UNIVERSITY OF CALIFORNIA

Los Angeles

Monitoring and Modeling of Pollutant Mass in Urban Runoff: Washoff, Buildup and Litter

A dissertation submitted in partial satisfaction of the
Requirements for the degree Doctor of Philosophy
in Civil Engineering

By

Lee-Hyung Kim

2002

UMI Number: 3078123

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

The dissertation of Lee-Hyung Kim is approved.

Irwin H. Suffet

Keith D. Stolzenbach

Thomas C. Harmon

Michael K. Stenstrom, Committee Chair

University of California, Los Angeles

2002

I wish to express heartfelt thanks
to my parents and parents-in-law who helped both materially and morally,
to my lovely son Eric,
to my wife So-Young,
and to my classmate Haejin.

This dissertation would not have been completed
without their love and help.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

VITA

December 11, 1969	Born, Kyungsangnam-Do, Korea
1994	B.S., Civil and Environmental Engineering Korea University Seoul, Korea
1996	M.S., Civil and Environmental Engineering Korea University Seoul, Korea
1995-97	Researcher The Research Institute for Environmental Technology and Sustainable Development, Korea University Seoul, Korea
1998	M.S., Civil Engineering University of California, Los Angeles
1999-2002	Graduate Student Researcher University of California, Los Angeles

PUBLICATIONS AND PRESENTATIONS

Kim, L.-H. (1996). A study on phosphorus release characteristics of sediments with environmental changes. *Master's thesis*, Dept. of Civil and Environmental Engineering, Korea University, Seoul, Korea, Aug.

Kim, L.-H., and Choi, E. (June, 1996), Phosphorus release from sediment with environmental changes in Han-river, *Proceedings of the 4th Conference of Korean Association of Water Quality*, Pusan, Korea.

Kim, L.-H., Hwang, H., and Choi, E. (1997). Water Quality of Han-river during dredging of sediments, 1994-1997, *Research report for KECC*.

Stenstrom, M.K., Lau, S., Lee, H-H., Ma, J-S., Ha, H., Khan, S., Kim, L.-H., and Kayhanian, M. (May, 2001). First Flush Stormwater runoff from Highways, *Proceedings of Environmental and Water Resources Institute's (EWRI's) World Water & Environmental Resource Congress*, Orlando, Florida.

Stenstrom, M.K., Kim, L.-H., and Ha, H. (May, 2000). Inlet Deflector Feasibility Study, *Research report for Department of California Transportation*.

Kim, L.-H., Kayhanian, M., and Stenstrom, M.K. (September, 2002). Prediction of event mean concentration and first flush effect using mass interpolation washoff model for highway runoff, *Conference proceedings of 6th International Conference on Diffuse Pollution*, pp 227-235, Amsterdam, The Netherlands.

Ma, M., Khan, S., Li, S., Kim, L.-H., Ha, H., Lau, S., Kayhanian, M., and Stenstrom, M.K. (September, 2002). Implication of Oil and Grease Measurement in Designing Stormwater Systems, *Proceedings of 9th International Conference on Urban Drainage*, Portland, Oregon.

Ma, M., Khan, S., Li, S., Kim, L.-H., Ha, S., Lau, S., Kayhanian, M., and Stenstrom, M.K. (September, 2002). First Flush Phenomena for Highways: How it can be meaningfully defined, *Proceedings of 9th International Conference on Urban Drainage*, Portland, Oregon.

Kayhanian, M., Kummerfeldt, S., Kim, L.-H., Gardiner, N., and Tsay, K. (September, 2002). Litter Pollutograph and Loadograph, *Proceedings of 9th International Conference on Urban Drainage*, Portland, Oregon.

Kim, L.-H., Choi, E., and Stenstrom, M.K. (2003). Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere*, 50(1): 53-61.

ABSTRACT OF THE DISSERTATION

Monitoring and Modeling of Pollutant Mass in Urban Runoff: Washoff, Buildup and Litter

by

Lee-Hyung Kim
Doctor of Philosophy in Civil Engineering
University of California, Los Angeles, 2002
Professor Michael K. Stenstrom, Chair

Stormwater pollution has displaced wastewater pollution in many cases as the major polluter of public waters. Paved areas such as highways and streets in urban areas are "stormwater intensive" land uses since they are highly impervious, and have high pollutant mass emissions from vehicular activity. To help manage this source of water pollution, a multiyear monitoring program was instituted at eight Southern California highway sites over two years. From the monitoring data, washoff and buildup models were developed.

The new model is semi-empirical and uses four fitting parameters. It is capable of fitting first flush events. The model was fit to more than 40 events for 8 pollutants, and the parameters were correlated to runoff conditions, such as total runoff, antecedent dry days, runoff coefficient and average runoff velocity. The model can be used in selecting best management practices. The model can also be used for estimating event mean concentrations for events with sparse data. First flush was noted in most storm events and an improved definition of first flush is presented. Using the criteria of "high" first flush and "medium" first flush, more than 30% of the storms showed high first flush and more than 80% showed a medium or high first flush.

The second goal of the research is to determine the pollutant mass accumulation during dry periods. Mass accumulation rates were determined for total suspended solids, chemical oxygen demand, oil and grease, total Kjeldahl nitrogen and total phosphorus, and are reported in g/m^2-day. A new two parameter model was developed, which can be used to predict pollutant buildup during dry days between storms.

Litter was also measured in the monitoring program. Litter production rates and event mean concentrations are reported. Vegetation composed approximately 90% of the gross pollutants (> 0.5 cm) from highways. Litter production is highly variable and few significant correlations were noted. A decreasing trend in event mean concentration was noted with total runoff volume or total rainfall. An increasing trend in event mean concentration was noted with antecedent dry days.

CHAPTER I.

INTRODUCTION

The United States has made tremendous advances in the past 30 years to clean up the aquatic environment by controlling pollution from point sources such as industries and sewage treatment plants. Although point source discharges have decreased during recent years, many water bodies or rivers are still impacted and are either eutrophic, with excess algae biomass and episodes of toxic algal blooms, or oxygen depleted (Horan 1990; Parr et al. 1998 Larsen et al. 1999). Non-point sources (NPSs) are the cause of many of the problems. Non-point source pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is widespread because it can occur at any time in any type of landuse. Agriculture, forestry, grazing, septic systems, recreational boating, urban runoff, construction, physical changes to stream channels, and habitat degradation are potential sources of NPS pollution. Careless or uninformed household management also contributes to NPS pollution problems. As the runoff moves, it picks up and carries away natural and anthropogenic pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, and even underground drinking water sources (EPA 1994; Jefferies et al. 1999; Smullen et al. 1999).

Many water bodies in developed countries remain polluted, in spite of the billions of dollars that have been spent on clean-up of municipal and industrial point pollutant sources. Non-point source pollution remains a major cause of degradation of receiving waters. NPS pollution in developing countries presents new challenges to the environmental and legal professions (Pratt and Adams 1984; Parr et al. 1998; Pegram 1999). Recent emphasis in the United States is to manage NPS.

The United States Environmental Protection Agency (USEPA) developed Nationwide Urban Runoff Program (NURP) to expand knowledge of urban runoff pollution by instituting data collection and applied research projects in selected urban areas throughout the United States (Driscoll et al. 1990; EPA 1994, 1995, 1996). The realization that significant quantities of nutrients, pesticides, herbicides and heavy metals are contained in runoff caused the U.S. EPA to require that regional planning agencies develop programs to reduce pollution from urbanized areas under section 208 of the Clean Water Act. Best Management Practices (BMPs), which refers to education, regulatory procedures, treatment systems and other methods to control pollutants in runoff were required (Silverman et al. 1986; Jefferies et al. 1999; Smullen et al. 1999).

Generally the sources of urban runoff pollution originate from wet and dry atmospheric deposition, street refuse, including litter, street dirt, vegetation and organic residues and vehicle emissions. Construction debris and road deicing materials are also pollutant sources. Paved areas such as highways and streets in urban areas are "stormwater intensive" land uses since they are highly impervious, and have high pollutant mass accumulation from vehicular activity.

Regulatory approaches to control NPS are institutionally difficult. It is not clear who "owns" the stormwater. Runoff from one property may discharge through a second property to a third property, accumulating pollutants as it travels. The final discharge into receiving water contains emissions from all land uses, and there is no clear responsibility to manage the runoff. Regulation becomes difficult to enforce due to the confusion about the source.

Therefore, methods to estimate pollutant emissions from different types of landuse are popular research and development topics. More recently methods to estimate pollutant accumulation over dry days and emissions during storm events are being developed and used to evaluate the impacts of urbanization. The methods are being used for analysis of existing conditions as well predictive tools for planners.

This dissertation concentrates on methods to estimate pollutant buildup and washoff from highways. The dissertation is contains five additional chapters. Chapter 2 is a literature review of processes for runoff and buildup along with previously developed models. Chapter 3 describes a washoff model and compares it to monitoring data from 8 highway sites over two rainy seasons. New definitions of first flush are suggested, and information useful for the development of best management practices is presented.

Chapter 4 describes a pollutant build-up model and its use for estimating accumulated mass during dry periods. Chapter 5 describes litter production from highways and its regression model. Usually, it is known to new pollution. Conclusions are presented in Chapter 6.

REFERENCES

Driscoll, E.D., Shelley, P.E., and Strecker, E.W. (1990). "Pollutant loading and impacts from stormwater runoff." Analytical Investigation and Research Report, Vol. III, FHWA-RD-88-008, *Federal Highway Administration*, USA.

EPA (1994). "Nonpoint sources pollution control program." *U.S. EPA*, Report 841-F-94-005, USA.

EPA (1995). "Economic benefits of runoff controls." *U.S. EPA*, Report 841-S-95-002, USA.

EPA (1996). "Managing nonpoint source pollution from households." *U.S. EPA*, Report 841-F-96-004J, USA.

Horan, N. J. (1990). "Biological wastewater treatment system-theory and operation." *John Wiley & Sons, INC.* England, U.K.

Jefferies, C., Aitken, A., McLean, N., Macdonald, K., and McKissock, G. (1999)." Assessing the performance of urban BMPs in Scotland." *Wat. Sci. & Tech.*, 39(12), 123-131.

Larsen, T., Broch, K., and Andersen, M.R. (1998). "First flush effects in an urban catchment area in Aalborg." *Wat. Sci. & Tec.*, 37(1), 251-257.

Parr, A., Zou, S., and McEnroe, B. (1998). "Runoff contamination." *J. of Environmental Engineering*. 124(9), 863-868.

Pegram, G. C., Quibell, G., and Hinsch, M. (1999). "The nonpoint source impacts of peri-urban settlements in South Africa: implications for their management." *Wat. Sci. & Tech.*, 39(12), 283-290.

Pratt, C. J., and Adams, J.R.W. (1984). "Sediment supply and transmission via roadside gully pots." *The Science of the Total Environment*, 33, 213-224.

Silverman, G. S., Stenstrom, M.K., and Fam, S. (1986). "Best management practices for controlling oil and grease in urban stormwater runoff." *The Environmental Professional*, 8, 351-362.

Smullen, J.T., Shallcross, A.L., and Cave, K.A. (1999). "Updating the U.S. nationwide urban runoff quality data base." *Wat. Sci. & Tech.*, 39(12), 9-16.

CHAPTER II.

LITERATURE REVIEW

2.1. POLLUTANT SOURCES IN NPS POLLUTION

Non-point source (NPS) pollution, unlike pollution from industrial and sewage treatment plants, comes from many diffuse sources. NPS pollution is widespread because it can occur any time and disturbs the land or water. Agriculture, forestry, grazing, septic systems, recreational boating, urban runoff, construction, physical changes to stream channels, and habitat degradation are potential sources of NPS pollution. Careless or uninformed household management also contributes to NPS pollution problems. As the runoff moves, it picks up and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, coastal waters, and even our underground sources of drinking water (EPA 1994; Jefferies et al. 1999; Smullen et al. 1999).

Broad ranges of pollutants are found in stormwater runoff. The nature of these pollutants depends strongly on the land use and the activities carried out on the site that generates the runoff. There are many kinds of non-point sources. Agricultural pollutants include nutrients from excess fertilizers, herbicides, and insecticides from agricultural or residential areas. Highways contribute oil and grease, heavy metals, suspended solids and toxic chemicals. Industries and commercial sites release pollutants related to their activities (e.g., heavy metals from metal recyclers, litter and oxygen demanding substances from commercial land use). Sediment from improperly managed construction sites, crop and forest lands are also NPS sources (Pratt and Horstead 1987; Pratt et al. 1987). Bacteria and nutrients caused by livestock, pet wastes and faulty septic systems, as well as sewage spills have high visibility because of their impact on recreational waters. Atmospheric deposition may contribute nitrogen and other pollutants (EPA 1994; Barrett et al. 1998; Andersen et al. 1999; Ekholm et al. 2000).

By definition, point source pollution is discharged from sewers, or treatment plant outfalls. Non-point sources, unlike point sources, are released into the environment form many locations and methods, such as wet deposition from rainfall, dry deposition from dust, and runoff. Biogenic and anthropogenic pollutants are released into rivers, lakes, wetlands, coastal waters, and groundwaters (EPA 1994; Braune and Wood 1999; Kawara et al. 1999; Lee and Bang 2000).

2.2. HYDROLOGICAL CHARACTERISTICS OF STORMWATER RUNOFF

Stormwater runoff volume and pollution load increase considerably when a catchment is urbanized. Stormwater runoff is produced when the capacity of the land to retain precipitation is exceeded and runoff occurs. Runoff will be affected from storm intensity, duration, antecedent dry days, land use types and site characteristics such as slope, slope type and imperviousness (Arnold and Gibbons 1996; Blackwell et al. 1999).

The extent of urbanization can be observed in changes in stream flows associated with storm events. Differences in runoff characteristics can be expected between undeveloped, natural watersheds and developed, urban watersheds. The differences include the volume of runoff, peak flow and time lags between rainfall and runoff. In developed areas, the capacity to retain rainfall is reduced; in fact, highly impervious landuse (e.g., parking lots, freeways) may produce conditions where nearly all rainfall becomes runoff. The result of the reduced capacity to retain rainfall is that storms of short duration and low intensity produce runoff.

Undisturbed areas have a greater capacity to retain rainfall. This increased retention is associated with interception and infiltration of rainfall. In natural areas we expect that runoff events will occur only for storms with longer duration or higher intensity (Dilks et al. 1993; Deletic and Mahsimivic 1998; Ferguson 1998; Blackwell et al. 1999). Runoff from smaller storms may be completely retained, and peak runoff flow is low.

2.2.1. Runoff Hydrograph

The runoff hydrograph will reflect the previously discussed differences in disturbed and undisturbed areas. In disturbed and urbanized areas, the runoff hydrograph will rise and fall rapidly and the discharge volume may nearly equal the rainfall volume in the catchment. In undisturbed areas, the rise and fall of the hydrograph will not be as sharp and the peak discharge will be much less reflecting the increased rainfall volume retained on the land surface (House and Warwick 1998; Iqbal 1998; Sansalone et al. 1998).

2.2.2. Hydrological Changes in an Urban Watershed

Generally urbanization changes a hydrologic cycle by reducing the degree of infiltration and increasing the volume of runoff. Development such as roads, parking lots, single family dwellings, will change the imperviousness, slope and amount of depression storage. It can also change the cycle by changing evapo-transpiration because of removal of vegetative cover, and by reducing the travel time to a receiving body of water because of the construction of efficient drainage systems.

An important characteristic of land use is the expected stormwater runoff rate. Previous investigators, through analysis of a large set of rainfall-runoff data from many studies on urban, agricultural and highway areas, have shown that the runoff coefficients (RC, defined as the overall average ratio of runoff to rainfall) are highly correlated to watershed imperviousness (Driscoll et al. 1990; EPA 1994, 1995, 1996; Sansalone et al. 1998). The relationship between imperviousness and runoff is worth considering in some detail. Figure 2.1 shows that runoff coefficients are correlated to site imperviousness.

The runoff coefficient can be calculated using equation 2.1 as follows:

$$Runoff\ coefficient(RC) = \frac{Event\ \ runoff\ \ volume}{Event\ \ rainfall\ \ volume} = \frac{\int_0^T Q_{TRu}(t)dt}{\int_0^T Q_{TR}(t)dt} \qquad (2.1)$$

Where, $Q_{TRu}(t)$ is stormwater runoff volume discharged and $Q_{TR}(t)$ is rainfall intensity at time t. The runoff coefficient ranges from 0 to 1. Figure 2.1 shows that the runoff coefficient is correlated with the percentage of impervious cover, except at very low imperviousness. At low levels, other factors like soil type, slope and total rainfall become important, and imperviousness is a less perfect predictor of the runoff coefficient.

Pavements are major surface covers in urban areas and highways. Modifying pavement material to maintain infiltration is a basic step in the restoration of hydrologic function.

The first rainfall on pavements may not runoff because it may infiltrate the pores in the material or evaporate. As the rain continues, the pavement becomes saturated and runoff flows from the surface or ponds. For safety and flood prevention, ponding is prevented by efficient stormdrains, and runoff with its associated pollutants is released into receiving waters. In extreme cases, the runoff may erode stream banks, destroying habitats and producing further sediment pollution. Stream bed materials may shift; stream banks may fail; and biota of all types are flushed out. Habitant is lost. After storm flow passes, base flow may decline much more rapidly and to lower levels than in undeveloped watersheds (Dilks et al. 1993; Barrett et al. 1998; Bertrand-Krajewski et al. 1998; Ferguson 1998; Braune and Wood 1999).

About 97% of the surface (930 million hectares) of the United States is land and only 7% of the land is classified as urban, but this is where 74% of the people live. As a result many cities and suburbs suffer from traffic congestion, high energy consumption, air pollution and other symptoms of high population density. By comparison, agricultural areas with low population comprise 54% of the area. Although the alteration of the land surface to accommodate urban development affects only 3% of the land surface, the hydrological and ecological effects often are more widespread, and occur in areas already stressed by point sources (Ferguson 1998).

The transformation of a watershed from a natural to urban conditions produces several major changes in the hydrologic characteristics of streams. Increased flow volume, decreased detention time and increased peak flow usually occur. The increase in flow volume primarily reflects changes in imperviousness. The transformation of vegetated surface into streets, sidewalks, and parking lots reduces hydraulic roughness and imperviousness, which increases the velocity and volume of overland flow. Taken together they increase peak discharge rate (Driscoll 1990; Arnold and Gibbons 1996; Bertrand-Krajewski et al. 1998).

2.3. RUNOFF QUALITY AND EVENT MEAN CONCENTRATION

Runoff quality or pollutant concentrations are a function of landuse. Larsen et al. (1998) studied the quality of runoff from similar, non-urbanized watersheds and compared it to runoff from urbanized watersheds. They found that pollutant concentrations were considerably higher in the urbanized areas than in undeveloped areas, such as forested regions. The mass emission of pollutants from NPS in urban areas can be as large as or greater than point source discharges. According to Jordan et al. (1997), NPS discharges to Chesapeake Bay contribute approximately two-thirds of the nitrogen and one-quarter of the phosphorus inputs. For Santa Monica Bay, model predictions suggest that urban runoff contributes 58% of the nitrogen input but only 3% of the phosphorus input (Wong et al. 1997).

These comparisons are difficult to make because of uncertainty associated with non-point sources. Atmospheric deposition is an important source of nitrogen but has not been well quantified. Watershed discharge of phosphorus are often difficult to quantify because phosphorus is strongly associated with suspended particles which may be discharged primarily during short, unpredictable periods of high flow (Line et al. 1996; Haygarth and Jarvis 1997; Heathwaite and Sharpley 1999). Monitoring programs for NPS are often lacking. For example, treatment plants in the Los Angeles area have been well monitored for 40 years or more, but it was not until the mid-90's that a comprehensive stormwater monitoring program was developed (Stenstrom and Strecker 1993)

These varied NPS are usually quantified with an event mean concentration (EMC). It is defined as the total mass load of a pollutant from a site during a storm divided by the total runoff water volume discharged during the storm. For sampling programs that are based on flow-weighted techniques, the EMC simply is equal to the flow weighted mean concentration. In studies employing sequential discrete sampling approaches, the EMC is calculated from the area under the loading rate curve (load-graph) divided by the area under the flow rate curve (hydro-graph, Bertrand-Krajewski et al. 1998). Equation 2.2 defines the EMC:

$$EMC = \frac{\textit{Discharged mass during an event}}{\textit{Discharged volume}} = \frac{\int_0 C(t) \cdot Q_{TRu}(t)dt}{\int_0 Q_{TRu}(t)dt} \qquad (2.2)$$

Where, *C(t)* is pollutant concentration at time t.

If a flow weighted composite sampler is used, no integration is required, and the samples are true EMCs. If grab samples are collected equation 2.2 must be integrated numerically. Typically there only may be 10 or 20 water quality samples, but flow measurements may exist on one-minute intervals. There are different methods for performing the integration, and the differences often relate to interpolation method. Larsen et al. (1998) suggested a medium point method to interpret concentrations for use in equation 2.2. Gupta and Saul (1996) suggested multiple linear regression to determine the EMCs. The Larsen procedure was used in this research.

One of the earliest studies in the United States was the Nationwide Urban Runoff Program (NURP) study (Sartor and Boyd 1972; Sartor et al. 1974; Smullen et al. 1999). Ten water quality pollutants were measured at more than 2,300 stations at 81 urban sites in 28 metropolitan areas. The NURP EMCs have been used for estimating pollutant loadings, the effectiveness of management measures and water quality impacts in a large number of investigations.

The most common use of the EMCs is for screening models where pollutant loads are estimated as the product of area of urban land, the rainfall runoff depth as estimated by a modified rational formula approach and a constant pollutant concentration, often estimated from the EMCs reported by NURP (Wong et al. 1997).

EMCs for urban runoff in the Unites States are shown in Table 2.1, which are referenced from US EPA, NURP, and USGS and NPDES sources. For total suspended solids (TSS), the US EPA mean was 200 mg/L, which is about 15% higher than that of NURP and approximately 150% higher than that of USGS and NPDES. The EMC for biochemical oxygen demand (BOD_5) is similar among the sources, but chemical oxygen demand (COD) varies among the sources by a factor of 2.

The EMCs are especially valuable for estimating pollutant loads. If the EMC is known, and the rational method for calculating runoff is assumed, it is easy to estimate loads. The load is the product of the rainfall, area and runoff coefficient. This approach is useful if the environment of the receiving water can be managed using average concentrations and loads (Corwin and Vaughan 1997; Irish Jr. et al. 1998). An important short coming of the simple EMC-Rational method models is their inability to express concentration change with time. If the receiving water is affected by transient inputs as opposed to mean inputs, more advanced approaches are needed.

2.4. FIRST FLUSH EFFECTS

A first flush is a commonly assumed phenomenon and means that the water quality of the first runoff is worse than subsequent runoff. Usually the stormwater that initially runs off an area will be more polluted than the stormwater that runs off later, after the rainfall has 'cleaned' the catchment. The stormwater containing this high initial pollutant load is called the 'First Flush'.

The definition of first flush is generally related to the observation of high concentrations of suspended sediments within the first part of the storm. The first flush can be affected by various conditions as follows: rainfall characteristics such as peak intensity and storm duration; runoff conditions, such as antecedent dry periods, slope, and catchment area. Very large catchments may not exhibit a first flush to the time of runoff travel.

Initially, Thornton and Saul (1987) defined the first flush as the initial period of storm flow during an event, when the concentration of pollutants is significantly higher than those observed during the latter stages of the storm event. Other approaches to define first flush have are more quantitative, and are based fractional mass loading of the early part of the runoff event.

The lack of consensus over first flush definitions has created a debate over the existence of first flush. Geiger (1987) defined a first flush as occurring when initial slope of normalized cumulative volume is greater than 45% using the point of maximum divergence from 45% slope to quantify the first flush as shown on Figure 2.2 (Gupta and Saul 1996; Larsen et al. 1998). Vorreiter and Hickey (1994) defined a first flush phenomenon in terms of the pollution load is in the first 25% of the event volume. Bertrand-Krajewski et al. (1998) described fractional, normalized, mass loading curves, which provides the most rational method for defining a mass first flush. Deletic (1998) calculated the mass using standard statistical methods including multiple regression model and used the mass carried in the first 20% of runoff volume to quantify the first flush. Saget et al. (1995) and Bertrand-Krajewski et al. (1998) concluded that a first flush exists when at least 80% of the pollution mass is transported in the first 30% of the runoff volume. Sansalone and Buchberger (1997) concluded that there are no restrictive criteria and first flush occurs when a mass cumulative curve is above the runoff volume curve.

Ma et al. (2002) proposed a continuous criteria and nomenclature for mass first flush. He suggested that MFF_n ratio be used, where n represents the volume of runoff in percent. The value of the ratio is the mass discharged in the first n% of the runoff divided by the total mass runoff. For example an MMF_{10} and MFF_{30} of 2.5 and 1.5 mean that 25% of the pollutant mass is discharged in the first 10% of the runoff and 45% of the runoff mass is discharged in the first 30% of the runoff, respectively. Ma et al. (2002)

reported mass first flush ratios for 52 storms and showed that *MFF20*'s ranged from 2.5 to 1.0 for more than 30 water quality parameters.

Then, does first flush always happen? The existence of first flush should not be assumed in all cases. Intensive monitoring of stormwater runoff from some catchments has failed to document this phenomenon. Clearly the existence or non-existence of first flush is critical in the design of stormwater pollution controls. While the concept of first flush is straightforward, first flush may not be observed for one or more of the following reasons:

(1) The drainage characteristics of the catchment may prevent it. In large catchments, the initial runoff from the most distant parts of the catchment may not reach the catchment outlet for some time after a storm starts. This time lag is rarely an issue for smaller catchments.

(2) The pollutants may not be very mobile or may be mobilized by rainfall intensity. Oil and grease is not easily scrubbed from pavements since it is hydrophobic. Bare soils or vegetated surfaces are generally not scrubbed as easily or effectively as impervious surfaces.

(3) Pollutant sources that are effectively continuous may exist within the catchment. First flush is generally seen only where the supply of pollutants is limited. Sediment runoff from soil erosion, for example, may not show a first flush because the supply of soil particles is unlimited.

2.5. WASHOFF MODEL

Usually the pollutant concentrations decline over time, which tends to create greater emission rates at the beginning of runoff (e.g. the first flush). The decline in concentration may sometimes be off-set by an increasing runoff rate as a storm progresses.

To evaluate first flush effects and BMP selection, models are often used to predict pollutant concentration. Regression models, stochastic and deterministic simulation models have all been used (Irish Jr. et al. 1998). The main difference among the models is the assumption of the origin of pollutants. Most of the models commonly use concentrations or loads of pollutants as variables that are dependent upon runoff volume, rainfall intensity, traffic intensity, antecedent dry days, surrounding land use, and other factors. Generally it is difficult to consider all factors because many different site-specific conditions exist, such as presence or absence of street sweeping, soil saturation, wind direction, etc. Regression models have been criticized as poor predictors of future events and too site specific (Driscoll et al. 1990). Detail washoff and buildup models developed by previous researchers are summarized on Table 2.2 and 2.3.

Many stormwater models assume that the rate of washoff is a function of the amount of pollutant present on the watershed. This formulation usually results in higher predicted concentrations at the beginning of the storm event, and can model first flush.

In 1987, Grottker used the washoff rate to derive the model shown in equations 2.3 and 4:

$$Washoff\ rate = -\frac{dM}{dt} = k_1 \cdot Q_{TRu}(t) \cdot M \qquad (2.3)$$

$$M_t = M_i \exp\left[-k_1 \cdot Q_{TRu}(t)\right] \qquad (2.4)$$

Where, M_t is the pollutant mass on the watershed at time, t, and M_i is initial mass. The unit of these two terms is mass per area and time. k_l is a washoff coefficient having units of mm^{-1}, and Q_{TRu} is total runoff volume to time, t, having units of volume per time.

Equation 2.4 states that the quantity of pollutants available for washoff decreases exponentially with runoff during an event.

Osuch-Pajdzinska and Zawilski (1998) described other washoff models based on Grotther model (1987). When the load prior to the rainfall (M_i) is considered, the equation 2.4 can be expressed to equation 2.5.

$$M_w = M_i - M_t = M_i \cdot \left\{1 - \exp\left[-k_1 \cdot Q_{Tru}(t)\right]\right\} \qquad (2.5)$$

Where, M_w is the washed off mass during a storm event.

2.6. BUILDUP MODEL

The sources of urban runoff pollution can be categorized as follows: wet and dry atmospheric deposition, street refuse deposition including litter, street dirt, vegetation and organic residues, Traffic emissions, erosion and road deicing. A significant portion of pollutant loadings from urban areas can be attributed to rain and snowfall (Duyzer and Vonk 2002). This is especially true for nitrogen.

Fugitive dust emissions and transport are the major sources of dry deposition from the atmosphere. The origin of dustfall is mostly from unpaved roads, parking lots, construction and demolition sites, urban refuse (garbage), surrounding soils and industrial emissions. Field and Turkeltaub (1981) estimated the atmospheric fallout rate to 0.05 g/m^2-day. Most of the traffic exhaust particles are dust-sized (<60 um). However, vehicle exhaust is not the only source of traffic-related pollution. Tire wear, solids carried on tires and vehicle bodies, wear and break-down of parts, and loss of lubrication fluids add to the pollution input attributed to traffic. Shaheen (1975) estimated that approximately 0.7 g/axle-km of solids was directly attributed to traffic. Direct traffic emissions were reported to be 0.2 g/vehicle-km from tire wear (Anon 1977).

Usually, the amount of polluted dust on highway surfaces should increase with the duration of the dry period. This would mean that pollutant loading of runoff flow during a storm event should depend on antecedent dry days (ADD). However, the role of ADD in the process of pollution generation has been questioned. Sartor and Boyd (1972) found a weak exponential relationship between ADD and mass of solids accumulated on asphalt surface with data obtained by vacuum cleaning of paved surfaces.

No one doubts that ADD largely affects pollutant mass accumulation, which was the original basis for developing buildup models. A buildup model generally can be expressed as a linear, power-law, exponential, or other function of time during a dry period. However, many models use the exponential representation because it is simple and has been previously used. The following buildup equation is a general buildup model described by Grottker (1987).

$$L_t = L_i\left[1 - Exp\left(-k_2 \cdot t\right)\right] \qquad (2.6)$$

Where, L_t is accumulated pollutant mass on the watershed during dry period, L_i is maximum pollutant mass accumulated on the watershed and k_2 is buildup coefficient (d^{-1}). Equation 2.6 shows the entire pollutant load accumulated during dry days. This equation is limited in that the accumulated mass can only be a function of dry days. To define more clearly the mass not washed-off from the previous rainfall event, Charbeneau and Barrett (1998) suggested an alternate buildup model as follows:

$$L_t = L_2 + \left(L_i - L_2\right)\left[1 - Exp\left(-k_2 \cdot t\right)\right] \qquad (2.7)$$

Where, L_2 is the pollutant mass not washed-off from the previous rainfall event, which can be called "the initial mass for the dry period".

Ball et al. (1998) tried to find the best reasonable buildup model using regression of ADD. Of the several regression functions, such as linear, exponential, power, reciprocal and hyperbolic, they concluded that the power and hyperbolic functions produced the best fit for road surfaces.

In many urban runoff models, ADD is one of the most important variables. The widely used Storm Water Management Model (SWMM, O'Loughlin et al. 1996) uses this approach. Other models ignore ADD; Deletic and Maksimovic (1998) compared event mean concentrations (EMCs) to ADD and concluded that they were weakly related. However, they also agreed that buildup and wash-off models should be related to each other, even though the relationship may not be precisely known. Buildup depends on the season, ADD, wind speed, land use, traffic, etc and wash-off may be a function of rainfall intensity, bottom shear stress and other factors (Mostaghimi et al. 1997; Ristenpart 1999). Novotny et al. (1985) and Osuch-Pajdzinska and Zawilski (1998) considered wind, street sweeping and mass accumulation rate in their buildup models.

However, the problems with the previously mentioned models are how to clearly estimate the initial mass and the pollutant accumulate rate during dry periods. Observing building up during dry days is the most reasonable method for estimating the initial retained mass and pollutant accumulate rate; however, to estimate the total accumulated mass during dry days, the experiment should be continued until a storm event. Sometimes these periods might be very long, which makes the research difficult to perform. Grottker (1987) found that high mass accumulation occurs during very short time periods after a rainfall, especially in the first day. This may occur because the surface is clean, which allows dust to accumulate. As the surface dust increases over time, other mechanisms such as wind may remove dust, which eventually establishes equilibrium. Grottker (1987) also suggested that the buildup should be related to washoff rate because many site specific conditions affect accumulated mass. Many factors such as street cleaning, wind speed, and traffic are known to affect to pollutant mass accumulation on highway surfaces. The variability in these factors make modeling of accumulated pollutant mass more difficult.

2.7. LITTER WASTE

Street litter, such as plastic bags, cups, and candy wrappers, is often swept away with stormwater into drains which terminate in receiving waters. This is the source of much of the litter this is observed floating in the ocean or washing up on beaches. A great deal of street litter is made up of plastic, which may take hundreds of years to break down and become harmless to the environment. Litter is considered one of the major pollutants of concern in protecting the integrity of California's receiving waters for beneficial use. As shown on Figure 2.3 and 2.4, many waters in United States and California are impaired from those pollutant sources. The California Water Resources Control Board has identified in their 303(d) list at least 36 water bodies where trash or litter is considered a pollutant of concern (CSWRCB 1999). On June 18, 2001 the California Regional Water Quality Control Board, Los Angeles Region, developed a total maximum daily load (TMDL) for trash in the Los Angeles River (CRWCB 2001). Figure 2.5 shows the impaired water bodies for affecting Santa Monica bay.

Faced with expected future trash regulations, the California Department of Transportation (Caltrans) is assessing the characteristics and potential impacts of litter generated from their highways (Caltrans 2000a). Caltrans is also evaluating the practical application and performance of several litter capturing devices (Caltrans 2001). Litter characterization has been an integrated part of the Caltrans First Flush Characterization Study (FFCS), where both water quality and litter characteristics are evaluated during the first flush as well as during the entire storm event

2.8. BEST MANAGEMENT PRACTICES

In an urban setting, best management practices (BMPs) can be of two types that address either the source of the problem or attempt to treat the stormwater. Source controls are practices that keep chemical pollutants or litter from entering the runoff. Examples include covering storage areas and/or diverting runoff away from such areas, street sweeping, household hazardous waste recycling programs and education. Treatment control BMPs refer to device that removes pollutants from the runoff, and examples include vegetated swales and buffers strips, infiltration, detention basins or catch basin inserts (EPA 1994; Jefferies et al. 1999).

The existence of a first flush of pollutants provides an opportunity for controlling stormwater pollution from a broad range of land uses. First flush collection systems are employed to capture and isolate this most polluted runoff, with subsequent runoff being diverted directly to the stormwater system or treated in some less expensive way. First flush is most readily observed on small catchments or individual premises, particularly if a high proportion of the catchment is impervious (Ferguson 1998). In such cases, the first flush collection system should be an integral part of the stormwater pollution control system. The first flush containment system also acts as an emergency backup if there is a chemical spill or similar incident. This reduces the risk of pollution and subsequent legal action.

The following principles are a general guide to controlling stormwater pollution from individual premises. Some of these principles apply to large-scale stormwater management.

(1) Minimize the availability of pollutants to be entrained by stormwater runoff.

(2) Install a first flush collection system and associated drainage works to capture the most polluted portion of the site's stormwater runoff.

(3) Re-use or dispose of first flush water quickly and properly.

It is important that the stormwater captured in the first flush collection pit be promptly re-used or disposed of before the catchment is contaminated.

REFERENCES

Andersen, H.E., Kronvang, B., and Larsen, S.E. (1999). "Agricultural practices and diffuse nitrogen pollution in Denmark: empirical leaching and catchment models." *Wat. Sci. & Tech.*, 39(12), 257-264.

Anon. (1977). "Control of reentrained dust from paved streets." *EPA 907/9-77-007, U.S. EPA*, Kansas City, MO.

Arnold, C., and Gibbons, J. (1996). "Impervious surface coverage: the emergence of a key environmental indicator." *J. of the American planning association*, 62(2), 243-258.

Ball, J.E., Jenks, R., and Aubourg, D. (1998). "An assessment of the availability of pollutant constituents on raod surfaces." *The Science of the Total Environment* 209, 243-254.

Barrett, M.E., Irish, Jr. L.B., Malina, Jr. J.F., and Charbeneau, R.J. (1998). "Characterization of highway runoff in Austin, Texas, area." *J. of Environmental Engineering*, 124(2), 131-137.

Becher, K.D., Schnoebelen, D.J., and Akers, K.K.B. (2000). "Nutrients discharged to the Mississippi River from Eastern Iowa watershed, 1996-1997." *J. of The American Water Resources Associa.*, 36(1), 161-173.

Bertrand-Krajewski, J., Chebbo, G., and Saget, A. (1998). "Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon." *Wat. Res.*, 32(8), 2341-2356.

Blackwell, M.S. A., Hogan, D.V., and Maltby, E. (1999). "The use of conventionally and alternatively located buffer zones for the removal of nitrate from diffuse agricultural run-off." *Wat. Sci. & Tech.*, 39(12), 157-164.

Braune, M.J., and Wood, A. (1999). "Best management practices applied to urban runoff quantity and quality control." *Wat. Sci. & Tech.*, 39(12), 117-121.

California Department of Transportation (2000a). "District 7 litter management study final report, June." *Caltrans Document No.* CTSW-RT-00-13.

California Regional Water Quality Control Board (CRWQCB, 2001). "Trash total maximum daily loads for the Los Angeles River watershed." June 18.

California State Water Resources Control Board (CSWRCB, 1999). "1998 California 303(d) List and TMDL Priority Schedule."
http://www.swrcb.ca.gov/tmdl/docs/303d98.pdf.

Charbeneau, R.J., and Barrett, M.E. (1998). "Evaluation of methods for estimating stormwater pollutant loads." *J. of Water Environmental Research*, 70(7), 1295-1302.

Chiew, F.H.S., and McMahon, T.A. (1999). "Modeling runoff and diffuse pollution loads in urban areas." *Wat. Sci. & Tech.* 39(12), 241-248.

Corwin, D.L., and Vaughan, P.J. (1997). "Modeling nonpoint source pollutants in the vadose zone with GIS." *Environmental Science & Technology*, 31(8), 2157-2175.

Deletic, A. (1998). "The first flush load of urban surface runoff." *Wat. Res.*, 32(8), 2462-2470.

Deletic, A.B., and Mahsimivic, C.T. (1998). "Evaluation of water quality factors in storm runoff from paved areas." *J. of Environmental Engineering*, 124(9), 869-879.

Dilks, D.W., Helfand, J.S., Bierman, V.J., and Burkhard, L. (1993). "Field application of a steady-state mass balance model for hydrophobic organic chemicals in an estuarine system." *Wat. Sci. & Tech.*, 28, 263-271.

Driscoll, E.D., Shelley, P.E., and Strecker, E.W. (1990). "Pollutant loading and impacts from stormwater runoff. Analytical Investigation and Research Report." Vol. III, FHWA-RD-88-008, *Federal Highway Administration*, USA.

