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Modelling the fate of a larviciding chemical, methoprene, at drainage systems

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MODELLING THE FATE OF A LARVICIDING CHEMICAL, METHOPRENE, AT DRAINAGE SYSTEMS

By

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ABSTRACT

Title: Modelling the fate of a larviciding chemical, Methoprene, at drainage systems

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With the recent occurrence of mosquito-borne West Nile Virus (WNV) in Canada, the City of Toronto and the surrounding municipalities have undertaken the larviciding program to control mosquitoes during the summer months. The larviciding chemical, methoprene, can be incorporated in clay pellets or chalks which sink to the bottom of a catch basin sump. The main concern is whether or not the methoprene pellets or chalks will still be in a catch basin sump or be flushed out during storm events. The objective of this thesis is to develop a water quality model, which is based on surface hydrology, mass balance and hydraulic characteristics of flushing at catch basin, in order to predict residual concentration of methoprene at catch basins and storm sewer outfalls. The findings of the research and all information from other contributing parties are expected to contribute to our understanding of the fate of methoprene at catch basins and storm sewer outfalls and improve the mosquito larviciding program in the Greater Toronto Area.

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Chapter 1 INTRODUCTION

1.1 Background

Prior to the summer of 1999, West Nile Virus (WNV) was never identified in the Western Hemisphere. Since the 1999 outbreak in the New York City metropolitan area, the disease has spread across North America. Ontario Ministry of Health and Long-Term Care (MOHLTC) described the Surveillance Plan for WNV in the Province of Ontario as well as the Prevention and Public Education measures aimed at reducing the risk of WNV disease for the population of Ontario (MOHLTC, 2001). Mosquito are the primary vectors of WNV, mainly the Culex pipens (Northern House Mosquitoes), found in sheltered or stagnant water, such as roof gutters, buckets, wheelbarrows, and catch basins with sump - one of the most mosquito breeding sites in urban areas.

In order to reduce human exposure to the disease vectors and the risk of WNV disease for the population of Ontario, Toronto Public Health has several initiatives to control and prevent the virus, including larviciding program to reduce the mosquito population. Larvicide methoprene pellets were applied in the city-owned catch basins in Toronto area during the peak mosquito breeding season.

Once added, they are supposed to remain effective for up to 30 days under typical environmental conditions as long as the pellets remain at the catch basin sump. However, some concerns have been raised that methoprene chemical or pellets and chalks may be flushed out from the catch basin or diluted with each rainfall, resulting in reduced larvicidal effect. Frequency of re-application and dosage may have to be increased, accordingly, and may pose hazards to human health and the environment. Therefore, field monitoring study within Toronto area have undertaken to predict the fate and transport of

methoprene larvicide in the storm water catch basin and sewer outfall (Des Lauriers, 2004)

The main sources of road surface pollutants are the atmospheric deposition and pollution caused by the traffic (Grottker, 1990). Pollutants are washed off from the surface to the catch basins. Some pollutants, such as metals, may adsorb onto the surface of solids, which is likely disturbed and flushed out during storm events. Sediment particle sizes are of great importance as fine particles are highly enriched with heavy metals when they reach the stormwater outfall (Morrison et al., 1988). Other pollutants such as nutrients and petroleum-based organics may be attached to their surfaces (Pyatt, 2003). Coarser sediment fractions, which are flushed out from the catch basin, may deposit in the drainage structures and cause the reduction in the hydraulic capacity of drainage system while fine sediment may pollute aquatic environment (Deletic et al., 2000). It is illustrated from Table 1.1 that medium size of 0.2-0.8 mm sediment could be deposited in the storm sewer. Rainbow trout died rapidly with mortality of 80-100% when exposed to silty water discharge whose particles are ranged in size from 0.1-0.17 mm (Pyatt, 2003). As a result, catch basins are cleaned periodically between once to twice per year or based on site inspection whether or not sediment is accumulated, to maintain its sediment-trapping ability and prevent the occurrence of local flooding.

Table 1.1: Median diameter of sediments found in storm drainage systems (Source: Deletic et al., 2000)

Place of sampling	Weather	Method of sampling	D50 (μm)
Urban (paved)	Dry	Dry vacuum cleaning	≈ 250
Surface (asphalt)	Dry	Dry vacuum cleaning	≈ 600
Inlet to drainage	Wet	Composite samples	81
system (before	Wet	Composite samples	≈ 60
deposition in gully)	Wet	Sieving	550
In gully	Dry	Wet sieving	200/1000+
In sewer	Dry	Sediment bed	200-800
	Wet and dry	In flow	30-40
At system outlet	Wet	In flow	1-50

This thesis is mainly intended to simulate the residual concentration of methoprene under dry and wet weather condition and investigate the hydraulic behaviors of methoprene pellets as well as chalks within catch basin. Once the critical flushing flows are determined, a hydrologic water quality model is developed to evaluate the potential effect of the larviciding program under local conditions and allows investigation of the fate and transport of methoprene.

1.2 Research Objectives and Scope

Since there are few research studies in North America focused on the hydraulic scouring of sediment as well as fate and transport of methoprene in catch basin, it is hoped that this thesis will be useful to gain a greater general understanding of these processes.

The objectives of this thesis are to: (1) determine the environmental fate of methoprene in field catch basins and quiescent condition; (2) analyze the discharge of methoprene mass at storm outfalls; (3) examine the hydraulic properties of sediment and methoprene product formulations; and (4) determine the risk of flushing of pellets and

chalks in catch basins. The scope of the research is limited to three study catch basins in North York area and laboratory experiments on a model catch basin.

1.3 Research Methodology and Organization

The schematic diagram which summarizes the research methodology is shown in Figure 1.1 and the thesis is presented as follows:

- Chapter 2: Review literature related to West Nile Virus, methoprene and catch basin hydraulics
- Chapter 3: Conduct field monitoring study on three catch basins and the storm sewer outfall of the Newtonbrook sewershed over three months in 2003 and 2004 as well as laboratory experiments on model catch basins
- Chapter 4: Analyze the catch basin sediment characteristics, such as particle size distribution, specific gravity, as well as organic and carbonate contents
- Chapter 5: Perform hydraulic scouring experiments on blended sediment and two methoprene products of pellets and chalks at the Canada Centre for Island Waters (CCIW)'s hydraulics laboratory.
- Chapter 6: Develop a hydrologic mass balance model which incorporates dry and wet weather conditions to simulate the concentration of methoprene at catch basins and the discharge of methoprene to the environment under local conditions in Toronto
- Chapter 7: Conclude the research and recommendation

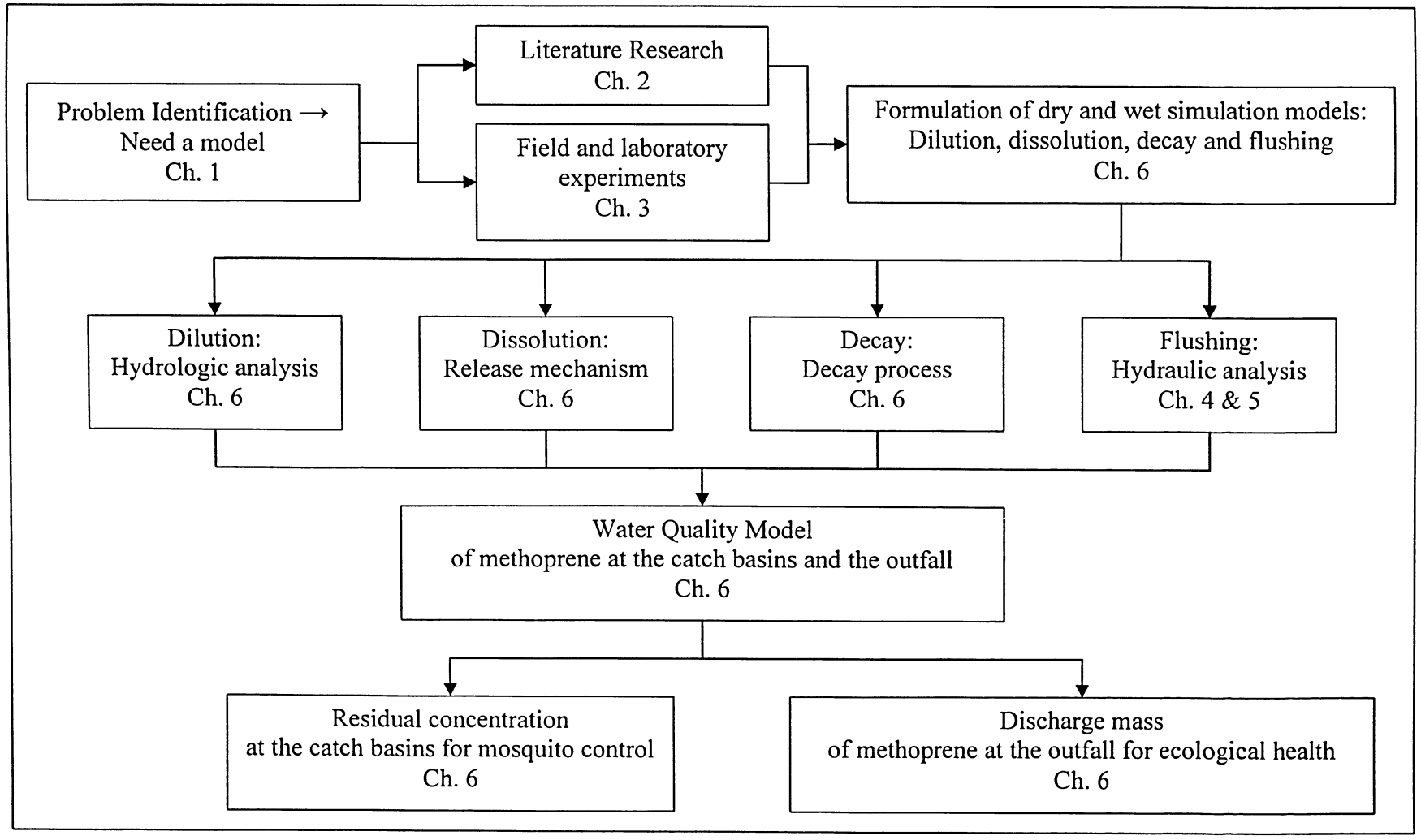


Figure 1.1: Research methodology

Chapter 2 LITERATURE REVIEW

2.1 West Nile Virus and Mosquito Control

West Nile Virus (WNV) is a mosquito-borne virus. It caused seven deaths when it first emerged in the United States in 1999. In Canada, the virus was first confirmed in birds in Ontario in 2001 and the first human case of WNV was confirmed in Ontario in September 2002. Infected people show various responses, from subclinical disease, to short duration flu-like illness, to frank encephalitis and death (Garmendia et al., 2001). Ten species of mosquitoes have been shown to be carriers of the virus. Of these species, Culex mosquitoes are the most likely species to transmit the virus. Birds, such as crows and blue jays, are preferred hosts to Culex mosquito species of pipiens, restuans, territans and salinarius. When their populations increase due to favourable weather and other conditions, they will often find other hosts, such as humans to feed on (Dohm et al., 2002). At this time, there is no licensed vaccine to protect people against West Nile Virus (Health Canada, 2004). As of October 31, 2004, six human cases of WNV have been reported in Toronto as well as thirty-one mosquito pools and eighteen birds have tested positive for the virus. In 2003, there were forty-four human cases of WNV reported to the City of Toronto as well as seventeen birds and fifty-five mosquito pools tested positive for WNV (Toronto Public Health, 2004).

Mosquitoes tend to breed in stagnant water in mid to late summer of extensive rainfall. They undergo four stages of their life cycle: egg, larva, pupa and adult to complete their metamorphosis. The first three stages take place in water. Eggs are laid singly or in groups called rafts for some species on the water surface. Culex females lay their eggs on water that is high in organic material and stagnant. Most eggs hatch into

larvae within 24 hours at 20-25°C and up to several days if cooler temperatures are prevalent. Most eggs are laid in early May but egg-laying continues until fall. Larvae feed on microorganisms and organic matter in the water. Temperature is an important condition for larval development, which is completed in approximately 60, 40 and 10 days at 10°C, 15°C and 25°C, respectively. Larvae emerge and eventually change to pupa, which, in turn, change to adults. Female mosquitoes bite and feed on blood of hosts, for example, amphibians, reptiles, birds, or mammals, including humans, in order to obtain a protein source for egg production. Male mosquitoes do not have mouthparts for taking blood and feed primarily on flower nectar and plant juices. The whole process from hatched egg to flying adult takes between 4 and 14 days. Variables such as food availability (micro-organisms or organic substances), temperature, and day-length have a large influence on the time necessary for mosquito development (Floore, 2003). Partial flushing of larvae from catch basin may happen by normal rainfall but not all catch basins could experience flushing thoroughly during average rainfall and heavy rain of 102 mm could substantially reduce larval numbers (Geery and Holub, 1989). Thus, control mosquito treatment in spite of rain is necessary.

Mosquito can be effectively reduced by source reduction, i.e., reducing the amount of standing water available for breeding; and controlled when they are larvae or adults. Products are called adulticides (mosquito repellants, for example, DEET) and larvicides (for example, Oil, Abate, Bti and methoprene). In general, the use of larvicides is preferred to the use of adulticides. Larval control is more effective at controlling mosquitoes and has the least effect on non-target species and the environment. It is because when mosquitoes are in the larval stage, their populations are concentrated and

located in catch basins, ponds, puddles and other stagnant bodies of water. More time and manpower are needed to track the adult mosquitoes down and kill them. In addition, adulticides provide only instant relief and the results are short-lived, thus, repeated applications are necessary. When insect hormone based larvicide is used, insects hardly develop resistance to their own hormones (Buchel, 1983).

2.2. Methoprene Larvicide

2.2.1. Properties

Methoprene, a juvenile hormone analogue, with IUPAC of Isopropyl (2E,4E)-11-methoxy-3,7,11-trimethyldodeca- 2, 4-dienoate, is an insect growth regulator for the control of mosquito larvae that was first registered for use in Canada in 1977. It is the third generation of insecticides. Figure 2.1 illustrates the structure of methoprene. Table 2.1 summarizes some properties of methoprene. The synthetic methoprene compounds are structurally similar to insect's natural juvenile hormones and therefore referred as juvenile hormone analogue. It prevents larvae from reaching maturity or reproducing by disrupting the action of the growth hormone, so its life cycle is disrupted. Methoprene works effectively during the late instar of larvae or pupal stage (Buchel, 1983).

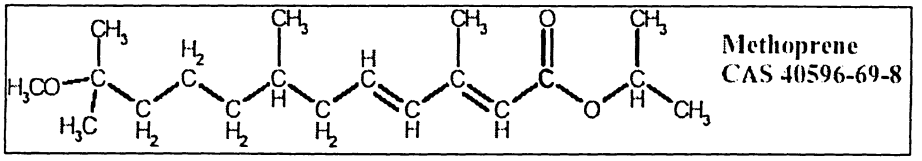


Figure 2.1: Structure of methoprene (Source: MOE, 2004)

Table 2.1: Physical and chemical properties of methoprene (Source: Wellmark International, 2003)

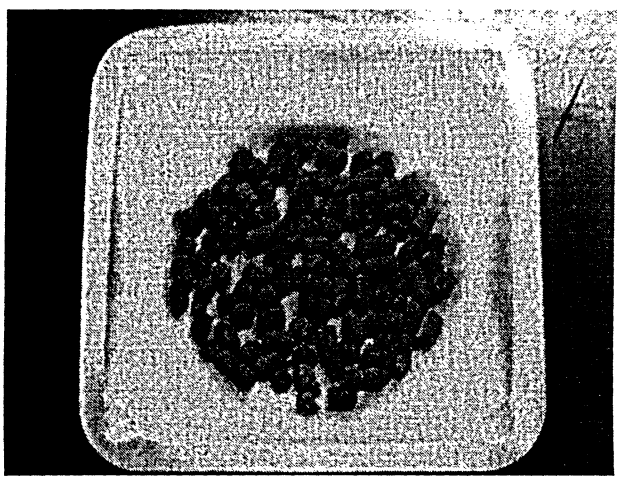
Properties	Description
Trade and Other Names	Altosid(R); Kabat(R); Apex(R); Diacon(R); Minex(R); Pharorid(R); Precor(R); Manta(R); Altosand(R); ZR-515
Molecular Weight	310
Appearance	Pale yellow liquid with a faint fruity odor
Water Solubility	1.4 mg/L @ 25°C
Solubility in Other Solvents	Miscible in organic solvents
Vapor Pressure	2.37 × 10-5 mm Hg at 25°C
Specific gravity	0.9261 g/ml at 20°C
Melting point	164°C.
Boiling point	135 - 136°C at 0.06 mm Hg and 100°C at 0.05 mm Hg.
Stability	Described as a stable compound though non-persistent due to rapid biodegradation mainly to CO_2. In water, less than one day in sunlight and over four weeks in dark
Flash Point	187°C - open cup method
Environmental Fate [Based on (RS)-Methoprene]:	
Hydrolysis	T1/2 > 4 weeks ((S)-Methoprene)
Photolysis	T1/2 < 10 hours ((S)-Methoprene)
Soil half life	~ 10 days ((S)-Methoprene)
Water solubility	< 2 ppm ((S)-Methoprene)
Toxicity: LD_{50} (Rat)	34,600 mg/kg

2.2.2. Formulations and Application

Methoprene is sold commercially as Zoecon Altosid and manufactured by Wellmark International. It can be a form of liquid, pellets, granules, as well as chalks, as shown in Figure 2.2. Altosid chalks are available in an "ingot" shape to allow the product to fit through the storm water catch basin grate without lifting the grate each time during treatment. The pellets or ingot stay positioned in the water at the bottom of the sump, gradually breaking down and releasing methoprene into the water. Pellets and ingots are slow-release formulations, which can provide residual concentration up to 30 and 150 days, respectively. Application rates vary depending on the type of habitat, water depth

and water quality (Wellmark International, 2003). They are applied to the water where mosquito larvae are found, such as catch basins especially with sump. Table 2.2 shows the information on the altosid products.

(a)



(b)

Figure 2.2: Forms of methoprene: (a) Altosid chalks; (b) Altosid pellets

Table 2.2: Altosid products (Source: Wellmark International, 2003)

Altosid® Product	EPA#	% Active Ingredient	Application Rate	Release Period
Liquid Larvicide	2724-392	5%	219 to 293 ml / hectare	5-7 days
Liquid Larvicide	2724-446	20%	55 to 73 ml / hectare	5-7 days
Altosid® SBG	2724-489	0.2%	5-10 lbs / acre	5-10 days
Briquets*	2724-375	8.62%	1 to 4	30 days
Briquets XR*	2724-421	2.1%	1 briquet / 100 sq. ft to 1 briquet / 200 sq. ft for non flow shallow (<2 feet) areas	150 days
Pellets*	2724-448	4.25%	2.5 – 10 lbs / acre	30 days
Granules XR*	2724-451	1.5%	5- 10 lbs / acre	21 days

* Slow release solids

Methoprene are classified by the Pest Management Regulatory Agency (PMRA) as restricted. That means applicator needs permit or certified to use this chemical. Larvicides are most effective when used early in the mosquito season, from May to July. According to Table 2.3, most suitable time for applying methoprene may be early-June when pupae begin to develop. In 2003 and 2004, the larvicide methoprene pellets of 0.7 g were placed into the 175,000 City of Toronto's owned catch basins during the summer months and early fall when the peak reproduction cycle of Cx. Pipiens was maximum. 0.7 g is calculated based on the application rate of 1.12 g/m^2 of water surface, assuming the catch basin is cylindrical with diameter of 0.9 m (MOE, 2003). One of the reasons using methoprene pellets is its longer persistence in water compared to others larvicides, which provide approximately 30-day mosquito control (McCarry, 1996).

Table 2.3: Typical presence and abundance of life stages of Culex in Ontario (Source: MOHLTC, 2001)

Month (s)	Life stages present and abundance
March to early May	Female adults (mostly fertilized females) overwintering
Mid-May	Adult females lay eggs
Late-May	Eggs hatch to larvae, adult numbers decrease
Early-June	Pupae develop and adults (male and female) emerge to mate
Mid-June	Adult females lay eggs, adult numbers decrease
Late June	Eggs hatch to larvae, pupae develop and adults emerge
Early August	Larvae and pupae continue to develop and more adults emerge
Mid-August	Egg laying by adult females
Late August	Larvae and pupae develop adult numbers decrease
Early September	Larvae and pupae continue to develop; females mate and ready for overwintering after first frost; males die
Mid September to February	Females overwinter

2.2.3 Environmental Persistence

Methoprene is extremely stable to hydrolysis (Schooley, 1975) and its half-life with respect to hydrolysis is over 4 weeks (Wellmark International, 2003). The main degradations in water are thought to be by photoisomerism and microorganism metabolism (Extoxnet, 1996). In the presence of sunlight in sterile water for 7 days, methoprene will decompose into four major and 40 minor products – the major products being Methoprene acid, Methoxycitronellal, Methoxycitronellic acid and Methoprene epoxide (LaClair et al., 1998). Temperature is another factor that would affect the persistence of methoprene in water. Higher temperature increases the rate of breakdown of methoprene (Schaefer and Dupras, 1973). Pree and Stewart (1975) found a difference in half-life of methoprene at 4.5°C between fresh (about 100 days) and salt water (35 days). Degradation at all temperatures and formulation was faster in salt water than in fresh water. Table 2.4 summarizes the half-lives of methoprene in different conditions.

Table 2.4: Half-lives of methoprene

Half-life	Condition	References
60 hrs (from data)	Water quality: Surface water (Humber River water) & stored in the dark at 4℃	Selected pesticide recovery studies (2004)
91 hrs (from graph)	Water quality: Surface water (Humber River water) & stored in the dark at 4℃	Selected pesticide recovery studies (2004)
2 hrs	Field pond water & Emulsifiable concentrates of aqueous solutions of methoprene	-McCarry (1996) -Schafer and Dupras (1973)
42 hrs	Tap water and stored in dark at 24℃	
30 hrs	Tap water and stored in dark at 38℃	
30 hrs	Pond water & initial conc. of 1 µg/L	EXTOXNET (1996)
40 hrs	Pond water & initial conc. of 10 µg/L	
> 4 weeks	Hydrolysis	Wellmark International (2003)
< 10 hrs	Photolysis	
< 1 day	Photolysis in water Done in laboratory	Quistad et al. (1975)
1-2 days	Water	Toronto Staff Report (2003)
~2 days	Field water	Wright (1976)
1-5 days	Exposed to UV	Degitz, et al. (2003)
30-45 hrs	Unsterilized field pond water	Starbarproducts (2002)
Short half-life (hour unit)	-	Integrated Pest Management Program (2004)
<7 days	In water	Draft (2000)
60-70 hrs	Sewage	Csondes (2004)

Altosid pellets produced S-methoprene residues that peaked at 2.0 μg/L on day 7 and declined to 0.2 μg/L at 14 days after applicaton while the Altosid XR ingot produced the concentration peaked at day 2 with average concentration of 0.7 μg/L and declined steadily through day 4 to 0.2 μg/L. The study was done in a static system (Ross et al., 1994). Rate of release and data generated under laboratory and field conditions with methoprene mosquito product formulations, including the slow release ingot formulations, indicate a maximal rate of release of less than 4 μg/L (USEPA, 2001).

Most studies done on methoprene pellets or briquets are focused on static experiment. The efficacy of methoprene is assessed by larvae or adult mosquito reduction. Few studies have been done on the dissolution and decay rate of methoprene as well as investigation of any possible influences on hydro-dynamic properties of methoprene. Little works have been undertaken to model the methoprene concentration and loadings within a drainage system.

2.2.4 Efficacy and Effect on Non-Target Species

Lethal concentration (LC50) of 0.3 to 2.3 μg/L has been reported for Culex mosquito species (Des Lauriers, 2003). Methoprene is effective for mosquito control at very low concentrations of 2 μg/L (West Nile Virus Prevention and Control Program, 2003). Methoprene was shown to be highly selective to mosquito larvae and showed a 90% emergence inhibition of Aedes nigromaculis at concentrations of 0.1 μg/L, while non-target organisms, including well-known mosquito predators, exhibited high tolerance to the larvicide (Miura and Takahashi, 1973). Pellets applied at a rate of 11.3 kg/ha or 7 g of pellets per catch basin can provide an average of 82% emergence inhibition of adult

mosquitoes over the 15 weeks trial period in field conditions (McCarry, 1996). In addition, 70% reduction in emergence of Culex pipens and Cx. restuans adults occurred during a test summer period of 15 weeks when methoprene ingot is applied in catch basin (Knepper et al., 1992). Methoprene is highly effective against mosquitoes, such as Culex pipiens and restuans, found in Peel region with efficacy rates of 80% or better (West Nile Virus Prevention and Control Program, 2003).

Methoprene is considered by the U.S. Environmental Protection Agency (USEPA) as a 'least toxic' insecticide, and USEPA claims that "methoprene used in mosquito control programs according to label directions does not pose unreasonable risks to wildlife or the environment" (USEPA, 2000). It has very little non-target species toxicity and virtually non-toxic to birds. However, there is some evidence of toxicity to fish, amphibians and freshwater invertebrates. Field studies of methoprene have demonstrated that there is little effect on non-target organism including dragonflies, water boatmen and fairy shrimp (West Nile Virus Prevention and Control Program, 2003). Methoprene levels in excess of 10 μg/L, which is the expected environmental concentration, could have detrimental effects on non-target invertebrates that are an important source of food for fish (Ross et al., 1994). The recommended Interim Provincial Water Quality Objective (IPWQO) for methoprene based on non-target and target species are 0.2 μg/L and 0.001 μg/L, respectively (MOE, 2004). Table 2.5 summarizes the benchmarks for environmental quality to ensure protection of ecological function over short-term exposures. Field application rates of 1.0 μg/L of methoprene have been reported to be adequate to eliminate the common target mosquitoes without producing lethality to most non-target aquatic biota (Glare and O'Callaghan, 1999).

Table 2.5: Benchmarks for environmental quality (Source: MOE, 2004)

Organism	Benchmark (μg/L)
Fish	80
Invertebrates	10
Amphibians	1.6
IPWQO	0.2

2.3 Urban Drainage Systems

2.3.1 Storm Water Catch Basin

Catch basin is one of the minor urban drainage systems which are designed to convey 2 to 5 years minor peak runoff to the storm sewer pipe system (Guo, 2000). Runoff from different sub-catchment areas is confined, channeled through street curbs and gutters and collected in underground concrete boxes called catch basins. A grate is a metal cover intercepted with the road surface. There are three major types of inlets: grate inlet, curb-opening inlet and combination inlet. Curb-opening inlet is not used by MTO. The interception capacity for combination inlets on grade is less than that of grate inlet (MTO, 1984). The fishbone type grate inlet is common to Southern Ontario (Townsend et al., 1980) with Ontario Provincial Standard Drawing of OPSD-400.01, as shown in Appendix A. Outlet pipe in catch basin is connected to storm sewer system. Catch basins may or may not have sumps, which acts as a settling basin to trap solids. Figure 2.3 shows a cast in place catch basin with 900 mm sump depth.

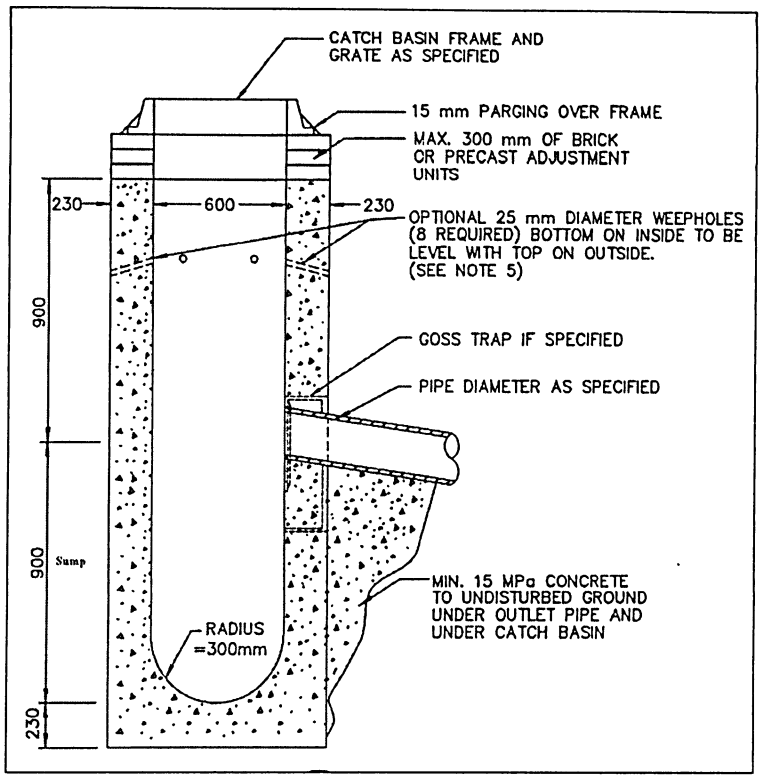


Figure 2.3: Cast in place catch basin with sump (Source: City of Toronto, 2001)

The standard catch basin heights for Ontario Provincial standard (OPS) are 1520, 1680, 1830 and 1980 mm. Common grate is square with 600 x 600 mm dimension. There are two standard sump depths: OPS with sump depths of 600 and 450 mm and Metro standard of 900 mm. The calculated sump capacities are 134, 188 and 300 L for sump depth of 450, 600 and 900 mm, respectively. Gully pot is another term for catch basin used in UK and Germany, as shown in Figure 2.4. The most common grate is circular with diameter of 450 mm and its small sump capacity is 90 L (Osborne et al., 1998).

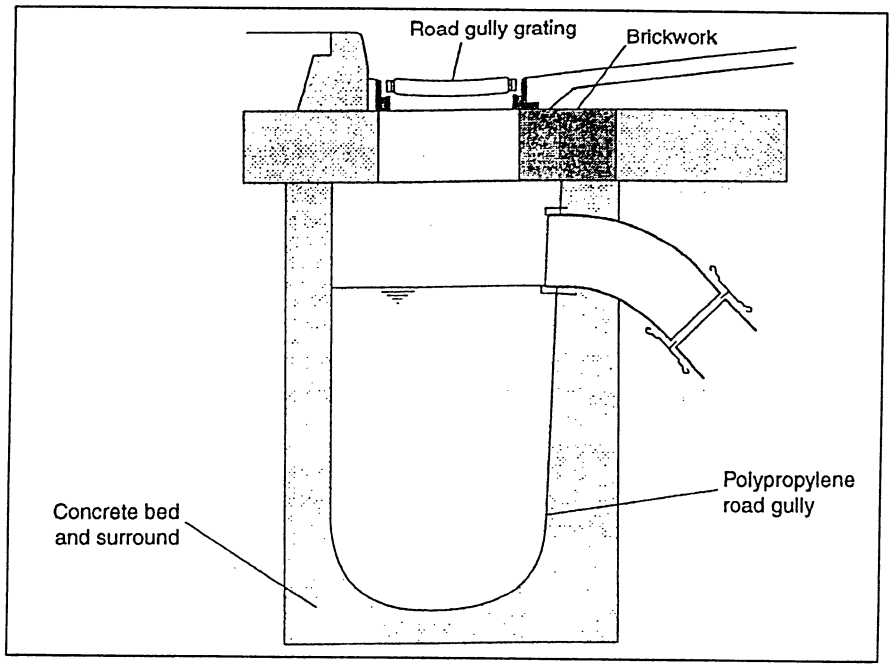


Figure 2.4: Typical gully pot (Source: Osborne et al., 1998)

Spacing of catch basins is approximately 60 to 120 m in an urban area. The catchment area for one catch basin is approximately 0.4 to 1.2 ha (Guo, 2000). Streets, gutters, catch basins and storm sewers are designed to minimize frequency surface ponding. The functions of catch basin are to collect surface runoff water and retain some sediment so that the polluting load can be reduced. Moreover, catch basin is an excellent breeding site for Culex pipiens and restuans because they retain water and much organic debris for long periods of time.

Inlet capacity of one fishbone cover catch basin was investigated by Townsend et al. (1980). It is observed from Figure 2.5 that catch basin can't capture all the runoff. Design charts for most common grate inlet capacity used by MTO are shown in Appendix B. Hydraulic efficiency of a grate inlet is defined as the ratio of the discharge

intercepted by the inlet to the total discharge approaching the inlet. Figure 2.5 indicates that inlet efficiency decreases with increasing flow rates.

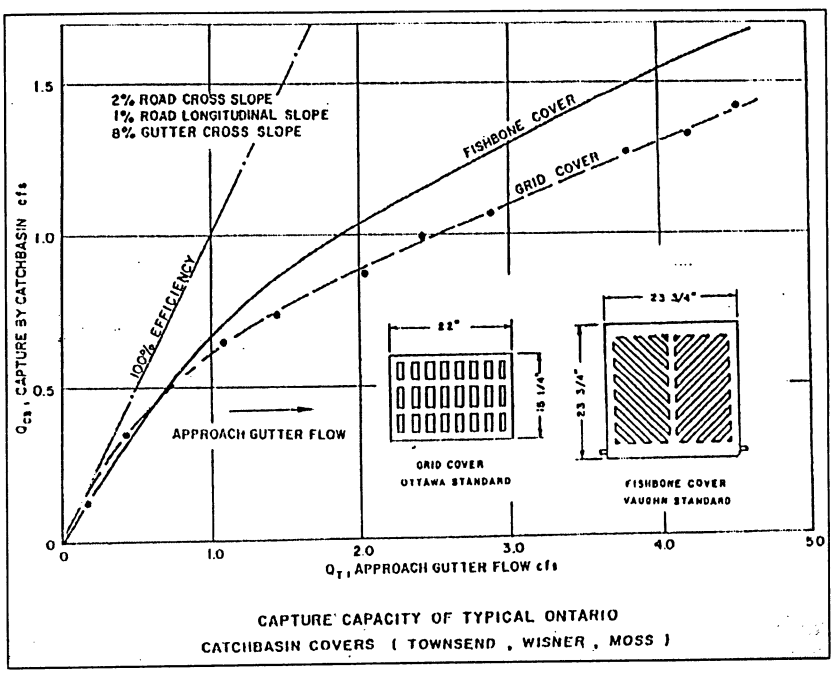


Figure 2.5: Inlet efficiency of fishbone catch basin grate (Source: Townsend et al., 1980)

2.3.2 Previous Studies on Gully Pot

Gully pot studies have been performed in UK and Germany. Few have been done in North America. Previous works done by Grottker (1990) was investigated catch basins for pollutant accumulation and removal processes. The catchment study area of a catch basin was in the City of Hannover, Germany. A flow rate of about 4 L/s was discharged. Test procedure included simulation of the pollutant removal and the flushing effect from different accumulation loads in the settling pit. The accumulated load level was adjusted by a metal sheet. It was concluded that there is no significant correlation between the passed load and the test duration as well as the level of accumulated load. The removal of

sediment is a function of flow rate and is expressed for different land area of the catchment.

Pratt and Adams (1984) studied sediment washoff to gully pots and stormwater runoff quality. The research was conducted on the Clifton Grove catchment, Nottingham, UK. Different openings of micron meshes were used to retain different fractions of the washoff material. It was pointed out that there is a correlation between the mass of sediment surface washoff and the runoff volume in the period between late December and early April when soil moisture deficit falls to zero. However, there is no correlation between them from April to December when soil moisture deficit is not zero. In addition, the author developed a relationship between the mean values of sediment supply to the gully pot and characteristics of gully catchment, such as impervious area, maximum drainage path length and slope, the number of houses served as well as soil moisture deficit. 92% of the total collected mass is retained on the 1.25, 0.6 and 0.4 mm meshes. The mean particle diameter of mesh-trapped sediment is 0.7 mm. The basal field catch basin sediment sample in the residential area of Nottingham obtained by a gully-emptying machine was measured the bulk density of 1492 kg/m^3 and the sediment size fractions of mean diameter of 1.75 mm. In addition, authors mentioned that peak flow rate of 1 L/s can wash out 9% of artificial city street sediment of size between 0.15 and 0.3 mm and 11% of 0.09 and 0.15 mm.

Fletcher et al. (1978) mentioned that solids are flushed out by scouring the bottom sediment. The scouring effect depends on four factors: 1) rate of inflow to the gully pot; 2) size of the gully pot; 3) depth of sediment deposited in the pot; and 4) mass of sediment available for release. Authors performed a laboratory simulation to predict

sediment removal from the gully pot under steady flow condition. Figure 2.6 shows the results of two inflow rates. The first part of the graph which sediment begins to release from the gully pot can be described by:

$$C = A\,(1\text{-}e^{Bt}) \tag{2-1}$$

where C = concentration of suspended solids in the outflow (mg/L); t = time (minutes); as well as A and B = constants which are dependent on flow rate. The second part of the graph can be described by:

$$C = A\,e^{-Bt} \tag{2-2}$$

The studies have shown that less than 0.5% of 50 mm gully basal sediment is flushed out with maximum flow rate of 1 L/s.

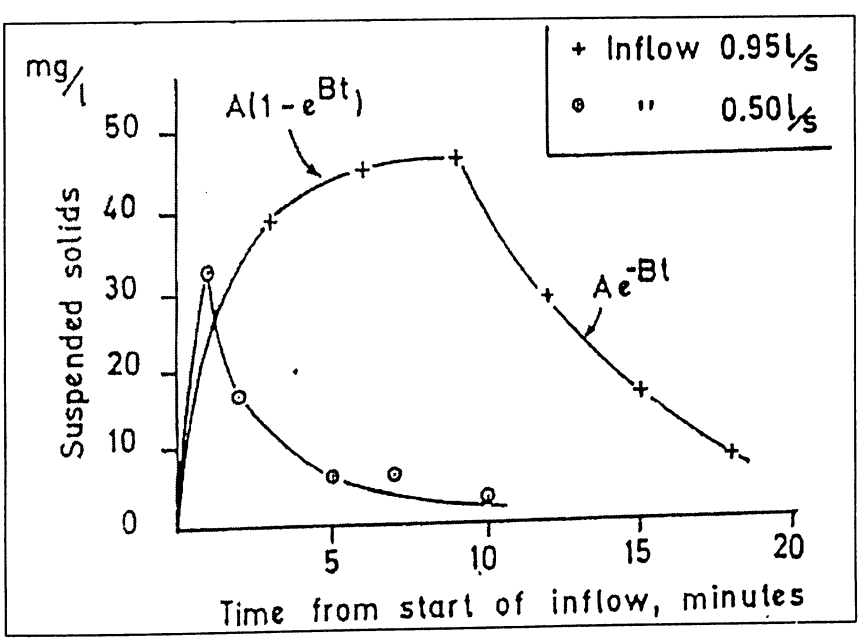


Figure 2.6: Experimental results (Source: Fletcher et al., 1978)

Clegg et al. (1993) conducted analytical tests on gully pot liquors and sediment in order to examine the ageing effects of sediments in gully pot. The selected gully pots are located in the Birmingham University campus, UK. Liquors were pumped out before sediment depth was measured by a metre rule. Gully pots liquor and sediment quality are examinated to represent different land use catchment area.

