, Tanfloc SH has been modified to have a higher molecular weight than Tanfloc SG (C. Wolf, personal communication, June 16, 2015). Otherwise, other physical and chemical properties of the polymers are the same as on the MSDS.

Figure 3.2: Tanfloc SH and Tanfloc SG powder

Prior to each jar test experiment, 2 g/L of Tanfloc SG and Tanfloc SH stock solutions as seen in Figure 3.3, were prepared by dissolving 0.2 g of the product completely in 100 mL of deionized water.

Figure 3.3: Tanfloc SH and Tanfloc SG stock solution

3.2.2 Dual Polymer System (DPS)

The sample of the dual polymer system was supplied by Stormtec Filtration Inc. (Delta British Columbia, Canada). The polymer is being marketed as a stormwater treatment solution and it is produced by Halosource Inc. (Bothell Washington, USA). The dual polymer system is a combination of two products which are LiquiFloc and LBP 2101 (Figure 3.4).

LiquiFloc and LBP 2101 are similar in terms of being polysaccharides but LiquiFloc is a cationic chitosan based polymer while LBP 2101 is anionic. The LiquiFloc solution received contained 2% of the active ingredient while LBP 2101 was received in an aqueous form containing 1% of the active ingredient. These concentrations are equivalent to 20 g/L and 10 g/L for LiquiFloc and LBP 2101, respectively.

Figure 3.4: The dual polymer system

For ease of dispensing during jar testing, both polymers were further diluted to 1 g/L of their active ingredient prior to each experiment. This was achieved by making 5 mL and 10 mL of LiquiFloc and LBP 2101, respectively up to 100 mL using deionized water.

3.2.3 Other Treatment Chemicals

Zetag 7873, Zetag Anionic, and alum were collected from the pollution control laboratory of the City of Windsor. Zetag 7873 is presently being used at the City of Windsor's RTB for the treatment of Windsor CSO. It was recommended for its ability to meet the requirements of procedure F-5-5 and for having the longest shelf life among the other polymers that were evaluated (Li, et al., 2003). Zetag 7873 is a polyacrylamide based cationic polymer. It was received in liquid form as 50% of the active ingredient and was diluted to 1 g/L prior to jar testing.

Zetag anionic is being used in combination with alum at LRWRP for municipal wastewater treatment and was received in granular form. The alum received contained 4.4% of aluminum. Prior to each jar test experiment, Zetag anionic was completely dissolved in deionized water to produce 1 g/L of the polymer and the alum was further diluted to 1 g (Al)/L.

3.2.4 Synthetic Wastewater

Synthetic wastewater was prepared by using bentonite. A stock solution of the synthetic wastewater was prepared by adding 10 g of the bentonite powder to 1 litre of water. The mixture was made using a magnetic stirrer to achieve uniform dispersion of the bentonite particles. The stock solution was further diluted to 200 mg/L to make up suspensions of 45 NTU turbidity.

3.3 Experimental Procedures

3.3.1 CSO Characterisation

Although there is presently no limit to the discharge of phosphorus as a result of CSO in Ontario, the recent influence the DRP may be having on the eutrophication in Lake Erie has made it interesting to explore. Hence, a total of 10 events were captured and analysed for SS, BOD, TP, TRP and DRP. Table 3.1 gives a summary of event dates, number of samples and the parameters analysed, for each of the events.

Table 3.1: Analysed Parameters for All CSO Captured

Event ID	Event Date	No. of Samples	SS	BOD	TP	DRP	TRP
Event 1	27 July 2014	16	ü			ü	
Event 2	11 - 12 August 2014	16	ü			ü	
Event 3	2 September 2014	16	ü	ü		ü	
Event 4	10 September 2014	16	ü	ü		ü	
Event 5	21 April 2015	11	ü	ü	ü	ü	ü
Event 6	18 May 2015	9	ü	ü	ü	ü	ü
Event 7	27 May 2015	10	ü	ü	ü	ü	ü
Event 8	31 May 2015	24	ü	ü	ü	ü	ü
Event 9	20 August 2015	24	ü	ü	ü	ü	ü
Event 10	31 August 2015	14	ü	ü	ü	ü	ü

3.3.2 Jar Test Experiments

A total of three natural polymers were evaluated based on their SS and BOD removal efficiencies using the jar test experimental procedure. Prior to the addition of the polymers, samples in beakers were continuously agitated at 100 rpm for 5 s to keep the solids in suspension. Samples were then rapidly mixed at 100 rpm (G = 90 s^{-1}) for 2 min after polymer addition; followed by slow mixing at of 25 rpm (G = 18 s^{-1}) for 5 min; samples were then allowed to settle for 5 min. The respective G-values were derived based on the graph shown in APPENDIX A. Afterwards, sample sizes 500 mL – 700 mL of the sample were collected in wide bore mouth sampling bottles for analysis.

3.3.2.1 Preliminary Experiments

Preliminary experiments were conducted using synthetic turbid water. The evaluation at this stage was based on the turbidity removal efficiency of the polymer. This was done to estimate the polymer concentration that result in a significant pollutant removal.

For the preliminary experiment, in addition to evaluating Tanfloc SG; Tanfloc SH; and the DPS, LiquiFloc, which is a component of DPS, was also evaluated independently. LiquiFloc has been reported (Bailey, et al., 2006; Curtis, 2007) to give the desired removal efficiency for solids and turbidity, respectively.

For each jar test run, controls were used as benchmarks to assess and compare the effectiveness of the polymers. In addition to blank control, Zetag 7873 and alum + anionic polymers were also used as chemical controls.

3.3.2.2 Polymer Selection

Based on the polymer concentration estimated from the preliminary experiment stage, the polymers were further evaluated on municipal wastewater between using a wider range of polymer concentrations. The evaluation at this stage was aimed at determining if the polymers were able to meet the requirements of Procedure F-5-5 guidelines which is 50% removal efficiency (RE) for SS and 30% RE for BOD_5. For the polymers that met the requirements, selection was based on the polymer that performed best based on their SS and BOD_5 removal efficiencies. The effect of the respective polymers on pH were also evaluated at this stage by measuring pH in the jars before and after the experiment.

Besides using Zetag 7873 as a control parameter for all jar test runs, it was also evaluated using a wide range of concentrations. This was done to assess its effectiveness under the same jar test operating conditions as the natural polymers. This also allowed a detailed comparison between the efficiencies of Zetag 7873 and the natural polymers. Tanfloc SG, Tanfloc SH, and DPS were evaluated more than once as a quality control measure to ascertain the performance achieved in the previous experiments.

As presented in Table 3.2, each polymer was evaluated at least twice except for LiquiFloc which was only evaluated once. DPS evaluation in Experiment #2 involved two stages, for the first stage, the concentration of LiquiFloc was initially kept constant while the concentration of LBP 2101 was varied. For the second stage, the concentration of LBP 2101 was varied and the concentration of LiquiFloc was kept constant. This was done with the aim of evaluating the polymer that most influences the effectiveness of the dual polymer system. Experiment #10 was performed to ascertain the difference between the treatment efficiencies of Tanfloc SG and Tanfloc SH.

Table 3.2: Polymers Assessed for the Preliminary Experiments

	Polymer used
Experiment 1	LiquiFloc
Experiment 2	DPS
Experiment 3	DPS
Experiment 4	DPS
Experiment 5	Tanfloc SH
Experiment 6	Tanfloc SH
Experiment 7	Tanfloc SG
Experiment 8	Tanfloc SG
Experiment 9	Zetag 7873
Experiment 10	Tanfloc SH and Tanfloc SG

The jar test experiments were performed on various dates between April 2015 and September 2015. Due to the limitation of not being able to perform all jar test experiments with wastewater with the same characteristics, controls were therefore applied as follows:

- Blank control: samples in the jar went through the jar testing process without the addition of polymer.
- 5 mg (Al)/L alum + 0.3 mg/L Zetag anionic polymer. This is the combination commonly used for the CEPT process at the LRWRP (Freund, 2013).
- 1 mg/L Zetag 7873: Zetag 7873 is presently being used at the Windsor RTB for the treatment of Windsor CSO.

In addition to calculating the pollutant removal efficiencies (RE) in relation to the raw wastewater using Equation 3.1, the removal efficiency of the polymers were also calculated with respect to treatment in the respective blank control of each jar test experiments (Equation 3.2). The adjustment to the removal efficiency was done to account for pollutants that are readily removed without the addition of polymer (Bailey, et al., 2006; Ebeling, et al., 2005; Miller, et al., 2008).

$$\text{Pollutant RE (\%)} = \frac{C_r - C_f}{C_r} \text{ X } 100 \qquad (3.1)$$

$$\text{Corrected Pollutant RE (\%)} = \frac{C_b - C_f}{C_b} \text{ X } 100 \qquad (3.2)$$

where: C_r = Initial pollutant concentration in the raw wastewater
C_b = Final pollutant concentration in blank control
C_f = Final pollutant concentration in jars

3.3.2.3 Further Evaluation of the Selected Polymer

Additional Experiments, #11 to #14, were performed using the selected natural polymer in order to estimate the minimum concentration of the selected natural polymer that meets the requirement of procedure F-5-5. However, while Experiments #11 and #12 were performed using municipal wastewater samples, Experiments #13 and #14 were performed using composite CSO samples obtained at the inlet of City of Windsor's RTB.

3.3.2.4 Phosphorus Removal

The effectiveness of Tanfloc SG for phosphorus removal was assessed in Experiments #2, #10, #13, and #14. For this purpose, TP and DRP were determined for the respective jar test experiments.

3.4 Analytical Methods

In this study, analyses of SS, BOD, and all forms of phosphorus were performed according to the procedures outlined in Standard Methods based on the respective section numbers presented in Table 3.3.

Table 3.3: Analytical Methods Used as per Standard Methods (APHA, 2005)

Parameter	Section ID	Method
Suspended Solids	2540 D	Filtration Method
BOD	5210 B	Carbonaceous BOD
Total Phosphorus	4500-P B	Persulfate Digestion
	4500-P D	Stannous Chloride Colourimetry
Total Reactive Phosphorus	4500-P D	Stannous Chloride Colourimetry
Dissolved Reactive Phosphorus	4500-P D	Stannous Chloride Colourimetry
pH	4500-H^+ B	Electrometric
Turbidity	2130 B	Nephelometric

DRP was filtered through a 0.45 µm pore size filter paper that had been soaked in deionised water for at least 48hours. In addition, prior to filtration, a minimum of 100 mL deionized water was filtered through the filter paper before running the sample through it. This was done to prevent leaching of pollutants from the filter paper (Khan & Pillai, 2006).

To reduce interference of solids with the colourimetry analysis during TP and TRP analysis, up to 25 mL aliquot of samples were pretreated based on the quantity of solids visually present. TRP was then further analysed according to the procedures outlined in Standard Methods. The details of TP analysis is presented in APPENDIX B.

3.5 Quality Control

For quality control purposes, reagent blanks, a standard solution and a spiked solution were also analysed with each set of samples. The percentage recovery of the spiked solution was used as a measure of accuracy. If the measured concentration of the standard solution falls within the 95% confidence interval of the calibration curve, the calibration curve is considered accurate.

Method detection limits (MDL) were determined with 99% confidence according to the method recommended by the USEPA (Oblinger Childress, et al., 1999). Measurements below the detection limit were recorded as at the method detection limit.

Calibration curves and method detection limit calculations are presented in APPENDIX C.

3.6 Analytical Equipment

3.6.1 Jar Test Apparatus

The Phipps and Bird jar test apparatus was used in this study to simulate the coagulation, flocculation and settling process. The apparatus shown in Figure 3.5 has an illuminated base and consists of six 2000 mL B-KER^2 square jars with corresponding paddle stirrers. The jars, which are also referred to as “gator” jars, provide the thermal insulation necessary to minimize temperature change during the experiment.

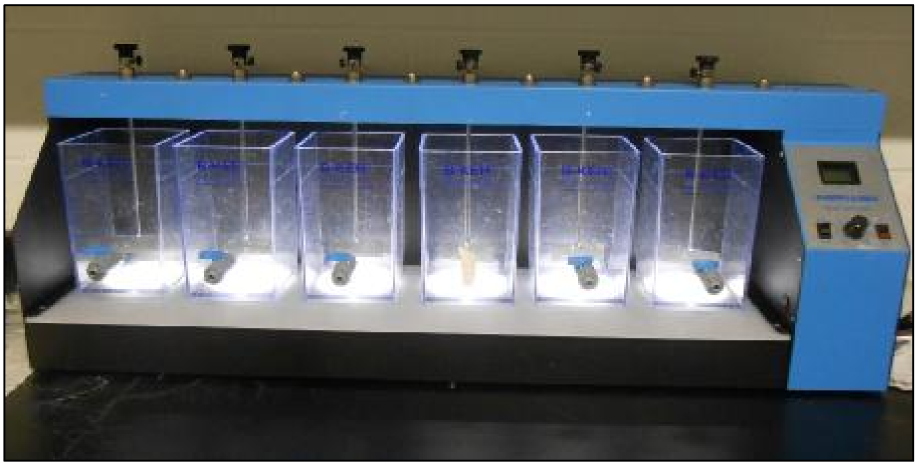


Figure 3.5: Phipps and Bird jar test apparatus

3.6.2 Other Equipment

Other equipment used includes: a UV- VIS spectrophotometer for phosphorus analysis; dissolved oxygen meter; HACH turbidimeter meter; pH meter. All the equipment was calibrated before analyses.

4 RESULTS AND DISCUSSION

4.1 Windsor CSO Characteristics

A total of 10 CSO events were captured and characterised for constituent pollutants between July 2014 and August 2015. A summary of pollutant concentrations for all events sampled is presented in Table 4.1. The concentrations of SS, BOD, TP and TRP vary widely within events as indicated by the high standard deviations, which were close in value to the mean concentrations of the pollutants.

Despite the wide variation in pollutant concentrations, a cumulative frequency percentage plot, as presented in Figure 4.1, shows that more than 50% of the SS concentrations were less than 50 mg/L, while over 80% of the SS concentrations were below 200 mg/L.

Table 4.1: Summary of Pollutant Concentrations

Event ID	**No. of Samples**	**Parameters**	**Minimum (mg/L)**	**Maximum (mg/L)**	**Average (mg/L)**	**Standard Deviation**
Event 1	16	SS	12	377	106	122
		DRP	0.18	0.47	0.33	0.10
Event 2	16	SS	2	385	110	117
		DRP	0.14	0.46	0.28	0.10
Event 3	16	SS	118	908	275	195
		BOD	23	121	44	25
		DRP	0.22	0.48	0.33	0.08
Event 4	16	SS	21	1199	328	328
		BOD	14	88	48	27
		DRP	0.05	0.26	0.46	.34
Event 5	11	SS	8	80	30	24
		BOD	3.8	16.4	8.7	3.9
		TP	0.22	1.37	0.60	0.39
		DRP	0.16	0.24	0.22	0.04
		TRP	0.24	0.44	0.36	0.06
Event 6	9	SS	30	100	57	25
		BOD	5.0	22.1	11.7	6.5
		TP	0.25	1.07	0.69	0.25
		DRP	0.23	0.39	0.32	0.05
		TRP	0.31	0.62	0.45	0.10
Event 7	11	SS	8	1674	309	506
		BOD	3.3	224	50.1	70.1
		TP	0.3	6.42	1.70	1.50
		DRP	0.13	0.43	0.24	0.11
		TRP	0.17	3.38	0.81	0.09
Event 8	24	SS	11	85	34	18
		BOD	1.9	17.6	5.9	4.0
		TP	0.18	1.09	0.42	0.18
		DRP	0.06	0.44	0.18	0.09
		TRP	0.16	0.60	0.27	0.09
Event 9	24	SS	4	334	57	66
		BOD	8	80	30.4	24.2
		TP	0.15	1.57	0.37	0.30
		DRP	0.02	0.10	0.04	0.03
		TRP	0.02	0.33	0.10	0.07
Event 10	14	SS	4	64	31	20
		BOD	1.7	9.8	4.9	2.8
		TP	0.13	0.71	0.30	0.16
		DRP	0.07	0.19	0.12	0.03
		TRP	0.13	0.39	0.19	0.07

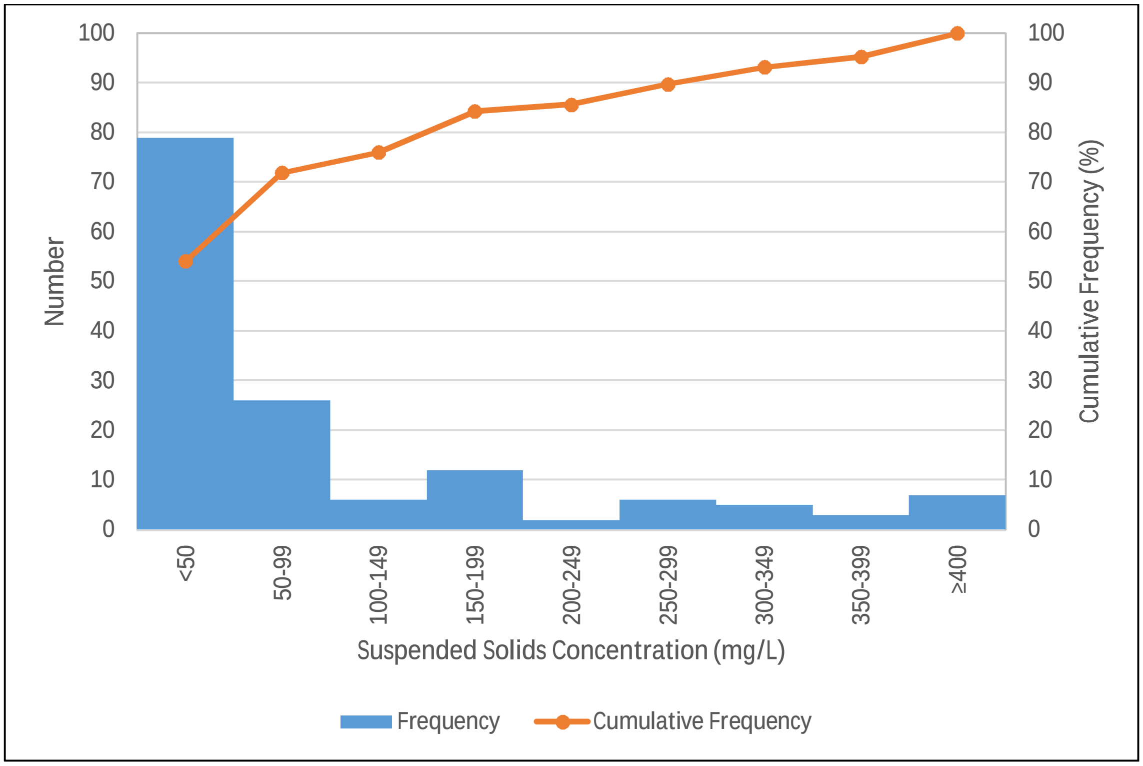


Figure 4.1: Suspended solids cumulative frequency curve

4.1.1 Categorization of CSO Events

The SS is commonly used as a control measure for stormwater, and is regarded as one of its most important constituents (Maestre & Pitt, 2005). Hence, all 10 events were ranked according to their SS event mean concentration (EMC) and divided into low, medium, and high concentration events. Since pollutant loading varies from one storm event to another (Berndtsson, 2014; Droste & Hartt, 1975), the grouping was based on the significant difference between the SS concentration. Hypothesis 1 was therefore, developed to determine the difference between the EMC SS for all the events.

Hypothesis 1

H_{01}: All the event mean concentrations are equal

H_{a1}: At least one of the event mean concentration is different

Hypothesis 1 was analysed using the one-way analysis of variance (ANOVA) test. The ANOVA test was done at the 95% confidence interval using the Minitab 17 software. To maintain the normality distribution assumption requirement of ANOVA, the SS concentration data were transformed to a normal distribution. Normalisation was done by converting the data to their natural log form.

Hence, based on the results of the ANOVA analysis of hypothesis 1 presented in APPENDIX D, the events were grouped as shown in Table 4.2. As shown in Table 4.2, BOD also conforms to the grouping.

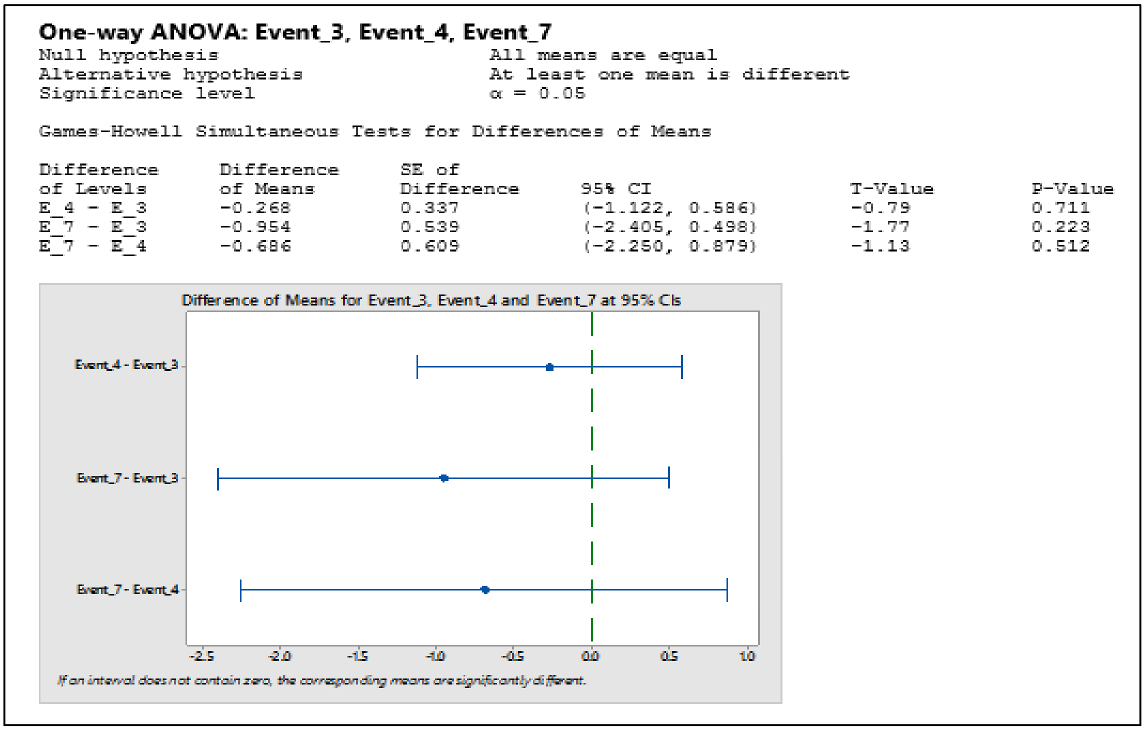
Table 4.2: Events Grouped According to Pollutant Concentrations

Event Grouping	**Events**	**Mean SS (mg/L)**	**Mean BOD (mg/L)**
High Concentration	Event 4	328	48
	Event 7	309	50
	Event 3	275	44
Medium Concentration	Event 2	110	ND*
	Event 1	106	ND*
	Event 9	57	30.4
	Event 6	57	12
Low Concentration	Event 8	34	6
	Event 10	31	5
	Event 5	30	9

* ND: Not determined

Hypothesis 2, 3, and 4 were also tested to confirm that the event mean concentrations of the high, medium, and low events, respectively do not vary significantly. Their null hypothesis states that all the means in each of the groups are equal while their corresponding alternative hypothesis states that at least one mean is different. The results of hypotheses 2, 3, and 4 are presented as follows:

Hypothesis 2



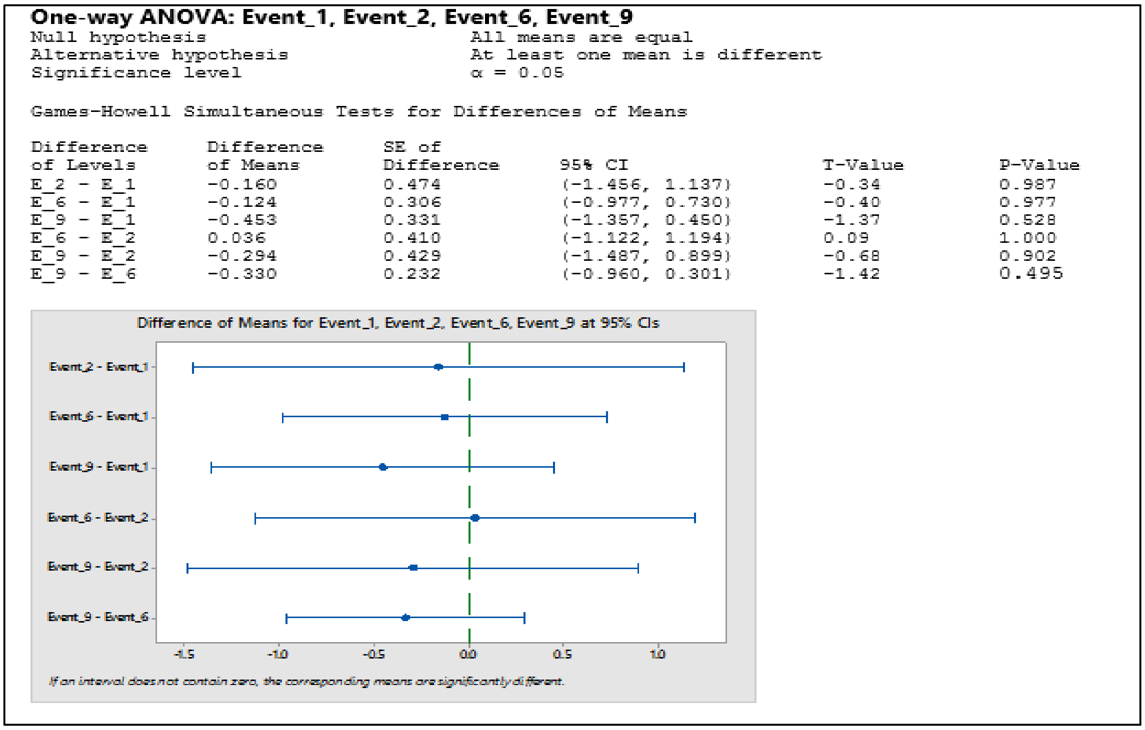
One-way ANOVA: Event_3, Event_4, Event_7

```
Null hypothesis                         All means are equal
Alternative hypothesis                  At least one mean is different
Significance level                      α = 0.05

Games-Howell Simultaneous Tests for Differences of Means

Difference       Difference       SE of
of Levels        of Means         Difference       95% CI                    T-Value          P-Value
E_4 - E_3        -0.268           0.337            (-1.122, 0.586)           -0.79            0.711
E_7 - E_3        -0.954           0.539            (-2.405, 0.498)           -1.77            0.223
E_7 - E_4        -0.686           0.609            (-2.250, 0.879)           -1.13            0.512
```

Hypothesis 3



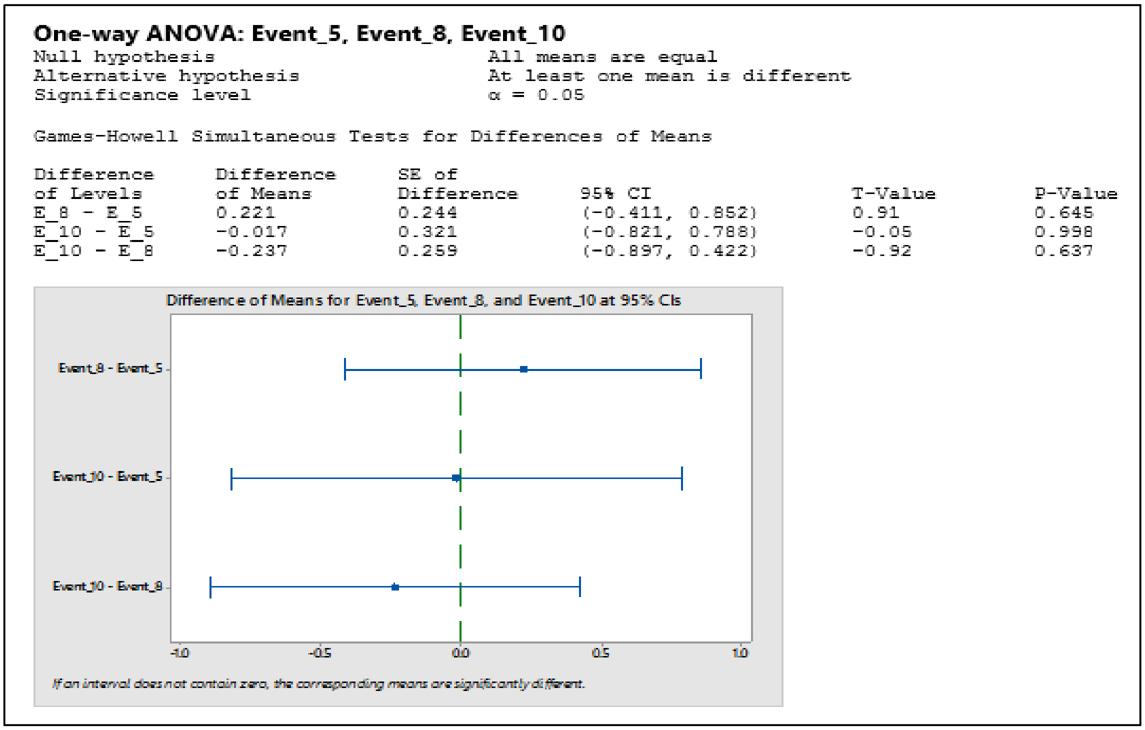
One-way ANOVA: Event_1, Event_2, Event_6, Event_9

```
Null hypothesis                         All means are equal
Alternative hypothesis                  At least one mean is different
Significance level                      α = 0.05

Games-Howell Simultaneous Tests for Differences of Means

Difference       Difference       SE of
of Levels        of Means         Difference       95% CI                    T-Value          P-Value
E_2 - E_1        -0.160           0.474            (-1.456, 1.137)           -0.34            0.987
E_6 - E_1        -0.124           0.306            (-0.977, 0.730)           -0.40            0.977
E_9 - E_1        -0.453           0.331            (-1.357, 0.450)           -1.37            0.528
E_6 - E_2        0.036            0.410            (-1.122, 1.194)           0.09             1.000
E_9 - E_2        -0.294           0.429            (-1.487, 0.899)           -0.68            0.902
E_9 - E_6        -0.330           0.232            (-0.960, 0.301)           -1.42            0.495
```

Hypothesis 4



One-way ANOVA: Event_5, Event_8, Event_10

```
Null hypothesis                        All means are equal
Alternative hypothesis                 At least one mean is different
Significance level                     α = 0.05

Games-Howell Simultaneous Tests for Differences of Means

Difference      Difference      SE of
of Levels       of Means        Difference      95% CI                 T-Value        P-Value
E_8 - E_5       0.221           0.244           (-0.411, 0.852)        0.91           0.645
E_10 - E_5      -0.017          0.321           (-0.821, 0.788)        -0.05          0.998
E_10 - E_8      -0.237          0.259           (-0.897, 0.422)        -0.92          0.637
```

From the results of hypotheses 2, 3, and 4, all p-values are greater than the 0.05 level of significance. Therefore, the null hypothesis that states that all means in each group are equal is valid. Hence, the events grouping based on their solids concentration is valid.