Duyzer, J., and Vonk, A-W. (2002). "Monitoring of POP concentrations and depositions in the Netherlands." *Proceedings of the 6th Int. Conf. on Diffuse Pollution*, 155-160, Amsterdam, The Netherlands.

Ekholm, P., Kallio, K., Salo, S., Pietilainen, O.P., Rekolainen, S., Laine, Y., and Joukola, M. (2000). "Relationship between catchment characteristics and nutrient concentrations in an agricultural river system." *Wat. Res.*, 34(15), 3709-3716.

EPA (1994). "Nonpoint sources pollution control program." *U.S. EPA*, Report 841-F-94-005, USA.

EPA (1995). "Economic benefits of runoff controls." *U.S. EPA*, Report 841-S-95-002, USA.

EPA (1996). "Managing nonpoint source pollution from households." *U.S. EPA*, Report 841-F-96-004J, USA.

Ferguson, B.K. (1998). "Introduction to stormwater: concept, purpose, design." *John Wiley & Sons, INC.* New York, USA.

Field, R., and Turkeltaub, R. (1981). "Urban runoff receiving water impacts: program overview." *J. of Environ. Engr. Div. Proc. Am. Soc. Civ. Engr.*, 107, EE1.

Geiger, W. (1987). "Flushing effects in combined sewer systems." *Proceedings of the 4th Int. Conf. on Urban Drainage.* 40-46, Lausanne, Switzerland.

Grottker, M. (1987). "Runoff quality from a street with medium traffic loading." *The Science of the Total Environment*, 59, 457-466.

Gupta, K., and Saul, A.J. (1996). "Specific relationships for the first flush load in combined sewer flows." *Wat. Res.*, 30(5), 1244-1252.

Haygarth, P.M., and Jarvis, S.C. (1997). "Soil derived phosphorus in surface runoff from grazed grassland lysimeters." *Wat. Res.* 31(1), 140-148.

Heathwaite, L., and Sharpley, A. (1999). "Evaluating measures to control the impact of agricultural phosphorus on water quality." *Wat. Sci. & Tech.*, 39(12), 149-155.

House, W.A., and Warwick, M.S. (1998). "Hysteresis of the solute concentration discharge relationship in rivers during storms." *Wat. Res.*, 32(8), 2279-2290.

Iqbal, M.Z. (1998). "Application of environmental isotopes in storm-discharge analysis of two contrasting stream channels in a watershed." *Wat. Res.*, 32(10), 2959-2968.

Irish, Jr. L.B., Barrett, M.E., Malina, Jr. J.F., and Charbeneau, R.J. (1998). "Use of regression models for analyzing highway storm-water loads." *J. of Environmental Engineering*, 124(10), 987-993.

Jefferies, C., Aitken, A., McLean, N., Macdonald, K., and McKissock, G. (1999). "Assessing the performance of urban BMPs in Scotland." *Wat. Sci. & Tech.*, 39(12), 123-131.

Jordan, T.E., Correll, D.L., and Weller, D.E. (1997). "Nonpoint source discharges of nutrients from piedmont watersheds of Chesapeake bay." *J. of The American Water Resources Association*, 33(3), 631-645.

Kawara, O., Uehara, M., and Ibaragi, K. (1999). "A study on the water quality of runoff from forest." *Wat. Sci. & Tech.*, 39(12), 93-98.

Larsen, T., Broch, K., and Andersen, M.R. (1998). "First flush effects in an urban catchment area in Aalborg." *Wat. Sci. & Tec.*, 37(1), 251-257.

Lee, H. L., and Bang, K.W. (2000). "Characterization of urban stormwater runoff." *Wat. Res.*, 34(6), 1773-1780.

Line, D.E., Arnold, J.A., Jennings, G.D., and Wu, J (1996). "Water quality of stormwater runoff from ten industrial sites." *Water Resources Bulletin of American Water Resources Association*, 32(4), 807-816.

Ma, M., Khan, S., Li, S., Kim, L-H., Ha, S., Lau, S., Kayhanian, M., and Stenstrom, M.K. (2002). "First flush phenomena for highways: how it can be meaningfully defined." *Proceedings of 9th International Conference on Urban Drainage*, September, Portland, Oregon.

Mostaghimi, S., Park, S.W., Cooke, R.A., and Wang, S.Y. (1997). "Assessment of management alternatives on a small agricultural watershed." *Wat. Res.* 31(8), 1867-1878.

Novotny, V., Sung, H.M., Bannerman, R., and Baum, K. (1985). "Estimating nonpoint pollution from small urban watersheds." *J. of WPCF*, 57(4), 339-348.

O'Loughlin, G., Huber, W.C., and Chocat, B. (1996). "Rainfall-runoff processes and modeling." *J. of Hydraulic Research.* 34(6), 733-751.

Osuch-Pajdzinska, E., and Zawilski, M. (1998). "Model of storm sewer discharge. I: description." *J. of Environmental Engineering*, 124(7), 593-599.

Pratt, C.J., and Horstead, J.R. (1987). "Interim developments towards design limits on Pollution." *The Science of the Total Environment*, 59, 431-436.

Pratt, C.J., Elliott, G.E.P., and Fulcher, G.A. (1987). "Suspended solids discharge from highway gully pots in a residential catchment." *The Science of the Total Environment*, 59, 355-364.

Ristenpart, E. (1999). "Planning of stormwater management with a new model for drainage best management practices." *Wat. Sci. & Tech.* 39(9), 253-260.

Saget, A., Chebbo, G., and Bertrand-Krajewski, J. (1995). "The first flush in sewer system." *Proceeding of the 4th Int. Conf. on Sewer Solids-Characteristics, Movement, Effects and Control*, 58-65, Dundee, UK.

Sansalone, J.J., and Buchberger, S.G. (1997). "Partitioning and first flush of metals in urban roadway storm water." *J. of Environmental Engineering*, 123(2), 134-143.

Sansalone, J.J., Koran, J.M., Smithson, J.A., and Buchberger, S.G. (1998). "Physical characteristics of urban roadway soils transported during rain events." *J. of Environmental Engineering*, 124(5), 427-440.

Sartor, J.D., and Boyd, G.B. (1972). "Water pollution aspects of street surface contaminants" *EPA-R2-72-081, U.S. EPA*, Washington, D.C.

Sartor, J.D., Boyd, G.B., and Agardy, F.J. (1974). "Water pollution aspects of street surface contaminants." *J. of WPCF*, 46(3), 458-467.

Shaheen, D.G. (1975). "Contribution of urban roadway usage to water pollution." *EPA 600/2-75-004, U.S. EPA*, Washington, D.C.

Smullen, J.T., Shallcross, A.L., and Cave, K.A. (1999). "Updating the U.S. nationwide urban runoff quality data base." *Wat. Sci. & Tech.*, 39(12), 9-16.

Stenstrom, M.K., and Strecker, E.W. (1993). "Assessment of storm drain sources of contaminants to Santa Monica Bay, Vol. III, Surface Drainage Water Quality Monitoring Program Plan." *UCLA-ENG-93-64*, Vol. III, 1-59.

Thornton, R.C., and Saul, A.J. (1987). "Temporal variation of pollutants in two combined sewer systems." *Proceedings of the 4th Int. Conf. on Urban Drainage*, 51-52, Lausanne, Switzerland.

Vorreiter, L., and Hickey, C. (1994). "Incidence of the first flush phenomenon in catchments of the Sydney region." *National Conf. Publication-Institution of Engineers*, Vol. 3, 359-364, Australia.

Wong, K., Strecker, E.W., and Stenstrom, M.K. (1997). "GIS to estimate storm-water pollutant mass loadings." *J. of Environmental Engineering*, 123(8), 737-745.

Wu, J.S., Allan, C.J., Saunders, W.L., and Evett, J.B. (1998). "Characterization and pollutant loading estimation for highway runoff." *J. of Environmental Engineering*, 124(7), 584-592.

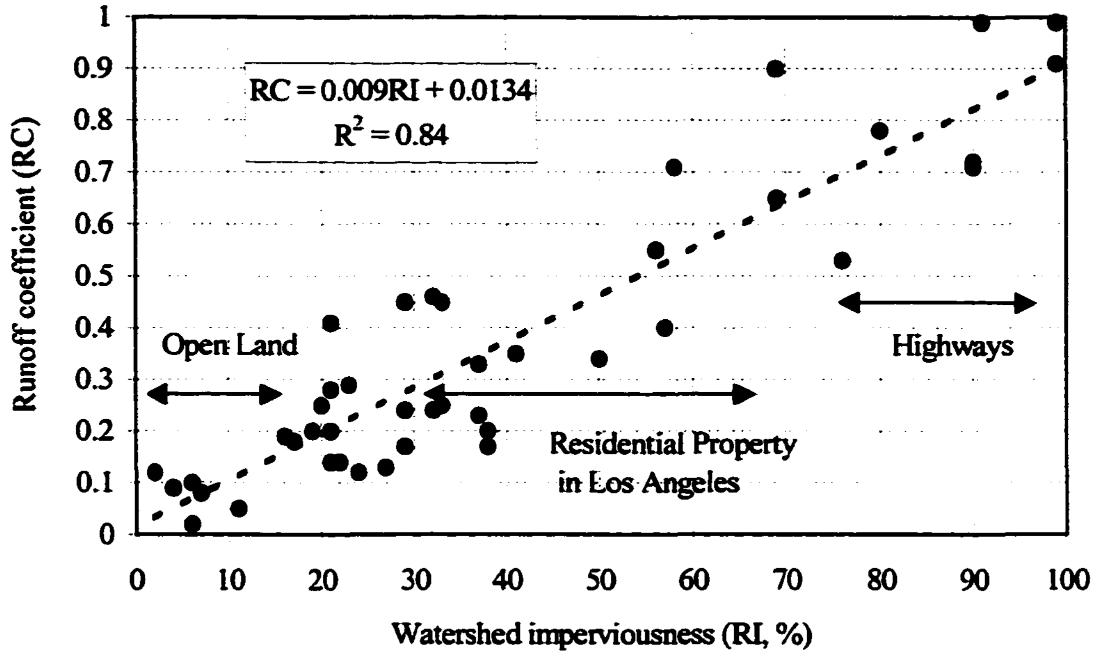


Figure 2.1. Watershed imperviousness and stormwater runoff coefficients [The figure was developed from more than 40 runoff monitoring sites throughout the U.S. (Dilks et al., 1993; Ferguson, 1998; Chiew and McMahon, 1999)].

Table 2.1. General urban runoff EMCs of US EPA, NURP and USGS

Unit: mg/L	US EPA (1)	NURP (2)	USGS and NPDES (3)
TSS	200.0	174.0	78.4
BOD	12.0	10.4	14.1
COD	103.0	66.1	52.8
Total P	0.52	0.34	0.32
PO_4P	0.17	0.10	0.13
TKN	2.40	1.67	1.73
NO_2 & NO_3	1.22	0.84	0.66

(1) United States Environmental Protection Agency (US EPA, 1983)
(2) Updated Urban Runoff data from Nationwide Urban Runoff Programs (NURP, 1999)
(3) United States Geological Survey (USGS) and National Pollutant Discharge Elimination System (NPDES, 1999)

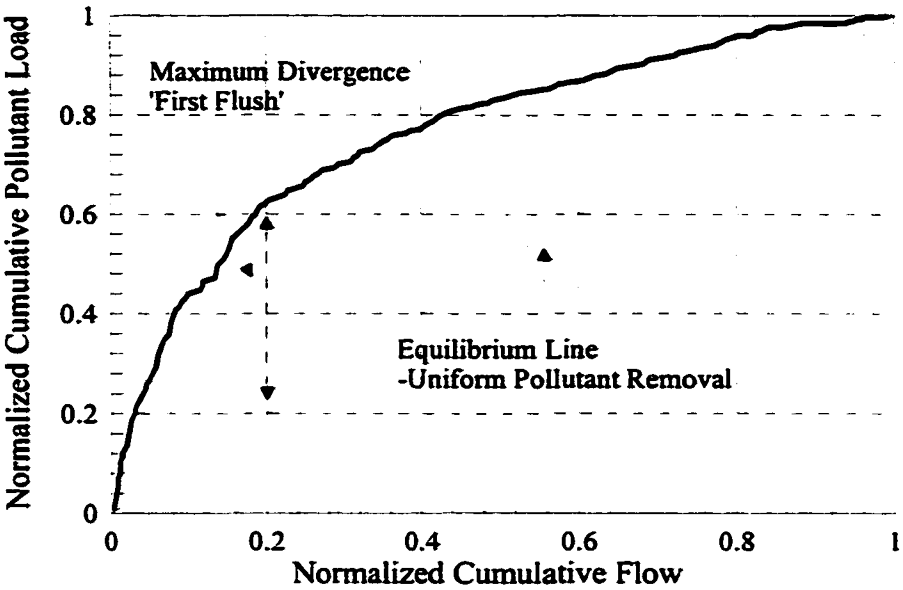


Figure 2.2. General type of normalized cumulative flow and mass and definition of first flush by Geiger (1987).

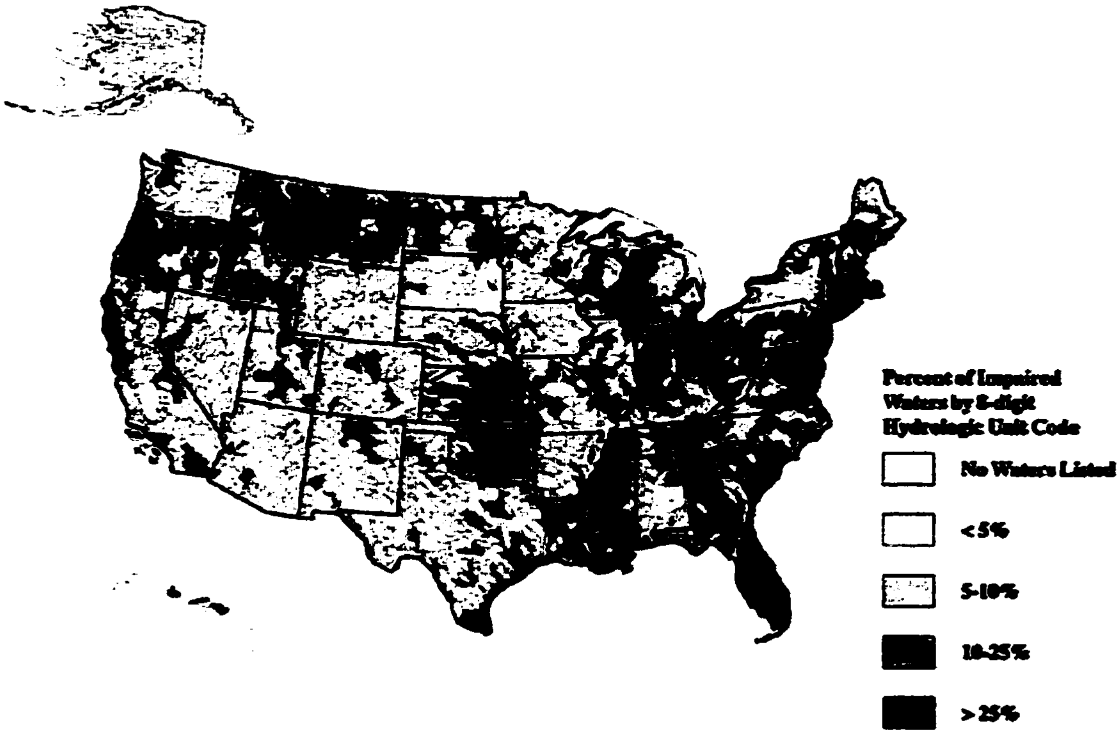


Figure 2.3. Impaired waters in United States.

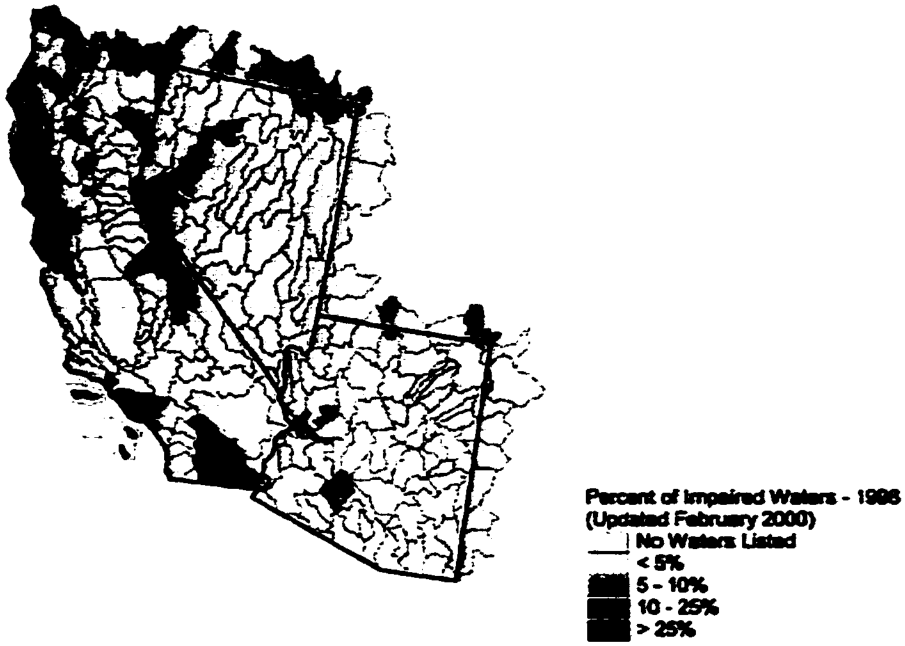


Figure 2.4. Impaired waters in California.

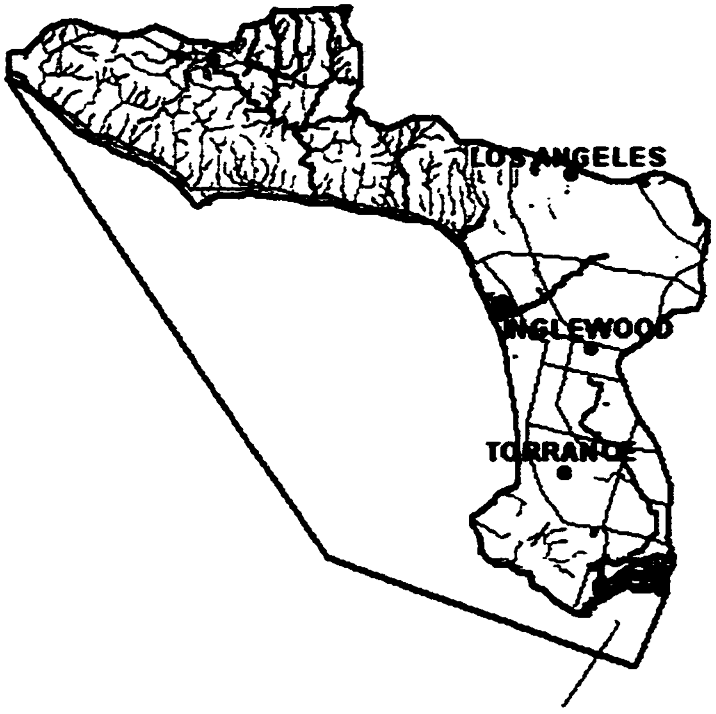


Figure 2.5. Impaired waters affecting to Santa Monica Bay (/\/: impaired waters)

Table 2.2. Previous washoff models

References (year)	Model objective	Classification	Model	Comments
Grottker (1987)	W	Regression	$L_w = L_{w0}\exp(k_1 R)$	R = effective rainfall
Gupta and Saul (1996)	W	Empirical	$Load_{ff} = f\left(EMC_f, EMF, RFINT, QIN_{max}, STDURN, ADWP, Flow\right)$ $Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + \ldots + A_nX_n$ $Load_{ff} = a(StDu)^b(RFINT)^c(ADD)^d$	$Load_{ff}$ = cumulative load in the first flush, kg EMF = event mean flow $RFINT$ = rainfall intensity ADD = antecedent dry weather periods $StDu$ = total storm duration QIN = inflow rate $R^2 > 0.5$
Saget et al. (1995)	W	Empirical	$Y = X^a$	Y = the fraction of discharged pollutant load X = the fraction of discharged volume
Barrett et al. (1998)	W	Empirical	$Conc. = a \cdot \exp(-k_1 \cdot H)$	$Conc.$ = concentration, mg/L
Bertrand-krajewski et al.(1998)	W	Empirical	$Y = X^a$	Y = the fraction of discharged pollutant load X = the fraction of discharged volume
Charbeneau and Barrett (1998)	W	Washoff rate	$L_w = L_2 + (L_o - L_2)\left[1 - Exp(-k_1 \cdot t)\right]$	
Deletic and Maksimovic (1998)	W	SL	$Load_w = a \cdot R_v$	R_v = runoff volume, L/m^2 $R^2 > 0.86$ No correlation between concentration and ADP
Irish et al. (1998)	W	Regression	$Load_w = a + b(Flow) + c(Intensity) + d(ADP) + e(PINT) + g(PFLOW)$	$PINT$ = the intensity of the preceding event(L/m^2-min) $PFLOW$ = the total volume per unit area(L/m^2) $R^2 > 0.9$
Osuch-Pajdzinska and Zawilski (1998)	W	Washoff Rate	$L_w = L_{w0}\left[1 - \exp(-kH)\right]$	
Wu et al. (1998)	W	Simple Linear	$L = a + b \cdot VDS$	* Loading attributed to vehicular traffic for an event VDS = total traffic count during a storm event
Chiew and McMahon (1999)	W		$Load = a(Runoff)^b$	
Becher et al. (2000)	W	Empirical	$\ln(L) = B_0 + B_1\ln(Q_m) + B_2\ln(Q_m)^2 + B_3t + B_4t^2 + B_5\sin(2\pi t) + B_6\cos(2\pi$	B_0, B_1, B_2, B_3, B_4, B_5 and B_6 = regression coefficient

$Load_w$ = the load of pollutant washed- off (kg/m^2); L_w = the load of pollutant washed- off (kg); L_{wo} = pollutant load accumulated on catchment surface prior to rainfall (kg); K = coefficient of washoff rate (1/m); H = total depth of runoff (m).

Table 2.3. Previous buildup models

References (year)	Model objective	Classification	Model	Comments
Novotny et al. (1985)	B	Empirical	$L_a(i)=\frac{L_T}{\xi}\left[1-\exp(-\xi)\right]+L_a(i-1)\cdot\exp(-\xi)$	L_T = true pollutant input ξ = removal coefficient $=0.00116\times(TS+WS)\cdot\exp(-8.8H)$
Grottker (1987)	B	Empirical	$L_a=L_{a\infty}\left[1-\exp(k_2 t)\right]$	
Ball et al. (1998)	B	Regression	$L_a=a\cdot t^b$ $L_a=\frac{t}{a+bt}$	Power: $R^2=0.6$ for sediment Hyperbolic: $R^2=0.65$ for sediment
Osuch-Pajdzinska and Zawilski (1998)	B	Builup rate	$L_a=\frac{a_1(A-A_u)\beta_1+a_2A_u\beta_2\eta}{w}\left[1-\exp(-wt)\right]$ $+L_{a0}\exp(-wt)$	A_u = area of the streets and squares, m^2 η = street sweeping effectiveness parameter
Novotny et al. (1985)	SS	Empirical	$L_{sw}=L^*+\left(L_{sw}-L^*\right)\cdot\exp(-k_3\cdot E)$	L^* = treshold pollutant accumulation E = street effort
Grottker (1987)	SS	Empirical	$L_{sw}=k_3\cdot L_{sw0}^{k_4}$	K_3 and K_4 = street sweeping constant

L_{ao} = pollutant load not washed-off catchment (kg); L_a=pollutant load accumulated on catchment surface prior to rainfall (kg); a_1 = dust fall (kg/m^2-day); a_2 = quantity of sweeping accumulated on streets and squares (kg/m^2-day); β_1 = conversion factor of the mass of the particular matter into parameters; β_2 = conversion factor of the mass of sweepings into parameters; ω = wind factor; t = time in days; A = catchment area (m^2); a, b, c, d, e, g = regression coefficients.

CHAPTER III.

DETERMINATION OF FIRST FLUSH CRITERIA USING MONITORING AND NEW CONCEPTUAL WASHOFF MODEL IN HIGHWAY RUNOFF

ABSTRACT

Highways are stormwater intensive landuses since they are impervious and have high pollutant mass emissions from vehicular activity. Vehicle emissions include different pollutants such as heavy metals, oil and grease and particulates from sources such as fuels, brake pad wear and tire wear. To understand the magnitude and nature of the stormwater emissions, a three-year study was conducted with the goal of quantifying stormwater pollutant concentrations, mass emission rates and the first flush of pollutants. Eight highway sites were monitored for three years for a large suite of pollutants. The monitoring protocol emphasized detecting the first flush and quantifying the event mean concentration. Grab and flow-weighted composite samples, rainfall and runoff data were collected. A new runoff model using four parameters was developed that describes first flush of pollutants for a variety of rainfall and runoff conditions. The model was fit to more than 40 events for 8 pollutants, and the parameters were correlated to runoff

conditions, such as total runoff, antecedent dry days and runoff coefficient. Improved definitions of first flush criteria are also presented.

Keywords

Best management practice; event mean concentration; first flush; highway; washoff, stormwater.

3.1. INTRODUCTION

The United States Environmental Protection Agency (USEPA) developed the Nationwide Urban Runoff Program (NURP) to expand the state of knowledge of urban runoff pollution by instituting data collection and applied research projects in selected urban areas throughout the country (Driscoll et al. 1990; EPA 1994, 1995, 1996). The discovery that significant quantities of organics, nutrients, pesticides, herbicides and heavy metals are present in runoff caused the U.S. EPA to require regional urban planning agencies to conduct planning studies regarding ways to reduce pollution from urbanized areas under section 208 of the Clean Water Act.

Best Management Practices (BMPs) are usually required to mitigate non-point source pollution and refer to management practices and engineering methods to control pollutants in runoff (Silverman et al. 1986; Jefferies et al. 1999; Smullen et al. 1999). In an urban setting, BMPs are of two types: source and treatment controls. Source controls are practices that keep chemical pollutants from entering the runoff, such as covering storage areas and/or diverting runoff away from such areas, street sweeping, and household hazardous waste recycling programs. Treatment control BMPs refer to devices that remove pollutants from the runoff, such as vegetated swales and buffers strips, infiltration, detention basins and catch basin inserts (EPA 1994; Jefferies et al. 1999).

The quantity and magnitude of runoff pollutants is a function of landuse and highways are among the higher emitters. Highway runoff contains pollutants from vehicular activities (metals from brake pad wear, combustion by-products, tire wear and corrosion products) pollutants from wet and dry atmospheric deposition, and gross deposition such as litter, vegetation and organic residues, erosion and road deicers. The runoff concentration from these varied sources is usually quantified with an event mean concentration (EMC), which is a flow weighted average (Bertrand-Krajewski et al. 1998). The EMC can be multiplied by the total runoff volume to determine the mass emission such as equation 3.1.

$$EMC = \frac{\textit{Discharged mass during an event}}{\textit{Discharged volume}} = \frac{\int_0^t C(t) \cdot Q_{TRu}(t)dt}{\int_0^t Q_{TRu}(t)dt} \qquad (3.1)$$

where, $C(t)$ = pollutant concentration; and $Q_{TRu}(t)$ = runoff flow rate discharged at time t.

One of the key problems in calculating the EMC is how to express the concentration. It is usually cost prohibitive to measure $C(t)$ at frequent intervals and some lesser number of samples is collected. Rainfall or runoff can usually be measured automatically and it is common to record them on one to five minute intervals. Flow-weighted automatic samplers can be used for many pollutants, but are expensive and provide no information on the time varying changes of concentration or mass emission rate. The EMC is useful in predicting the total mass emission rate. The total mass emission can be calculated as the product of rainfall, catchment area, runoff coefficient and EMC. Historical records for rainfall as well as runoff coefficients and areas are usually available, which has made the EMC critical parameter for estimating the contribution of runoff to receiving waters (Corwin and Vaughan 1997; Irish Jr. et al. 1998).

The EMC does not provide information on the time varying changes in pollutant concentration or mass emissions, which are often important for BMP development, or understanding shock loads. Pollutant concentration often declines over time, which tends to create greater emission rate at the beginning of runoff. This phenomenon is often called a "first flush", and the existence of a first flush can influence the selection of best management practices. The decline in concentration is sometimes offset by an increasing runoff rate as a storm progresses.

To evaluate first flush effects and BMP selection, models are often used to predict pollutant concentration. Regression models, stochastic and deterministic simulation models have all been used (Irish Jr. et al. 1998). The main difference among the models is the assumption of the origin of pollutants. Most of the models commonly use mass emission rate as a governing equation, express concentrations or loads of pollutants as function of time. The variables are usually dependent upon runoff volume, rainfall intensity, traffic intensity, antecedent dry days, surrounding landuse, etc. Generally it is difficult to consider all affecting factors for a governing equation because many different site-specific conditions exist, such as presence or absence of street sweeping, soil saturation, wind direction, etc. These regression models have been criticized as poor predictors of future events or other regions (Driscoll et al. 1990).

The existence of first flush is debated and many defining criteria exist (Bertrand-Krajewski et al. 1998). Thornton and Saul (1987) defined the first flush as the initial period of storm flow during a storm event. Geiger (1987) defined a first flush as occurring when the slope of normalized cumulative mass emission plotted against normalized cumulative volume is greater than 45%. Later investigators have also used this definition (Gupta and Saul 1996; Sansalone and Buchberger 1997; Larsen et al. 1998; Sansalone et al. 1998). Vorreiter and Hickey (1994) proposed using only the first 25% of runoff volume in defining first flush. Deletic (1998) used standard statistical methods including a multiple regression model, and restricted first flush to the first 20% of runoff. Saget et al. (1995) and Bertrand-Krajewski et al. (1998), defined a first flush as occurring when at least 80% of the pollutant load is emitted in the first 30% of the runoff volume. First flushes have most often been observed in small watersheds, particularly if imperviousness is high. Large watersheds may have long time of travel, so that the early runoff from areas far from the sample location is mixed with later runoff from areas adjacent to the sample location.

In this research we investigate the existence of first flush as a function of site-specific variables as well as stormwater characteristics. The watersheds or sites are small, and avoid problems associated with time of travel in large watersheds. The objectives of the study are to show determination approaches for EMCs and mass loading with new derived washoff model and to suggest a clear definition and criteria of first flush.

3.2. METHODS

Rainfall, runoff rate and runoff quality were monitored at 8 freeway sites in Southern California over two rainy seasons (1999 to 2001). The sites were equipped with recording flow meter and rainfall gage and flow-proportional automatic sampler for taking composite water sample. Four-liter grab samples were also collected. Generally 5 samples were collected in the first hour. The first sample was collected at the very beginning of runoff. Additional samples were collected each hour until the end of runoff. EMCs were calculated by integrating the product of runoff rate and concentration and compared to the results from the automatic sampler. A large suite of water quality parameters was measured, including oxygen demand parameters, metals, nutrients and ions (Stenstrom et al. 2001).

3.2.1. Descriptions of Sites and Events

Figure 3.1 shows the monitoring locations. All events above a minimum rainfall (generally > 0.3 cm rainfall) were monitored. Detail summaries of sites and events are shown in Table 3.1, which includes site area, date, average daily traffic (ADT), antecedent dry days, rainfall, storm duration and total volume of runoff. The event rainfall varies from 0.3 cm to 5.64 cm and antecedent dry days vary from 1 to about 69 days. The smallest catchment area is 1,700 m^2 at site URS6-20F and the largest area is 48,100 m^2 at site CDM7-10.

3.2.2. Derivation of New Washoff Model

It is well known that the EMCs cannot be determined by simple statistical averaging of measured pollutant concentration in stormwater runoff because of random characteristics of runoff quality and quantity. The sources of uncertainty are broadly caused by uncertainties in rainfall intensity and magnitude, experimental errors, and lack of sufficient data.

Gupta and Saul (1996) used multiple linear regression analysis for data interpolation and Larsen (1998) calculated EMCs using medium point method. In many previous papers (Charbeneau and Barrett 1998; Deletic and Mahsimivic 1998; Irish Jr. et al. 1998; Osuch-Pajdzinska and Zawilski 1998; Deletic et al. 2000), the exponential washoff model derived using mass emission rate was applied for estimating EMCs.

Many different trends in concentrations were observed during monitoring. Figure 3.2 shows the pollutographs observed during monitoring periods. Only a few of the graphs such as oil and grease and COD (upper left box) can be easily fit with an exponential function. Dilution is a mechanism that is not possible to predict with an exponential model. Concentration reduction occurs whenever a particular quantity of pollutants mixes with a large runoff volume. The dilution in stormwater occurs essentially as a continuous process, and varies with rainfall rate.

It is generally assumed that a pollutant has an initial mass on the watershed area that existed before the rainfall, and a remaining mass that still exists after the rainfall. The wash-off mass is the difference between total and remaining mass. The total mass on the watershed changes with time due to inputs from wet or dry deposition, automobiles, and other sources. During the storm event, the mass input from automobiles can be high and it can affect runoff concentrations during the storm (Shaheen 1975).

As mentioned earlier, the mechanism affecting the concentration changes with time is the dilution of initial pollutant mass. However, the mass from air and automobiles during a storm event can be creates the opposite trend, continuously adds to the washed-off mass.

The washoff rate can be described such as equation 3.2.

$$\frac{d[C(t)]}{dt} = -\alpha \cdot \frac{Q_{Ru}(t) \cdot C(t)}{V_{TRu}} \qquad (3.2)$$

α = Washoff rate coefficient,

$C(t)$ = Pollutant concentration at time t

V_{TRu} = Total runoff volume = $\int_0^T Q_{Ru}(t)\ dt,\ m^3$

Rearranging equation 3.2.

$$\frac{d[C(t)]}{C(t)} = -\alpha \cdot \frac{Q_{Ru}(t)}{V_{TRu}} dt \tag{3.3}$$

Integrating equation 3.3, we obtain:

$$\ln[C(t)] = -\alpha \cdot \frac{\int_0^t Q_{Ru}(t)dt}{V_{TRu}} + \ln(\beta) \tag{3.4}$$

β = Intergration constant

In equation 3.4, the initial concentration is as follows at $t = 0$: $\ln[C(0)] = \ln(\beta)$

By letting $\frac{\int_0^t Q_{Ru}(t)dt}{V_{TRu}} = \frac{\int_0^t Q_{Ru}(t)dt}{\int_0^T Q_{Ru}(t)dt} = V_{nRu}(t)$, equation 3.4 becomes:

$$\ln[C(t)] = -\alpha \cdot V_{nRu}(t) + \ln(\beta) \tag{3.5}$$

Where, $V_{nRu}(t)$ = Normalized Cumulative Volume, $0 \leq V_{nRu}(t) \leq 1.0$

Taking the exponential of both sides, equation 3.5 becomes:

$$C(t) = \beta \cdot Exp[-\alpha \cdot V_{nRu}(t)] \tag{3.6}$$

Finally, as stated earlier, the mass input during a storm event can be considered as another concentration term (γ), which originates from automobiles, air and other impacting factors. Thus,

$$C(t) = \beta \cdot Exp\left[-\alpha \cdot V_{nRu}(t)\right] + \gamma \tag{3.7}$$

Where, the concentration can also be defined from mass emission rate:

$$M(t) = C(t) \cdot Q_{Ru}(t) \tag{3.8}$$

$M(t)$ = Pollutant mass emission rate at time, t

$$C(t) = \frac{\Delta M(t)}{\Delta Q_{Ru}(t)} = \frac{\int_{t-1}^{t} M(t)dt}{\int_{t-1}^{t} Q_{Ru}(t)dt} = \frac{\int_{t-1}^{t} M(t)dt}{\int_{0}^{t} Q_{Ru}(t)dt - \int_{0}^{t-1} Q_{Ru}(t)dt} \tag{3.9}$$

The denominator of equation 3.9 after integrating becomes

$$\int_{0}^{t} Q_{Ru}(t)dt - \int_{0}^{t-1} Q_{Ru}(t)dt = \left[V_{nRu}(t) - V_{nRu}(t-1)\right] \cdot V_{TRu} \tag{3.10}$$

The difference in two normalized volumes over time t and $t\text{-}1$, which is a normalized flow rate for prediction, let

$$\beta_1 = \frac{\left[V_{nRu}(t) - V_{nRu}(t-1)\right]}{V_{nRu}(t)} \tag{3.11}$$

By substituting equation 3.11 into 3.9 and rearranging, we obtain;

$$C(t) = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot \frac{\int_{t-1}^{t} M(t)dt}{V_{TRu}} \tag{3.12}$$

The normalized flow rate will not be known if the model is used for prediction. If a parameter is used for this value, the parameter can be estimated from previous storms, which allows the model to be used for prediction. Later it will be shown that this parameter is correlated to average runoff velocity, or the average flow rate divided by the catchment area.

The right side of equation 3.12 has units of m/L^3 or concentration. This new concentration term is a key premise of the model. If we let

$\int_{t-1}^{t} M(t)dt \Big/ V_{TRu} = NewConc.\left[V_{nRu}(t)\right]$, equation 3.12 can be expressed such as follows:

$$C(t) = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot \left\{NewConc.\left[V_{nRu}(t)\right]\right\} \qquad (3.13)$$

By equating equations 3.7 and 3.13, we obtain:

$$\beta \cdot Exp\left[-\alpha \cdot V_{nRu}(t)\right] + \gamma = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot \left\{NewConc.\left[V_{nRu}(t)\right]\right\} \qquad (3.14)$$

Summarizing and letting $\beta \cdot \beta_1 = \beta^*$ and $\gamma \cdot \beta_1 = \gamma^*$, the new wash-off model is expressed as follows:

$$NewConc.\left[V_{nRu}(t)\right] = \beta^* \cdot V_{nRu}(t) \cdot Exp\left[-\alpha \cdot V_{nRu}(t)\right] + \gamma^* \cdot V_{nRu}(t) \qquad (3.15)$$

In equation 3.15, a parameter is needed to describe the initial condition, which ideally should be related to antecedent dry periods. The new washoff model is finally expressed as follows:

$$NewConc.\left[V_{nRu}(t)\right] = \delta + V_{nRu}(t) \cdot \left\{\gamma^* + \beta^* \cdot Exp\left[-\alpha \cdot V_{nRu}(t)\right]\right\} \qquad (3.16)$$

The new washoff model has two different parts or functions. The first is a linear, $\gamma^* V_{nRu}(t) + \delta$, and the second takes the form of a gamma type function, $\beta^* \cdot V_{nRu}(t) \cdot Exp\left[-\alpha \cdot V_{nRu}(t)\right]$.

In order to use the model as a predictive tool, it is necessary to predict the total runoff volume, which must be based upon weather forecast or other information. Equation 3.13 has four parameters that are related to antecedent dry periods, rainfall intensity and runoff coefficient. The δ is an initial concentration related to antecedent dry periods. The parameters α and γ^* are related to total runoff. The β^* is related to rainfall, runoff coefficient and storm duration.