Particulate matter washoff to the gully pot depends on three primary factors: rainfall intensity, street surface characteristics and particle size. Exponential equation can be used to simulate the sediment washoff from street surface. Field studies indicated that fine solids and most organic matter cannot be effectively removed from storm runoff by catch basin, thereby contributing to water pollution problems (Sartor et al., 1974)

Wada et al. (1987) developed a mathematical runoff model to simulate the removal of BOD, COD and SS from a model gully pot. Catch basin physical model with 35 cm square is made of transparent acrylic resin, shown in Figure 2.7. The model has 10 cm sump depth. Pollutant load is flushed from the gully pot by two mechanisms: removal of dissolved materials of water and removal of materials that are re-suspended from bottom sediments. Authors mentioned that gully liquor is fully mixed with the inflow and sediment scouring begins when water flow rate is exceeded of 0.12 L/s. Total mass of materials available for release per bottom sediment load (M', mg / (mg/L)) are expressed as function of inflow rate (Q) and given as:

$$M'_{BOD} = 5.517\ Q + 0.861$$

$$M'_{COD} = 4.783\ Q + 0.101$$

$$M'_{SS} = 5.712\ Q + 0.083 \qquad (2\text{-}3)$$

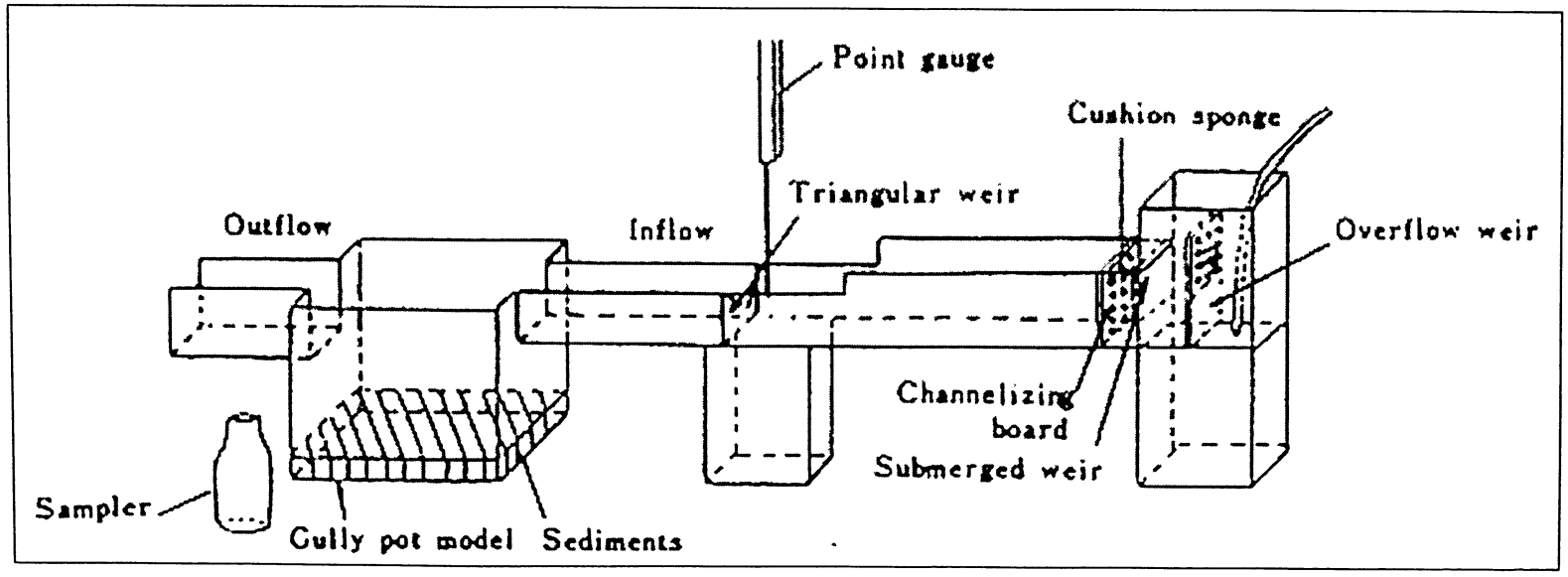


Figure 2.7: Catch basin model for experiment (Source: Wada et al., 1987)

Chapter 3 MONITORING STUDY OF METHOPRENE LARVICIDE

3.1 Field Monitoring

The field study was to examine the concentration of methoprene released from pellets and ingots over time in storm water catch basins and storm sewer outfalls under local conditions in Toronto.

3.1.1 Newtonbrook Sewershed Area and Study Site Description

The Newtonbrook sewershed is located at the North-Eastern region of Toronto, shown in Figure 3.1. Storm water is drained by catch basins to local storm sewers and then to the storm trunk sewer with diameter of around 2.74 m, which eventually discharges to the Newtonbrook Creek, a tributary of the Don River. Its drainage area and perimeter are measured as 359 ha and 14,349 m, respectively. Information, such as land use areas, locations and numbers of catch basins within the catchment area as well as sewershed maps were collected from site reconnaissance and analyzed using Geographic Information System. The land uses in the Newtonbrook sewershed is illustrated in Table 3.1. Numbers of catch basins in the Newtonbrook sewershed were marked on a map by survey, and summarized in Table 3.1.

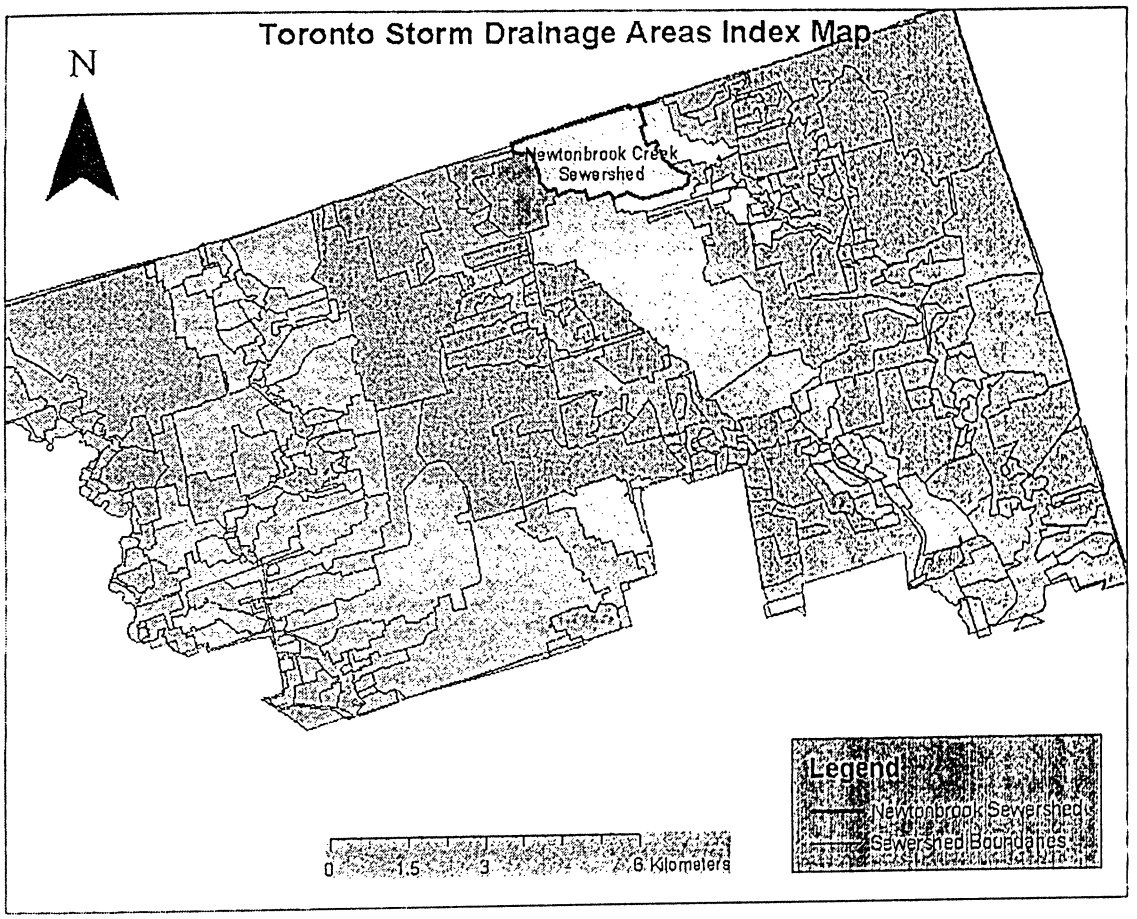


Figure 3.1: Newtonbrook Creek sewershed (Source: Des Lauriers, 2003)

Table 3.1: Information of land uses

Land use	Percent (%)	Numbers of catch basins
Residential	77	920
Commercial	11	244
Institutional	7	50
Park/Recreational	5	29
Industrial	0	0

The study site for this study is located at Willowdale Avenue and Silverview Drive, North York, Ontario. Three roadside catch basins are selected for monitoring, identified as W1, S1 and S2, shown in Figure 3.2. W1 catch basin is on the Willowdale Avenue while catch basins, S1 and S2 are on the Silverview Drive. In addition, sediment depth and water level of each catch basin are varied and they can be used to study the effect of sump depths on the residual methoprene concentration. Half of the sediment and all sediment were removed by a vacuum truck for W1 and S2, respectively. S1 was remained the same. Table 3.2 shows the sump characteristics of the three catch basins. The water depths and sediment depths are used as references for the subsequent hydraulic experiments. The catch basin catchment is residential area with high imperviousness, as shown in Table 3.3.

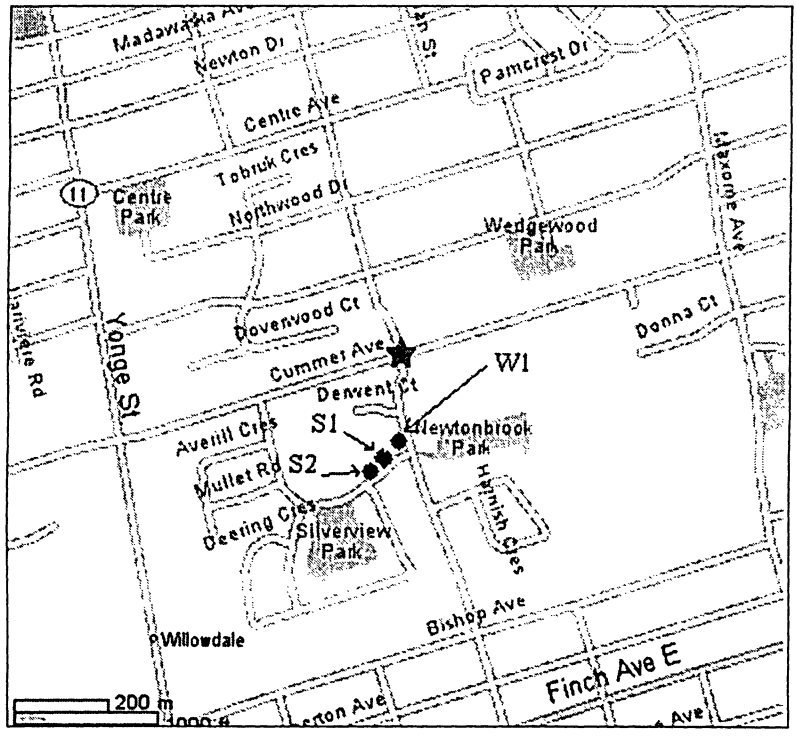


Figure 3.2: Location of the three study catch basins

Table 3.2: Characteristics of the study catch basins

Catch basin	W1	S1	S2
Water level (cm)	31.0	11.5	106.0
Sediment depth (cm)	52.0	66.5	3.0
pH	7.21	6.97	7.41
Temperature (℃)	20	22	22

Table 3.3: Drainage area and percentage of impervious area

Catch basin	Total area m^2	Impervious area m^2	Pervious area m^2	Percentage of impervious	Percentage of pervious
W1	1838.60	1334.30	504.30	72.57	27.43
S1	688.17	612.17	76.00	88.96	11.04
S2	1338.50	1338.50	0.00	100	0

3.1.2 Material and Methods

Water sampling:

During the field study of 2003, automatic samplers were not properly installed yet so the catch basin water was sampled through a small battery-operated pump attached to a long stainless steel tube, as shown in Figure 3.3. Automatic samplers (American Sigma Model No. 1350) were installed at each of the catch basins for the field study of 2004. In order to monitor concentration of methoprene at the storm sewer outfall during wet-weather, a concrete hut located at Willowdale and Silverview was installed where an automatic sampler (American Sigma Model 900MAX) was used to collect the water samples. The Newtonbrook Creek monitoring station is illustrated in Appendix C.

Figure 3.3: Catch basin monitoring study in progress

Flow and Rain measurements:

The automatic sampler (American Sigma Model 900MAX) has built-in area-velocity sensor to measure the flow. A local rain gauge was installed on the roof of the concrete hut to measure the amount of precipitation. The rain gauge and sampler began data collection on August 11, 2003. Therefore, the rain data prior to that day was taken from two separate rain gauges, E. Bales station at Bathurst and Sheppard (approximately 4.50 km apart to the local rain gauge) as well as Mitchell field station at Church Avenue (approximately 1.62 km apart to the local rain gauge).

Pellets and ingot size distribution analysis:

Three batches were made and each contains fifty blank clay pellets obtained from the manufacturer. They were randomly sampled and analyzed for their diameter, length and mass. Digital Vernier Caliper is used to do the measurement. It is observed from Figure 3.4 that 61 to 73% of pellets have diameters of 4.06 to 4.83 mm (0.16 to 0.19 in). However, the length distributions differ greatly for each batch, indicating that pellets do

not have a uniform length, as shown in Table 3.4. Dimensions of eight ingots are measured while densities of two ingots were determined. Volume of ingot is determined by immersing the ingot in the water and measuring the weight in water. It is observed from Table 3.5 that the dimensions for ingot are quite uniform.

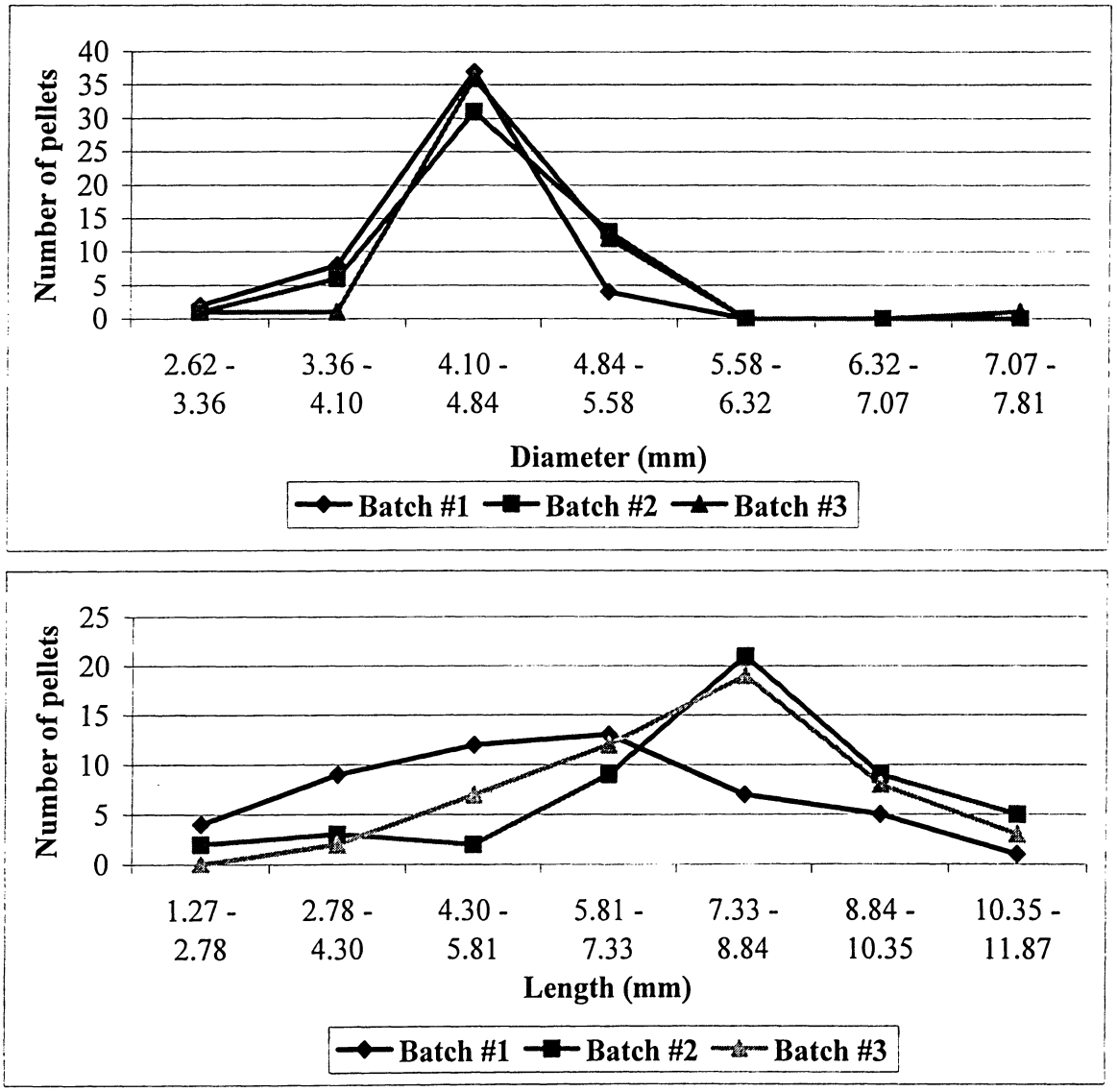


Figure 3.4: Size distribution of the pellets

Table 3.4: Physical characteristics of pellets

Pellets	Mean	S.D.	CV (%)
Length	7.11 mm	2.06 mm	28.97
Diameter	4.57 mm	0.48 mm	10.50
Mass	0.152 g	0.028 g	18.42
Density	1.31 g/cm^3	0.028 g/cm^3	2.14

Table 3.5: Physical characteristics of ingots

Ingot	Mean	S.D.	CV (%)
Length	77.98 mm	0.28 mm	0.36
Width	28.45 mm	0.13 mm	0.46
Height	25.40 mm	0.58 mm	2.28
Mass	45.37 g	1.70 g	3.75
Density	1.41 g/cm^3	0.0082 g/cm^3	0.58

Methoprene chemical anlaysis:

Methoprene concentrations in the water samples were analyzed by the City of Toronto laboratory, using the United States Geological Survey (USGS) method of liquid-liquid extraction and gas chromatography/mass spectrometry. The detection limit is 0.03 μg/L. The detail procedures are shown in Appendix D.

3.1.3 Field Study Investigation

Methoprene pellets of 0.7 g were added manually into each of the three catch basins (W1, S1 and S2) on July 4, August 9 and September 9, 2003. The concentrations were monitored daily under dry-weather condition. The 250 mL water samples were taken from top 5-10 cm of the water surface, collected in amber and teflon-lined jars and stored in cooler with ice. In 2004, 0.7 g of long pellets with average length of 11.05 mm were added in W1 catch basin on July 16 and 0.7 g of short pellets with average length of 4.29 mm were applied in W1 on August 23. S1 and S2 catch basins were dosed ingots

and monitored daily from July 16 to Oct 25. The outfall water was sampled during wet-weather from July to August and to September in 2003 and 2004, respectively, by the City of Toronto Works and Emergency Services.

3.2 Laboratory Experiment

3.2.1 Experimental Investigations

Control laboratory experiments were conducted in 2003 and 2004 to determine the residual concentration of methoprene over time in a quiescent condition for pellets and ingot. A plastic tank was fitted with three spouts at different heights of MT = 900 mm, MM = 600 mm and ML = 450 mm from the bottom of the tank, shown in Figure 3.5. The tank is round in shape and the dimensions are close to the OPS and Metro standard storm sewer catch basin sump depths, described in Section 2.3.1. The tank was filled with tap water with temperature of 16°C and pH of 7.26 to just above the top spout. Methoprene pellets and ingot were added to the water and concentration was monitored daily from each spout, starting from the top to down. An equal withdrawal amount of tap water was added to the tank after each sampling. The testing conditions are summarized in Table 3.6.

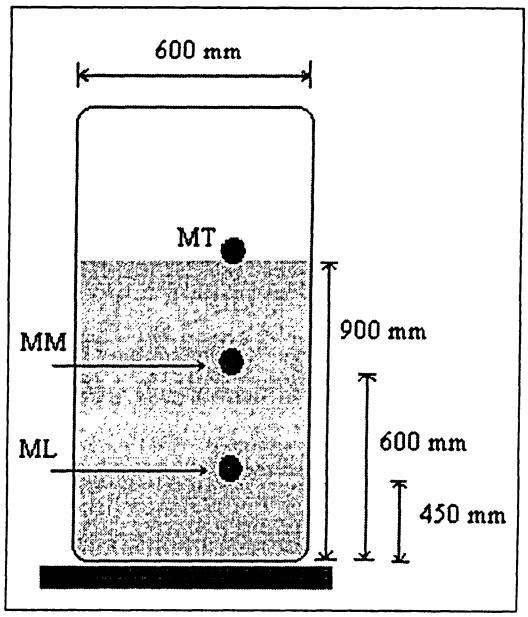


Figure 3.5: Lab tank (Source: Des Lauriers, 2003)

Table 3.6: Laboratory experiments

Starting date	Description	Duration (days)	Water depth (mm)	Methoprene pellets / ingot (g)
July 14, 2003	Pellets	25	900	0.71
August 9, 2003	Pellets	30	900	3.53
September 9, 2003	Pellets	28	900	35.07
February 3, 2004	Pellets	30	600	0.71
February 3, 2004	Pellets	30	450	0.73
July 25, 2004	Ingot	92	900	~45
July 25, 2004	Ingot	92	450	~45

3.3 Results and Discussion

The 2003 results and discussion are presented by Des Lauriers (2003) while the 2004 results and discussion can be found in Li (2005).

3.3.1 Field Catch Basin Study and Storm Outfall

The general descriptions of catch basin and storm outfall monitoring study are summarized as follows:

Pellets:

- The general patterns for W1 and S1 catch basins show double peak methoprene concentrations with first peak within 1-2 days. W1 has residual methoprene concentration above the detection limit of 0.03 μg/L until 7-11 days after application while S1 is 10-19 days after application. This shows that the less water in a catch basin, the longer the residual life of methoprene. Methoprene concentrations in S2 remain undetectable until 12-22 days after application. In 2003 field study, the percent of days of three-month larvicidng periods (or 97 days) that residual methoprene concentration maintain above the minimal lethal concentration of 0.3 μg/L were 3.09%, 23.71%, and 0% for W1, S1 and S2, respectively. In 2004 field study, the residual concentration was below the minimal lethal concentration of 0.3 μg/L over the whole monitoring period.
- It is observed in W1 and S1 that rain may have some effect on the residual methoprene concentration. Firstly, rain may flush and dilute the methoprene, resulting in the decline of the concentration. Secondly, rain may affect the release rate of methoprene from pellets or re-suspend the pellets in the bottom sediment,

resulting in the rise of the methoprene concentration. Rain seems to have no effect on methoprene concentration for S2 catch basin because it contains much water depth of 1 m, thereby having less turbulence effect on pellets.

Ingot:

- Multiple peaks are observed and first peak occurs 1-2 days after application. Ingot can provide residual concentration of 90 days after application. Rain has significant effect on the release or flushing of ingots. In addition, it is observed that the effect of rain is more apparent in S1 than in S2. In 2004 field study, the percent of days of three-month larvicidng periods (or 100 days) that residual methoprene concentration maintain above the minimal lethal concentration of 0.3 μg/L are 11.9% and 24.9% for S1 and S2, respectively.

Storm sewer outfall:

- Two events were analyzed: August 16, 2003 and July 19, 2004. In general, concentration of methoprene increases with flow, shown in Figures 3.6 and 3.7. The variations of methoprene concentration at the outfall resemble those of the hydrographs. The storm event on August 16 was high intensity and short duration, resulting in a large flushing effect of methoprene at the catch basins and instantaneous response of methoprene concentration at the outfall. The storm event on July 19 was low intensity and long duration, resulting in a mild flushing effect of methoprene at catch basins and delay of methoprene concentration at the outfall. Multiple peaks of concentration are observed in Figure 3.6 because methoprene continued to be released from the pellets during rain and flushed out from catch basins to the outfall. The highest methoprene concentrations of the two

events are much lower than the USEPA recommended environmental concentration of 10 µg/L and the IPWQO of 0.2 µg/L.

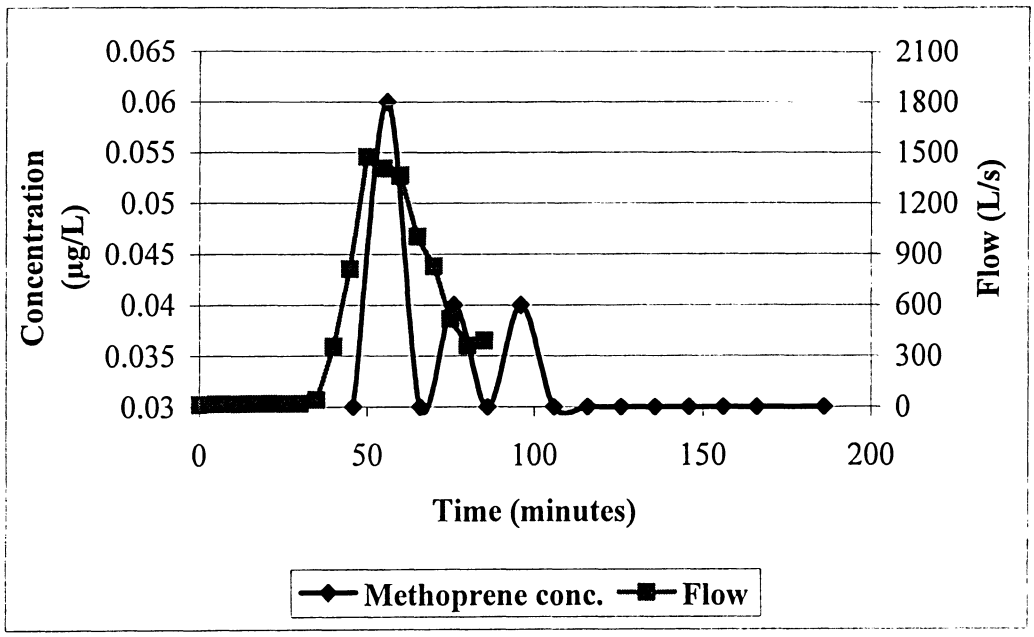


Figure 3.6: Concentration of methoprene at the outfall for a rain event of August 16, 2003

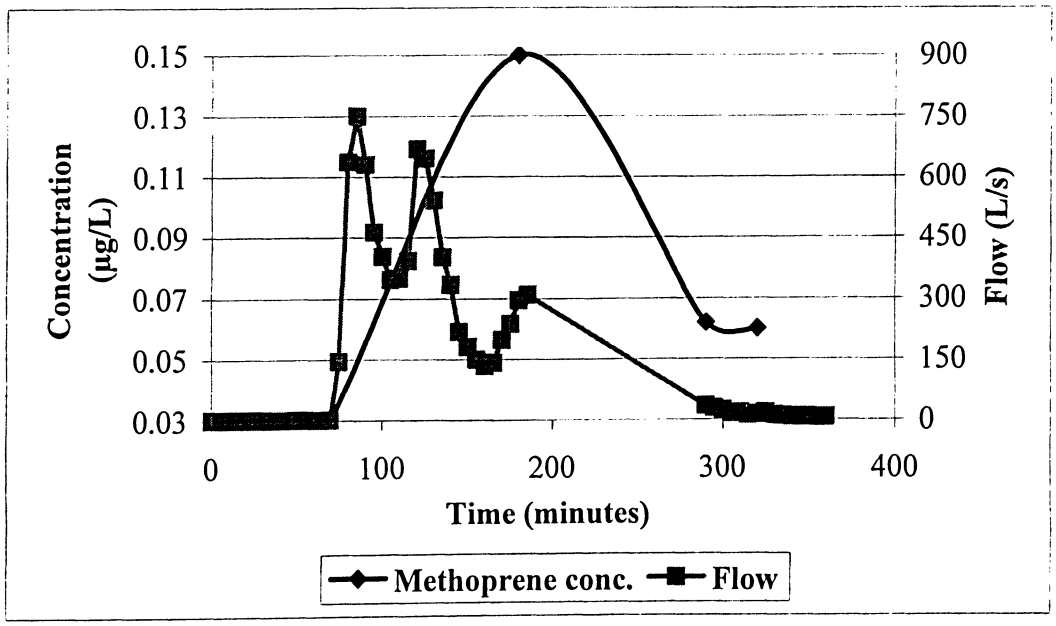


Figure 3.7: Concentration of methoprene at the outfall for a rain event of July 19, 2004

3.3.2 Control Laboratory Experiment

The general descriptions of control laboratory monitoring study are summarized as follows:

Pellets:

- Each of the spouts (MT, MM and ML) shows similar methoprene concentration patterns over time and double peak concentration similar to the field study. The first peak is within 1-2 days after application. The average ratio between methoprene concentration at the bottom and at the top surface is 0.988, indicating that the methoprene concentration was fairly uniform over the whole depth.

Ingot:

- In general, double peaks are observed in the quiescent environment condition, compared to multiple peaks in the field study. This concludes that rain have effects on the release of methoprene from ingot. First peak occurs 1-2 days after application as well as second peak occurs after 65 days of application and continue to release. The reasons may be due to the physical breakdown of the ingot at around 65 days, resulting in large release of methoprene. The methoprene concentration at top (C_{MT}) is close at the bottom concentration (C_{ML}) with ratio of (C_{ML} / C_{MT}) 0.996.

Chapter 4 SEDIMENT FROM CATCH BASIN

4.1. Experimental Study

The study started with the sediment collection from two different locations. The properties of catch basin sediment: grain-size, specific gravity, organic matter and carbonate contents were then determined. In addition, compositions as well as percent of crushed particles in catch basin sediment are determined. Part of this study is to characterize the catch basin sediment and to simulate the sediment found in the field in the subsequent hydraulic experiments.

4.2 Test Procedure

4.2.1. Sediment Sample Preparation

The disturbed sediments were first collected at the Scarborough District's public works yard where the sediment was stored temporarily after it was removed from the catch basin sump by vacuum cleaning machines. It represents all the mixed sediment from urban catch basins in eastern Toronto. Samples were taken from the bottom of the pile and a garden shovel was used to transfer the sample to plastic bag for transport. Sediment from one catch basin located at 93 Wedgewood Dr., North York (a residential area) was also collected using shovel and posthole digger.

4.2.2 Grain Size Distribution

It was observed that the sediment samples tended to form hard lumps after dried and had to be ground and crushed in order to separate the particles. The original true cohesive grain size can't be recovered. Therefore, fines (clay and silt) must be separated

from sand before drying. It is standard to do wet-sieving first to separate these groups and then perform in accordance with the appropriate American Society for Testing and Materials (ASTM) test methods to quantify size distributions for each fraction. In addition, wet-sieving is helpful to remove all organic debris in a coarse sieve. The procedures and parameter calculations are shown in Appendix E. Figure 4.1 shows the apparatus for wet-sieving.

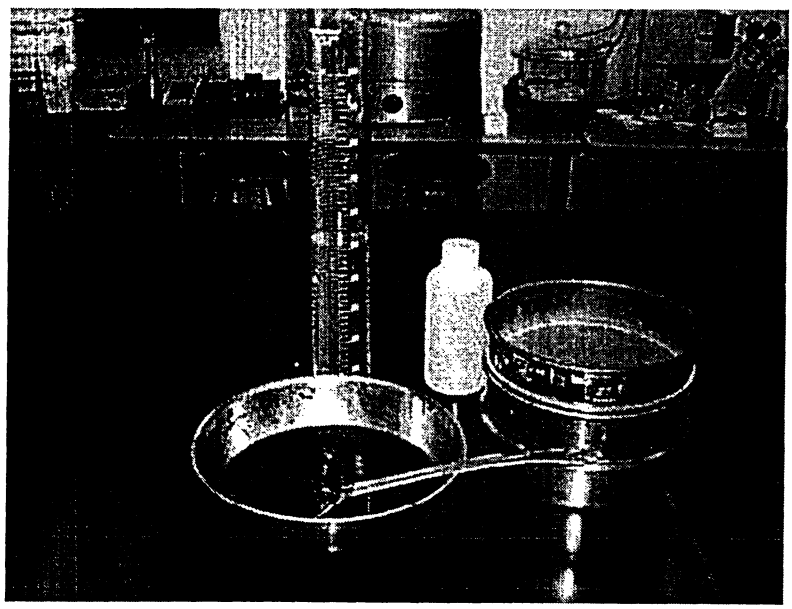


Figure 4.1: Wet-sieving in progress

4.2.3. Composition and Visual Determination of the Percent of Crushed Particles

Fresh catch basin sediment is black in color, smells foul and contains leaves and branches. Solid grain is felt when robbing. Figure 4.2 shows a picture of dried coarse and fine catch basin sediment after sieving. These observations would give us a general idea of how to blend the soil used for subsequent hydraulic experiments. Sediment samples may contain a large proportion of organic material, such as small leaves, branches and

other miscellaneous items. The samples were heated to around 150°C for about 10-15 minutes if any asphalts are present, it would be melted and identified. A crushed particle is defined as a piece of coarse aggregate (particles size larger than 4.75 mm), which has at least one fractured face, shown in Figure 4.3. The coarse aggregate fraction is separated into crushed and uncrushed particles. The procedure and calculations are outlined in Appendix E.

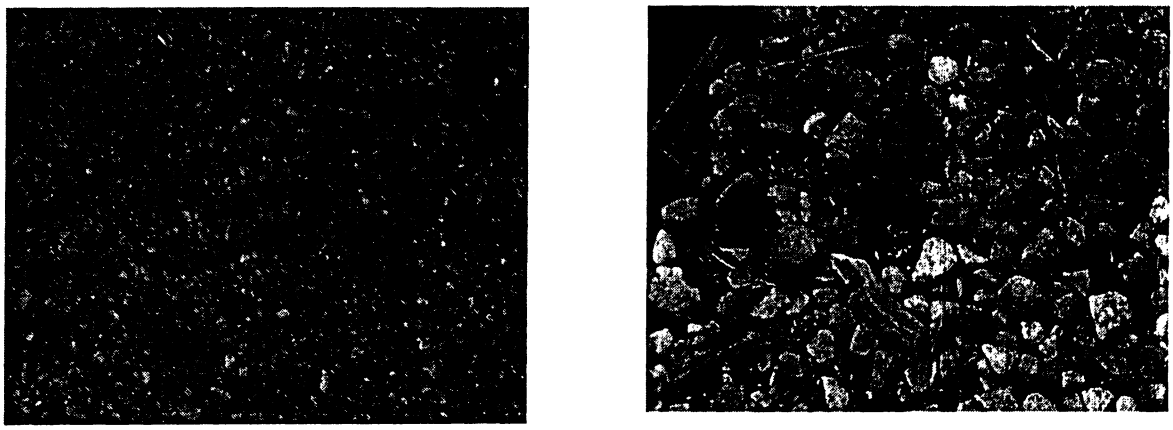


Figure 4.2: Catch basin sediment

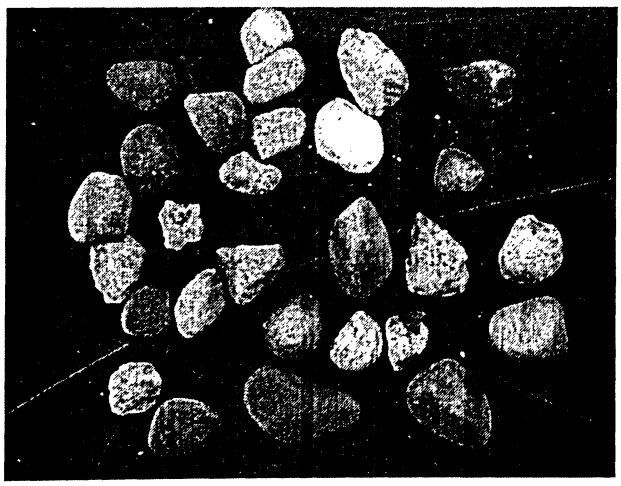


Figure 4.3: Crushed and round particles

4.2.4. Specific Gravity

The method involves the Archimedes' principle of displacement. Specific gravity (SG) of solids finer than 4.75 mm sieve is determined by means of a pycnometer whereas materials retained on 4.75 mm sieve is determined by test method ASTM C127. The procedure and calculations are outlined in Appendix E. Specific gravity of mixed soil is a weighted average of the two values, given by:

$$Gavg = \frac{1}{\frac{R1}{100G1} + \frac{R2}{100G2}} \tag{4-1}$$

where Gavg = weighted average specific gravity of soils; R1 = percentage of soil particles retained on 4.75 mm sieve; R2 = percentage of soil particles passing 4.75 mm sieve; G1 = apparent specific gravity of coarse aggregates; and G2 = specific gravity of fines aggregates.

4.2.5. Organic and Carbonate Content Tests

Loss-on-ignition (LOI) is a simple and inexpensive way to estimate the amount of organic and carbonate contents on sediments. It is a routine analysis performed on most sediment. The procedure and calculations are outlined in Appendix E. Organic matter is oxidized at a temperature of around 55°C to carbon dioxide and ash. The weight difference between the dry sediment and the 550°C ash is the amount of organic matter. Further increase of temperature to 900-1000°C will oxidize carbonate to oxide. The weight difference between the 550°C ash and the 1000°C ash is the amount of CO_2 evolved from carbonate. The LOI_{550} and LOI_{950} are determined by measuring the weight loss in samples after burning at selected temperatures. However, the original percent

content of carbonate theoretically in sample is the multiplication between the LOI_{950} and 1.36, which is calculated by the molecular weight of carbonate (60 g/mol) / molecular weight of carbon dioxide (44 g/mol).

One challenge of determining organic content is the ignition hour because samples will have a strong initial weight loss from the destruction of organic matter and continue to lose its weight at a slow rate up to 64 hrs. The reason is due to the effect of loss of volatile salts and structural water from clay minerals or metal oxides, which may overestimate organic matter content in soils (Heiri et al., 2001). A trial run is performed to determine one ignition hour and used for the whole samples.

4.3 Analysis of Results and Discussion

The particle-size distribution curves of the catch basin sediment collected from Scarborough yard and one catch basin are shown in Figure 4.4. Most of the catch basin sediment is within 0.85-2 mm, as shown in Figure 4.5. Particle size distribution curve can be used to determine four parameters: effective size (D10), median size (D50), uniformity coefficient (Cu) and coefficient of gradation (Cc). The results are shown in Table 4.1. Sediments collected in Scarborough yard have small median size. Most of the sediment at the Scarborough yard was already taken to a landfill so the remaining sediment was at the bottom of sediment pile and rain could wash the fines to the bottom of the sediment pile. Therefore, it may not be truely representative of the sediment characteristics from typical catch basins.