4.1.2 Variability of Pollutant Concentrations

Multiple flow proportional discrete samples were collected for each CSO event, with one 1000 mL sample collected for every 500 m^3 of flow. The SS and DRP were monitored for ten events, BOD for eight events while TP and TRP were monitored for six events.

As shown in Figures 4.2 - 4.11, all pollutant concentrations vary significantly over time which explains the high standard deviations in Table 4.1.

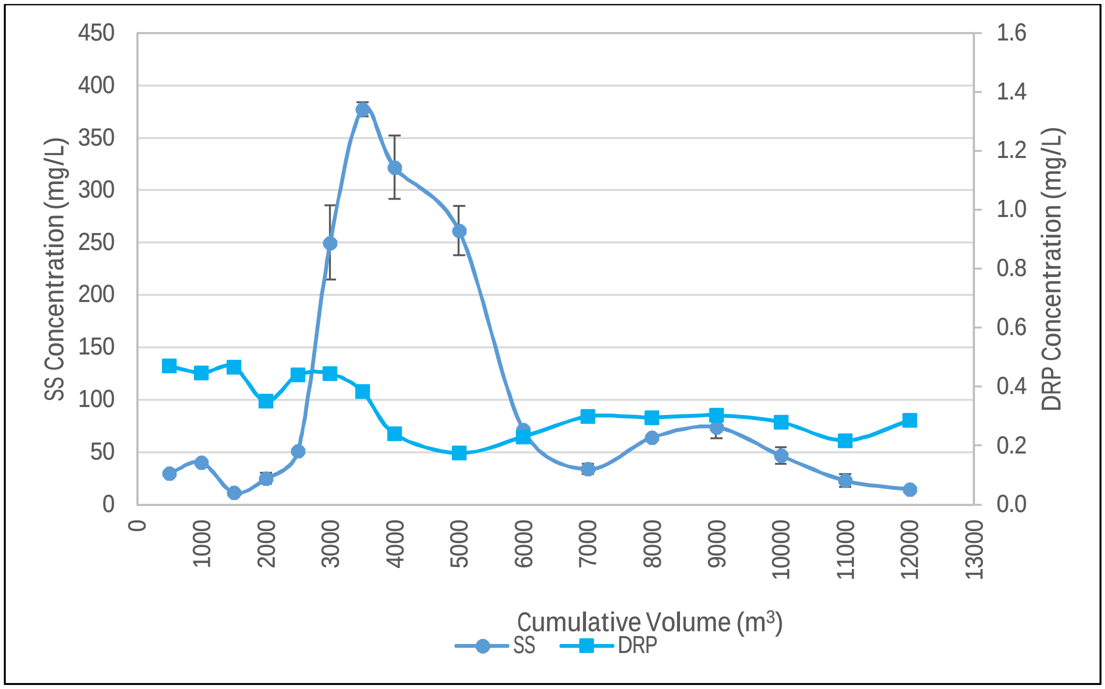


Figure 4.2: Pollutant concentration curve for Event 1

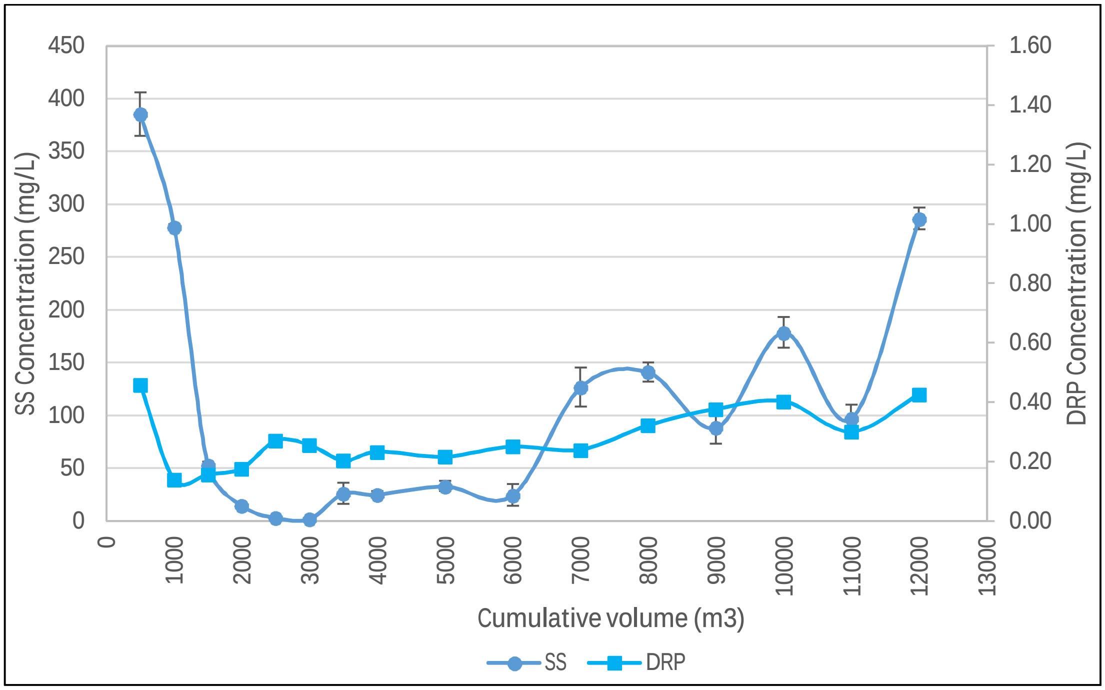


Figure 4.3: Pollutant concentration curve for Event 2

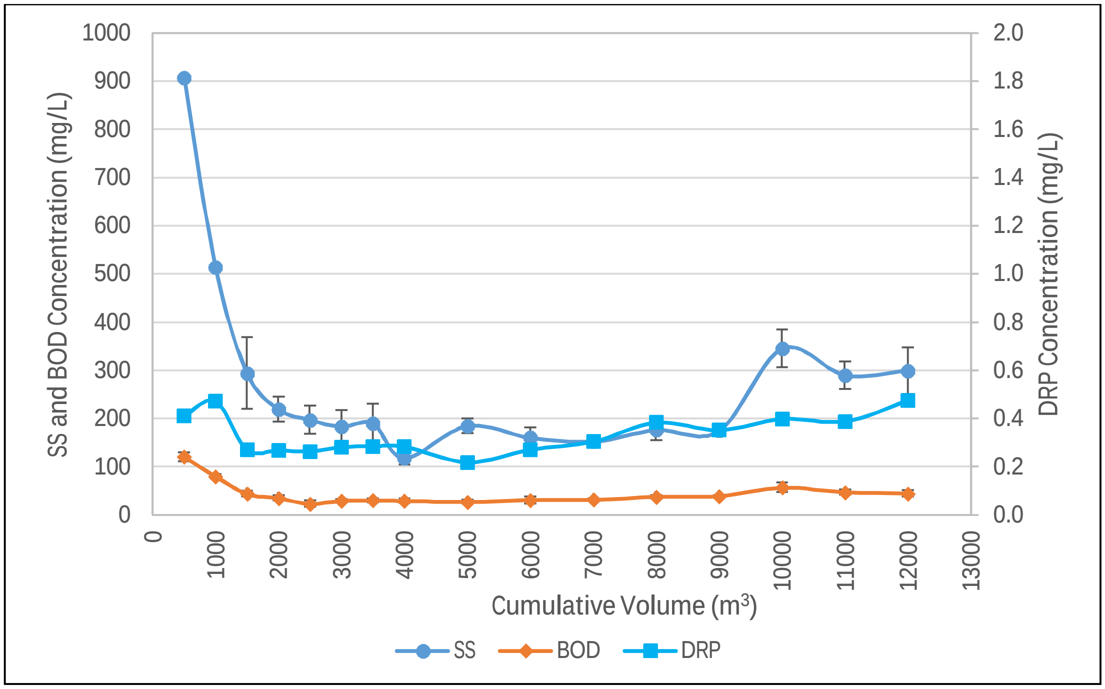


Figure 4.4: Pollutant concentration curve for Event 3

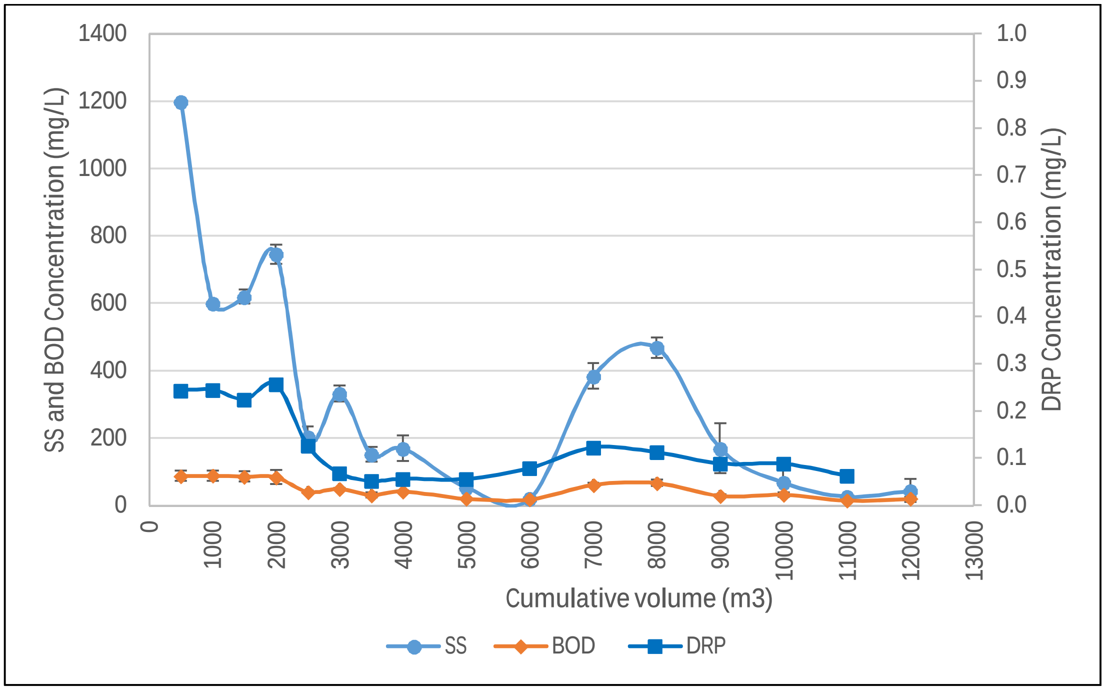


Figure 4.5: Pollutant concentration curve for Event 4

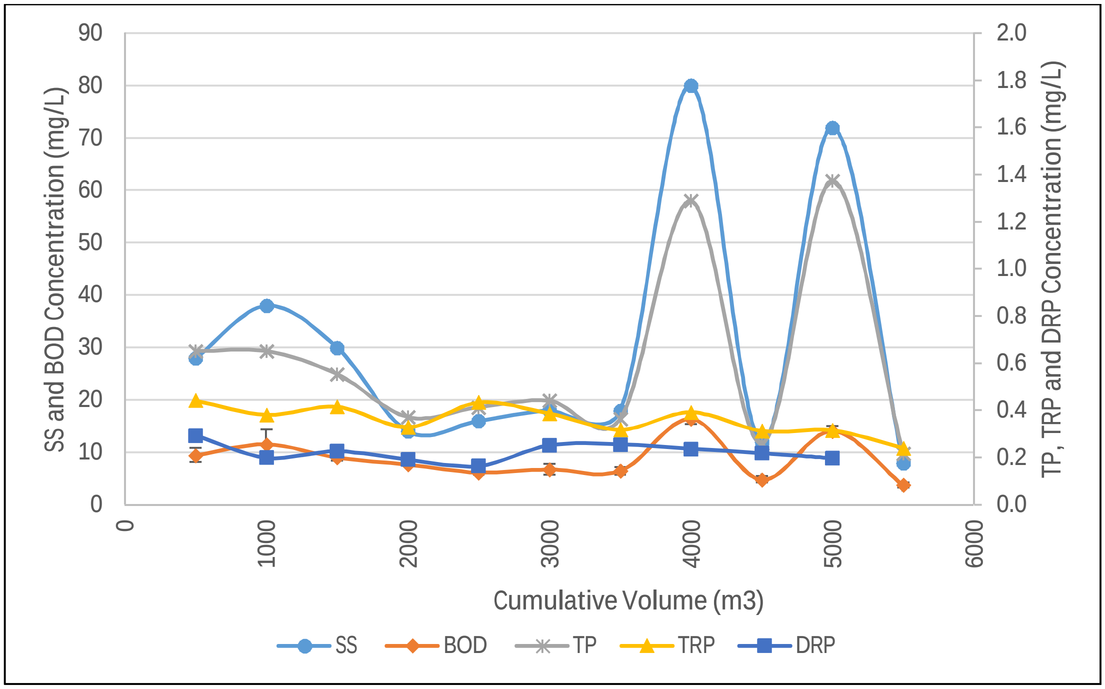


Figure 4.6: Pollutant concentration curve for Event 5

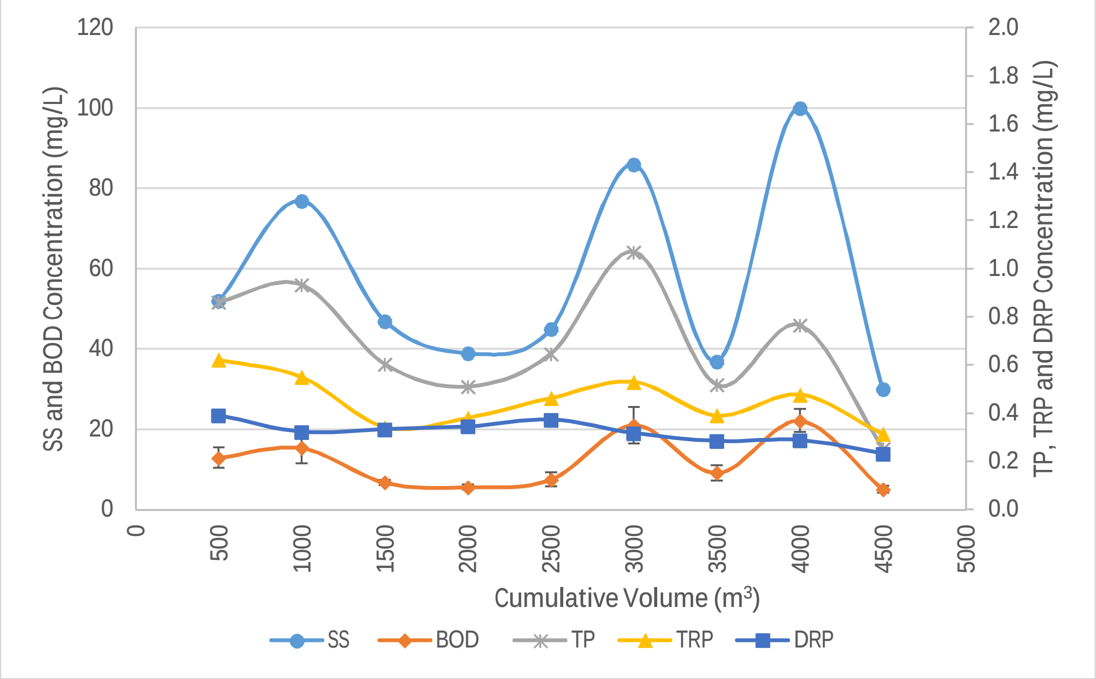


Figure 4.7: Pollutant concentration curve for Event 6

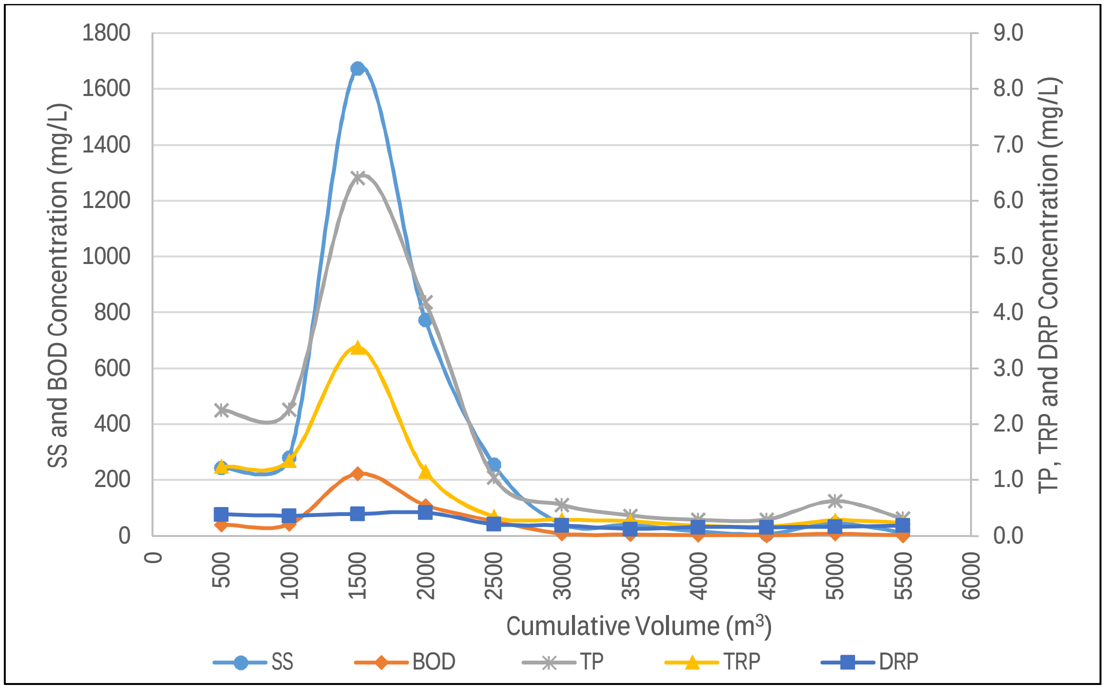


Figure 4.8: Pollutant concentration curve for Event 7

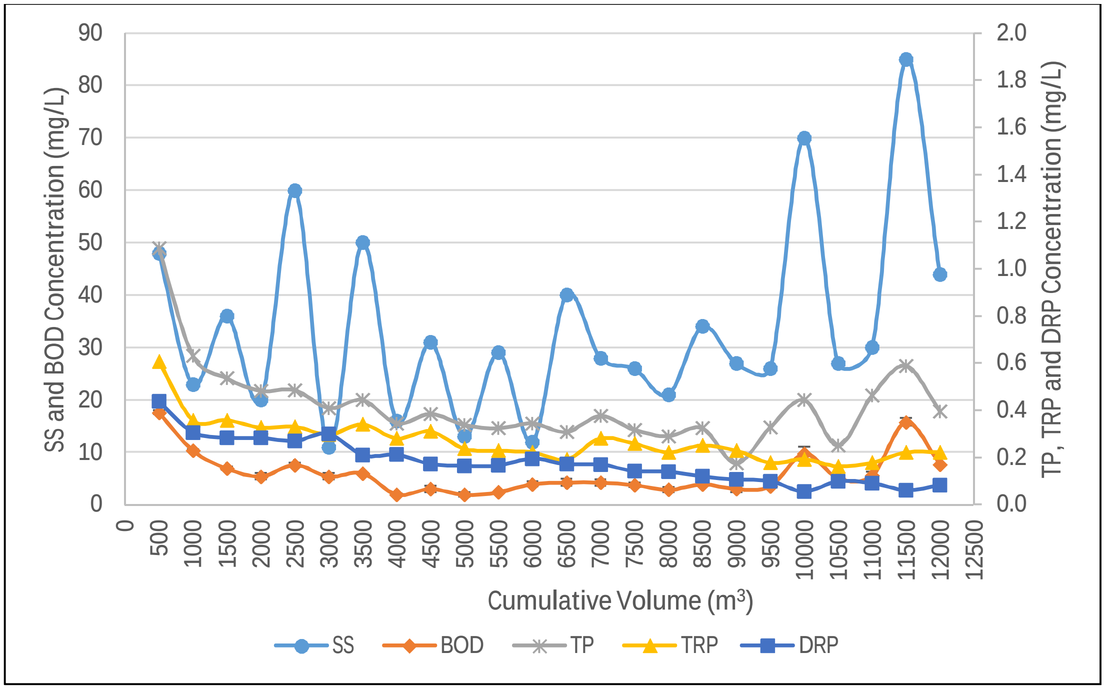


Figure 4.9: Pollutant concentration curve for Event 8

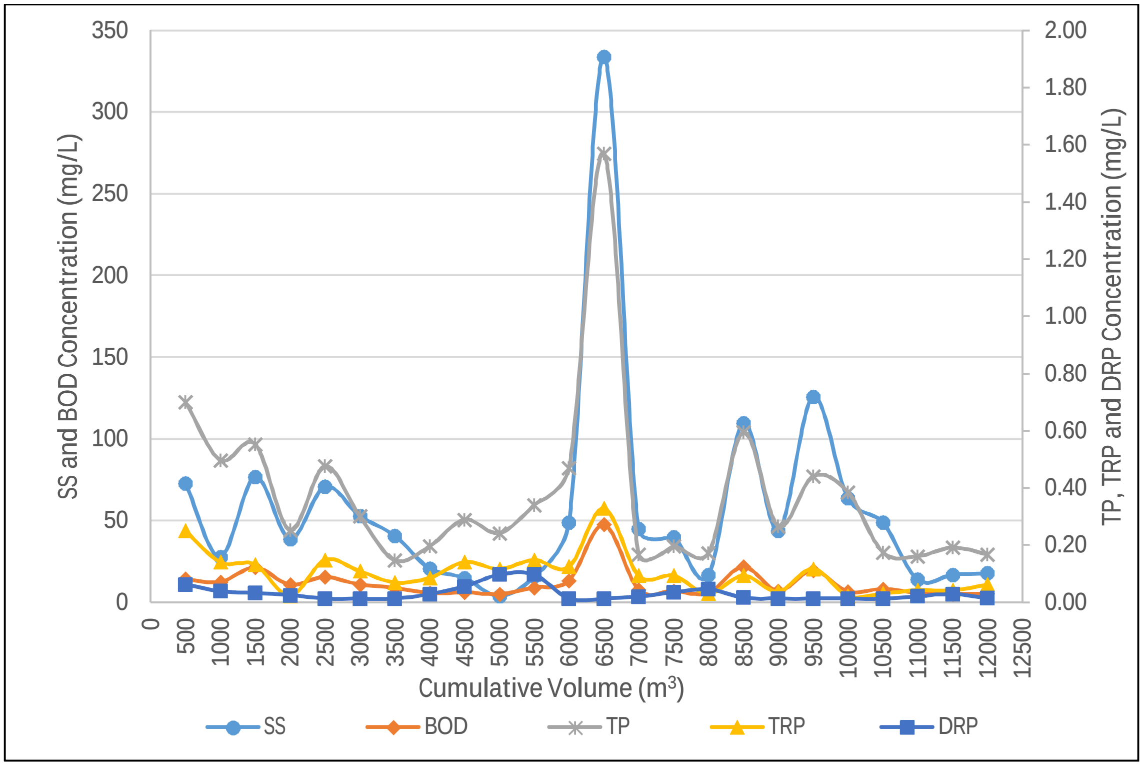


Figure 4.10: Pollutant concentration curve for Event 9

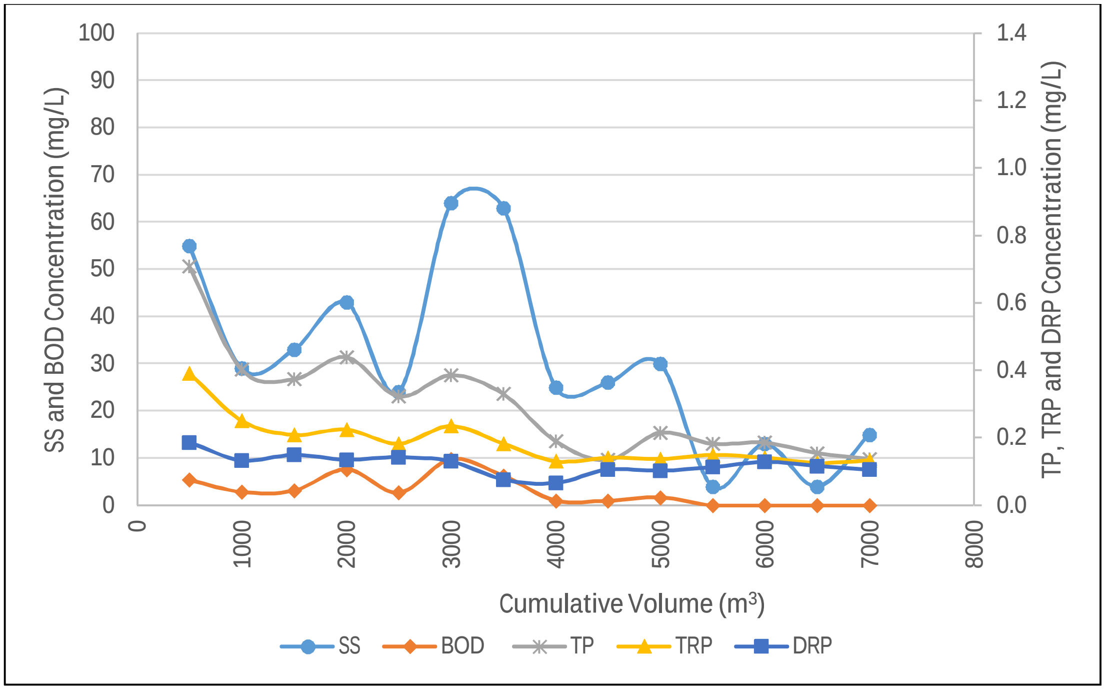


Figure 4.11: Pollutant concentration curve for Event 10

4.1.2.1 First Flush Effect

The first flush phenomenon is described by an increased pollutant concentration that is generally assumed to occur at the beginning of a storm event. As reported by Gutteridge, Haskins and Davey Pty Ltd (1981), the first flush effect is more evident in particulate pollutants than in soluble pollutants. This is similar to the findings of Droste & Hartt (1975) where the concentration of all pollutants except for colour and dissolved phosphorus were reported to be higher during the first third of a storm event. The load generated by the first flush has been quantified by Droste & Hartt (1975), Gutteridge, Haskins and Davey Pty Ltd (1981) and Cheng-qing, et al. (2007) as a function of the percentage runoff volume for their respective catchments studied.