3.2.3. Sensitivity Analysis

A sensitivity analysis was performed to define the model's sensitivity with each parameter. The model has more flexibility than previous model, which can be important because many storms do not shown the ideal, decreasing exponential trend in concentration. The model can more accurately predict a greater number of storm events.

Figure 3.3 shows four sets of model responses for changing parameters. Increasing β^* generally increases the peak concentration. As β^* tends to zero, the concentration trend becomes linear. Increasing γ^* increases the final remaining pollutant concentration. Increasing α increases the rate and mass of runoff. All trends are consistent with the governing equation.

One potential use of this model is for data interpolation after a storm event to calculate EMCs and mass loading. The model provides a smooth estimate of concentration and can be used in lieu of discrete data points. Another use is for predictions of pollutant loading and EMCs before a storm event. This will require reliable parameter estimates.

Storm duration varies from event to event, which makes it difficult to predict concentration as a function f time. The new model avoids the problem by using is normalized cumulative flow.

3.3. RESULTS

The model was applied to the data collected from the eight freeway sites over two years and shows good agreement. This is shown in this section and its application for estimating EMCs and impacts on BMP selection are demonstrated.

3.3.1. Runoff Coefficient

The variations of the runoff coefficients are shown on Figure 3.4. The runoff coefficients are ranged from 0.35 to 0.95 depending on rainfall intensity, antecedent dry days and catchment area. The mean value was determined to 0.87. It is higher, approaching unity for large rainfall events, and lower in small rainfall events. This is expected and is caused by depression storage and the limited infiltration that occurs in paved areas. The depression storage and infiltration is low when compare to large rainfall events. For very small rainfall events, evaporation may be significant. Antecedent dry periods are also important because it will affect infiltration.

3.3.2. Comparison of Monitored and Modeled Concentration

The new washoff model was applied for all events as mentioned earlier to predict concentration profiles. The model can predict the various functional types such as linear, exponential and Gamma distributions. The existing models such as exponential and power types have limitations for presenting various types of distributions. However, the new model has flexibility to fit various types of concentration and it fits well. Figure 3.5 shows concentration distributions of monitored and modeled. It shows good agreement for most types of concentration distributions. To use this for prediction, the parameters should be generalized to show their relationship to storm characteristics such as total runoff, ADD, ADT, etc.

The comparison of distributions between measured and estimated concentrations is another important way to assess the model's accuracy. Figure 3.6 shows the comparison of the monitored and modeled results. The R^2 for all water quality constituents are between 0.84 and 0.98 and the residuals (not shown) are generally equally distributed and unbiased. The model can be used to estimate EMCs for an entire event, or could be integrated over a subset of the storm to obtain flow-weighted average concentrations. In this way the concentration in one part of the storm can be compared to concentrations in other parts of the storm.

3.3.3. Washed-off Mass Loading and EMCs for Each Parameter

Washed-off mass was calculated using the continuous model and the measured runoff flow rate with one-minute time intervals. Concentrations at one-minute intervals were generated using the washoff model. Table 3.2 summarizes the statistical analysis for washed-off mass loading and EMCs for each water quality parameter, which shows minimum, maximum, median, outliers and 95% upper/lower confidence intervals. The ranges of washed-off mass loading are from about 0.06 g/m^2 to 17.27 g/m^2 for TSS and about 0.1 to 3.23 g/m^2 for COD. The volume of runoff can affect on mass loading and EMCs because of dilution effect during a storm event. Generally the differences between minimum and maximum washed-off mass and EMCs are large because of event and site characteristics, such as rainfall intensity, area, runoff coefficient and antecedent dry periods. As shown in the tables, large amounts of pollutant are washed-off during storm events, which may affect receiving waters. This process could be expanded to an entire watershed to estimate freeway loadings in a TMDL analysis.

Table 3.2 also shows the summary of EMCs determined with new wash-off model. Appendix 1.2 shows graphical relationships among the EMCs and parameters. The TSS EMCs ranged from 5 mg/L to 880 mg/L and COD EMCs range from 13 mg/L to about 780 mg/L. The EMC ranges for oil and grease range from 0.5 mg/L to 34 mg/L. The large range shows the difficulty of predicting EMCs for even a single land use type.

3.3.4. Comparison of Event Mean Concentrations

It is interesting and useful to compare EMCs calculated in different ways. Three methods for estimating EMCs were used: 1) predicting concentration using the new washoff model; and 2) generating the concentrations from an exponential model, and 3) the medium point method suggested by Larsen (1998). The results are shown in Figure 3.7. The median value is similar, but the 50% interquartile ranges are smaller for new model than other methods, suggesting less variability in of the new method is less. The reductions in variability are even greater if one considers the maximum and minimum values. For example, the maximum TSS EMC calculated using the exponential method is 1200 mg/L. The maximum using the medium point method is 750 mg/L, which compares more favorably to the maximum calculated using the new model, 890 mg/L. The large values calculated with the exponential model occur when the fit is poor. The medium point method is easy to apply, but it potentially inaccurate if there are few monitored samples.

3.3.5. Factors Affecting the EMC

The relationships of pollutant EMCs and factors affecting are shown in Figure 3.8. The correlation matrix shows the relationships of pollutant parameters and possible affecting factors such as ADD, storm duration, total rainfall, total runoff volume, total rainfall volume and average rainfall intensity. The EMCs are negatively correlated to storm duration, total rainfall, total volume of runoff and rainfall, and average rainfall intensity. Large storms have smaller EMCs because of dilution effects or exhaustion of pollutant mass.

3.3.6. First Flush Criteria

Fractions of washed-off mass for each 10% flow volume interval are shown on Figure 3.9. The figure is an example for selected parameters such as oil and grease, TKN and TSS. The fractions of washed-off mass are very high in first 30% of runoff, which is a distinctive feature of the first flush effect. As shown in the figure, after 30% volume, the differences in washed off mass over subsequent flow volume intervals decreases. Using this approach, the first flush can be characterized in mass terms. It is useful to characterize the first flush in terms normalized mass discharged in the first fraction of the normalized runoff volume.

Figure 3.10 shows two ways of plotting the normalized washed off mass as a function of normalized flow. The left side of Figure 3.10 shows the mass washed off in each 10% of normalized washed off volume. The right side of Figure 3.10 shows the cumulative washed off mass. Notched box plots are used in both cases, and all events for all sites are represented in the figures. Both graph types are useful for visualizing the potential for BMPs to remove material form the first flush. The fractional mass diagrams show the opportunity for treatment in each fraction of runoff volume. The cumulative diagrams are useful in visualizing the performance of BMPs that might treat the first fraction of a storm event.

The washed-off mass generally decreases with time, and a point of diminishing returns can be envisioned for BMPs that are sized based on flow rate, or total volume treated. Each subsequent volume fraction provides less opportunity for removal. After 30% of the runoff volume, the washed-off mass does not show large differences. It is apparent that treatment capacity in the early part of a storm (i.e., less than 30%) is more valuable that treatment capacity in the later part of the storm. TSS in the lower left of Figure 3.10 provides the clearest example.

Figure 3.11 shows another method of graphing to illustrate the first flush. The difference between the normalized washed off mass (curved line) and the normalized flow (diagonal line) is plotted. The maximum value of the function is the point of maximum first flush, or the point where the normalized washed off mass most TSS and COD are shown and all events are plotted. The maximums vary significantly, but generally the maximums are in the 20 to 30% range of normalized runoff. The non-first flush effects are clearly shown in the figures. Therefore, the figures are also a reasonable approach for determining the first flush criteria and first flush effects.

Figure 3.12 shows the storms classified into three categories of first flush. The first are high first flush, when 50% or more of the washed-off mass occurs in the first 30% of flow, medium first flush, when 30 to 50% of the mass is washed off in the first 30% of the flow, and non-first flush, when 30% or less mass in washed off in the first 30% of flow. These results are also useful in visualizing the impact of first flush on

BMPs. A "first flush friendly" BMP, meaning a BMP that can treat a high percentage or all of the initial flow, would be advantageous for 80% of the events for TSS, 90% for COD and 95% for TOC.

3.3.7. Model Parameter Estimation

As stated earlier, the new washoff model has four different coefficients, which are α, β^*, γ^* and δ. All coefficients have a different meaning such as washoff rate for α, coefficient affected by runoff for β^*, coefficient representing additional pollutant sources during a rainfall event for γ^* and initial concentration affected by antecedent dry days for δ.

The new model can be directly used for a past rainfall event to determine EMCs and to calculate the mass loading when monitoring program were performed. However, for future use, each coefficient of the model should be generalized. According to the derivations, we can anticipate the factors that affect each parameter. Figure 3.13 shows a correlation matrix with tabular values of correlation coefficient (R) and probability of a random correlation (p). The values of p are below the diagonal and the correlation coefficients are above the line. The model parameters are compared with ADT, catchment area, ADD, storm duration, total rainfall, total runoff, runoff coefficient and average runoff velocity (total rainfall divided by area and storm duration). For all pollutant parameters, α shows strong positive relationship with total runoff, but γ^* shows negative relationship with total runoff. δ is strongly and positively related with antecedent dry days. However, β^* are generally related with rainfall, runoff coefficient and storm duration and shows negative relationship with "average runoff velocity". Figure 3.14 shows the relationship of model parameters and affecting factors for TSS. The correlations of the model parameters with event and site characteristics allow the model to be used for prediction or design. The determination of model parameters is summarized in Table 3.3 for each water quality parameter with affecting parameters.

3.4. CONCLUSIONS

This paper has presented a new semi-empirical model for describing stormwater runoff. The model uses four parameters which gives it flexibility to fit first flush as well as non-first flush events. The model's parameters are correlated to measurable or predictable storm events such as total runoff volume, antecedent dry days and storm duration. The model shows good fit for eight water quality constituents and will be tested for other constituents, which were collected over two years from eight highway sites. Future uses of the model include improving estimates of event mean concentrations from sparse data and designing BMPs to take advantage of the first flush. The following additional conclusions are made:

(1) Model comparison: The median value is similar, but the 50% interquartile ranges are smaller for the new model than for other methods, suggesting less variability for the new model. The reductions in variability are even greater if one considers the maximum and minimum values. The large values calculated with the

exponential model occur when the fit is poor. The medium point method is easy to apply, but it potentially inaccurate if there are few samples.

(2) Washed-off mass loading and EMCs are presented for eight water quality parameters. Generally the differences between minimum and maximum washed-off mass and EMCs are large because of event and site characteristics, such as rainfall intensity, area, runoff coefficient and antecedent dry periods.

(3) The EMCs are negatively correlated to storm duration, total rainfall, total runoff volume of runoff, and average rainfall intensity. Large storms have smaller EMCs because of dilution effects or exhaustion of pollutant mass.

(4) The fractions of washed-off mass are very high in first 30% of runoff, which suggests a first flush. The washed-off mass stabilizes after 30% of the runoff volume and it is apparent that treatment capacity in the early part of a storm (i.e., less than 30%) is more valuable that treatment capacity in the later part of the storm.

(5) Using the criteria of "high" first flush and "medium" first flush, as 50% of the mass in the first 30% of the volume, and 30 to 50% in the first 30% volume, respectively, more than 30% of the storms showed high first flush for TSS and COD, and more than 45% showed a medium first flush. The frequency of first flushes is tabulated for the other parameters, which generally less frequent. A "first flush friendly" BMP, meaning a BMP that can treat a high percentage or all of the initial flow, would be advantageous for 80% to 90% of the events for TSS, COD and TOC.

REFERENCES

Bertrand-Krajewski, J., Chebbo, G., and Saget, A. (1998). "Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon." *Wat. Res.*, 32(8), 2341-2356.

Charbeneau, R.J., and Barrett, M.E. (1998). "Evaluation of methods for estimating stormwater pollutant loads." *J. of Water Environmental Research*, 70(7), 1295-1302.

Corwin, D.L., and Vaughan, P.J. (1997). "Modeling nonpoint source pollutants in the vadose zone with GIS." *Environmental Science & Technology*, 31(8), 2157-2175.

Deletic, A., (1998). "The first flush load of urban surface runoff." *Wat. Res.*, 32(8), 2462-2470.

Deletic, A.B., and Mahsimivic, C.T. (1998). "Evaluation of water quality factors in storm runoff from paved areas." *J. of Environ. Engineering*, 124(9), 869-879.

Deletic, A., Ashley, R., and Rest, D. (2000). "Modeling input of fine granular sediment into drainage systems via gully-pots." *Wat. Res.*, 34(15), 3836-3844.

Driscoll, E.D., Shelley, P.E., and Strecker, E.W. (1990). "Pollutant loading and impacts from stormwater runoff." Analytical Investigation and Research Report, Vol. III, FHWA-RD-88-008, Federal Highway Administration, USA.

EPA (1994). "Nonpoint sources pollution control program." U.S. EPA Report 841-F-94-005, USA.

EPA (1995). "Economic benefits of runoff controls." U.S. EPA Report 841-S-95-002, USA.

EPA (1996). "Managing nonpoint source pollution from households." U.S. EPA Report 841-F-96-004J, USA.

Geiger, W. (1987). "Flushing effects in combined sewer systems." *Proceedings of the 4th Int. Conf. on Urban Drainage*. 40-46, Lausanne, Switzerland.

Gupta, K., and Saul, A.J. (1996). "Specific relationships for the first flush load in combined sewer flows." *Wat. Res.*, 30(5), 1244-1252.

Irish, Jr. L.B., Barrett, M.E., Malina, Jr. J.F., and Charbeneau, R.J. (1998). "Use of regression models for analyzing highway storm-water loads." *J. of Environmenal Engineering*, 124(10), 987-993.

Jefferies, C., Aitken, A., McLean, N., Macdonald, K., and McKissock, G. (1999). "Assessing the performance of urban BMPs in Scotland." *Wat. Sci. & Tech.*, 39(12), 123-131.

Larsen, T., Broch, K., and Andersen, M.R. (1998). "First flush effects in an urban catchment area in Aalborg." *Wat. Sci. & Tec.*, 37(1), 251-257.

Osuch-Pajdzinska, E., and Zawilski, M. (1998). "Model of storm sewer discharge. I: description." *J. of Environmental Engineering*, 124(7), 593-599.

Saget, A., Chebbo, G., and Bertrand-Krajewski, J. (1995). "The first flush in sewer system." *Proceeding of the 4th Int. Conf. on Sewer Solids-Characteristics, Movement, Effects and Control*, 58-65, Dundee, UK.

Sansalone, J.J., and Buchberger, S.G. (1997). "Partitioning and first flush of metals in urban roadway storm water." *J. of Environ. Engineering*, 123(2), 134-143.

Sansalone, J.J., Koran, J.M., Smithson, J.A., and Buchberger, S.G. (1998). "Physical characteristics of urban roadway soils transported during rain events." *J. of Environmental Engineering*, 124(5), 427-440.

Shaheen, D.G. (1975). "Contribution of urban roadway usage to water pollution." *EPA Report 600/2-75-004, U.S. EPA*, Washington, D.C.

Silverman, G.S., Stenstrom, M.K., and Fam, S. (1986). "Best management practices for controlling oil and grease in urban stormwater runoff." *The Environmental Professional*, 8, 351-362.

Stenstrom, M.K., Lau, S-L., Lee, H-H., Ma, J-S., Ha, H., Khan, S., Kim, L-H., and Kayhanian, M. (2001). "First flush stormwater runoff from highways." *Proceedings of Environmental and Water Resources Institute's (EWRI's) World Water & Environmental Resource Congress*, May, Orlando, Florida.

Smullen, J.T., Shallcross, A.L., and Cave, K.A. (1999). "Updating the U.S. nationwide urban runoff quality data base." *Wat. Sci. & Tech.*, 39(12), 9-16.

Thornton, R.C., and Saul, A.J. (1987). "Temporal variation of pollutants in two combined sewer systems." *Proceedings of the 4th Int. Conf. on Urban Drainage*, 51-52, Lausanne, Switzerland.

Vorreiter, L., and Hickey, C. (1994). "Incidence of the first flush phenomenon in catchments of the Sydney region." *National Conf. Publication-Institution of Engineers*, Vol. 3, 359-364, Australia.

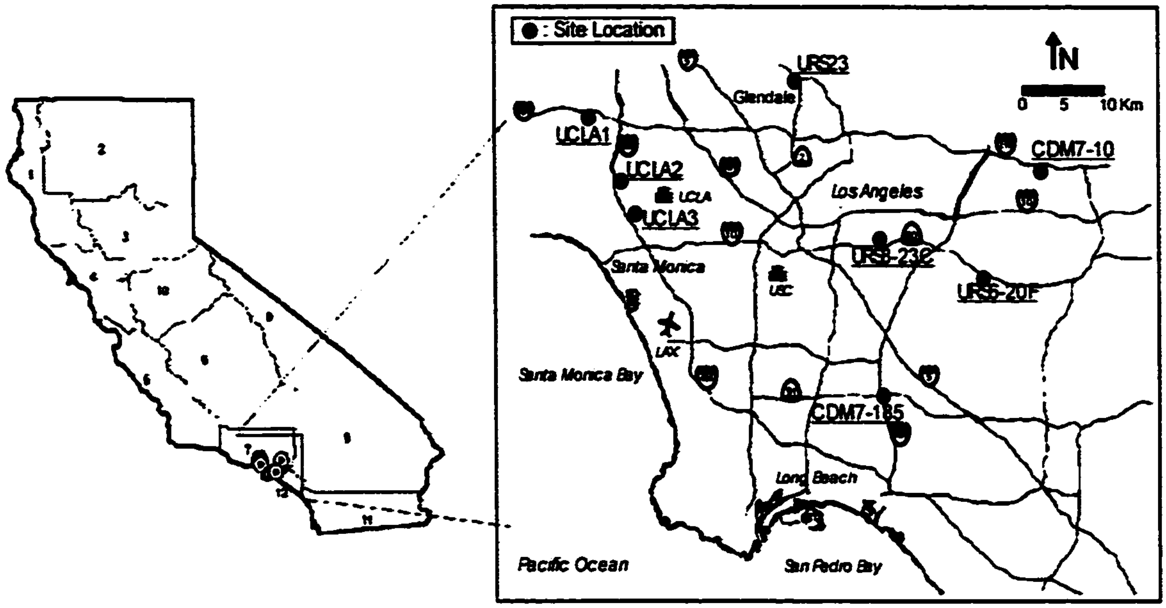


Figure 3.1. Study Areas in Southern California, USA.

Table 3.1. Monitoring site descriptions

Sites	Watershed Area (m^2)	ADT (Cars/day)	Event Date (mm/dd/yy)	Antecedent Dry Days (days)	Storm Duration (hrs:min)	Total Rainfall (cm)	Total Volume of Runoff (m^3)
UCLA 1	12800	328000	01/25/00	8.00	19:21	1.68	213.18
			02/27/00	3.90	4:26	0.30	16.14
			10/26/00	33.60	10:57	2.34	255.20
			01/08/01	69.40	6:34	0.38	43.70
			02/19/01	5.40	4:08	0.71	80.86
			03/04/01	4.00	10:32	1.17	136.13
UCLA 2	16900	260000	01/25/00	7.90	19:23	2.36	396.70
			02/10/00	9.90	19:01	0.69	106.47
			04/17/00	39.80	8:34	4.42	300.78
			10/26/00	33.60	10:57	2.31	194.41
			01/08/01	69.40	4:18	0.48	49.60
			03/04/01	4.00	5:05	0.89	140.17
UCLA 3	3900	322000	01/25/00	8.20	7:53	1.75	68.02
			02/12/00	1.10	4:42	1.78	59.46
			03/04/00	5.00	1:33	0.58	20.50
			10/26/00.	33.60	11:47	2.59	94.53
			02/19/01	5.30	6:56	2.97	110.53
			02/24/01	1.00	11:36	1.12	37.29
			04/07/01	31.60	10:46	2.16	55.43
CDM7-10	48100	176000	01/25/00	25.20	10:04	1.50	557.23
			02/12/00	2.10	2:50	2.31	950.31
			02/20/00	3.20	13:05	5.64	2598.24
			02/23/00	2.10	13:00	4.24	1737.42
			02/27/00	4.00	5:45	1.09	400.49
			03/08/00	1.00	10:06	2.74	1145.46
			04/17/00	38.90	7:20	4.24	1745.43
CDM7-185	2300	220000	01/25/00	25.00			
			02/12/00	2.00	2:30	1.88	36.98
			02/23/00	2.00	9:35	2.49	56.53
			02/27/00	4.00	1:05	0.38	4.00
			03/08/00	3.00	8:45	2.06	45.70
			04/17/00	39.00	6:55	3.18	70.39
URS23	29100	122000	01/26/01	33.00	7:48	0.89	95.61
			02/10/01	14.60	9:12	0.99	120.42
			02/19/01	5.70	6:24	0.94	116.82
URS6-20F	1700	216600	10/26/00	33.00	10:00	3.18	33.13
			01/26/01	33.00	7:18	1.19	10.53
			02/10/01	14.50	6:36	0.51	2.75
			02/19/01	5.60	5:40	1.04	7.72
URS8-23C	2500	229000	01/26/01	33.00	12:48	0.53	6.59
			02/19/01	5.50	7:12	0.43	10.66

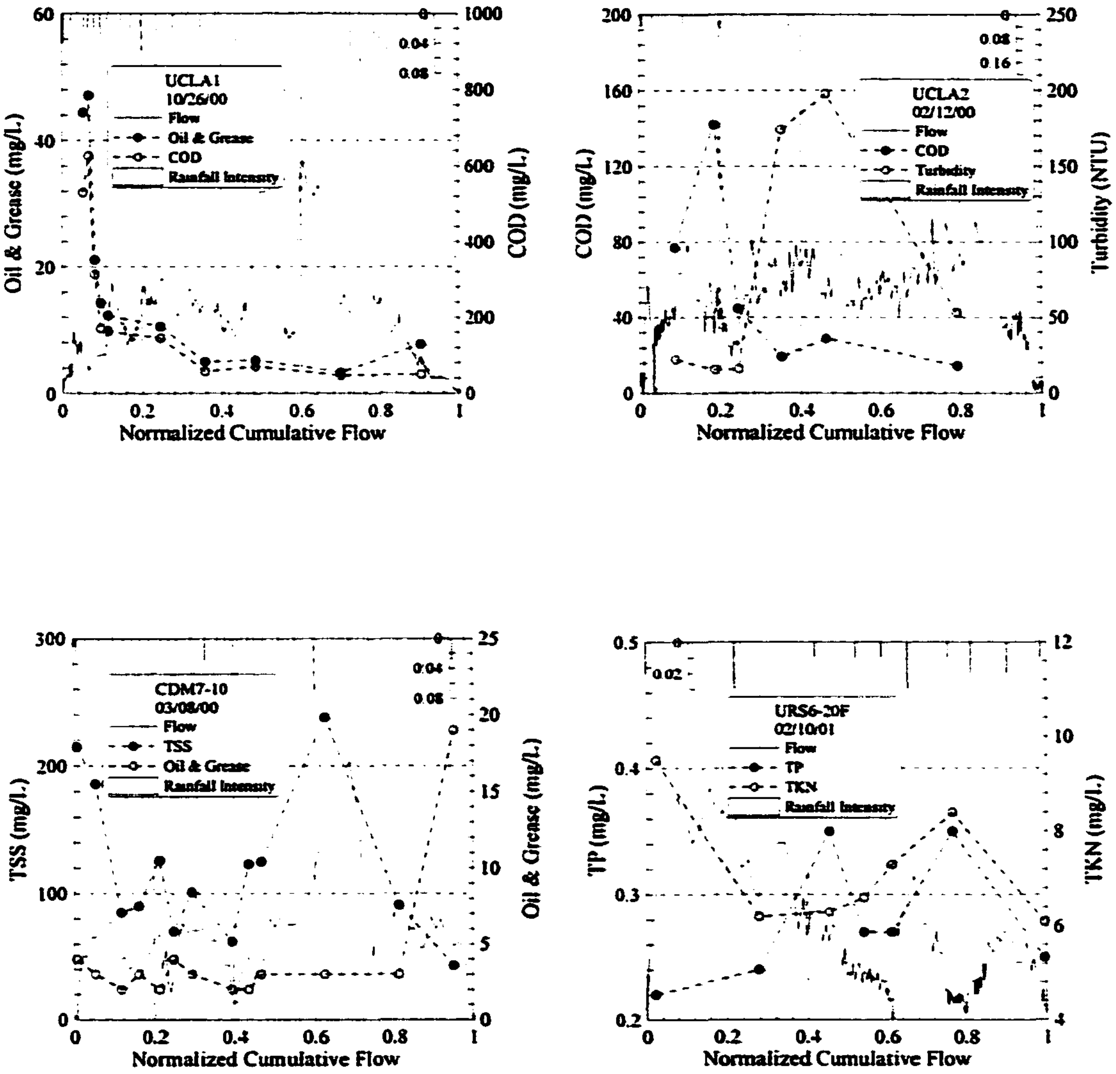


Figure 3.2. Types of observed polluto-graphs.

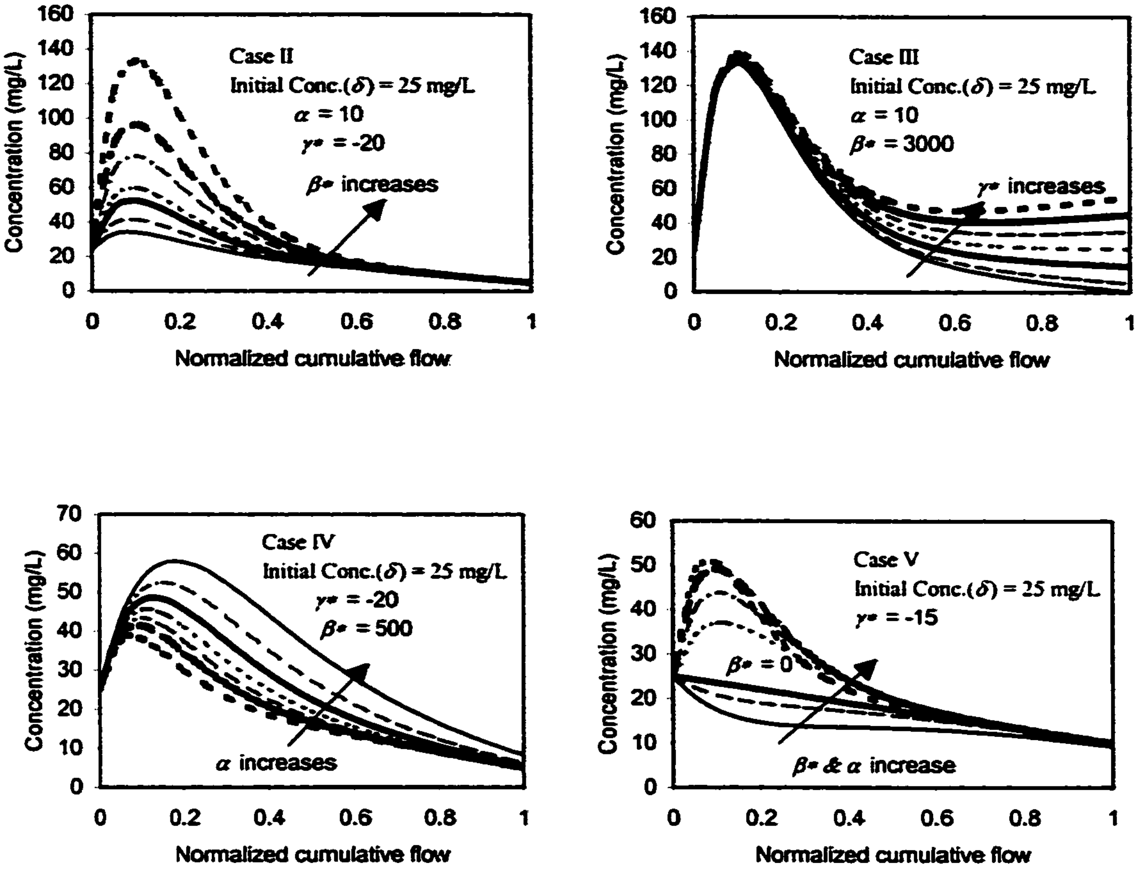


Figure 3.3. Sensitivity analysis for new model.

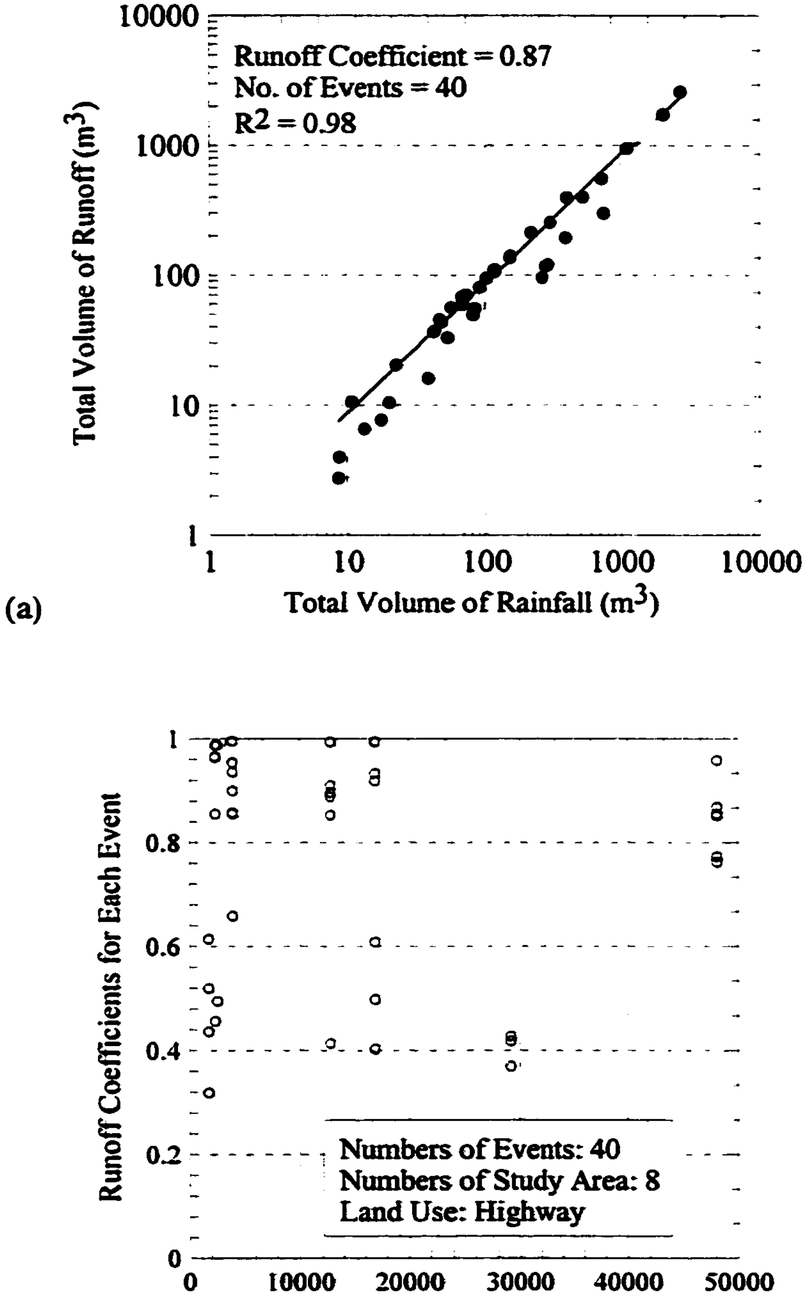
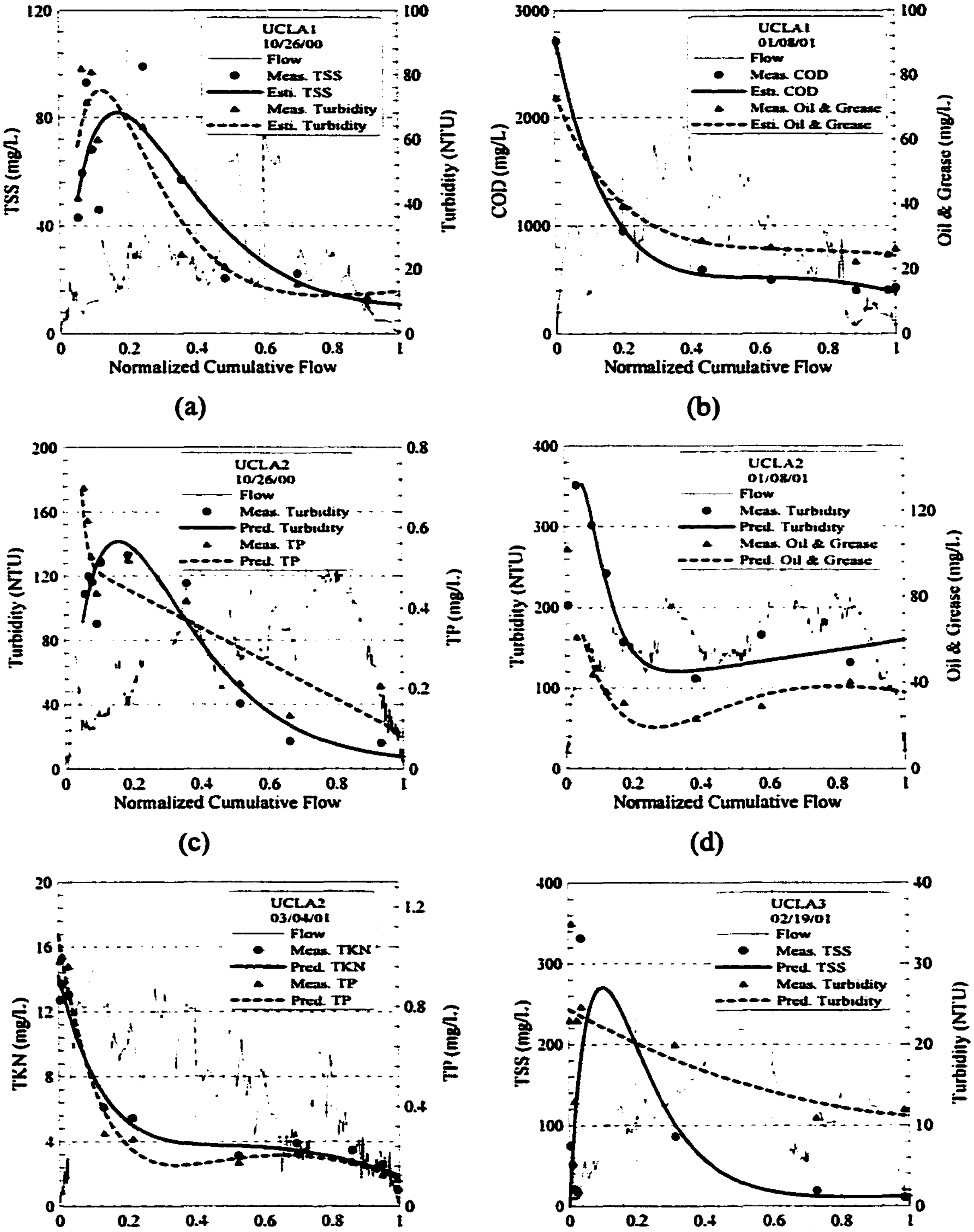


Figure 3.4. Runoff coefficients.



(a) (b)

(c) (d)

(e) (f)

Figure 3.5. Concentrations distributions for monitored and modeled results.

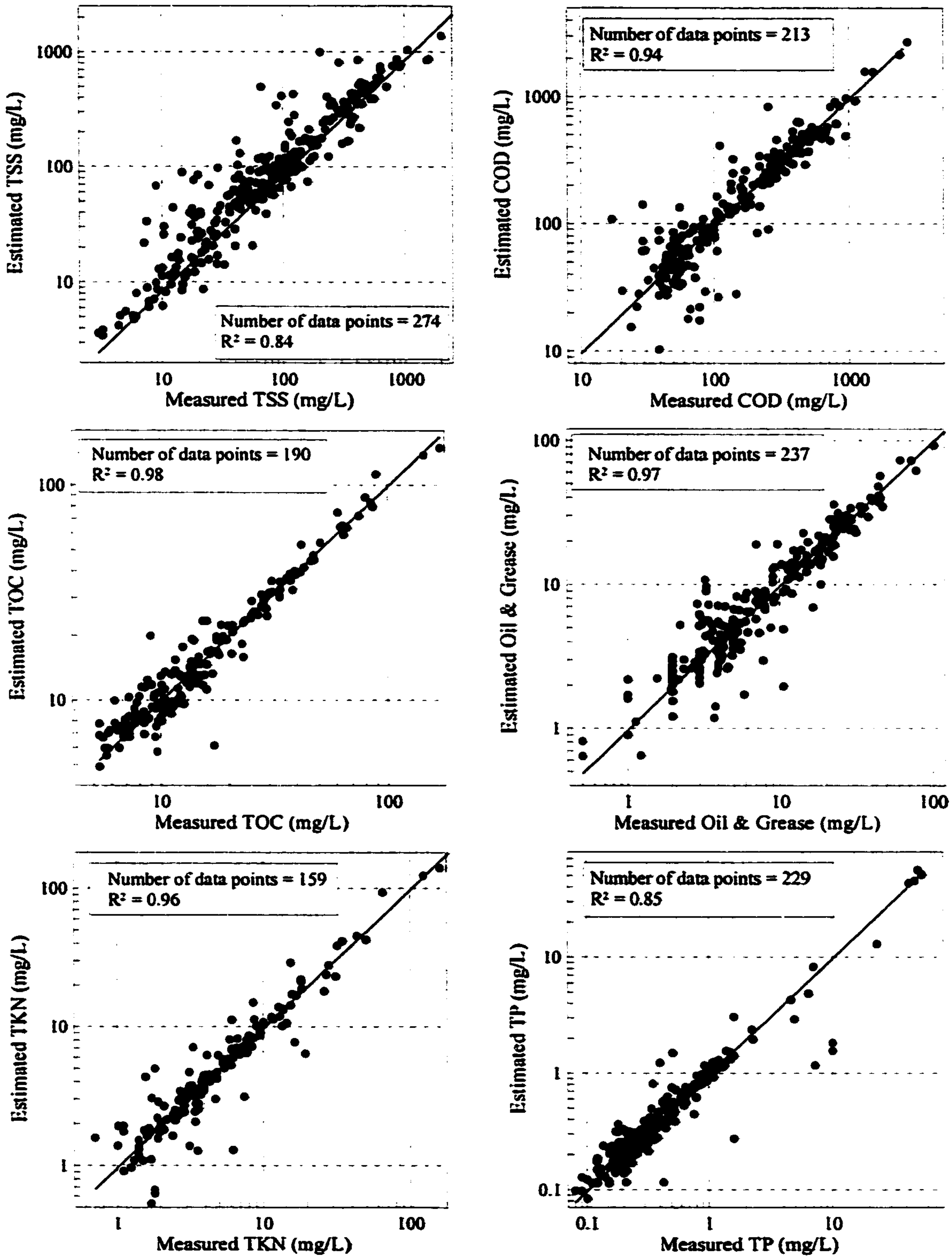


Figure 3.6. Relationships between measured and estimated concentrations.