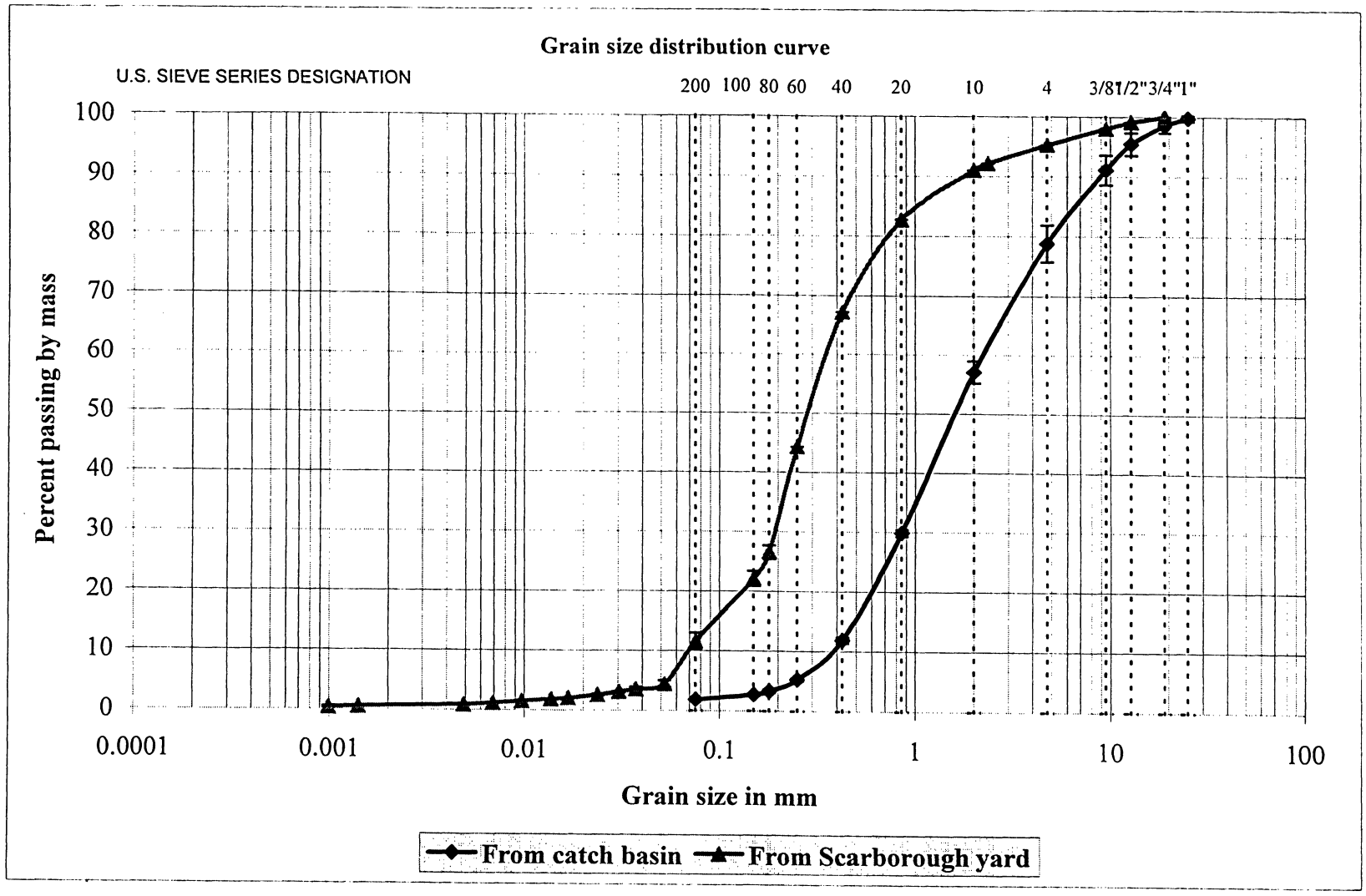


Figure 4.4: Particle-size distribution curve of catch basin sediment

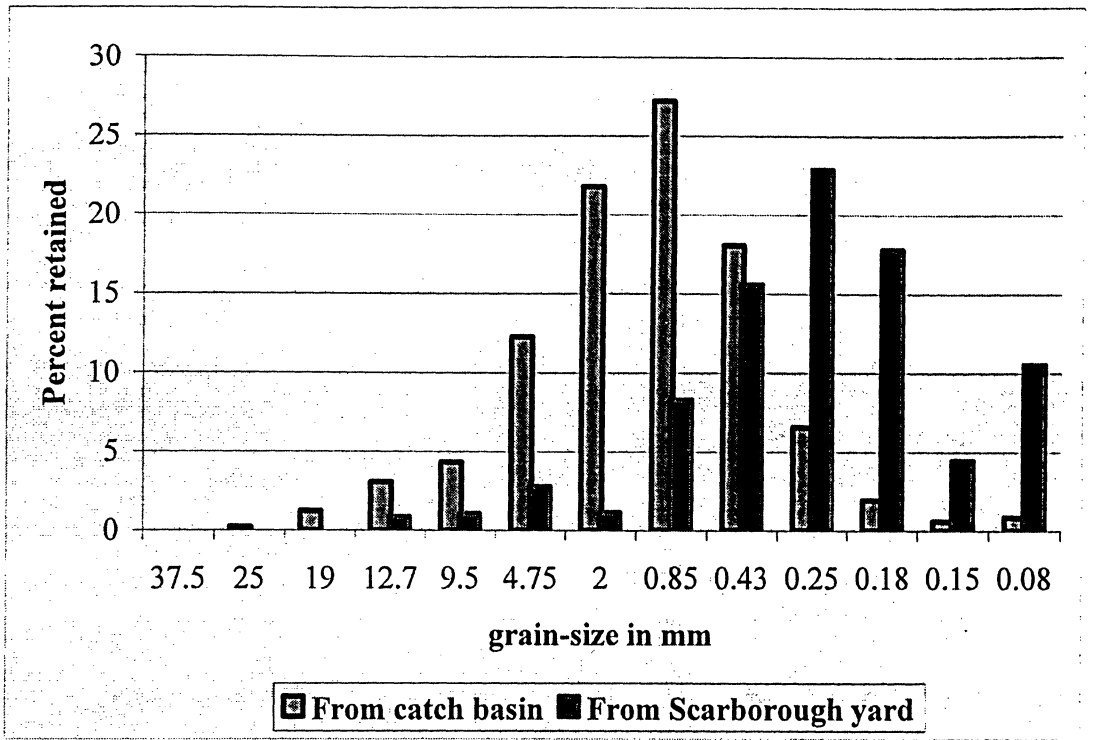


Figure 4.5: Percent mass retained of catch basin sediment

Table 4.1: Sediment parameters

Sediment sources	Parameters			
	D10 (mm)	D50 (mm)	Cu	Cc
Catch basin	0.38	1.62	5.68	0.88
Scarborough yard	0.065	0.28	5.38	1.42

Particle-size classifications are used the Unified Soil Classification System (USCS), which is now almost universally accepted and has been adopted by ASTM (Das, 1998). Table 4.2 shows the particle-size classification system. The percent of gravel (including asphalt amounts), sand and fines are 21.16%, 76.98% and 1.86%, respectively, and the catch basin sediment is classified as poorly graded sand with gravel with symbol

of SP (S = sand and P = poorly graded) according to the Unified Soil Classification System.

Table 4.2: Particle-size classification (Das, 1998)

Name of organization	Grain size (mm)			
	Gravel	Sand	Silt	Clay
Unified Soil Classification System (U.S. Army Corps of Engineers, U.S. Bureau of Reclamation, and American Society for Testing and Materials	76.2 to 4.75	4.75 to 0.075	Fines (i.e. silts and clays) <0.075	

It is observed that there are certain amounts of asphalts (black solids) present in the sediment, shown in Figure 4.6. The percent of crushed particles in each class are illustrated in Table 4.3. The weighted average percent crushed is 77.09%. In addition, the percent of asphalts in each class are illustrated in Table 4.4. The adjusted percent of sediment fractions are shown in Table 4.5.

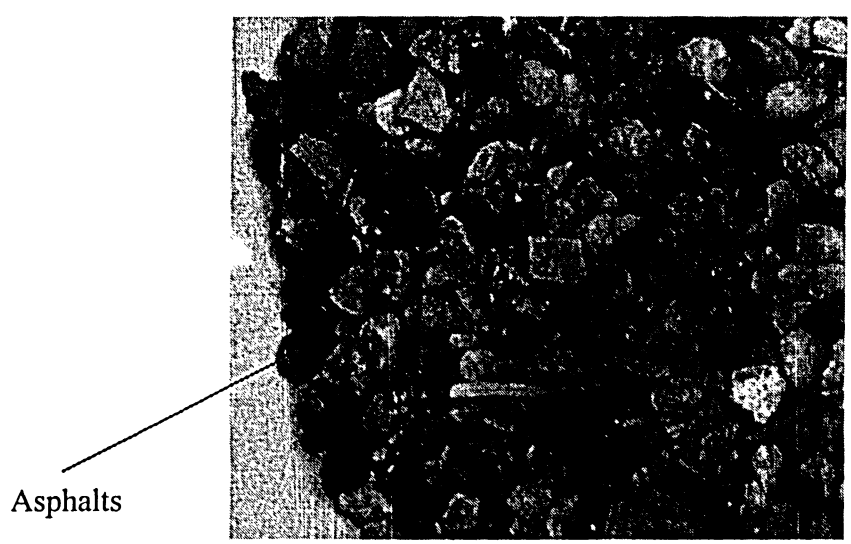


Figure 4.6: Asphalts present in the sediment

Table 4.3: Determination of percent of crushed particles

Sieve size fraction mm	% Retained	% Crushed	Product (% Ret. * % Crushed)
Pass 25.0 / Retained 19.0	5.93	100	593
Pass 19.0 / Retained 13.2	14.71	69.37	1020.43
Pass 13.2 / Retained 9.5	20.67	72.61	1500.85
Pass 9.5 / Retained 4.75	58.69	78.28	4594.25
Totals	100		7708.53
Weighted Average*			7708.53 / 100 or 77.09 %

* Weighted Average = $\sum$ ((% Retained) * (% Crushed)) / $\sum$ (% Retained)

Table 4.4: Percent of asphalts

Sieve size fraction mm	% of asphalt of whole sample
Pass 37.5 / Retained 25.0	0
Pass 25.0 / Retained 19.0	0.19
Pass 19.0 / Retained 13.2	1.95
Pass 13.2 / Retained 9.5	3.00
Pass 9.5 / Retained 4.75	5.57
Pass 4.75 / Retained 2	2.24

Table 4.5: Sediment compositions

Sediment composition	Percent of mixed sediment
Asphalt	12.95
Gravel	10.45
Sand	74.74
Fines	1.86

The specific gravity of gravel as well as sand and fines fraction is summarized in Table 4.6. The weighted average specific gravity of the catch basin sediment is 2.52, which is smaller than the typical SG of quartz minerals of 2.65. The reasons may be due to the presence of organic matter and asphalts in the samples.

Table 4.6: Specific gravity results

Size fraction (mm)	% in sample	Specific gravity	S.D.	CV (%)
Gravel (>4.75)	21.16	2.59	0.083	3.20
Sand and fines(<4.75)	78.84	2.50	0.056	2.24

The ignition hour is set 3 hrs and 2 hrs for sand and fine fractions, respectively, based on the trial runs, as shown in Figure 4.7. The LOI value reaches a plateau by these times and continues increase at a more or less constant rate. LOI_{550} for sand and fine fractions is shown in Table 4.7. The fine fractions may contain a high percent of organic matter which indicates some pollutants, such as hydrocarbons may be adhered to these particles. It is hard to correlate any relationship between organic C and organic matter unless additional experiments like dichromate oxidation methods are performed to estimate of soil organic C in catch basin sediment.

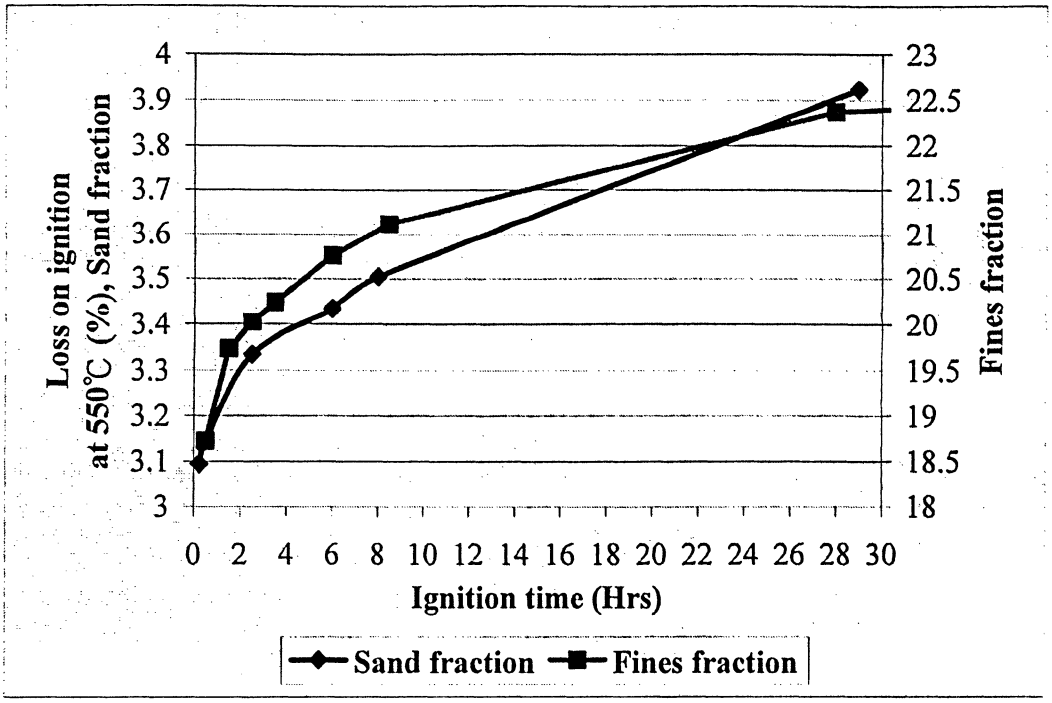


Figure 4.7: Sediment exposed to 550℃ for ignition

Table 4.7: Organic content test results

Size fraction (mm)	% LOI	S.D. (%)	CV (%)
Sand (2-0.075)	2.74	0.31	11.31
Fines (<0.075)	19.87	3.28	16.51

Carbonate content in sand fraction of catch basin sediment is theoretically equal to average of LOI_{950} * 1.36 ± S.D (standard deviation) or 33.53 ± 1.86%. The ignition time is 1 hr. No significant weight loss was detected upon further ignition, indicating that the carbonate was completely burnt out within the ignition time.

Chapter 5 HYDRAULIC EXPERIMENT

5.1. Experimental Study

In order to determine the critical flow conditions that may flush out methoprene pellets and ingot during storm events, a physical model study was conducted. The study results are used as input critical flows for subsequent hydrologic water quality model to predict the fate of methoprene concentration at catch basins and storm sewer outfall. The flushing effect of solids at catch basin is a function of the inflow rates, the fall depths, the sump depths and the sump water levels. Various combinations of the sump and water depths were investigated in the experiments. The physical model study involved the preparation of blended soil, construction of the hydraulic model as well as a study on scouring effect of sediment and different methoprene formulations.

5.2 Preparation of Sediment

5.2.1 Origin of Sediment

Field sediments from catch basins are not allowed for the test because of potential hazard concern. Clean soils were used instead to simulate the field sediment. In order to find soils comparable to the field sediment found in catch basins, concrete sand and stone, winter sand as well as ditch soils were collected to obtain their grain size distribution, and compared to that of the sediment in the catch basins (Figure 5.1). Concrete sands and stones were obtained from Dufferin Aggregates. There are two types of concrete stone in the aggregate company: 100% crushed particles of limestone and around 75% crushed particles of crushed gravel both with 20 mm nominal size.

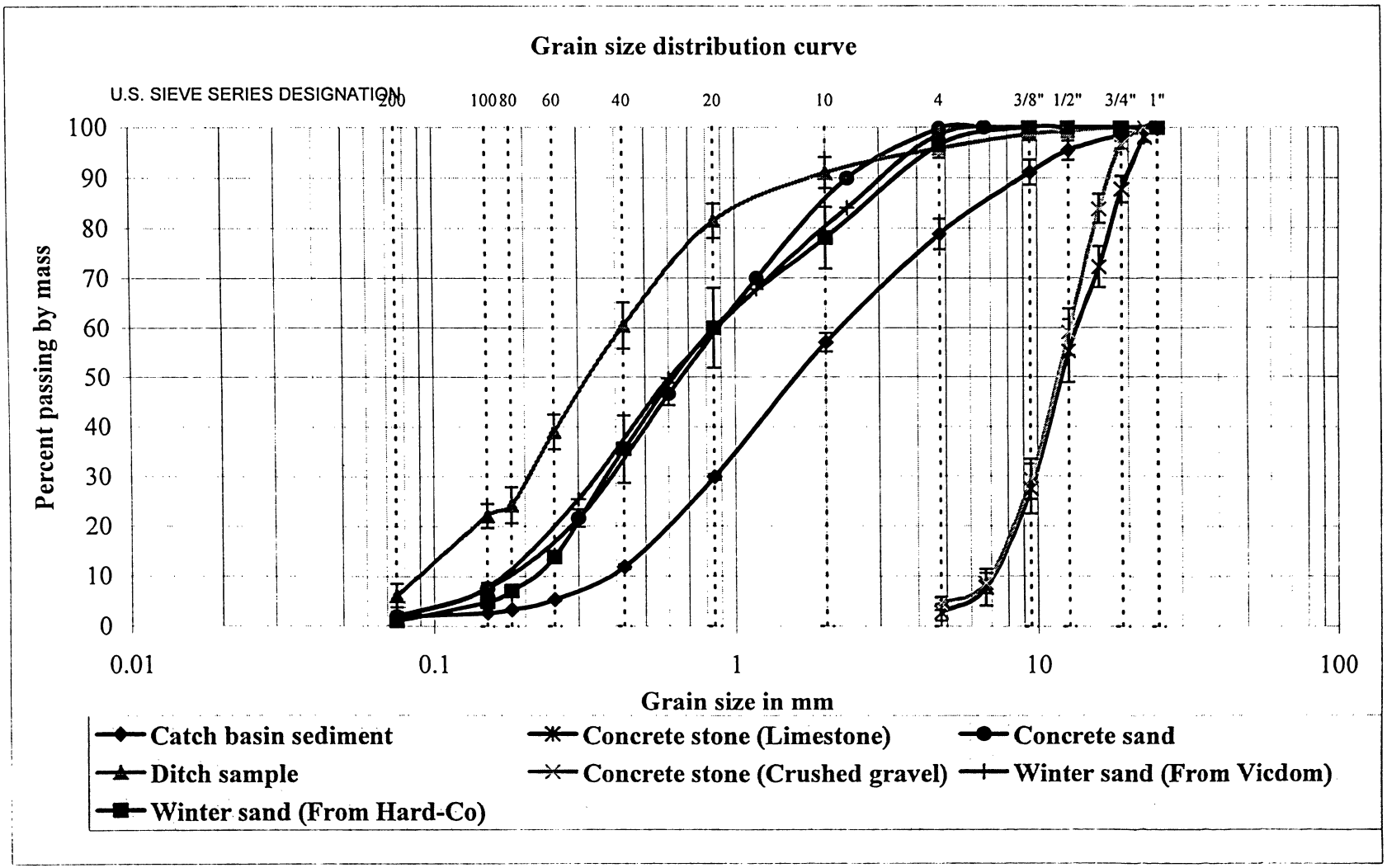


Figure 5.1: Comparison of soil materials from different origins

Winter sand is sand mixed with salts and applied to roads during winter to provide traction. Sand materials are screened out most of the gravel fractions, which can cause potential damage to the windshield. Winter sand samples and gradation distribution were supplied by Hard-Co Construction Limited and Vicdom Sand & Gravel (Ontario) Limited. Another soil sample was collected from the roadside ditch in the Rosedale area of Toronto. The sediment along the ditch represents years of sediment left along the roadway. Runoff can transport those sands from the road pavement into the catch basin sump, which is settled as sediment.

5.2.2 Blended Sediment

It is observed from Figure 5.1 that sands from different sources have finer particle sizes than found in catch basins. None of them is comparable in size to the field catch basin sediment. Therefore, concrete sand and concrete stone were sieved into individual size fraction by the aggregate shaker and blended to obtain the required grain size particles for the hydraulic experiment, as illustrated in Figure 5.2. Crushed gravel was used for the gravel fraction of blended sediment because it has 75% crushed particles compared to the weighted average of catch basin sediment of 77%. The blending was based on the percent retained in each fraction, as tabulated in Table 5.1. Each required amount of retained materials in each size fraction was weighted and blended in the concrete mixer with leaves to make one batch. Table 5.2 shows the quantity of one batch soils. Blended soils were sub-sampled to check the quality, as shown in Figure 5.3. It is shown that blended soil can reproduce the field catch basin sump sediment.

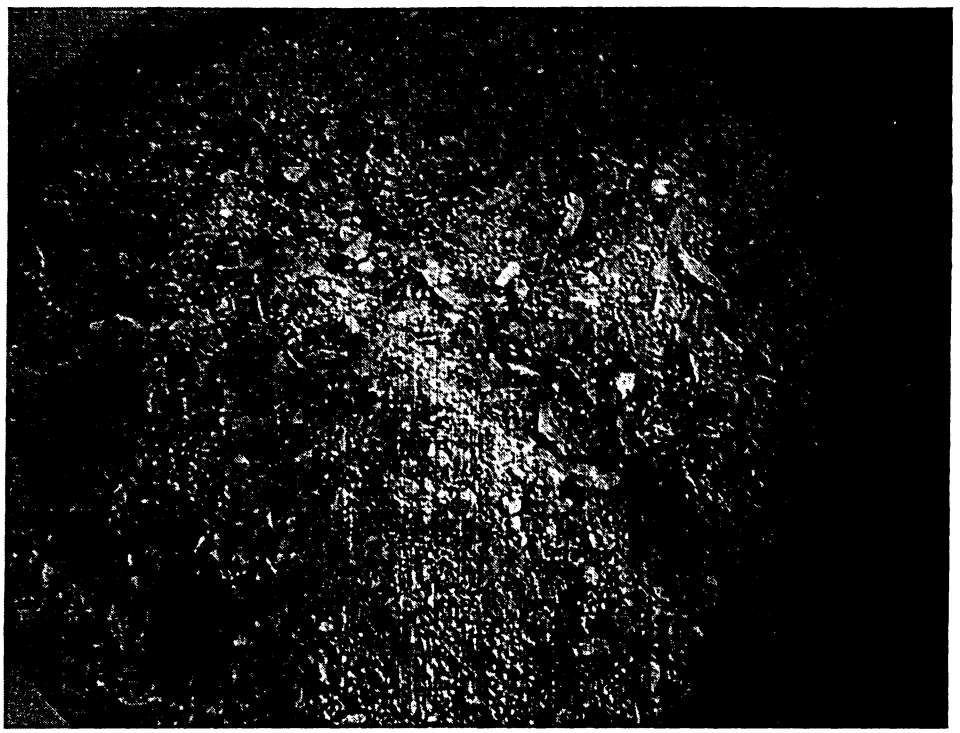


Figure 5.2: Blended samples

Table 5.1: Sieve size for blended samples

Sieve size	mm	Percent asphalt	Percent crushed gravel	Percent concrete sand	Percent retained
1-1/2	37.5	0	0		0
1	25.00	0	0.24		0.24
3/4	19.00	0.19	1.05		1.24
1/2	12.70	1.95	1.13		3.08
3/8	9.50	3	1.32		4.32
4	4.75	5.57	6.71		12.28
10	2.00	2.24		19.51	21.75
20	0.85			27.22	27.22
40	0.43			18.04	18.04
60	0.25			6.56	6.56
80	0.18			1.96	1.96
100	0.15			0.61	0.61
200	0.075			0.84	0.84
Pan	<0.075			1.86	1.86
Total		12.95	10.45	76.60	100.00

Table 5.2: Quantity of one batch

50kg for one batch					
Sieve size	mm	Asphalt (kg)	Crushed gravel (kg)	Concrete sand (kg)	Percent retained
1-1/2	37.5	0.00	0.00		0.00
1	25	0.00	0.12		0.24
0.75	19	0.10	0.53		1.24
0.5	12.7	0.98	0.56		3.08
0.375	9.5	1.50	0.66		4.32
4	4.75	2.79	3.35		12.28
10	2	1.12		9.76	21.75
20	0.85			13.61	27.22
40	0.425			9.02	18.04
60	0.25			3.28	6.56
80	0.18			0.98	1.96
100	0.15			0.30	0.61
200	0.075			0.42	0.84
Pan	<0.075			0.93	1.86
Total		6.48	5.23	38.30	100.00

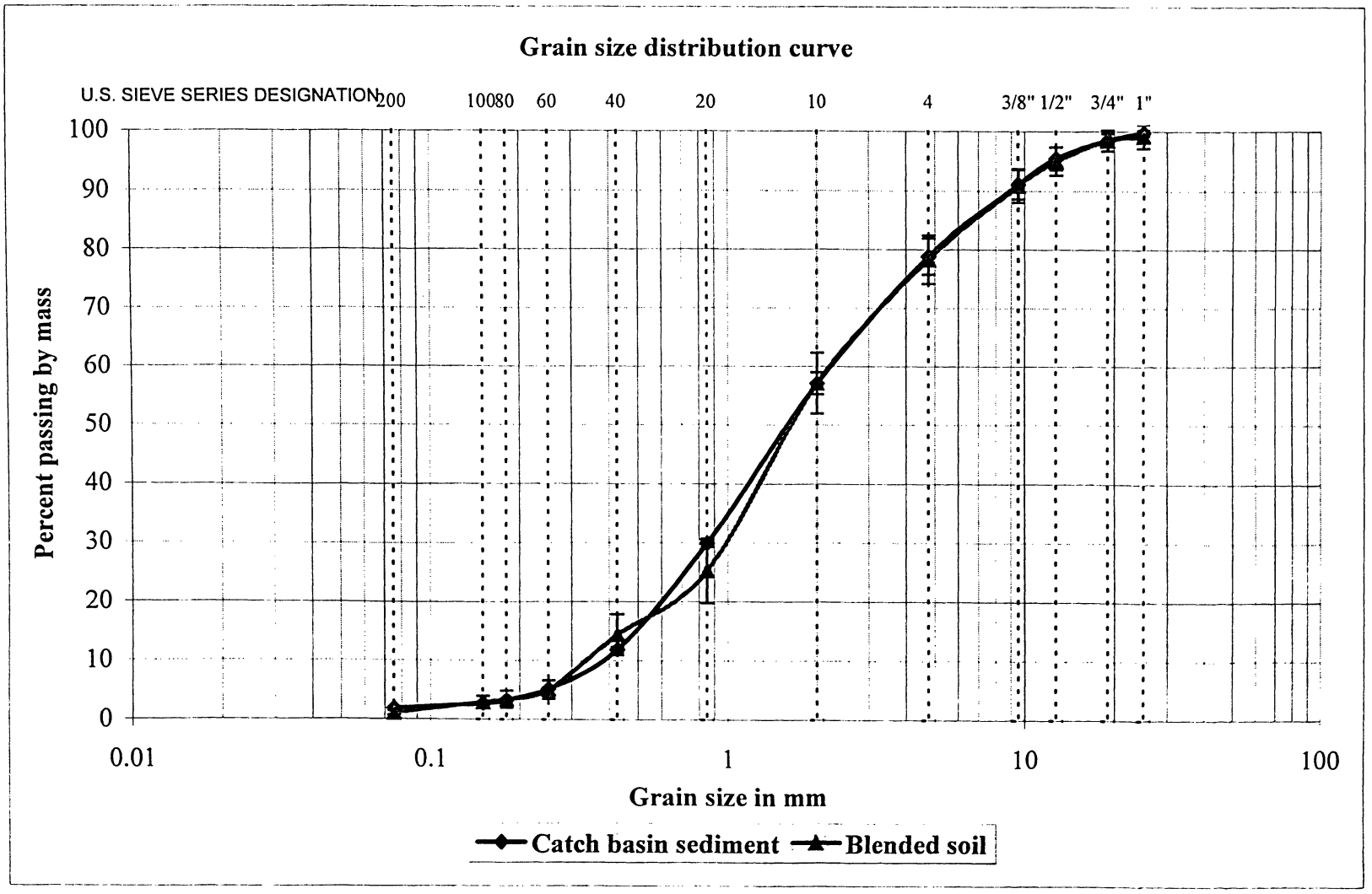


Figure 5.3: Grain size distributions of blended soil

5.3. Hydraulic Experiment Set-up

5.3.1 Hydraulic Model Construction

Hydraulic experiments were conducted in the Canada Centre for Island Waters (CCIW)'s Hydraulics Laboratory, Burlington, Ontario. The physical model is a full-scaled typical roadside street of a single inlet catch basin, as shown in Figure 5.4. The detail drawing is shown in Appendix F. The model consists of the following components:

- A 0.85 x 0.85 x 1.83 m high precast concrete catch basin with plexiglass windows was manufactured by Wilkinson Concrete Precast Ltd. It has three 200 mm outlet openings and two 200 x 1200 mm plexiglass windows installed for observation. Three mechanical plugs were used to plug two of the three outlets. The catch basin shown in Figure 5.5 has three different sump depths, which represents the Ontario Provincial standard and Metro standard of 600 and 450 as well as 900 mm, respectively. The inside catch basin had been marked with a permanent marker to indicate levels of sump and standing water depth.

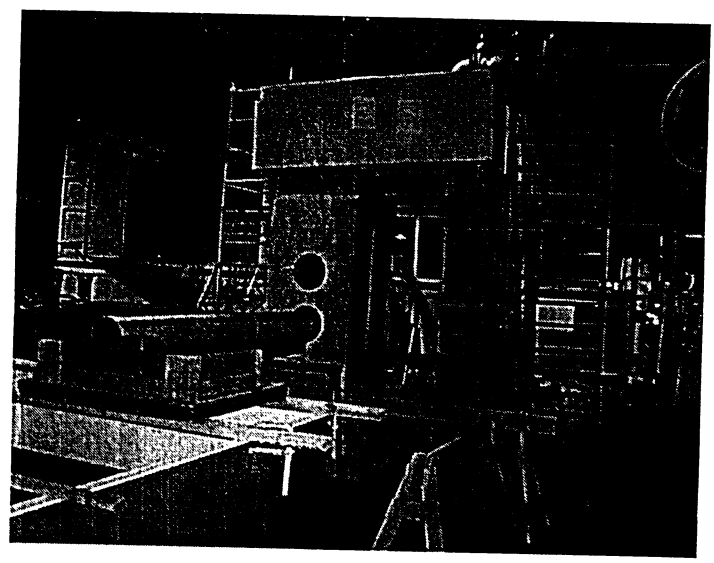


Figure 5.4: Hydraulic model

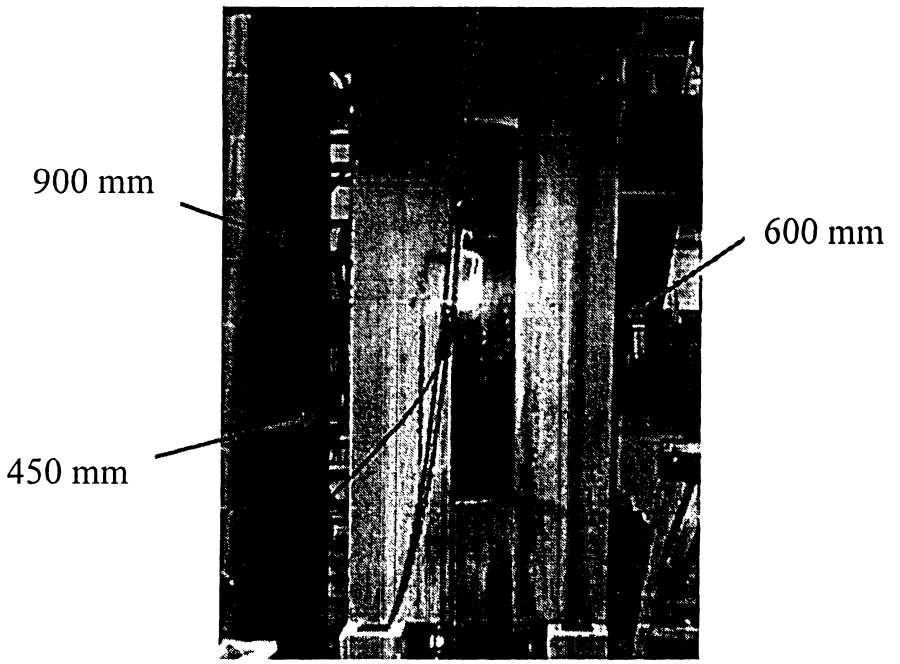


Figure 5.5: Catch basin with different sump depths

- A 2134 x 3048 mm roadside platform:

  The size represents a typical half width of a local street surface. The road deck contains a 600 x 600 mm "fishbone" inlet grate, as shown in Figure 5.6. The platform is constructed of plywood with 2% gutter slope and longitudinal slope as well as 2% cross slope, as shown in Figure 5.7. It is noticed that the entire flow enters into the catch basin from all edges of the grate and no spill overflow condition occurs.

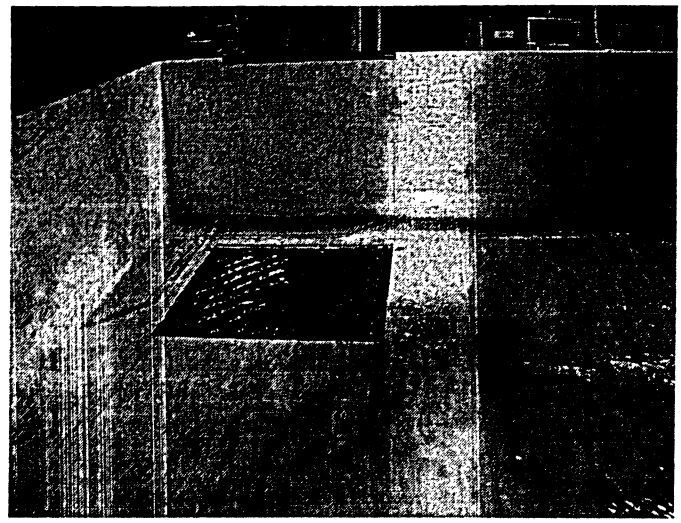


Figure 5.6: Catch basin inlet grate

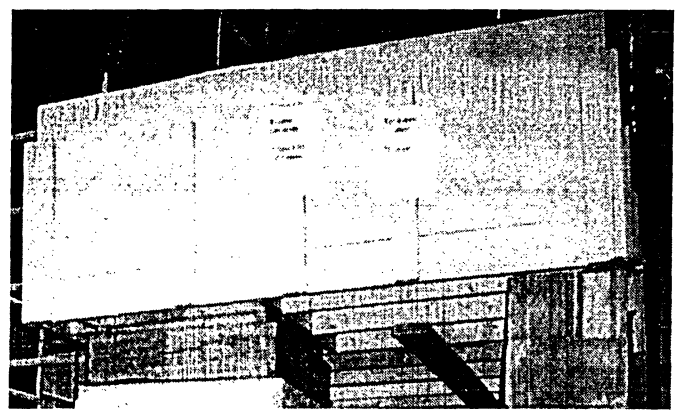


Figure 5.7: Road deck

- Flow distribution weir and perforated pipe:

  The simulated runoff fills up the first chamber via a white down pipe and a perforated horizontal pipe. A sheet flow on the road deck is made by overflowing the flow distribution weir in order to simulate the runoff in typical roadside condition. The flow distribution weir in front of the perforated pipe is slightly elevated above the road deck to allow water to travel underneath in a laminar flow action, as seen in Figure 5.8.

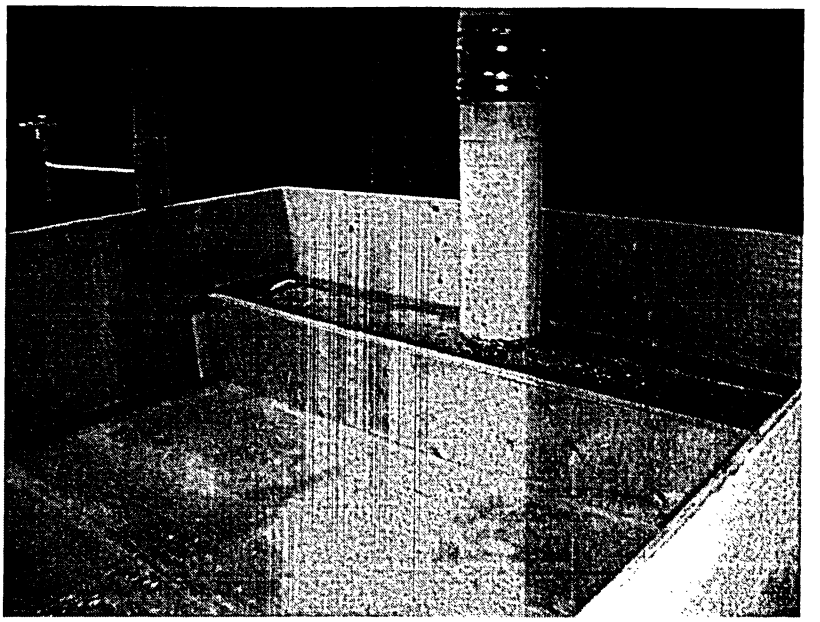


Figure 5.8: Perforated pipe

- A rectangular weir measurement box and outlet components:

  The discharge from the catch basin is measured by a rectangular weir box because it is expected that high flow scenarios may occur. The flow rate is determined by measuring the head over the weir box. A screen with opening size of 0.063 mm is used to capture sediments as well as pellets and ingots when they are flushed out from the catch basin, shown in Figure 5.9. The weir is calibrated with the volumetric flow method. Water exited from the weir box is channelled to an underground trench for drainage or recirculation.

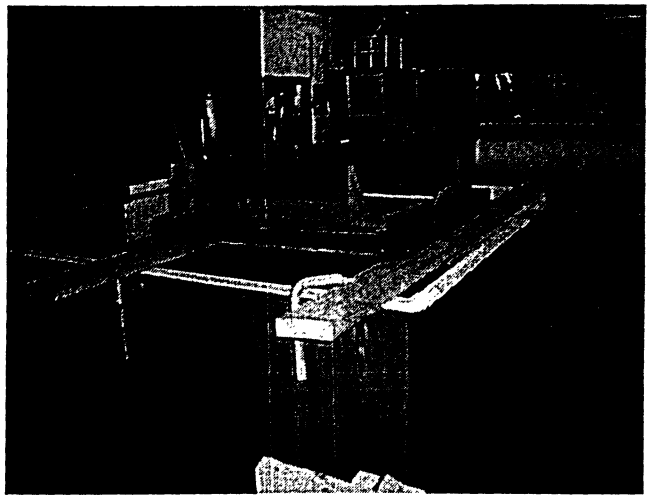


Figure 5.9: Weir box and screen

5.3.2 Weir Flow Calibration and Valve Operation

Before starting the experiment, a series of calibration tests were run to adjust the weir parameters. The simplest way for small flows is volumetric test, which is direct measurement of the time to fill a container of known volume and the time to fill is measured by a stop watch. The basic equation for a rectangular weir flow is given by:

$$Q = A * H^B \qquad (5\text{-}1)$$

where Q = flow rate (L/s); A and B = weir parameters; and H = weir head (cm). A and B can be determined by plotting log (volumetric flow) versus log (weir head) and B is equal to the slope and A is equal to $10^{intercept}$. The log-log plot is given in Figure 5.10. The weir flow equation is

$$Q = 1.80 * H^{1.37} \qquad (5\text{-}2)$$

The flow is not regulated by a digital meter but a valve controlled by a long chain. The chain needs to be marked for repeated experiments. When experiment starts, the valve is fully opened first and then partially closed to get the desired flow level. The fully opened

valve at the beginning of the experiment does not affect the flow going into the catch basin because the flow is quickly restricted by partially closing the valve.