Similar to previous studies, a spike in pollutant concentration is more evident for SS, BOD, TP, and TRP which are the pollutants in particulate form and less evident for DRP, which dissolved pollutant, as shown in Figures 4.2 – 4.11. Although the first flush is noticeable for events 2, 3, 4 and 7 as shown in Figure 4.3, Figure 4.4, Figure 4.5, and Figure 4.8, respectively, the spike in the pollutant concentrations did not always occur at the beginning of the storm event as observed in the pollutographs of other events. This is contrary to the first flush phenomenon but similar to findings in the literature (Maestre & Pitt 2005), in which the source of the contaminants and how fast they travel within the watershed were reported as important factors determining if a spike of pollutant arrives at the first flush.

4.1.3 Pollutant Mass Loadings

The mass loading for each pollutant was calculated using Equation 4.1.It was assumed that the measured pollutant concentration for each sample collected is representative of the corresponding 500 m^3 of flow. The cumulative loads were then quantified for each pollutant and the results are presented in Figures 4.12 – 4.16 for SS, BOD, TRP, TP, and DRP, respectively.

$$m_n(kg) = 10^{-3}\, c_n\, (kgm^{-3})\, X\, 500\, (m^3) \qquad (4.1)$$

where: m_n = pollutant mass load per sample,

c_n = sample concentration

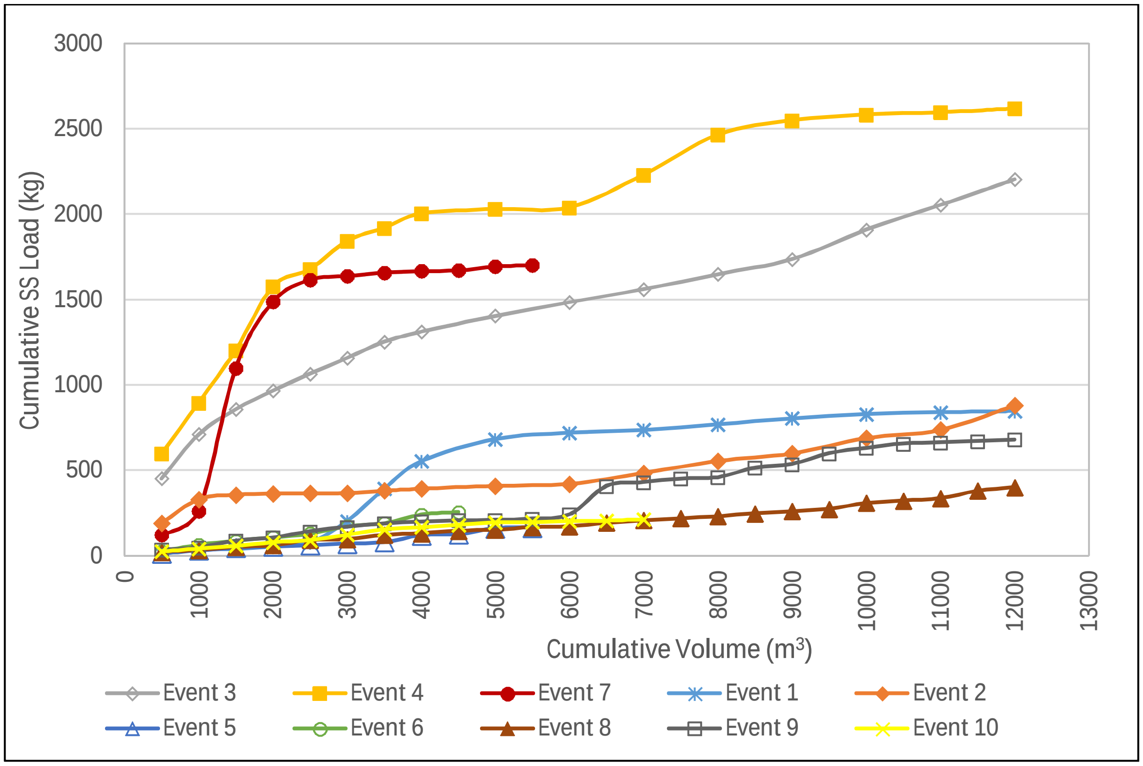


Figure 4.12: Cumulative SS load per event

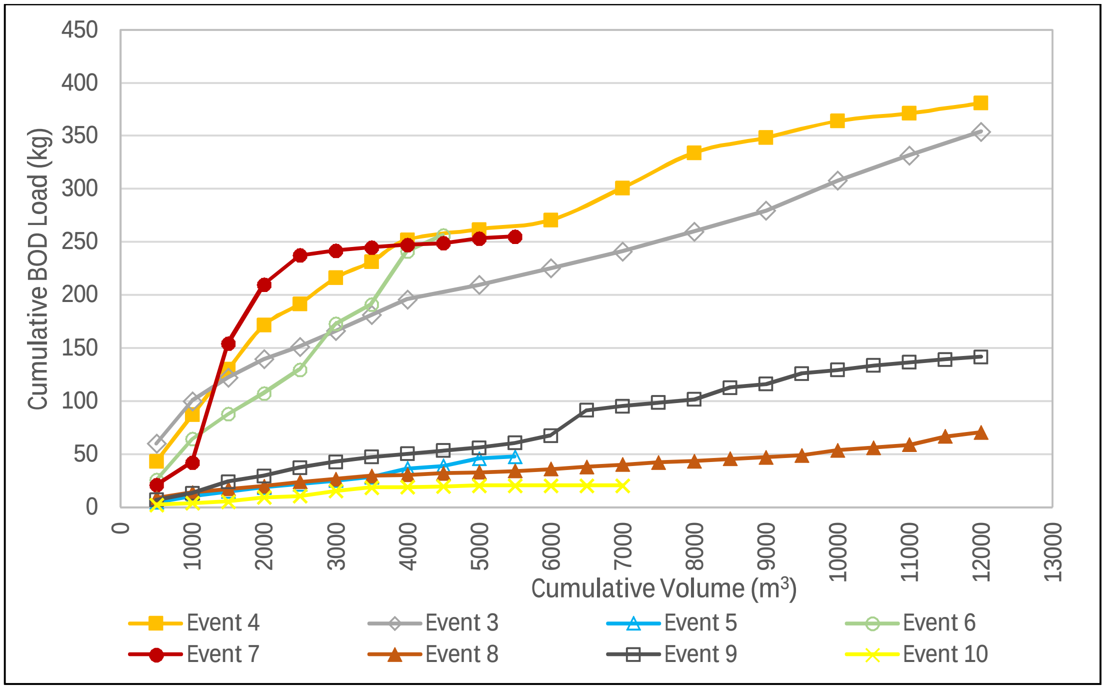


Figure 4.13: Cumulative BOD load per event

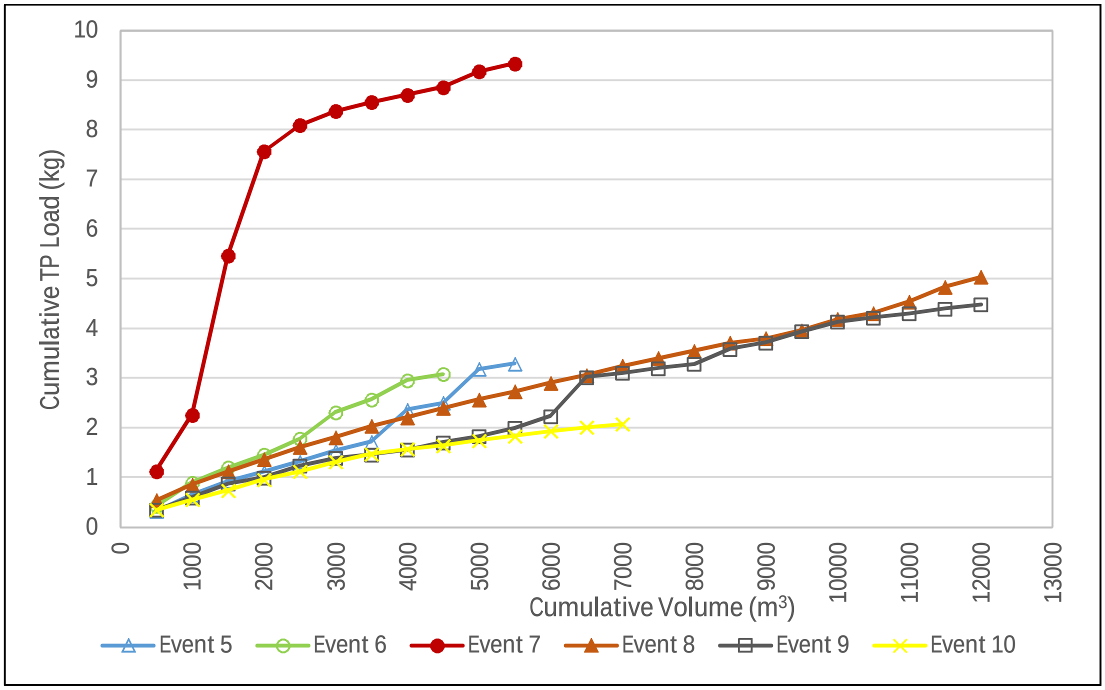


Figure 4.14: Cumulative TP load per event

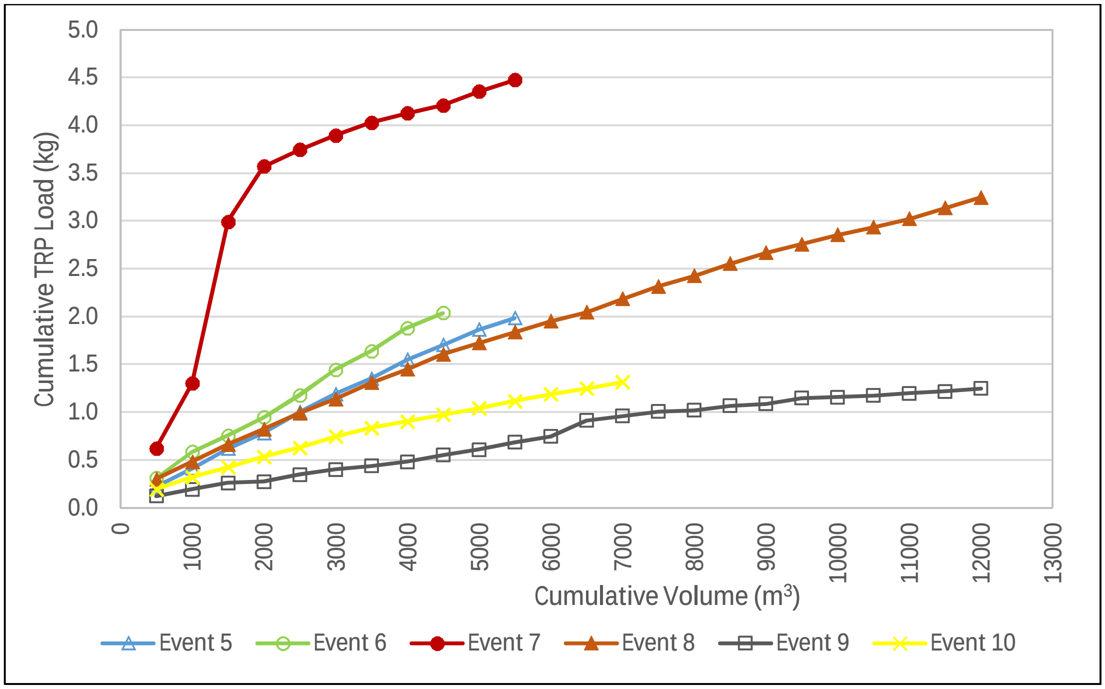


Figure 4.15: Cumulative TRP load per event

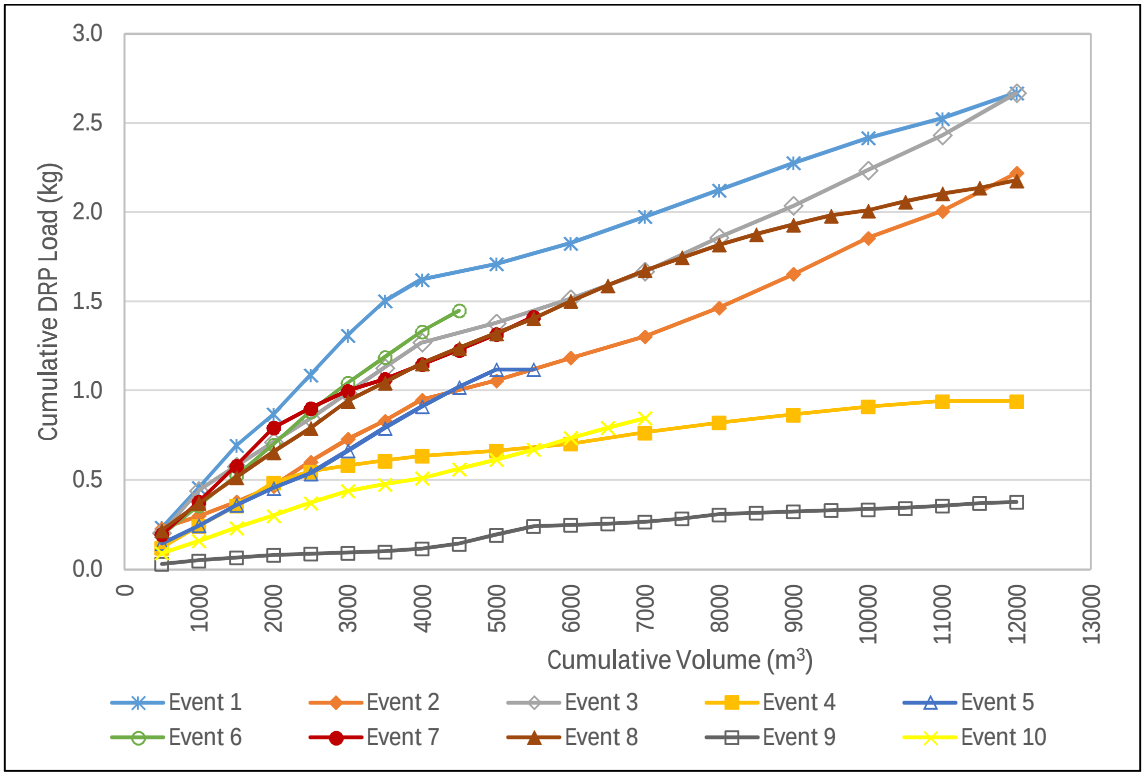


Figure 4.16: Cumulative DRP load per event

4.1.4 Effect of Rainfall Intensity on Pollutant Loadings

Rainfall characteristics such as runoff volumes and rainfall intensity may have an effect on pollutant loadings for storm flows. High rainfall intensity, which is a measure of the rainfall energy, may lead to erosion and may subsequently increase pollutant wash off, however, a significant runoff volume is required to transport the pollutant (Maestre & Pitt, 2005).

The return period (RP), being a measure of the magnitude and intensity of a storm event, was used to classify the captured storm events into low, moderate, and high intensity storms. The classification was based on 60 year rainfall Intensity-Duration-Frequency (IDF) curve for Windsor (APPENDIX E). The storms with less than 2 years return period (RP < 2yrs) were classified as low intensity storm. Storms with a RP between 2years and 5years (2yrs < RP > 5yrs) were classified as moderate intensity storms while storms with over 5 years RP (RP > 5yrs) were classified as a high intensity storm.

As shown in Figure 4.17, Event 2 only contributed ~1000kg of solids load despite being a high intensity storm. However, Event 4, which is a high load event, resulted from a moderate intensity storm while Events 7 and 3 which were similarly high load events resulted from low intensity storms. This phenomenon is similar for the BOD load as shown in Figure 4.18. Hence, there is no observed significant effect of rainfall intensity on the SS loading.

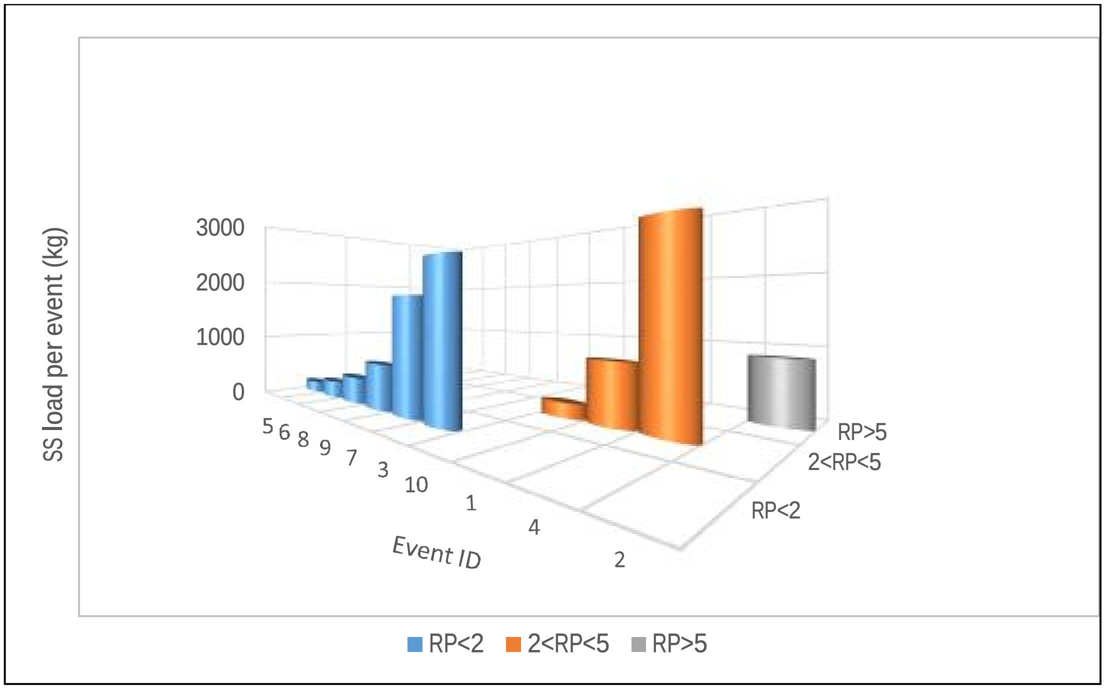


Figure 4.17: Cumulative SS load with respect to rainfall return period

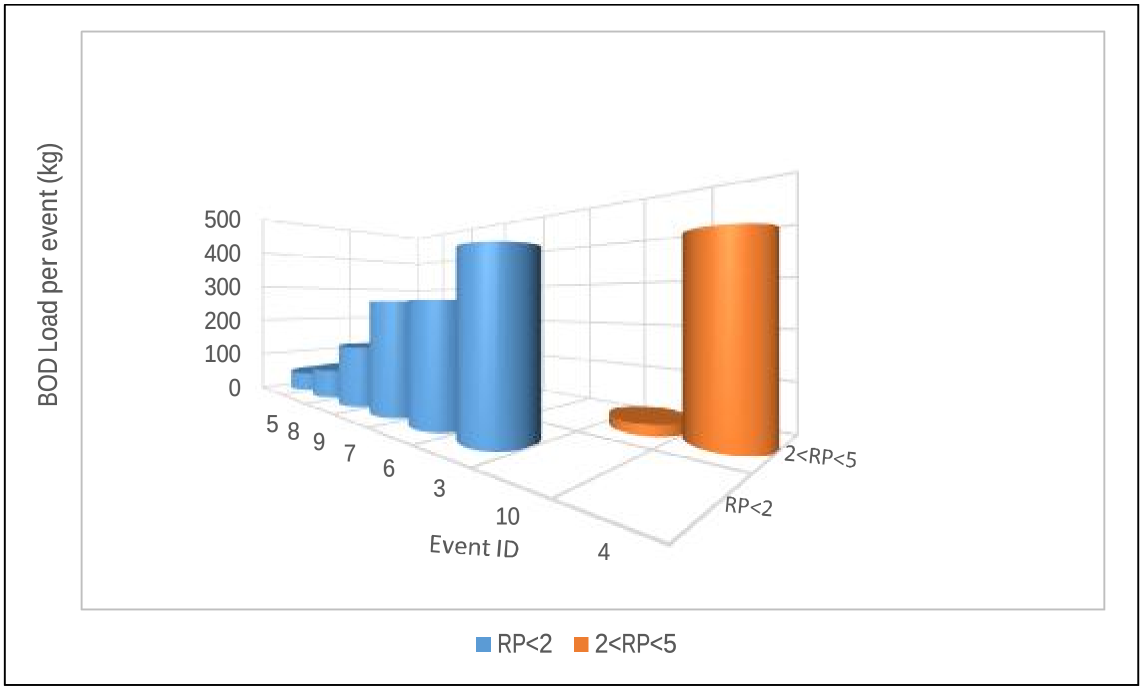


Figure 4.18: Cumulative BOD load with respect to rainfall return period

4.1.5 Effects of Antecedent Dry Weather Period

As reported in the literature Droste & Hartt (1975), three of an antecedent dry weather period caused an increase in BOD concentration although the SS concentration of the same study was not significantly affected by the antecedent dry weather condition. Moreover, it has been reported that days and weeks of antecedent dry period did not have a significant effect on runoff volumes and total pollutant loading (Gutteridge, Haskins and Davey Pty Ltd, 1981). A study (Maestre & Pitt 2005), has indicated that the increase in BOD and nutrient concentration as a result of antecedent dry weather periods may, however, be dependent on the land use type of the catchment.

A simple correlation between the antecedent dry days (ADD) and the event mean concentration was determined for the all the storm events captured. Similarly, the correlation between the ADD and the event mean concentration for the low intensity storms, according to the classification in described 4.1.4, was also determined. This was done to determine the effect of storm intensity on the relationship between ADD and the event mean concentration. This effect was not determined for moderate and high intensity storms due to insufficient data.

As shown in Figures 4.19a – e, when all the storms were considered, there were no significant relationships between the ADD and pollutant concentrations for all the pollutants sampled. However, as shown in Figures 4.20a – b, an increase in the antecedent dry days significantly increased the event mean concentration for SS and BOD for the low intensity storms. The effect of the intensity of the storms is thus evident in the relationship between the ADD and each of the SS and BOD concentration. For the DRP, similar to when all the storm events were considered, an increase in ADD did not have an effect on the event mean concentration for the low intensity storms as shown in Figure 4.20e.