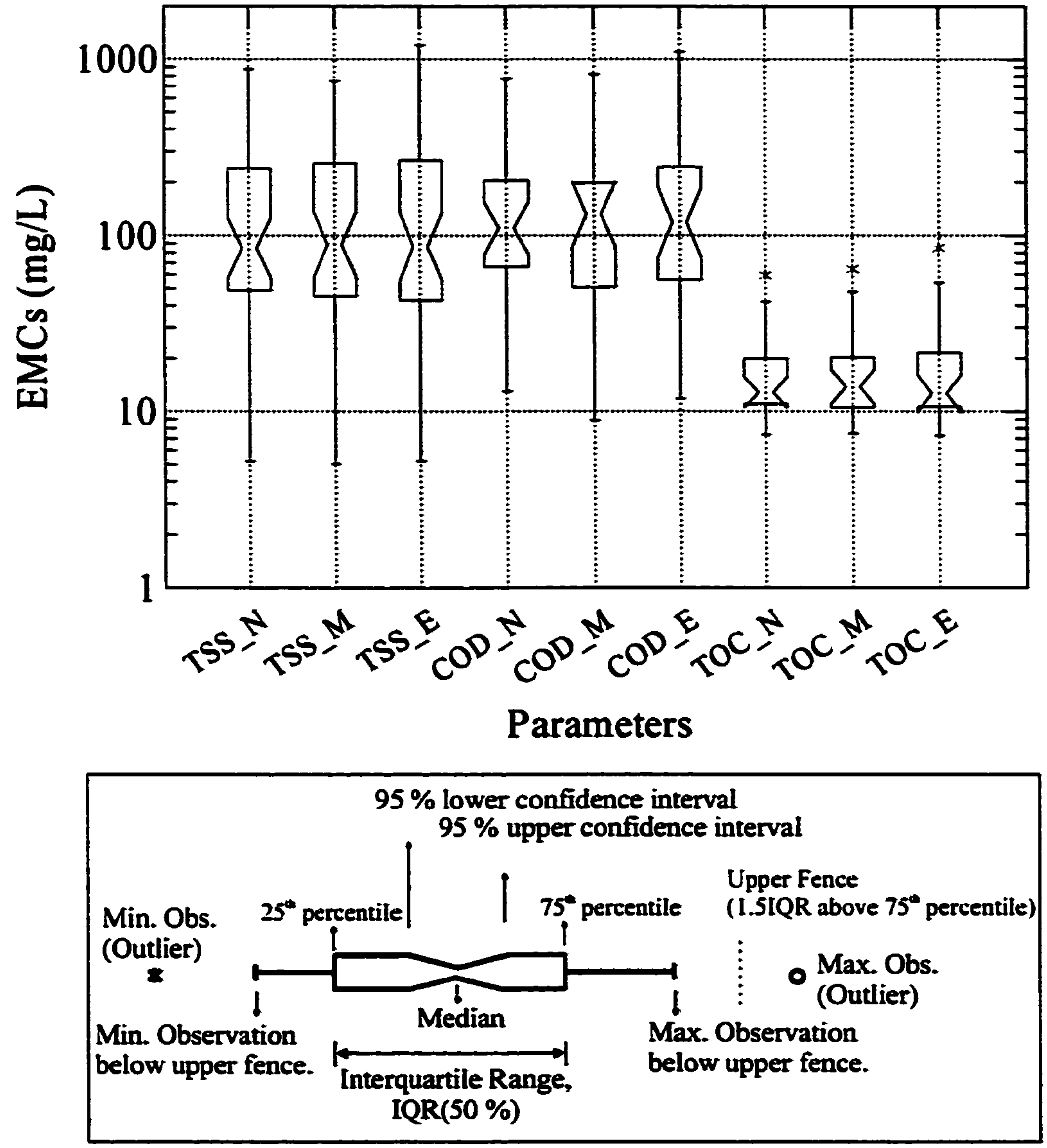
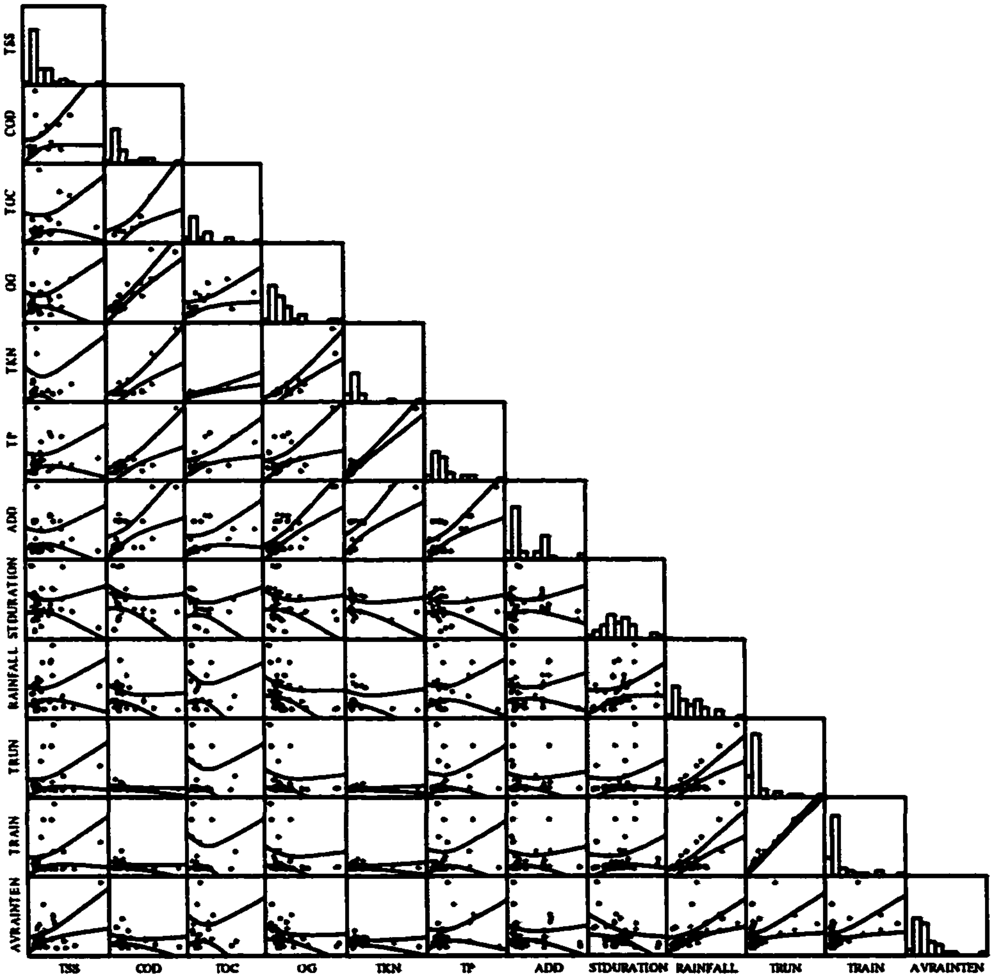


Figure 3.7. Comparison of event mean concentrations (N=New model, M=Medium point method, and E=Exponential model).

Table 3.2. Statistical summaries of event mean concentrations and mass loading

Parameters		Basic Statistics						Confidence Interval	
		No. of Events	Min.	Max.	Median	Mean	StDev.	95% Upper	95% Lower
TSS	EMC	39	5.21	874.23	87.54	159.57	175.22	216.37	102.78
	Mass Loading		0.06	17.27	0.83	2.43	3.91	3.71	1.14
COD	EMC	26	13.51	776.71	102.87	178.16	182.30	251.79	104.53
	Mass Loading		0.10	3.23	0.98	1.19	0.91	1.56	0.83
TOC	EMC	21	7.36	59.26	12.82	18.09	13.27	24.13	12.05
	Mass Loading		0.03	0.85	0.14	0.22	0.23	0.33	0.12
TKN	EMC	19	1.93	33.85	3.15	6.30	8.06	10.18	2.42
	Mass Loading		0.01	0.15	0.02	0.04	0.04	0.06	0.02
TP	EMC	31	0.11	1.54	0.31	0.41	0.32	0.53	0.30
	Mass Loading		0.00	0.04	0.00	0.01	0.01	0.01	0.00
Oil & Grease	EMC	37	0.52	34.57	5.23	8.00	7.73	10.58	5.42
	Mass Loading		0.01	0.39	0.05	0.08	0.08	0.11	0.05
Hardness	EMC	36	8.36	291.58	44.63	70.83	59.82	90.49	51.17
	Mass Loading		0.00	5.68	0.52	0.82	1.02	1.16	0.49
Alkalinity	EMC	17	8.98	75.54	21.82	26.88	18.58	36.43	17.32
	Mass Loading		0.05	0.49	0.22	0.24	0.13	0.31	0.18

* Units of EMC and mass loading are mg/L and g/m^2.
EMC's and mass loading are calculated using the new model.



	TSS	COD	TOC	OG	TKN	TP	ADD	STDURATION	RAINFALL	TRUN	TRAIN	AVRAINTEN
TSS		0.82	0.75	0.61	0.74	0.18	0.51	0.09	-0.13	-0.70	-0.68	-0.19
COD	0.05		0.87	0.92	0.81	0.16	0.03	-0.44	0.05	-0.66	-0.64	0.16
TOC	0.08	0.03		0.86	0.99	-0.08	-0.16	-0.43	-0.13	-0.38	-0.35	0.04
OG	0.20	0.01	0.03		0.77	0.07	-0.30	-0.55	-0.08	-0.60	-0.59	0.14
TKN	0.09	0.05	0.00	0.07		-0.06	-0.13	-0.40	-0.17	-0.29	-0.26	-0.01
TP	0.73	0.77	0.88	0.89	0.91		0.15	0.11	-0.49	-0.36	-0.40	-0.55
ADD	0.31	0.95	0.77	0.56	0.80	0.78		0.70	0.12	-0.38	-0.37	-0.21
STDURATION	0.86	0.39	0.39	0.26	0.43	0.84	0.12		-0.41	-0.24	-0.24	-0.65
RAINFALL	0.80	0.93	0.80	0.89	0.75	0.33	0.83	0.43		0.27	0.29	0.94
TRUN	0.12	0.16	0.45	0.21	0.58	0.48	0.46	0.64	0.60		1.00	0.30
TRAIN	0.14	0.17	0.49	0.22	0.62	0.43	0.47	0.64	0.58	0.00		0.32
AVRAINTEN	0.72	0.77	0.94	0.79	0.98	0.26	0.70	0.16	0.01	0.56	0.54	

Note: ADD (Antecedent Dry Days, days), STDURATION (Storm Duration, hours), TRUN (Total Volume of Runoff, m^3), TRAIN (Total Volume of Rainfall, m^3) and AVRAINTEN (Average Rainfall Intensity, cm/hr)

Figure 3.8. Relationships of EMCs and affecting parameters.

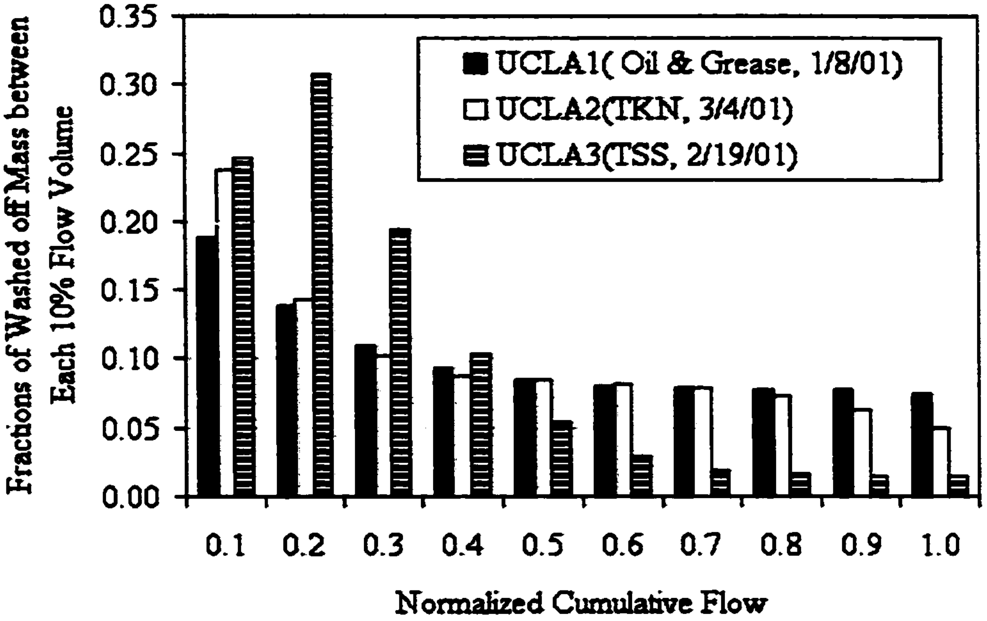


Figure 3.9. Normalized fractional mass washed-off as function of flow.

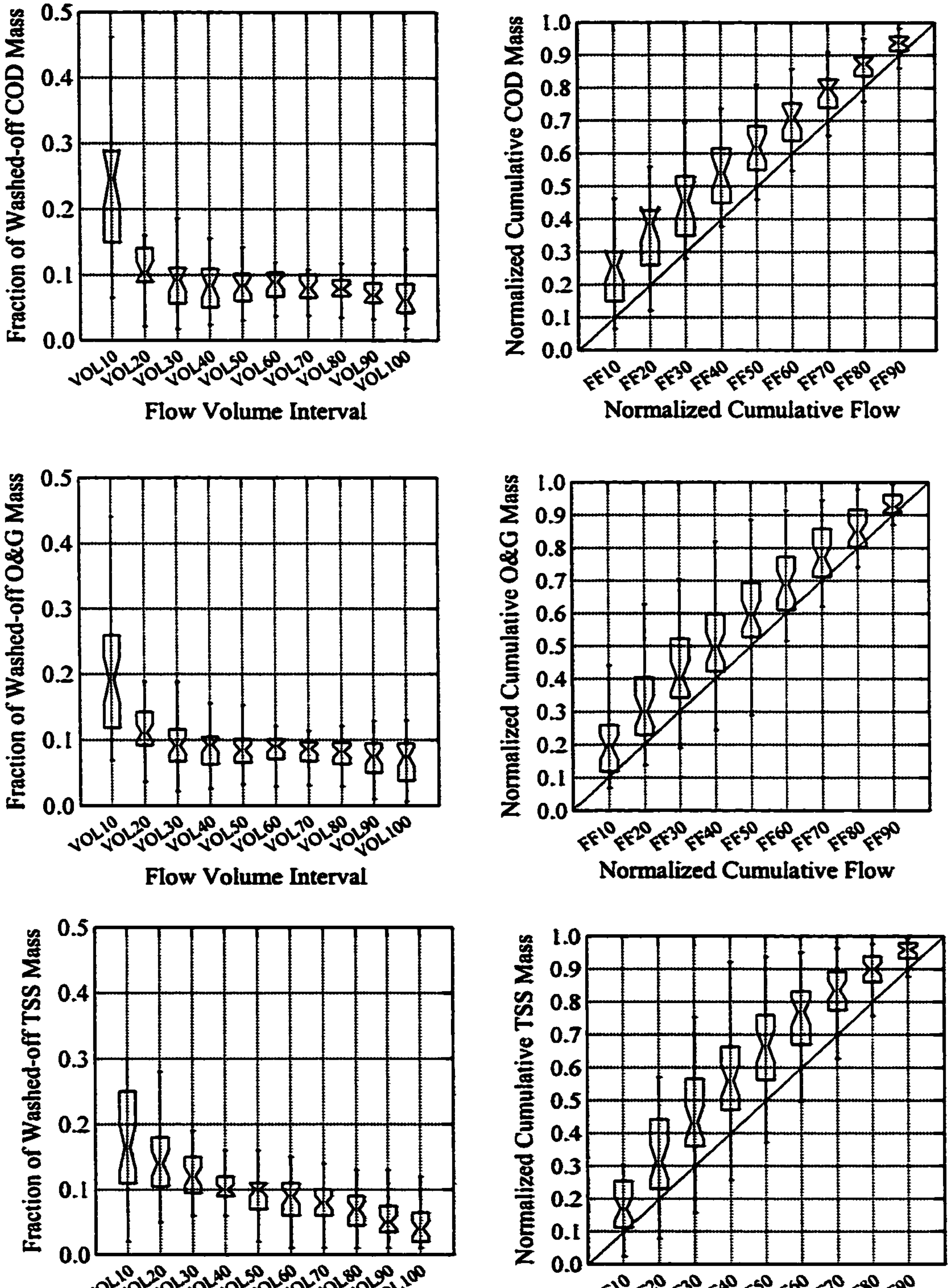


Figure 3.10. Washed-off pollutant mass and volume with new washoff model.

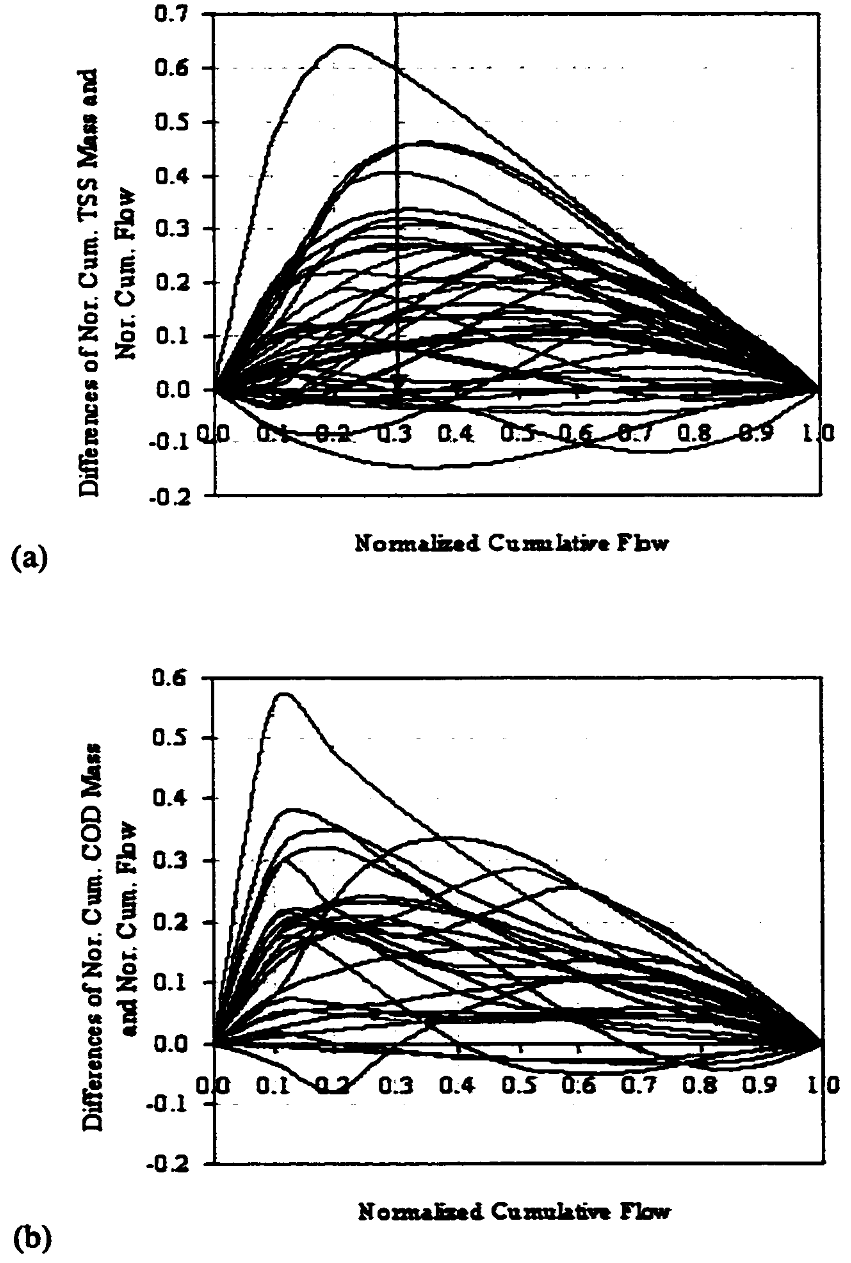


Figure 3.11. Differences of normalized cumulative mass and flow for TSS and COD.

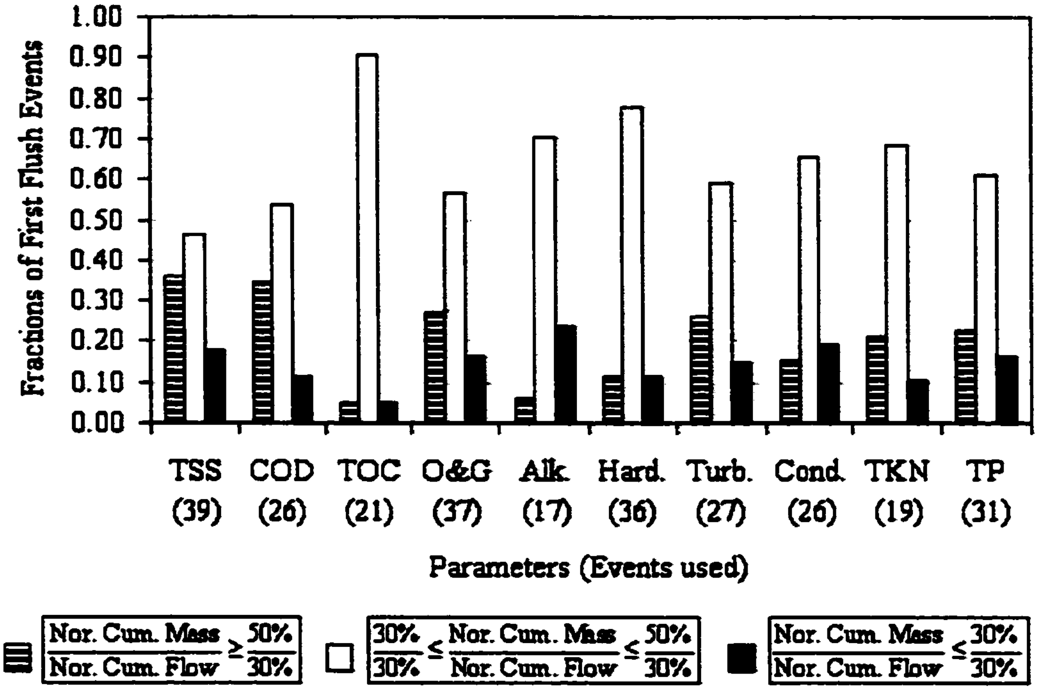
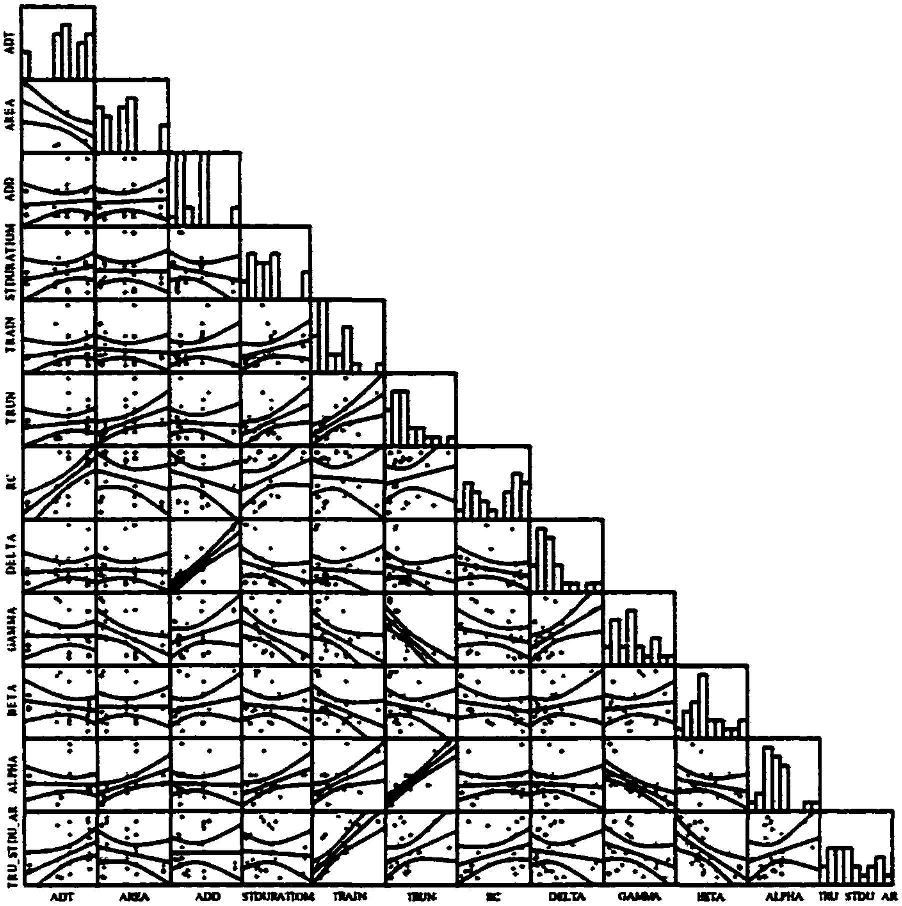


Figure 3.12. Frequency of first flush events.



	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	ARV
ADT		-0.51	0.08	0.22	0.19	0.13	0.71	0.06	0.00	-0.16	-0.03	0.46
AREA	0.01		0.06	-0.01	-0.07	0.45	-0.25	-0.06	-0.49	-0.01	0.50	-0.22
ADD	0.72	0.78		-0.20	0.14	-0.06	-0.24	0.86	0.30	0.20	-0.04	0.01
STDURATION	0.32	0.95	0.36		0.27	0.49	0.35	-0.31	-0.47	-0.09	0.46	-0.06
TRAIN	0.38	0.74	0.51	0.21		0.58	-0.05	-0.06	-0.45	-0.36	0.52	0.75
TRUN	0.57	0.03	0.78	0.02	0.00		0.18	-0.21	-0.75	-0.19	0.88	0.36
RC	0.00	0.25	0.27	0.10	0.82	0.41		-0.25	-0.25	-0.19	0.08	0.33
δ	0.79	0.77	0.00	0.14	0.80	0.33	0.25		0.52	0.19	-0.08	-0.14
γ*	0.99	0.02	0.17	0.02	0.03	0.00	0.26	0.01		0.12	-0.68	-0.33
β*	0.46	0.98	0.35	0.67	0.09	0.40	0.38	0.39	0.58		-0.22	-0.57
α	0.89	0.01	0.86	0.03	0.01	0.00	0.73	0.73	0.00	0.32		0.23
ARV	0.03	0.30	0.98	0.78	0.00	0.10	0.12	0.53	0.13	0.00	0.28	

Note: ADT (Average Daily Traffic, cars/day), ADD (Antecedent Dry Days, days), STDURATION (Storm Duration, hours), TRAIN (Total Volume of Rainfall, m^3), TRUN (Total Volume of Runoff, m^3), RC (Runoff Coefficient, -) and ARV (Average Runoff Velocity, m/hr)

Figure 3.13. Correlation matrix and table for COD.

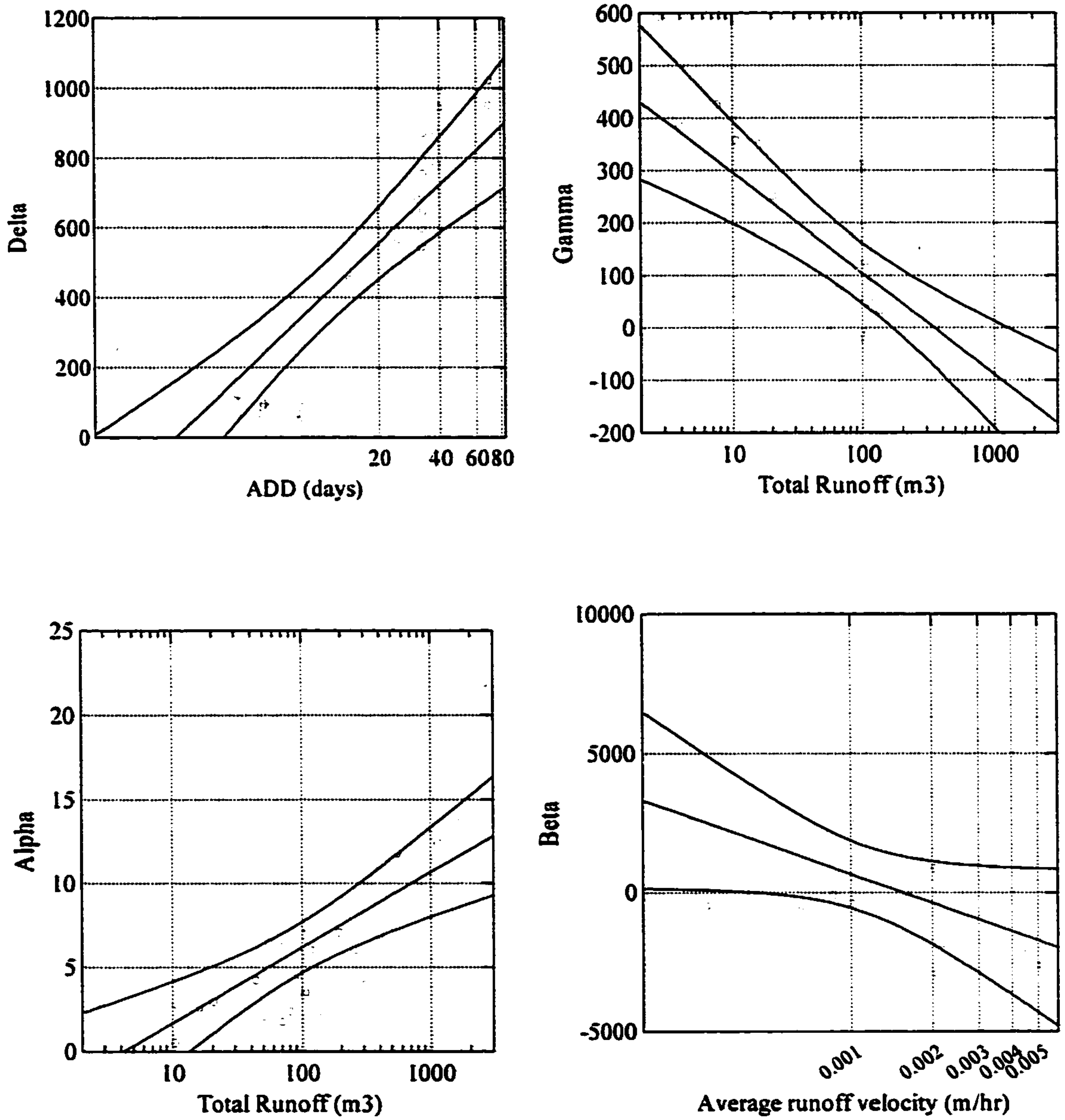


Figure 3.14. Relationships of model parameters and affecting factors for TSS.

Table 3.3. Summaries of model parameters

Parameters	δ	γ^*	α	β^*
TSS	240.8Ln(ADD)-164.8	-83.74Ln(TRun)+489.1	0.007(Trun)+3.83	-1475Ln(ARV) – 9539
COD	305.9Ln(ADD)-135.5	-259.1Ln(TRun)+1480.1	0.035(Trun)+2.30	-3016Ln(ARV) - 22138
TOC	2.32(ADD)+12.9	-72.61Ln(TRun)+488	1.044(Trun)+0.54	-196.4Ln(ARV) – 1106
Oil & Grease	14.24Ln(ADD)-1.61	-39.76Ln(TRun)+194	0.0046(Trun)+3.82	-526Ln(RC) - 353.67
Alkalinity	28.98Ln(ADD)+5.1	-64.72Ln(TRun)+485.3	0.023(Trun)+2.06	-786963(ARV) + 828
Hardness	8.52(ADD)+44.2	-0.219Ln(TRun)+131.8	0.003(Trun)+4.55	-4270(RC) + 2620
TKN	1.75(ADD)-10.6	-26.17Ln(TRun)+148.9	1.173(Trun)-0.02	-68.9Ln(ARV) – 523
TP	19.81(ADD)+430.9	-117Ln(TRun)+955.4	1.35Ln(Trun)-0.54	-6325(RC) + 2930

CHAPTER IV.

ESTIMATION OF ACCUMULATED POLLUTANT MASS DURING DRY DAYS USING NEW BUILDUP MODEL IN HIGHWAY LANDUSE

ABSTRACT

A new washoff model was applied to two years of monitoring data from 8 highway sites in Southern California. The model facilitated estimation of retained pollutant mass. Using retained pollutant mass and washoff from the following storm, buildup over antecedent dry days was calculated. Mass accumulation rates were determined for total suspended solids, chemical oxygen demand, oil and grease, total Kjeldahl nitrogen and total phosphorus, and are reported in g/m^2-day. A new build-up model is proposed. This research suggests a new modeling approach to describe buildup during dry days between storms.

Keywords

Antecedent dry days; buildup; event mean concentration; mass accumulation rate; stormwater.

4.1. INTRODUCTION

Many of the waters of the United States are classified as impaired because of pollutant inputs from point and non-point sources. The Nationwide Urban Runoff Program (NURP) expanded the state of knowledge of urban runoff pollution by instituting data collection at many different sites (Driscoll et al. 1990; EPA 1994, 1995, 1996). The study showed that significant quantities of organics, nutrients, pesticides, herbicides and heavy metals are contained in runoff, and caused the U.S. EPA using the authority of section 208 of the Clean Water Act to require that regional urban planning agencies develop ways to reduce pollution from nonpoint sources

Most developed plans to minimize nonpoint source pollution use Total Maximum Daily Loads (TMDLs) as a control mechanism. A TMDL is the sum of the allowable loads of a single pollutant from all contributing point and nonpoint sources. The calculation must include a margin of safety to ensure that the receiving water can still be used for its designated purpose (e.g., drinking water supply, contact recreation, etc.). The success in developing and implementing a TMDL depends largely a better understanding of nonpoint sources, since most point sources (e.g., domestic wastewater treatment plants) have already been addressed. From 40% to 80% of the total annual organic pollutant loading that enters receiving waters from a typical city originates from nonpoint sources (EPA 1995, 1996). Other pollutants also have high fractions originating from nonpoint sources.

The origins of pollutants from nonpoint sources are varied, and range from illegal discharges to washoff of natural substances to atmospheric deposition. Buildup of pollutants from various deposition sources is of interest and a better understanding may assist in BMP selection or justification.

The paper analyzes the buildup of pollutants from of 8 highway sites over two years of monitoring. Estimates are made for 6 water quality parameters and a new buildup model is proposed.

4.2. BACKGROUND

The sources of urban runoff pollution can be categorized as follows: wet and dry atmospheric deposition, street refuse deposition including litter, street dirt, vegetation and organic residues, traffic emissions, erosion and road deicing chemicals. Dry deposition includes dust particles, which arise from unpaved roads, parking lots, construction and demolition sites, urban refuse (litter or garbage), surrounding soils and industrial activities. A significant portion of pollutant loadings from urban areas can be attributed to rain or snowfall. This is especially true for nitrogen, and precipitation is one of major source of nitrogen (Crittenden 1998).

Yuzhou et al (2002) measured the wet and dry atmospheric nitrogen deposition on the east coast of the United States. The mean values were 0.611 and 3.37 mg N/m^2-day for wet and dry deposition, respectively. Lang et al (2002) estimated 0.186 ug/m^2-day and 0.814 ug/m^2-day for wet and dry PAHs deposition, respectively, in metropolitan Miami. Park et al (2002) also measured the atmospheric wet and dry deposition for PAHs in urban areas in Texas. The authors found 0.499 and 0.185 ug/m^2-day for wet and dry deposition, respectively.

Deposition from automobile exhausts is composed of dust-sized particles (<60 um), but is not the only source of traffic-related pollution. Tire wear, solids carried on tires and vehicle bodies, wearing parts such as brake pads, and loss of lubrication fluids add to the pollution input attributed to traffic. Shaheen (1975) estimated that approximately 0.7 g/axle-km of solids was directly attributed to traffic. Direct traffic emissions were reported to be 0.2 g/vehicle-km from tire wear (Anon 1977). Bannerman et al. (1984) estimated atmospheric dry deposition of solids in urban watersheds as 50 mg/m^2-day. Of the atmospheric dry deposition rate, organic content was 40%.

The dust mass on highway surfaces should increase with the duration of the dry period before rainfall events. This means that pollutant mass washed-off during a storm event should depend on antecedent dry days (ADD); however, the role of ADD in the process of pollution generation has been questioned. Sartor and Boyd (1972) found a weak exponential relationship between ADD and mass of solids accumulated on asphalt surface using data obtained by vacuum cleaning paved surfaces. The buildup depends on the season, ADD, wind speed, land use, traffic. Wash-off may be a function of rainfall intensity, bottom shear stress and other factors (Mostaghimi et al. 1997; Ristenpart 1999). Osuch-Pajdzinska and Zawilski (1998) and Novotny et al. (1985) considered the loss coefficient, street sweeping and mass accumulation rate in their buildup models.

Grottker (1987), after experimenting on impervious surfaces, suggested that the buildup should be related to ADD, washoff and site-specific parameters such as street cleaning, wind speed, and traffic intensity. Deletic and Maksimovic (1998) compared event mean concentrations (EMCs) to ADD and concluded that they were weakly related, and suggested that buildup and wash-off models should be related, even though the exact mechanism or relationship is not presently known.

Most previously published buildup models are based on ADD and the buildup models have been expressed as a linear, power-law, exponential, or other function of time. Many models are adapting the exponential representation because it is simple and can be derived as a first-order process. Grottker (1987) proposed the following buildup model:

$$M_t = M_o\left[1 - Exp\left(-k_1 \cdot t\right)\right] \tag{4.1}$$

where, M_t is accumulated pollutant mass on the watershed during dry period, M_0 is the maximum possible pollutant mass accumulated on the watershed and k_1 is buildup coefficient (d^{-1}). This equation is only considers buildup between storm events as function of dry days.

Charbeneau and Barrett (1998) proposed the following model which accounts for masses not washed off during previous rainfall events.

$$M_t = M_2 + (M_o - M_2)\left[1 - Exp(-k_1 \cdot t)\right] \qquad (4.2)$$

where, M_2 is the pollutant mass not washed-off from the previous rainfall event, which can be called "the initial mass for the dry period".

Ball et al. (1998) tried to find a more reasonable buildup model using regressions of ADD. Of the several regression functions such as linear, exponential, power, reciprocal and hyperbolic, they concluded that the power and hyperbolic functions produced the best fit of pollutant buildup.

The challenge of using the previously mentioned model is estimating the initial mass after a previous storm event, and the pollutant accumulate rate during dry days. Experiments are required but are cumbersome because the experiments must be continued until the next rainfall event, which is generally unknown, and may occur at inconvenient times. It is also necessary to obtain data over a range of dry days, which means that the rainfall frequency must accommodate the experimental design, which can only occur by fortuitous conditions. It is believed that accumulation occurs most rapidly during the first few days after a rainfall event (Grottker 1987), and short and long ADDs are needed to describe the rate. As a consequence, it is difficult to characterize buildup, and several seasons of data may be needed. Other issues such as street cleaning, construction, shock pollutant spills, wind speed must be controlled and complicate experimental design.