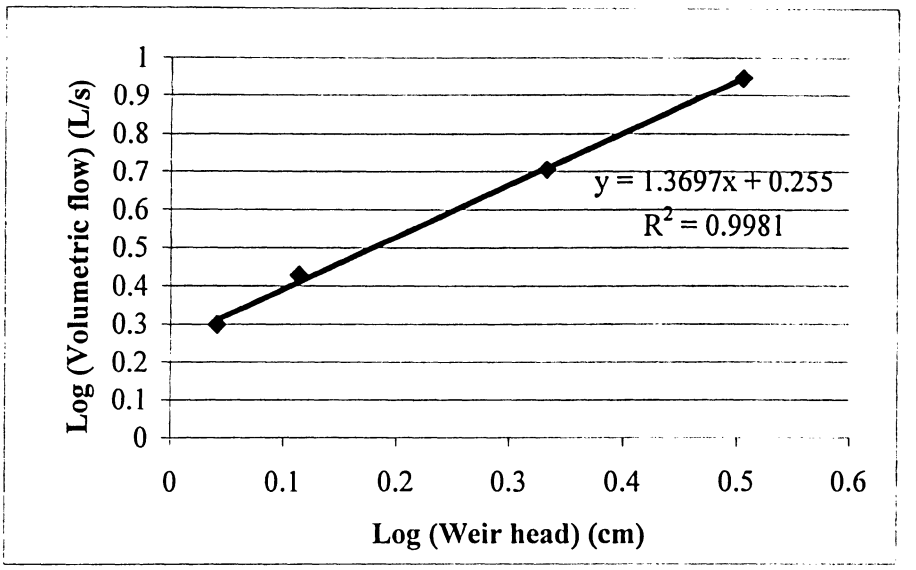


Figure 5.10: Log-Log plot

5.4 Hydraulic Analysis of Different Methoprene Formulation Products

Two types of methoprene formulation products (i.e. pellets and ingots) were tested for their hydro-dynamic properties. The blended soil materials were first added to the base of the catch basin model and water was slowly added until it reached the invert of the outlet pipe. Methoprene pellets or ingot were dropped from the grate similar to how applicators drop them in the field. Tests were performed for different sump depths, starting from the lowest position and for different water levels.

The inlet water flow was varied to simulate wet weather condition. The minimum critical flow (Qmin) is defined as the flow (Q) which initiates the flushing of methoprene pellets or ingots (i.e. $Q > Qmin$). The maximum critical flow (Qmax) is defined as the

flow (Q) which flushes out the majority of the pellets (i.e. Q = Qmax). In addition, two types of flow patterns are used in the hydraulic experiments: Instantaneous (I) and Gradual (G). Instantaneous flow is the flow starting from 0 to the desired flow value and is the simulation of the summer short-duration rainfalls. Gradual flow is the flow starting from 0 and increasing incrementally to the desired flow value and is the simulation of the fall and winter long-duration rainfalls. Each experiment run at the steady-state condition (or no fluctuation of weir head) and continued for 5-10 minutes. It should be noticed that no compaction on sediment is required based on the field penetrometer test. Field sediment compaction is by the natural compaction of sand itself. The followings summarize the different study scenarios on the hydraulic scouring:

1) Sediment: No sediment, sediment alone and sediment with leaves
2) Rainfall pattern: Short and long duration
3) Methoprene products: Pellets and Ingots
4) Sump water levels: 11.4 cm and 22.8 cm
5) Sump depth: 450, 600 and 900 mm

The experimental procedures of sediment with leaves scenarios were described in the following steps:

1) Experiment was started for the lowest 450 mm sump depth. The catch basin was loaded with blended soils to the appropriate level so that there was 11.4 cm water below the invert. The valve was open to add water up to the invert (Figure 5.11).

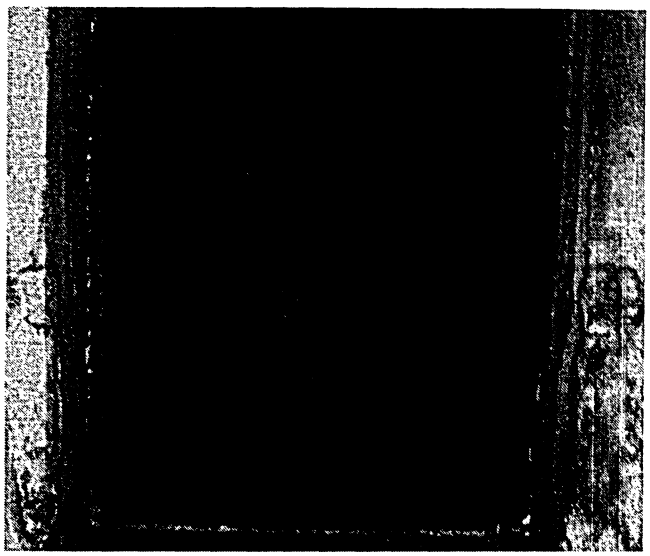


Figure 5.11: Catch basin with sediment

2) Few minutes were waited to allow the blended soils with leaves to settle and 0.7 g of methoprene pellets or a piece of ingot was dropped through the grate opening.
3) The valve was open and head was recorded. Experiment was run for 5-10 minutes more after the head was not fluctuated or no pellets were flushed out, as seen in Figure 5.12. Flushed pellets or the ingot trapped on the screen were collected and counted.

Figure 5.12: Hydraulic experiment in progress

4) In case of gradual flow, flow rate was increased and step 3 was repeated. For instantaneous flow, the flow was stopped after step 3 and steps 1-3 were repeated for different flow rates. Each flow rate was repeated few times to confirm the percent of flushed pellets. After each set of experiment, remaining pellets inside catch basin were removed and new batch of 0.7 g pellets or a piece of ingot was dropped.
5) Experiment was started for the highest 900 mm sump depth. Steps 1-4 were repeated for 11.4 cm and 22.8 cm water levels (Figure 5.13).

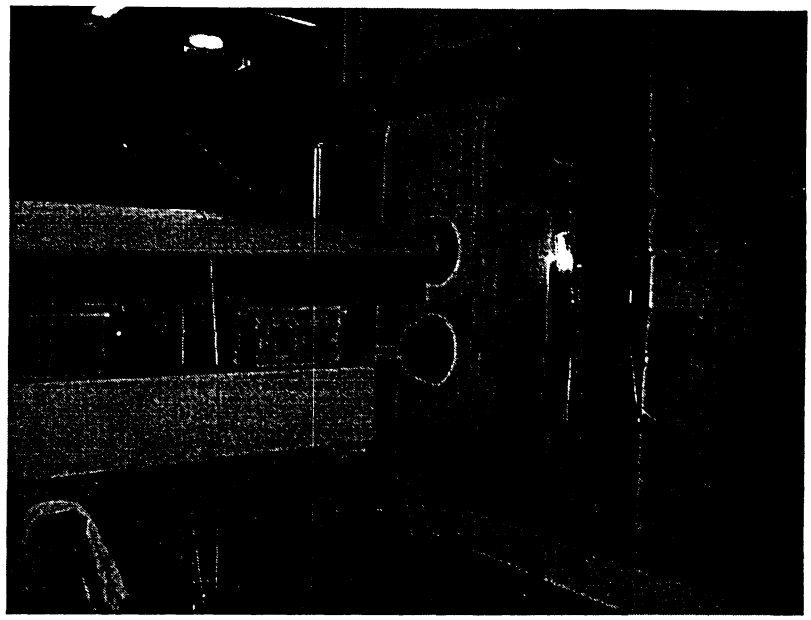


Figure 5.13: Experiment on 900 mm sump depth

6) Road platform was lifted up and catch basin was turned 180°. Experiment was started for the middle 600 mm sump depth and steps 1-4 were repeated.

5.4.1 Results and Discussions

It is observed from the hydraulic experiment that in order to flush out the pellets or ingots from the catch basin, the plunging water jets must penetrate the water down to the sediment to create the scouring or lift force, which is greater than the submerged weight of pellets or ingots. Pellets are moved on the sediment to the falling water jets during the experiments. After the experiments, some pellets and parts of the ingots are covered by the sediment. It is expected that pellets may be re-suspended from the sediment and ingots may be exposed to release in the next rain event.

Figure 5.14 and Table 5.3 show the effect of sediment and leaves on the pellets and ingots. It is shown that the critical flows are increased by 3-15% and 7-10% for

pellets and ingots, respectively, when comparing between sediment and sediment with leaves. The reason may be due to the protective layer of leaves. Figures 5.15 and 5.16 show the critical flow is increased 5-18% for pellets and around 8% for ingot if the flow is gradual flow. However, there is not the case for 600 mm.

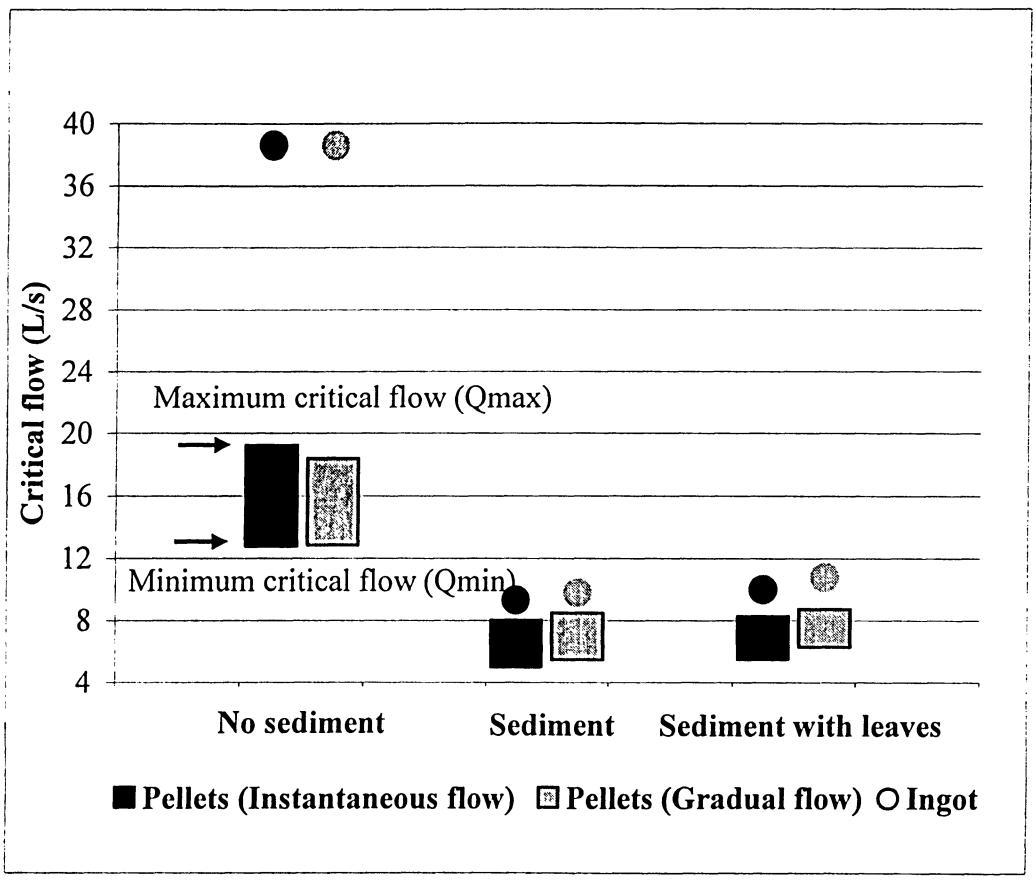


Figure 5.14: Comparison of critical flows for sediment and leave experiments (450 mm sump depth and 11.4 cm water depth)

Table 5.3: Detail results of sediment and leaves scenarios

(a) Formulation – Pellets; 450 mm sump depth; and 11.4 cm water level						
Critical flow (L/s)	No sediment		Sediment		Sediment with leaves	
	Instantaneous	Gradual	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	12.77	12.85	5.00	5.47	5.50	6.30
Maximum	19.24	18.41	8.04	8.50	8.30	8.75
(b) Formulation – Ingot; 450 mm sump depth; and 11.4 cm water level						
Critical flow (L/s)	No sediment		Sediment		Sediment with leaves	
	Instantaneous	Gradual	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	> 38.63		9.33	9.78	10.01	10.80

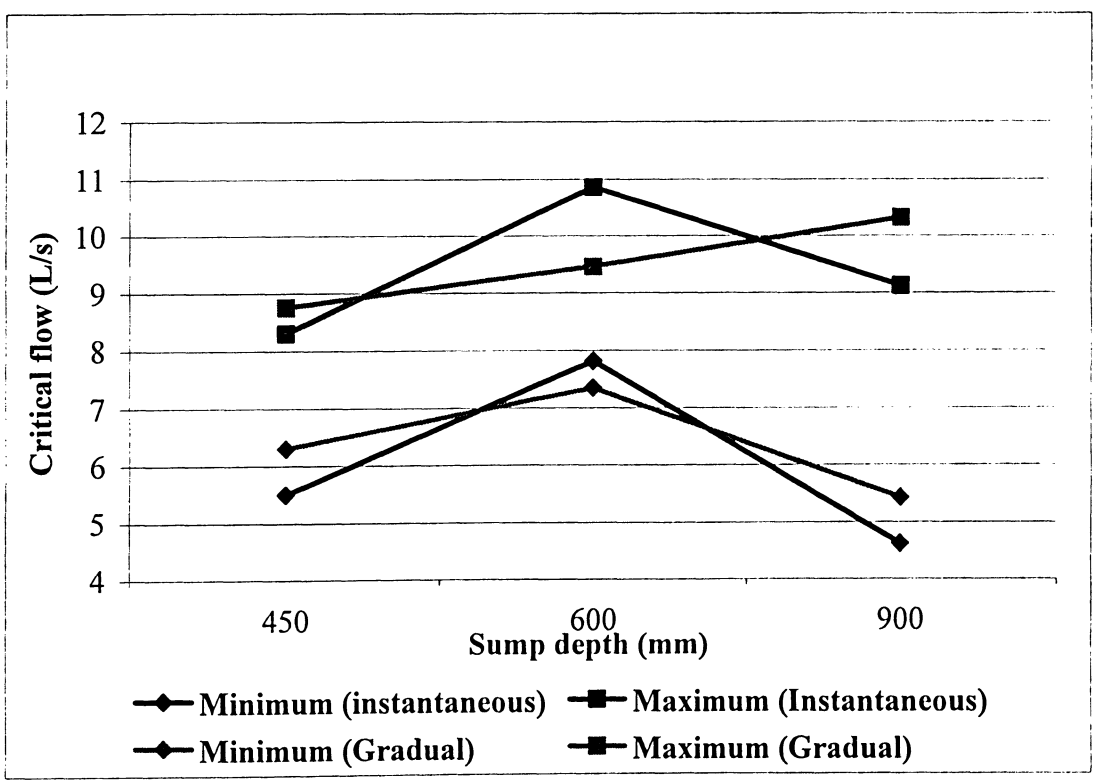


Figure 5.15: Gradual and instantaneous flow comparison for pellets (sediment with leaves and 11.4 cm water depth)

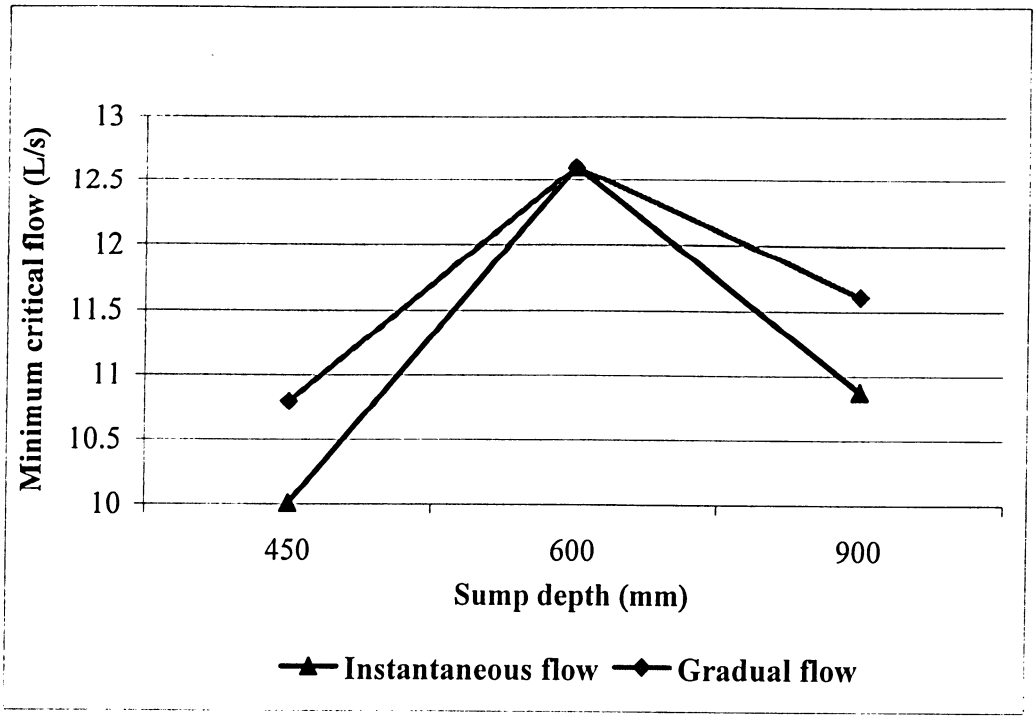


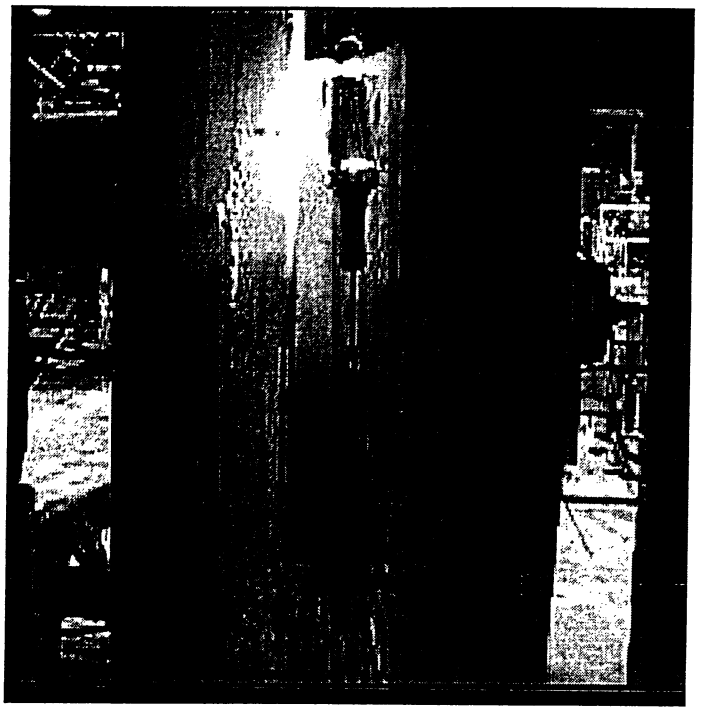
Figure 5.16: Gradual and instantaneous flow comparison for ingot (sediment with leaves and 11.4 cm water depth)

It is shown in Table 5.4 that when the catch basin is completely clean, it needs more than 30-40 L/s to flush out pellets and ingots. For the no sediment condition, the falling water jet could not plunge to the bottom of the catch basin to create a scouring force even the water flows keep increasing, as illustrated in Figure 5.17. The flow to flush out the pellets for 450 mm sump depth is around 130% increase compared to sediment with leaves. The reason is that water provides much cushion effect to dissipate the potential energy of the falling water. That also explains the larger the depth of water, the higher the critical flow, as shown in Table 5.5. It is observed from Figures 5.18 and 5.19 that even when the flow is increasing, the percent flushed pellets are decreasing because most sediments start to flush out at higher flow and block the pellets from flushing out. It

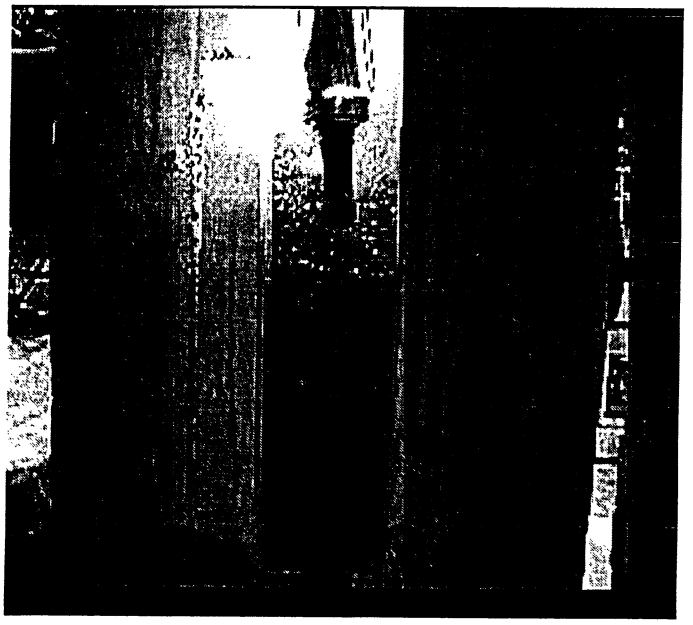
is observed that the 450 mm sump depth has smaller percent flushed pellets because more sediment is flushed out at that sump depth.

Table 5.4: No sediment and sediment with leaves for different sump depths

(a1) Formulation – Pellets; 450 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	12.77	12.85	5.50	6.30
Maximum	19.24	18.41	8.30	8.75
(a2) Formulation – Ingot; 450 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	> 38.63		10.01	10.80
(b1) Formulation – Pellets; 600 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum			7.81	7.34
Maximum	>32.13		10.86	9.46
(b2) Formulation – Ingot; 600 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	>28.96		12.60	12.60
(c1) Formulation – Pellets; 900 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum			4.62	5.43
Maximum	>41.02		9.12	10.32
(c2) Formulation – Ingot; 900 mm sump depth; and 11.4 cm water level				
Critical flow	No sediment		Sediment with leaves	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	>41.02		10.88	11.61



(a)



(b)

Figure 5.17: No sediment experiment in progress: (a) low flow condition; (b) high flow condition

Table 5.5: Different water depths for 900 mm sump depth

(a) Formulation – Pellets				
Critical flow	11.4 cm water level		22.8 cm water level	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	4.62	5.43	10.96	10.28
Maximum	9.12	10.32	11.57	12.06
(b) Formulation – Ingot				
Critical flow	11.4 cm water level		22.8 cm water level	
(L/s)	Instantaneous	Gradual	Instantaneous	Gradual
Minimum	10.88	11.61	11.98	14.12

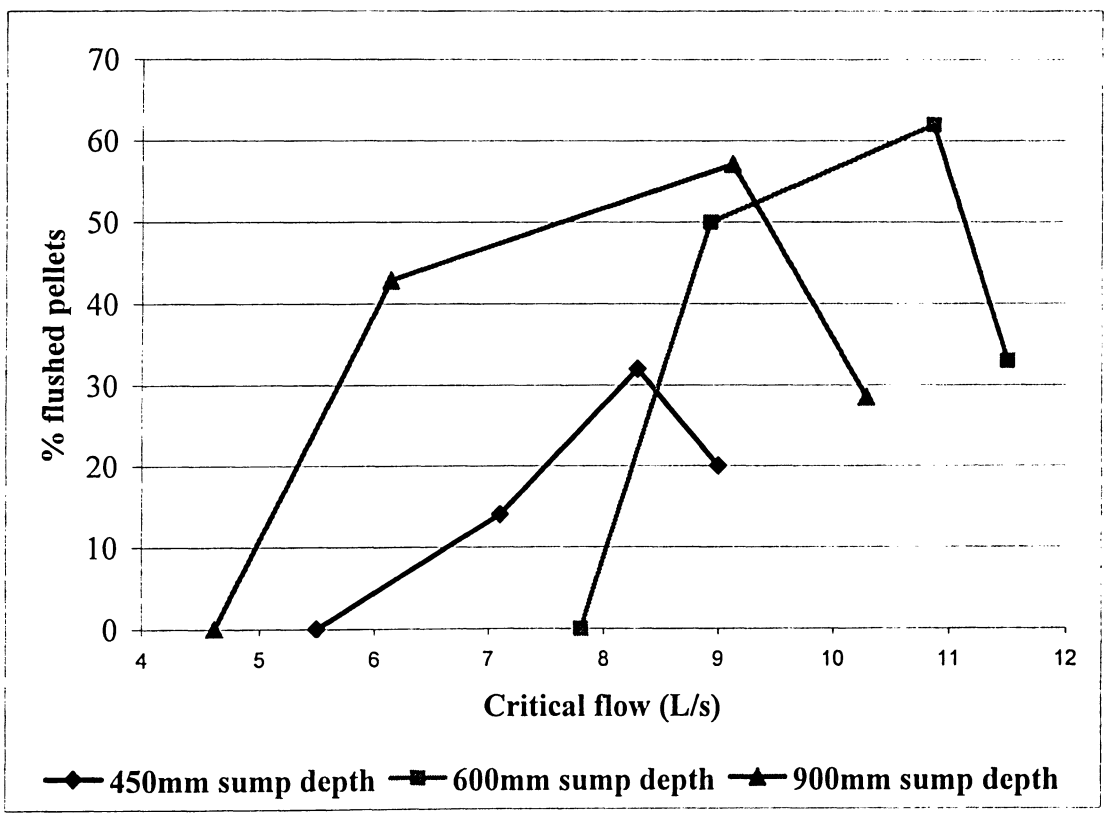


Figure 5.18: Percent of flushed pellets with different sump depths (instantaneous flow and 11.4 cm water depth)

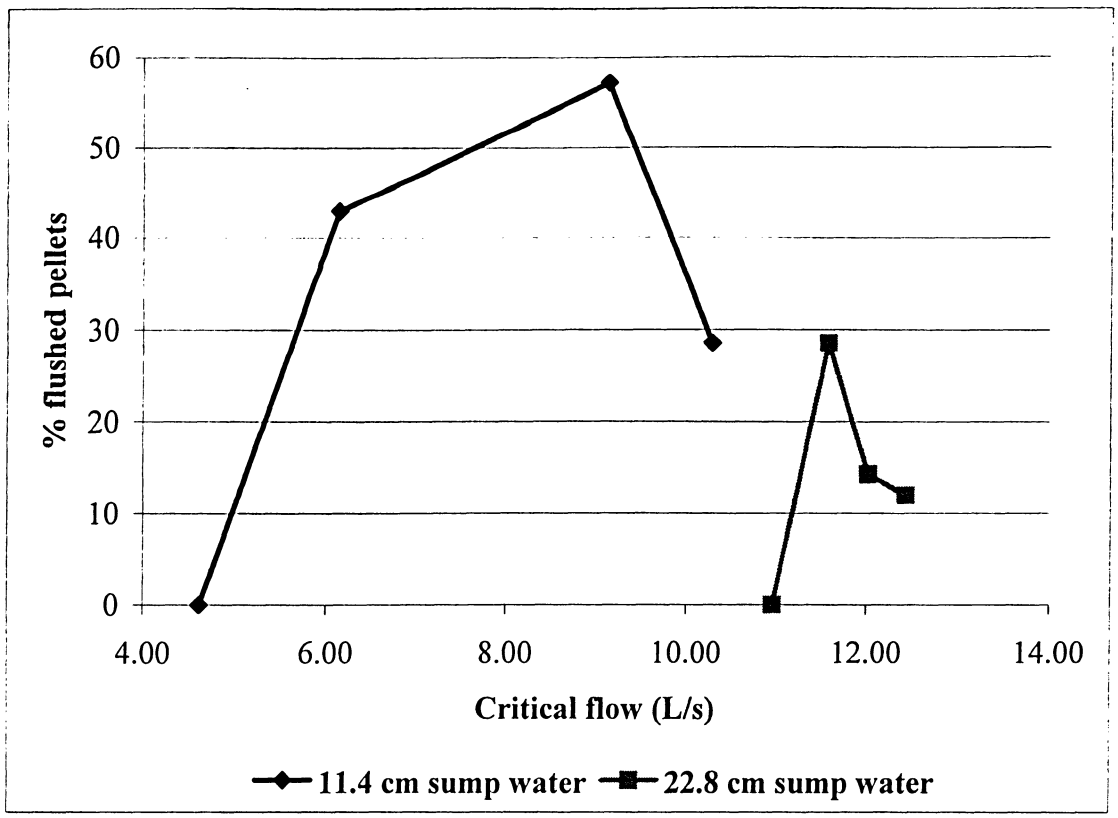


Figure 5.19: Percent of flushed pellets with different water levels (instantaneous flow and 900 mm sump depth)

The sediment depth and water level of the field catch basin W1 is similar to a 900 mm sump depth with water level of 22.8 cm; S1 is similar to a 900 mm sump depth with water level of 11.4 cm; S2 is similar to a 900 mm sump depth with no sediment. Based on the rainfall intensity duration frequency curves (IDF) of Toronto region, the critical storm events to flush out the pellets and ingot are tabulated in Table 5.6. Based on residential land use area in Newtonbrook watershed, the peak flow into catch basin for 3-month storm is calculated to be 9.50 L/s with runoff coefficient of 0.4, indicating that the chance to flush out the pellets or ingot is much higher. IDF curve and peak flow rate return periods are shown in Figures 5.20 and 5.21, respectively.

Table 5.6: Critical storm events for flushing out methoprene pellets and ingots

Condition	Pellets			Ingot		
	Minimum critical flow (L/s)	Return period (years)	Rainfall intensity (mm/hr)*	Minimum critical flow (L/s)	Return period (years)	Rainfall intensity (mm/hr)*
W1						
No sediment	>41.02	>25	>185	>41.02	>25	>185
Sediment with leaves	10.96	0.29	41.22	11.98	0.33	45.67
S1						
No sediment	>41.02	>25	>185	>41.02	>25	>185
Sediment with leaves	4.62	<0.25	<38	10.88	1.44	93.80
S2						
No sediment	>41.02	>25	>185	>41.02	>25	>185

* Time of concentration = 5 minutes (MTO, 1984)

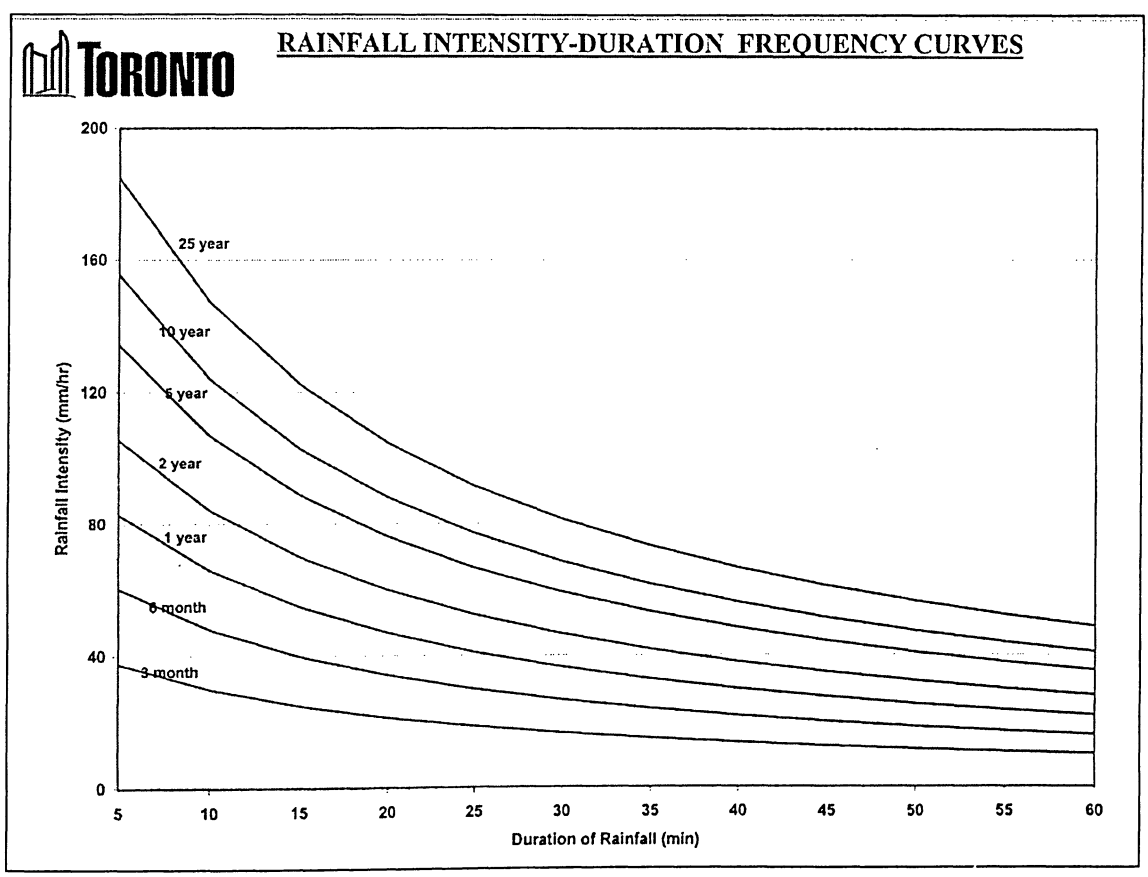


Figure 5.20: IDF of Toronto region (Source: City of Toronto)

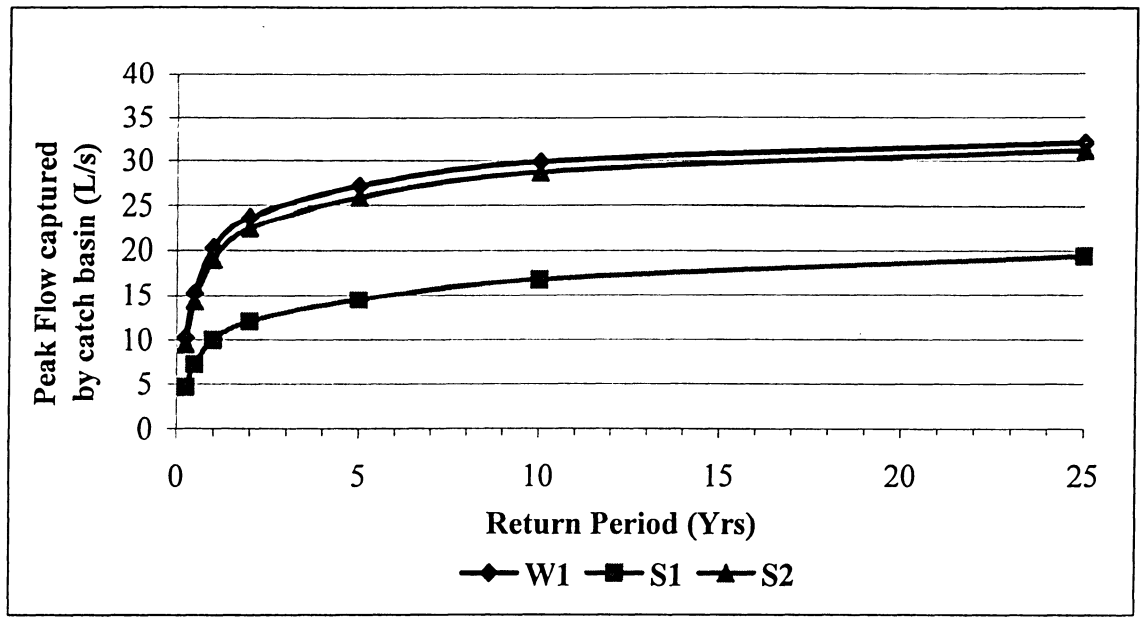


Figure 5.21: Peak flow rate return period

The long term rainfall data from 1939 to 1997 is used to calculate the risk of flushing of pellets and ingot from July to September, given as:

P[Q>Qmin at least once in 3 months) = 1 – (P[Q<Qmin] in July * P[Q<Qmin] in August * P[Q<Qmin] in September) (5-3)

The catch basins are assumed as S1 and W1 and drainage area is based on the Newtonbrook watershed. The peak monthly flows are calculated by the average drainage area drained by one residential catch basin and runoff coefficient of 0.4. Based on the runoff coefficient, the fraction of impervious areas is 0.29, taken runoff coefficient of 0.9 and 0.2 for entire impervious and pervious areas, respectively (Brodie, 1987). Area-weighted average depression storage is 4.7 mm, which is calculated by:

$$Savg = h * Sdi + (1-h) * Sdp \quad (5\text{-}4)$$

where Savg = area-weighted depression storage (mm); h = fraction of impervious areas; and Sdi & Sdp = depression storage of the entire impervious and pervious areas at 1.5 mm and 6.0 mm, respectively (Viessman Jr. and Lewis, 1996). Average duration of rainfall events in Toronto is taken as 3.5 hrs (Adams and Papa, 2000) and it is assumed that the depression storage of 4.7 mm is averaged over the 3.5 hrs rainfall event and determined to be 1.34 mm/hr. The peak runoff is calculated by using a rainfall and runoff transformation employed in STORM, as expressed by (Adams and Papa, 2000):

$$Rp = Cv * (Ip - S) * A * 2.78x10^{-4} \quad (5\text{-}5)$$

where Rp = peak runoff (L/s); Cv = runoff coefficient; Ip = peak hourly rainfall intensity (mm/hr); S = depression storage (mm/hr); A = drainage area (m^2) and $2.78x10^{-4}$ = unit conversion. Peak flow captured by one catch basin is determined by using catch basin inlet hydraulics, as shown in Figure 5.22, and the computed peak runoff. The peak monthly flows are ranked and sorted in ascending order of magnitude to do the frequency analysis, as illustrated in Figure 5.23. The results are presented in Table 5.7. The risk for flushing of pellets is high with risk of 74% when catch basin is not clean. When half of sediment is removed, the risk can be reduced to 8.1%. The risk for flushing of ingot is low with value of 9%.