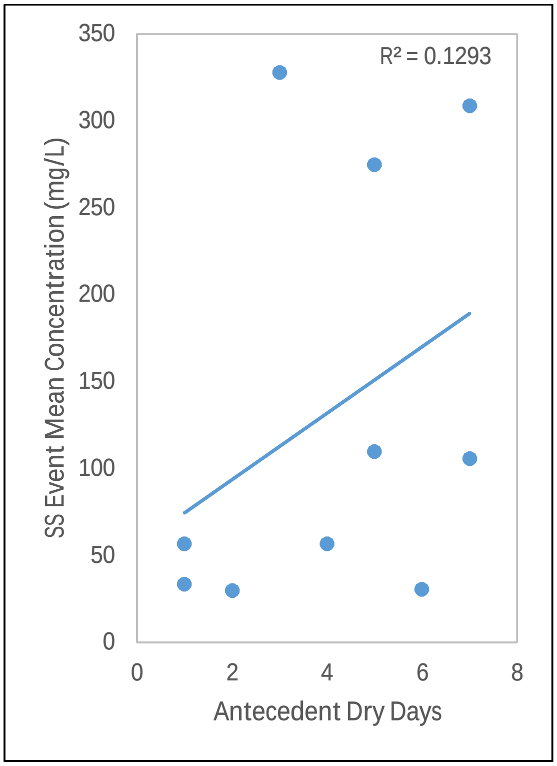


Figure 4.19a: SS load vs ADD for all storms

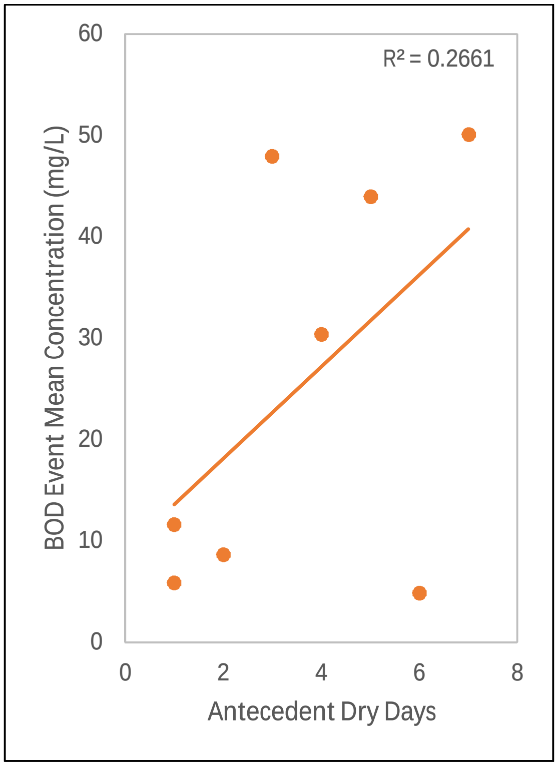


Figure 4.19b: BOD load vs ADD for all storms

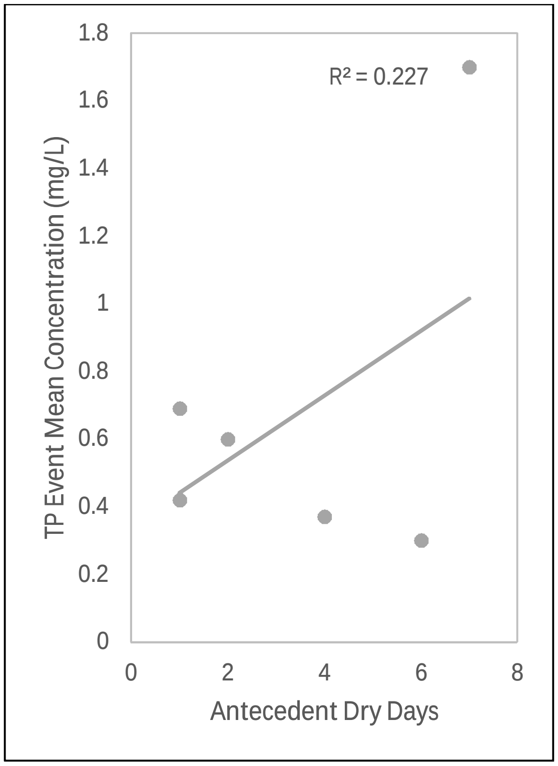


Figure 4.19c: TP load vs ADD for all storms

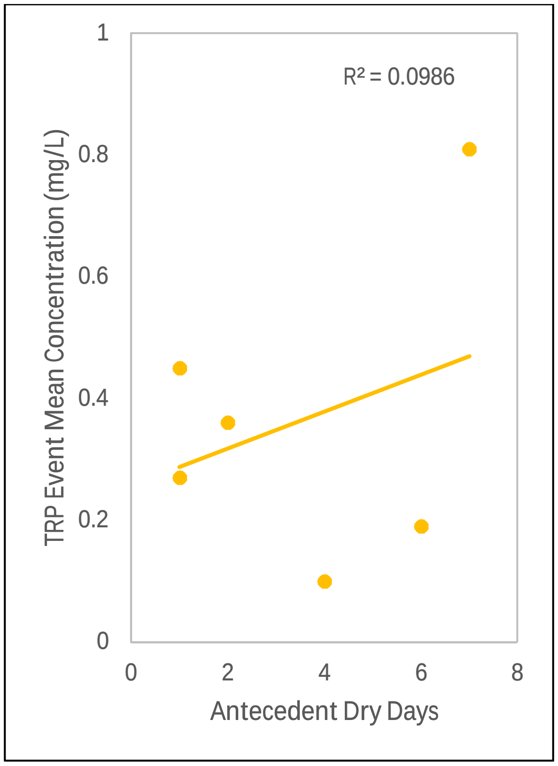


Figure 4.19d: TRP load vs ADD for all storms

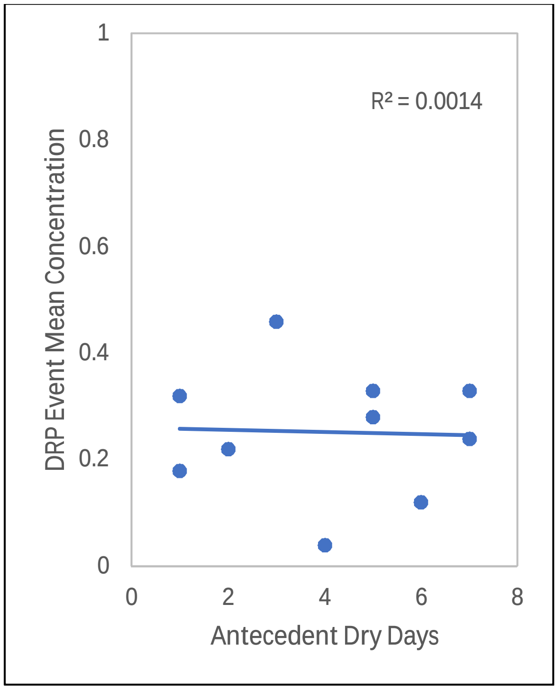


Figure 4.19e: DRP load vs ADD for all storms

Figure 4.19a - e: Pollutant concentrations vs ADD for all storm events

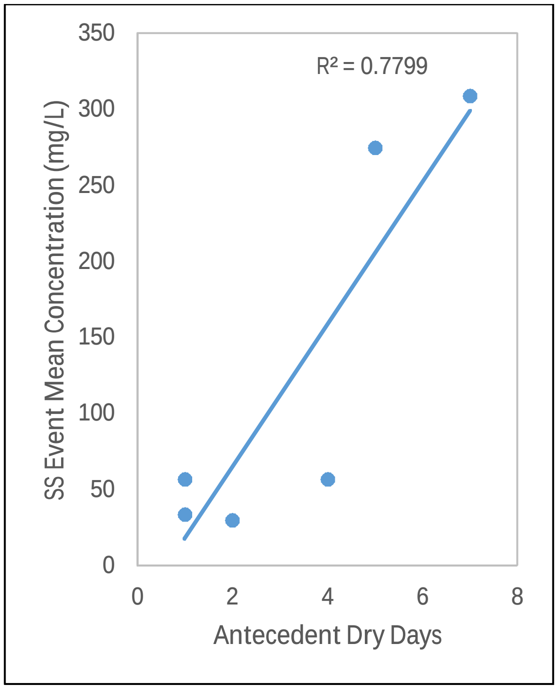


Figure 4.20a SS load vs ADD for low intensity storms

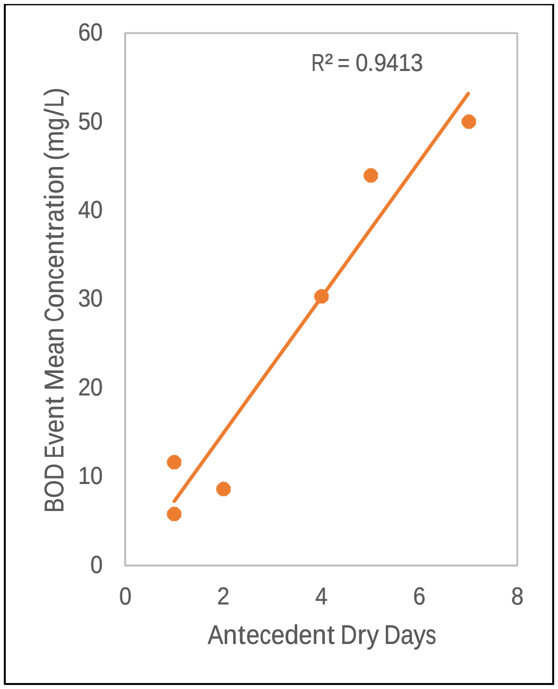


Figure 4.20b: BOD load vs ADD for low intensity storms

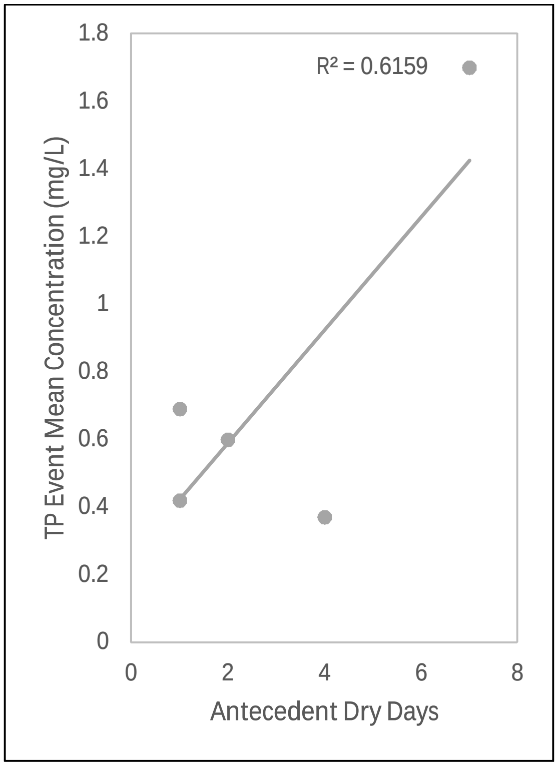


Figure 4.20c: TP load vs ADD for low intensity storms

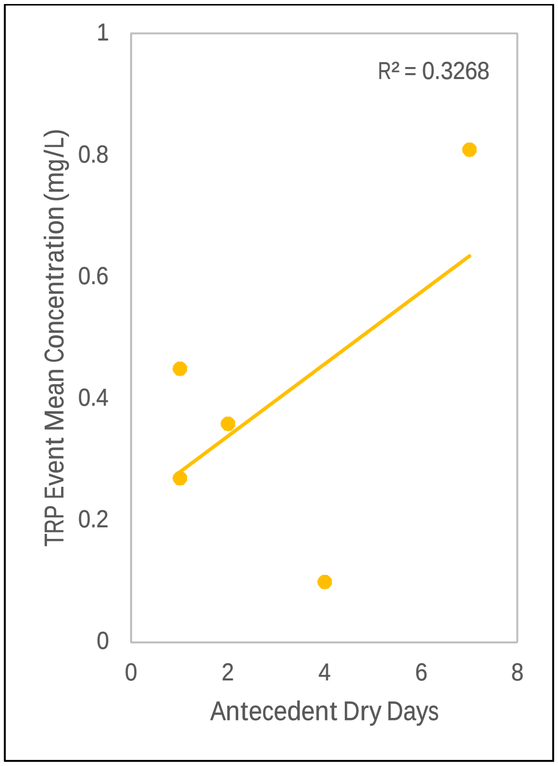


Figure 4.20d: TRP load vs ADD for low intensity storms

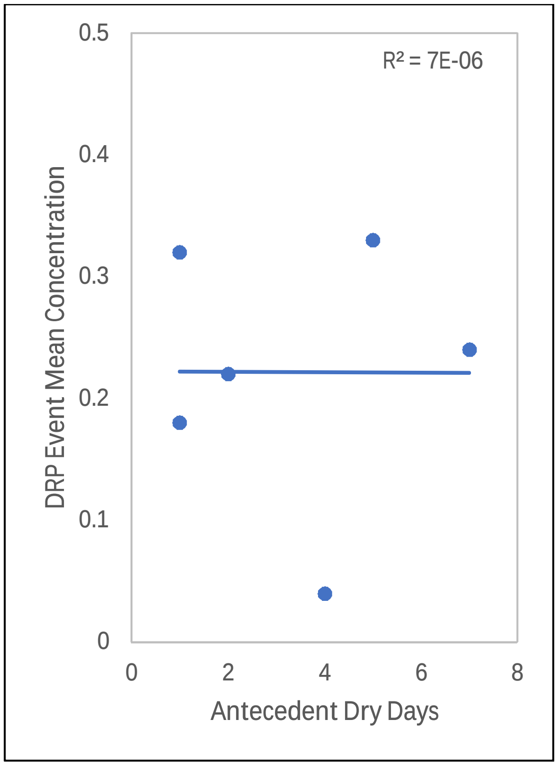


Figure 4.20e: DRP load vs ADD for low storms intensity storms

Figure 4.20a - Figure 4.20e: Pollutant concentrations vs ADD for low intensity storm events

4.1.6 Phosphorus Speciation and their Variability

Events 5 - 10 were monitored for three forms of phosphorus: TP, TRP and DRP. Previous work on municipal wastewater (Freund, 2013) and lakes as well as rivers in Canada (Bradford & Peters, 1987) has shown that DRP is the dominant part of total dissolved phosphorus (TDP), typically 80%-90%. Based on this, sample TDP concentrations were calculated using monitored DRP values, assuming DRP to be 90% of TDP. Particulate phosphorus (PP) concentrations were then determined using Equation 4.2.

$$PP = TP - \frac{DRP}{0.9} \qquad (4.2)$$

As shown in Figure 4.21 the DRP concentration was below 0.5 mg/L for all storms monitored, accounting for 36% ± 23% of TP with a 95% confidence interval (CI) as shown in Figure 4.22. PP accounts for 64% ± 23% of the TP, while 54% ± 21% of TP is TRP.

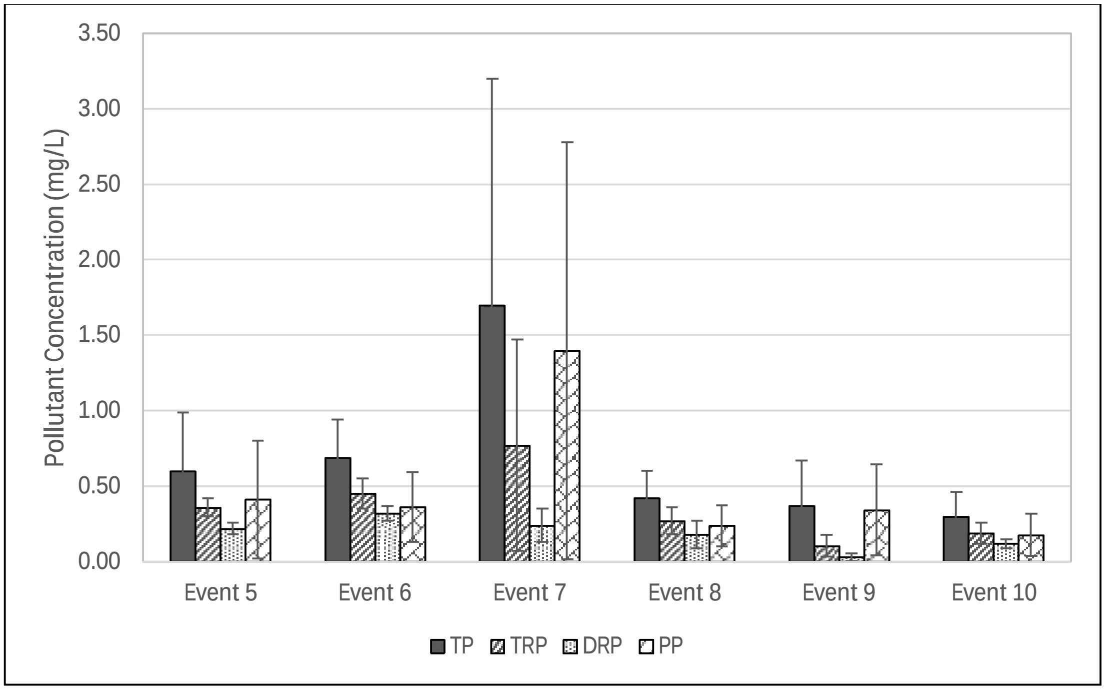


Figure 4.21: Various forms of phosphorus for Events 5 - 10

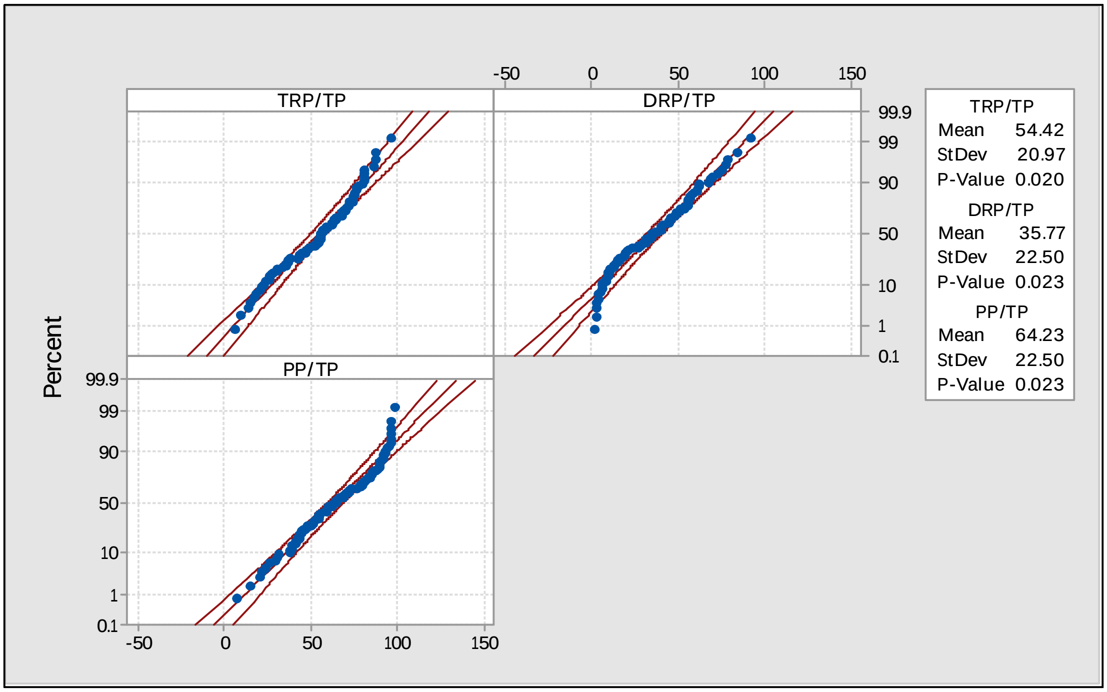


Figure 4.22: Probability plot of TRP, DRP and PP as a percentage of TP at 95% CI.

As shown in Figure 4.23, PP correlates strongly with TP with an R^2 value of 0.93 and has a minimal correlation with TRP ($R^2 = 0.57$). However, PP has a weak correlation with DRP. Therefore, the wide variation in the TP and TRP, unlike DRP, may be due to the influence of particulate phosphorus.

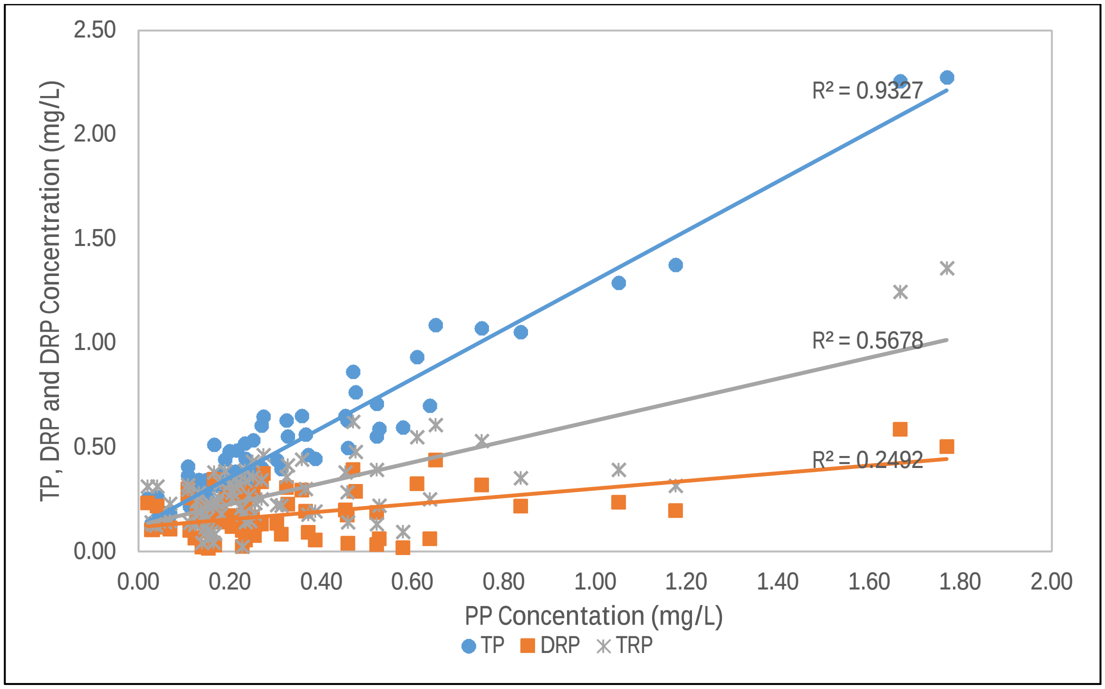


Figure 4.23: Relationship between PP and other forms of phosphorus.

4.1.7 Correlation between Pollutants

As shown in Figures 4.24 a – c, when all the concentration ranges were considered, there was a strong correlation between the SS and each of the BOD, TP, and TRP with R^2 values of 0.98, 0.90, and 0.79, respectively. The DRP showed a minimal correlation with the SS with an R^2 value of 0.10, as shown in Figure 4.24d.

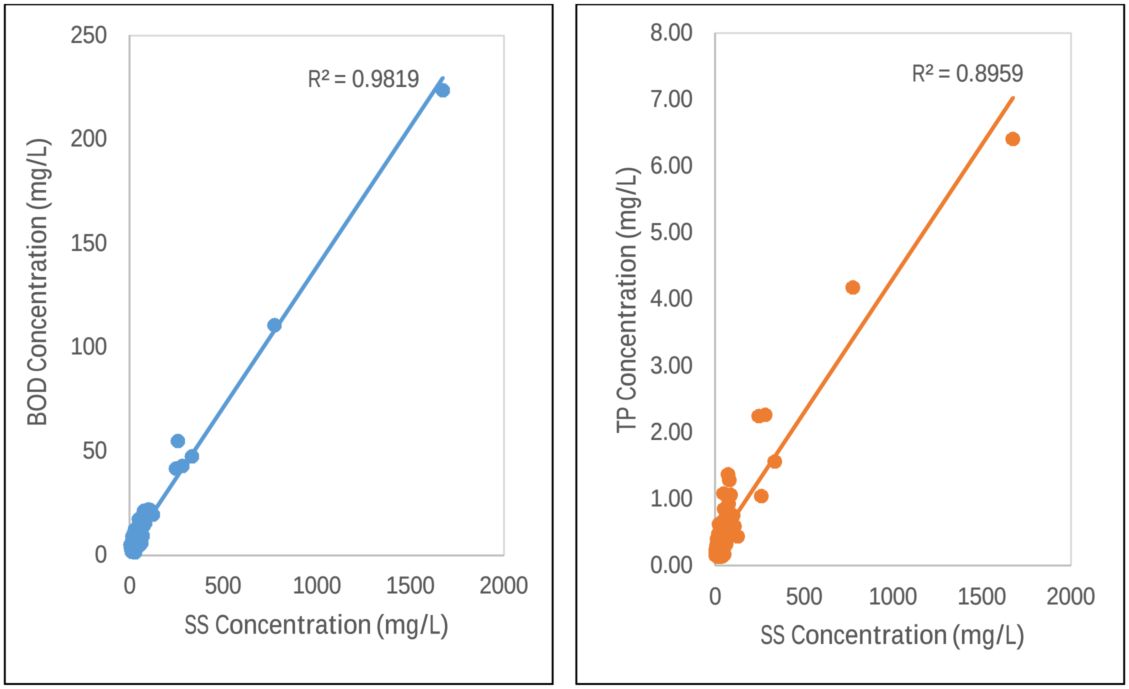


Figure 4.24a: SS vs BOD. Figure 4.24b: SS vs TP.

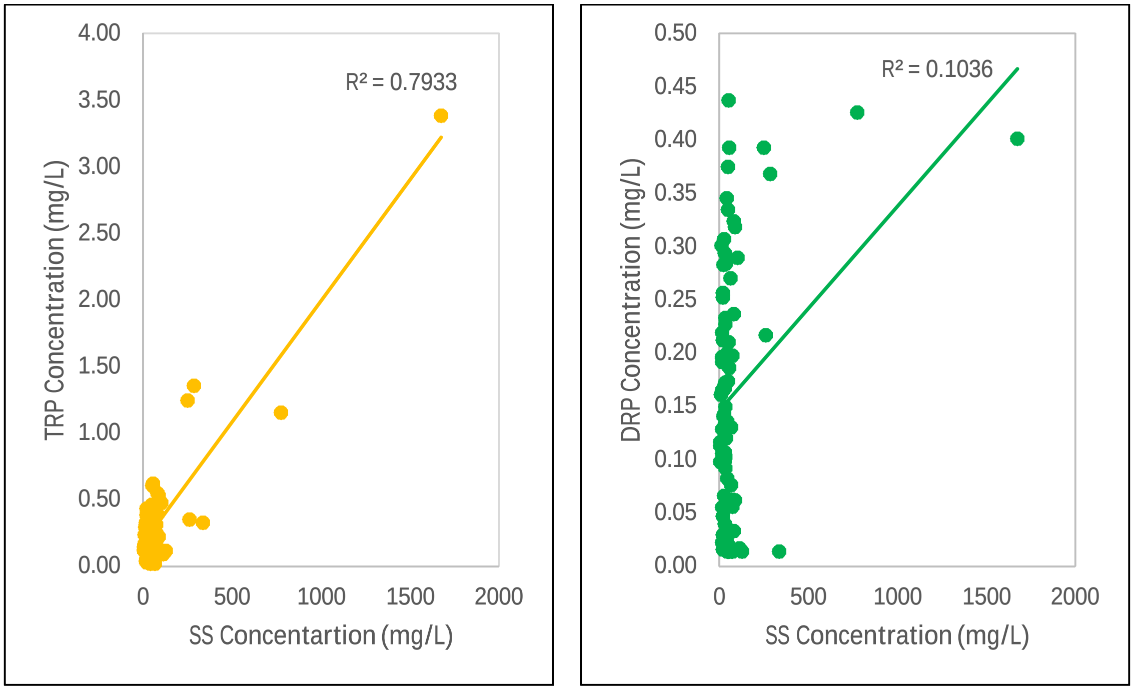


Figure 4.24c: SS vs TRP. Figure 4.24d: SS vs DRP.

Figure 4.24a - d: Correlation between pollutant concentrations for all concentration ranges.

Since more than 80% of the SS concentration is lower than 200 mg/L, as discussed in Section 4.1, samples with a SS concentration greater than 200 mg/L were removed and correlation between the pollutants were also determined for the low concentration ranges. For the low SS concentration range, there is still a moderate correlation ($R^2 = 0.64$) between the SS and BOD as shown in Figure 4.25a. The correlation between SS and each of TP and TRP is lower for the low SS concentration range as shown in Figure 4.25b and Figure 4.25c respectively.

Thus, the high correlation observed when all the pollutant concentrations ranges were considered for the relationship between the SS and each of TRP and TP may have been influenced by high pollutant concentration.

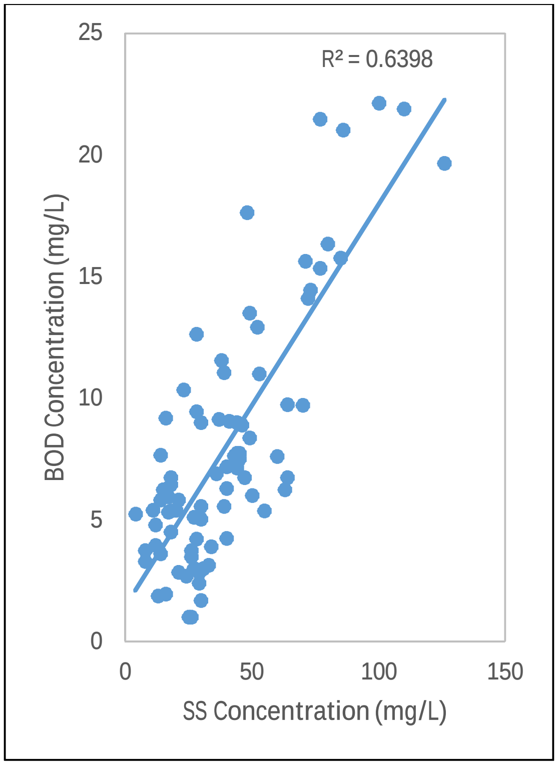


Figure 4.25a: SS vs BOD.

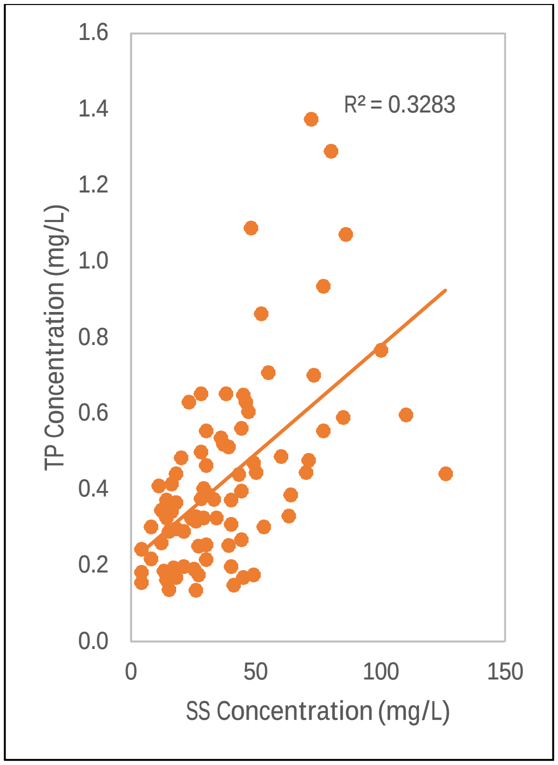


Figure 4.25b: SS vs TP.

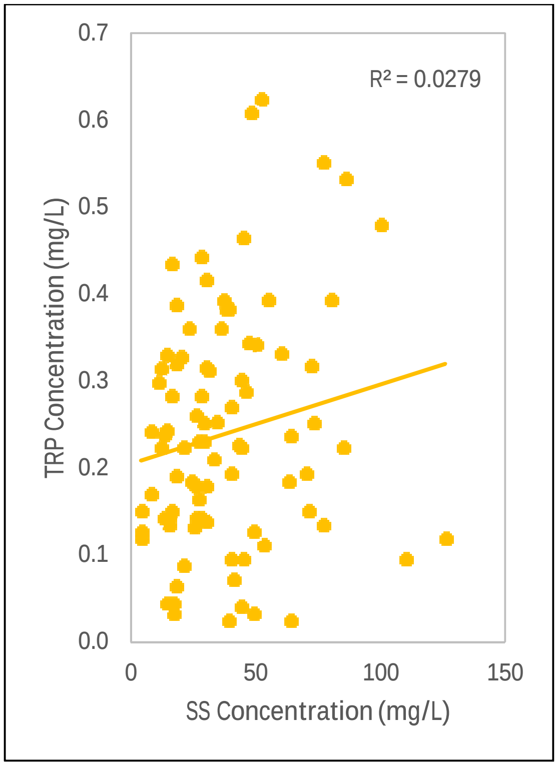


Figure 4.25c: SS vs TRP

Figure 4.25a - c: Correlation between pollutant concentrations for low concentration ranges.