Using two years of stormwater monitoring data, we found a weak relationship between ADD and pollutant EMCs (Ma et al. 2002). The comparison of total mass, which includes washed-off mass and retained mass, is compared to ADD, shows a stronger relationship. Thus, using total mass can be a reasonable approach to estimate the mass accumulation during the dry days. Additionally, when the remaining mass is linked with total washed-off mass for a storm event, the mass accumulation can be estimated. The method is a new approach for mass accumulation model based on relationship of washoff and buildup models.

4.3. METHODS

As stated earlier, the direct measurement of mass accumulation on watershed, especially highways, is very difficult because of high traffic, random street sweeping, shock pollutant spills and other uncontrolled conditions. Therefore, if an indirect estimation method can be developed, it might be more useful (Deletic and Maksimovic 1998). Accumulated pollutant mass can be inferred from the amount of pollutant that is washed-off during storm events. Some of the pollutant mass is washed-off the watershed, but some mass remains on the watershed and contributes to the buildup for the next dry period (Charbeneau and Barrett 1998; Deletic and Maksimovic 1998; Fraser et al. 1999). The monitoring results obtained in our study (Ma et al. 2002) provide an opportunity to estimate buildup from washed off mass, which is an indirect method.

4.3.1. Monitoring Area

Rainfall, runoff flow rate and runoff quality were monitored at 8 highway sites in Southern California (Figure 4.1) over two rainy seasons. The stations were equipped with a flow meter, rain gage and an automatic water sampler. Grab samples were also collected and compared to composite samples. A total of 41 storm events were monitored.

Detail summaries of sites and events are shown in Table 4.1. The table shows the area of each site, event date, average daily traffic (ADT), ADD, event rainfall, storm duration, total runoff volume, and runoff coefficients for each storm event. More information on the methodologies is available (Stenstrom et al. 2001; Ma et al. 2002)

4.3.2. Derivation of the New Buildup Model

Two mechanisms are proposed for the buildup model. The first is a buildup mechanism that should be related to ADD, ADT and other factors that affect pollutant input. The second mechanism accounts for pollutant reduction, and should include factors as wind, degradation, street sweeping, etc. The individual factors for buildup and reduction are lumped into single terms for simplicity. Figure 4.2 shows the approach of mass buildup and washoff phenomena. Equation 4.3 shows the mass changes with time.

$$\frac{dM}{dt} = \xi P \cdot A - \psi \cdot M \tag{4.3}$$

M = Pollutant mass accumulated on the watershed surfaces at time t, mg

P = Pollutant mass fallen on watershed surface from air and vehicles, $mg / m^2 \cdot day$

ξ = Capture Coefficient (-)

ψ = Loss Coefficient, $1 / day$

A = Catchment area, m^2

Rearranging equation 4.3, we obtain equations 4.4

$$\int_0^{Ma_i} \frac{dM}{\xi P \cdot A - \psi \cdot M} = \int_0^{T_i} dt \tag{4.4}$$

where T_i is the dry period to the next storm event, I, and Ma is the accumulated mass during the dry period.

After integration we obtain:

$$\left(-\frac{1}{\psi}\right) \ln\left(\xi P \cdot A - \psi \cdot M\right)\Big|_0^{Ma_i} = T_i \tag{4.5}$$

$$\ln\left[\frac{\xi P \cdot A - \psi \cdot Ma_i}{\xi P \cdot A}\right] = -\psi \cdot T_i \tag{4.6}$$

Rearranging the equation 4.6, we obtain:

$$Ma_i = \frac{\xi P \cdot A}{\psi} \cdot \left[1 - Exp\left(-\psi \cdot T_i\right)\right] \tag{4.7}$$

Therefore, the total mass accumulation during dry periods on a catchment can be determined by adding the retained mass from a previous rainfall event and accumulated mass after an event. The total mass (Ma_T) affecting to next storm can be described such as equation 4.8.

$$Ma_T = Mr_{i-1} + Ma_i = Mr_{i-1} + \frac{\xi P \cdot A}{\psi} \cdot \left[1 - Exp\left(-\psi \cdot T_i\right)\right] \qquad (4.8)$$

where, Mr_{i-1} is the retained mass that is not washed-off by the previous storm.

Equation 4.8 has two fitting parameters ψ, ξP, which ideally would be measured directly. For the previously cited reasons, this is difficult and the parameters must be estimated by fitting washoff and buildup observations. Acquisition of the high quality data needed to support modeling efforts, either through literature reviews or field surveys, will affect the level of effort and costs associated with management program.

4.4. RESULTS

The averaged weather descriptions for research areas are shown in Figure 4.3, which are averaged historical records of air temperature, wind speed and rainfall during 43 years proceeding the research period. Figure 4.3(a) shows monthly average temperature during 43 years, which ranged from 57 to 78 °F and wind speed ranged from 6 to 9 MPH. The wind speed will affect pollutant buildup during dry periods, especially when the shear stress among the pollutant particles is low. This typically occurs soon after a rainfall.

Monthly and cumulative rainfall during monitoring periods is shown in Figure 4.3(b). The vertical bars show the 43-year monthly average and the observed rainfall during the study period. The lines show the cumulative rainfall for the same conditions. The number of dry days per month ranges from 23 to 31 days; therefore, even in the wet season, the highways are usually dry. The first year of the research period was an average year, while the second as a wet year, having near 50% more rainfall that average.

4.4.1. Monitored Event Descriptions

Table 4.1 summarizes the site information and event descriptions. Monitoring was performed for all events having at least one antecedent dry day. The average daily traffic (ADT) is very high, ranging from 122,000 to 328,000 cars/day. Table 4.1 also summarizes selected event characteristics such as date, ADD, rainfall duration, total rainfall, runoff volume and runoff coefficients. Event rainfall varies from 0.3 cm to 5.64 cm and antecedent dry days vary from 1 to about 70 days. The smallest watershed site, URS6-20F, is 1700 m^2 and the largest area, CDM7-10 is 48,100 m^2. The runoff coefficients vary from 0.35 to 0.96 with lower values occurring during smaller events. The lower coefficient reflects infiltration and evaporation during the event, which are more significant in smaller events. Antecedent dry periods are also known to affect to runoff coefficients.

4.4.2. Comparison of Monitored Pollutant Concentrations

Figure 4.4(a) shows a concentration correlation matrix of water quality parameters. The ellipses indicate 90% confidence ranges. Confidence ellipse is Gaussian bivariate confidence intervals on the centroid. The correlations are represented by middle line with the 90% confidence intervals represented by bordering lines (SYSTAT, SPSS Inc., Chicago, Illinois). COD shows strong correlations with all parameters except total phosphorus. Statistical summaries for monitored concentrations are shown in Figure 4.4(b). The number of observations for each parameter range from 451 to 785.

4.4.3. Calculation of Accumulated Pollutant Mass during Dry Days

The retained mass is assumed to be the product of the final runoff concentration and retained water. The retained water is equal to the total rainfall times one minus the runoff coefficient. The buildup mass can be quantified by the washed off mass in the following rainfall event, as shown in Figure 4.2. The retained mass for the next event is calculated as before. The analysis can be performed after the second event. Thus, the mass accumulated on highway surface can be calculated by following equation 4.9 to 4.10.

$$Ma_2 = Mw_2 - (Mr_1 - Mr_2) = Mw_2 + Mr_2 - Mr_1 \qquad (4.9)$$

$$Ma_3 = Mw_3 - (Mr_2 - Mr_3) = Mw_3 + Mr_3 - Mr_2 \qquad (4.10)$$

$$\vdots$$

$$Ma_n = Mw_n - (Mr_{n-1} - Mr_n) = Mw_n + Mr_n - Mr_{n-1} \qquad (4.11)$$

Where,

$Ma_{1,\,2,3 \text{ and } n}$ = Mass accumulated on catchment during dry periods between events, kg
$Mw_{1,\,2,3 \text{ and } n}$ = Mass washed-off by an storm event, kg
$Mr_{1,\,2,3 \text{ and } n}$ = Mass retained in catchment after an event, kg

Figure 4.5(a) shows a correlation matrix for accumulated pollutant masses for the five pollutants calculated using equations 4.9 to 4.11. Figure 4.5(b) shows a statistical summary for accumulated pollutants using notched box plots. The accumulated masses are normalized per unit are over the eight sites. Figure 4.6 shows the accumulated masses versus ADD, and the buildup trends are apparent. There are fewer TKN observations since TKN was not measured at site UCLA1, 2, and 3 in the first year.

4.4.4. Model Application using Normalized Accumulated Mass

Equation 4.7 can be applied to the data shown in Figure 4.6 and used to fit the parameters ξP and ψ. Two parameters were estimated using non-linear, least squares regression (NLREG, Phillip H. Sherrod, Brentwood, TN). The results are shown in Table 4.2, which summarizes the model fit and presents R^2, F, other statistical parameters and the Durbin-Watson parameter for autocorrelation. Small values of the Durbin-Watson statistic indicate the presence of autocorrelation. Usually a value less than 0.80 indicates that autocorrelation is likely. The R^2 for all parameters are greater than 0.8, suggesting that the model and data are well matched.

The "adjusted coefficient of multiple determination (Ra^2)" is an R^2 statistic adjusted for the number of parameters in the equation and the number of data observations. It is a more conservative estimate of the percent of variance explained, especially when the sample size is small compared to the number of parameters. It is defined by equation 4.12.

$$R_a^2 = 1 - \frac{n-1}{n-N_p} \cdot \left(1 - R^2\right) \tag{4.12}$$

Where n is the number of observations, N_p is the number of parameters, and R^2 is the unadjusted coefficient of multiple determination.

4.4.5. Model Parameters

As stated earlier, it is difficult to measure mass buildup rates because of difficulty in controlling or accessing sites. Deletic and Maksimovic (1998) proposed indirect estimation methods. They correlated event mean concentrations (EMCs) with antecedent dry days and found only a weak relationship.

The technique used here is also an indirect method. The modeled mass accumulation rate (ξP) and loss coefficient (ψ) are summarized in Table 4.3. The mass accumulation rates are 0.653 g/m^2-day for TSS, 0.125 g/m^2-day for COD, and 0.0096 g/m^2-day for oil and grease. The table also shows standard errors, t and *Prob(t)* for all of parameters. The table also shows "t" statistics that is computed by dividing the estimated value of the parameter by its standard error. This statistics is a measure of the likelihood that the actual value of the parameter is not zero. The larger the absolute value of t, the less likely that the actual value of the parameter could be zero. The "*Prob(t)*" value is the probability of obtaining the estimated value of the parameter if the actual parameter value is zero. The smaller the value of *Prob(t)*, the more significant the parameter and the less likely that the actual parameter value is zero. The *Prob(t)* values of Table 4.3 are very small (mostly <0.03%), which suggests a non-random relationship.

The values of mass accumulation rate and loss coefficients are different for each water quality parameter. This is to be expected since each pollutant has different transport and transformation behavior.

An alternate method for estimating buildup is to use only the early part of the data shown in Figure 4.6. The data between 1 and 10 ADD show nearly linear buildup. Also the proposed model assumes linear buildup during this period, in that the product of the loss coefficient and accumulated mass are small. Table 4.4 shows the slopes of the buildup between 1 and 10 ADD and compares them to the model parameters presented in Table 4.3. The linear buildup coefficients are less than the model parameters and the agreement is good. The mass buildup rates were 0.544 g/m^2-day for TSS, 0.114 g/m^2-day for COD, and 0.0113 g/m^2-day for oil and grease form zero to 10 days. After 10 days, the mass buildup rates decreased to 0.113 g/m^2-day (79% less than the buildup rate before 10days) for TSS, 0.0252 for COD (78% less), and 0.0044 for Oil & Grease (61% less) in the ADD ranges of 10 to 70 days.

Total suspended solids are often used as a master parameter or "tracer" in stormwater modeling. The individual measurements of COD, TOC, oil and grease, TKN and TP are correlated to TSS with R^2 ranging from 0.65 (TKN) to 0.83 (TOC). The correlations ratio of the parameters to TSS and the ratio of the buildup coefficients to the buildup coefficients for TSS are poor. Therefore one does not expect the relationship among pollutant concentrations to be useful in predicting buildup coefficients.

Table 4.3 also summarized values and statistics of loss coefficient for each parameter. It is determined from 0.025 to 0.062 day $^{-1}$ for all parameters. The *Prob(t)* is shown mostly below than 2.4% except for TKN.

4.4.6. Sensitivity Analysis with Changes of Model Parameters

The mass accumulated on the catchment during dry days can be predicted using the new buildup model. The model has several parameters, which include measurable variables such as area, ADD, etc. and two fitting parameters. The product of capture coefficient with pollutant accumulation rate and loss coefficient will affect the rate of mass buildup. A sensitivity analysis of the loss coefficient is shown in Figure 4.7. The final buildup is impacted by the value of the coefficient as well as the rate of buildup. The net mass accumulation of TSS becomes nearly constant after 20 to 40 days. For COD, the net mass accumulation continues to increase until 100 days or more. For pollutants that have a high loss coefficient, BMPs such as street sweeping must be performed regularly if the mass removal is to be maximized. Also the model could be used to assist in comparing the cost of various BMPs, such as frequency of street sweeping. .

4.5. CONCLUSIONS

Pollutant buildup over dry days between storms was investigated using data from the monitoring program and a new model. The following conclusions are made:

(1) Pollutant on highways are highly varied and buildup over time. The concentrations of organic constituents (e.g. chemical oxygen demand, total organic carbon) are highly correlated, and are more correlated to each other than to total suspended solids. The various pollutants also accumulate at different rates.

(2) Pollutant buildup over 41 storm events at 8 sites were calculated from washoff data and show good agreement with a new buildup model using two calibration parameters. The model can be used to assist in best management practice selection and will be useful in predicting their cost effectiveness.

(3) The mass accumulation rate was 0.653 g/m^2-day for TSS, 0.125 g/m^2-day for COD, and 0.0096 g/m^2-day for oil and grease. The parameters show high statistical significance at the 0.03 level or less. Results are also presented for total Kjeldahl nitrogen, total phosphorus and total organic carbon.

(4) An alternate method for estimating buildup using a simple linear assumption was also presented. Between 1 and 10 antecedent dry days, the mass buildup rates were 0.544 g/m^2-day for TSS, 0.114 g/m^2-day for COD, and 0.0113 g/m^2-day for

oil and grease. Between 10 and 70 days the buildup rates decreased by 79% for TSS, 78% less for COD (78% less), and 61% less for oil and grease (61% less)

(5) The loss coefficient ranged from 0.025 to 0.062 day^{-1} for all parameters. The significance was less than 0.024 except for TKN, which was 0.05.

REFERENCES

Anon. (1977). "Control of reentrained dust from paved streets." *EPA Report 907/9-77-007, U.S. EPA*, Kansas City, MO.

Ball, J.E., Jenks, R., and Aubourg, D. (1998). "An assessment of the availability of pollutant constituents on road surfaces." *The Science of the Total Environment*, 209, 243-254.

Bannerman, R., et al. (1984), "Evaluation of urban nonpoint source pollution management in Milwaukee County, Wisc." US EPA-Region V, Madison, WI.

Charbeneau, R.J., and Barrett, M.E. (1998). "Evaluation of methods for estimating stormwater pollutant loads." *J. of Water Environ. Research*, 70(7), 1295-1302.

Crittenden, P.D. (1998). "Nutrient exchange in an Antarctic macrolichen during summer snowfall snowmelt events." *New Phytologist*, 139 (4), 697-707.

Deletic, A.B., and Mahsimivic, C.T. (1998). "Evaluation of water quality factors in storm runoff from paved areas." *J. of Environmental Engineering*, 124(9), 869-879.

Driscoll, E.D., Shelley, P.E., and Strecker, E.W. (1990). "Pollutant loading and impacts from stormwater runoff." *Analytical Investigation and Research Report, Vol. III, FHWA-RD-88-008, Federal Highway Administration*, USA.

EPA (1994). "Nonpoint sources pollution control program." *U.S. EPA Report 841-F-94-005*, USA.

EPA (1995). "Economic benefits of runoff controls." *U.S. EPA Report 841-S-95-002*, USA.

EPA (1996). "Managing nonpoint source pollution from households." *U.S. EPA Report 841-F-96-004J*, USA.

Fraser, A. I., Harrod, T.R., and Haygarth, P.M. (1999). "The effect of rainfall intensity on soil erosion and particulate phosphorus transfer from arable soils." *Wat. Sci. & Tech.*, 39(12), 41-45.

Grottker, M. (1987). "Runoff quality from a street with medium traffic loading." *The Science of the Total Environment*, 59, 457-466.

Lang, Q., Zhang, Q., and Jaffé, R. (2002). "Organic aerosols in the Miami area, USA: temporal variability of atmospheric particles and wet/dry deposition." *Chemosphere*, 47(4), 427-441.

Ma, M., Khan, S., Li,, S., Kim, L-H., Ha, S., Lau, S., Kayhanian, M., and Stenstrom, M.K. (2002). "First flush phenomena for highways: how it can be meaningfully defined." *Proceedings of 9th International Conference on Urban Drainage*, September, Portland, Oregon.

Mostaghimi, S., Park, S.W., Cooke, R.A., and Wang, S.Y. (1997). "Assessment of management alternatives on a small agricultural watershed." *Wat. Res.*, 31(8), 1867-1878.

NLREG version 5.2 (2001), *Phillip H. Sherrod*, Brentwood, TN.

Novotny, V., Sung, H.M., Bannerman, R., and Baum, K. (1985). "Estimating nonpoint pollution from small urban watersheds." *J. of WPCF*, 57(4), 339-348.

Osuch-Pajdzinska, E., and Zawilski, M. (1998). "Model of storm sewer discharge. I: description." *J. of Environmental Engineering*, 124(7), 593-599.

Park, J-S., Wade, T.L., and Sweet, S.T. (2002). "Atmospheric deposition of PAHs, PCBs, and organochlorine pesticides to Corpus Christi Bay, Texas." *Atmospheric Environment*, 36(10), 1707-1720.

Ristenpart, E. (1999). "Planning of stormwater management with a new model for drainage best management practices." *Wat. Sci. & Tech.*, 39(9), 253-260.

Sartor, J.D., and Boyd, G.B. (1972). "Water pollution aspects of street surface contaminants." *EPA Report R2-72-081, U.S. EPA*, Washington, D.C.

Shaheen, D.G. (1975). "Contribution of urban roadway usage to water pollution." *EPA Report 600/2-75-004, U.S. EPA*, Washington, D.C.

Stenstrom, M.K., Lau, S., Lee, H-H., Ma, M., Ha, H., Khan, S., Kim, L-H., and Kayhanian, M. (2001). "First Flush Stormwater runoff from Highways." *Proceedings of Environmental and Water Resources Institute's (EWRI's) World Water & Environmental Resource Congress*, May, Orlando, Florida.

SYSTAT version 9 (1998), *SPSS Inc.*, Chicago, Illinois.

Yuzhou, L., Xiusheng, Y., Robert, J., Carley, and Christopher, P. (2002). "Atmospheric deposition of nitrogen along the Connecticut coastline of Long Island Sound: a decade of measurements."

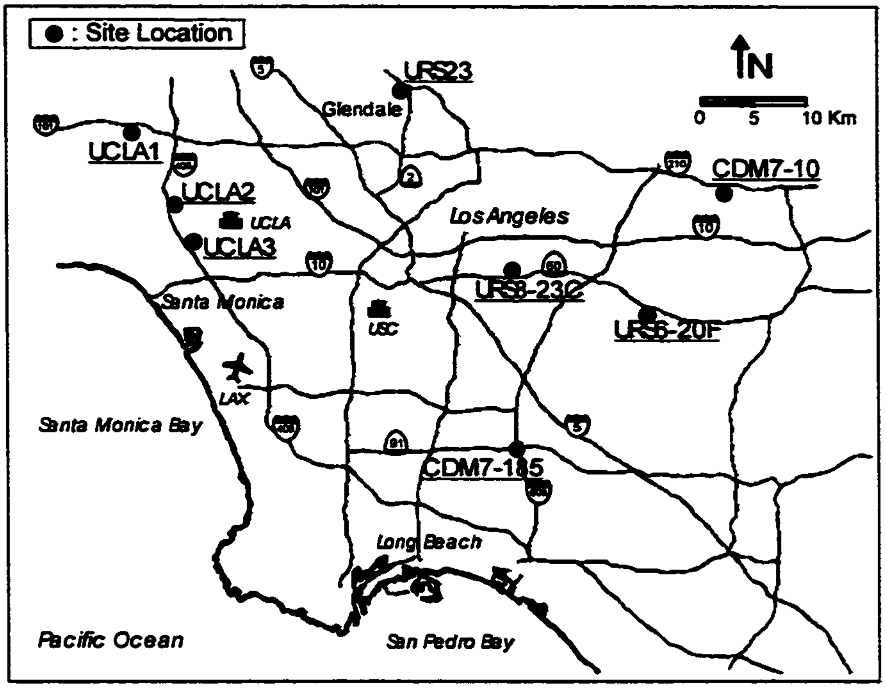


Figure 4.1. Monitoring area in Southern California, USA.

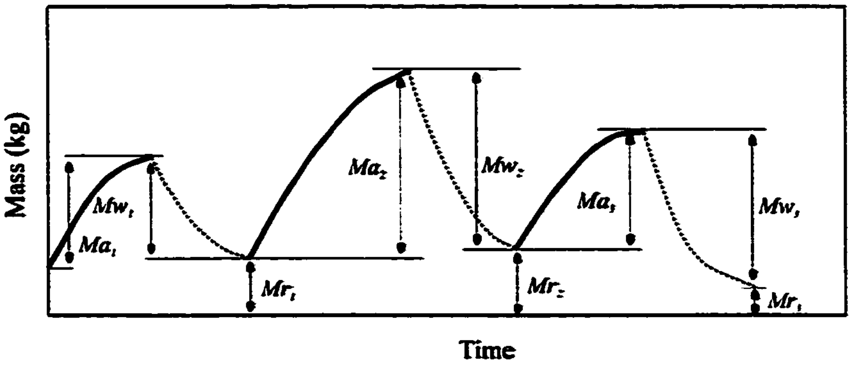


Figure 4.2. Mass accumulation and washoff model approaches.

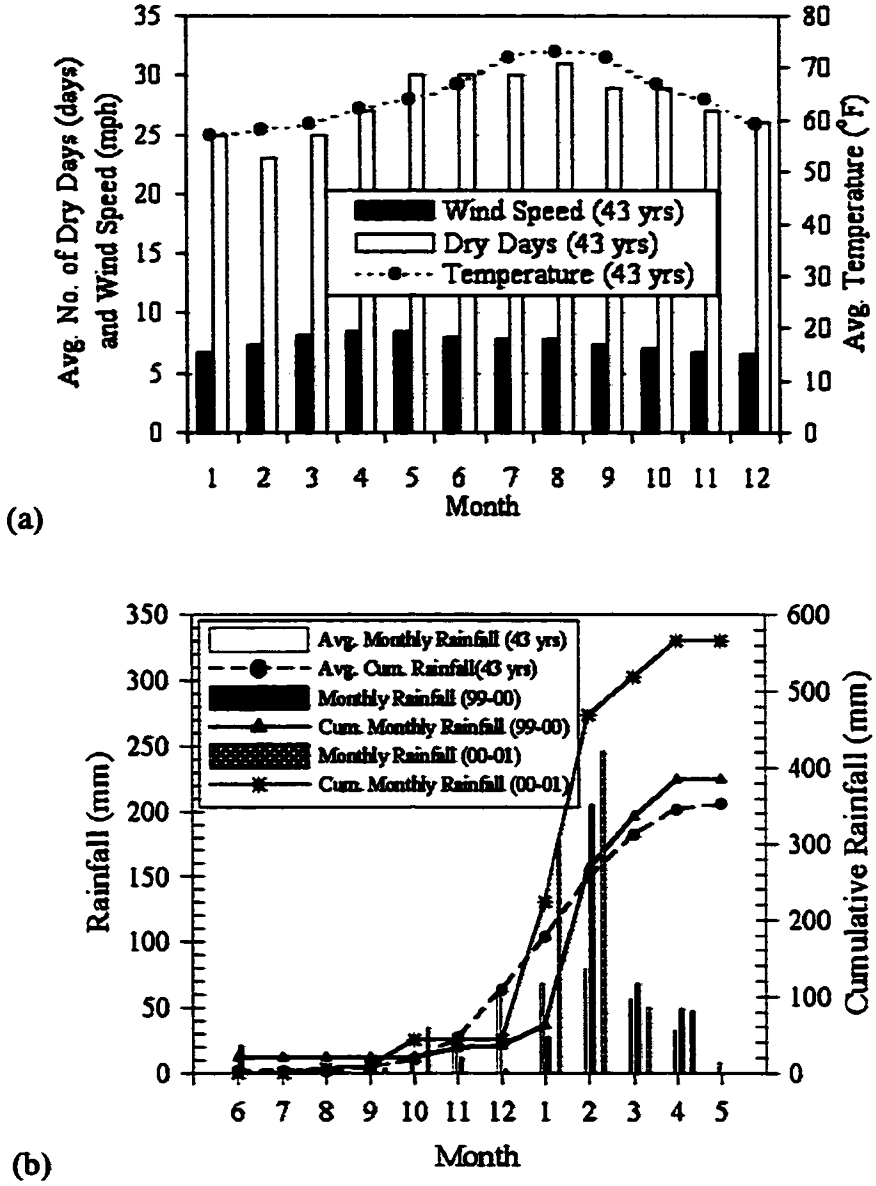


Figure 4.3. Basic historical and monitored information: (a) average dry days, wind speed, temperature during 43 years. (b) monthly rainfall for research periods and 43 years.

Table 4.1. Site and event descriptions

Site	Event Date (m/d/y)	ADT* (cars/day)	Watershed Area (m^2)	Antecedent Dry Days (days)	Storm Duration (hrs:min)	Total Rainfall (cm)	Total Volume of Runoff (m^3)	Runoff Coefficient
UCLA 1	01/25/00	328,000	12800	8.00	19:21	1.68	213.18	0.87
	02/27/00			3.90	4:26	0.30	16.14	0.37
	10/26/00			33.60	10:57	2.34	255.20	0.85
	01/08/01			69.40	6:34	0.38	43.70	0.90
	02/19/01			5.40	4:08	0.71	80.86	0.89
	03/04/01			4.00	10:32	1.17	136.13	0.91
UCLA 2	01/25/00	260,000	16900	7.90	19:23	2.36	396.70	0.92
	02/10/00			9.90	19:01	0.69	106.47	0.92
	04/17/00			39.80	8:34	4.42	300.78	0.40
	10/26/00			33.60	10:57	2.31	194.41	0.50
	01/08/01			69.40	4:18	0.48	49.60	0.61
	03/04/01			4.00	5:05	0.89	140.17	0.93
UCLA 3	01/25/00	322,000	3900	8.20	7:53	1.75	68.02	0.96
	02/12/00			1.10	4:42	1.78	59.46	0.86
	03/04/00			5.00	1:33	0.58	20.50	0.75
	10/26/00			33.60	11:47	2.59	94.53	0.94
	02/19/01			5.30	6:56	2.97	110.53	0.95
	02/24/01			1.00	11:36	1.12	37.29	0.86
	04/06/01			31.60	10:46	2.16	55.43	0.66
CDM7-10	01/25/00	176,000	48100	25.20	10:04	1.50	557.23	0.77
	02/12/00			2.10	2:50	2.31	950.31	0.85
	02/20/00			3.20	13:05	5.64	2598.24	0.96
	02/23/00			2.10	13:00	4.24	1737.42	0.85
	02/27/00			4.00	5:45	1.09	400.49	0.76
	03/08/00			1.00	10:06	2.74	1145.46	0.87
	04/17/00			38.90	7:20	4.24	1745.43	0.86
CDM7-185	01/25/00	220,000	2300	25.00				
	02/12/00			2.00	2:30	1.88	36.98	0.86
	02/23/00			2.00	9:35	2.49	56.53	0.96
	02/27/00			4.00	1:05	0.38	4.00	0.46
	03/08/00			3.00	8:45	2.06	45.70	0.95
	04/17/00			39.00	6:55	3.18	70.39	0.96
URS23	01/26/01	122,000	29100	33.00	7:48	0.89	95.61	0.37
	02/10/01			14.60	9:12	0.99	120.42	0.42
	02/19/01			5.70	6:24	0.94	116.82	0.43
URS6-20F	10/26/00	216,600	1700	33.00	10:00	3.18	33.13	0.61
	01/26/01			33.00	7:18	1.19	10.53	0.52
	02/10/01			14.50	6:36	0.51	2.75	0.32
	02/19/01			5.60	5:40	1.04	7.72	0.44
URS8-23C	01/26/01	229,000	2500	33.00	12:48	0.53	6.59	0.49
	02/19/01			5.50	7:12	0.43	10.66	0.94

* ADT: Average Daily Traffic flow at, or near, monitoring site.

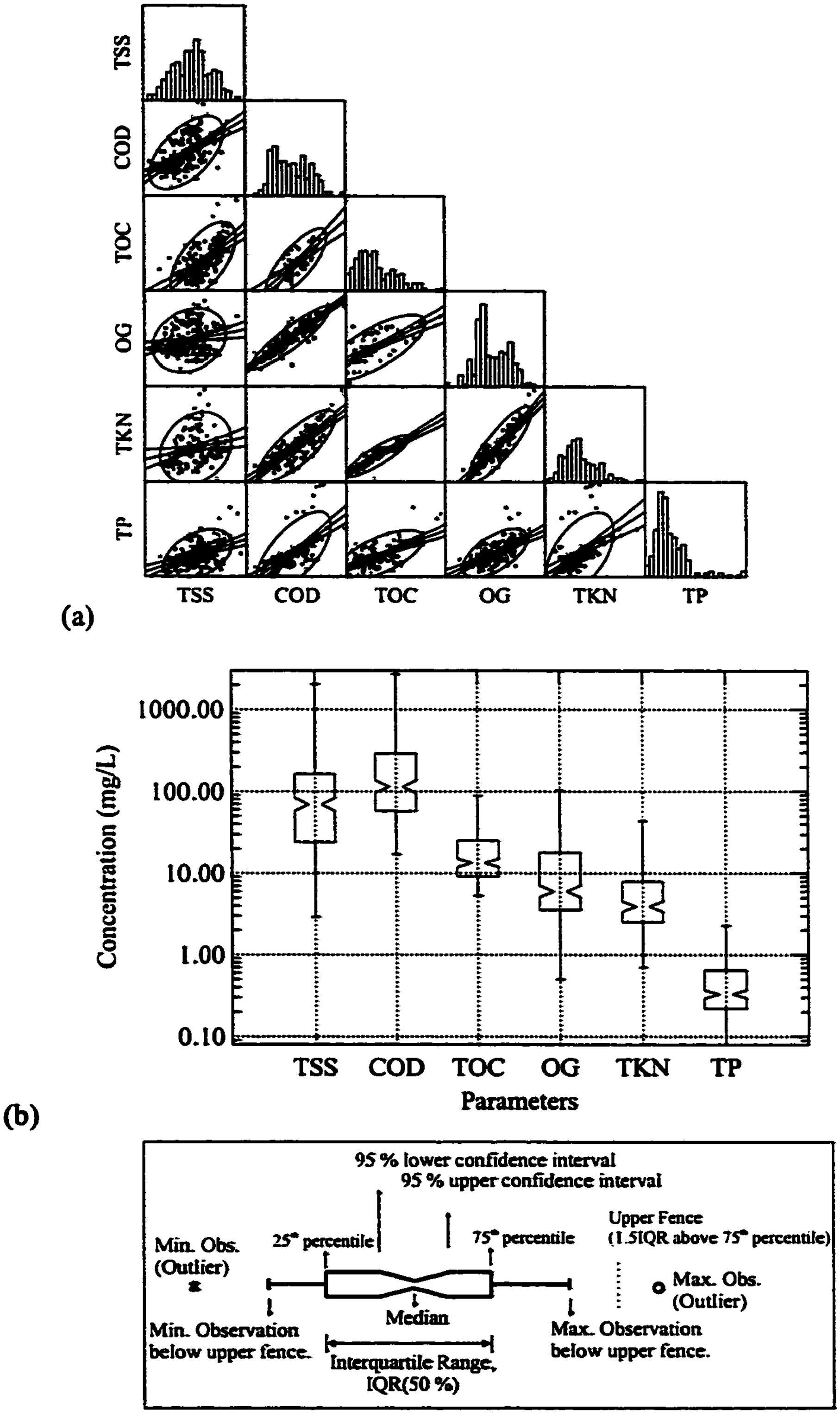


Figure 4.4. Correlation matrix (a) and notched box plots for concentration distributions (b).

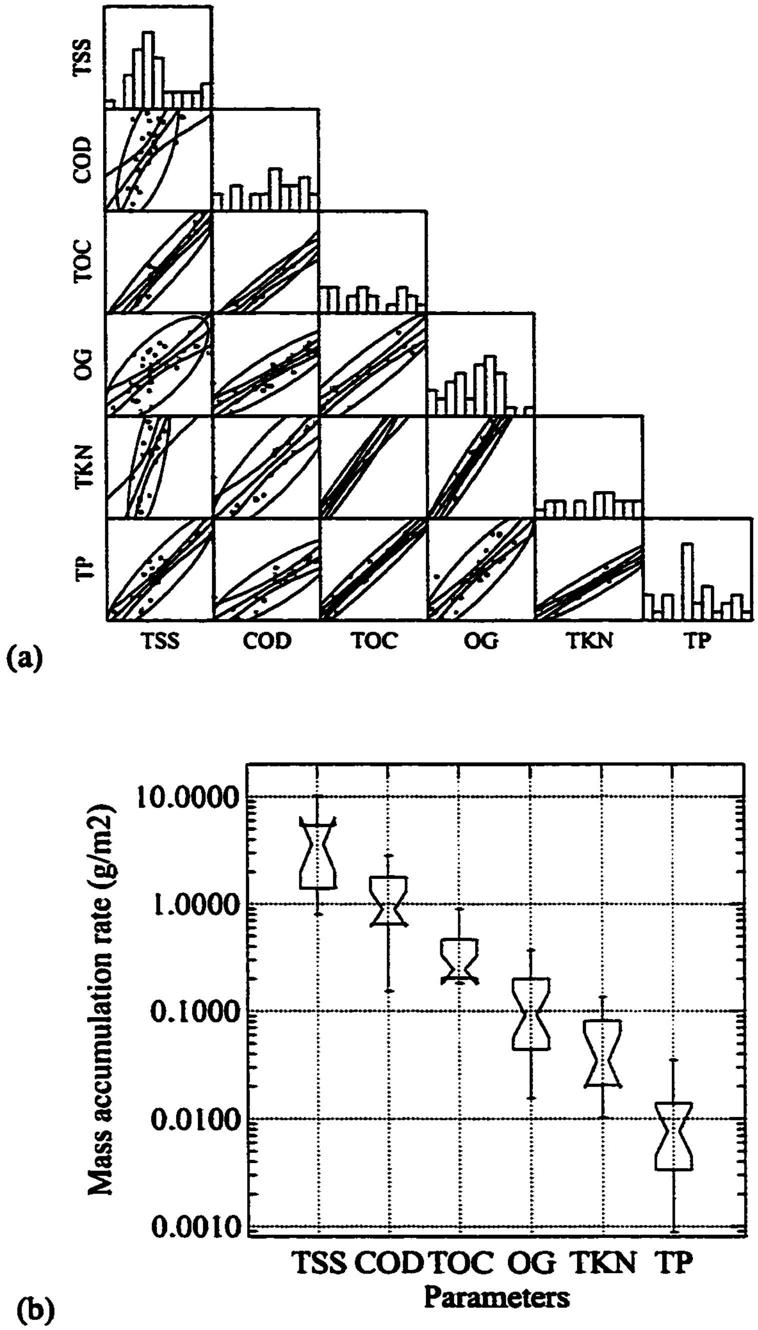


Figure 4.5. Correlation matrix (a) and notched box plots (b) for accumulated pollutant mass rate.

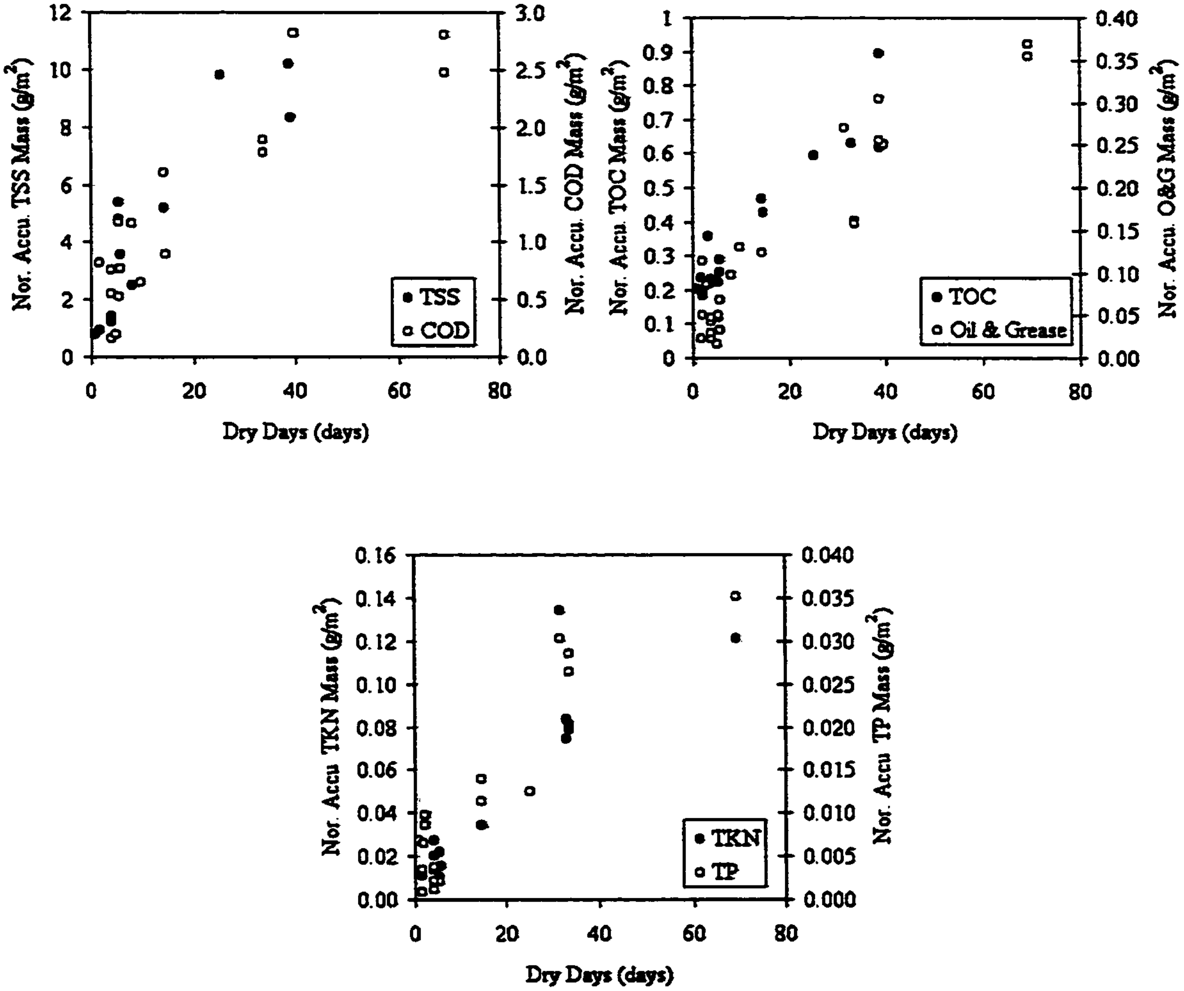


Figure 4.6. Normalized accumulated pollutant mass for model application.