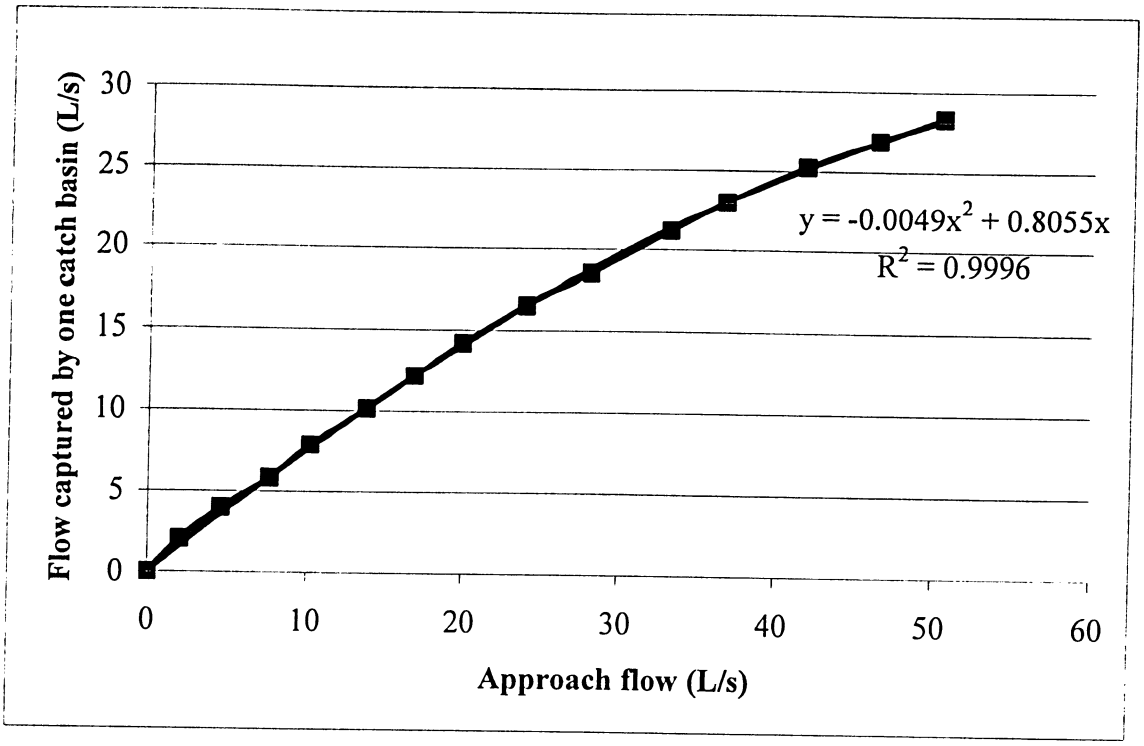


Figure 5.22: Hydraulic performance of the fishbone grate (Source: Townsend et al., 1980)

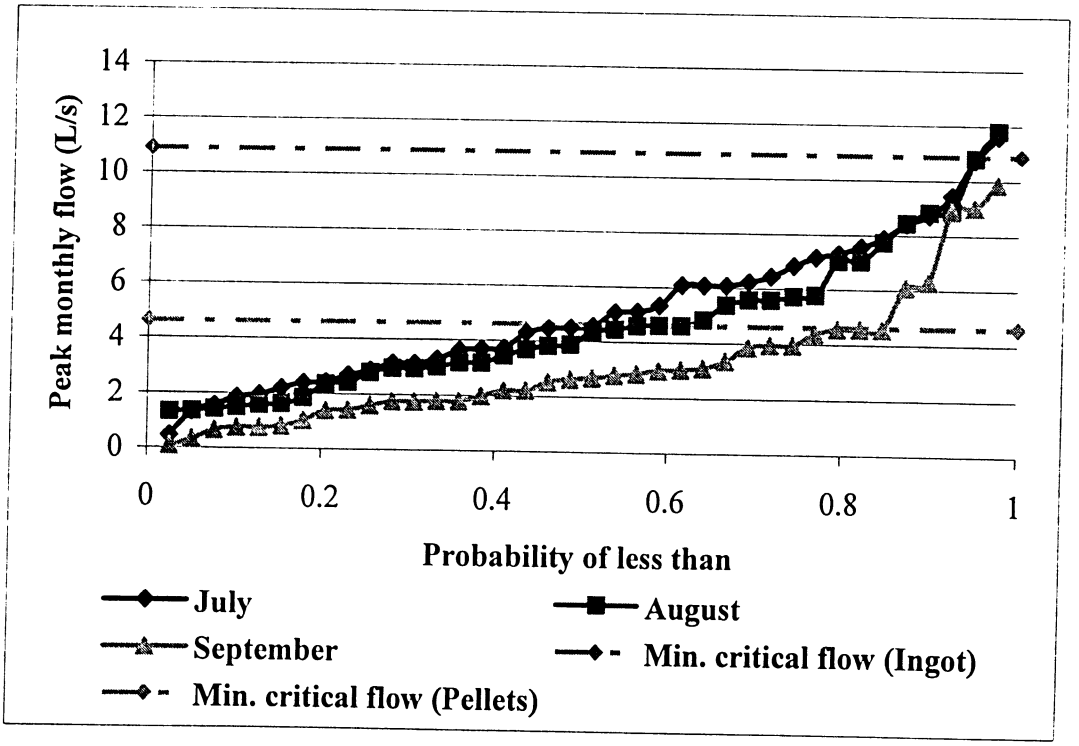


Figure 5.23: Storm event risk analysis (11.4 cm water level)

Table 5.7: Results of risk analysis

Rainfall station: Toronto Pearson Airport, 1960-1997		
Water level: 11.4 cm	Formulation	Risk
	Pellets	0.74
	Ingot	0.098
Water level: 22.8 cm	Formulation	Risk
	Pellets	0.088
	Ingot	0.00
Rainfall station: Toronto Bloor St., 1939-1997		
Water level: 11.4 cm	Formulation	Risk
	Pellets	0.73
	Ingot	0.073
Water level: 22.8 cm	Formulation	Risk
	Pellets	0.074
	Ingot	0.030

5.5 Sediment Washout from Catch Basin

The washout amount of sediment is not monitored with time. The bottom sediments were re-suspended and flushed by the incoming water flow and collected in the screen, weighted and analyzed for the particles sizes. Tests were done for instantaneous flow. The test procedures are similar to the hydraulic analysis of methoprene pellets and ingot.

5.5.1 Data Analysis and Discussion

It is observed from the experiments that sediment washout (Mr) lasts only for a certain period of time until soil available for release (M) is exhausted. Each fixed flow rate has certain total mass of soils available for release from the bottom of catch basin. The sediment scouring is eased when Mr = M. Figure 5.24 illustrates the values of M for different situations. It is indicated that few sediments are eroded at low flow until it

reaches a critical flow (Qc) that sediments begin to flush out. A critical flow of 7 to 8 L/s is needed in order to flush out sediment for the three sump depths with 11.4 cm water depth whereas a critical flow of 11 L/s is needed for the 22.8 cm water level. It is observed in Figure 5.23 that the chance of having $Q < Qc$ is almost 70%. The 22.8 cm water level provides a large cushion effect to dissipate the potential energy of the free-falling water, thereby reducing the impact force on the sediment particles. Thus, the amount of soils washout for 11.4 cm is more than that for 22.8 cm water depth. In addition, more sediments were flushed out at 450 mm sump depth because the larger fall of water resulted in greater impact force on the sediment particles. M and Qc values are important parameters to model sediment erosion and inflow rate exceeded of 7-8 L/s was found to cause significant disturbance and mixing of the sediments. It is observed from the Table 5.8 that 3-month storm can create sediment scouring from catch basin in all land uses except the park/recreational land-use area. A 4-month storm over a park/recreational land-area can cause the sediment scouring.

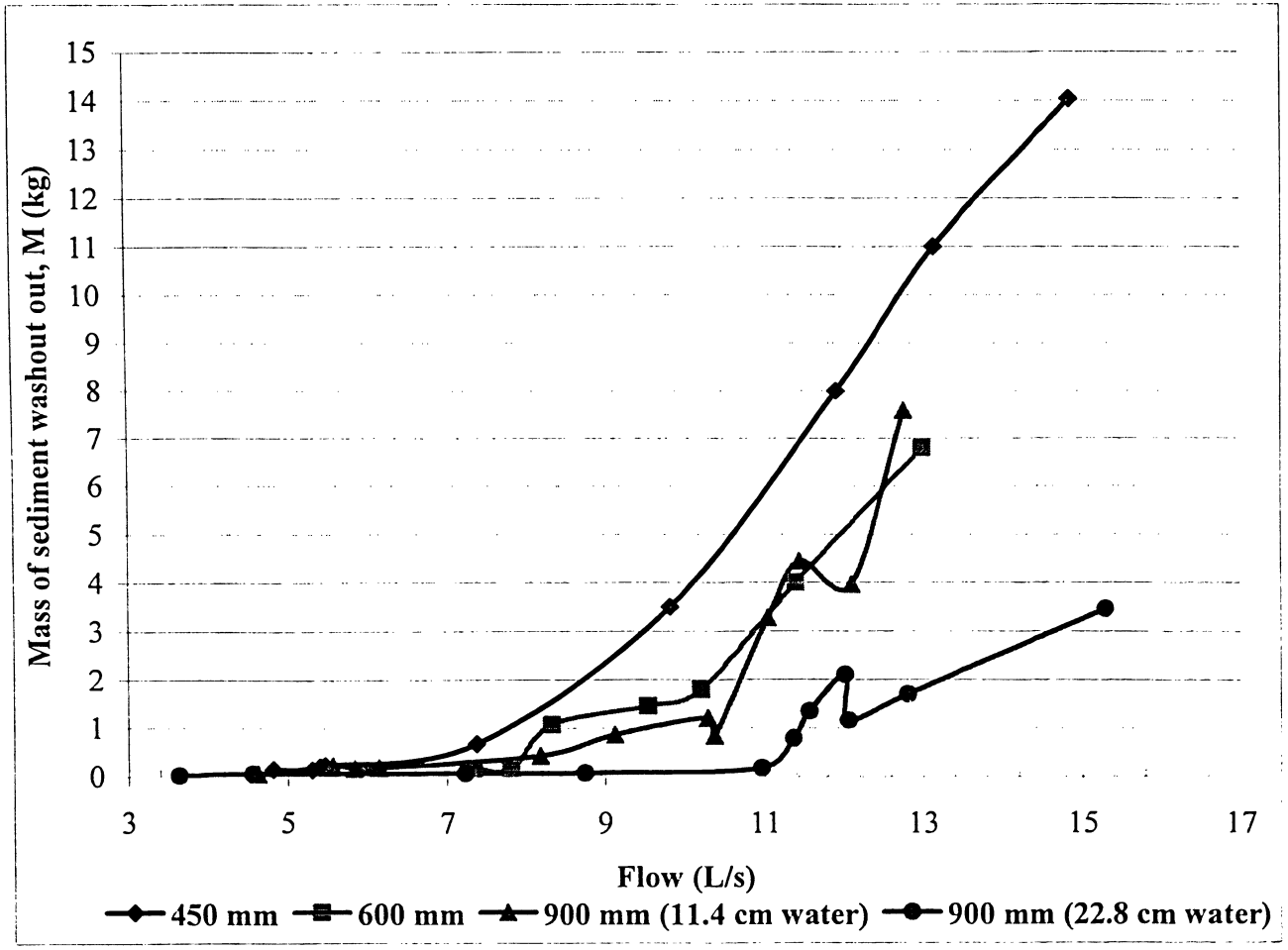


Figure 5.24: Mass of sediment washout

Table 5.8: 3-month peak flows of catch basin

Newtonbrook watershed land-area	C (Source: Brodie, 1987)	3-month peak flow into catch basin (L/s)
Residential	0.4	9.50
Park/Recreational	0.1	5.10
Commercial	0.6	7.80
Institutional	0.6	20.80

D50 is used to represent the average particle size of the mixed soil sample. Figure 5.25 illustrates the underlying sediment particle sizes scouring from catch basin under various flow conditions. In general, D50 increases with inflow rates for all the situations. Medium sand particles can be flushed out during a 3-month storm over residential and commercial areas and gravel particles are left in the catch basins.

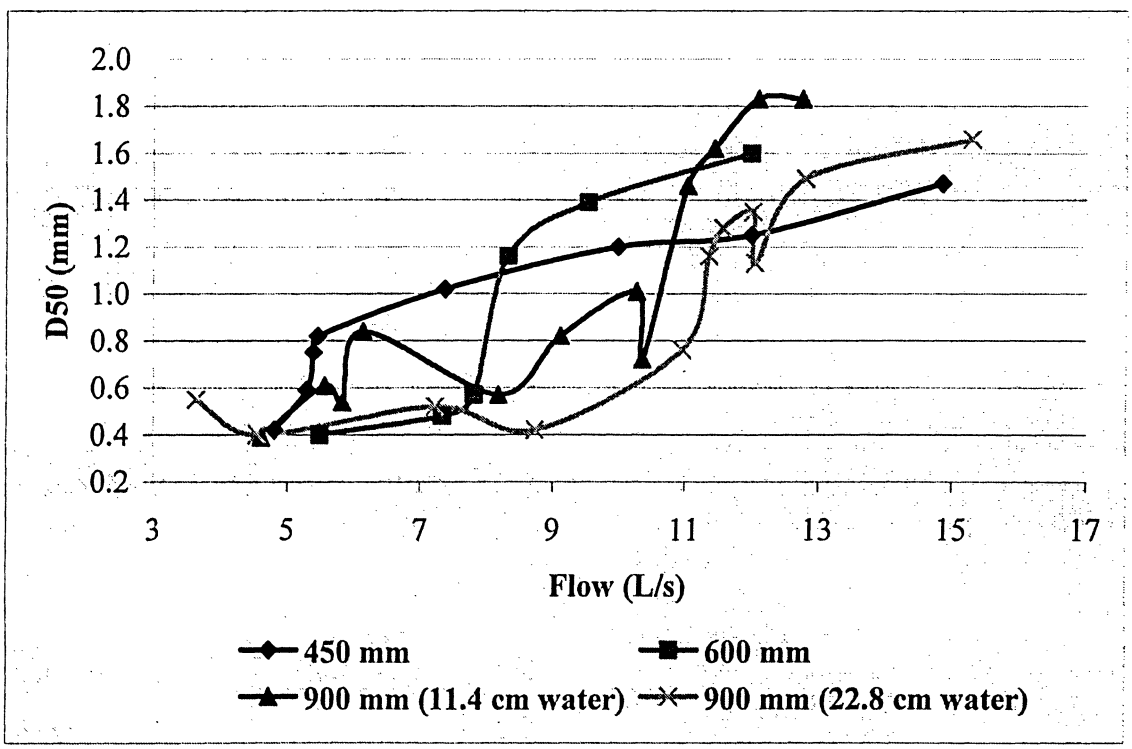


Figure 5.25: Sediment washout at different flows

Chapter 6 MODELLING METHOPRENE CONCENTRATION AT CATCH BASINS AND STORM OUTFALLS

6.1 Model Concept

The catch basin sump can be conceptualised as a completely well-mixed reactor. Many factors such as rainfall volume, physical dissolution of methoprene, catch basin physical characteristics and complicated reactions inside catch basin, affect the residual concentration of methoprene at the catch basin sump. A hydrologic water quality model is developed to predict the fate and transport of the methoprene chemical in the catch basin and sewer outfall. The model simulates the residual concentration of methoprene at a catch basin under dry and wet weather conditions. The following processes are modelled: (a) methoprene loading; (b) methoprene reaction; (c) flushing of methoprene and pellets; and (d) dilution.

6.1.1. Mass Balance Model – Dry Weather Condition

The mass balance for a completely mixed system is expressed as:

$$\text{Accumulation} = \text{Loading} - \text{Reaction} - \text{Output} \qquad (6\text{-}1)$$

When there is no rain, methoprene released from the pellets or ingots undergoes decay in the catch basin sump. There are many different types of loading functions, such as pulse, step, linear, exponential and sinusoidal for chemical release (Chapra, 1997). However, there is no literature which gives the release function of methoprene. It is expected that the methoprene releasing functions are complicated and difficult to identify. Therefore, a simplified loading function is assumed in the model. It is observed from the field and laboratory studies that residual methoprene concentration reaches a peak and decline exponentially. Thus, the mass releasing rate is assumed to be exponential:

$$W(t) = W_e e^{-\beta_e t} \tag{6-2}$$

where We = initial rate of mass loading (μg/d) at t = 0; and β_e is the rate of mass decay (d^{-1}). An exponential relationship between the amount of release of methoprene and the time of elapsed is proposed. By integrating the mass loading function over time, the total methoprene mass available for release from pellets or ingot is given by:

$$\text{Pellets: } \frac{We}{\beta_e} = 0.7\,g \times 4.25\% \times r$$

$$\text{Ingot: } \frac{We}{\beta_e} = 45\,g \times 2.1\% \times r \tag{6-3}$$

where r = fraction of methoprene release (r = 1, claimed value by manufacturer). The decay of methoprene in catch basin sump is assumed to be a first-order reaction, expressed by:

$$\text{Reaction} = KM \tag{6-4}$$

where K = first order decay coefficient (d^{-1}) and M = mass of methoprene in the sump (μg). The mass balance equation of methoprene for dry weather condition is expressed as:

$$\frac{dM}{dt} = W(t) - KM \tag{6-5}$$

The above differential equation is solved for the mass of methoprene over time, or:

$$M = \frac{W_e}{(K - \beta_e)} \left(e^{-\beta_e t} - e^{-Kt} \right) \tag{6-6}$$

6.1.2. Mass Balance Model – Wet Weather Condition

When rain occurs, two cases have to be considered. The first case is the dilution and flushing of methoprene chemical when runoff is not strong enough to flush out the methoprene pellets. The second case is the dilution as well as flushing of methoprene chemical and pellets when runoff is strong enough to flush out the pellets. The mass equation for the first case is expressed as:

$$\begin{aligned} \frac{dM}{dt} &= W(t) - K\left(M - M \times \frac{R_r}{V_T} \right) - \left(M \times \frac{R_r}{V_T} \right) \\ &= W(t) - \left(K - K \times \frac{R_r}{V_T} + \frac{R_r}{V_T} \right) M \\ &= W(t) - K' M \end{aligned} \tag{6-7}$$

where R_r = runoff volume (m^3); V_T = runoff and water sump volume (m^3); and K' = net decay coefficient. Methoprene mass is assumed to be equally distributed in the completely mixed catch basin sump when runoff is introduced to the catch basin. Figure 6.1 shows the mass of methoprene flushed out and remaining after a daily runoff event. The remaining mass of methoprene will undergo decay.

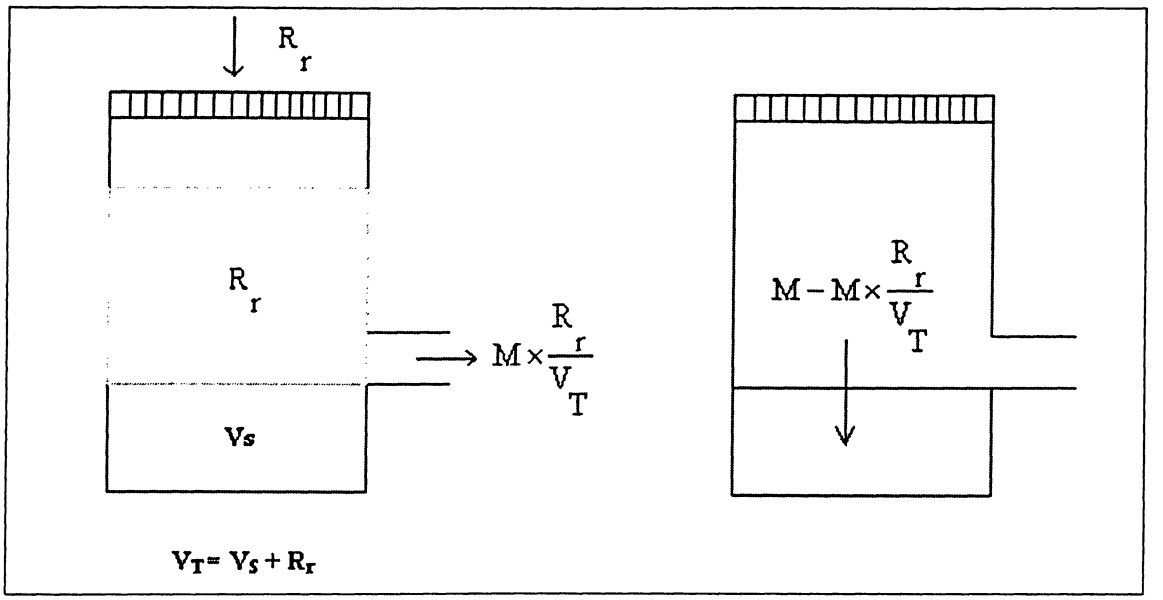


Figure 6.1: Flushing of methoprene description

Equation 6-7 is solved for the mass of methoprene over time, or:

$$M = \frac{W_e}{(K' - \beta_e)} \left(e^{-\beta_e t} - e^{-K' t} \right) \tag{6-8}$$

When the rain occurs, K will become K' in the model.

The mass balance equation for the second case is:

$$\begin{aligned} \frac{dM}{dt} &= W'(t) - K\left(M - M \times \frac{R_r}{V_T} \right) - \left(M \times \frac{R_r}{V_T} \right) \\ &= W'(t) - \left(K - K \times \frac{R_r}{V_T} + \frac{R_r}{V_T} \right) M \\ &= W'(t) - K'M \end{aligned} \tag{6-9}$$

where

$$W'_e(t) = W'_e e^{-\beta_e t} = R W_e e^{-\beta_e T} e^{-\beta_e t}$$

in which We' = new initial rate of mass loading (μg/d) at t = T after flushing of methoprene pellets; T = time of flushing of pellets (day); and R = percent of remaining pellets. Flushing of methoprene chemical is still occurred during the wet weather except the rain is strong enough to flush out some of the methoprene pellets and W'(t) takes this into consideration. It should be noted that the area under the mass loading curve is equal to methoprene mass available for release from pellets at time t. When some pellets are flushed out at time T, the methoprene mass available for release is reduced by R% (or area of ABC is reduced by R%), as indicated in Figure 6.2.

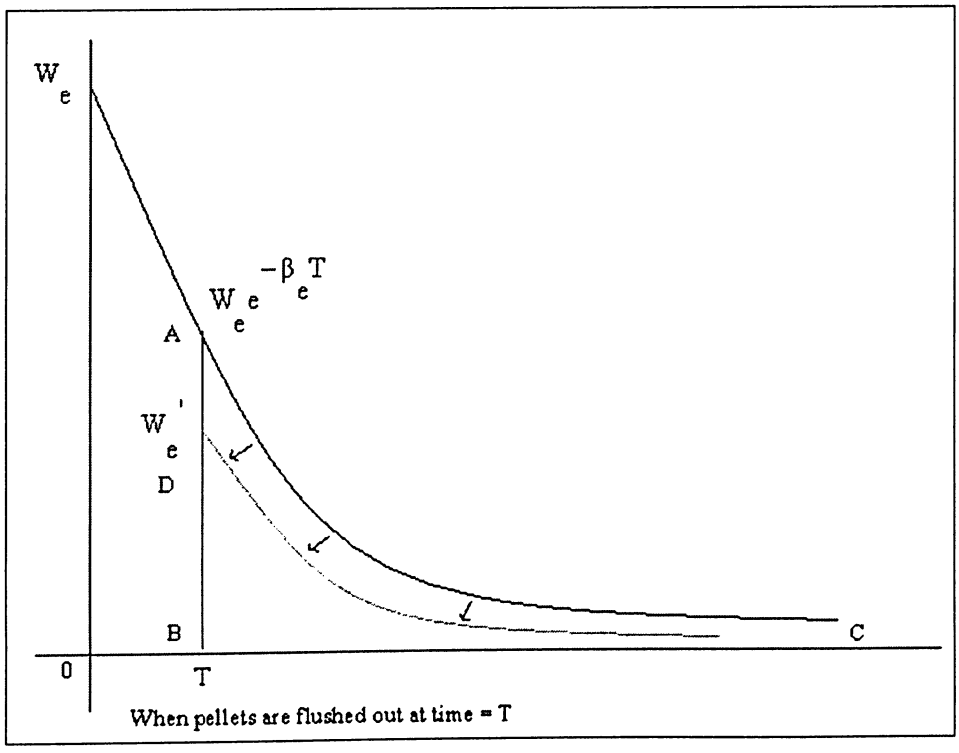


Figure 6.2: Mass balance after flushing of pellets

Therefore, W_e' can be determined by:

Area of DBC = R * (Area of ABC) or

$$\int_0^{\infty} W_e' e^{-\beta_e t} dt = R \int_0^{\infty} (W_e e^{-\beta_e T}) e^{-\beta_e t} dt \tag{6-10}$$

Solve the above equation and get:

$$W_e' = R W_e e^{-\beta_e T} \tag{6-11}$$

The Equation 6-9 is solved for the M over time and get:

$$M = \frac{W_e'}{(K' - \beta_e)} \left(e^{-\beta_e t} - e^{-K' t} \right) \tag{6-12}$$

When pellets are flushed out, We will become We' and K will become K' in the model. We' will also be used in the dry weather model after the pellets are flushed out. It is assumed that the β_e parameter is the same when the pellets are flushed out.

The general equation for We in case of multiple flushing is given as:

$$W_e^n = R_n * W_e^{n-1} * e^{-\beta_e (T_n - T_{n-1})} \tag{6-13}$$

where n = no. of flushing ($n \geq 1$). When n is equal to 1 (i.e. first time of flushing), equation becomes:

$$W_e^1 = R_1 W_e^0 e^{-\beta_e (T_1 - T_0)} = R_1 W_e^0 e^{-\beta_e (T_1)} \tag{6-14}$$

where We^0 = the rate of mass loading in dry weather (μg/d) at t = 0 and To is the origin.

If second flushing occurs at T_2, put n = 2 and get:

$$W_e^2 = R_2 * W_e^1 * e^{-\beta_e (T_2 - T_1)} \tag{6-15}$$

6.2 Peak Flow Determination

In order to determine peak daily flow into the catch basin, the 5-min continuous daily rainfalls are separated into independent storm events. A minimum interevent time is required. Shorter minimum interevent time is appropriate for a small and quick response urban catchment. 1 to 6 hrs of minimum interevent time have been suggested for most urban applications (Adams and Papa, 2000). A 5-min rainfall can be considered to be a separate event if the time period between the two 5-min rainfalls is longer than the minimum interevent time. Summer storm is short duration in nature so the minimum interevent time of about two hours is appropriate. After events are separated, each 5-min rainfall is transformed into runoff by applying a volumetric runoff coefficient. The catchment area is separated into pervious and impervious portion and rainfall-runoff transformation is applied to each portion and given by the following equation used in the STORM type hydrology model:

$$Vr = 0 \qquad \text{if } P \leq Sd$$

$$Vr = 0.001 * Cv * (P-Sd) * A \text{ if } P > Sd \tag{6-16}$$

where Vr = runoff volume (m^3); P = rainfall (mm); Sd = depression storage (mm); Cv = volumetric runoff coefficient; and A = drainage area (m^2). It is assumed that infiltration occurs at a uniform rate after the initial depression storage loss. The overall daily runoff

generation from the catchment is equal to:

$$Rr = \sum Vrp + \sum Vri \quad (6\text{-}17)$$

where Vrp = runoff generated from pervious area (m^3); and Vri = runoff generated from impervious area (m^3). The typical Sd and Cv values in the model are summarized in Table 6.1.

Table 6.1: Rainfall-runoff parameters

Urban catchment	Sd (mm)*	Cv (mm)**
Impervious	1.5	0.9
Pervious	6.0	0.2

* From Viessman Jr. and Lewis (1996) ** From Brodie (1987)

The drainage areas of the three catch basins are shown in Table 3.3. The runoff rate is calculated as:

$$Q = (Vr / 5) * 16.67 \quad (6\text{-}18)$$

where Q = 5-min flow (L/s). However, certain percent of approaching flow is captured by the catch basin, as shown in Figure 5.22. The daily peak flow (Qp) is given as:

$$Qp = \text{Max } \{Qcb\} \quad (6\text{-}19)$$

where Qcb = captured catch basin flow for each 5-min flow (L/s). Figure 6.3 illustrates one daily event of W1.

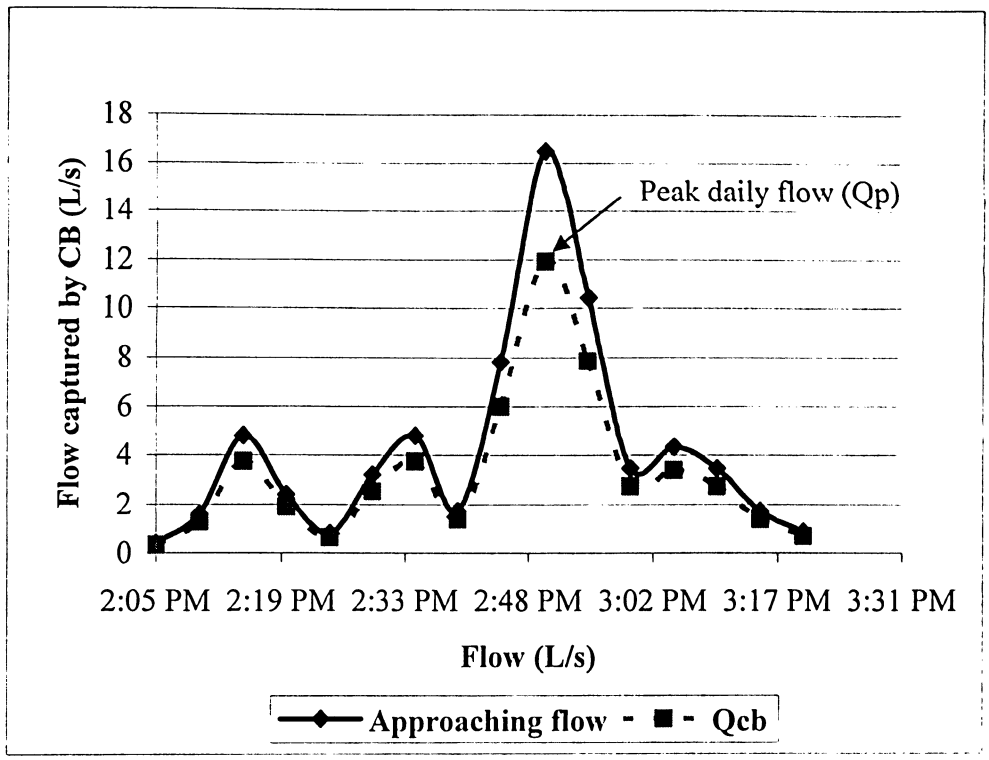


Figure 6.3: Peak flow determination of one daily event

6.3 Model Description

A spreadsheet model was developed to predict the concentration of dissolved methoprene at a typical catch basin and the associated outfall during dry and wet weather periods. The simulation model is based on the following assumptions:

- The time step of the model is daily.
- The model is based on a completely well-mixed sump system for methoprene mass.
- The decay rate constant (K), rate of release (β_e) and exponential release function do not change with runoff volume.
- There is no interaction between sediment or suspended solids and methoprene chemical.

- The mass of dissolved methoprene at time t is the mass available to flush out from catch basin during a rainfall event at time t.
- The inflow rate is equal to the outflow rate.
- The runoff is applied at the beginning of the time t. The mass of dissolved methoprene at time t + 1 is determined by the methoprene mass release from the pellets or ingots during that interval and the decay of the remaining of the dissolved methoprene mass at time t.

The columns in spreadsheet model are named and described as follows:

1) Date: date/month/year
2) Day No.: modeling time and used for no flushing of pellets.
3) Day No. for flushing of pellets: modeling time and used for flushing of pellets. The time is set zero for new release when pellets are flushed out.
4) Rainfall volume: daily rainfall volume in mm
5) Runoff volume (Rr): calculated by Equation 6-17.
6) Peak flow (Qp): calculated by Equation 6-19 and used to determine the percent of flushed pellets.
7) Percent flushed pellets: determined by the peak flow and Figure 5.18
8) Percent remaining pellets (R): equal 100 – (7) and used to calculate new We.
9) Dry weather (M1): mass of methoprene calculated in dry-weather condition of Equation 6-6.
10) Dry weather after flushing of pellets (M2): mass of methoprene calculated in dry-weather condition after flushing of pellets.
11) Wet weather (K'): calculated by Equation 6-7.

12) Wet weather and no flushing of pellets (M3): mass of methoprene calculated in wet-weather condition of Equation 6-8 but no flushing of pellets occurs, i.e. first case of wet weather

13) Wet weather (We): change each time when pellets are flushed out, calculated by Equation 6-13.

14) Wet weather and flushing of pellets (M4): mass of methoprene calculated in wet-weather condition of Equation 6-12 with flushing of pellets, i.e. second case of wet weather.

15) Final mass (M): choose M from column 9, 10, 12 or 14 based on dry or wet weather condition.

16) Final concentration (C): final mass divided by volume of water of W1, S1, and S2 catch basins.

17) Mass at outfall (M): mass of methoprene at outfall during a runoff event at time t taken from column 15 and multiple by Rr/V_T.

6.4 Model Sensitivity and Calibration

Before modeling, sensitivity analysis is performed to identify the most sensitive parameters and give a general idea of how the model behaves when one variable is changed. The model parameters are varied one at a time over a reasonable range while holding other parameters constant and the relative change in the state variable is determined. The model parameters are K, β_e, and We and state variable is the methoprene concentration. Table 6.2 summarizes the half-lives from the liternature values, as

presented in Table 2.4. The half-life of 30 hrs is chosen or K of 0.555 d^{-1}. Assume the time to peak (Tp) is 2 days, β_e can be estimated by Chapra (1997):

$$Tp = \frac{Ln(\beta_e / K)}{\beta_e - K} \tag{6-20}$$

and β_e of 0.45 d^{-1} is determined. Using the peak methoprene concentration (Cp) from the field monitoring study of S1 catch basin (i.e. 15 μg/L), We can be estimated by Chapra (1997):

$$Cp = \frac{We}{KV}\left(\frac{\beta_e}{K}\right)^{\frac{\beta_e}{K-\beta_e}} \tag{6-21}$$

where V = water sump volume of S1 (L) and We is determined to be 846.70 μg/d based on matching the peak concentration. As indicated in Figures 6.4-6.6, Cp is more sensitive to We and Tp is more sensitive to K and β_e. We is calibrated to match the peak concentration, while K & β_e are calibrated to match the shape of curve, especially the recession part.

Table 6.2: Summary of the range of methoprene half-lives

Literature values*	Range (hr)
Field water	24-48
Pond water	2-45
Surface water	8-63**
Lab (Tap water)	46**
Sewage	60-70

* Summarized by Table 2.4

** Data in Table 2.4 converted to temperature at 20℃ using Arrhenius equation

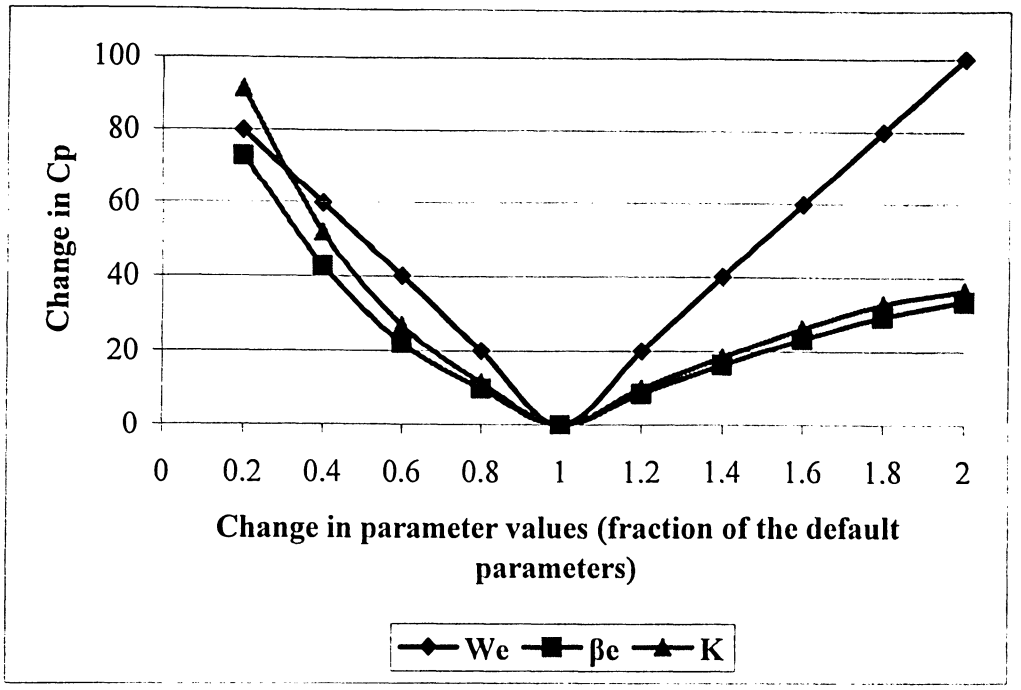


Figure 6.4: Sensitivity analysis (percent change of peak concentration)

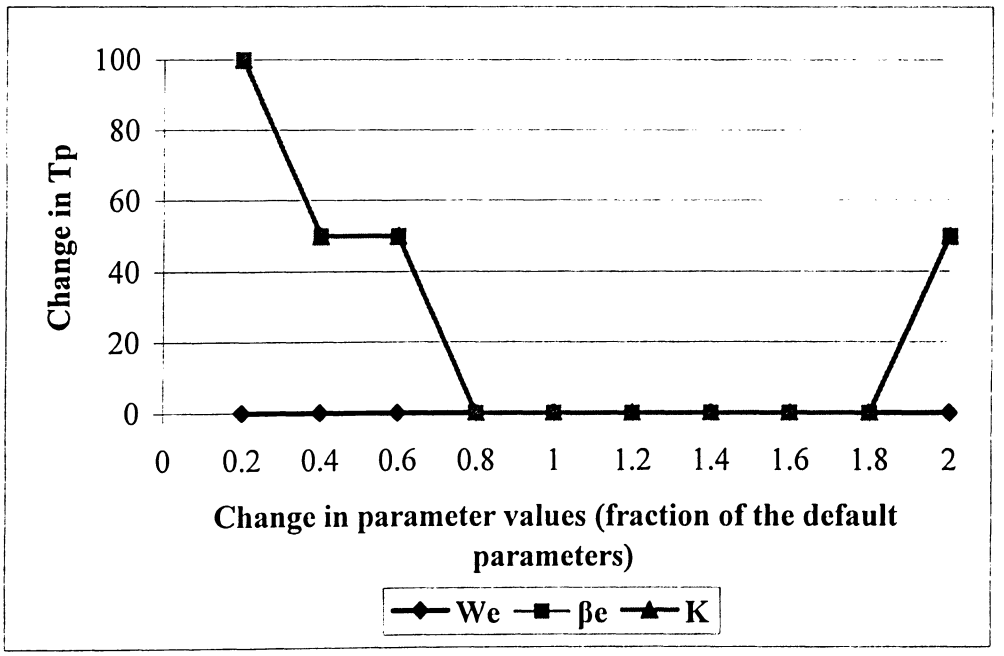


Figure 6.5: Sensitivity analysis (percent change of time to peak)

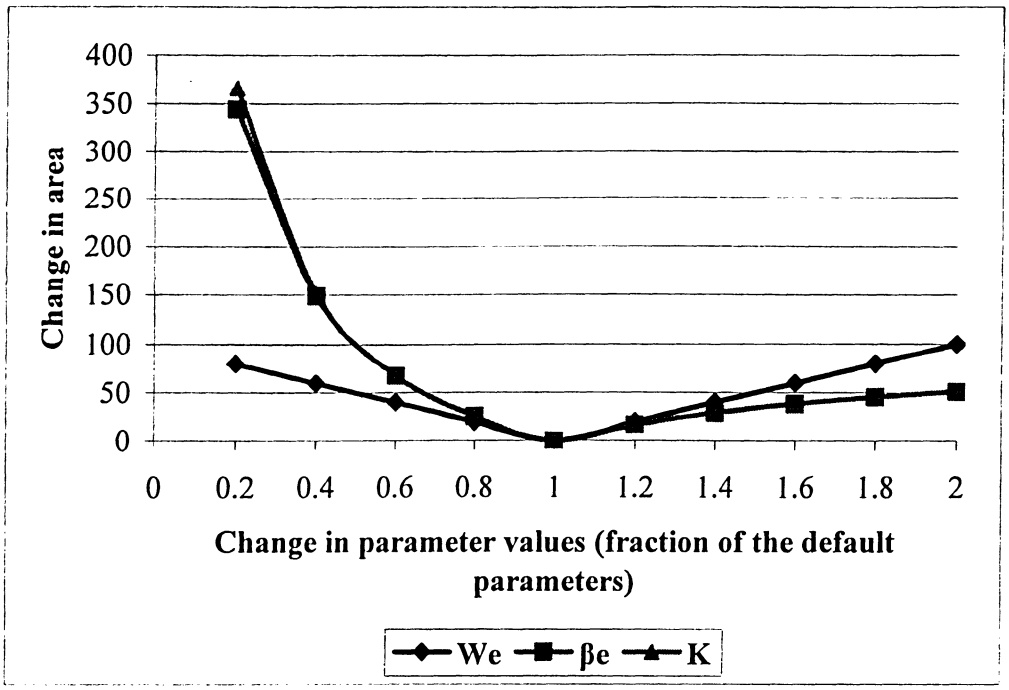


Figure 6.6: Sensitivity analysis (percent change of area under the pollutograph)

The field and laboratory experiment data are used to calibrate the hydrologic model. The 2003 (W1, S1, and S2) data are used to calibrate the residual methoprene concentration released from pellets while the 2004 (S1 and S2) data are used to calibrate the residual methoprene concentration released from ingots. Comparison between the model results and field measurements are based on: percent difference in peak concentration (Cp); time to peak (Tp); area of concentration versus time (%A) and root mean square (RMS) of concentration duration curves, which represent the percent of total time that different levels of concentration are equalled or exceeded. The RMS percent difference is defined as:

$$\text{RMS \% difference} = \sqrt{\frac{\sum_{i=1}^{n}\left(\frac{Cm,i - Cp,i}{Cm,i}\right)^2}{n}} \times 100 \qquad (6\text{-}22)$$

where Cm,i = measured concentration for ith percent of equalled or exceeded; Cp,i = model predicted concentration for ith percent of equalled or exceeded; and n = numbers of data points between measured and model computed concentration. The best of fit is based on minimizing the above percent differences between measured and model predicted values. Sets of parameters are obtained by using the relationship between the parameters and rainfall.