4.2 Selection of Natural Polymer

4.2.1 Preliminary Evaluation

As detailed in section 3.2.4, simulated wastewater was used for preliminary evaluation of the selected natural polymers at two concentrations, representing the lower and upper limit of a test range. For Tanfloc SH and Tanfloc SG, the test ranges were chosen based on results in the literature (Beltran-Heredia, et al., 2011; Sanchez-Martin, et al., 2010; Beltran-Heredia, et al., 2010). For the DPS, the range was chosen based on additional preliminary experiments (results not shown). The evaluation of the polymers at this stage was based on their turbidity removal efficiencies (RE) as well as their efficiencies relative to the efficiencies of alum and Zetag 7873 which were used as controls. Table 4.3 summarises the results of the preliminary experiments.

The results show that turbidity removal efficiencies for Tanfloc SG and Tanfloc SH at the two concentrations were in the range of 85% - 90%. These efficiencies were similar to those obtained with alum and Zetag 7873 control while the efficiencies of DPS were higher than 90%. Thus, these polymers were selected for further evaluation. For LiquiFloc, although its removal efficiencies of 69% and 70% were lower than 85% - 90% with the controls, its values were significantly higher than 50% and it was also selected for further evaluation.

Table 4.3: Turbidity Removal Efficiency of Polymers

Polymer Type	**Polymer Concentration (mg/L)**	**Turbidity Removal Efficiency (%)**
Alum	3	85
Alum	5	87
Zetag 7873	0.5	89
Zetag 7873	1	90
Tanfloc SG	10	89
Tanfloc SG	40	86
Tanfloc SH	10	90
Tanfloc SH	40	87
Liquifloc	6	69
Liquifloc	10	70
DPS	2.75 mg/L LBP 2101 + 6 mg/L Liquifloc	95
DPS	5 mg/L LBP 2101 + 6 mg/L Liquifloc	95

4.2.2 Polymer Selection

All the natural polymers were further evaluated using raw municipal wastewater over the range selected based on the preliminary experiments. The polymer selection process resulted in nine jar test experiments using wastewater of different characteristics as shown in Table 4.4. A tenth experiment was conducted for the evaluation of Zetag 7873.

Table 4.4: Wastewater Characteristics for Polymer Selection Process

	Polymer used	Initial SS (mg/L)	Initial BOD (mg/L)
Experiment 1	LiquiFloc	114	ND*
Experiment 2	DPS	127	75
Experiment 3	DPS	119	105
Experiment 4	DPS	192	195
Experiment 5	Tanfloc SH	99	132
Experiment 6	Tanfloc SH	64	61
Experiment 7	Tanfloc SG	137	156
Experiment 8	Tanfloc SG	119	105
Experiment 9	Zetag 7873	109	76
Experiment 10	Tanfloc SH & Tanfloc SG	132	101

*ND: Not determined

DPS evaluation in Experiment #2 was aimed at determining the individual effects of LBP 2101 and LiquiFloc on the efficiency of DPS. In Experiment #9, the effectiveness of Tanfloc SG was compared to that of Tanfloc SH. The efficiency of all polymers will be discussed in the following subsections.

4.2.2.1 LiquiFloc

LiquiFloc was assessed at 2 mg/L, 5 mg/L, 10 mg/L, and 15 mg/L concentrations. As shown in Figure 4.26, the highest removal efficiency of 47% was reached at a 5 mg/L polymer concentration. However, this removal efficiency is lower than the minimum 50% required by the Ontario’s Procedure F-5-5 guidelines also, it is similar to the 46% removal efficiency achieved with the blank control. In addition to these measurements, it was observed that no visible flocs were formed within this concentration range. Thus, LiquiFloc was eliminated from any further consideration, except with LBP 2101 as part of the DPS evaluation, which will be discussed later.

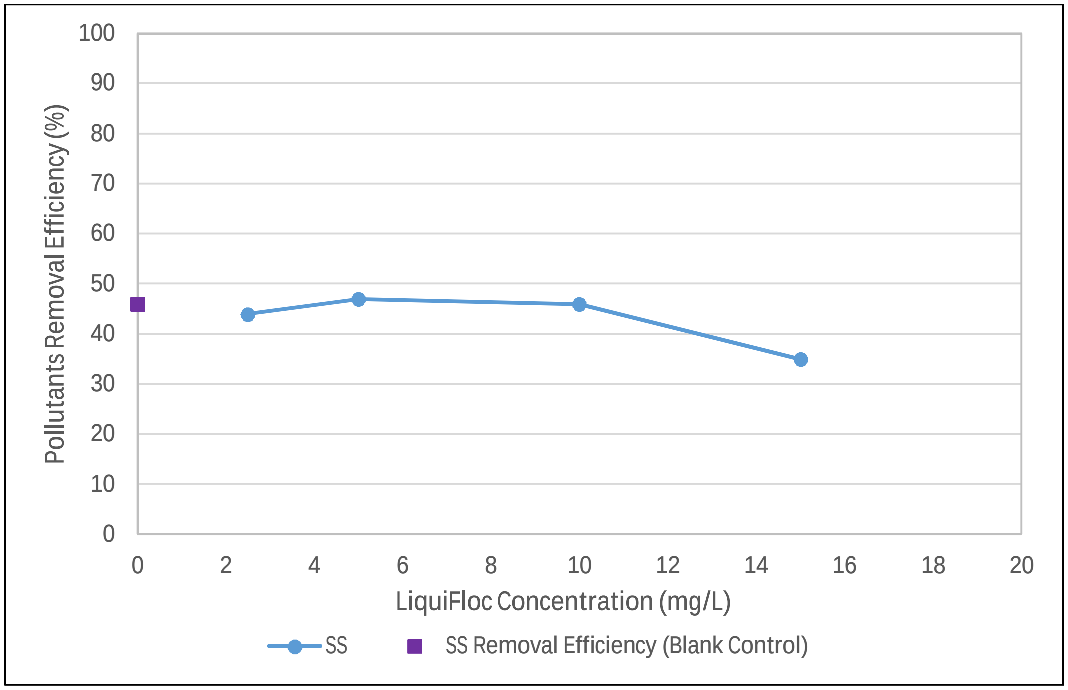
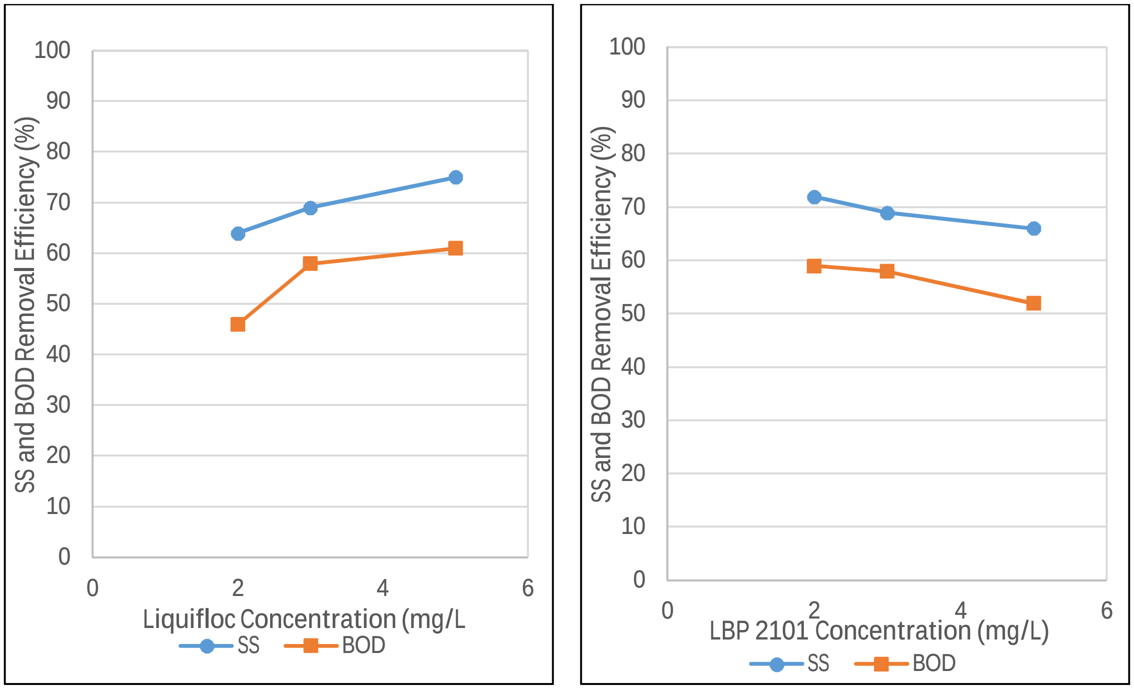


Figure 4.26: Effect of LiquiFloc concentration on SS removal (Experiment #1).

4.2.2.2 Dual Polymer System (DPS)

Since DPS treatment includes two polymers, (LiquiFloc and LBP 2101), the evaluation was conducted over three experiments. The results of Experiment #2 presented in Figure 4.27a shows that the SS and BOD removal efficiencies of DPS increase with increasing LiquiFloc concentration. When the concentration of LBP 2101 was increased, the removal efficiency of the SS and BOD removal efficiencies of DPS were reduced as shown in Figure 4.27b. Hence, for subsequent DPS evaluation in Experiments #3 and #4, the concentration of LBP 2101 was kept constant at 3 mg/L while the concentration of LiquiFloc was varied between 2 mg/L and 15 mg/L.



a) b)

Figure 4.27: DPS evaluation for Experiment #2: a) 3 mg/L LBP 2101 + varying LiquiFloc concentration; b) 3 mg/L LiquiFloc + varying LBP 2101 concentration.

In Experiment #3, SS and BOD removal efficiencies of 43% - 46% and 23% - 29% respectively, were obtained over the range of DPS concentration used. Thus, the requirements of procedure F-5-5 were not attained for both SS and BOD removal, as shown in Figure 4.28.

The requirements of Procedure F-5-5 were attained in Experiment #4. As shown in Figure 4.29, the SS and BOD removal efficiencies over the range of DPS concentration used were 70% - 73% and 47% - 49%, respectively.

In comparison, the range of removal efficiencies obtained with DPS polymer in both experiments was similar to those of the blank control (no polymer). These results suggest that DPS treatment is not expected to be very effective in the treatment of Windsor CSO over the range of concentration used.

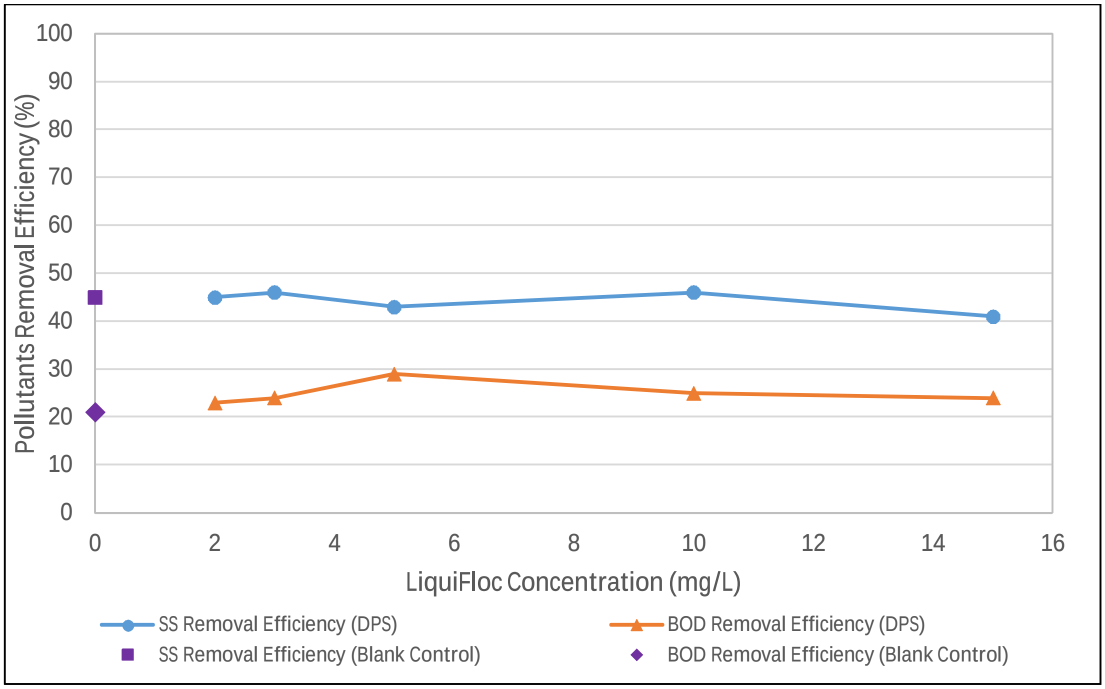


Figure 4.28: DPS evaluation for Experiment #3.

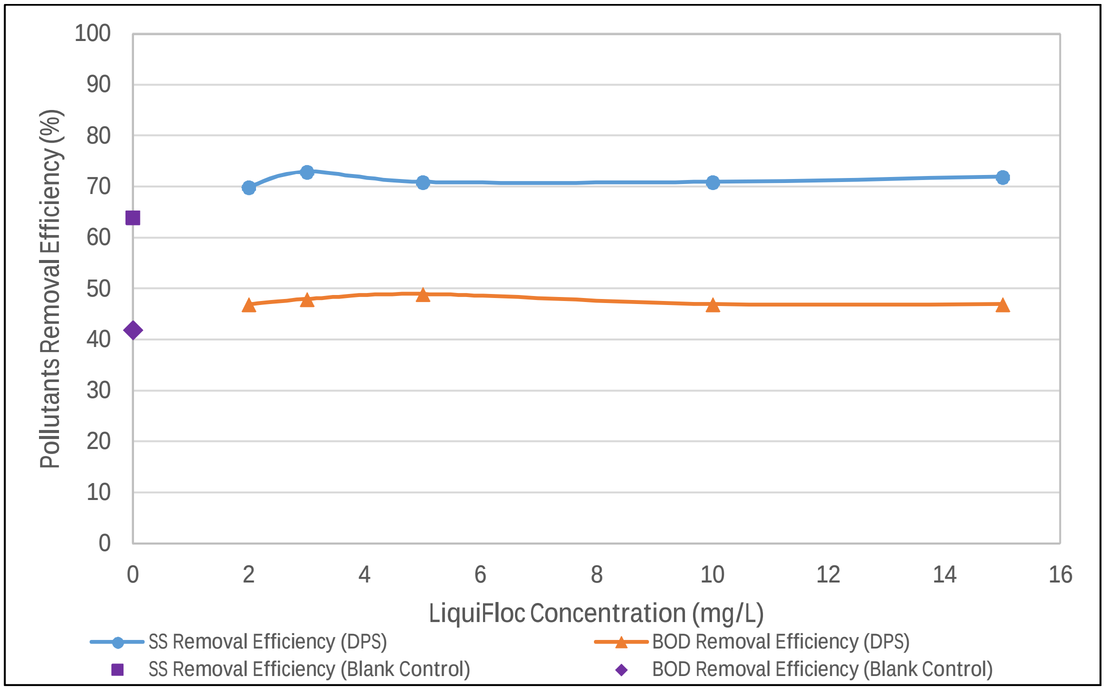


Figure 4.29: DPS evaluation for Experiment #4.

4.2.2.3 Tanfloc SH

For Experiment #5, Tanfloc SH was evaluated over a concentration range of 1 mg/L – 10 mg/L. For Experiment #6, the concentration range evaluated was 5 mg/L – 30 mg/L. In

Experiment #5, the SS removal efficiency of 37%-49% achieved over a polymer range of 1 mg/L – 7.5 mg/L did not meet the requirements of procedure F-5-5. However, with 10 mg/L, the SS treatment requirement of Procedure F-5-5 was achieved with 64% removal efficiency. For BOD treatment, the Procedure F-5-5 requirements were not achieved for concentrations ranging from 1 mg/L – 5 mg/L with BOD removal efficiencies of 21% - 26%. With polymer concentrations of 7.5 mg/L and 10 mg/L however, the BOD removal efficiencies of 33% and 42% were achieved which was more than the required removal efficiency, as shown in Figure 4.30.

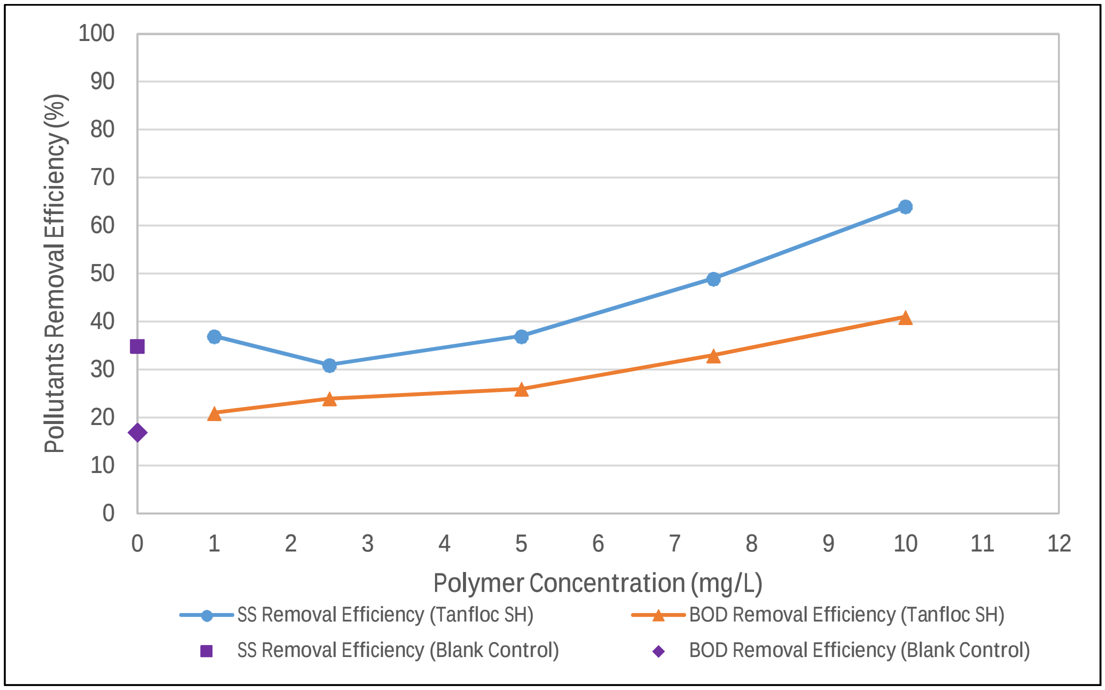


Figure 4.30: Tanfloc SH evaluation for Experiment #5.

In Experiment #6, the SS and BOD treatment requirements of procedure F-5-5 were achieved for a concentration range of 10 mg/L – 30 mg/L. This polymer range resulted in 78% - 87% and 55% - 58% removal efficiencies for SS and BOD, respectively, as shown in Figure 4.31. However, at 5 mg/L, the 37% and 29% removal efficiencies for SS and BOD, respectively, did not meet the requirements of Procedure F-5-5.

The SS and BOD removal efficiencies were achieved with a polymer concentration range of 10 mg/L – 30 mg/L were higher than those achieved with the blank control. Based on these results Tanfloc SH may be suitable for Windsor CSO treatment.

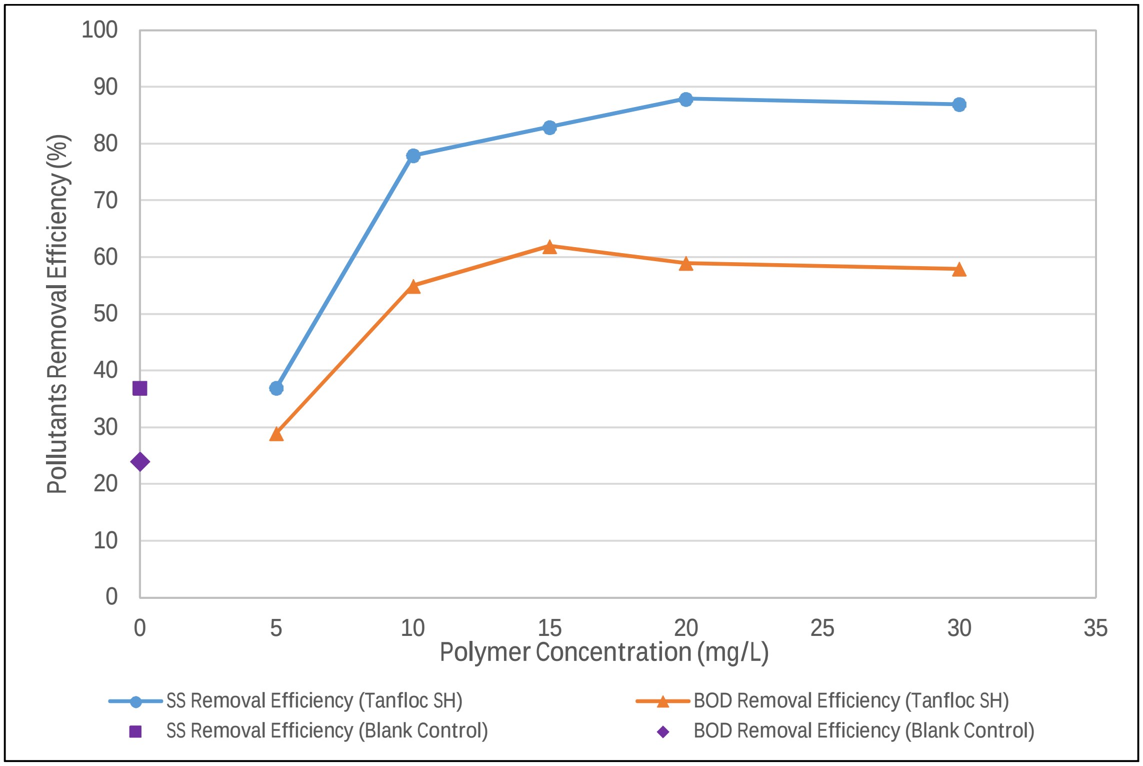


Figure 4.31: Tanfloc SH evaluation for Experiment #6.

4.2.2.4 Tanfloc SG

For Experiments #7 and #8, Tanfloc SG was evaluated over a concentration range of 1 mg/L – 10 mg/L and 5 mg/L – 30 mg/L respectively.

From the results of Experiment #7, presented in Figure 4.32, the Procedure F-5-5 SS treatment requirement was achieved for a concentration range of 5 mg/L–10 mg/L, resulting in 62% - 80% removal efficiencies. For BOD, the treatment requirement was attained at 7.5 mg/L and 10 mg/L polymer concentrations resulting in 38% and 41% BOD removal efficiencies, respectively.

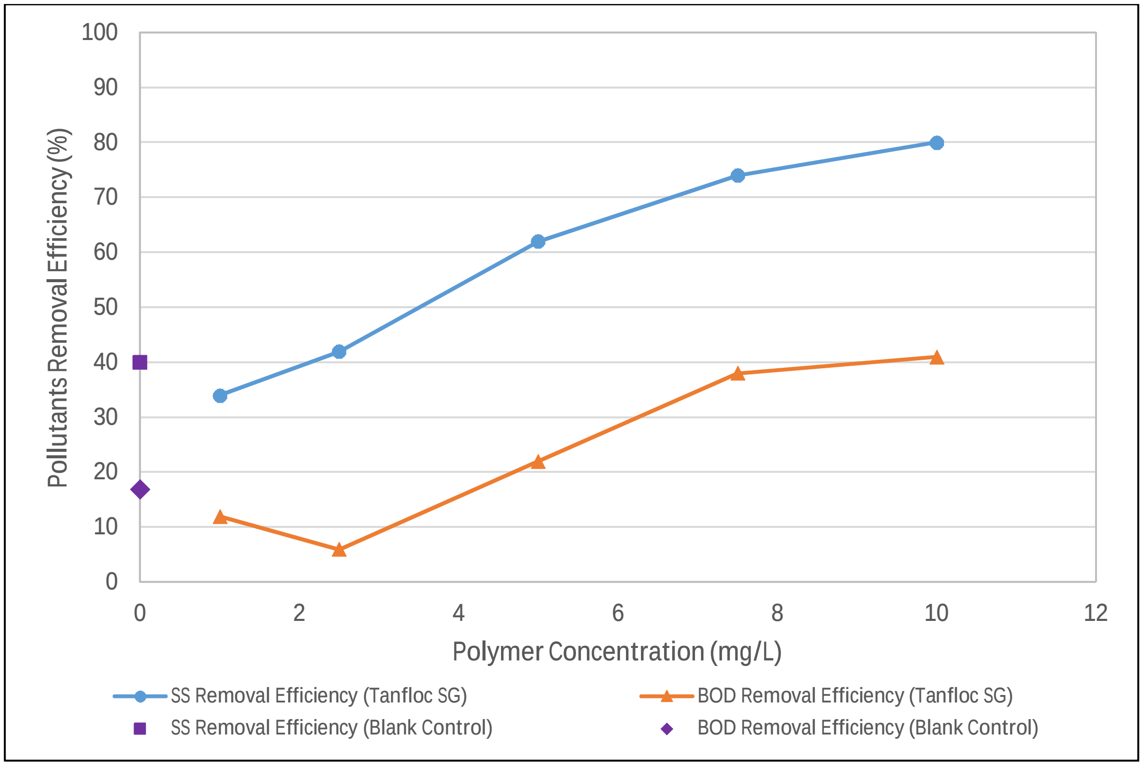


Figure 4.32: Tanfloc SG evaluation for Experiment #7.

In Experiment #8, the Procedure F-5-5 SS and BOD treatment requirements were achieved for concentration in the ranges of 10 mg/L – 30 mg/L resulting in 82% - 89% and 50% – 56% SS and BOD removal efficiencies respectively. However, at 5 mg/L, the SS and BOD removal efficiencies were less than the F-5-5 requirements as shown in Figure 4.33.

The SS and BOD removal efficiencies achieved with the Zetag 7873 control were 60% and 41% respectively. The SS and BOD removal efficiencies for the concentration range of 10 mg/L – 30 mg/L suggest that Tanfloc SG may be suitable for Windsor CSO treatment.

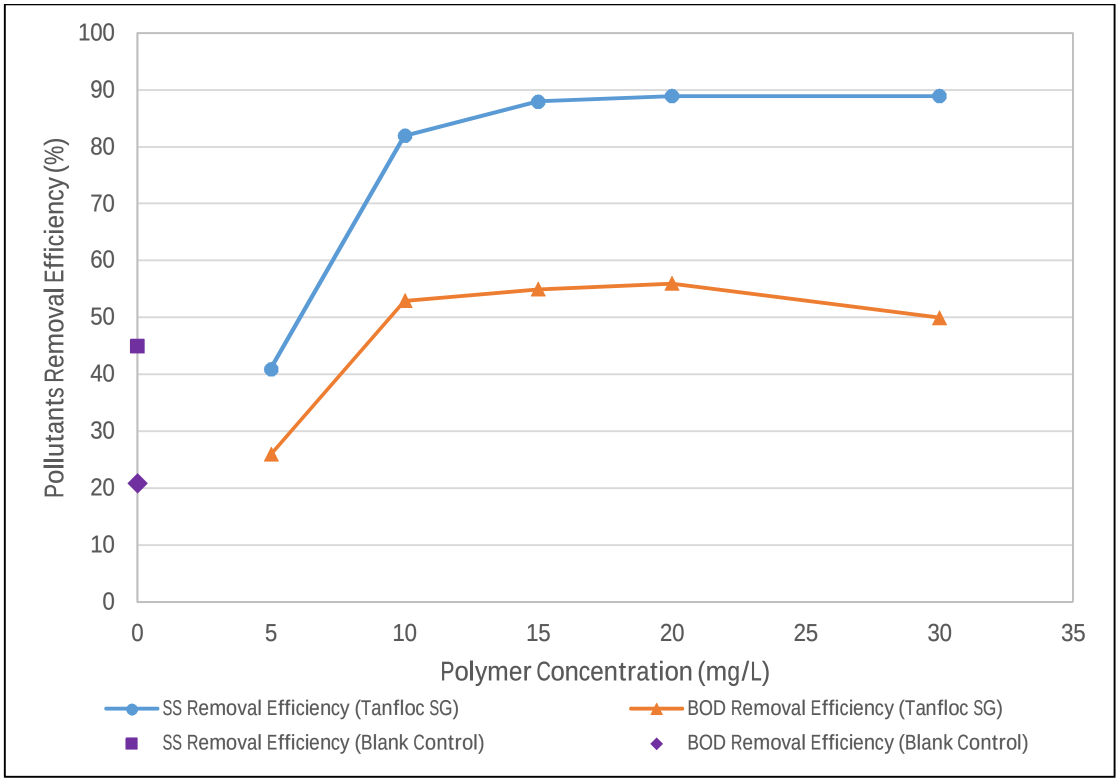


Figure 4.33: Tanfloc SG evaluation for Experiment #8

4.2.2.5 Zetag 7873

Zetag 7873 was evaluated under the same jar test operating conditions as the natural polymers, and the resulting SS and BOD removal efficiencies are presented in Figure 4.34. It is shown that the requirements of procedure F-5-5 were attainable for SS and BOD removal at all polymer concentrations assessed. The 5 mg (polymer)/g (SS) dose presently used at the City of Windsor's RTB resulted in about 60% and 45% removal efficiencies for SS and BOD, respectively.