Table 4.2. Statistical comparison between modeled and measured mass rate

Parameters	No. of Events	St. Error of Estimate	Max. Dev. for Any Event	R^2	R_a^2	F value	Durbin-Watson Test for Autocorrelation
TSS	13	1.33	2.36	0.85	0.84	64.27	2.09
COD	17	0.37	0.61	0.82	0.81	69.69	1.47
TOC	18	0.10	0.21	0.80	0.79	64.73	1.21
Oil & Grease	24	0.04	0.09	0.88	0.88	165.80	1.89
TKN	14	0.02	0.05	0.85	0.83	65.93	2.55
TP	18	0.00	0.01	0.86	0.85	95.16	2.37

Table 4.3. Determined model parameters and statistical summaries

Parameters	Mass Accumulation Rate			
	ξP (g/m^2-day)	Standard Error	*t*	*Prob(t)*
TSS	0.6525	0.124	5.27	0.00026
COD	0.1245	0.022	5.78	0.00004
TOC	0.0678	0.011	5.94	0.00002
Oil & Grease	0.0096	0.001	6.74	0.00001
TKN	0.0039	0.0008	4.90	0.00037
TP	0.0009	0.0002	5.59	0.00004

Parameters	Loss Coefficient			
	ψ (1/day)	Standard Error	*t*	*Prob(t)*
TSS	0.062	0.019	3.280	0.007
COD	0.045	0.012	3.850	0.002
TOC	0.021	0.007	2.900	0.008
Oil & Grease	0.097	0.022	4.390	0.000
TKN	0.026	0.012	2.180	0.050
TP	0.025	0.010	2.480	0.024

Table 4.4. Mass accumulation rate using linear assumptions

Parameters	Mass Accumulation Rate (g/m^2-day)		
	0 to 10 days	10 to 70 days	% decrease
TSS	0.544	0.1133	0.79
COD	0.114	0.0252	0.78
TOC	0.059	0.0122	0.79
Oil & Grease	0.0113	0.0044	0.61
TKN	0.0037	0.0013	0.65
TP	0.0011	0.0004	0.64

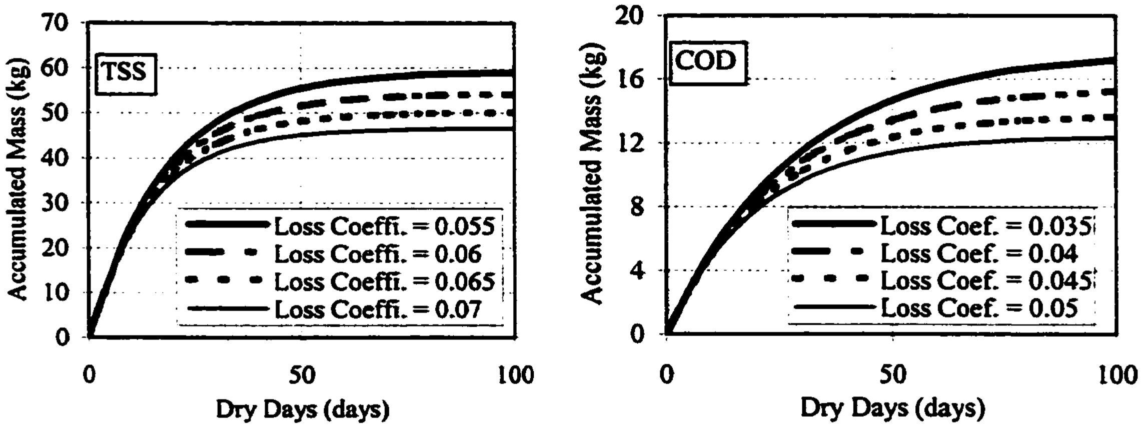


Figure 4.7. Sensitivity analysis for TSS and COD with changes of loss coefficient (ψ) at 5000 m^2 area.

CHAPTER V.

CHARACTERISTICS OF LITTER, OBSERVATION OF FIRST FLUSH AND DETERMINATION OF EVENT MEAN LITTER CONCENTRATIONS IN NON-POINT SOURCES

ABSTRACT

Litter in stormwater was monitored at six Southern California highway sites for two years. Total captured gross pollutants, defined as larger than 0.5 cm, 90% vegetation with only 10% being litter. Event mean concentrations and mass emission rates for five litter parameters are presented. No significant correlations of litter production were noted, although the event mean concentrations show an increasing trend with antecedent dry days and a decreasing trend with total runoff volume or total rainfall. The mass emission rates should be useful to estimate total litter production for developing total maximum daily loads.

Keywords

Event mean concentrations; litter, power model, nonpoint sources, stormwater.

5.1. INTRODUCTION

The United States has made advances in the past 30 years to clean up the aquatic environment by controlling pollution from industries and sewage treatment plants. In spite of these efforts, the aquatic environment is still impacted due to diffuse, or non-point source pollution. Currently non-point source pollution remains the Nation's largest source of water quality problems.

Section 303(d) of the Clean Water Act mandated the implementation of total maximum daily loads (TMDL). A TMDL is a calculation of the maximum amount of pollutant that a waterbody can receive and still meet water quality standards. The TMDL also includes the allocation of loads to the various discharges to meet the goal. States, territories, and tribes can set a TMDL. The process requires the identification of the uses for each waterbody (e.g., drinking water supply, contact recreation, and aquatic life support) and the scientific criteria to support that use. A TMDL becomes the sum of the allowable loads of a single pollutant from all contributing point and nonpoint sources. The calculation must include a margin of safety to ensure that the waterbody can be used for the designated purposes. The calculation must also account for seasonal variation in water quality.

The California State Water Resources Control Board has identified in their 303(d) list at least 36 water bodies where trash is considered a pollutant of concern (CSWRCB 1999). Los Angeles Region of the California Regional Water Quality Control Board developed a total maximum daily load (TMDL) standard for trash in the Los Angeles River (CRWCB 2001). Figure 5.1 shows the parameters that impact California waters and lists them by percentage of total area or linear miles impacted. The major parameters are sediments, nutrients, pathogens, inorganic toxics or metals, organic toxics, mercury, pesticides and others. Seventy percent of the waters are impacted by the stated parameters. Litter is included in sediments and other categories.

The California Department of Transportation (Caltrans) is actively assessing the characteristics and potential impacts of litter generated from their highways (Caltrans 2000a). Caltrans is also evaluating the practical application and performance of several litter capturing devices (Caltrans 2001). Currently, litter characterization is an integrated part of the Caltrans First Flush Characterization Study (FFCS) where both water quality and litter characteristics during the first flush and the entire storm event are evaluated. These data will provide a basis for Caltrans to develop potential treatment technologies and best management practices (BMPs) to control pollutants in runoff from Caltrans freeways. As part of this study, litter weight and volume were evaluated from 6 monitoring sites in the Los Angeles area for up to 17 storm events during the 2000-2002 rainy season.

Street litter, such as plastic bags, cups, cigarette butts, and candy wrappers accumulate during dry seasons. The litter is swept away with stormwater into storm drains and ends up floating in the ocean or washing up on our beaches. A great deal of street litter is made up of plastic, which may take hundreds of years to break down and become harmless to the environment. Litter is considered one of the major pollutants of concern in protecting the integrity of receiving waters for beneficial use.

5.2. METHODOLOGY

5.2.1. Study Area

The first flush characteristic study (FFCS) was developed to obtain first flush water quality and litter data that were representative of stormwater runoff from standard highway drainage outfalls in the Los Angeles area. The locations of the FFCS monitoring sites in Southern California area are shown in Figure 5.2. The characteristics of monitoring sites are summarized in Table 5.1, which shows average daily traffic (ADT), catchment area and approximate impervious rate. Rainfall, runoff flow rate and runoff quality were monitored at 6 freeway sites in Southern California over two rainy seasons (two others were monitored but not for litter). The stations were equipped with a rainfall gage, flow meter and flow-weighted composite sampler. Rainfall and flow data were recorded at one-minute intervals. The monitoring sites were designed to capture litter for off-site evaluation. Each site generally had a corrugated or reinforced concrete pipe that discharged stormwater from grated drain vaults located along the edge of the highway. The circular storm drain outfalls were modified by a metal collar extension to mount and secure litter collection bags with ½ -centimeter openings.

5.2.2. Litter Collection Procedure

Gross pollutant samples were collected in accordance with the procedures detailed in the FFCS Sampling and Analysis Plan (SAP) (Caltrans 2000b). Gross pollutants refer to the combination of litter and vegetation that is initially collected in the bags. Samples were collected throughout each storm event, with particular emphasis on the first flush of storm water flow. Prior to the start of a storm event, a new collection bag was placed on the outfall and securely fastened with the strap. During the event, up to four bags might be used at each monitoring site. To the extent possible, bags were collected after the first 30 minutes of storm water flow, after the end of the first hour, and after the end of the second hour of storm water flow. The fourth and final bag was collected after the storm event. At the completion of each sample interval, the filled collection bag was removed from the outfall and placed inside a plastic trash bag. The trash bag was secured with a large, plastic tie-wrap and labeled with a Tyvek sample tag with the appropriate sample information. Following the storm event, the collected bags were delivered to the laboratory for analysis.

5.2.3. Litter Analysis

Litter analysis were conducted for weight and volume for the following constituents: gross pollutants, vegetation, wet litter, dry litter, biodegradable dry litter, and non-biodegradable dry litter according to the procedures specified in Caltrans Litter Monitoring Guidance Manual (Caltrans 2000c). Litter was defined as material larger than ½-cm that is not vegetation.

All material trapped by the bag's ½-cm openings was analyzed. The weight and volume of the gross pollutants were initially measured. The gross pollutants were then emptied into a tray, where vegetation was separated. The wet weight and volume of litter and vegetation were measured and recorded. The wet litter fraction was then air dried for a minimum of 24 hours. After drying, the litter dry weight and volume were measured and recorded. The dry litter fraction was then sorted into non-biodegradable and biodegradable fractions and weighed. Non-biodegradable litter is defined as litter that does not naturally degrade in the environment, such as metals and plastics. Biodegradable litter consists primarily of paper products. Mass balances were used to for quality control. Twenty percent of the samples were remeasured, and the replicates were generally less than 15% different in volume and 5% different in weight.

5.2.4. Calculation of Event Mean Litter Concentrations and Litter Emission Parameters

The classical event mean concentration was used to characterize litter loading as shown in 5.1:

$$EMC_T\ (g/L) = \frac{Captured\ Litter\ Mass}{Discharged\ Runoff\ Volume} = \frac{\int_0^T M(t)dt}{\int_0^T V_{TRu}(t)dt} \qquad (5.1)$$

where, $M(t)$ is captured litter weight, $V_{TRu}(t)$ is runoff volume during integration interval, and T is the period of the storm. The equation can also be applied to portions of the storm by applying the appropriate integration limits. EMCs are frequently used to characterize stormwater loadings and can be multiplied by the runoff volume to estimate the mass discharge (Corwin and Vaughan 1997; Irish Jr. et al. 1998).

Pollutant concentrations often decline over time, and it is generally believed that the first runoff is the most polluted. The mass emission rate is generally greater at the beginning of rainfall. This phenomena is often called a "first flush", and the existence of a first flush can influence the selection of best management practices (BMPs). The decline in concentration is sometimes off-set by an increasing runoff rate as a storm progresses. Mass emission based definitions of first flush have been proposed (Ma et al. 2002). In this paper, the first flush of litter refers to the mass collected during the first two hours of the event. This corresponds to the first three bags.

Site and event specific parameters were calculated in order to investigate the sources or nature of litter emissions. Factors such as average daily traffic (ADT), antecedent dry days (ADD), total rainfall and runoff volume were correlated with litter emission rates and first flush masses. Litter emission was normalized by dividing by catchment area.

5.3. RESULTS AND DISCUSSION

Table 5.2 shows storm event summaries for each monitored event and site, which includes event rainfall, maximum rainfall intensity, total runoff volume and (ADD). The event date means litter sampled date. The hydrologic data were used to prepare hydrographs and to calculate event mean litter concentrations. During the monitoring periods, antecedent dry days were observed from 1 day to 190 days and event rainfalls were monitored from 0.28 cm to 15.6 cm. The total runoff volume varied from 8 m^3 to 1420 m^3 among the sites.

5.3.1. Statistical Summary of Litter

The gross pollutant and litter for each site were analyzed for all of the storm events. The results of a statistical analysis for normalized weight and volume by area are summarized in Table 5.3 for the 2000-2002 monitoring seasons. URS23, the largest site, had the highest total weight and volume of gross pollutants and litter collected over the storm season. The net volume of litter collected from URS23 was greater than observed at other sites, but less when normalized by area. Sites URS6-20F and URS8-23C had larger pollutant loadings compared to other sites. The mean mass loading for wet gross pollutant in URS6-20F is 18.63 kg/ha and volume loading is 73.46 L/ha. Comparatively UCLA3 and URS23 sites had smaller mean mass and volume loadings, which are 5.34 kg/ha and 12.81 L/ha for UCLA3 and 5.88 kg/ha and 17.65 L/ha for URS23.

Figure 5.3 shows notched box plots for mass and volume loadings of the combined data of all sites and events. Figure 5.4 shows ratios of selected components of the collected material. The notched box plots show the median value and interquartile range with flared sides that terminate at the 95% confidence limit. The various columns are significantly different at the 95% confidence interval if the flared sides do not overlap.

The wet gross pollutants are composed of wet vegetation and wet litter. Figure 5.3(a) shows that vegetation composed approximately 90% of the total gross pollutants by wet weight. The ratio for the litter fraction is shown in Figure 5.4 (left column, ~ 12%). The biodegradable and non-biodegradable portions of the dry litter were nearly equal. The mean volume of wet litter expands slightly upon drying, but the difference is not significant.

Table 5.4 shows the cumulative litter parameters totaled for the 2000-2001 season, normalized by site area. The site UCLA1 is missing due to collection failures. The normalized litter values vary for each site from 2.69 to 17.35 kg/ha for dry litter weight, 0.40 – 8.99 kg/ha for dry biodegradable litter weight, and 0.85 – 6.61 kg/ha for non-biodegradable litter weight. The ratio of net weight of biodegradable to non-biodegradable litter at UCLA3, URS8-23C, and URS23, was very similar, approximately 1 to 1. A higher fraction of biodegradable litter (up to 2 times) was observed at URS6-20F and a higher fraction of non-biodegradable litter (up to 2 times) at UCLA2. The 2000-2001 season was a normal rainfall year with total rainfall nearly equal the mean 43 year record.

5.3.2. Litter Fraction

The fractions of each parameter are shown in Figure 5.4. The data used for this comparison was the combined data from all sites and events. The mean fraction of wet litter weight was about 12% of the wet gross pollutant weight while the remainder was vegetation. Mean wet litter volume was 21% of the total gross pollutant volume, but varied widely, from 3 to 45%. The mean portions of biodegradable dry litter weight and volume were approximately 50% of the dry litter weight and volume; the fractions of biodegradable and non-biodegradable were nearly equal.

5.3.3. Litter Polluto- and Load-graphs

Gross pollutant and litter data were evaluated as polluto-graphs (concentration versus time) and load-graphs (mass loading rate versus time) for each event and site. The litter concentrations were calculated as the dry litter mass divided by the total flow volume during the time of the litter sample collection. The litter mass loading rates were calculated as the dry litter mass divided by the elapsed time of litter collection, and normalized by the catchment area. These plots were compared to the respective hydrographs to determine the potential relationships to flow intensity and storm duration. The plots were also used to determine whether a first flush effect (i.e., relatively higher litter concentrations early in the event, followed by a decrease in concentration after a period of time) was present. Figure 5.5 shows combined litter polluto-graphs and load-graphs for the first event of the season. The first event of the season at site UCLA1 shows very high dry litter concentration and load in first hour.

5.3.4. First Flush

Caltrans' first flush criteria for litter is defined by the litter mass fraction within the first two hours of the storm event. If more than 50% of the mass is emitted during the first two hours, it is a first flush. If this condition occurs, the concentration or load of litter gradually decreases throughout the hydrograph. The litter first flush observation based on the litter ratio is presented in Table 5.5 for selected events. The occurrence of a first flush was not consistently observed at all monitoring sites during the same storm event. Similarly, review of the litter pollutographs and loadographs indicate that, the first flush phenomenon was occasionally observed in all sites during certain storm events. Table 5.5 shows that site URS 6-20F most consistently exhibited a first flush. During the storm event of January 10, 2001, URS6-20F, URS8-23C and URS23 showed significant first flush effects, but there was none present for UCLA2 and UCLA3. This storm event also had the highest relative rainfall intensity of the season.

Evaluation of the litter loadographs, however, presented no clear observations of a first flush phenomenon. In many instances, the litters mass loading rates were not highest during the first portion of a storm event. The highest litter mass loading rate was observed later in the storm event, after the peak flow had occurred.

Gross pollutant and litter data were also reviewed and compared on a multi-event basis to evaluate a potential effect of the first storm event of the season. It was hypothesized that the first storm event of the season would have the highest relative amount of litter mass, volume and mass loading compared to subsequent storm events. Table 5.4 shows that the first monitored storm event of the season did not produce a relatively greater amount of litter when compared to the subsequent storm events.

The ratio of biodegradable to non-biodegradable litter was calculated for each event and site. The values varied considerably during each storm event. Site URS6-20F, the site with the highest normalized litter mass loading, consistently had higher amounts of biodegradable litter. Site UCLA2 had more non-biodegradable litter. On average for all sites, a slightly greater percentage (approximately 60%) of biodegradable litter was measured in the first flush of the storm events. This was consistent with individual storm event observations where lighter biodegradable litter appeared to be washed out first, leaving the relatively heavier non-biodegradable litter to wash out with the remainder of the storm event during the peak flow periods.

Figure 5.6 shows the normalized wet gross, vegetation and litter rates for each event at UCLA3 site. The storm event, October 30, 2001, is the first storm at UCLA3 site. The mass rate is not higher compared to other events. The mass rates vary to event to event, which means the mass rates do not depend on total rainfall.

5.3.5. Factors Affecting Litter Production

Each parameter normalized by area was compared with potential affecting factors such as total rainfall, maximum rainfall intensity and antecedent dry days to determine whether there are any potential relationships. The matrix of small figures represents mass loading relationship with affecting parameters. Figure 5.7(a) shows the mass-based parameters and Figure 5.7(b) shows the volume-based parameters. The two lines means 90% confidence intervals of data. There are no obvious correlations with storm characteristics, such as ADD and total rainfall (TR). The relationship between wet gross pollutant mass or volume and wet vegetation mass or volume is striking. The wet gross pollutant mass is primarily vegetation. There are also significant relationships between wet and dry volumes, which is expected.

Figure 5.8 shows the litter EMC as a function of ADD and event rainfall. The wet gross pollutant weight shows no trend with ADD or rainfall; however, the EMC shows a slight increasing trend with ADD for litter, suggesting accumulation during dry periods. The EMCs for litter show a small decreasing trend with total rainfall. This has been observed for other pollutants and suggests that the large rainfall has washed out sufficiently large masses of litter from the catchment so that the concentration decreases.

Figure 5.9(a) shows the litter EMC as a function of maximum rainfall. There is no obvious trend; also the rainfall intensity is correlated with total rainfall (see Figure 5.7) so that any trends may be due to total rainfall or maximum intensity. Figure 5.9(b) shows the EMC as a function of total runoff. This result is similar to Figure 5.8(b) and is expected since the total runoff volume and total rainfall are related by the runoff coefficient.

Figure 5.10 shows EMCs represented by notched box plot for the six previously defined litter parameters. The EMCs can be used to estimate litter production in planning models. The variability of litter emission is 2 orders of magnitude in some cases.

5.3.6. Regression Model for Event Mean Concentrations of Litter

In order to predict the litter EMC to measurable or predictable rainfall parameters and power regression was performed using the following equation:

$$EMC_{litter} = \varepsilon(ADD)^{a}(TR)^{b} \tag{5.2}$$

where, *ADD* is antecedent dry days (unit: days), and *TR* is total rainfall (unit: cm). ε, *a* and *b* are fitting parameters.

The mass and volume loadings, which are normalized by watershed area, show no correlations with impacting parameters such as antecedent dry periods, total rainfall and maximum rainfall intensity. The EMCs were not tested using the simple correlations.

The regression in equation 5.2 explains approximately 40 to 80 % of the variability as shown in Table 5.6. The fitting parameters are also shown. The value of *a* is positive, suggesting that EMC increases with increasing ADD. The parameter *b* is negative, suggesting that EMC decreases with total rainfall or runoff. These two results match mechanisms. The litter should build up over dry days, and the high rainfall or runoff should washout litter from the catchment, reducing the concentration.

5.4. CONCLUSIONS

Litter has become an important aspect of stormwater pollution prevention. Litter is observable by the public and has attracted increased interest. The first TMDL for Southern California was for litter. There is less information about litter since it has not been considered a traditional water pollutant. This paper presents the results of litter observation at 6 highway sites in Southern California over two years.

Vegetation composed almost 90% of the total gross pollutants (> 0.5 cm). Litter composed approximately 10% of the mass captured in litter traps. The normalized litter loadings vary from 2.69 to 17.35 kg/ha for dry litter weight, 0.40 to 8.99 kg/ha for dry biodegradable litter weight, and 0.85 to 6.61 kg/ha for non-biodegradable litter weight.

EMCs for 5 gross mass parameters are presented. The event mean concentration for total gross pollutants ranged from 2.1 to 259 mg/L (wet basis). The concentrations of non-biodegradable (metals, plastics, etc.) and biodegradable litter (paper, etc.) were nearly equal and ranged from 0.03 to 5.5 mg/L (dry basis). There were few meaningful correlations of litter parameters with storm parameters such as total rainfall, antecedent dry days, etc. A decreasing trend in litter EMC was observed with total rainfall or total runoff volume. An increasing trend of EMC was observed with antecedent dry days. An empirical power series model was developed that can be used to estimate litter production. The trend observations and the model are considered developmental and need verification.

REFERENCES

California Department of Transportation (2000a). "District 7 litter management study, final report." June, Caltrans Document No. CTSW-RT-00-13.

California Department of Transportation (2001). "Gross solids removal devices (GSRD) pilot study 2000-2001 interim report." Caltrans Document No. CTSW-RT-01-047.

California Department of Transportation (2000c). "Litter monitoring guidance manual." October, Caltrans Document No. CTSW-RT-00-025.

California Department of Transportation (2000b). "Sampling and analysis plan, Caltrans 2000-2001, first flush characterization study." November, Caltrans Document No. CTSW-RT-00-044.

California Regional Water Quality Control Board (CRWQCB, 2001). "Trash total maximum daily loads for the Los Angeles River watershed." June 18.

California State Water Resources Control Board (CSWRCB, 1999). "1998 California 303(d) list and TMDL priority schedule."
http://www.swrcb.ca.gov/tmdl/docs/303d98.pdf.

Jefferies, C., Aitken, A., McLean, N., Macdonald, K., and McKissock, G. (1999). "Assessing the performance of urban BMPs in Scotland." *Wat. Sci. & Tech.*, 39(12), 123-131.

Ma, M., Khan, S., Li,, S., Kim, L-H., Ha, S., Lau, S., Kayhanian, M., and Stenstrom, M.K. (2002). "First flush phenomena for highways: how it can be meaningfully defined." *Proceedings of 9th International Conference on Urban Drainage*, September, Portland, Oregon.

U.S. EPA (1994). "Nonpoint sources pollution control program." U.S. EPA Report 841-F-94-005, USA.

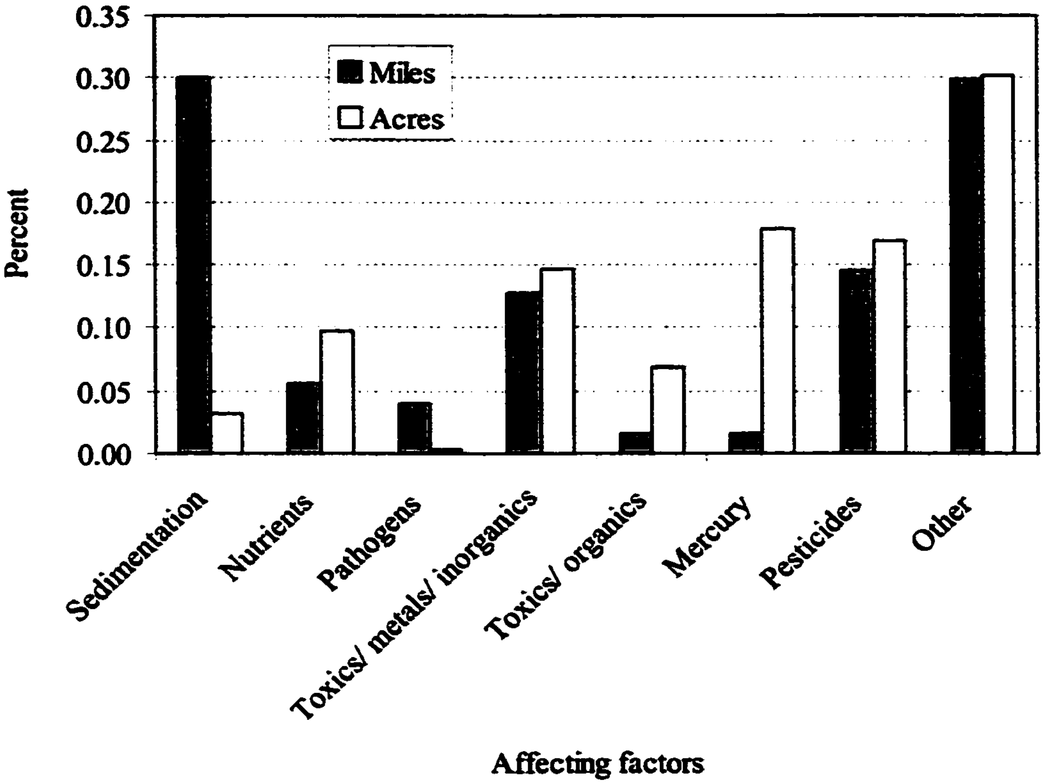


Figure 5.1. Percentage of impacting parameters to waters in California.

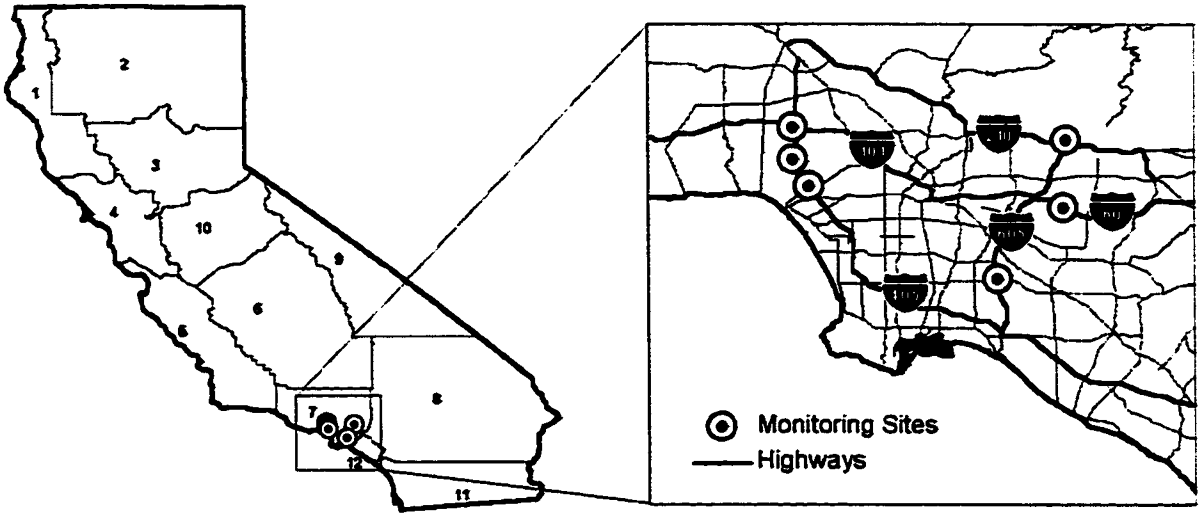


Figure 5.2. Monitoring sites in Southern California.

Table 5.1. Descriptions of monitoring sites

Site Name	Site Location	Post Kilometers	ADT (cars/day)	No. of Drain Inlets	Catchment Area (ha.)	Approx. Percent Impervious (%)
UCLA1	101 Freeway	29.2	328,000	1	1.3	100
UCLA2	405 Freeway	53.6	260,000	1	1.7	95
UCLA3	405 Freeway	49.7	322,000	1	0.4	100
URS6-20F	60 Freeway	8.2/25.1	216,600	1	0.2	100
URS8-23C	605 Freeway	9/9.6	229,000	1	0.3	100
URS23	210 Freeway	29.8	122,000	20	2.9	100

Table 5.2. Event summary for all monitored events

Event Date (m/d/y)	UCLA Monitoring Sites											
	UCLA1				UCLA2				UCLA3			
	Event Rainfall (cm)	Max Rainfall Intensity (mm/hr)	Total Flow (m³)	ADD (days)	Event Rainfall (cm)	Max Rainfall Intensity (mm/hr)	Total Flow (m³)	ADD (days)	Event Rainfall (cm)	Max Rainfall Intensity (mm/hr)	Total Flow (m³)	ADD (days)
10/26/00	2.39	6.10	260.7	33.6	2.39	5.84	200.8	33.6	2.59	4.06	94.7	33.6
01/08/01	0.38	1.78	43.7	69.4	0.51	1.78	52.2	69.4	0.53	2.03	17.9	69.4
01/10/01	12.70	30.23	1327.4	1.9	15.60	32.26	1416.2	1.9	12.85	22.35	481.1	2.0
02/10/01	1.32	7.87	155.2	14.2					1.55	4.57	58.6	14.2
02/19/01	0.71	2.79	80.9	5.4	2.39	7.11	261.6	4.8	3.02	12.19	112.4	5.3
02/24/01	1.45	1.78	165.6	1.0	1.91	2.29	241.6	1.0	1.14	2.29	38.1	1.0
03/04/01	1.19	3.05	139.1	4.0	0.89	4.83	140.2	4.0	0.51	2.29	11.4	4.0
04/07/01					3.02	5.33	501.9	31.5	2.54	7.62	65.2	31.6
04/20/01	0.81	2.79	79.0	13.2								
10/30/01					0.33	2.03	47.5	192.20	0.28	2.29	8.1	192.30
11/12/01					1.19	9.91	172.3	12.98	0.74	5.33	24.8	12.99
11/24/01					5.03	26.67	737.8	11.69	2.97	14.48	108.7	11.60
12/14/01					0.36	2.03	52.0	19.73				
01/27/02					3.18	8.13	445.6	27.13	2.46	5.08	92.2	27.14
02/17/02									0.74	4.32	25.6	20.31
03/07/02									0.46	3.30	14.4	17.74
03/17/02					0.23	2.29	23.53	10.69	1.04	9.40	37.0	10.70
	URS Monitoring Sites											
	URS6-20F				URS8-23C				URS23			
10/26/00	0.89	15.20	33.9	33.0		7.60	11.2		3.20			33.0
01/08/01	0.23	3.00	2.0	70.6	0.33			108.0	0.43			70.4
01/10/01	7.11	18.30	130.6	72.2	10.26	24.40	168.0	2.0	8.74	27.40	1673.5	2.0
01/26/01	0.71	6.10	10.7	1.7	1.45	6.10	14.6	1.7	1.19	21.30	156.1	1.7
02/10/01	0.71	6.10	4.3	14.5	1.25	12.20	7.3	2.9	0.79	9.10	152.7	14.6
02/19/01	0.46	6.10	7.9	5.6	0.94	1.50	12.0	5.5	1.04	6.10	117.6	5.7
02/24/01	9.04	9.10	80.8	1.1	6.43	9.10	118.3	0.0	9.55	12.20	1047.4	5.1
04/09/01	1.55	15.20	21.7	31.8		24.40	31.4	28.1	2.29	15.20	564.6	31.8

Table 5.3. Statistical summary of normalized litter for the 2000-2002

Parameters	Monitoring Sites	Gross Pollutants		Litter				Biodegradable		Non-biodegradable		Vegetation	
		Wet		Wet		Dry		Dry		Dry		Wet	
		Weight (kg/ha)	Volume (L/ha)	Weight (kg/ha)	Volume (L/ha)	Weight (kg/ha)	Volume (L/ha)	Weight (kg/ha)	Volume (L/ha)	Weight (kg/ha)	Volume (L/ha)	Weight (kg/ha)	Volume (L/ha)
Minimum	UCLA2	0.302	0.412	0.020	0.088	0.010	0.082	0.005	0.000	0.005	0.000	0.280	0.323
	UCLA3	0.625	1.875	0.221	0.000	0.104	0.000	0.036	0.000	0.034	0.000	0.625	1.875
	URS6-20F	0.350	2.400	0.033	0.500	0.012	0.400	0.010	0.249	0.000	0.100	0.305	1.400
	URS8-23C	0.497	2.833	0.172	0.900	0.084	0.934	0.053	0.600	0.031	0.334	0.313	1.834
	URS23	0.407	1.793	0.066	0.345	0.030	0.145	0.008	0.072	0.007	0.072	0.335	1.448
Maximum	UCLA2	49.42	35.76	1.38	22.94	0.90	10.00	0.37	4.41	0.39	4.71	48.65	33.84
	UCLA3	11.45	32.50	0.88	5.75	0.40	7.00	0.35	5.00	0.21	4.75	10.75	31.00
	URS6-20F	80.00	292.00	6.80	52.00	4.17	39.30	2.60	19.70	1.15	12.80	72.50	234.00
	URS8-23C	43.33	82.33	7.70	27.73	6.07	26.37	2.30	11.33	3.31	12.37	35.00	53.00
	URS23	20.77	50.00	2.22	8.97	1.30	8.97	0.58	4.14	0.63	4.66	18.22	40.34
Median	UCLA2	3.78	4.44	0.27	1.07	0.16	0.86	0.05	0.16	0.04	0.15	3.30	3.29
	UCLA3	4.78	10.13	0.46	1.63	0.25	2.24	0.12	1.05	0.08	0.56	4.24	7.25
	URS6-20F	5.81	35.00	0.66	2.37	0.26	2.68	0.14	1.72	0.08	0.92	5.40	33.08
	URS8-23C	6.60	10.58	1.27	4.48	0.72	4.50	0.30	1.97	0.36	2.36	5.27	6.10
	URS23	2.25	8.79	0.26	1.55	0.14	1.67	0.05	0.33	0.02	0.24	2.11	5.69
Mean	UCLA2	9.28	10.76	0.46	3.69	0.30	2.75	0.09	0.57	0.13	0.60	8.78	7.06
	UCLA3	5.34	12.81	0.49	2.28	0.25	2.60	0.14	1.31	0.10	1.05	4.88	10.36
	URS6-20F	18.63	73.46	1.58	10.03	0.85	8.38	0.54	4.86	0.24	2.62	16.59	60.94
	URS8-23C	13.97	23.78	2.31	8.66	1.62	7.90	0.67	3.45	0.85	3.93	11.51	14.83
	URS23	5.88	17.65	0.59	2.63	0.33	2.69	0.14	1.09	0.13	1.25	5.21	11.59
Standard Deviation	UCLA2	14.00	13.12	0.44	6.56	0.30	3.53	0.12	1.23	0.16	1.33	13.76	9.56
	UCLA3	3.02	8.82	0.22	1.88	0.10	2.22	0.08	1.37	0.06	1.25	2.95	8.33
	URS6-20F	26.70	93.71	2.29	17.63	1.41	13.29	0.88	6.94	0.39	4.24	24.13	73.93
	URS8-23C	17.22	30.85	2.88	10.43	2.30	9.67	0.88	4.09	1.26	4.59	14.18	19.89
	URS23	7.45	17.54	0.77	3.07	0.45	3.12	0.21	1.57	0.23	1.70	6.58	14.20

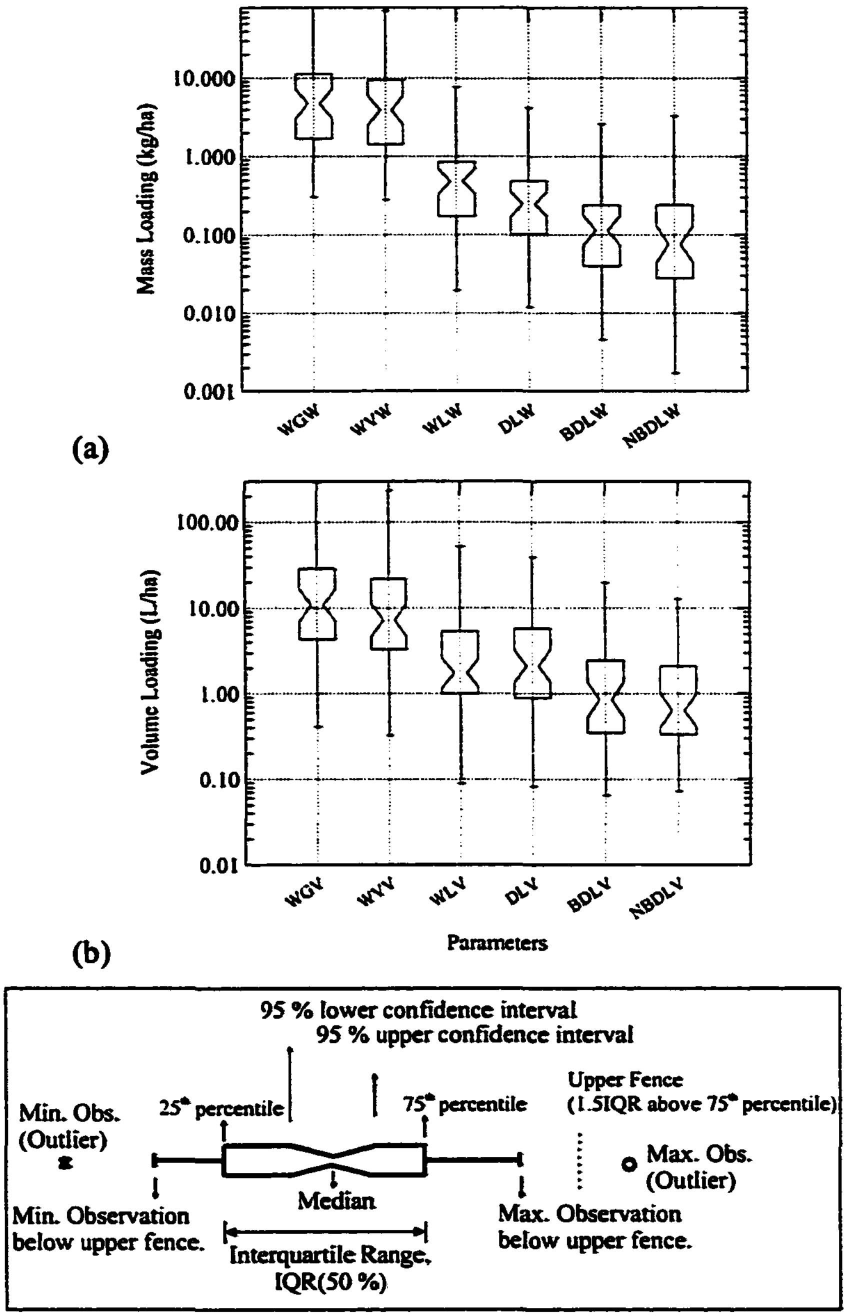


Figure 5.3. Mass (a) and volume (b) loadings normalized by area for combined sites (WGW: wet gross weight, WVW: wet vegetation weight, WLW: wet litter weight, DLW: dry litter weight, BDLW: biodegradable dry litter weight, NBDLW: non-biodegradable dry litter weight, WGV: wet gross volume, WVV: wet vegetation volume, WLV: wet litter volume, DLV: dry litter volume, BDLV: biodegradable dry litter volume, NBDLV: non-biodegradable dry litter volume).