6.5 Model Verification and Application

For verification, a set of calibrated parameters are put into the model and run for the Year of 2004 (W1). There is no data for verification of the ingots as the 2004 data were used for calibration. The 1980 rainfall record, which matches the long-term annual average rainfall, is used to do the "What if" scenario analysis. After the simulation of residual methoprene concentration in individual catch basin, methoprene mass at the Newtonbrook storm sewer outfall is estimated. The flow data of 2003 and 2004 are used to calibrate the runoff coefficients for the catchment. Total predicted methoprene mass for each event at the storm outfall is calculated by the multiplying the methoprene mass discharged from one catch basin with the number of catch basins in the residential area. The measured methoprene mass for one event (EM) is calculated as:

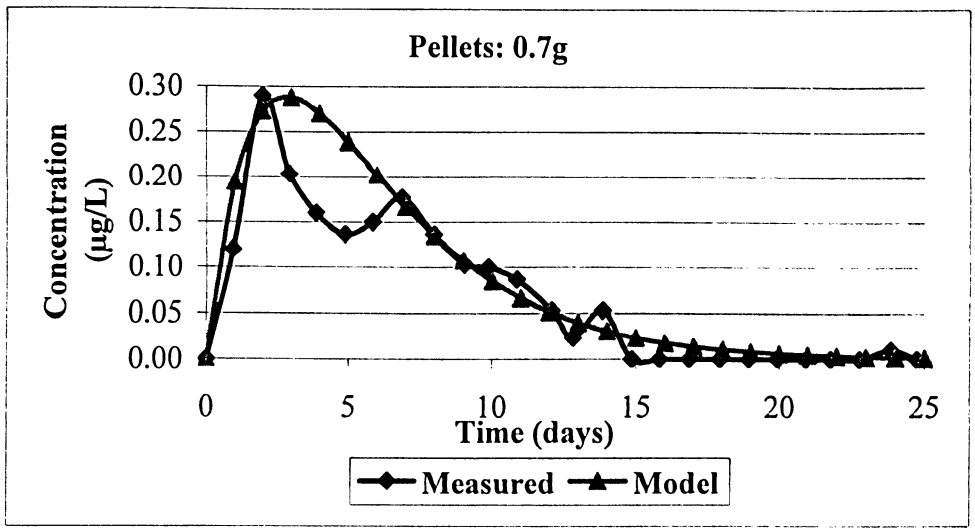
$$EM = \sum (Ci * Qi * \Delta ti) \qquad (6\text{-}23)$$

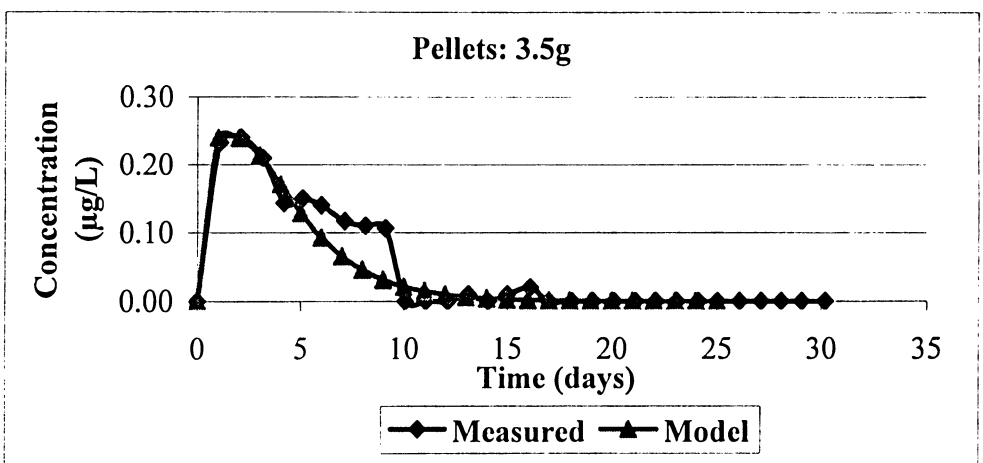
where Ci = concentration of sample at time interval i (μg/L); Qi = flow rate at time interval i (L/s); and Δti = time interval i (min).

6.6 Results and Discussion

6.6.1 Methoprene Pellets

Figures 6.7-6.10 show the measured and simulated values for the laboratory experiments and field studies. It is observed that the model can generally match the peak concentration and the shape of the field measurements. The percent differences between the model and measured values are summarized in the Table 6.3. The model is generally in good agreement with the measured concentrations within ±30%. The best-fit model parameter values are shown in Table 6.4. It is observed from Figure 6.11 that for S1, the model parameter K is more or less the same with the range of 0.416 to 1.666 d^{-1}; We is in the range of 50 to 5000 μg/d and β_e is in the range of 0.29 to 5 d^{-1} with respect to rainfall. There are no general patterns of the three parameters with respect to rainfall amount. It is shown from Table 6.5 that the entire mass release fraction r is much smaller than 1 with range of 0.0014 to 0.047 in the field. By comparing between the field catch basins and laboratory control laboratory, the r values are higher under the quiescent conditions. The catch basin environment (e.g. chemical constituents and adsorption to sediment) may suppress the release of methoprene. It is observed from Figure 6.12 that r decreases with rainfall. In addition, sump water depth could affect methoprene release from pellets. S1 has least amount of water and rain could cause significant disturbance to the pellets, resulting in large release.





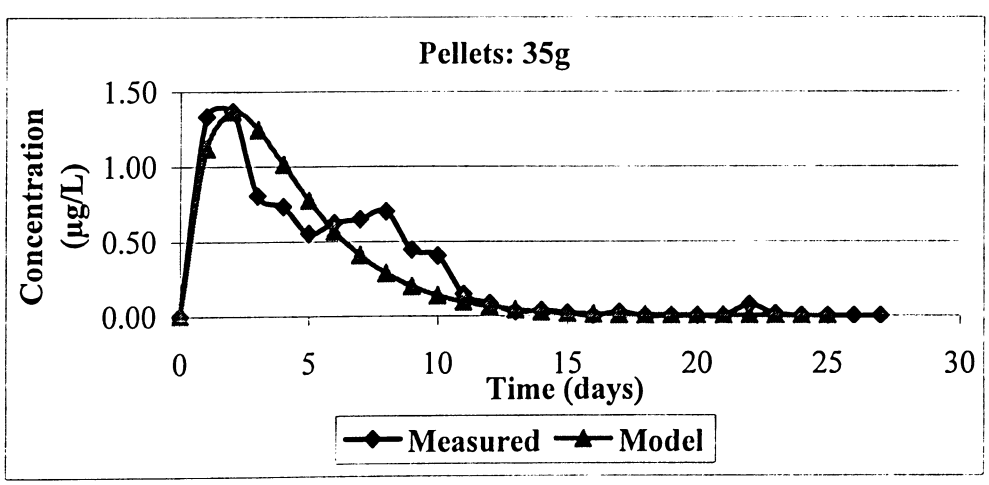
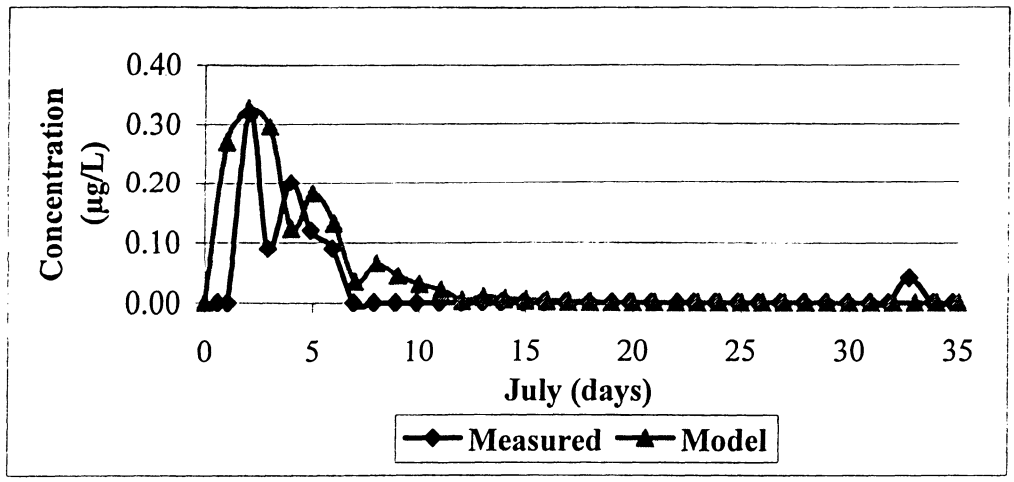
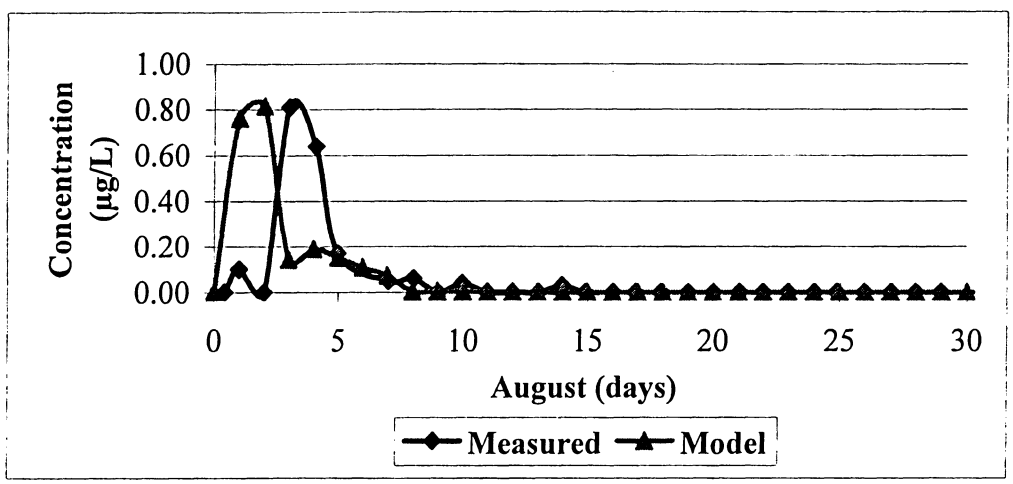


Figure 6.7: Measured and predicted methoprene concentration for Lab experiments (Pellets)





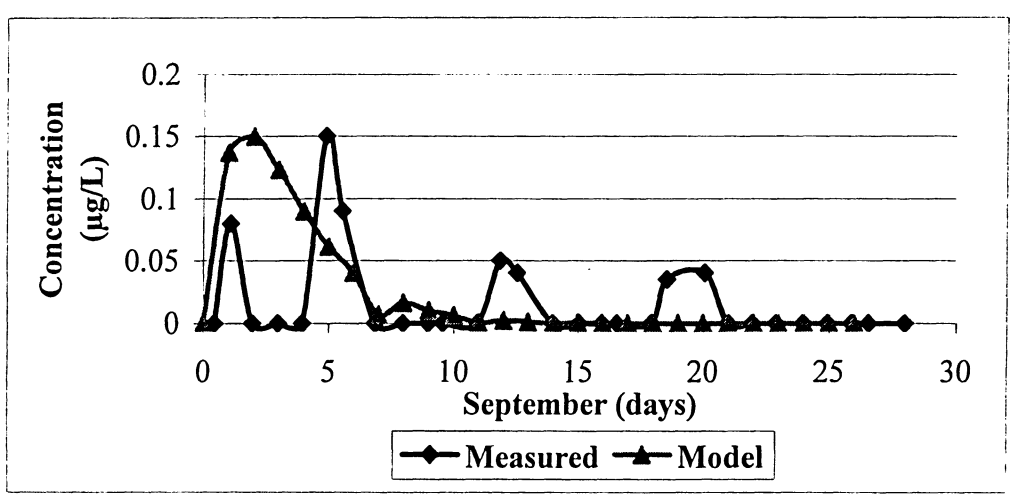


Figure 6.8: Measured and predicted methoprene concentration at W1 (Pellets)

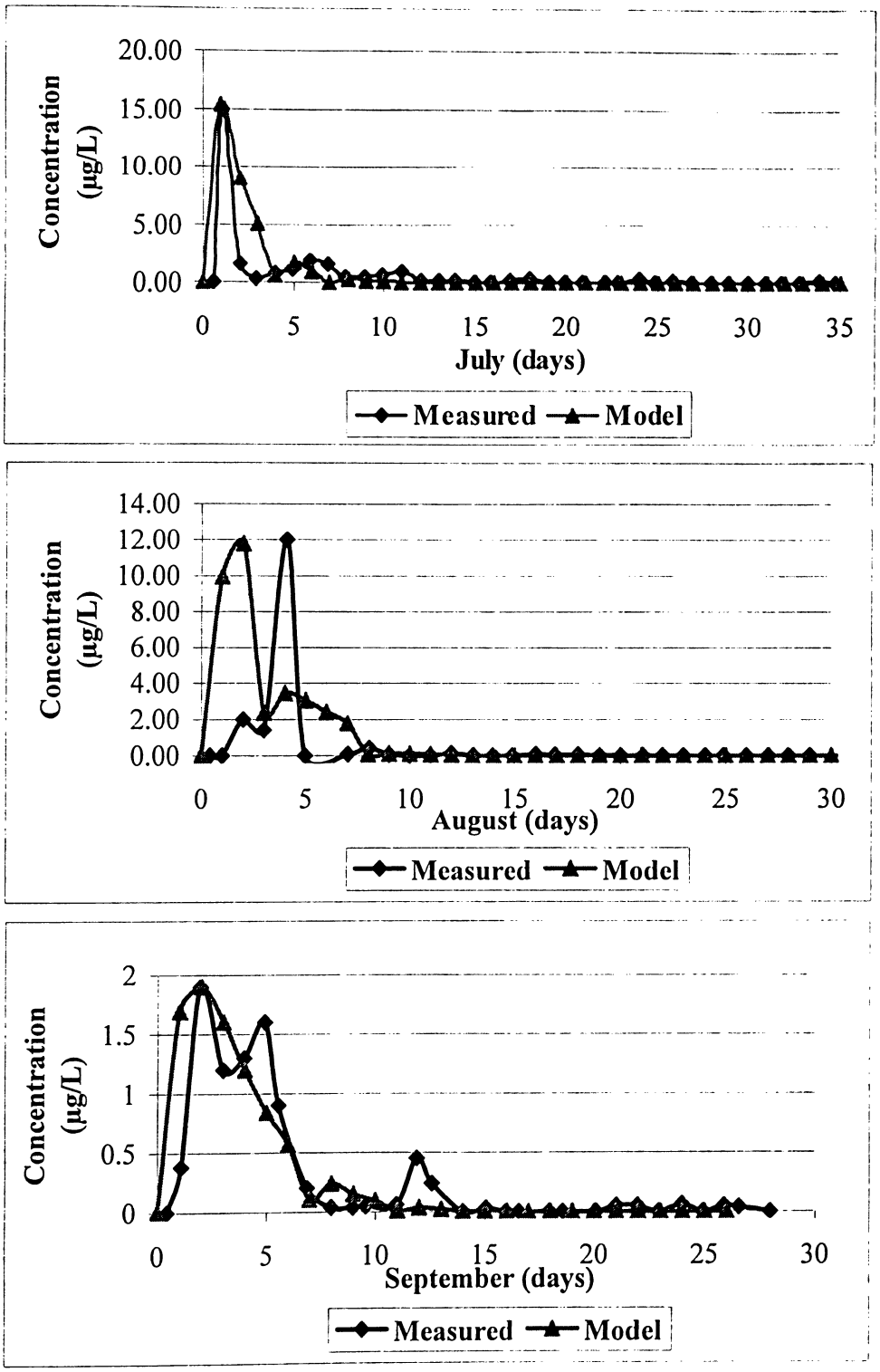
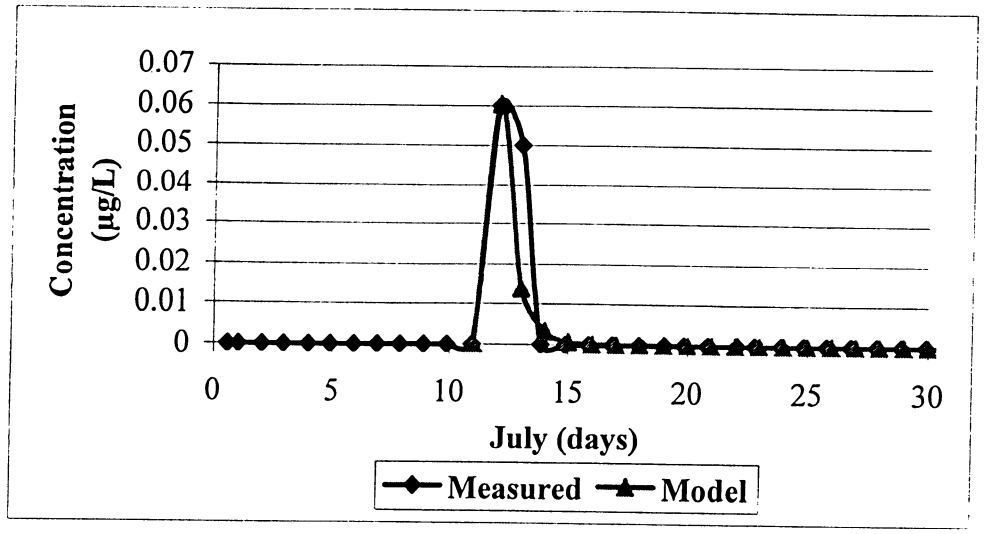
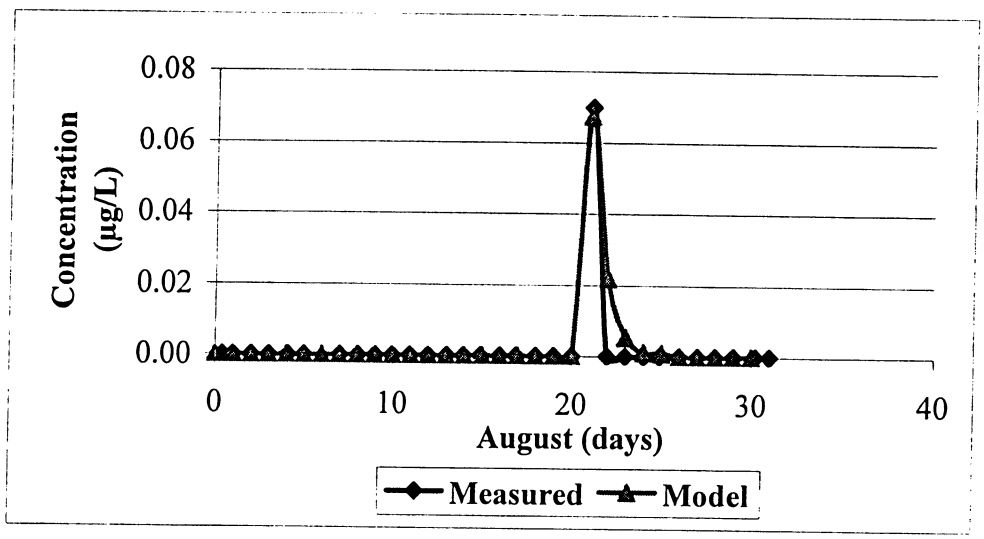


Figure 6.9: Measured and predicted methoprene concentration at S1 (Pellets)





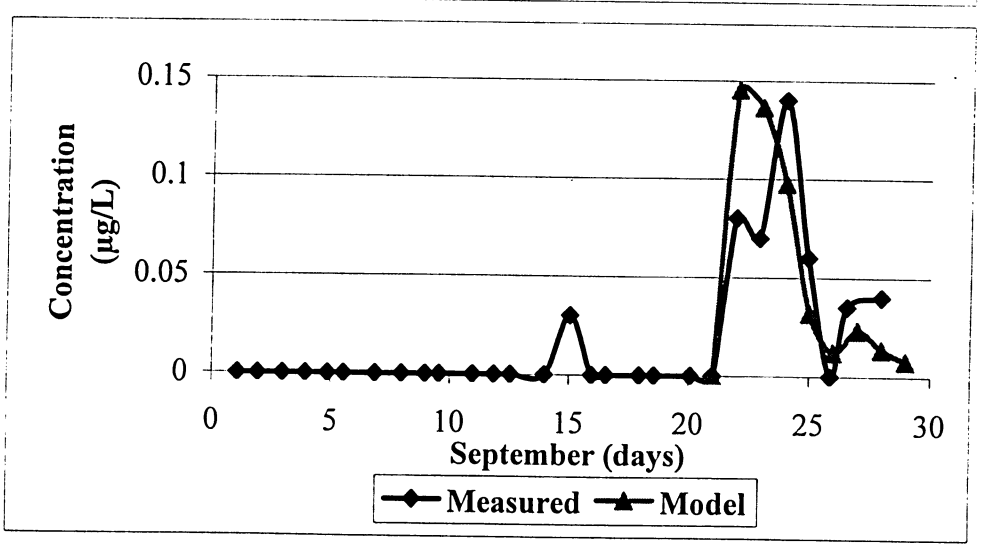


Figure 6.10: Measured and predicted methoprene concentration at S2 (Pellets)

Table 6.3: Comparison of model and measured concentration (Pellets): (a) Laboratory experiments; (b) field catch basin study

(a)

Methoprene pellets (g)	Percent difference			
	Cp[1]	Tp[2]	A[3]	RMS[4]
0.7	0.70	50.75	8.35	19.15
3.5	0.15	52.38	36.45	71.04
35	0.24	2.56	10.62	15.57

(b)

	W1		
Percent difference	July	Aug.	Sept.
Cp	2.19	0.74	0.11
Tp	1.48	33.33	59.10
A	8.31	6.77	38.74
RMS	37.57	26.02	22.91
	S1		
Percent difference	July	Aug.	Sept.
Cp	2.77	1.83	0.17
Tp	4.00	51.10	2.56
A	49.96	111.34	2.30
RMS	359.90	72.96	98.40
	S2		
Percent difference	July	Aug.	Sept.
Cp	0.75	3.45	3.80
Tp	0.17	0.21	8.24
A	26.63	40.95	1.45
RMS	50.00	13.56	35.15

Note: [1] Peak concentration
[2] Time to peak
[3] Area of concentration versus time
[4] Root mean square of concentration duration curves

Table 6.4: Best fit model parameters for (a) Lab. experiments; (b) W1; (c) S1; (d) S2

(a)

	Methoprene pellets (g)		
Best-fit parameters	0.7	3.5	35
We (µg/d)	70.44	86.99	473.13
β_e (d^{-1})	0.29	0.64	0.59
K (d^{-1})	0.42	0.42	0.42

(b)

W1	Year 2003		
Best-fit parameters	July	Aug.	Sept.
We (µg/d)	50.00	160.00	28.00
β_e (d^{-1})	0.45	0.70	0.65
K (d^{-1})	0.56	0.56	0.56

(c)

S1	Year 2003		
Best-fit parameters	July	Aug.	Sept.
We (µg/d)	5000.00	700.00	125.00
β_e (d^{-1})	5.00	0.50	0.60
K (d^{-1})	0.56	0.56	0.56

(d)

S2	Year 2003		
Best-fit parameters	July	Aug.	Sept.
We (µg/d)	100.00	160.00	120.00
β_e (d^{-1})	2.00	2.00	1.00
K (d^{-1})	1.66	1.66	0.56

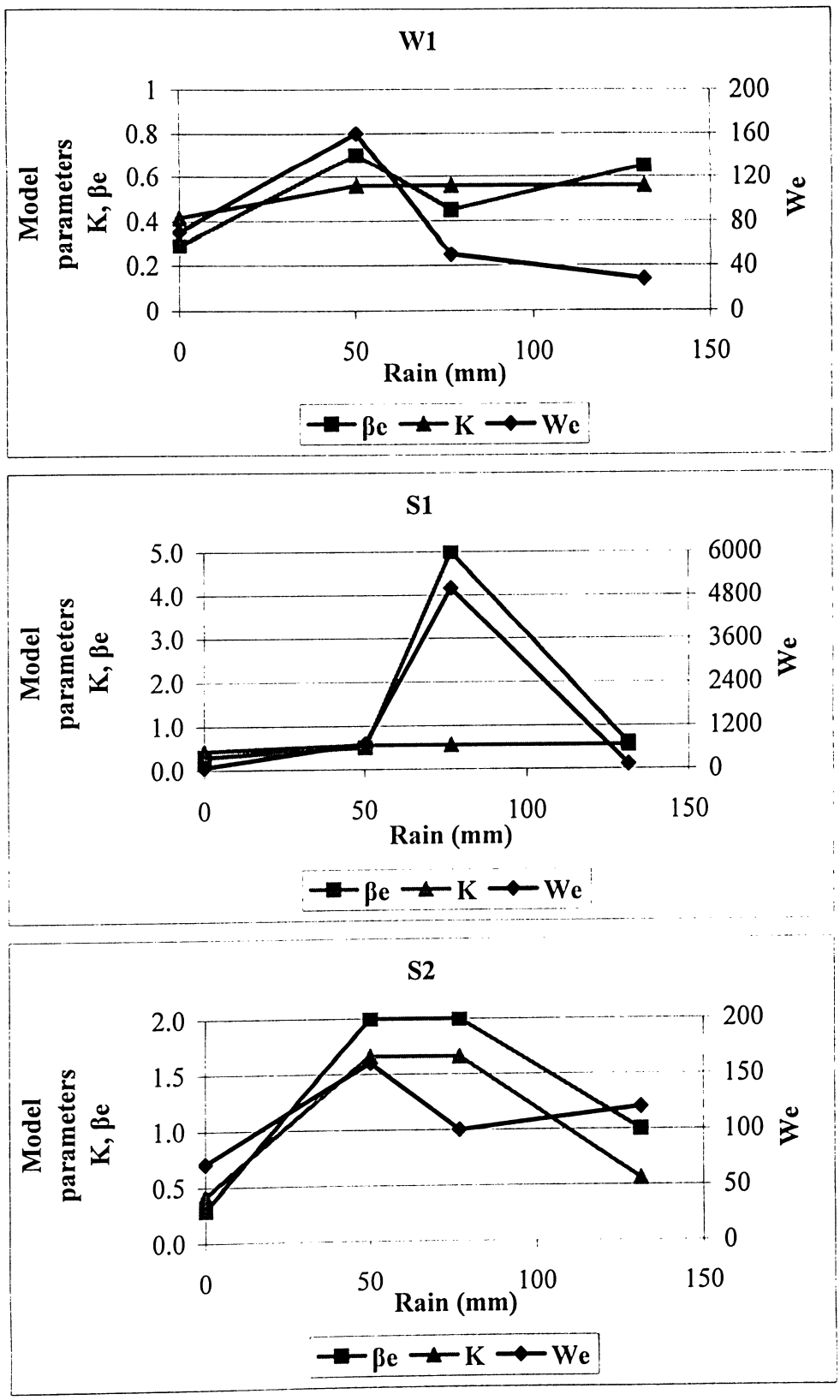


Figure 6.11: Model parameters with rain (Pellets)

Table 6.5: r values (Pellets)

r (Field catch basin study)	Year 2003		
	July	August	September
W1	0.0037	0.0077	0.0014
S1	0.034	0.047	0.0070
S2	0.0017	0.0014	0.0040
r (Laboratory experiments)	Methoprene pellets (g)		
Water level (mm)	0.7	3.5	35
900	0.0082	0.00091	0.00054
450	0.07	-	-

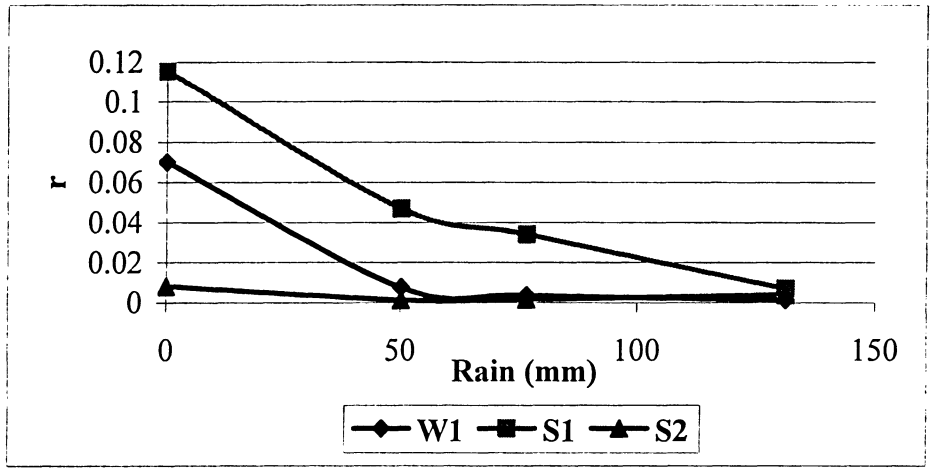


Figure 6.12: Relationship between r and rain for pellets

A set of parameters (0.56 d^{-1}, 43.55 μg/d, and 0.51 d^{-1} for K, We, and β_e, respectively) is chosen from Figure 6.11, based on the rainfall amount of 92.8 mm in 2004's summer in verification of the model. There are three missing methoprene concentration measurements in the first three days. Therefore, it is hard to make any conclusion of the model verification, shown in Figure 6.13. There are two peaks after 21 days of application, as shown in Figure 6.13. The reason may be the release of

methoprene caused by rainfall. The 1980 rainfall data are used for scenario analysis, as the 1980 is considered to be a typical rainfall year in Toronto. The sets of parameters for S1 and S2 simulations are chosen based on the monthly rainfall in 1980, as shown in Table 6.6. The model predicts the residual methoprene concentration over 1980 summer months in Figures 6.14 and 6.15. As the range of lethal concentration for Culex mosquito is 0.3 μg/L and 2.3 μg/L. For S1, there are 7 days (or 20% of 35 days) in July, 13 days (43% of 30 days) in August and 7 days (23% of 30 days) in September in which the residual methoprene concentrations exceed 0.3 μg/L. As indicated in Figure 6.16, there are 0 days in July, 7 days in August (25% of 30 days) and 4 days in September (13% of 30 days) in which the residual methoprene concentrations exceed 2.3 μg/L. For S2, there is none of days in which the residual concentrations exceed 0.3 μg/L, except in July that there are 5 days (or 14% of 35 days) in which the residual concentrations exceed 0.3 μg/L. It can be concluded that the sump water depth could dilute the residual methoprene concentration.

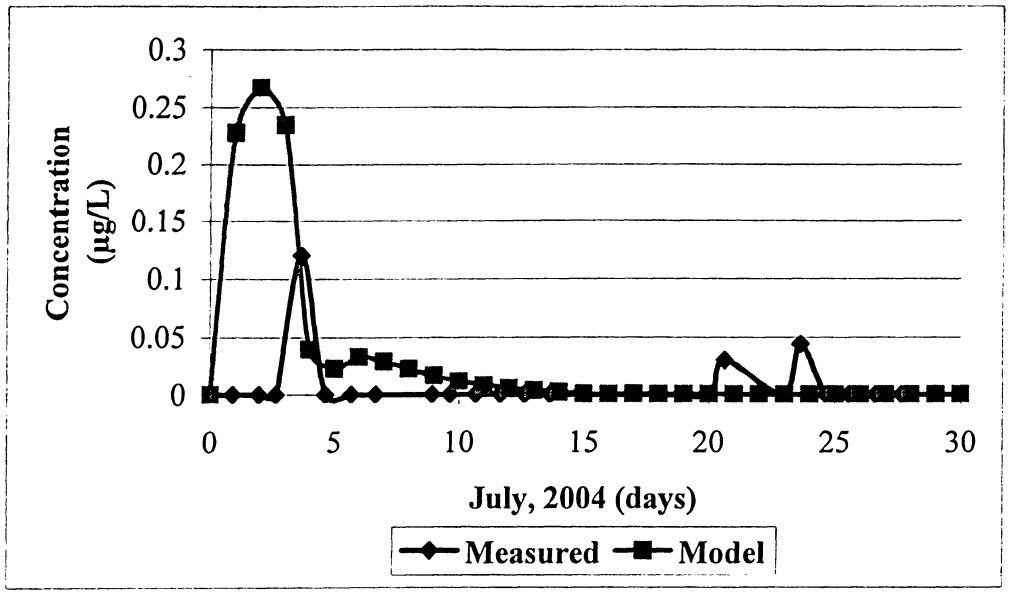
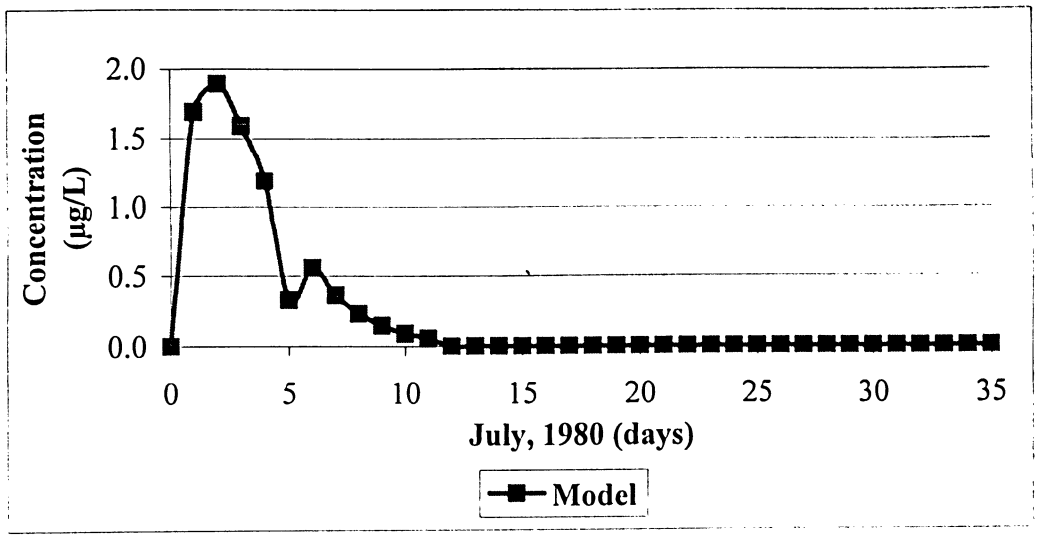
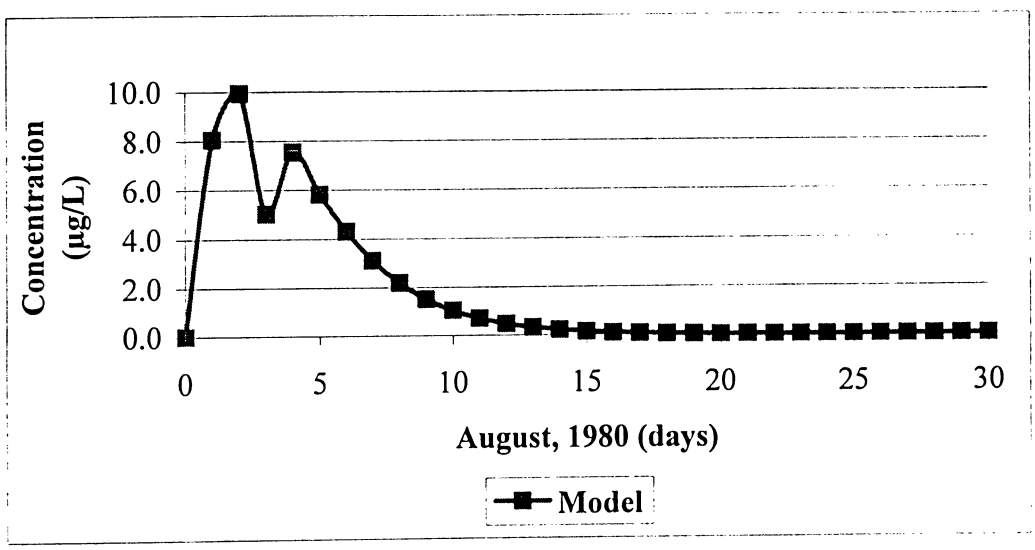


Figure 6.13: Measured and predicted methoprene concentration at W1 (for verification)

Table 6.6: Model parameters for the 1980 analysis

Year 1980	Rainfall (mm)	Model parameters (S1)		
		We (µg/d)	β_e (d^{-1})	K (d^{-1})
July	179.30	125.00	0.60	0.56
Aug.	37.6	541.98	0.45	0.52
Sept.	77.7	4919.64	4.93	0.56
		Model parameters (S2)		
July	179.30	137.55	0.12	0.56
Aug.	37.6	137.52	1.57	1.35
Sept.	77.7	100.33	1.98	1.64