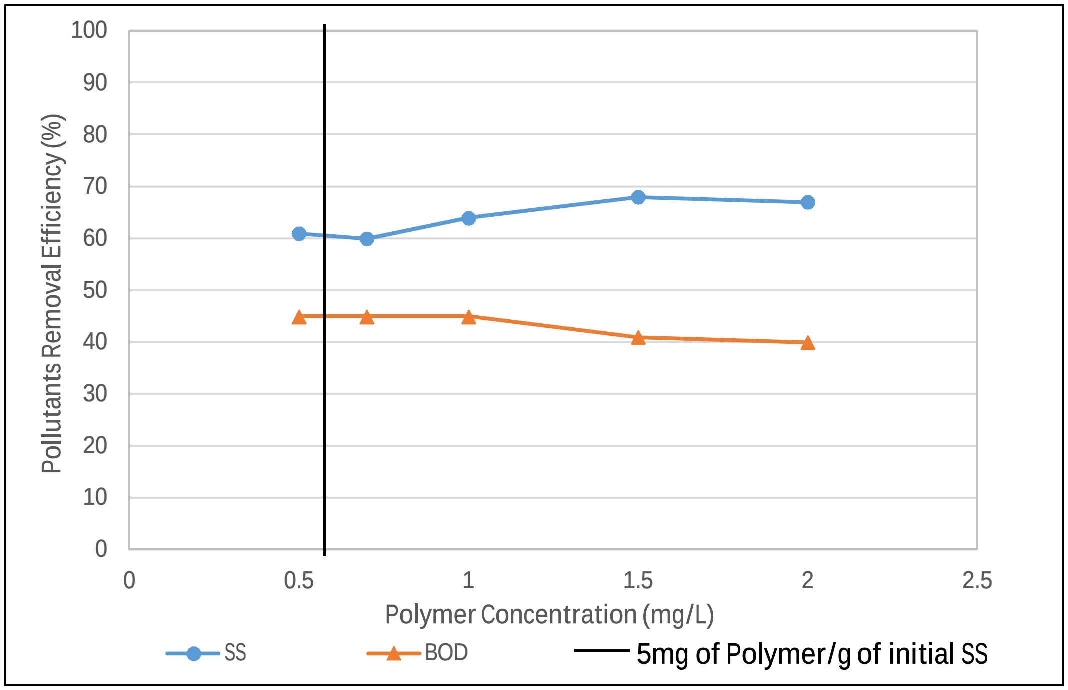


Figure 4.34: Zetag 7873 evaluation for Experiment #9

4.2.2.6 Adjusted Polymer Efficiency

Due to the limitation of not being able to assess the polymers using wastewater of identical characteristics, the SS removal efficiencies of the polymers were adjusted with respect to the removal efficiency of the blank, which was used as the control, as presented in Section 3.3.2.2. This was done to account for solids that were readily removed without the addition of polymers. Comparison of the polymers was therefore based on the adjusted SS removal efficiency. The adjusted SS removal efficiencies of the polymers, as shown in Figure 4.35, represent the proportion of pollutants removed due to polymer addition while the remaining proportion may be due to settling alone.

Compared to Zetag 7873, which accounted for 30% to 50% of the solids removed, DPS only accounted for less than 20% of the solids removed in the range of the polymer tested. In the case of Tanfloc SG and Tanfloc SH however, over 60% of the solids removed were due to polymer additions.

Of all the natural polymers evaluated, Tanfloc SG and Tanfloc SH performed best in terms of their SS and BOD removal efficiencies. However, the results of Experiments #6 and #8 show that Tanfloc SG and Tanfloc SH exhibited similar treatment efficiencies despite being tested with wastewater with slightly different characteristics. Thus, Tanfloc SG and Tanfloc SH were further evaluated using wastewater with similar characteristics to determine which of the two polymers worked better.

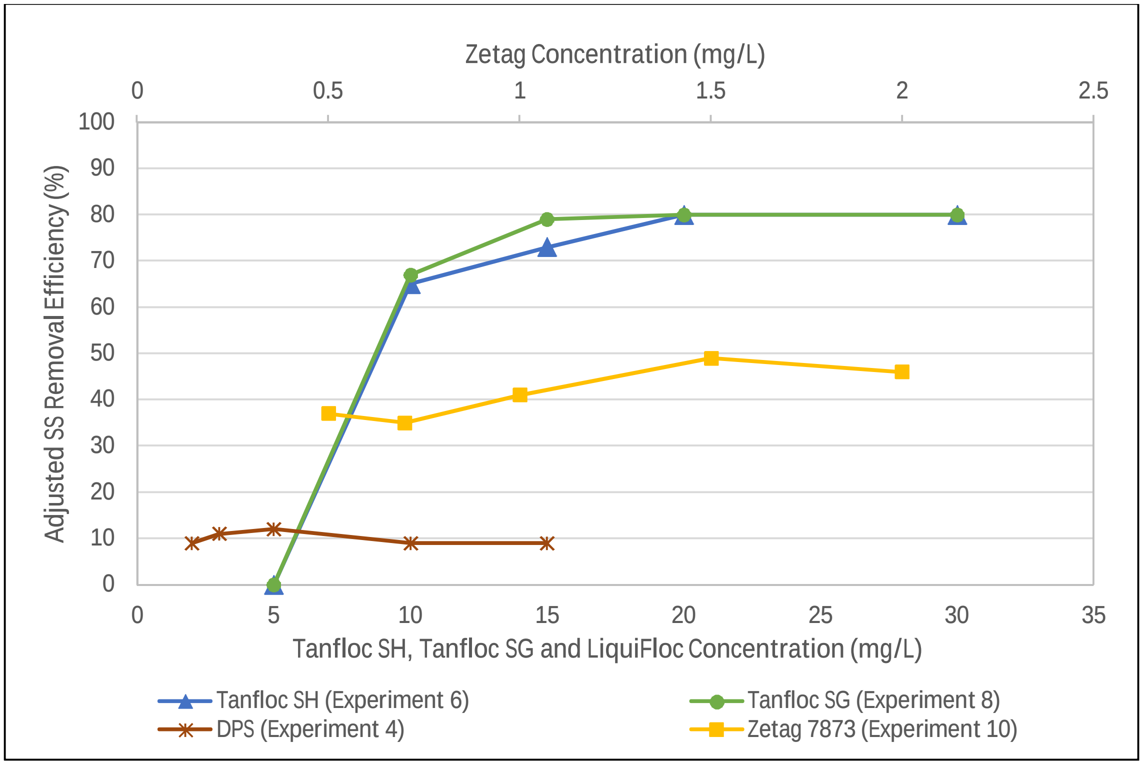


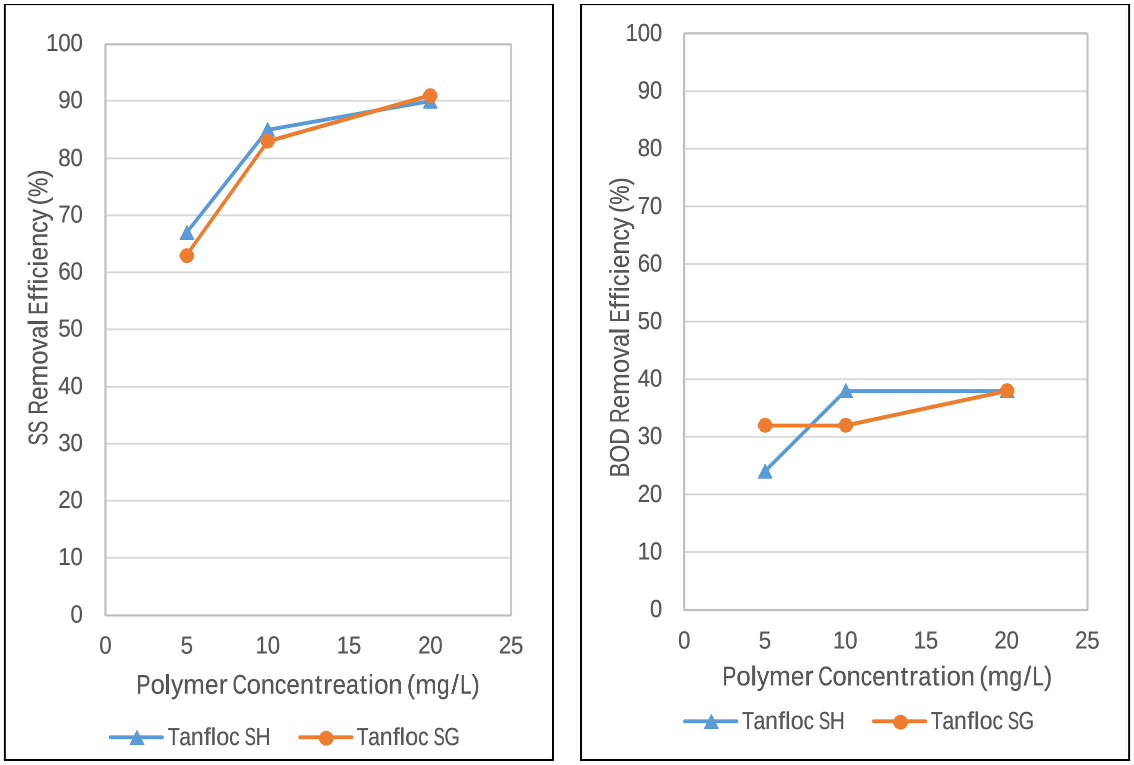
Figure 4.35: Adjusted SS removal efficiency

4.2.2.7 Comparison of Tanfloc SG and Tanfloc SH

Further evaluation of Tanfloc SG and Tanfloc SH was required to determine if there is a difference between their efficiencies and to ascertain which of them worked better. The assessment was done with wastewater of the same characteristics. As performed in

Experiment #10 and shown in Figure 4.36a and b the treatment efficiencies of Tanfloc SG and Tanfloc SH are comparable. This is similar to the study done by (Wolf, et al., 2015) where both polymers exhibited the same treatment efficiencies for dairy wastewater treatment.

Of the two polymers used, Tanfloc SG is certified by NSF international for drinking water treatment (NSF, 2012). Therefore, Tanfloc SG was selected for further evaluation.



a)

b)

Figure 4.36: Tanfloc SG vs Tanfloc SH: a) SS removal efficiency; b) BOD removal efficiency

4.3 Evaluation of Tanfloc SG

In order to estimate the concentration Tanfloc SG that meets the requirements of Procedure F-5-5, additional Experiments #11 - #14 were performed using Tanfloc SG. In Experiments #11 and #12, Tanfloc SH raw municipal wastewater was used for the evaluation, while in Experiments #13 and #14 CSO samples were used.

In Experiment #11, Tanfloc SG was evaluated over a concentration range of 1.5 mg/L – 10 mg/L, in Experiment #12, it was evaluated over a concentration range of 3 mg/L – 15 mg/L while for Experiments #13 and #14, the concentration ranges used were 3 mg/L – 10 mg/L. The SS and BOD removal efficiencies of Tanfloc SG for wastewater and CSO treatment are presented in the following subsections.

4.3.1 Wastewater Sample

The SS and BOD removal efficiencies of Experiments #2, #7, #10, #11, and #12 have been presented in Figure 4.37 and Figure 4.38 respectively.

As shown, Tanfloc SG did not meet the treatment requirements of procedure F-5-5 for concentrations less than 5 mg/L. However, at 5 mg/L, the polymer was sometimes able to meet the required removal efficiency for both SS and BOD removal. When the concentration was set at 7.5 mg/L the SS removal efficiencies was always above the required 50% RE while for BOD, the required 30% RE was not met at all times. For polymer concentrations of 10 mg/L and above, Tanfloc SG met the required SS and BOD removal efficiencies at all times irrespective of the wastewater sample used.

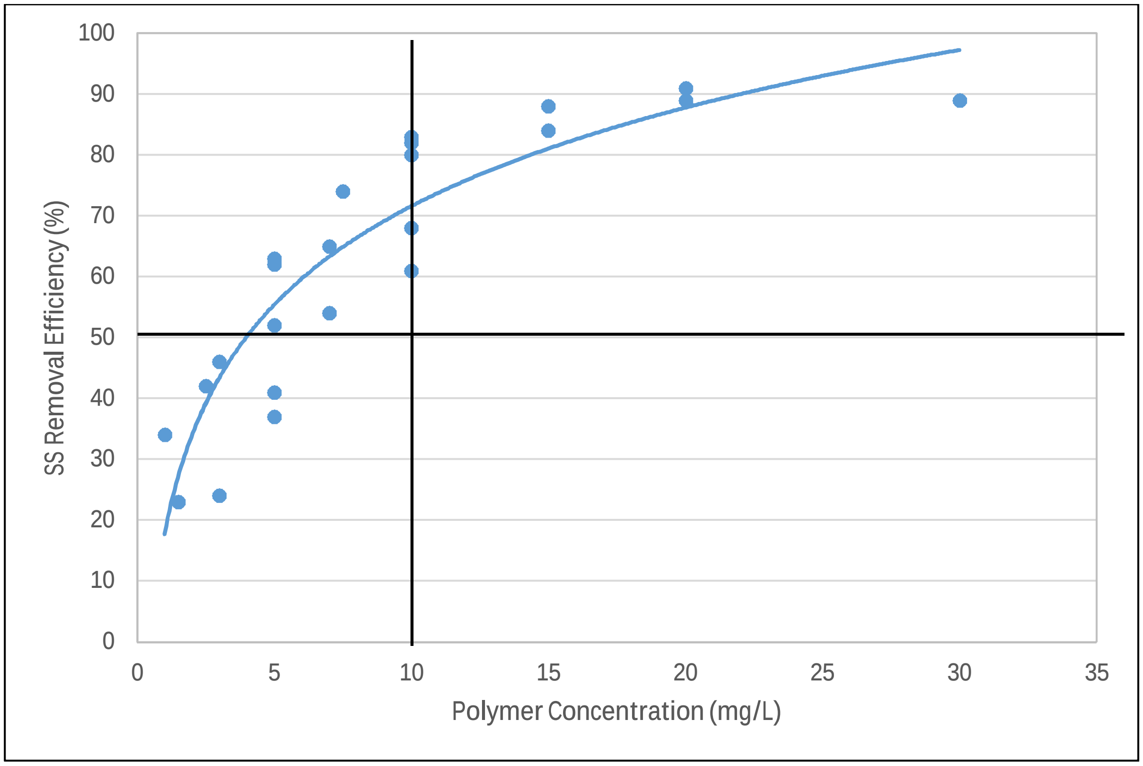


Figure 4.37: Effects of varying Tanfloc SG polymer dose on SS removal.

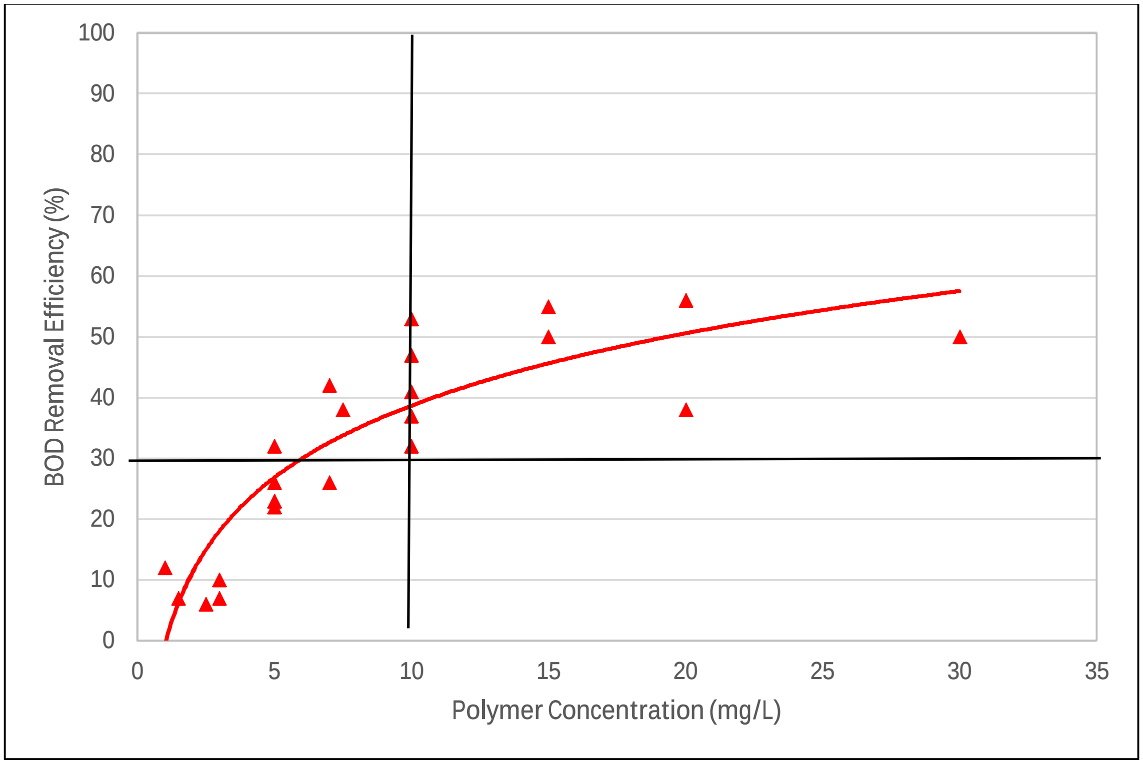


Figure 4.38: Effects of varying Tanfloc SG polymer dose on BOD removal.

4.3.2 CSO Samples

In section 4.3.1, the evaluation of the selected natural polymer (Tanfloc SG), using municipal raw wastewater as a surrogate of Windsor CSO was presented. As discussed in section 3.1.2, only one actual CSO sample could be captured to test and confirm the effectiveness of Tanfloc for its treatment. The CSO sample was used as sampled in Experiment #13 and diluted in Experiment #14 to vary the initial characteristics of the sample. The corresponding characteristics are presented in Table 4.5.

Table 4.5: CSO Characteristic for Experiments #13 and #14

	Initial SS (mg/L)	**Initial BOD (mg/L)**
Experiment 13	197	34
Experiment 14	112	19

The SS and BOD removal efficiencies for Experiments #13 and #14, where CSO samples were used for Tanfloc SG evaluation are presented in Figure 4.39 and 4.40 respectively. For Tanfloc SG, at a concentration range of 3 mg/L – 10 mg/L, the SS and BOD removal efficiencies were greater than 90% and 75% respectively. The unusually high removal efficiencies obtained may be due to better settling characteristics of the CSO sample captured as compared to the wastewater samples. This is based on the equivalent removal efficiencies obtained with the blank control of both experiments (92% and 95% SS removal efficiencies and 63% and 73% BOD removal efficiencies).

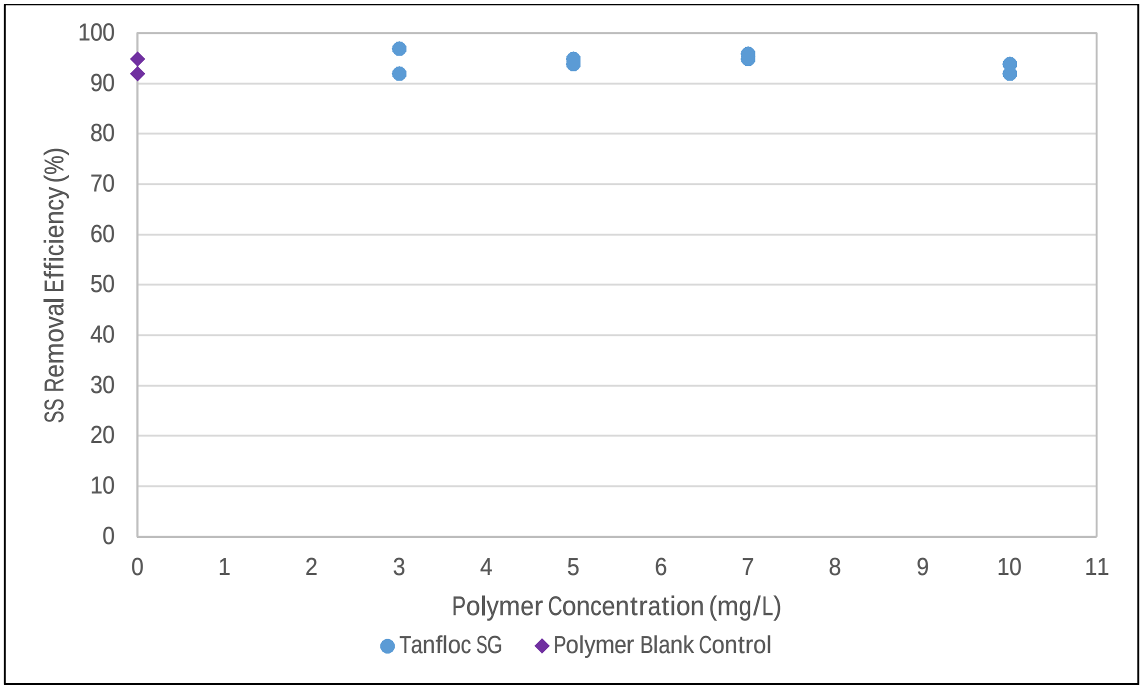


Figure 4.39: SS removal efficiencies for Tanfloc SG with CSO samples.

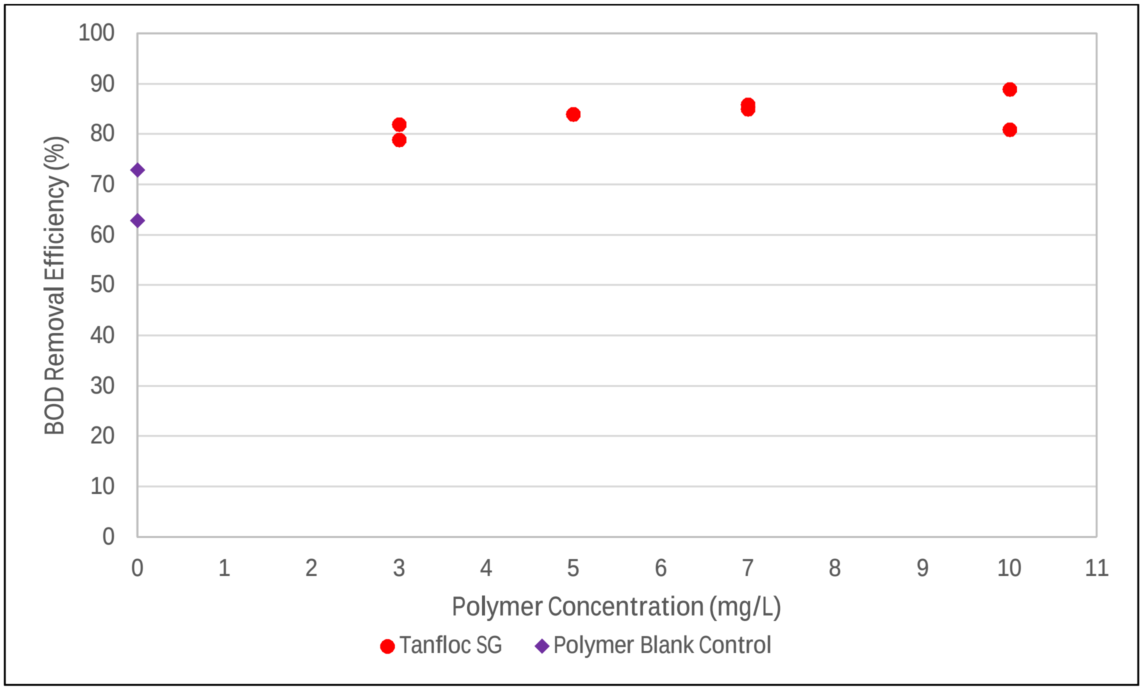


Figure 4.40: BOD removal efficiencies for Tanfloc SG with CSO samples.

4.3.3 Phosphorus Removal

The TP and DRP concentrations were monitored during the evaluation of Tanfloc SG with municipal wastewater in Experiments #5 and #10. The TP and DRP were also monitored when Tanfloc SG was evaluated with CSO in Experiments #13 and 14. However, since Ontario’s Procedure F-5-5 does not currently regulate phosphorus removal in CSO effluent, there is no guideline to compare the phosphorus removal efficiencies obtained in this study.

From the results of Experiments #5, #10, #13 and #14, Tanfloc SG was able to remove DRP to a maximum removal efficiency of 2%. Thus, Tanfloc SG has a minimal effect on DRP removal. The TP removal efficiency, on the other hand, ranged from 30% to 86% for polymer dosages ranging between 5 mg/L – 15 mg/L as shown in Figure 4.41, while PP removal efficiency ranged between 32% - 99% for the same polymer range as shown in Figure 4.42.

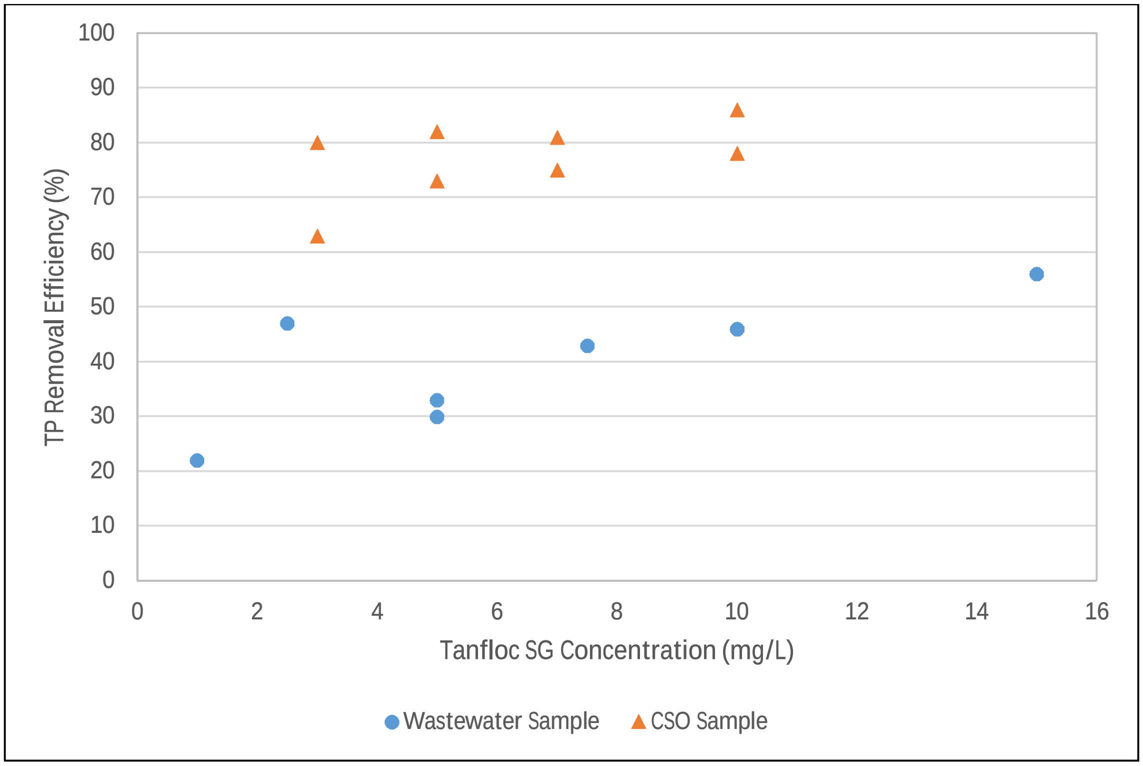


Figure 4.41: TP removal efficiency with Tanfloc SG.