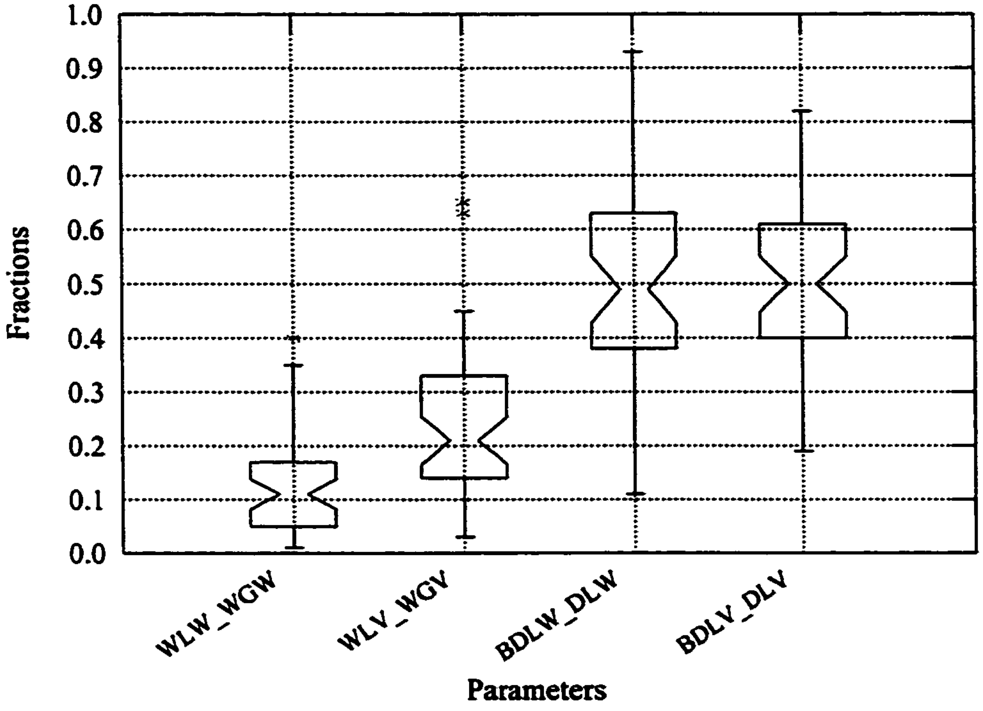


Figure 5.4. Fractions of litter for all of the combined data (WLW_WGW = wet litter weight/wet gross weight, WLV_WGV = wet litter volume/wet gross volume, BDLW_DLW = biodegradable dry litter weight/dry litter weight, BDLV_DLV = biodegradable dry litter volume/dry litter volume)

Table 5.4. Normalized litter wastes as function of catchment area during 2000-2001 rainy season

Parameter			Cumulative Pollutant				
Monitoring Sites			UCLA2	UCLA3	URS6-20F	URS8-23C	URS23
Gross pollutants	Wet	Weight (kg/ha.)	64.8	36.4	329	121	48
		Volume (L/ha.)	56.1	78.6	1,440.00	178	138
Litter	Wet	Weight (kg/ha.)	1.8	4	25.3	19.1	4.87
		Volume (L/ha.)	6.25	18.1	165	69.3	22.1
	Dry	Weight (kg/ha.)	5.8	17.35	14.1	13.3	2.69
		Volume (L/ha.)	1.3	1.8	149	63.7	22.3
Biodegradable	Dry	Weight (kg/ha.)	0.4	0.8	8.99	6.01	1.1
		Volume (L/ha.)	2.8	9.5	82.3	28.3	8.28
Non-biodegradable	Dry	Weight (kg/ha.)	0.85	0.85	4.4	6.61	1.01
		Volume (L/ha.)	3	7.8	58.3	31.7	9.55

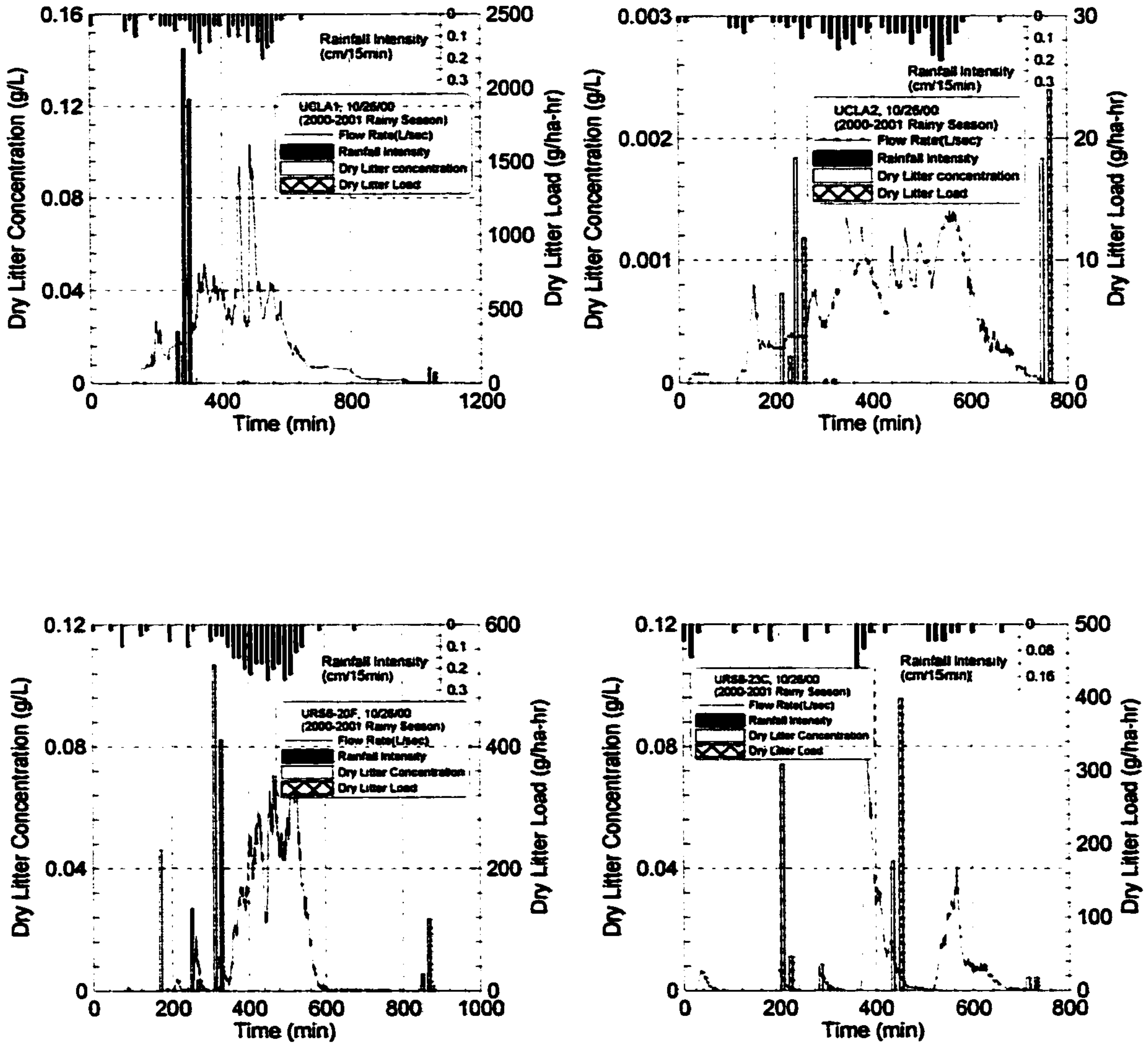


Figure 5.5. Litter polluto- and load-graphs for first storm event (with hydrograph shown in background).

Table 5.5. Fraction of litter occurring in the first two hour of runoff

Parameters		Gross Pollutant Wet Weight (g)	Gross Pollutant Wet Volume (ml)	Litter Wet Weight (g)	Litter Wet Volume (ml)	Litter Air Dry Weight (g)	Litter Air Dry Volume (ml)	Biodegradable Dry Weight (g)	Biodegradable Dry Volume (ml)
UCLA2	10/26/01	0.02	0.03	0.04	0.05	0.03	0.06	0.03	0.04
	1/8/01	0.98	0.95	0.98	0.97	0.96	0.97	0.97	0.98
	1/10/01	0.05	0.11	0.53	0.39	0.48	0.5	0.5	0.63
UCLA3	10/26/01	0.92	0.73	0.85	0.62	0.81	0.61	0.64	0.4
	1/8/01	0.94	0.9	0.98	0.96	0.98	0.96	0.98	0.95
	1/10/01	0.2	0.27	0.59	0.31	0.38	0.34	0.49	0.37
	2/10/01	0.25	0.26	0.15	0.13	0.12	0.1	0.15	0.1
	2/19/01	0.61	0.57	0.85	0.71	0.92	0.74	0.75	0.57
URS6-20F	10/26/00	0.23	0.29	0.33	0.35	0.29	0.34	0.24	0.31
	1/10/01	0.98	0.96	0.94	0.96	0.96	0.94	0.97	0.94
	1/26/01	0.87	0.88	0.94	0.96	0.96	0.96	1	0.93
	2/10/01	0.97	0.95	0.99	0.93	0.99	0.94	0.99	0.93
URS8-23C	10/26/00	0.19	0.2	0.14	0.12	0.12	0.12	0.16	0.14
	1/10/01	0.77	0.68	0.58	0.7	0.53	0.62	0.77	0.7
	2/24/01	0.22	0.32	0.37	0.43	0.37	0.33	0.46	0.33

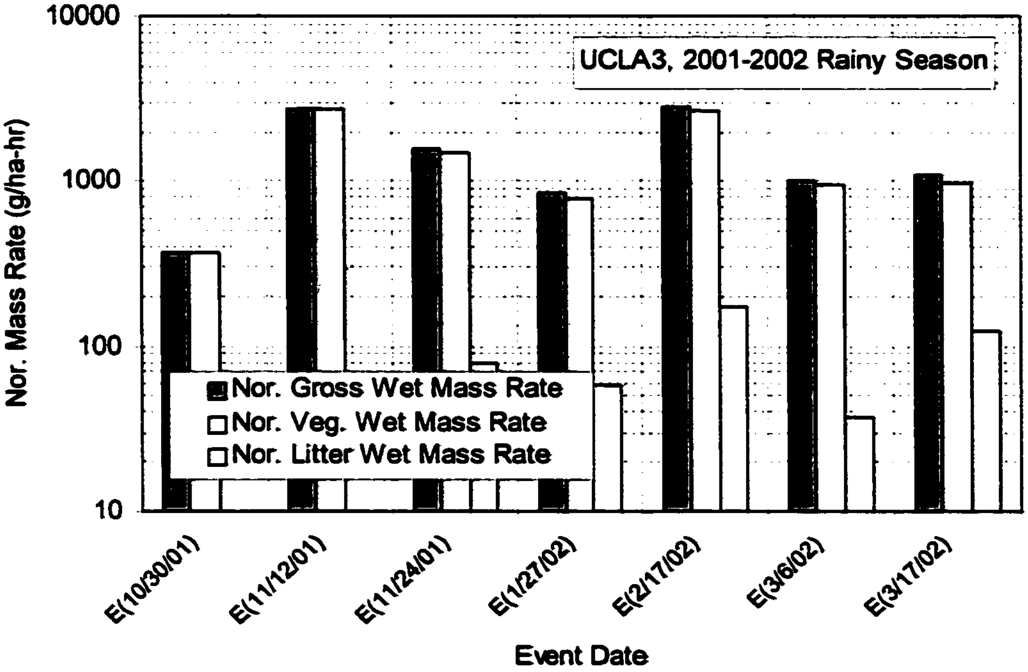


Figure 5.6. Normalized mass rates as function of catchment area and storm duration.

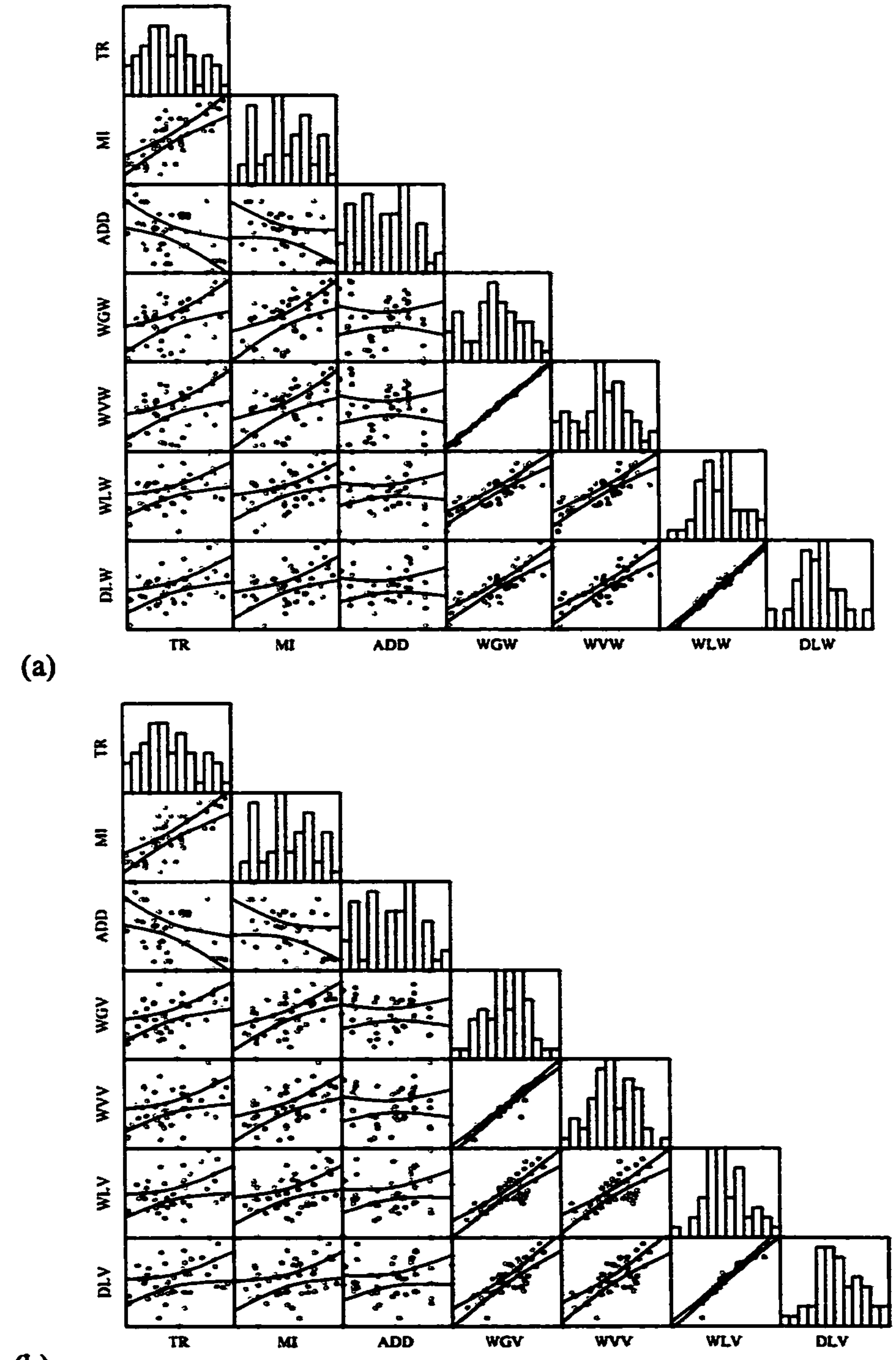


Figure 5.7. Correlation matrix for mass (a) and volume (b) loading with impacting parameters such as total rainfall, maximum rainfall intensity and antecedent dry days (TR: total rainfall, MI: Maximum rainfall intensity, ADD: antecedent dry days).

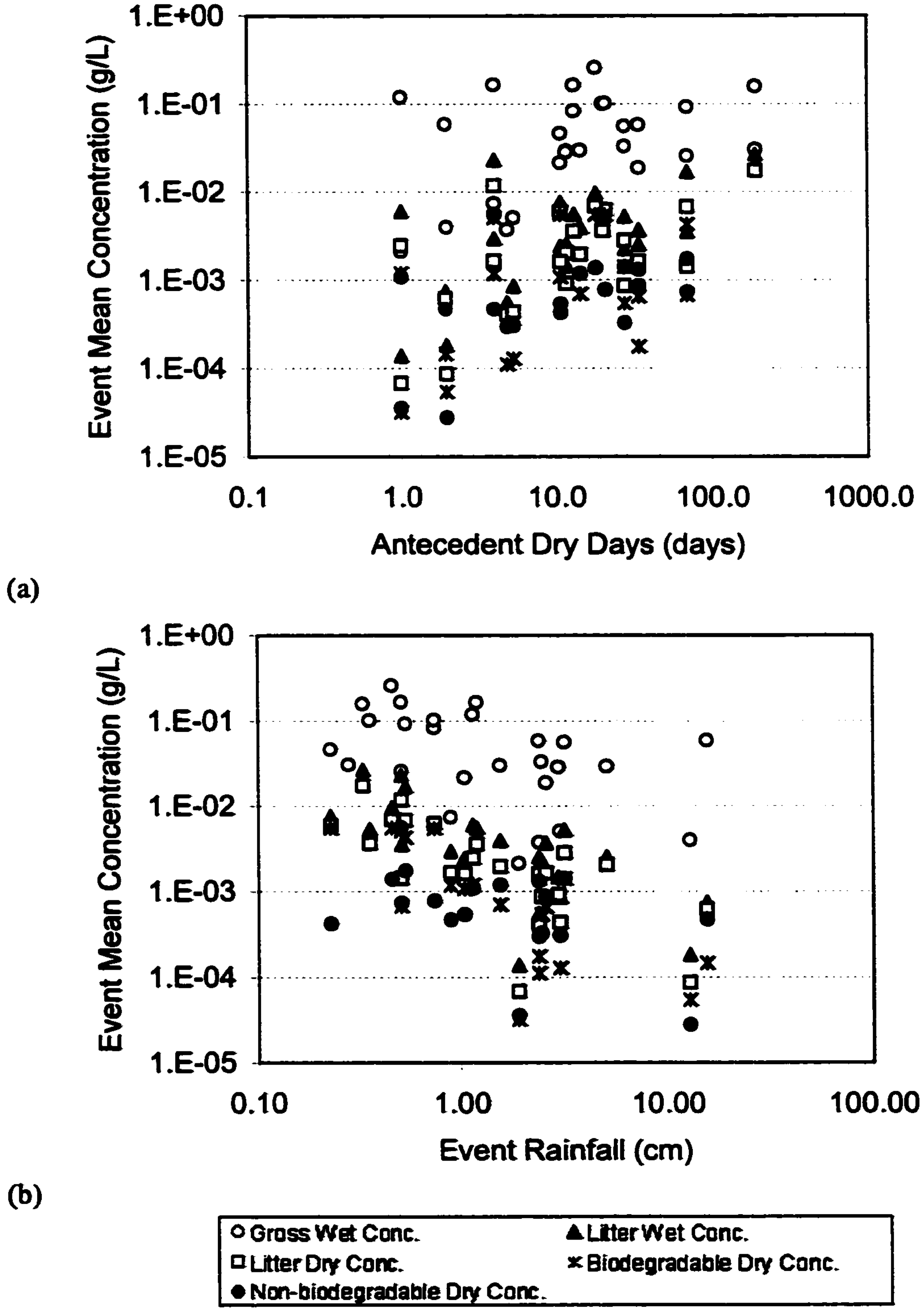
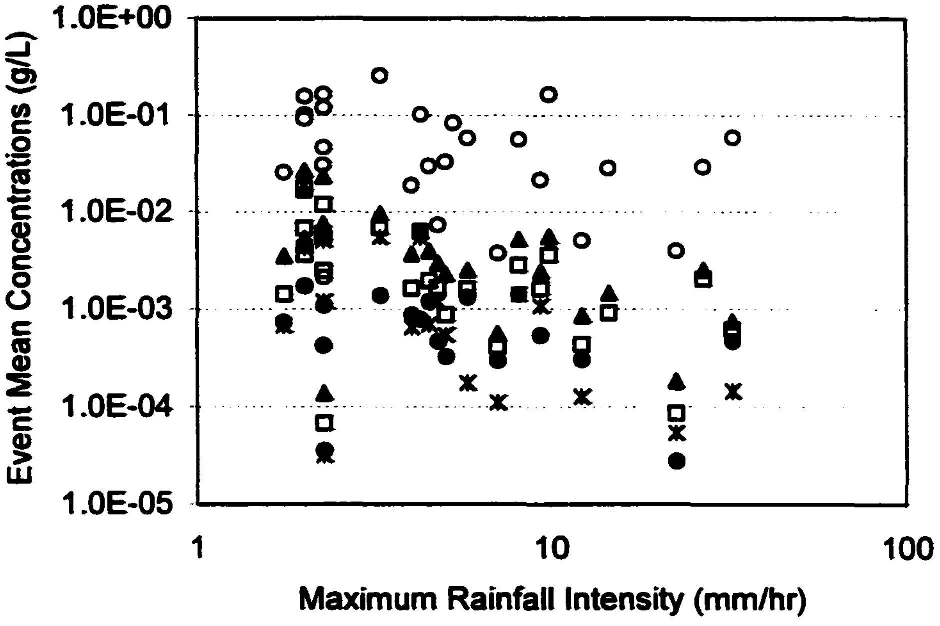
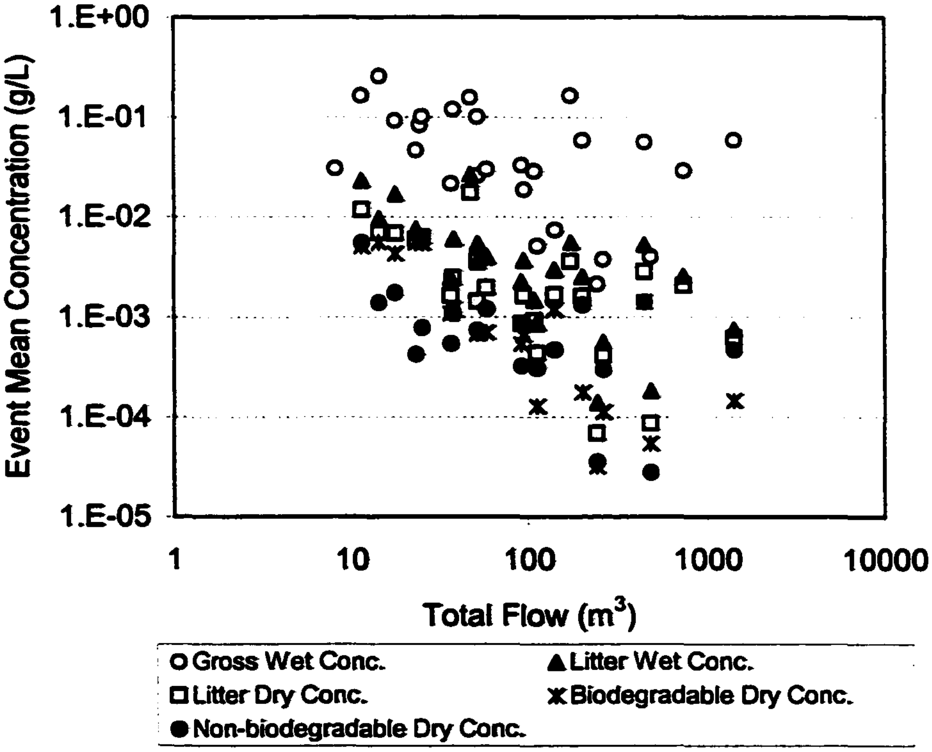


Figure 5.8. Event mean concentrations with ADD and event rainfall.



(a)



(b)

Figure 5.9. Event mean concentrations with maximum rainfall intensity and total flow.

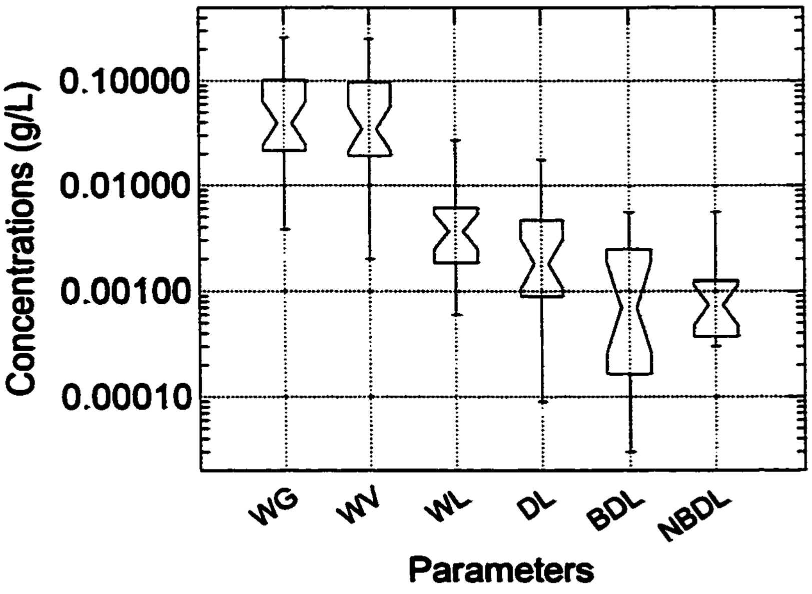


Figure 5.10. Notched box plot for event mean concentrations (WG: wet gross, WV: wet vegetation, WL: wet litter, DL: dry litter, BDL: biodegradable dry litter, NBDL: non-biodegradable dry litter).

Table 5.6. Coefficient determination and statistical summaries

Parameters	ε	a	b	R^2	Durbin-Watson D
Wet gross pollutant	0.0239	0.206	-0.408	0.500	2.009
Wet vegetation	0.02056	0.215	-0.387	0.490	1.964
Wet litter	0.0016	0.360	-0.683	0.790	1.933
Dry litter	0.00095	0.354	-0.694	0.770	2.061
Dry biodegradable litter	0.00061	0.245	-1.034	0.570	1.676
Dry non-biodegradable	0.00032	0.336	-0.408	0.590	2.252

CHAPTER VI.

CONCLUSIONS

This dissertation was divided into three parts. The first part developed a semi-empirical runoff model. The second part developed a pollutant build up model. Both were based on data collected during an intensive two year monitoring project. The third part of the dissertation reports litter production parameters from highways, which were also observed in the monitoring project.

6.1. Pollutant Washoff from Highways

Forty-one storms were monitored from 8 different highway locations. A large suite of water quality parameters was sampled and was used in developing a new washoff model. The model uses four parameters which gives it flexibility to fit first flush as well as non-first flush events. The model's parameters are correlated to measurable or predictable storm events such as total runoff volume, antecedent dry days and storm duration. The model shows good fit for eight water quality constituents and will be tested for other constituents, which were collected over two years from eight highway sites. Future uses of the model include improving estimates of event mean concentrations from sparse data and designing BMPs to take advantage of the first flush. The following additional conclusions are made:

(1) Washed-off mass loading and EMCs are presented for eight water quality parameters. Generally the differences between minimum and maximum washed-off mass and EMCs are large because of event and site characteristics, such as rainfall intensity, area, runoff coefficient and antecedent dry periods.

(2) The EMCs are negatively correlated to storm duration, total rainfall, total runoff volume of runoff, and average rainfall intensity. Large storms have smaller EMCs because of dilution effects or exhaustion of pollutant mass.

(3) The fractions of washed-off mass are very high in first 30% of runoff, which suggests a first flush. The washed-off mass stabilizes after 30% of the runoff volume and it is apparent that treatment capacity in the early part of a storm (i.e., less than 30%) is more valuable that treatment capacity in the later part of the storm.

(4) Using the criteria of "high" first flush and "medium" first flush, as 50% of the mass in the first 30% of the volume, and 30 to 50% in the first 30% volume, respectively, more than 30% of the storms showed high first flush for TSS and COD, and more than 45% showed a medium first flush. The frequency of first flushes is tabulated for the other parameters, which generally less frequent. A "first flush friendly" BMP, meaning a BMP that can treat a high percentage or all

of the initial flow, would be advantageous for 80% to 90% of the events for TSS, COD and TOC.

(5) When using the model to calculate event mean concentrations, the mean is similar to results using previous models, but the 50% interquartile ranges are smaller for the new model, suggesting less variability for the new model. The reductions in variability are even greater if one considers the maximum and minimum values. The large values calculated with the exponential model occur when the fit is poor. The medium point method is easy to apply, but it potentially inaccurate if there are few samples.

6.2. Pollutant Accumulation during Dry Days

Pollutant build up over dry days between storms was investigated using data from the monitoring program and a new model. The following conclusions are made:

(1) Pollutant on highways are highly varied, and buildup over time. The concentrations of organic constituents (e.g. chemical oxygen demand, total organic carbon) are highly correlated, and are more correlated to each other than to total suspended solids. The various pollutants also accumulate at different rates.

(2) Pollutant build up over 41 storm events at 8 sites were calculated from washoff data and show good agreement with a new build up model using two calibration parameters. The model can be used to assist in best management practice selection and will be useful in predicting their cost effectiveness.

(3) The mass accumulation rate was 0.653 g/m^2-day for TSS, 0.125 g/m^2-day for COD, and 0.0096 g/m^2-day for oil and grease. The parameters show high statistical significance at the 0.03 level or less. Results are also presented for total Kjeldahl nitrogen, total phosphorus and total organic carbon.

(4) An alternate method for estimating buildup using a simple linear assumption was also presented. Between 1 and 10 antecedent dry days, the mass buildup rates were 0.544 g/m^2-day for TSS, 0.114 g/m^2-day for COD, and 0.0113 g/m^2-day for oil and grease. Between 10 and 70 days the build up rates decreased by 79% for TSS, 78% less for COD (78% less), and 61% less for oil and grease (61% less)

(5) The loss coefficient ranged from 0.025 to 0.062 day^{-1} for all parameters. The significance was less than 0.024 except for TKN, which was 0.05.

6.3. Litter Waste Loading

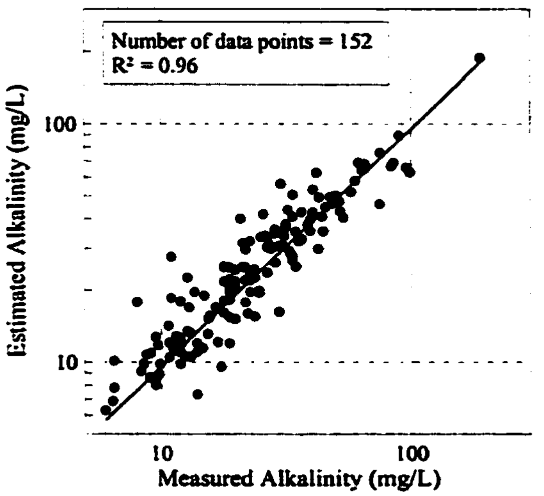
Litter has become an important aspect of stormwater pollution prevention. Litter is observable by the public and has attracted increased interest. The first TMDL for Southern California was for litter. There is less information about litter since it has not been considered a traditional water pollutant. This paper presents the results of litter observation at 6 highway sites in Southern California over two years.

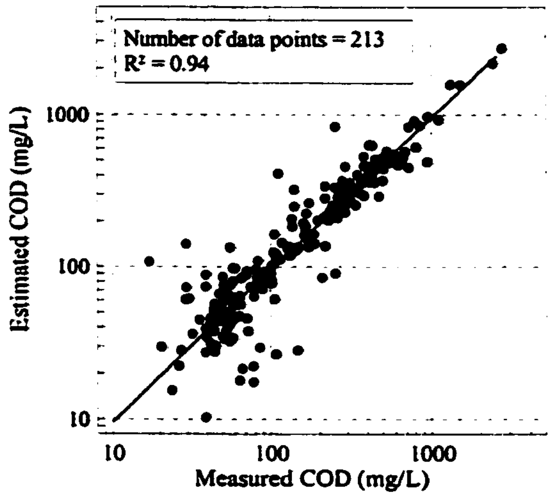
Vegetation composed almost 90% of the total gross pollutants (> 0.5 cm). Litter composed approximately 10% of the mass captured in litter traps. The normalized litter loadings vary from 2.69 to 17.35 kg/ha for dry litter weight, 0.40 to 8.99 kg/ha for dry biodegradable litter weight, and 0.85 to 6.61 kg/ha for non-biodegradable litter weight.

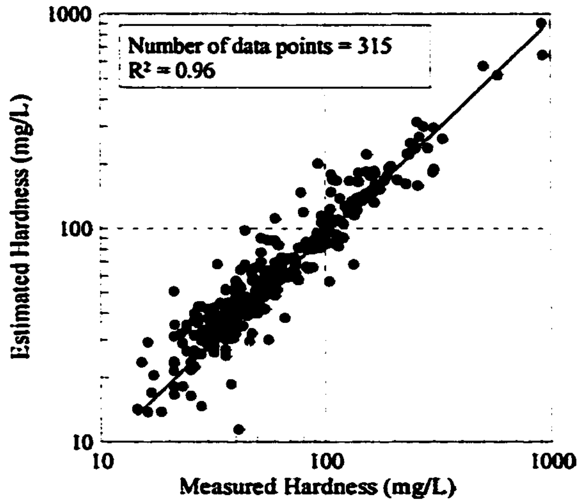
EMCs for 5 gross mass parameters were presented. The event mean concentration for total gross pollutants ranged from 2.1 to 259 mg/L (wet basis). The concentrations of non-biodegradable (metals, plastics, etc.) and biodegradable litter (paper, etc.) were nearly equal and ranged from 0.03 to 5.5 mg/L (dry basis). There were few meaningful correlations of litter parameters with storm parameters such as total rainfall, antecedent dry days, etc. A decreasing trend in litter EMC was observed with total rainfall or total runoff volume. An increasing trend of EMC was observed with antecedent dry days. An empirical power series model was developed that can be used to estimate litter production. The trend observations and the model are considered developmental and need verification.