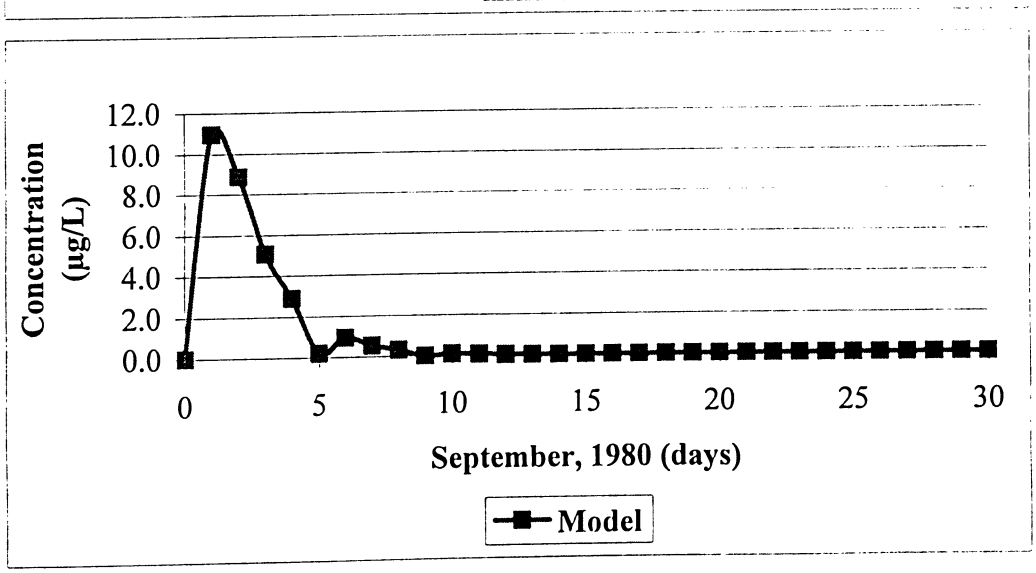
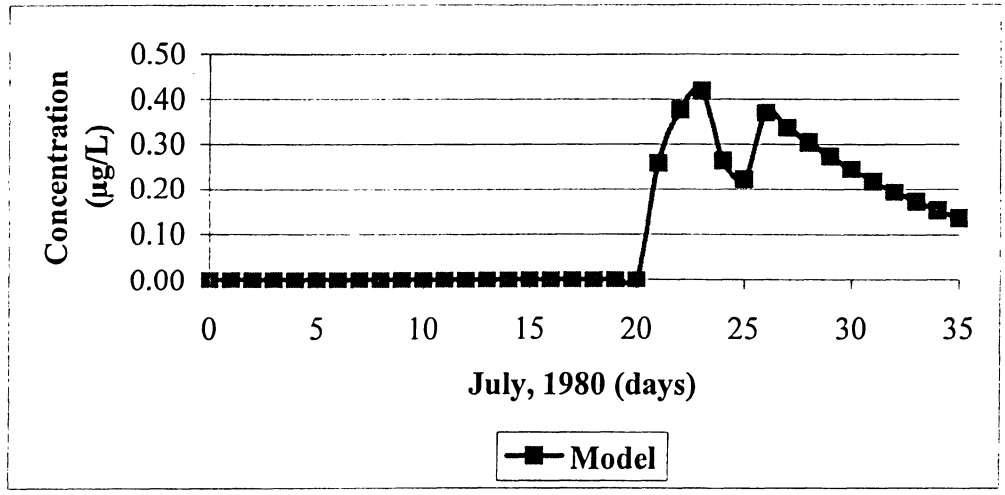
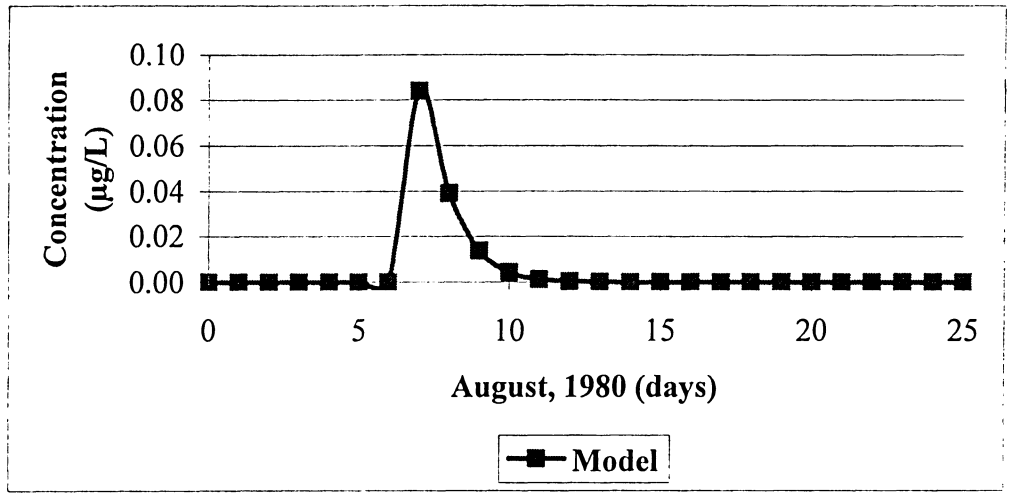


Figure 6.14: Predicted methoprene concentration in 1980 (S1)





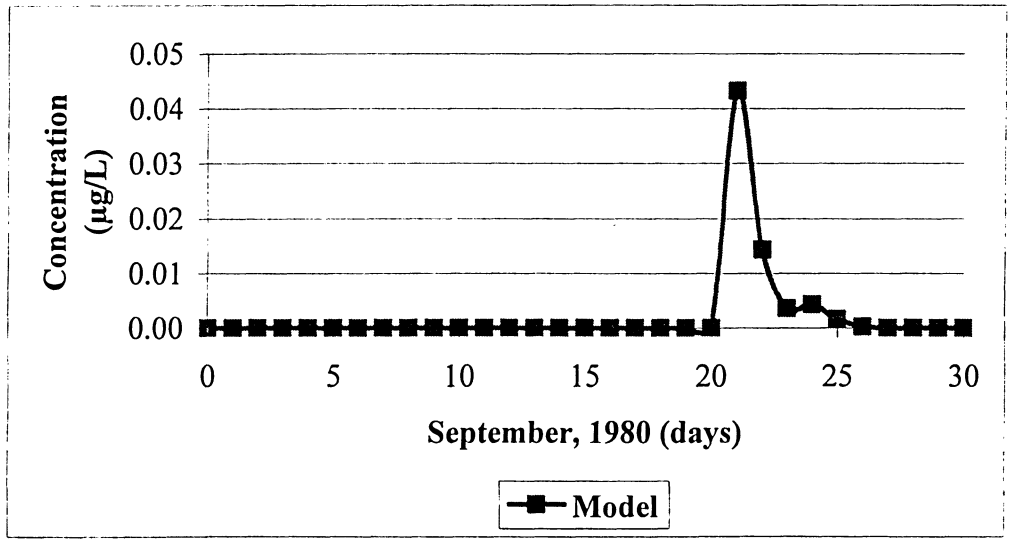


Figure 6.15: Predicted methoprene concentration in 1980 (S2)

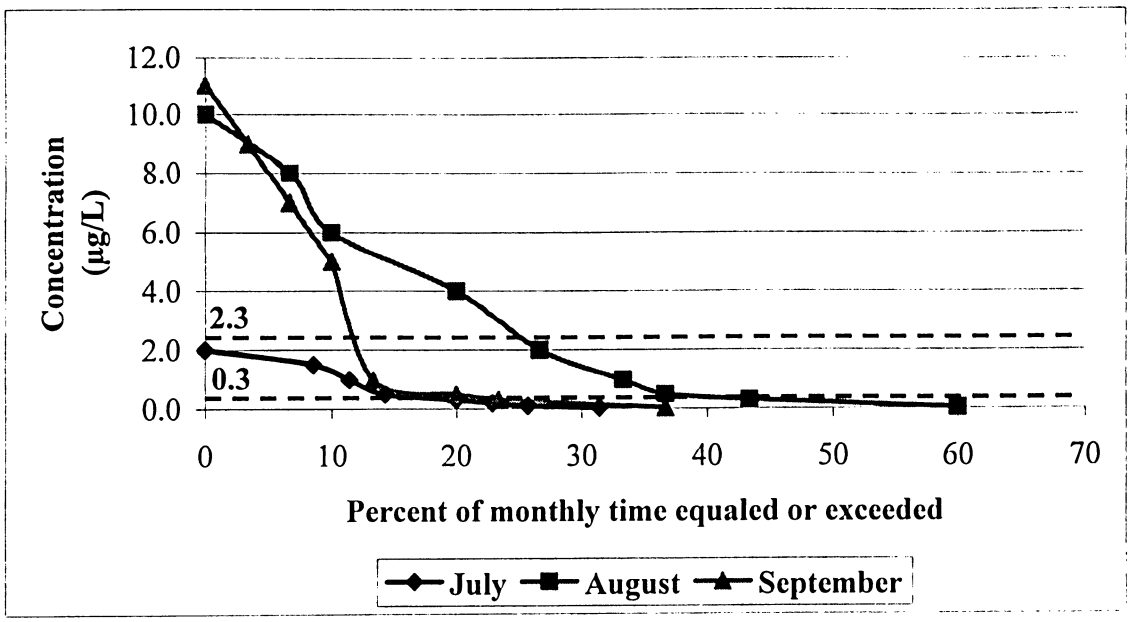


Figure 6.16: Concentration duration curves for S1 (Pellets)

A sensitivity analysis is performed to analyze the sensitivity of calibrated parameters on the model outputs. The large variation of model results is a combination of the overestimation of the We and underestimation of K and β_e parameters, as demonstrated in Table 6.7.

Table 6.7: Sensitivity on calibrated parameters

Case	% difference			
	Cp	Tp	A	≥ 0.3 μg/L*
July (1980)				
We: +50% β_e : -50% K : -50%	+ 201.06	+ 50	+ 418.63	+ 57.15
We: -50% β_e : +50% K : +50%	- 66.67	- 50	- 77.45	- 57.15
August (1980)				
We: +50% β_e : -50% K : -50%	+ 197.08	+ 100	+ 491.89	+ 92.31
We: -50% β_e : +50% K : +50%	- 68.18	- 50	- 77.80	- 53.84
September (1980)				
We: +50% β_e : -50% K : -50%	+ 318.89	+ 100	+ 550.77	+ 128.59
We: -50% β_e : +50% K : +50%	- 68.80	0	- 78.98	- 42.86

* Percent of days that residual methoprene concentrations exceed 0.3 μg/L

The first part of outfall simulation is the calibration of catchment hydrologic parameters. By plotting the measured runoff against rainfall, the Cv and S_d were determined from the slope and intercept of the graphs. Table 6.8 shows the results of the parameters for 2003 and 2004. Based on the land-use information of the Newtonbrook watershed, 77% of the total watershed area is residential uses. However, the small Cv is typical for the suburban residential areas with Cv of 0.25 (Brodie, 1987). According to the field staff of City of Toronto, the flow area at the outfall was calculated based on a circular pipe instead of the elliptic shape. This assumption may underestimate the flow

rate measured during the monitoring periods. In addition, rainfall variability may be another reason. Typical Cv parameters are chosen as 0.6, 0.6, 0.1 and 0.4 for institutional, commercial, park or recreational and urban residential land use area, respectively (Brodie, 1987). Methoprene mass at the sewer outfall for two rain events obtained from 2003 and 2004 are compared to the model output, as shown in Table 6.9. Model values are different from the measured values by average of 29%. The model event concentrations of methoprene for August 16 and July 19 are 0.033 and 0.072 μg/L, respectively, which is calculated by dividing the methoprene mass from model to the event runoff volume. The outfall methoprene concentrations are smaller than the recommended interim provincial water quality objective for non-target species of 0.2 μg/L.

Table 6.8: Catchment parameters

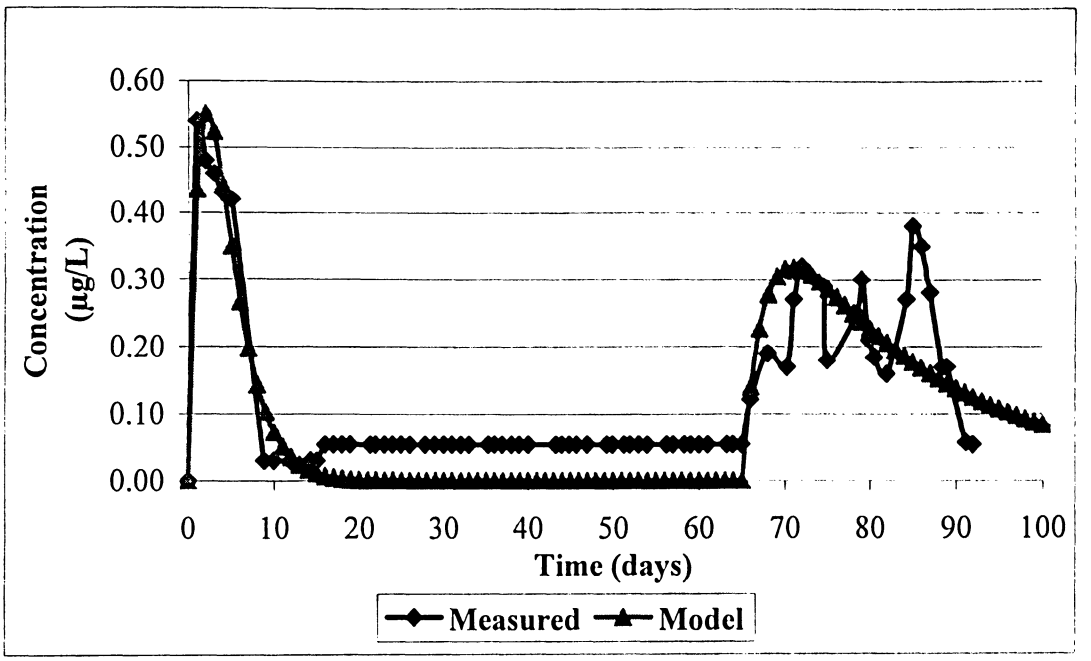
	Parameters		
Year	Cv	Sd (mm)	R^2
2003	0.19	2.25	0.91
2004	0.06	2.23	0.87

Table 6.9: Mass of methoprene discharged at outfall

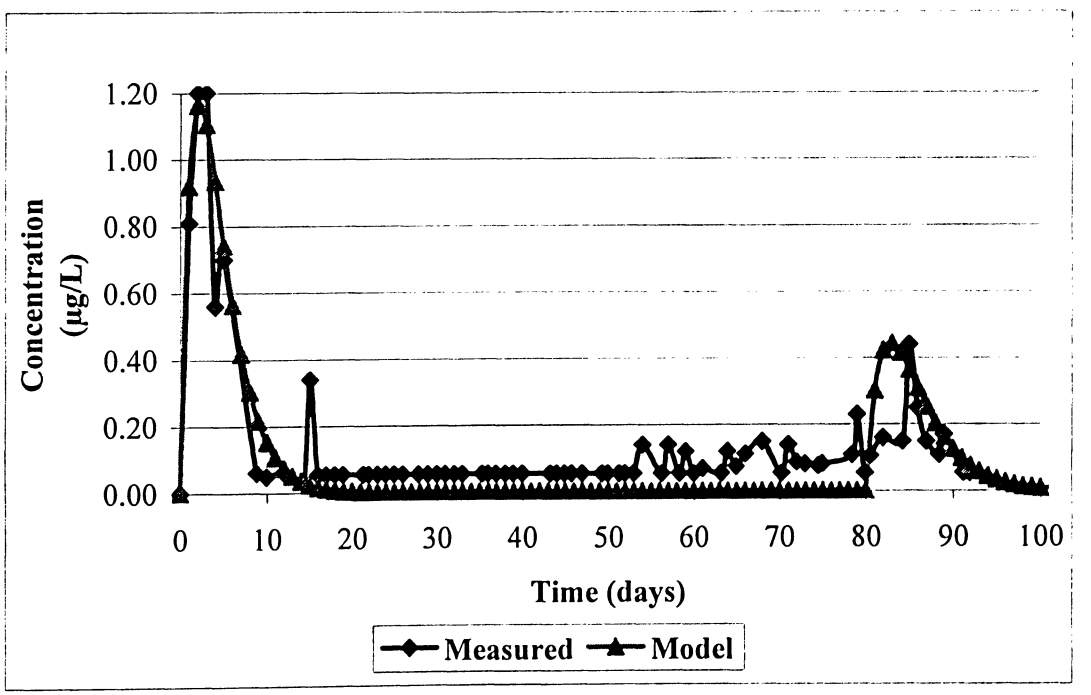
Rain event	EM (μg)	Model (μg)	Percent difference (%)
Aug 16, 2003	100047	82957	17
Jul 19, 2004	189103	266188	41

6.6.2 Methoprene Ingots

Figures 6.17-6.19 show the measured and modelled concentration of methoprene values for the laboratory experiments and field study using methoprene ingot. There are multiple concentration peaks, possibly due to the rain effect. In order to simulate the laboratory and field measurements, methoprene masses are assumed to be released again at certain days. The release time is defined as the time between the beginning of the rain storm and the next methoprene mass released. It should be noticed that first release always begins at t = 0 and the second as well as subsequent releases are illustrated in Figures 6.18 and 6.19. The percent differences between the model and measured values are summarized in Table 6.10 and the best-fit model parameter values for each release are shown in Table 6.11. The model is considered accepted by the author because the majority of the four percent differences are within ±30%. It is shown from Figure 6.20 that there seems to be a minimum and maximum rain to create the release of methoprene mass in S1. This statement needs to be verified by more experiments.



(a)



(b)

Figure 6.17: Measured and predicted methoprene concentration for lab. experiments (Ingot): (a) 900 mm; (b) 450 mm

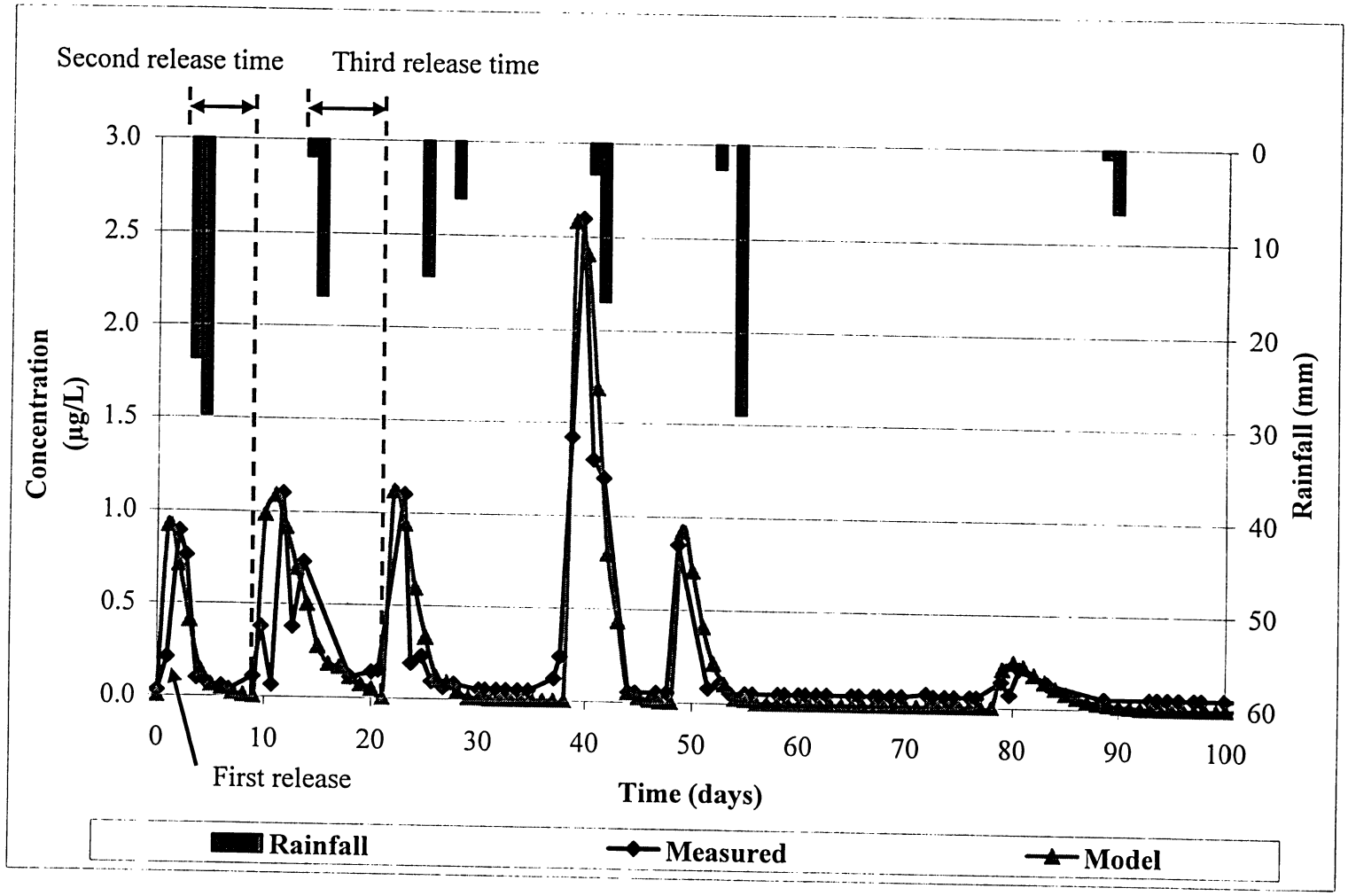


Figure 6.18: Measured and predicted methoprene concentration at S1 (Ingot)

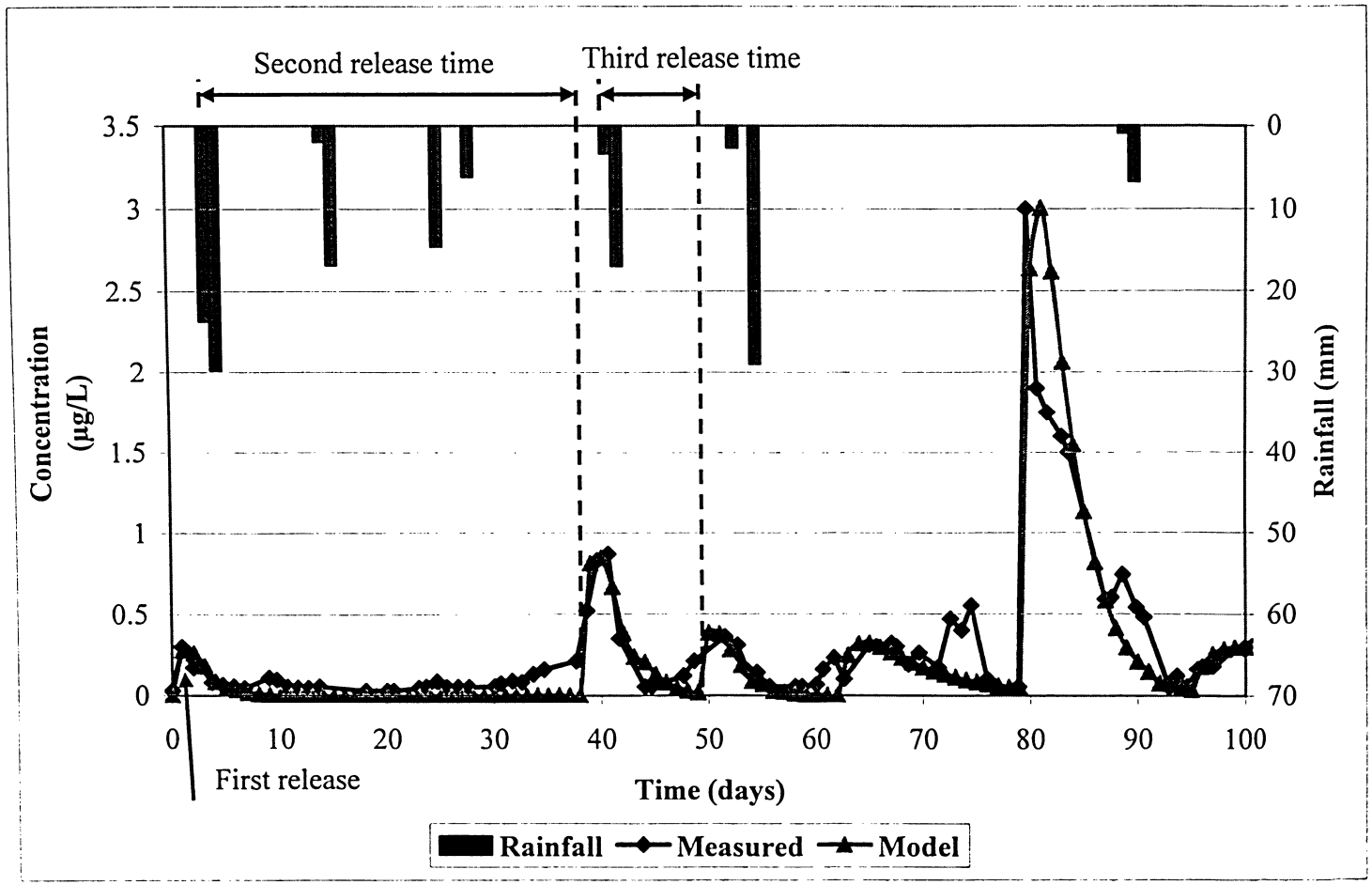


Figure 6.19: Measured and predicted methoprene concentration at S2 (Ingot)

Table 6.10: Comparison of model and measured concentration (Ingot)

Water level (mm)		
Percent difference (Laboratory expts)	450	900
Cp	2.92	2.03
Tp	1.48	98
A	21.01	21.66
RMS	33.54	29.34
Percent difference (Field catch basins)	S1	S2
Cp	5.3	3.95
Tp	10.36	3.23
A	3.69	11.75
RMS	34.18	27.33

Table 6.11: Best fit model parameters (Ingot) for
(a) laboratory experiments; (b) S1 and S2 field catch basins

(a)

Water level (mm)	900		450	
Best-fit parameters	First release	Second release	First release	Second release
We (μg/d)	175	45	185	55
β_e (d^{-1})	0.5	0.05	0.5	0.30
K (d^{-1})	0.42	0.42	0.42	0.42

(b)

S1 (July-Oct.)						
Best-fit parameters	First release	Second release	Third release	Fourth release	Fifth release	Sixth release
We (μg/d)	100.00	75.00	110.00	230.00	100.00	15.00
β_e (d^{-1})	1.10	0.40	0.90	0.70	1.10	0.30
K (d^{-1})	0.83	0.83	0.83	0.83	0.83	0.83
S2 (July-Oct)						
Best-fit parameters	First release	Second release	Third release	Fourth release	Fifth release	Sixth release
We (μg/d)	230.00	600.00	300.00	150.00	1800.00	100.00
β_e (d^{-1})	0.70	0.50	0.60	0.15	0.35	0.01
K (d^{-1})	0.83	0.83	0.83	0.83	0.83	0.83

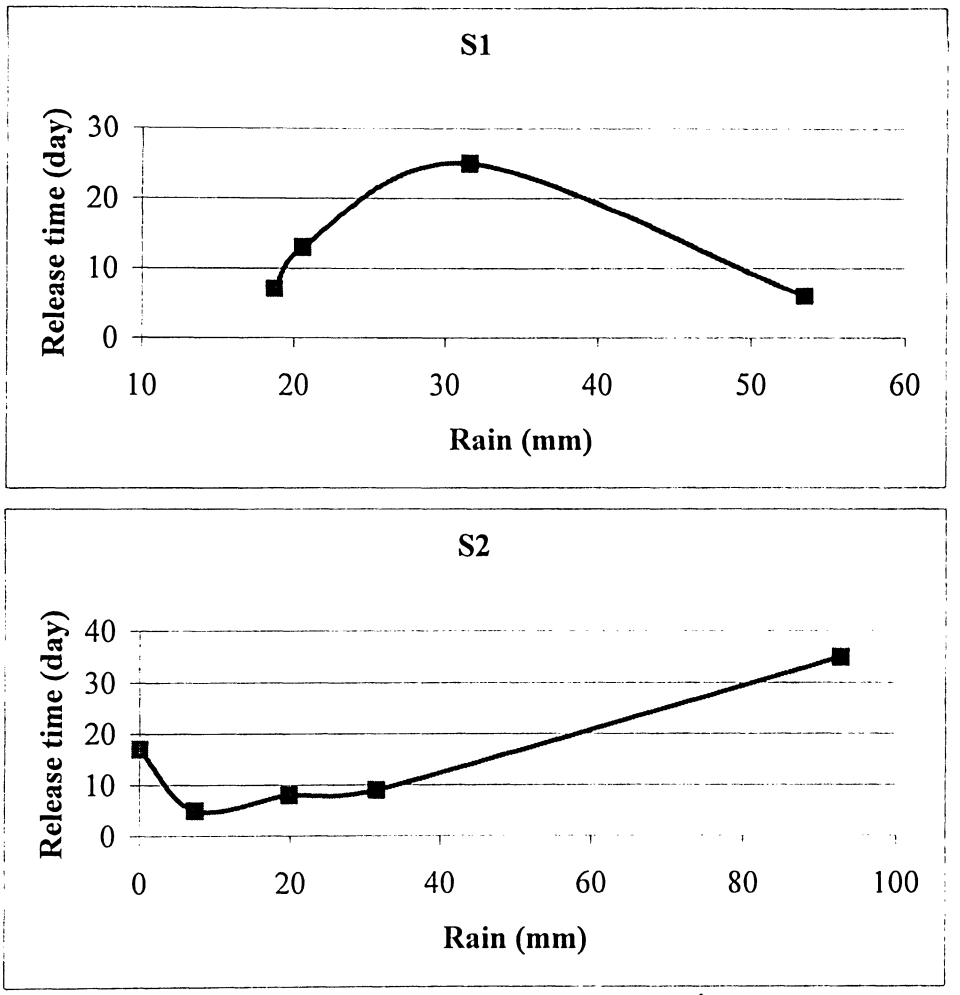


Figure 6.20: Determination of release time

The 1980 rainfall data is used for scenario analysis. Sets of parameters and release times for S1 are chosen from Figures 6.20 and 6.21, based on the rainfall data. Four rain events can create the release of methoprene, as shown in Figure 6.22 and Table 6.12. The maximum residual methoprene concentration is 0.92 μg/L and continues to release up to three months. The concentration duration curve from Figure 6.23 shows that only 12% of the three months (or 11 days) that residual methoprene concentrations are above the

minimum lethal concentration of 0.3 μg/L and the methoprene concentrations never exceed the upper bound of lethal concentration of 2.3 μg/L. Table 6.13 shows the combination effect of parameters on the sensitivity of model results. The large variation of model results is the combination of the overestimation of the We and underestimation of K and β_e parameters.

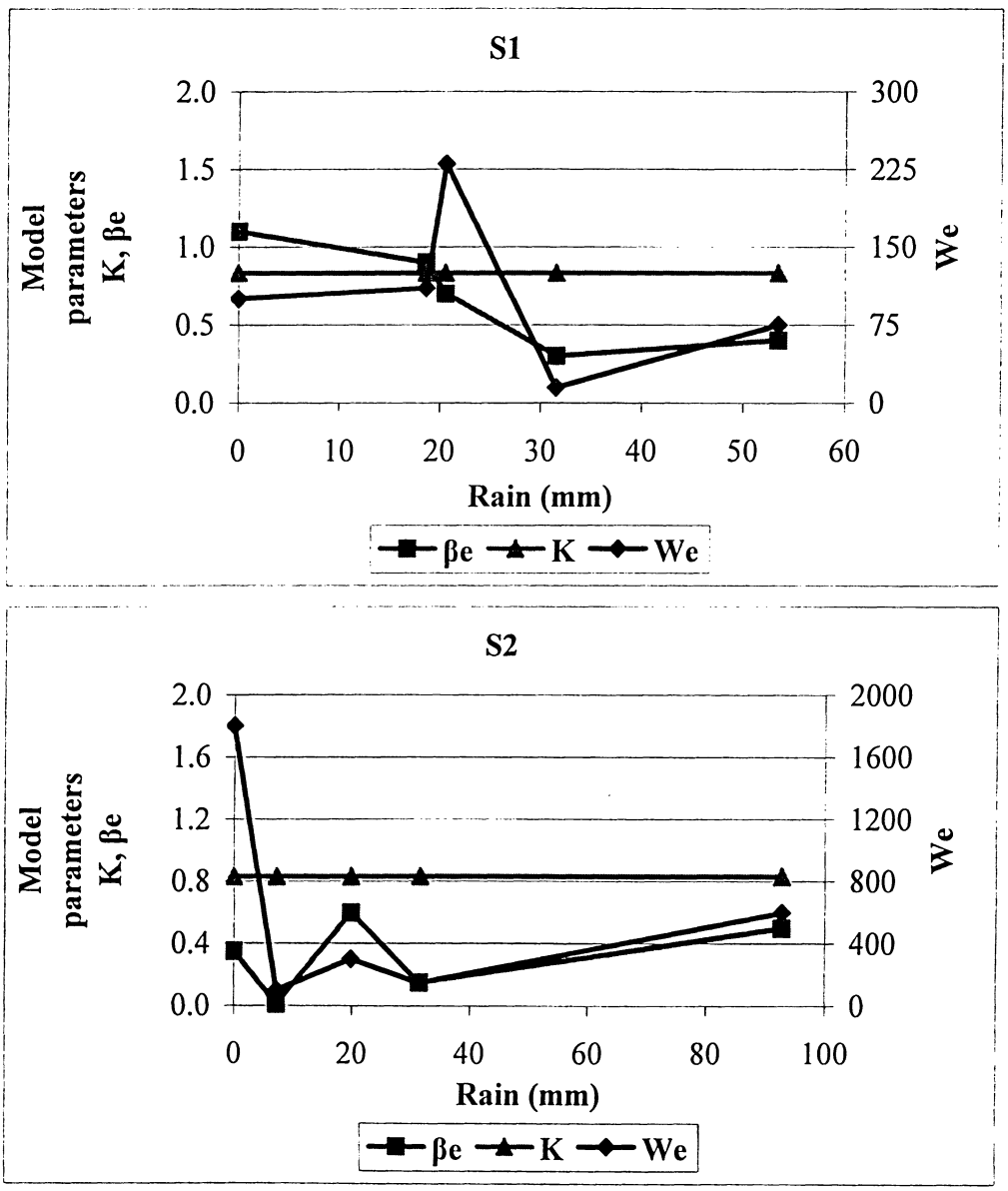


Figure 6.21: Model parameters with rain (Ingot)

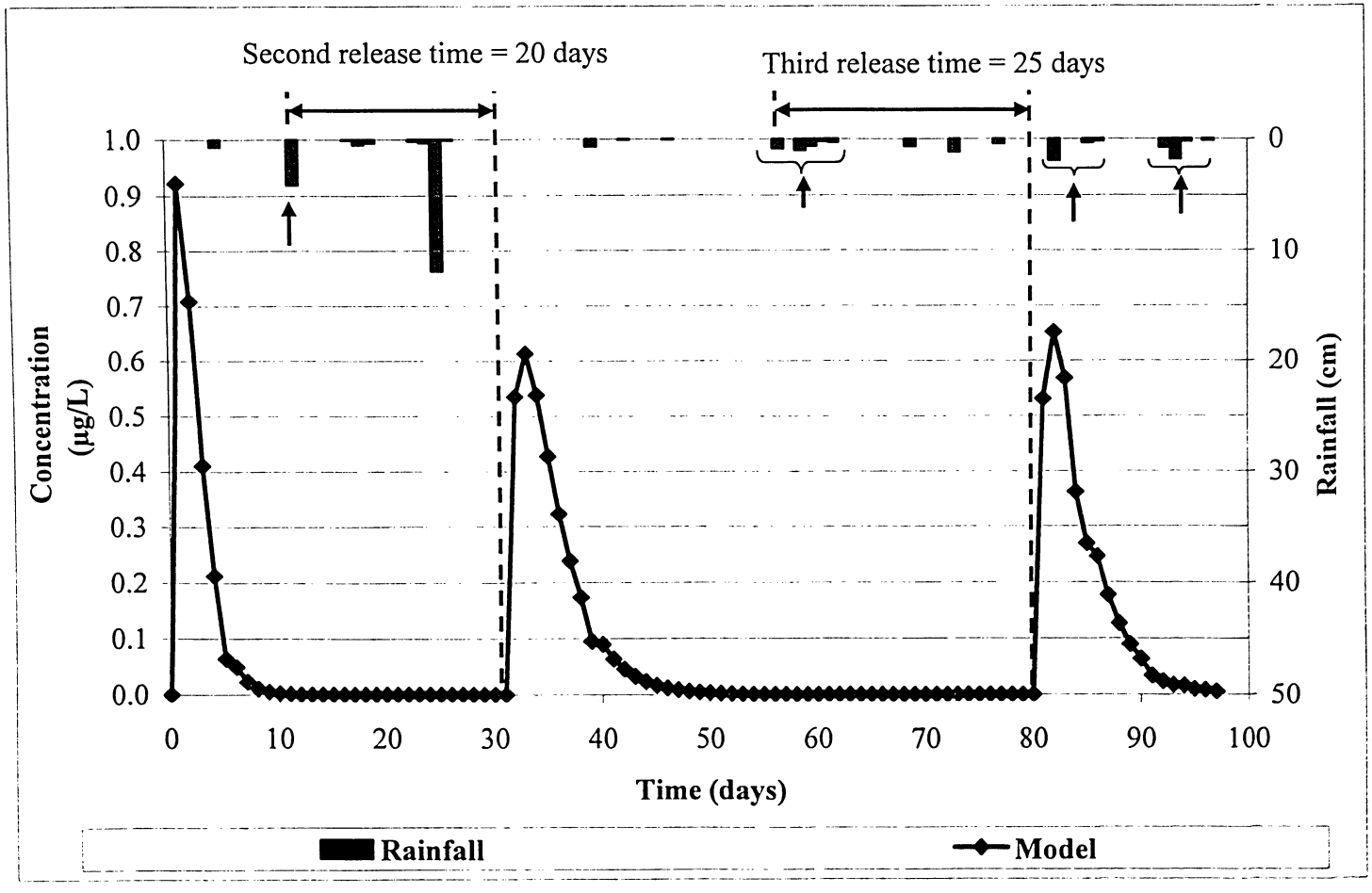


Figure 6.22: Model scenario of 1980 rainfall record (Ingot)

Table 6.12: Model parameters for each new release

Release	Rainfall (mm)	Release time (Day)	We (µg/d)	β_e (d^{-1})	K (d^{-1})
First	-	0	100.00	1.10	0.83
Second	40.5	20	39.38	0.34	0.83
Third	30.2	25	42.36	0.35	0.83
Fourth	24.8	20	147.91	0.55	0.83
Fifth	29.9	25	48.23	0.36	0.83

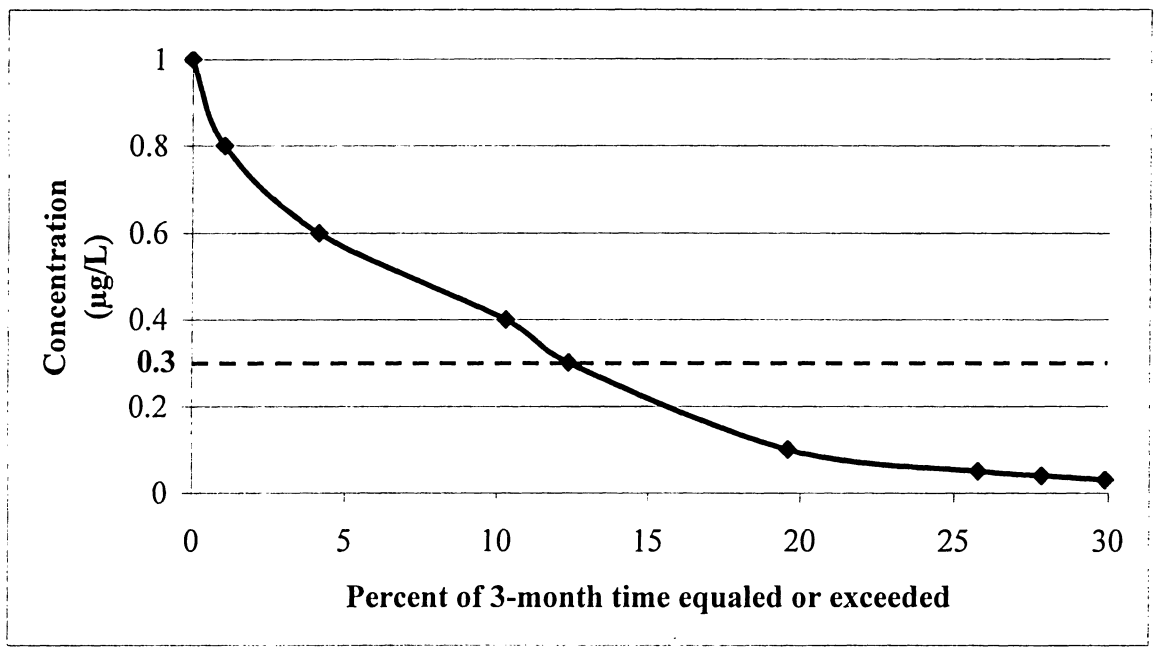


Figure 6.23: Concentration duration curve (Ingot)

Table 6.13: Sensitivity on calibrated parameters

Case	% difference			
	Cp	Tp	A	≥ 0.3 μg/L*
We: +50% β_e : -50% K : -50%	+ 198.91	+ 100	+ 434.50	+ 225.06
We: -50% β_e : +50% K : +50%	- 68.48	0	- 77.23	- 100

* Percent of days that residual methoprene concentrations, which are exceeded or equalled 0.3 μg/L

It is shown from Table 6.14 that the r is much less than 1. By comparing the r value of S2 field catch basin and 900 mm model catch basin, it is noted that ingot applied in field has high r or total available methoprene mass for release than in quiescent condition. When compared between pellets and ingot in quiescent state, in general, pellets release more methoprene mass than ingots for 450 mm water depth. The field and laboratory study indicate that the more water in the catch basin, the larger the release of more methoprene.