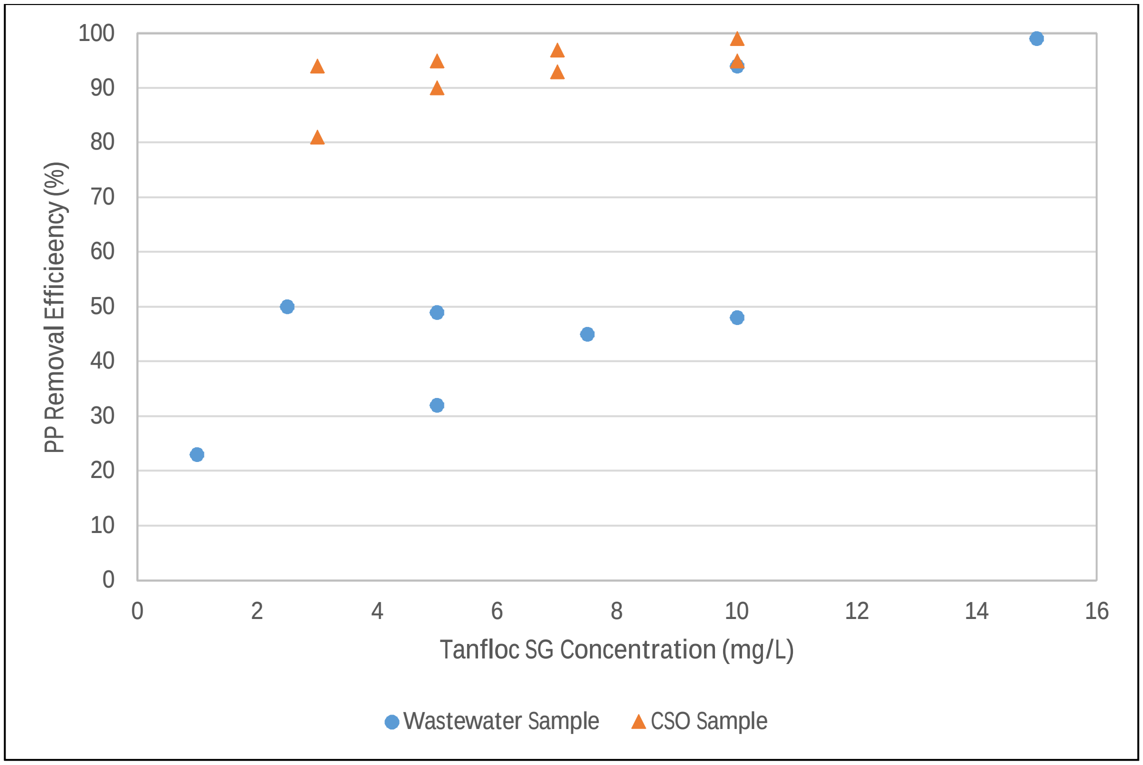


Figure 4.42: PP removal efficiency with Tanfloc SG.

4.3.4 Comparison with Present Practise

Based on the jar test operating parameters used in this study, the SS removal efficiency of all Tanfloc SG and Zetag 7873 evaluations are presented in Figure 4.43. As shown, the SS removal efficiency of Zetag 7873 at 5 mg/g, which is the present polymer dose used at the City of Windsor's RTB, is equivalent to 60%. With a minimum of 7.5 mg/L Tanfloc SG dose, the removal efficiency of Tanfloc SG was either similar or more than the treatment efficiency of Zetag 7873 at 5 mg/g.

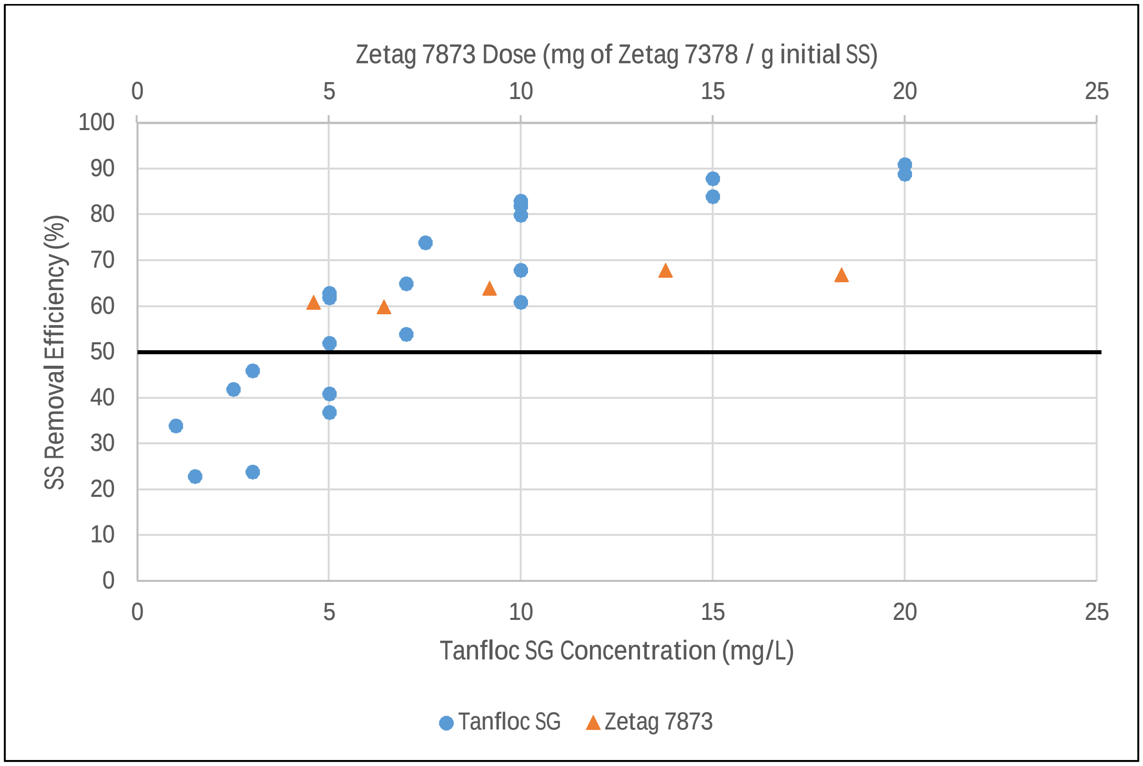


Figure 4.43: Comparison between the treatment efficiency of Tanfloc SG and Zetag 7873.

Based on this study, 10 mg/L of Tanfloc SG met the SS and BOD treatment requirements of Procedure F-5-5 at all times, when assessed with wastewater of initial SS concentration range of 119 mg/L – 137 mg/L. Therefore the cost of treating 1 megalitre of CSO with 10 mg/L of Tanfloc SG was compared to the cost of using 5 mg (Zetag) /g (SS) that is currently used for treatment for treating Windsor CSO at the RTB (Stantec, 2014). Since the Zetag 7873 dose depends on the influent SS, the cost of using Zetag 7873 was based on the initial SS concentration range of 119 mg/L – 137 mg/L, which is the same as the initial SS concentration used for Tanfloc SG evaluation in this study.

The cost evaluation was based on an estimated cost of USD 1.8 per tonne of Tanfloc SG and USD 8.83 per tonne of Zetag 7873. The information about the cost of Tanfloc SG was obtained through from the research and development manager of TANAC SA (C. Wolf, personal communication, July 21, 2015) and the cost of Zetag 7873 was from Promag Enviro Systems Ltd (2015).

As shown in Table 4.6, despite the low cost of purchase of Tanfloc SG, its cost of treatment may be higher than the cost of Zetag 7873 due to the high Tanfloc SG dose requirement.

Table 4.6: Cost Comparison between Tanfloc SG and Zetag 7873

Polymer	**Estimated Polymer Dose (mg/L)**	**Cost required to Treat 1 Ml of Sample (USD)**
Tanfloc SG	10	18
Zetag 7873	0.595 – 0.685	5.3 – 6.0

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CSO Characterisation

The following conclusions were drawn based on the results of this study:

- The SS, BOD, TP as well as TRP concentration in Windsor CSO vary significantly within an event and from one storm event to the other. However, the DRP did not vary significantly for each storm event and was less than 0.5 mg/L throughout the period of the study.
- Although there are noticeable spikes in pollutant concentrations, especially for those in the particulate form, the spikes did not always occur at the beginning of the storm event as would be explained by the first flush phenomenon.
- In general, the antecedent dry weather periods did not have an effect on pollutant concentrations. However, for the low intensity storms, there was a significant increase in pollutant concentrations as the antecedent dry weather days increased. However, rather than determining the individual effect of these factors on the pollutant concentrations, the level of pollutant concentrations may be due to a combination of factors such as rainfall volume, antecedent dry, and rainfall intensity.
- PP accounts for 64% ± 23% of the TP while TRP and DRP account for 54% ± 21% and 36% ± 23% respectively.
- There is a strong relationship between PP and TRP, while DRP exhibits a minimal correlation with PP.

5.2 Natural Polymer Evaluation

- Tanfloc SG was able to meet and surpass the requirements of Procedure F-5-5 up to a treatment efficiency of 91% and 56% for SS and BOD_5 respectively for polymer dosages ranging between 5 mg/L – 30 mg/L. However, based on the jar test operating parameters used in this study, the minimum dose of Tanfloc SG required for efficient treatment is equivalent to 10 mg/L
- Tanfloc SG has a minimal effect on DRP removal for polymer dosages ranging between 3 mg/L and 15 mg/L. However, the removal efficiencies for TP and PP ranged between 30% - 86% and 32% - 99%, respectively for 3 mg/L – 15 mg/L polymer range. Since Tanfloc SG has a minimal effect on the DRP removal, the majority of the TP that was removed was due to PP removal. Hence, Tanfloc SG is expected to significantly reduce the TP in Windsor CSO, since PP accounts for 64% ± 23% of TP in Windsor CSO based on the results of characterisation study.
- Based on the evaluation done in this study, the cost of using Tanfloc SG for Windsor CSO treatment may be more than the cost of using Zetag 7873.

5.3 Recommendations

Based on the results of this study, it is evident that Tanfloc SG is able to meet the requirements of Ontario's procedure F-5-5. The following recommendations are thus provided for future research:

- The use of Tanfloc SG should be optimized for possible reduced dose requirement
- The effect on initial solids concentration on the effectiveness of Tanfloc SG should be determined to better improve polymer dosing for CSO treatment.
- Further testing of Tanfloc SG should be done with actual CSO.

REFERENCES

Ahmed, E.-G., Jian, G. L. & Biswas, N., 2008. Treatment of Combined Sewer Overflow Using Treatment Basin Assisted with Polymer Chemical Coagulation. *Water Environmental Research,* 80(9), p. 774.

Aktas, T. S., Fujibayashi, M., Maruo, C. & Nomura, M., 2013. Influence of Velocity Gradient and Rapid Mixing Time on Flocs Formed by Polysilica (PSI) and Polyaluminum Chloride (PACl). *Desalination and Water Treatment,* Volume 51, pp. 4729 - 4735.

Ammary , B. Y. & Cleasby, J. L., 2004. Effect of Addition Sequence on Dual-Coagulant Performance. *Journal (American Water Works Associatio)n,* 2(96), pp. 90 - 101.

Anderson, D. M., Glibert, P. M. & Burkholder, J. M., 2002. Harmful Algal Blooms and Eutrophication: Nutrient Sources, Composition, and Consequences. *Estuaries,* 25(4b), pp. 704 - 726.

APHA, AWWA & WEF, 2005. Standard Methods for the Examination of Water and Wastewater. 21th ed. Washington DC: *American Public Health Association, American Water Works Association, Water Environment Federation.*

Aryal, R., Vigneswaran, S., Kandasamy, J. & Naidu, R., 2010. Urban Stormwater Quality and Treatment. *Korean Journal of Chemical Engineering,* 25(5), pp. 1343-1359.

Gilcreas, F.W., 2002. Simplified Procedures for Water Examination. *Public Health Nations Health,* 55(7), pp. 1109-1110

Bailey, S. E., Hwang, S., Brooks, M. C. & Schroeder, P. R., 2006. Evaluation of Chemical Clarification Polymers and Methods for Removal of Dissolved Metals from CDF Effluent. *Engineer Research and Development Center,* July, 2006.

Beltran-Heredia, J., Davila-Acedo, J. & Sanchez-Martins, J., 2011. Optimization of the Synthesis of a New Coagulant from a Tannin Extract. *Journal of Hazardous Materials,* Volume 186, pp. 1704-1712.

Beltran-Heredia, J., Sanchez-Martin, J. & Gomez-Munoz, M., 2010. New Coagulant Agents form Tannin Extracts: Preliminary Optimisation Studies. *Chemical Engineering Journal ,* Volume 162, pp. 1019-1025.

Berndtsson, J. C., 2014. Stormwater Quality of First Flush Urban Runoff in Relation to Different Traffic Characteristics. *Urban Water Journal,* 11(4), pp. 284-296.

Bolto, B. & Gregory, J., 2007. Organic Polyelectrolyte in Water Treatment. *Water Research,* Volume 41, pp. 2301-2324.

Booker, N., Ocal, G. & Priestly, A., 1996. Novel High-Rate Processses for Sewer Overflow Treatment. *Water Science & Technology,* 34(3-4), pp. 103-109.

Boyd, D., 1988. The Effect of Contamination Associated with Suspended Sediments on Water Quality in the Toronto Waterfront During 1985, *Ministry of the Environment.*

Bradford , M. E. & Peters, H. R., 1987. The Relationship between Chemically Analysed Phosphorus Fractions and Bioavailable Phosphorus. *Limenology and Oceanography,* 32(5), pp. 1124-1137.

Carpinteyro-Urban, S., Vaca, M., & Torres, L. G., 2012. Can Vegetal Biopolymer Work as Coagulant-Flocculant Aids in the Treatment of High-Load Cosmetic Industrial Wastewater. *Water Air & Soil Pollution,* Volume 223, pp. 4925-4936.

Chang, E. E., Chiang, P.-C., Tang, W.-Y. & Chao, S.-H., 2005. Effects of Polyelectrolytes on Reduction of Model Compounds via Coagulants. *Chemosphere,* Volume 58, pp. 1141-1150.

Chapra, S. C. & Dolan, D. M., 2012. Great Lakes Total Phosphorus Revisited: 2. Mass Balance Modelling. *Journal of Great Lakes Research,* Volume 38, pp. 741-754.

Cheng-qing, He, Q.-c., Kong, L.-l. L. L.-q. & Yin, 2007. First Flush of Storm Runoff Pollution from an Urban Catchment in China. *Journal of Environmental Sciences,* Volume 19, pp. 295-299.

Chung, Y.-C., Wu, L.-C. & Chen, C.-Y., 2013. The Removal of Kaolimnite Suspensions by Acid-Soluble and Water-Soluble chitosans. *Environmental Technology,* 34(3), pp. 283-288.

Cornwell, D. A. & Bishop, M. M., 1983. Determining Velocity Gradients in Laboratory and Full-Scale Systems. *Journal* (*American Water Works Association),* 75(9) pp. 470-475.

Curtis, J. G., 2007. Laboratory-Scale Investigation of Stormwater Treatment in the Lake Tahoe Basin Using Chemical Coagulants, *University of Nevada, Reno: Doctoral Dissertation*

Denault, C., Miller, R. G. & Lence, B. J., 2006. Assessment of Possible Impacts of Climate Change in an Urban Catchment. *American Water Resources Association,* 3(42), pp. 685-697.

Droste, R. L. & Hartt, J. P., 1975. Quality and Variation of Pollutant Loads in Urban Stormwater Runoff. *Canadian Journal of Civil Engineering,* Volume 2, pp. 418-430.

Ebeling, J. M., Rishel, K. L. & Sibrell, P. L., 2005. Screening and Evaluation of Polymers as Flocculation aids for the Treatment of Aquacultural Effluents. *Aquacultural Engineering,* Volume 33, pp. 235-249.

Ebeling, J. M., Sibrell, P. L., Ogden, S. & Summerfelt, S. T., 2003. Evaluation of Chemical Coagulation-Flocculation aids for the Removal of Suspended Solids and Phosphorus from Intensive Recirculating Aquaculture Effluent Discharge. *Aquacultural Engineering,* Volume 29, pp. 23-42.

Environment Canada, 2013. Phosphorus and Excess Algal Growth. Available at: https://www.ec.gc.ca/grandslacs-greatlakes/default.asp?lang=En&n=6201FD24-1 *[Accessed 4 December 2015].*

Environment Canada, 2015. Engineering Climate Datasets. Available at: http://climate.weather.gc.ca/prods_servs/engineering_e.html *[Accessed 20 December 2015].*

Erickson, A. J., Gulliver, J. S. & Weiss, P. T., 2007. Enhanced Sand Filtration for Storm Water Phosphorus Removal. *Journal of Environmental Engineering,* Volume 133, pp. 485-497.

Exall, K. & Jiri, M., 2013. A Coagulant Survey for Chemically Enhanced Primary Treatment of Synthetic CSOs. *Water Air & Soil Pollution,* Volume 224, pp 1414 - 1423

Freund, K., 2013. Phosphorus Management in Primary Treatment at the Lou Romano Water Reclamation Plant, *Uinveristy of Windsor, Windsor Ontari: Masters Thesis.*

Ghosh, M. M., Cox, C. D. & Prakash, T. M., 1985. Polyelectrolyte Selection for Water Treatment. *American Water Works Association,* 77(3), pp. 67-73.

Graham, N., Fang, G., Fowler, G. & Watts, M., 2008. Characterisation and Coagulation Performance of a Tannin-based Cationic Polymer: A preliminary Assessment. *Colliods and Surfaces: Physicochemical and Engineering Aspects,* Volume 327, pp. 9-16.

Green N.D., Carginelli L., Briggs T., Child M., Esberge J., Valiante M., Henderson T., Mcgregor D., & Munro D., 2010. Detroit River Canadian Remedial Action Plan: Stage 2 Report, *Detroit River Cleanup,* Volume 1, Essex, Ontario, Canada.

Gutteridge, Haskins and Davey Pty LTD, 1981. Characterisation of Pollution in Urban Stormwater Runoff. *Australian Water Resources Council, Canberra, No, 60*

He, J., Valeo, C., Chu, A. & Neumann, N. F., 2011. Stormwater Quantity and Quality Response to Climate Change using Artificial Neural Network. *Hydrological Processes,* Issue 25, pp. 1298-1312.

Henze, M., Loosdrecht, M. C. & Ekama, G. A., 2008. Biological Wastewater Treatment: Principles, Modelling, and Design. 1st ed. *London: IWA Publishing..*

Hsu, Y.-L., Wu, H., Yeh, M., Liu, C., Tung, C., Lin, Y., Lin, P., & Chen, H., 2009. Turbidity Removal Efficiency of Biocoagulant and verification of its Biological Safety. *The Practice Periodical of Hazardous, Toxic and radioactive Waste management,* Volume 13, pp. 278-286.

Hu, C., Lo S., Chang, C., Chen, F., Wu, Y. and Ma, J., 2013. Treatment of Highly Turbid Water Using Chitosan and Aluminum Salts. *Separation and Purification Technology,* Volume 104, pp. 322-326.

IJC, 2014. A Balanced Diet for Lake Erie: Reducing Phosphorus Loadings and Harmful Algal Blooms. International Joint Commission - Report of the Lake Erie Ecosystem Priority.

Irvine, K. N., Perrelli, M. F., McCorkhill, G. & Caruso, J., 2005. Sampling and Modelling Approaches to Assess Water Quality of Combined Sewer Overflows - The Importance of a Watershed Perspective. *Journal of Great Lake Research,* Issue 31, pp. 105-115.

Kan, C., Huang, C. & Pan, J. R., 2002. Timr Requirement for Rapid-Mixing in Coagulation. *Colloids and Surfaces,* Volume 203, pp. 1-9.

Kawamura, S., 1991. Effectiveness of Natural Polyelectrolytes in Water treatment. *American Water Works Association,* 83(10), pp. 88-91.

Kerr, J. L., Lumsden, J. S., Russel, S. K., Jasinska, E. J., Goss, G. G., 2014. Effects of Anionic Polyacrylamide Products on Gill Histopathology in Juvenile Rainbow Trout (Oncorhynchus Mykiss). *Environmental Toxicology and Chemistry,* 33(7), pp. 1552-1562.

Khan, E. & Pillai, S. S., 2006. Effect of Leaching from Filters on Laboratory Analyses of Collective Organic Constituents. *Journal (Water Environment Federation),* Volume 18, pp. 901-918.

Lai, R. J., Hudson Jr., H. E. & Singley, J. E., 1975. Velocity Gradient Calibration of Jar-Test Equipment. Journal (*American Water Works Association),* pp. 553-557.

Lee, J.-F., Liao, P.-M., Tseng, D.-H. & Wen, P.-T., 1998. Behaviour of Organic Polymers in Drinking Water Purification. *Chemosphere,* 37(6), pp. 1045-1061.

LeFevre, G. H., Paus, K. H., Natarajan, P., Gulliver, J. S., Novak, P., Hozalski, R. M., 2014. Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. *Journal of Environmental Engineering.* 141(1), pp. 14-50

Li, J. G., Horneck, H., Averill, D., McCorquodale, A., Biswas, N., 2004. High-Rate Retention Treatment Basins for CSO Control in Windsor, Ontario. *Water Quality Research Journal Canada,* 39(4), pp. 449-456.

Li, J. G., Samir, D., Averill, D. & Biswas, N., 2003. Windsor Combines Sewer Overflow Treatability Study with Chemical Coagulation. *Water Quality Research Journal Canada,* 38(2), pp. 317-334.

Liu, J. & Davis, A. P., 2013. Phosphorus Speciation and Treatment Using Enhanced Phosphorus Removal Bioretention. *Environmental Science & Technology,* Volume 48, pp. 607 - 614.

Maestre, A. & Pitt, R., 2005. The National Stormwater Quality Database, Version 1.1. *Center for Watershed Protection, Ellicott, Maryland.*

Michigan Department of Natural Resources (MDNR) and Ontario Ministry of the Environment (MOE), 1991. *Detroit River Remedial Action Plan,* Michigan Depertment of natural Resources, Lansing. Report No. 1

Menezes, F., Amal, R. & Luketina, D., 1996. Removal of Particles using Coagulation and Flocculation in a Dynamic Separator. *Powder Technology,* Volume 88, pp. 27-31.

Metcalf and Eddy, 2003. Wastewater Engineering: Treatment and Reuse. 4th ed. *McGraw Hill Education* New York.

Mhaisalkar, V. A., Paramasivam, R. & Bhole, A. G., 1991. Optimizing Physical Parameters of Rapid Mix Design for Coagulation-Flocculation of Turbid Water. *Water Research,* 25(1), pp. 43-52.

Miller, S. M., Fugate, E. J., Craver, V. O., Smith J. A., and Zimmerman J. B., 2008. Towards Understanding the Efficacy and Mechanism of Opuntia spp. as a Natural Coagulant for Potential Application in Water Treatment. *Environment Science & Technology,* Volume 42, pp. 4274-4279.

Muthuraman, G. & Sasikala, S., 2013. Removal of Turbidity from Drinking Water Using natural Coagulants. *Journal of Industrial and Engineering Chemistry.*

Muyibi, S. A. & Evison, L. M., 1995. Optimizing Physical Parameters Affecting Coagulation of Turbid Water with Moringa oleifera. *Water Research,* 29(12), pp. 2689-2695.

Ndabigengesere, A. & Narasiah, K., 1996. Influence of Operating Parameters on Turbidity Removal by Coagulation with Moringa oleifera Seeds. *Environmental Technology,* Volume 17, pp. 1103-1112.

NSF, 2012. *NSF* Product and Service Listings.Available at: http://info.nsf.org/Certified/PwsChemicals/Listings.asp?Company=79000&Standard=060 *[Accessed 16 December 2015].*

Oblinger Childress, C. J., Foreman, W. T., Connor, B. F. & Maloney, T. J., 1999. New Reporting Procedures Based on Long-Term method Detection Levels and Some Considerations for Interpretations for Water-Quality Data, *Denver: U.S. Geological Survey National Quality Laboratory.* Report No. 99-193

2014. F-5-5 Determination of Treatment Requirements for Municipal and Private Combined and Partially Separated Sewer Systems. Available at:

https://dr6j45jk9xcmk.cloudfront.net/documents/1753/193-partially-seperated-sewer-systems-en.pdf
[Accessed 18 March 2015].

Pennsylvania DEP, 2006. Pennsylvania Stormwater Best Management Practices Manual. *Pennsylvania Department of Environmental Protection, Bureau of Watershed Management.*

Phipps & Bird Inc, 2015. G- Curves. Available at:
http://www.phippsbird.com/pbinc/WaterWasteWater/Gcurve.aspx
[Accessed 22 December 2015].

Promag Enviro, 2015. Liquid Cationic Flocculant. Available at:
http://www.promagenviro.com/Cationic-Liquid-Flocculant?whence=
[Accessed 31 Dec 2015].

Renault, F., Sancey, B., Badot, P.-M. & Crini, G., 2009. Chitosan for Coagulation/Flocculation Process: An Eco-Friendly Approach. *European Polymer Journal,* Volume 45, pp. 1337-1348.

Rossini, M., Garrido, G. J. & Galluzzo, M., 1999. Optimization of the coagulation-Flocculation Treatment: Influence of Rapid Mix Parameters. *Water Research,* 33(8), pp. 1817-1826.

Rushton, H. J., 1952. Mixing of Liquids in Chemical Processing. *Industrial and Engineering Chemistry,* 44(12), pp. 2931-2936.

Sanchez-Martin, J., Beltran-Heredia, J. & Solera-Hernandez, C., 2010. Surface Water and Wastewater Treatment using a new Tannin-based Coagulant - Pilot Plant Trials. *Journal of Environmental Management,* Volume 91, pp. 2051-2058.

Semadeni-Davies, A., Hernebring, C., Svensson, G. & Gustafsson, L.-G., 2008. The Impact of Climate Change and Urbanisation on Drainage in Helsingborg, Sweden: Combined Sewer System. *Journal of Hydrology,* Issue 350, pp. 100-113.

Shu, W.-P., 2004. The Use of a Water Quality Model to Evaluate the Impacts of Combined Sewer Overflows on the Lower Hudson River. *New Jersey Instutute of Technology, New Jersey: Doctoral Dissertation.*

Spivakov, B. Y., Maryutina, T. A. & Muntau, H., 1999. Phosphorus Speciation in Water and Sediments, *Pure & Applied Chemistry,* 71(11), pp. 2161-2176.

Stanley, D. W., 1996. Pollutant Removal by a Stormwater dry Detention Pond. *Water Environment Research,* 68(6), pp. 1076-1083.

Stantec, 2001. City of Windsor Combined Sewer Overflow (CSO) Characterisation / Treatability Study - Final Report. *Stantec Consulting Limited, Windsor, Ontario.*

Stantec, 2014. Optimization Study for the Windsor Riverfront Retention Treatment Basin, *Stantec Consulting Limited, Windsor, Ontario.*

Tacchi, K. J. & Churchill, R. J., 1977. Polyelectrolyte Usage in Industrial Wastewater Treatment. *Petrolite Corporation, Tretolite Division*, December 1977

USEPA, 1999. *Combined Sewer Overflow Technology Fact Sheet,* Washington, D.C.: Office of Water.

USEPA, 2004. *Report to Congress - Impacts and Control of CSOs and SSOs,* Washington, D.C.: s.n.

USEPA, 2008. A Screeing Assessment of the Potential Impact of Climate Change on Combined Sewer Overflow Mitigation in the Great Lakes and New England Regions, *Global Research Program, Washington, DC.*

USEPA, 2015. Great Lakes: Nutrient Policy and Data. Available at: http://www2.epa.gov/nutrient-policy-data/great-lakes *[Accessed 17 December 2015].*

USEPA, 2015. Recommended Binational Phosphorus Target to Combat Lake Erie Algal Blooms. Available at: http://www.epa.gov/sites/production/files/2015-06/documents/recommended-binational-phosphorus-targets-20150625-8pp.pdf *[Accessed 4 December 2015].*

Wakida, F. T., Martinez-Huato, S., Garcia-Flores, E., Pinon-Colin, T. D. J., Espinoza-Gomez, H., & Ames-Lopez, A., 2014. Pollutants Association with Suspended Solids in Stormwater in Tijuana Mexico. *International Journal of Science and Technology,* Volume 11, pp. 319-325.

Wolf, G., Schneider, R. M., Bongiovani, M. C. & Garcia Do Amaral, A., 2015. Application of Coagulation/ Flocculation Process of Diary Wastewater from Conventional Treatment Using Natural Coagulant for Reuse. *Chemical Engineering Transactions,* Volume 43, pp. 2041-2046.

Wu, H.-Z., Hsu, Y.-L., Huang, H.-L. & Chen, J.-P., 2007. Application of Biocoagulant on Drinking Water Treatment. *Practice Periodical of Hazardous, Toxic and Radioactive Waste Management,* Volume 11, pp. 92-96.

Yin, C.-Y., 2010. Emerging Usage of Plant-Based Coagulants for Water and Wastewater Treatment. *Process Biochemistry,* Volume 45, pp. 1437-1444.

Young, S., Stanley, S. J. & Smith, D. W., 2000. Effect of Mixing on the Kinetics of Polymer-aided Flocculation. *Water Supply Research and Technology,* 49(1), pp. 1-8.

Zhu, W., Seth, R. & Lalman, J., 2007. Evaluation of a Micro carrier Weighted Coagulation Flocculation Process for the Treatment of Combined Sewer Overflow. *Environmental Technology,* Volume 28, pp. 761-770.

APPENDIX A VELOCITY GRADIENT VS AGITATION SPEED

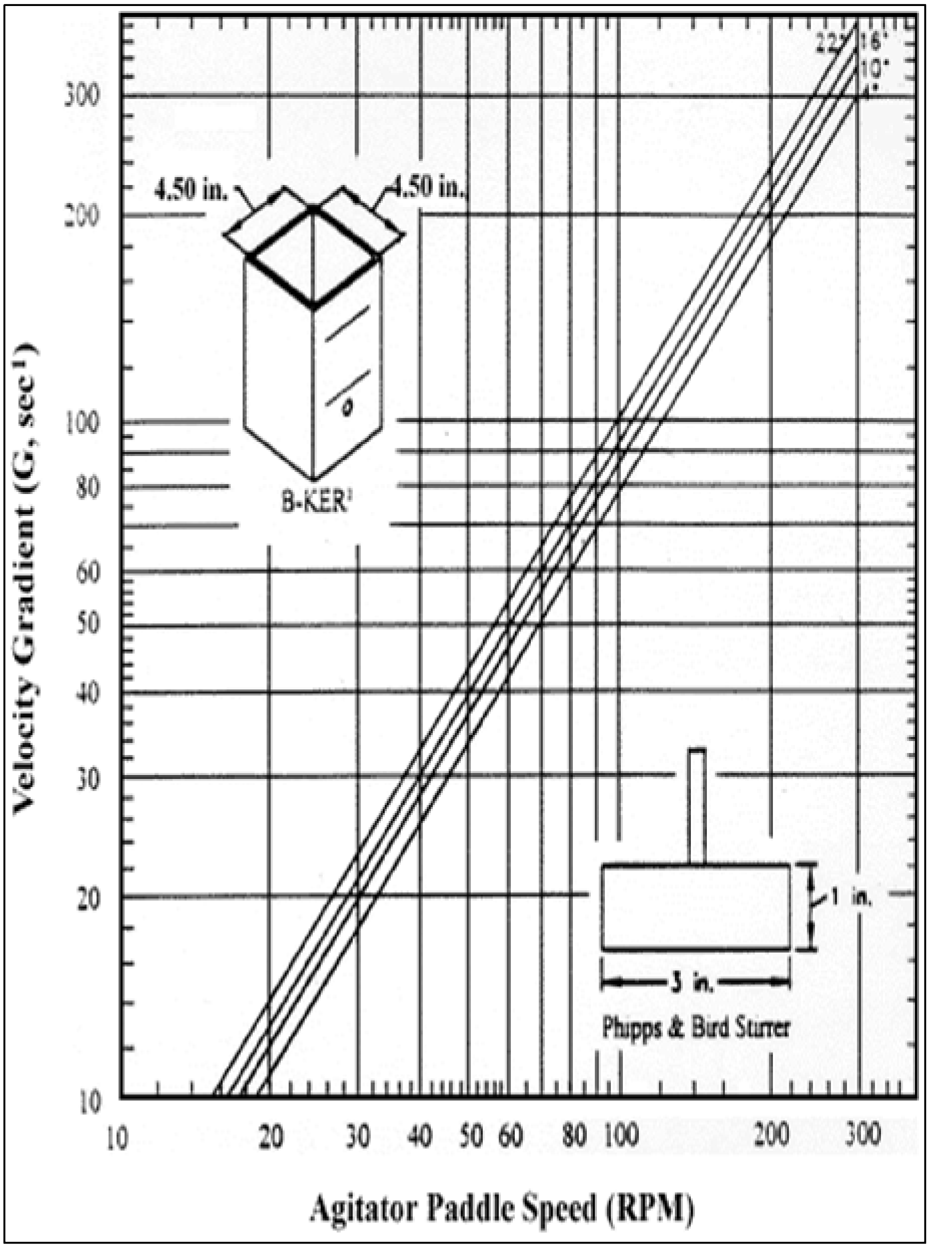


Figure A 1: Velocity gradient vs agitator speed for a 2-litre square Beaker (B-KER^2), Using a Phipps and Bird stirrer.

(Phipps & Bird Inc, 2015)

APPENDIX B PRE-TREATMENT FOR TOTAL PHOSPHORUS ANALYSIS

The following procedure was used for all the total phosphorus:

- Depending on the amount of solids visually present, about 5 mL-25 mL aliquot of sample is added to a beaker.
- 4 mg of potassium persulfate and 1 mL of 30% H_2SO_4 were added to the sample in the beaker.
- The solution was made up to 50 mL with deionised water while thoroughly rinsing the side of the beaker.
- The mixture was thereafter heated on a hotplate and allowed to digest to about 1 mL.
- After complete cooling, the volume was increased slightly by rinsing the side of the beaker with deionised water and a drop of phenolphthalein indicator was then added.
- 6N sodium hydroxide was added dropwise until the sample turned slightly pink
- The solution was transferred to a 50 ml volumetric flask.
- 4 ml ammonium molybdate was added followed by six drops of stannous chloride. Timing starts after the first drop of stannous chloride has been added.
- The solution was made up to 50 mL and moderately shaken.
- The absorbance was measured after 10 mins using spectrophotometer at 690 nm wavelength.

APPENDIX C CALIBRATION CURVES AND DETECTION LIMIT

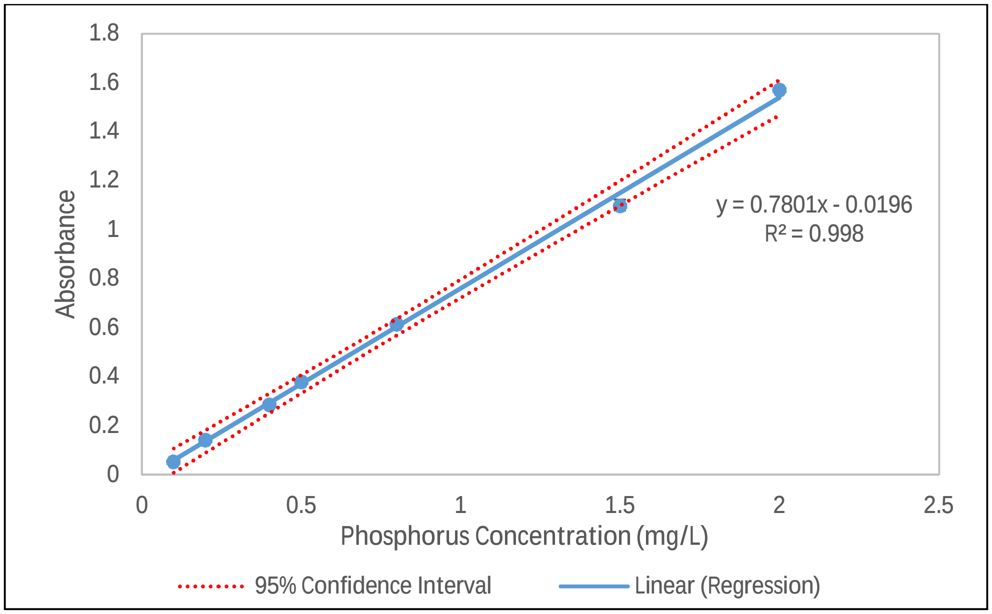


Figure C 1: Orthophosphate calibration Curve 1.

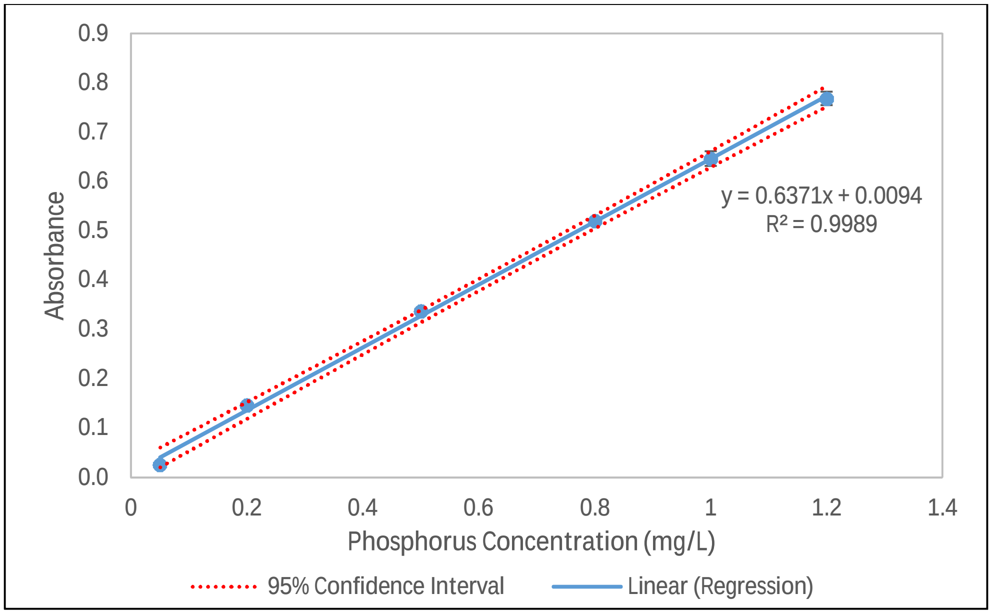


Figure C 2: Orthophosphate calibration Curve 2

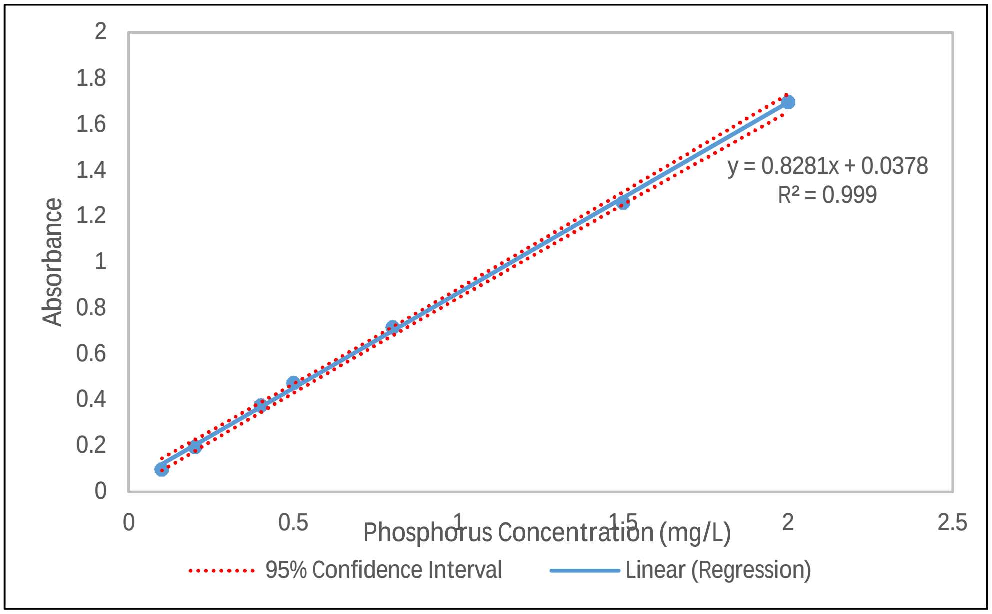


Figure C 3: Total phosphorus calibration Curve 1.

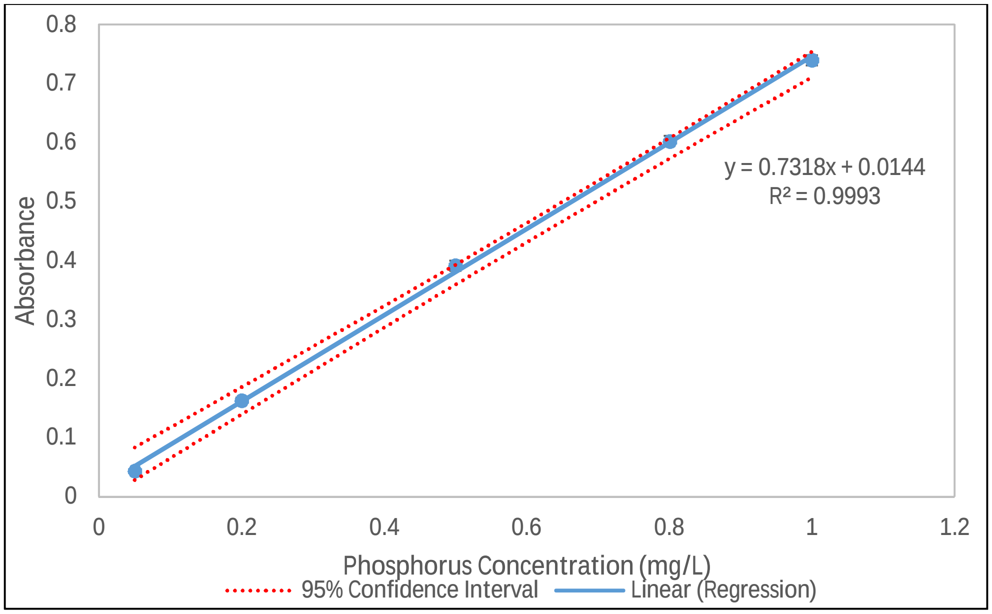


Figure C 4: Total phosphorus calibration Curve 2.

METHOD DETECTION LIMIT (MDL)

Table C 1: Method Detection Limit for Total Phosphorus and Orthophosphate

	Total Phosphorus	**Orthophosphate**
n	10	10
α	0.01	0.01
t	2.82	2.82
M (mg/L)	0.045	0.037
S (mg/L)	0.0099	0.0059
MDL (mg/L)	0.028	0.017

$$MDL = s\ X\ t_{(n-1,\ 1-\alpha=0.99)}$$

Concentration of spiked sample = 0.05 mg/L

n: number of spiked replicates

m: mean of measured spiked sample

s: standard deviation of the measured spiked sample

t: student’s t value at n-1 degree of freedom and 99% confidence level

α: level of significance

APPENDIX D   STATISTICAL ANALYSIS OF SUSPENDED SOLIDS DATA

One-way ANOVA: Event_1, Event_2, Event_3, Event_4, Event_5, Event_6, Event_7, Event_8, Event_9, Event_10

```
Null hypothesis         All means are equal
Alternative hypothesis  At least one mean is different
Significance level      α = 0.05

Games-Howell Simultaneous Tests for Differences of Means

Difference of Levels      Difference of Means SE of Difference    95% CI              T-Value   P-Value
Event_2 - Event_1          -0.160              0.474              (-1.787, 1.468)    -0.34     1.000
Event_3 - Event_1           1.382              0.302              ( 0.318,  2.445)    4.58     0.005
Event_4 - Event_1           1.114              0.415              (-0.304,  2.532)    2.68     0.227
Event_5 - Event_1          -0.927              0.350              (-2.139,  0.286)   -2.65     0.248
Event_6 - Event_1          -0.124              0.306              (-1.202,  0.955)   -0.40     1.000
Event_7 - Event_1           0.428              0.591              (-1.735,  2.591)    0.72     0.999
Event_8 - Event_1          -0.706              0.294              (-1.750,  0.338)   -2.40     0.375
Event_9 - Event_1          -0.453              0.331              (-1.588,  0.682)   -1.37     0.927
Event_10 - Event_1         -0.944              0.361              (-2.182,  0.295)   -2.61     0.258
Event_3 - Event_2           1.541              0.407              ( 0.084,  2.998)    3.78     0.033
Event_4 - Event_2           1.273              0.497              (-0.428,  2.974)    2.56     0.280
Event_5 - Event_2          -0.767              0.444              (-2.318,  0.784)   -1.73     0.770
Event_6 - Event_2           0.036              0.410              (-1.430,  1.502)    0.09     1.000
Event_7 - Event_2           0.587              0.651              (-1.718,  2.893)    0.90     0.995
Event_8 - Event_2          -0.546              0.401              (-1.991,  0.898)   -1.36     0.924
Event_9 - Event_2          -0.294              0.429              (-1.799,  1.212)   -0.68     0.999
Event_10 - Event_2         -0.784              0.453              (-2.356,  0.788)   -1.73     0.768
Event_4 - Event_3          -0.268              0.337              (-1.464,  0.927)   -0.79     0.998
Event_5 - Event_3          -2.308              0.253              (-3.224, -1.392)   -9.12     0.000
Event_6 - Event_3          -1.505              0.188              (-2.171, -0.840)   -8.01     0.000
Event_7 - Event_3          -0.954              0.539              (-3.037,  1.130)   -1.77     0.741
Event_8 - Event_3          -2.088              0.167              (-2.654, -1.522)  -12.49     0.000
Event_9 - Event_3          -1.835              0.226              (-2.595, -1.075)   -8.12     0.000
Event_10 - Event_3         -2.325              0.268              (-3.273, -1.377)   -8.67     0.000
Event_5 - Event_4          -2.040              0.381              (-3.363, -0.717)   -5.35     0.001
Event_6 - Event_4          -1.237              0.341              (-2.446, -0.028)   -3.62     0.042
Event_7 - Event_4          -0.686              0.609              (-2.888,  1.516)   -1.13     0.975
Event_8 - Event_4          -1.820              0.330              (-2.999, -0.640)   -5.51     0.001
Event_9 - Event_4          -1.567              0.364              (-2.824, -0.310)   -4.31     0.007
Event_10 - Event_4         -2.057              0.391              (-3.405, -0.709)   -5.26     0.001
```

```
Difference of Levels       Difference of Means SE of Difference    95% CI              T-Value   P-Value
Event_6 - Event_5           0.803               0.258              (-0.136,  1.741)     3.11     0.128
Event_7 - Event_5           1.354               0.567              (-0.767,  3.476)     2.39     0.400
Event_8 - Event_5           0.221               0.244              (-0.673,  1.114)     0.91     0.994
Event_9 - Event_5           0.473               0.287              (-0.523,  1.470)     1.65     0.812
Event_10 - Event_5         -0.017               0.321              (-1.140,  1.106)    -0.05     1.000
Event_7 - Event_6           0.552               0.541              (-1.534,  2.637)     1.02     0.984
Event_8 - Event_6          -0.582               0.175              (-1.208,  0.043)    -3.33     0.080
Event_9 - Event_6          -0.330               0.232              (-1.121,  0.462)    -1.42     0.910
Event_10 - Event_6         -0.820               0.273              (-1.789,  0.149)    -3.00     0.142
Event_8 - Event_7          -1.134               0.534              (-3.212,  0.944)    -2.12     0.548
Event_9 - Event_7          -0.881               0.556              (-2.983,  1.220)    -1.59     0.833
Event_10 - Event_7         -1.371               0.574              (-3.502,  0.759)    -2.39     0.397
Event_9 - Event_8           0.253               0.215              (-0.472,  0.977)     1.17     0.972
Event_10 - Event_8         -0.237               0.259              (-1.163,  0.688)    -0.92     0.994
Event_10 - Event_9         -0.490               0.300              (-1.521,  0.540)    -1.63     0.822
```

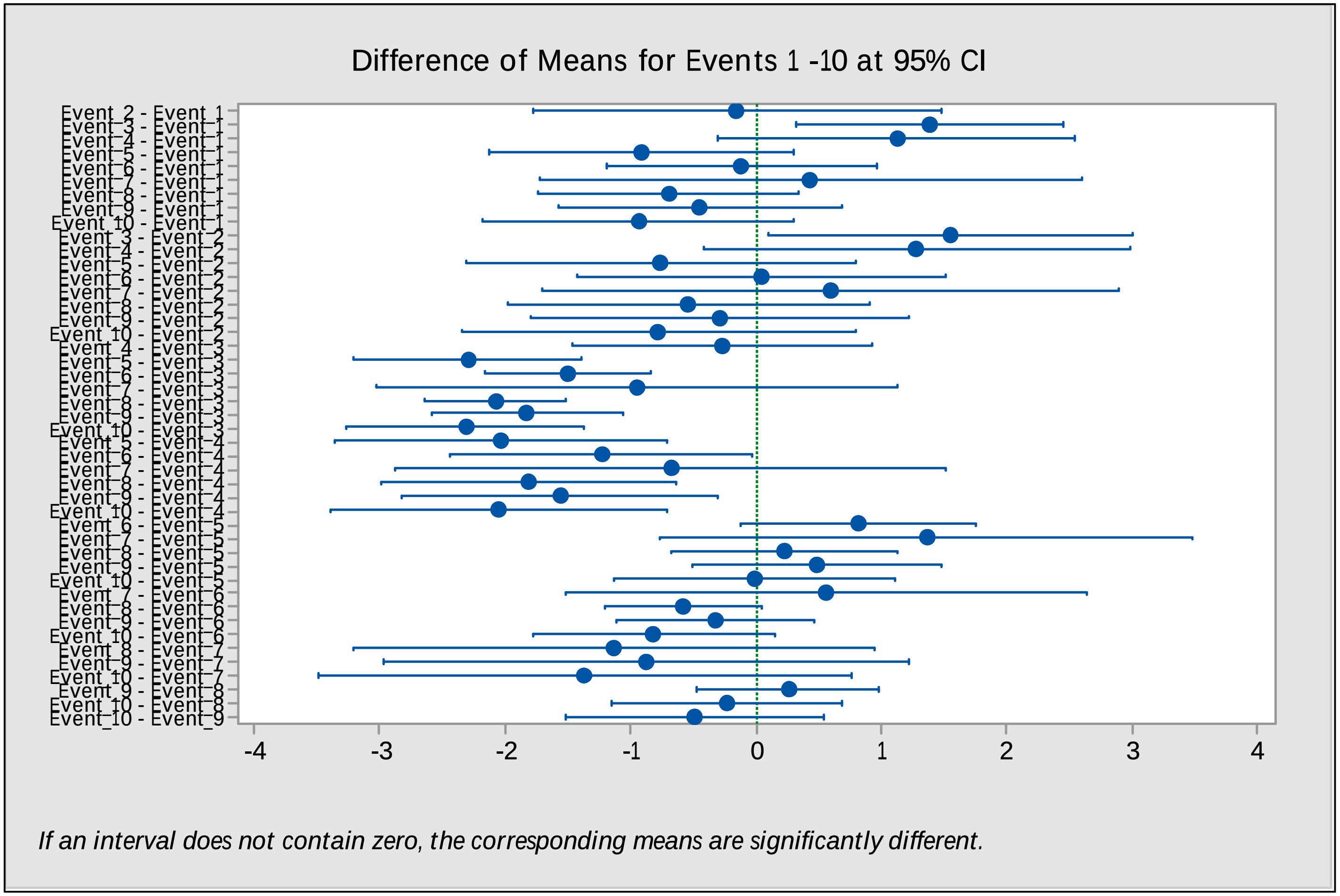


Figure D 1: Hypothesis 1 test result.

APPENDIX E RETURN PERIOD OF STORM EVENTS

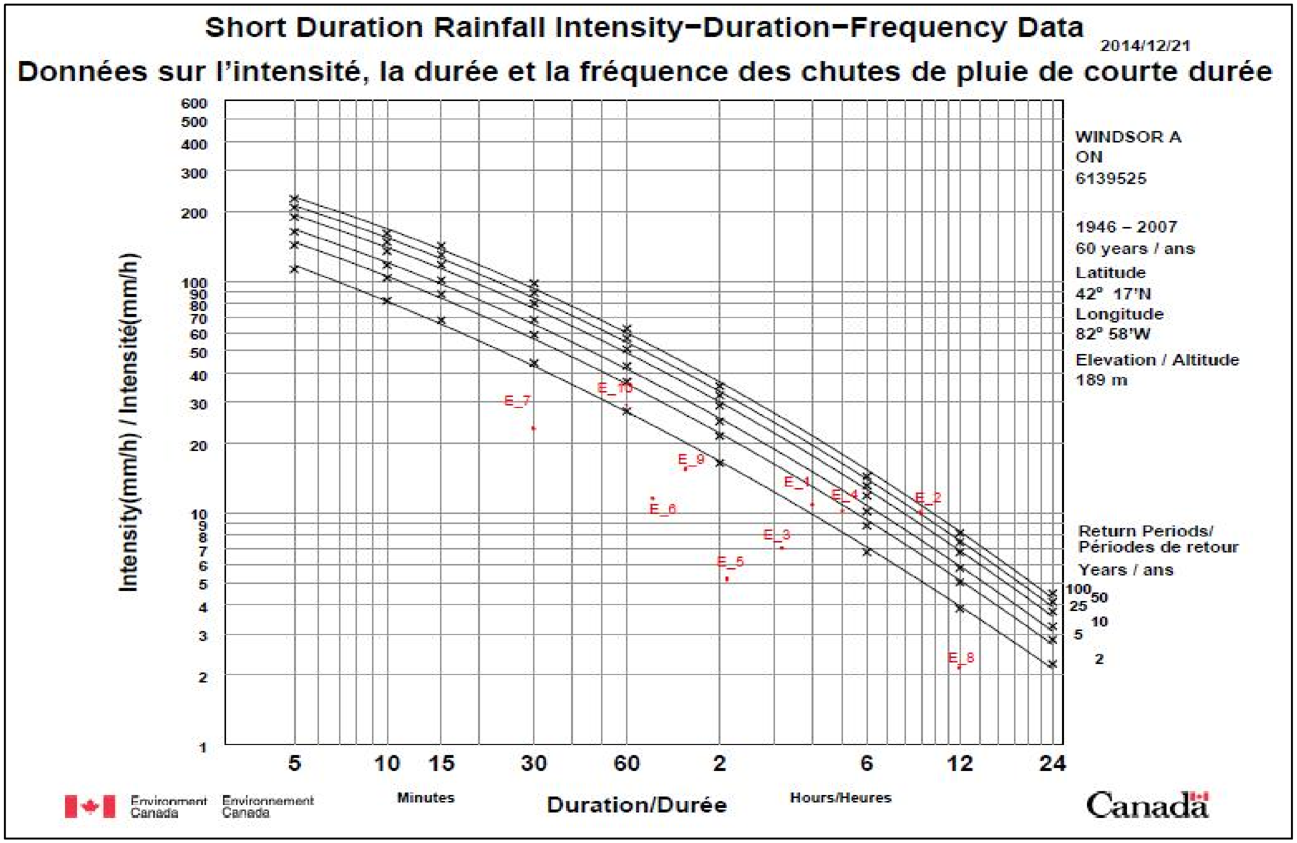


Figure E 1: Return periods of all monitored storm events.
(Environment Canada, 2015)

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