Table 6.14: r values (Ingot)

Laboratory experiments	Total r
900 mm	1.17×10^{-3}
450 mm	5.85×10^{-4}
Field experiments	
S1	9.19×10^{-4}
S2	9.05×10^{-3}

Chapter 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

As West Nile Virus has become a public health concern in North America, the mosquito larviciding programs have been initiated in many jurisdictions to reduce the likelihood of human infection of the virus. The City of Toronto has applied methoprene pellets in roadside catch basins since the outbreak of the virus in 2002. The potential flushing of the small larviciding pellets after heavy rainfall should be considered when developing a larviciding program.

Based on the field monitoring study, the residual concentration for pellets in the three study catch basins can provide 0 to 12 days protection with concentration above the minimum lethal concentration. For methoprene ingot, the numbers of days in which the residual concentrations exceed the minimum lethal concentration ranges from 12 to 25 days of the summer larvicidng periods. Multiple peaks of methoprene concentration indicate that flushing, dilution, degradation and dissolution could be factors affecting the concentration of methoprene over time in catch basins. It is concluded from the field study that there may be some difficulty of maintaining the minimum lethal concentration of 0.3 μg/L over the larviciding period at catch basins, which are either half-cleaned or completely cleaned. Dilution due to rainfalls or sump water volume may be the reasons to account for the difficulty. The sustained release pellet formulation examined in this study did not release methoprene, at Newtonbrook sewer outfall during rain events, at a concentration larger than the lethal environmental concentration of 10 μg/L as recommended by USEPA and IPWQO of 0.2 μg/L.

The grain-size of sediment found in one catch basin of residential uses ranges from 0.85 to 2 mm with a median size of 1.62 mm. Fines may be flushed out from catch basin during rain and contribute to water pollution problems. However, this statement needs to be verified by comparing the grain-size distribution of catch basin sump sediment and sediment washoff from road surfaces. The hydraulic experiments on sediment demonstrate that sediment scouring starts at about 7-8 L/s, which is equivalent to a 3-month peak flow. It means that the chance of re-suspension of the bottom sediment is high and the retained fines associated with high organics are likely to be eroded from catch basins. The grain size of the flushed sediment at that flow is around 0.6-1.0 mm, whose sizes may be deposited in the storm sewer. Thus, catch basin cleaning or street sweeping is essential.

According to the hydraulic experiments of instantaneous flow, which is similar to rain storm pattern in summer period, methoprene pellets started to flush out before sediment came out and the percent of flushed pellets dropped when most sediments were flushed out. However, this was not the case for ingot, which was flushed out with sediment. It can be concluded that 450 mm sump depth can trap 74% more pellets comparing the maximum percent flushed pellets. Half-clean catch basin can trap 22% more pellets. Low return period storm (< 3 months storm) can create scouring of pellets and 1.44 years storm can flush out the ingot if catch basin is not cleaned (e.g. catch basin S1). The critical storm to flush out the pellets and ingots when catch basin is completely clean-out is more than 25 years. Thus, cleaning catch basins can improve the trapping efficiency of methoprene pellets or ingots. The risk of flushing of pellets is very high with value of 74% during a typical three months summer period. The way to reduce the

risk is to clean the catch basin or use the ingot. However, the cost of cleaning the catch basin has to be considered and the ecological health of using ingot needs to be considered.

A hydrologic mass balance model has been developed. The model provides a general prediction of the residual concentration of methoprene over time at a catch basin. It simulates the processes of dissolution, dilution, degradation and flushing of methoprene within catch basin during dry and wet weather conditions. The model predicts that total methoprene mass available for release in methoprene formulation products may be small. The actual total methoprene mass available for release was found to be two to three orders of magnitude less than the theoretical value in quiescent state. Rain may suppress the release of methoprene from pellets by resuspension of sediment; however, rain can enhance the release of methoprene from ingots through breakdown. For long term average rainfall scenario analysis, the methoprene pellets can allow 1-2 weeks larvicide protection with concentrations exceeding the lower bound of mosquito lethal dosage. Methoprene ingot provides less than 2 weeks larvicide protection in accordance to the model prediction. The individual catch basin model provides a good estimation of the event output mass of methoprene at the storm sewer outfall. Model values are different from the measured values by average of 29%. This difference may be caused by the phenomenon that methoprene mass may be degraded during the travelling from the catch basins to the storm outfall or pellets may be re-suspended from the catch basin sediment during rain event.

7.2 Recommendations

As the current larviciding program of 0.7 g methoprene pellets may not be effective to have 30 days larviciding control, there are three options to achieve: (1) to use ingots; (2) to use more methoprene pellets (>0.7 g); and (3) to apply methoprene pellets twice a month. Ingot may be a better option. The second option needs to be verified by more field experiments and cost consideration may upset the third option.

Sediment was collected from only one catch basin and the scenario analysis is applied in S1 catch basin whose sump water and sediment depth were measured in the field. However, those information may be not representative of all the catch basins. Therefore, it is important to conduct more field investigations at other catch basins.

Different amount of methoprene pellets can be applied to the field study catch basins and the results can assist in calibrating the model to evaluate the larvidicing program. Continuation of field monitoring using pellets and ingots at catch basins is essential to improve the model predictions. Wet weather sampling at outfall should be continued in order to obtain more rain event data to assess and increase confidence of the model output of the methoprene mass.

Interaction or partitioning studies of methoprene between sediment and water is an important study. This can be achieved by loading the catch basin model with sediment and monitoring the concentration of methoprene over time in the laboratory quiescent experiment. Hydraulic experiments incorporated with concentration monitoring can be performed to investigate any methoprene adsorption on suspended or re-suspended sediment and re-suspension of methoprene pellets from catch basin sediment. The results could be useful information to increase the performance of the model.

In the model, the K parameter is assumed to be constant during rain. However, the surface runoff to catch basin may not be the same in terms of the water temperature during the hot weather in summer. Monitoring temperature within the catch basin can modify the K model parameter.

The integration of the Geographic Information System (GIS) with the mass balance model and hydraulic model could further accurately route the mass of methoprene discharge to the storm sewer outfall.

The potential for enzyme-linked immunosorbent assay (ELISA) for methoprene is under investigation. It might overcome the disadvantages of conventional methoprene analysis (solvent extraction and gas chromatography/mass spectrometry): costly; long turn around time and low workload; rapid breakdown of methoprene upon storage and large sample size (250 mL in our experiments).

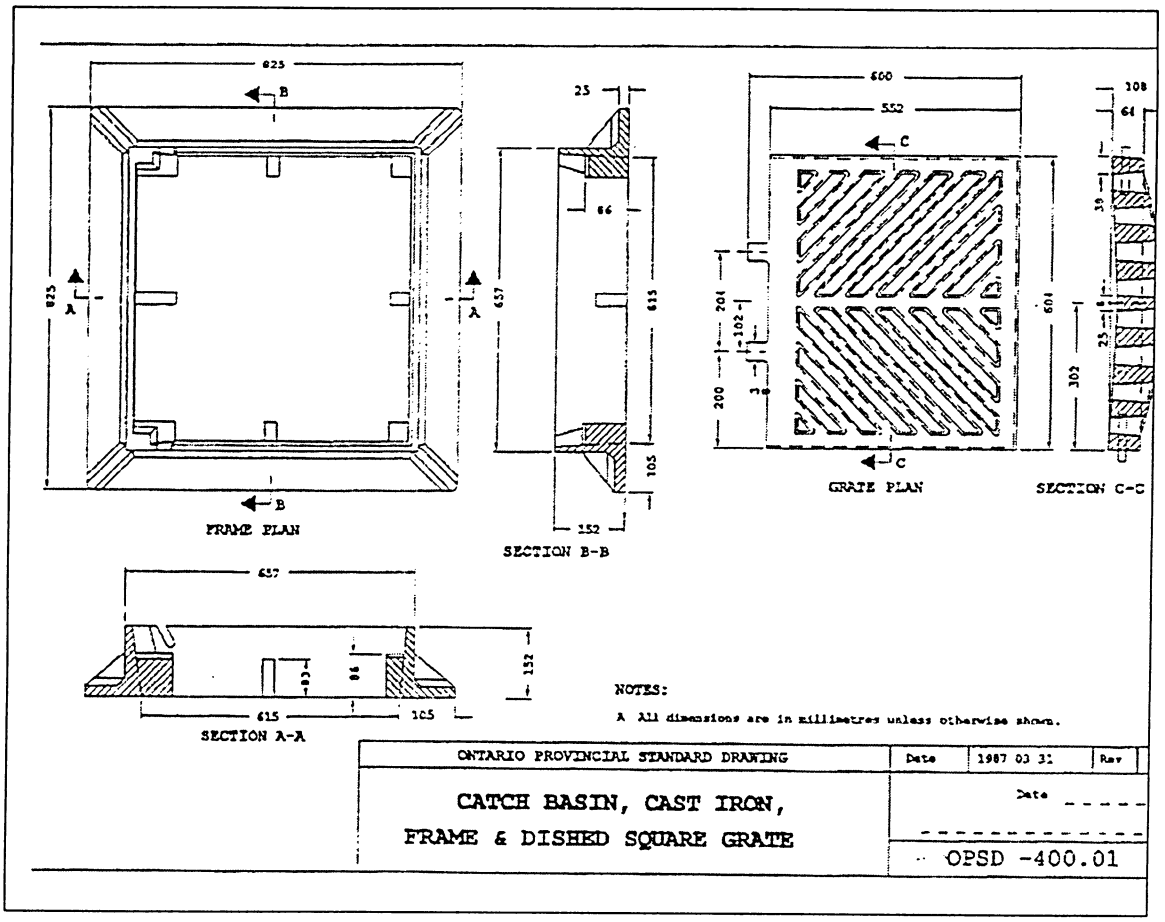
Tests should be done on methoprene pellets and ingots to find out the actual mass of methoprene in the altosid products.

In order to further evaluate the current schedule of catch basin cleaning, field study on what type of solids washoff from road surfaces to the catch basins is investigated. The sediment washoff from road surfaces, deposition, and flushing processes can be quantified in a hydraulic model.

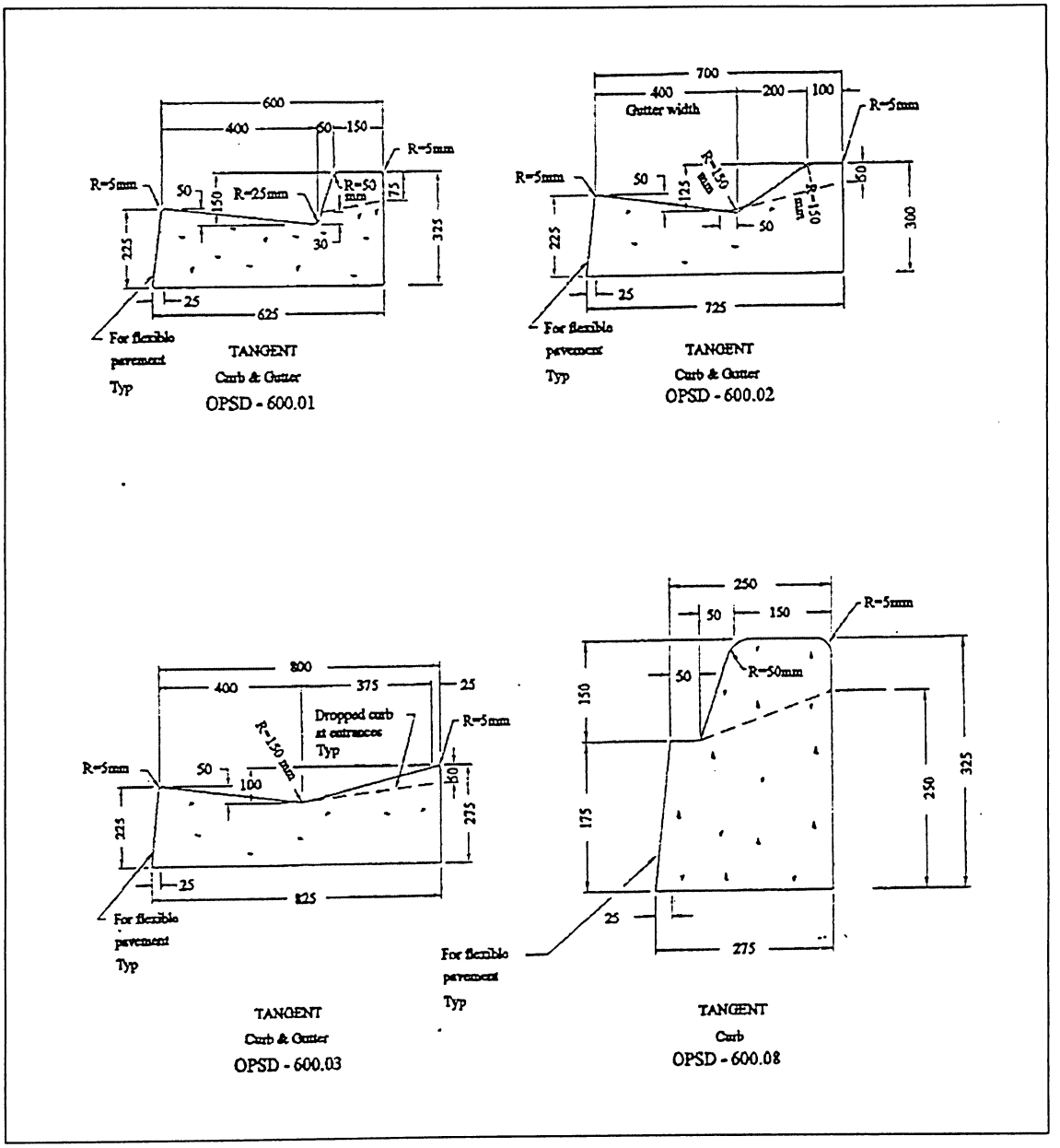
The efficacy of methoprene and its degradation products in controlling mosquito larval emergence in catch basins as well as physical and chemical dissolution of pellets or ingots should be further investigated.

APPENDIX A

Standard Drawings of Grate Inlet as well as Curbs and Gutters



Source: MTO (1995-1997)



Source: MTO (1995-1997)

APPENDIX B

MTO Design Charts

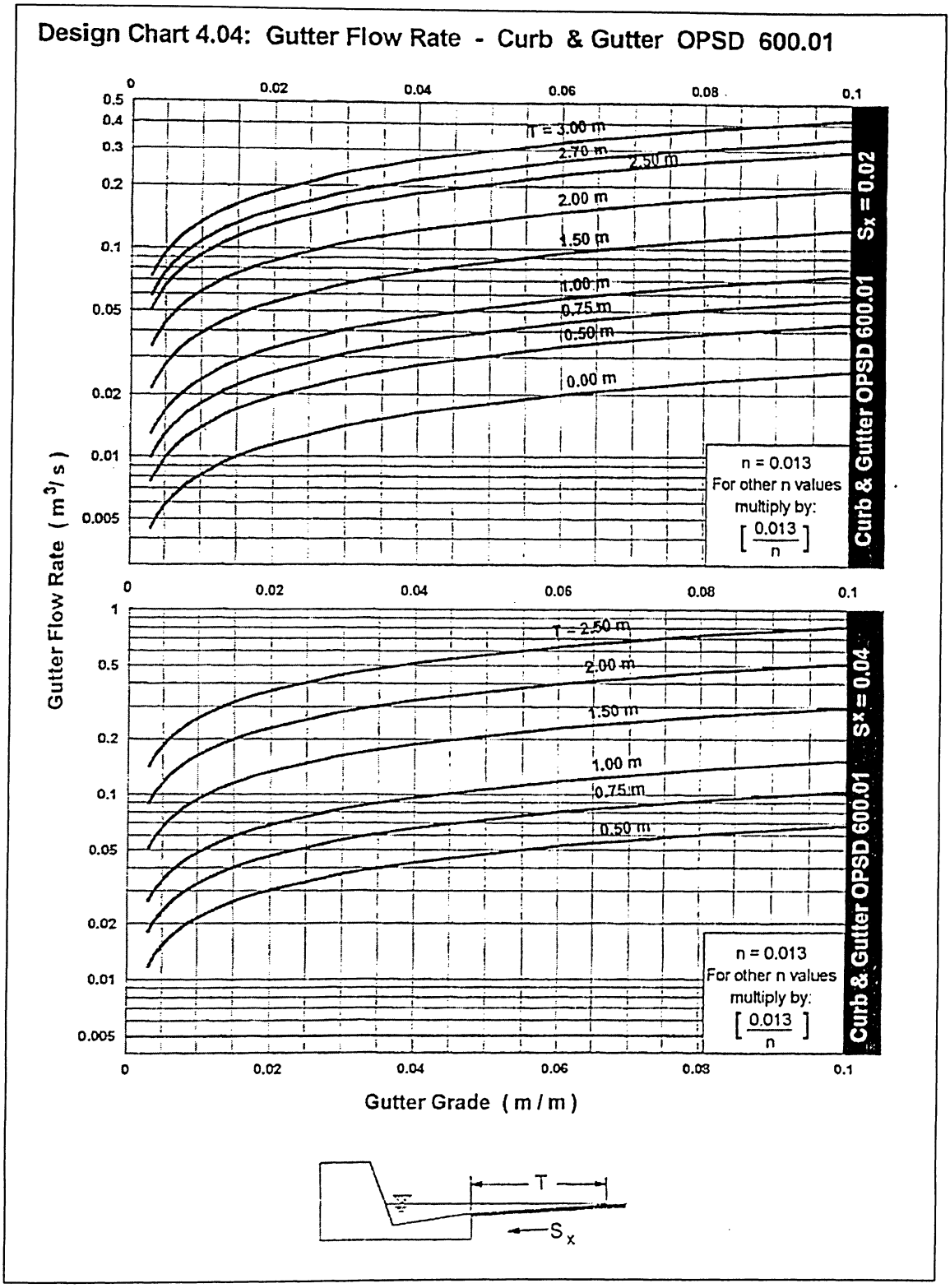


Figure B.1: Gutter flow design chart

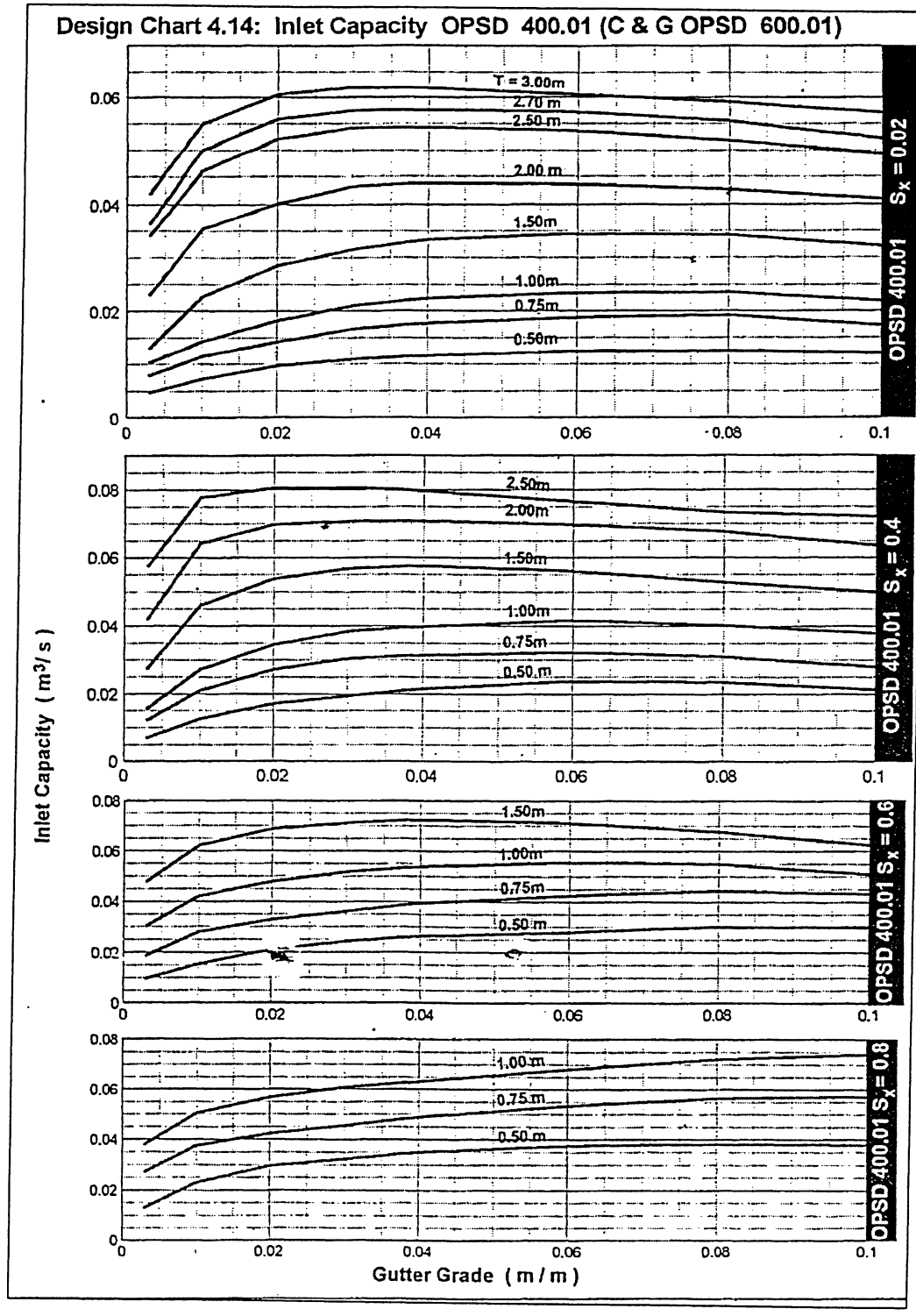
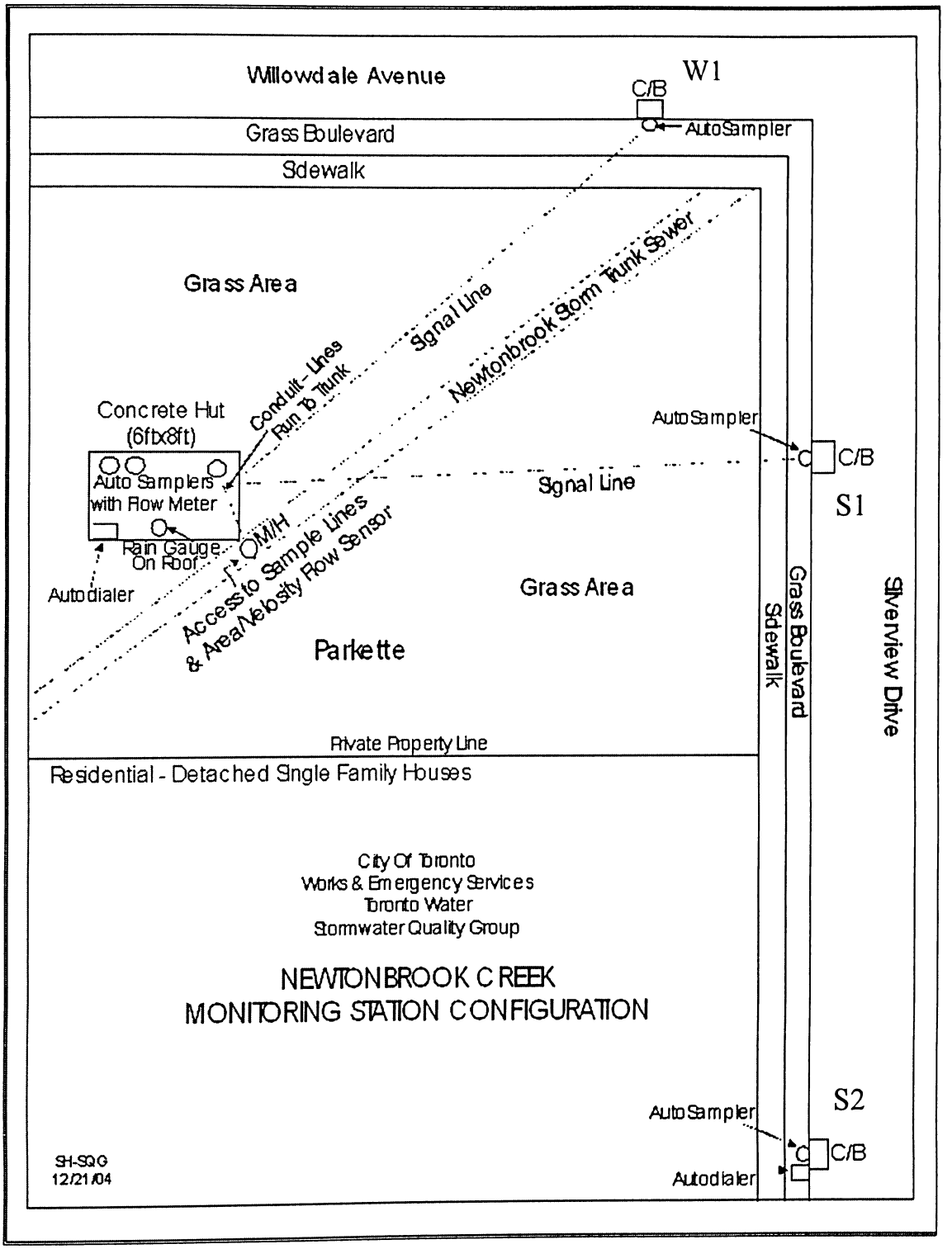


Figure B.2: Grate inlet capacity design chart

The approaching gutter flow is determined by Figure B.1. The curb and gutter are assumed to be OPSD 600.01. The gutter grade and cross slope are assumed to be 2%. From Figure B.1, the gutter flow for spread, say 0.5 m, is 0.02 m^3/s. Grate inlet is assumed to be OPSD 400.01. The corresponding grate inlet capacity for spread of 0.5 m is 0.01 m^3/s, as shown in Figure B.2.

APPENDIX C

Newtonbrook Creek Monitoring Station Configuration



Source: City of Toronto (2004)

APPENDIX D

Methoprene Chemical Detection Method

These methods involve using liquid-liquid extraction to isolate the organic larvicide methoprene from the water samples and gas chromatography/mass spectrometry (GC/MS) to identify and quantify these compounds. This method was adapted from U.S. Geological Survey Open-File Report 01-273 "Methods of Analysis and Quality-Assurance Practices by the U.S. Geological Survey Organic Geochemistry Research Group--Determination of Four Selected Mosquito Insecticides and a Synergist in Water Using Liquid-Liquid Extraction and Gas Chromatography/Mass Spectrometry".

Sample collection procedure: The water sample was collected in a 250 mL amber bottle with Teflon-lined lid by using a pump inserted in the catch basins and filled to the bottle's neck. No chemical preservation and sample pre-treatment are required. The water sample was stored in a cooler before analysis, labeled and sent to the City of Toronto's Laboratory for pesticide analysis.

Liquid-Liquid extraction procedure: The water sample is transferred to a glass bottle. The full-bottle and empty-bottle are weighed to determine the amount of water sample processed (required volume of sample processed = 247 mL, if a sample contain less than 247 mL, distilled water is added to bring the volume to the required 247 mL and any volume added is recorded) by subtracting, assuming 1 mL is equal to 1 g. 0.1 mL Surrogate Standard solution of Terbuthylazine is added to the sample. The bottle is swirled to mix. 7 mL of Hexane is added to the bottle using bottle-top dispenser, which is capped and shaked on a mechanical shaker for few minutes. The bottle is then allowed to stand for 10 minutes so that the organic hexane phase can separate from the aqueous phase. Two distinct layers are formed in the bottle and the pesticide will be transferred into the organic hexane phase. Deionizated distillated water (DDW) is added to bring the

Hexane layer up into the neck of the bottle for easier removal of the Hexane. The Hexane layer is removed using a pasteur pipette and filtered through a drying tube into a 15 mL centrifuge tube to which 0.1 mL Internal Standard solution of Phenanthrene-d10 in ethyl acetate has been added. A drying tube (4 mL TRANSFER PIPETTE) contains a small amount of glass wool and sodium sulfate rinsed with Hexane for drying out any water in the Hexane layer. A 24 mm holed Septa is used to support the drying tube above the 15 mL centriguge bottle. The Hexane extract is evaporated under nitrogen stream using a TurboVap LV Evaporator to a volume of approximately 60 μL and transferred to a 0.1 mL autosampler vial using an autopipette with disposable tips. The extracts are stored at the freezer until analysis by GC/MS.

APPENDIX E

Sediment Analysis

Grain-size distribution test procedure (Pasternack):

1) Prepare 0.5% sodium hexametaphosphate (SHMP) dispersant, which is a dispersant that helps prevent particles from aggregating.
2) Get replicate sets of the samples
3) Soak the sample under the SHMP solution, mix and wait for few minutes
4) Do the wet-sieving: pour the moist sediment through the No. 10 and 200 sieves into a pan. Some macro organics like twigs and roots can be removed.
5) Empty bottom pan into a container (fine fractions)
6) Wash the sediment retained on each sieve with SHMP to remove any fines, until the water is clear.
7) Rinse the sediment with distilled water to remove any SHMP residue, fines and any dissolved salts.
8) Flush all the sediment retained on each sieve (No. 10 and 200) into containers and dry at ~80℃ in oven for overnight.
9) Measure the mass retained on each sieve.
10) Pass the retained sample again through No 10 and 200 sieves into a pan and calculate the percent of gravel, sand and fine fractions.
11) Do the dry-sieving for the gravel and sand fraction (>0.075mm or sieve No. 200) and hydrometer for fine fraction (<0.075mm or sieve No. 200) if necessary in accordance with ASTM D 422.

Parameter calculations:

D10, D30, D50 and D60: diameters corresponding to percents finer of 10%, 30%, 50% and 60%.

Cu: uniformity coefficient $\left(Cu = \frac{D60}{D10}\right)$

Cc: coefficient of gradation $\left(Cc = \frac{D30^2}{D60 * D10}\right)$

Determination of the percent crushed particles (ASTM D 5821):

1. Obtain the dried sample with size retained the 4.75 mm sieve.
2. Spread the sample on a clean and flat surface to inspect of each particles
3. Separate the particles into crushed and uncrushed portions for each sieve size fraction
4. Weigh each crushed and uncrushed portion of the sample

Calculations:

$$CP = \left(\frac{Mcp}{Mt} \right) * 100$$

where CP = percent of crushed particles (%); Mcp = mass of crushed particles (g); and Mt = total mss of crushed and uncrushed particles (g).

Specific gravity of soils finer than 4.75 mm sieve (ASTM D 854):

1) Clean and dry the pycnometer, then determine and record its mass in grams.
2) Fill the pycnometer with distilled water up to the line and determine as well as record the mass
3) Measure the water temperature
4) Take around 50 (for cohesive) or 100 (for non-cohesive) g of oven-dried sample and place in the pycnometer. Add distilled water to the flask until the sample is completely soaked.
5) Left sample for overnight
6) Remove the entrapped air by subjecting a vacuum (~20 in-Hg) for about 10 to 15 mins
7) Fill the flask to the ring marked on the neck with distilled water, clean and dry the outside as well as the neck of the flask after the air has been removed
8) Determine and record the mass of pycnometer as well as sample
9) Stir the soil-water suspension to assure even temp distribution and measure the water temperature

Calculations:

Specific gravity:

$$Gs = \frac{kMs}{Ms + Mpw - Mpws}$$

where Gs = specific gravity of sample at 20℃; k = conversion factor, which is equal to:

$k = \frac{\text{density of water at temperature Tx}}{\text{density of water at 20°C}}$; Ms = mass of oven-dried sample (g); Mpw = mass of pycnometer filled with water at temperature Tx (g); and Mpws = mass of pycnometer filled with water and sample at Tx (g)

Specific gravity of soils retained on 4.75 mm sieve (ASTM C 127):

1) Dry the aggregate to constant weight and measure weight of sample. Subsequently immerse the aggregate sample in water at room temperature for period of 24 +/- 4 hours
2) Remove the test sample from the water and put it in a basin and dry it using a paper tower until all surface water film is removed. Weigh the test sample in the saturated surface-dry condition
3) After weighing, immediately place the saturated-surface-dry test sample in the sample container and determine its weight in water. Take care to remove all entrapped air before weighing by shaking the container while immersed.

Calculations:

$$Gs = \frac{kMs}{Ms - Mms}$$

where Gs = apparent specific gravity of sample at 20℃; and Mms = mass of saturated test sample in water at Tx (g).

Organic and carbonate contents test by loss on ignition (LOI):

1. Obtain cleaned and dried crucibles and weigh the empty dried crucibles
2. Sub-sample oven-dried sediment of about 10g (Samples should be grounded into small fraction. If samples are taken from refrigerator, oven-dry the sample for at least two hours at 105℃)
3. Weigh the oven-dried sample and crucible after cooling in the desiccators for half an hour.
4. Allow the muffle furnace to reach the desired temperature first and place the crucibles in the muffle furnace and ignite the samples for certain hours at 550℃
5. Place the crucibles into the 100℃ oven to balance the pressure (Note: the desiccators in the lab doesn't have a pressure release valve) and prevent any moisture absorption, then place in the desiccators to cool to room temperature for 1 hour (Note: Make sure the desiccant is blue in color)
6. Weigh the ashed sample and crucible
7. Set the muffle furnace temperature to 950℃ and leave the ashed sample for 1 hour.
8. Repeat steps 5-6 to obtain the mass of sample and crucible.

Calculations:

$$LOI_{550} = \left(\frac{Ms - M_{550}}{Ms} \right) * 100$$

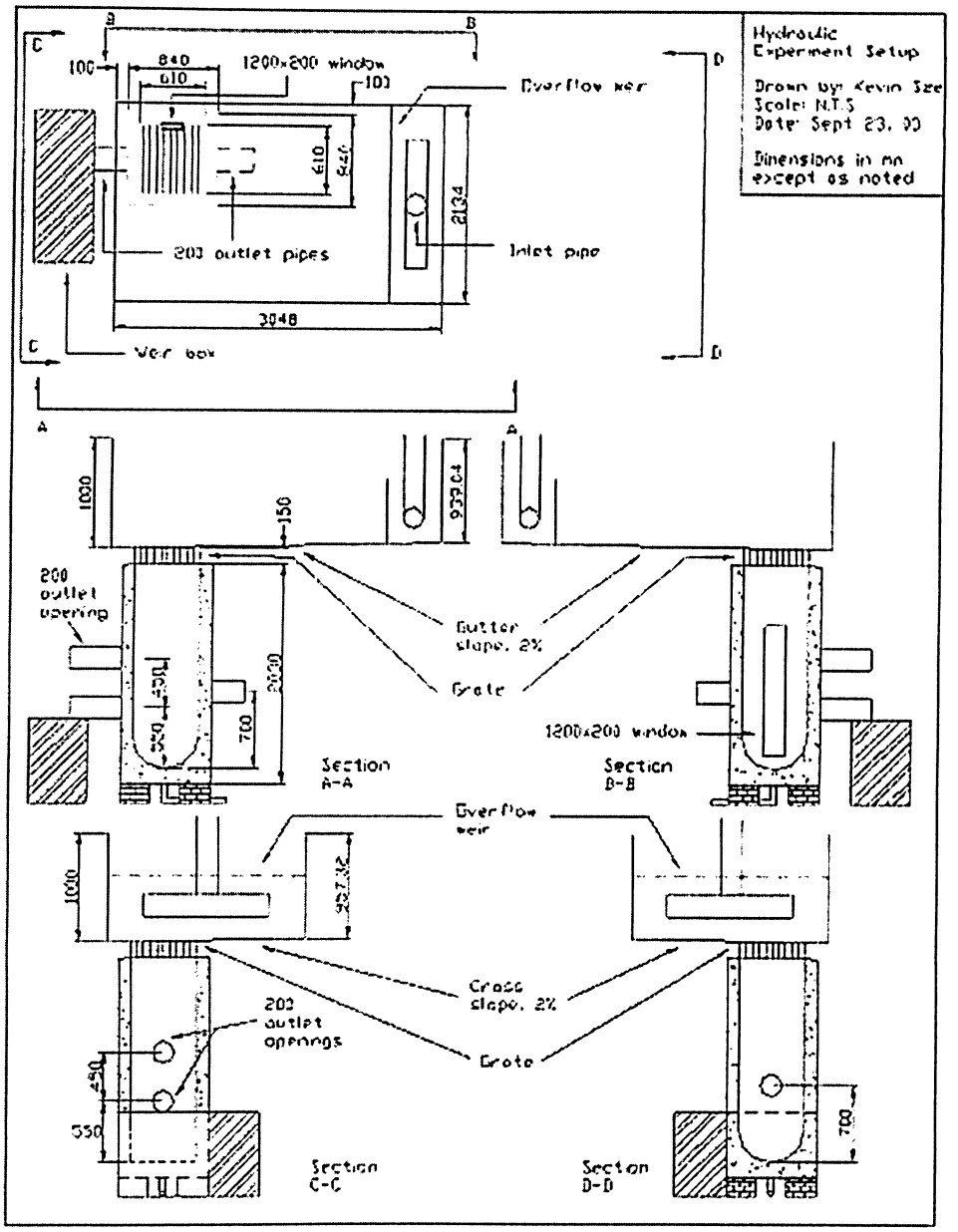
where LOI_{550} = LOI at 550℃; and M_{550} = mass of ashed sample after ignited at 550℃ (g)

$$LOI_{950} = \left(\frac{M_{550} - M_{950}}{Ms} \right) * 100$$

where LOI_{950} = LOI at 950℃; and M_{950} = mass of ashed sample after ignited at 950℃ (g)

APPENDIX F

Drawings of Hydraulic Model


Hydraulic
Experiment Setup
Drawn by: Kevin Sze
Scale: N.T.S
Date: Sept 23, 00
Dimensions in mm
except as noted
1200x200 window
Overflow weir
200 outlet pipes
Inlet pipe
Weir box
3048
2134
200
outlet
opening
Gutter
slope, 2%
Grate
Section
A-A
Section
B-B
Overflow
weir
Cross
slope, 2%
202
outlet
openings
Section
C-C
Section
D-D

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