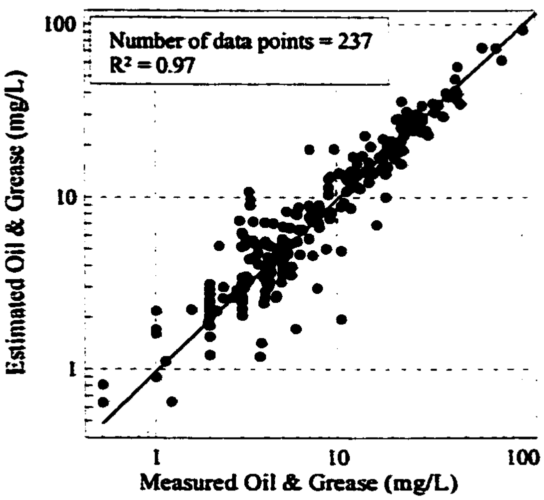
Appendix 1. New Washoff Model Results

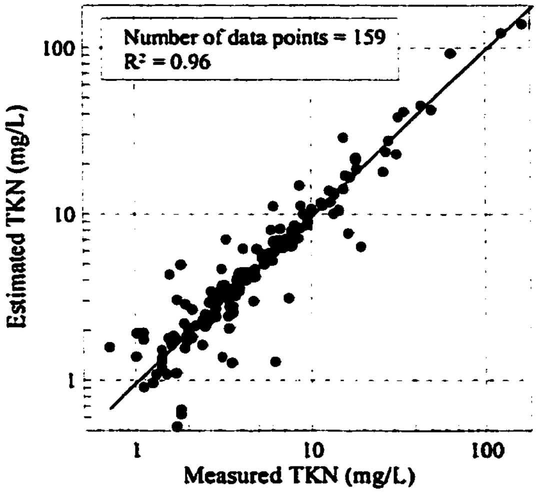
Appendix 1.1. Relationships of Measured and Estimated Concentrations

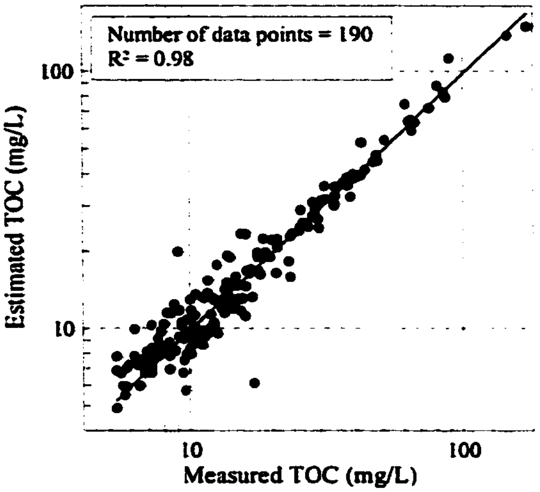


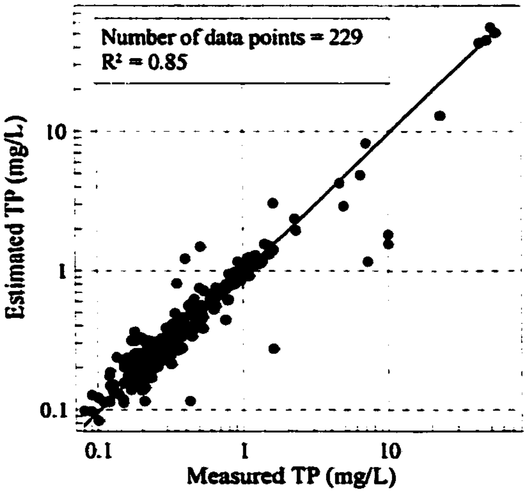


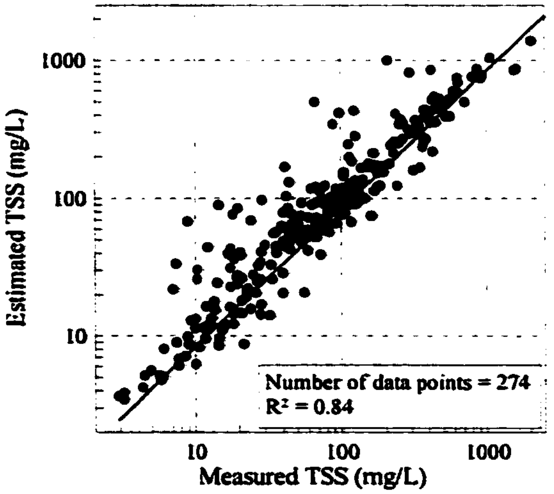




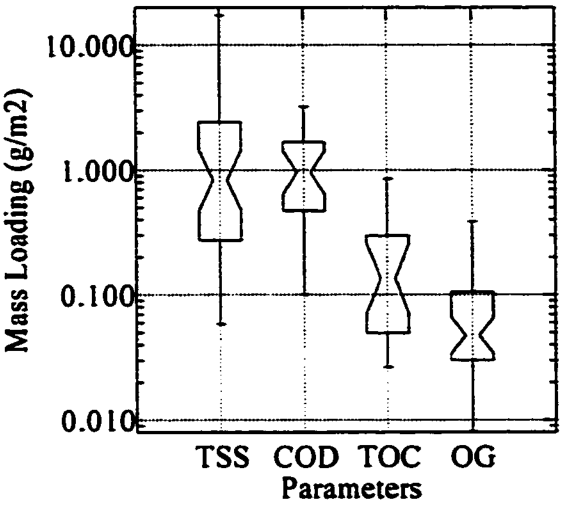

Number of data points = 159
R^2 = 0.96
Estimated TKN (mg/L)
Measured TKN (mg/L)
1
10
100

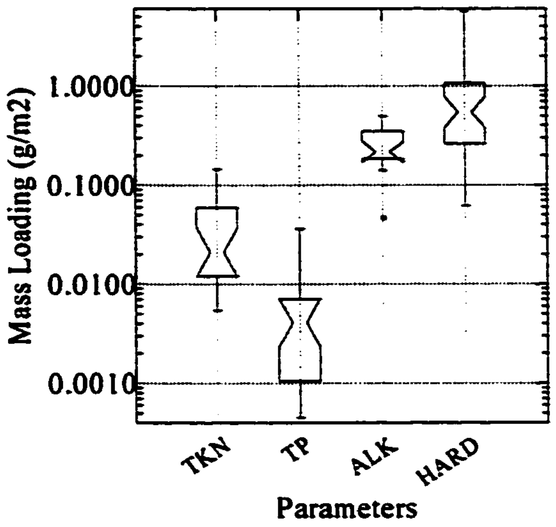

Number of data points = 190
R^2 = 0.98
Estimated TOC (mg/L)
Measured TOC (mg/L)
10
100

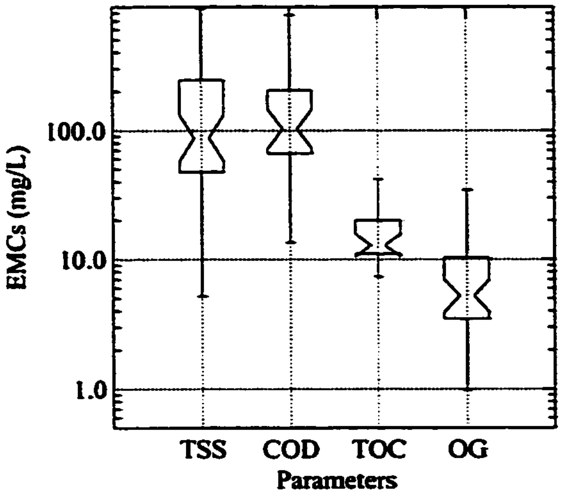

Number of data points = 229
R^2 = 0.85
Estimated TP (mg/L)
Measured TP (mg/L)
0.1
1
10

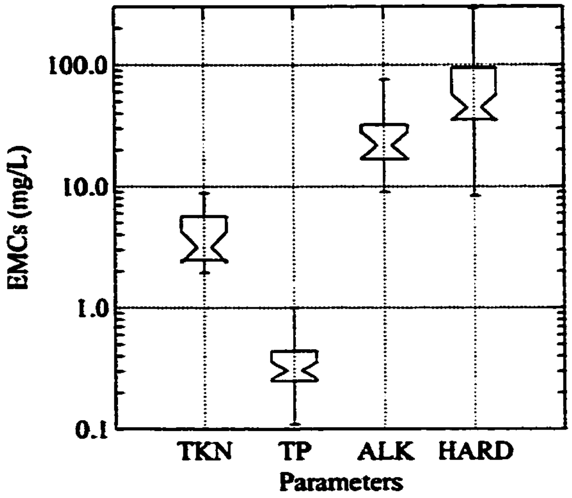

Number of data points = 274
R^2 = 0.84
Estimated TSS (mg/L)
Measured TSS (mg/L)
10
100
1000

Appendix 1.2. Notched Box Plots for Mass Loading Rate and EMCs

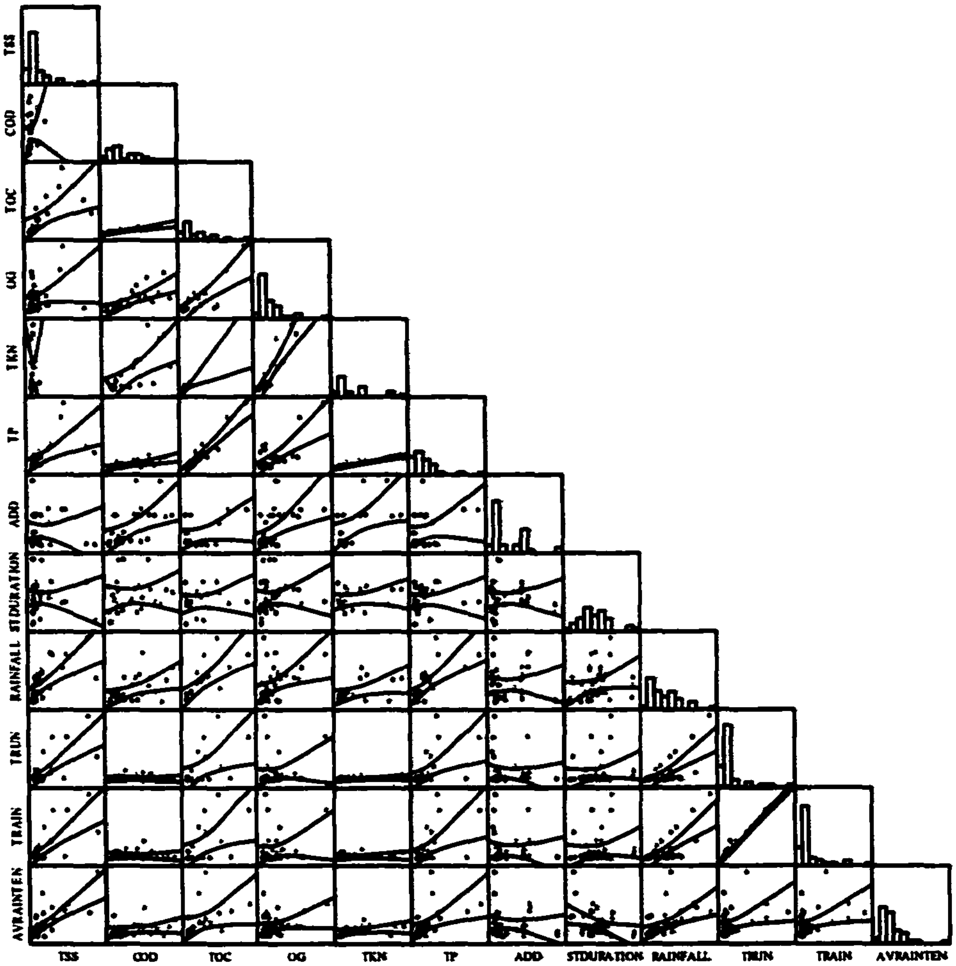








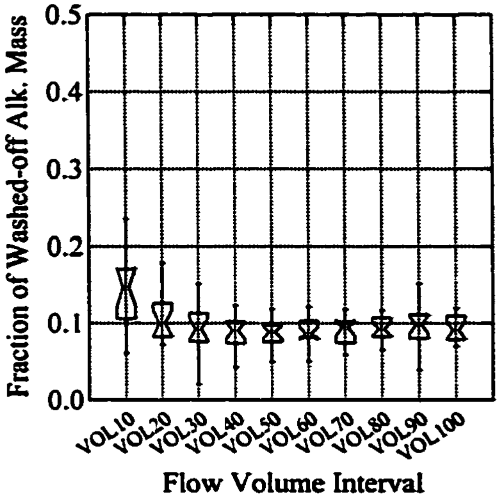
Appendix 1.3. Relationships of Mass Loading and Affecting Parameters

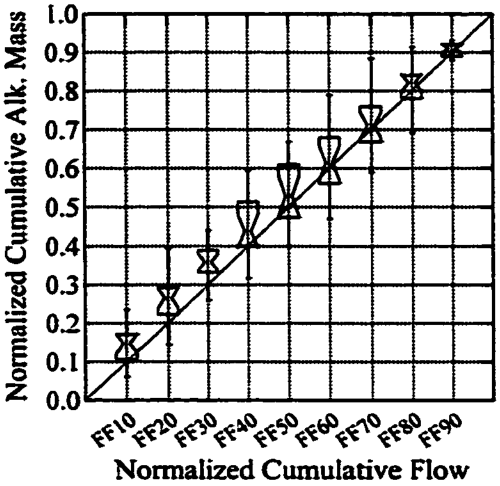


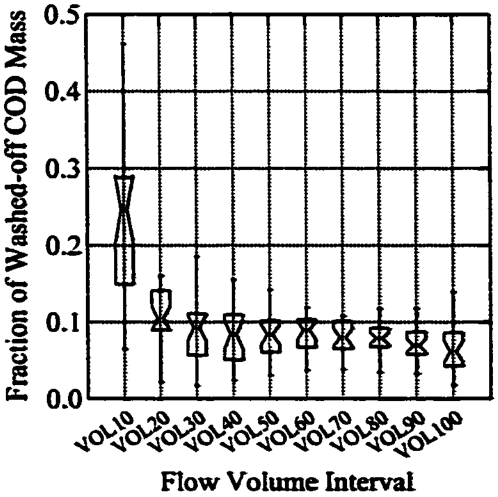
	TSS	COD	TOC	OG	TKN	TP	ADD	STDURATION	RAINFALL	TRUN	TRAIN	AVRAINTEN
TSS	▨	0.88	0.73	0.62	0.75	0.60	0.62	-0.05	0.54	-0.52	-0.52	0.37
COD	0.02	▨	0.92	0.89	0.92	0.67	0.21	-0.40	0.66	-0.41	-0.42	0.61
TOC	0.10	0.01	▨	0.91	0.98	0.38	-0.04	-0.63	0.72	-0.31	-0.30	0.78
OG	0.19	0.02	0.01	▨	0.84	0.47	-0.16	-0.55	0.48	-0.48	-0.48	0.58
TKN	0.08	0.01	0.00	0.04	▨	0.47	0.01	-0.65	0.80	-0.16	-0.15	0.82
TP	0.21	0.14	0.46	0.34	0.34	▨	0.20	-0.13	0.27	-0.14	-0.18	0.15
ADD	0.19	0.70	0.95	0.76	0.99	0.71	▨	0.70	0.12	-0.38	-0.37	-0.21
STDURATION	0.93	0.43	0.18	0.26	0.16	0.81	0.12	▨	-0.41	-0.24	-0.24	-0.65
RAINFALL	0.27	0.16	0.11	0.34	0.06	0.61	0.83	0.43	▨	0.27	0.29	0.94
TRUN	0.29	0.42	0.56	0.34	0.76	0.79	0.46	0.64	0.60	▨	1.00	0.30
TRAIN	0.29	0.41	0.57	0.33	0.77	0.74	0.47	0.64	0.58	0.00	▨	0.32
AVRAINTEN	0.47	0.20	0.07	0.23	0.05	0.78	0.70	0.16	0.01	0.56	0.54	▨

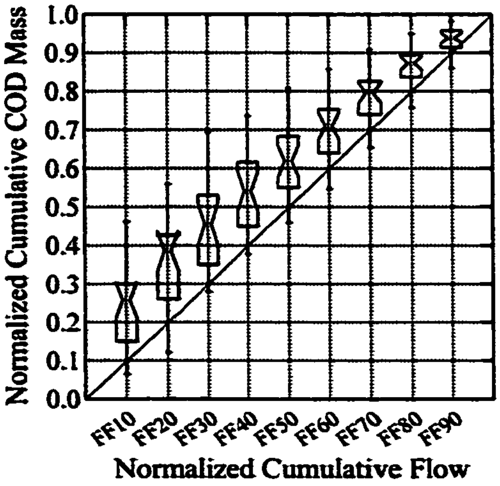
Note: ADD (Antecedent Dry Days, days), STDURATION (Storm Duration, hours), TRUN (Total Volume of Runoff, m^3), TRAIN (Total Volume of Rainfall, m^3) and AVRAINTEN (Average Rainfall Intensity, cm/hr)

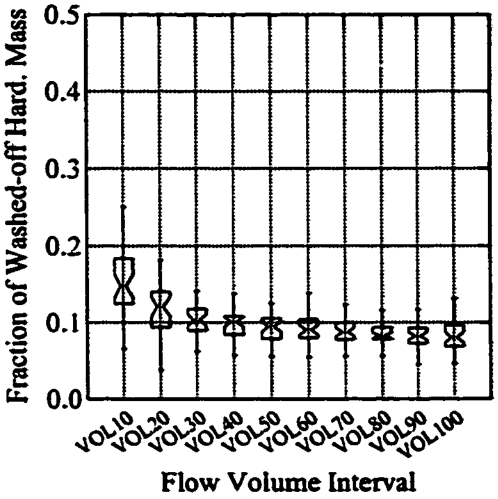
Appendix 1.4. Washed-off Pollutant Mass using Monitoring and New Washoff Model

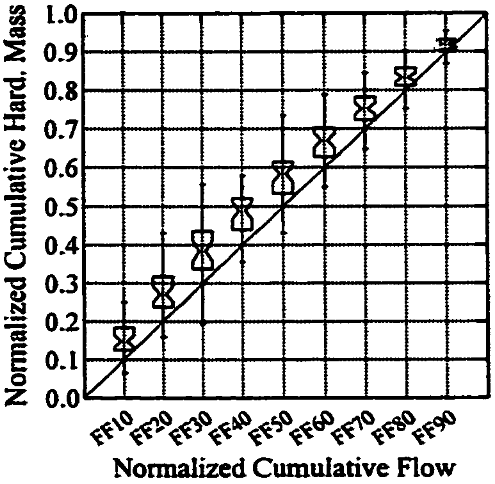


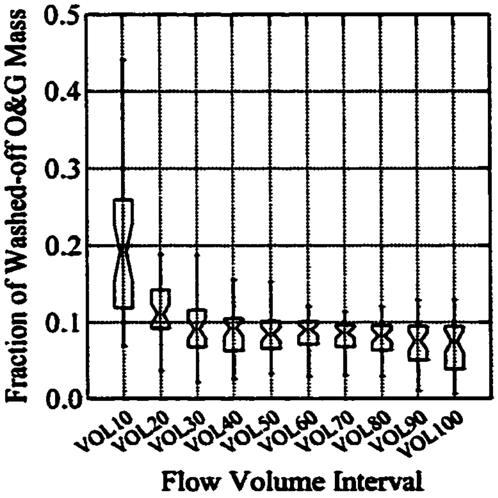


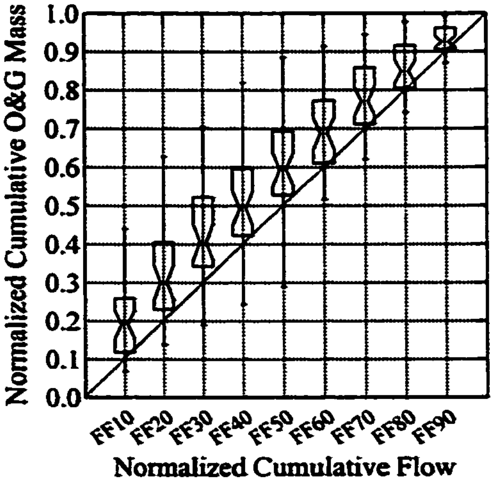


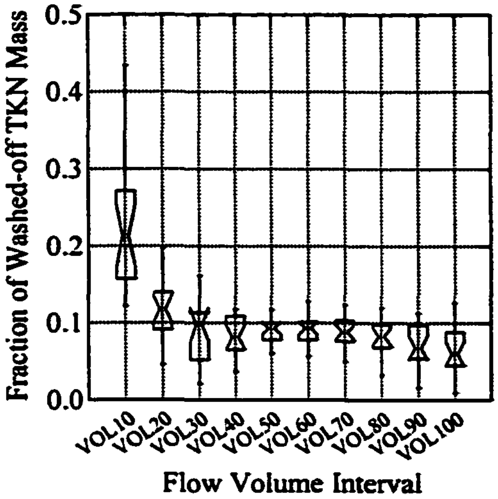



Fraction of Washed-off Hard. Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval

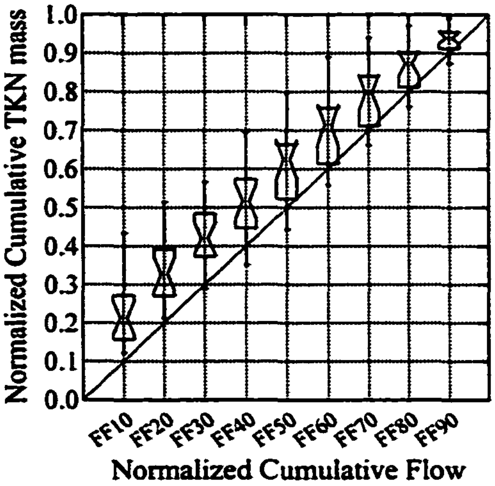

Normalized Cumulative Hard. Mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow


Fraction of Washed-off O&G Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval

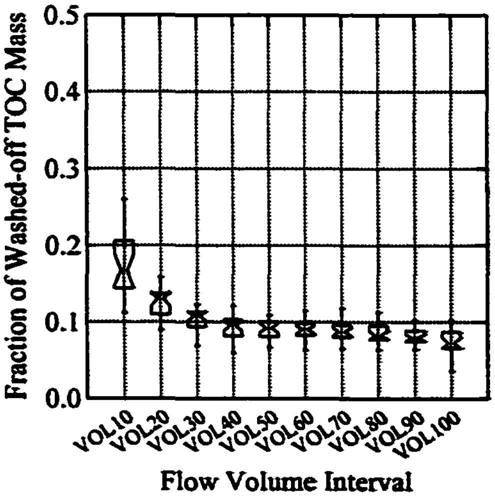

Normalized Cumulative O&G Mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow



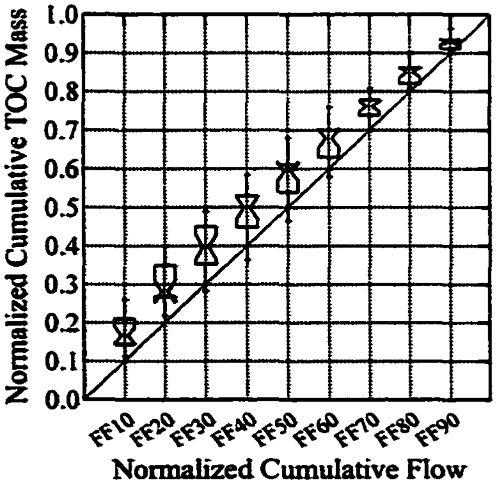
Fraction of Washed-off TKN Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval



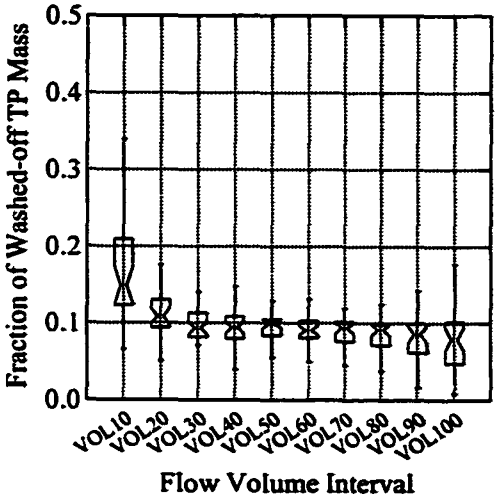
Normalized Cumulative TKN mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow

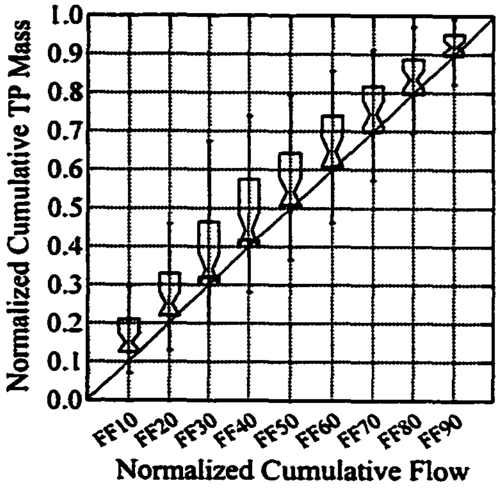


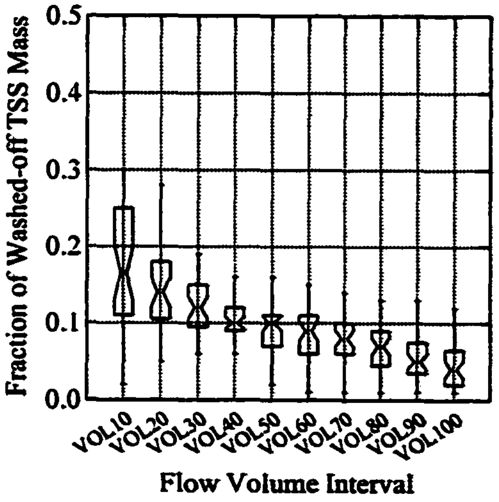
Fraction of Washed-off TOC Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval

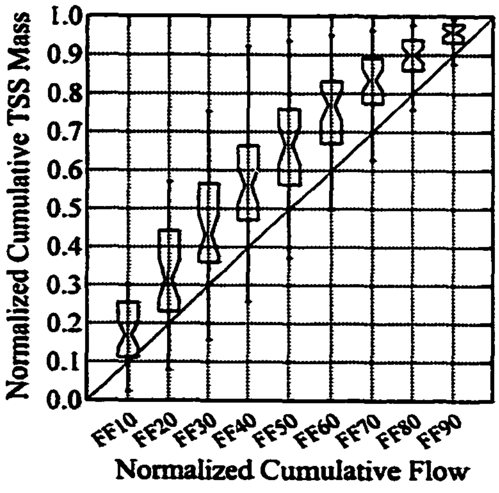


Normalized Cumulative TOC Mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow

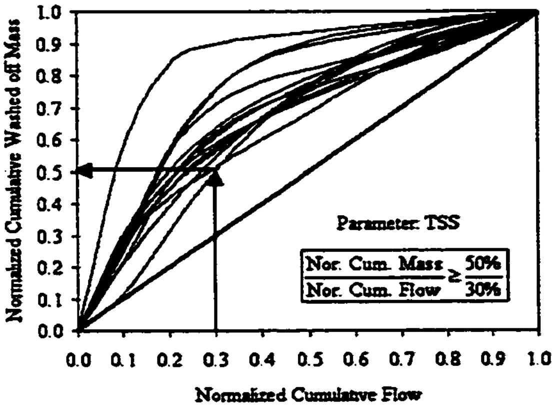

Fraction of Washed-off TP Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval

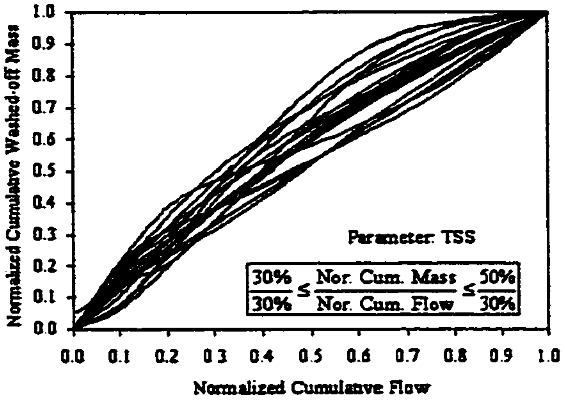

Normalized Cumulative TP Mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow

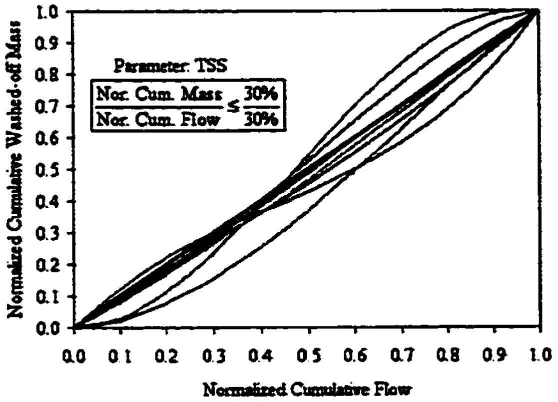

Fraction of Washed-off TSS Mass
0.5
0.4
0.3
0.2
0.1
0.0
VOL10
VOL20
VOL30
VOL40
VOL50
VOL60
VOL70
VOL80
VOL90
VOL100
Flow Volume Interval

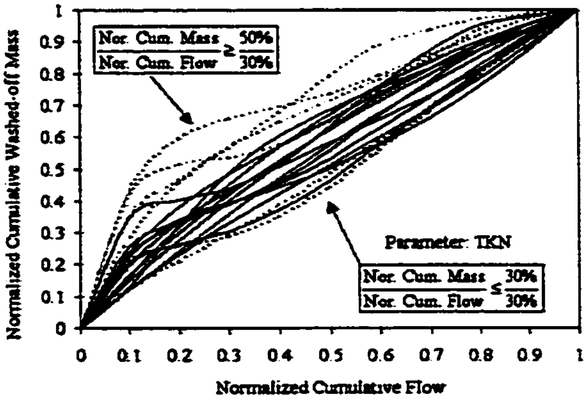

Normalized Cumulative TSS Mass
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
FF10
FF20
FF30
FF40
FF50
FF60
FF70
FF80
FF90
Normalized Cumulative Flow

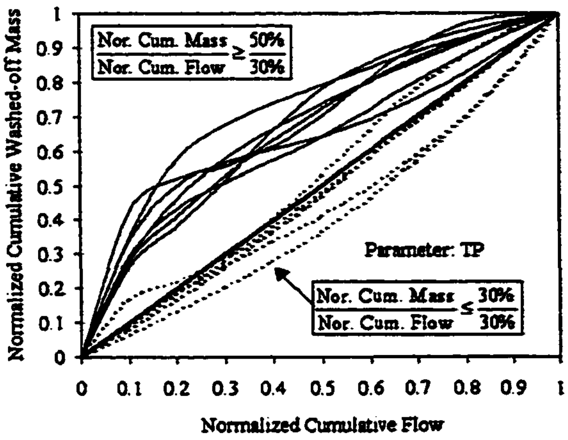
Appendix 1.5. Fractions of Normalized Cumulative Mass and Flow

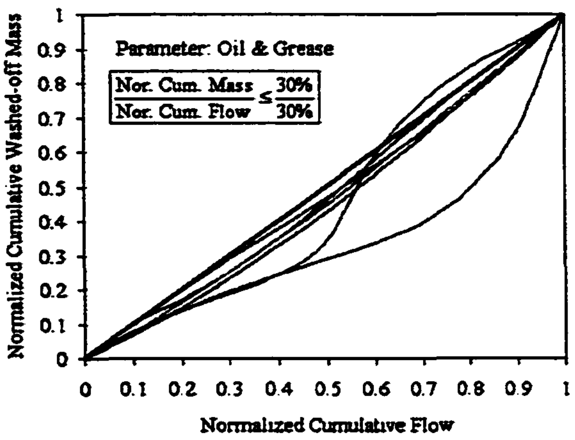


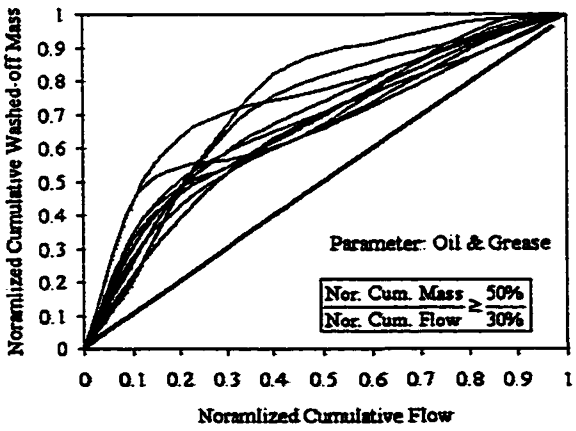






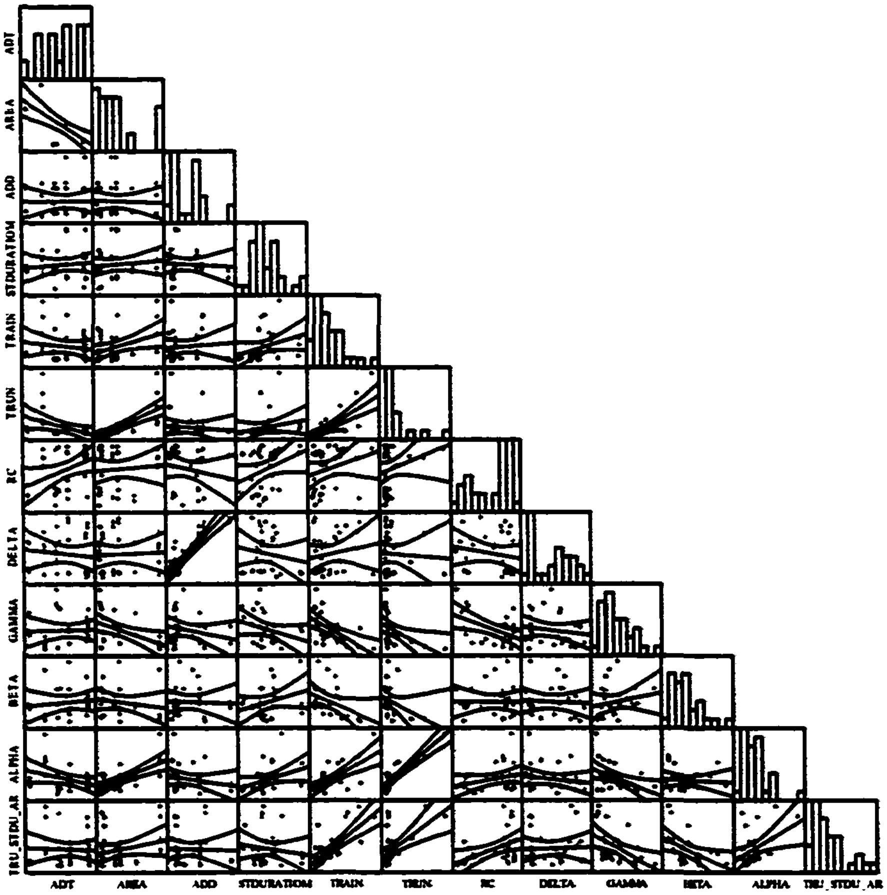

Normalized Cumulative Washed-off Mass
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Nor. Cum. Mass / Nor. Cum. Flow ≥ 50% / 30%
Parameter: TP
Nor. Cum. Mass / Nor. Cum. Flow ≤ 30% / 30%
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Normalized Cumulative Flow


Normalized Cumulative Washed-off Mass
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Parameter: Oil & Grease
Nor. Cum. Mass / Nor. Cum. Flow ≤ 30% / 30%
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Normalized Cumulative Flow


Noramlized Cumulative Washed-off Mass
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Parameter: Oil & Grease
Nor. Cum. Mass / Nor. Cum. Flow ≥ 50% / 30%
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Noramlized Cumulative Flow

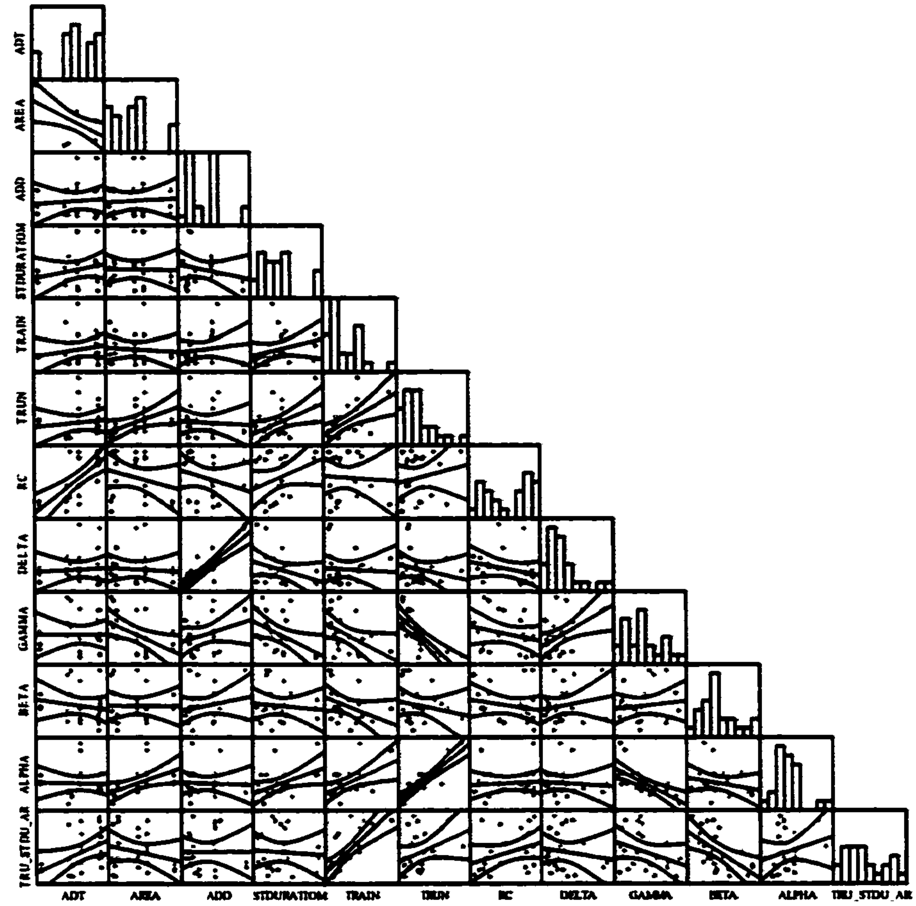
Appendix 2. Correlation Tables and Matrices for New Washoff Model

Appendix 2.1. Correlation Table and Matrix for TSS



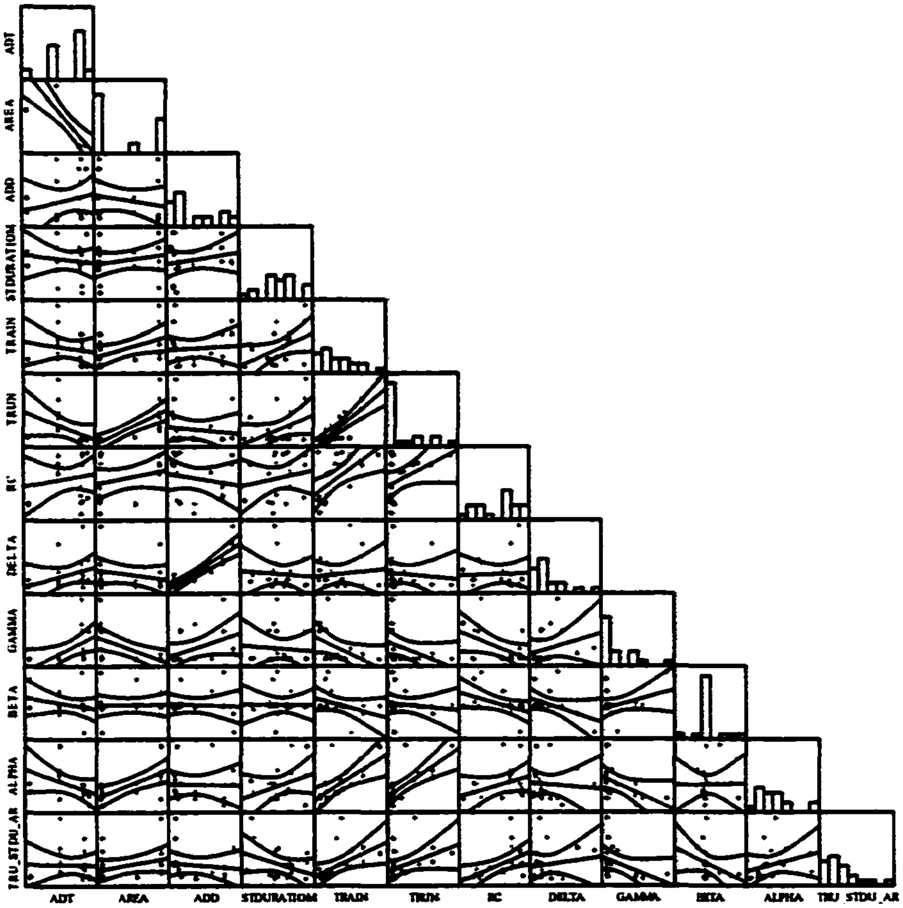
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.65	0.02	0.16	-0.10	-0.41	0.40	-0.13	0.04	0.12	-0.32	-0.08
AREA	0.00	1.00	0.02	0.05	0.26	0.76	-0.07	0.11	-0.41	-0.17	0.69	0.15
ADD	0.92	0.93	1.00	-0.11	0.26	0.05	-0.12	0.87	-0.27	-0.04	-0.06	0.12
STDURATION	0.42	0.82	0.61	1.00	0.29	0.12	0.40	-0.16	-0.25	0.30	0.35	-0.21
TRAIN	0.63	0.19	0.20	0.15	1.00	0.61	0.14	0.40	-0.54	-0.38	0.52	0.67
TRUN	0.04	0.00	0.81	0.57	0.00	1.00	0.17	0.15	-0.42	-0.31	0.80	0.55
RC	0.05	0.75	0.56	0.05	0.51	0.41	1.00	-0.13	-0.40	0.00	0.21	0.35
δ	0.52	0.60	0.00	0.43	0.04	0.47	0.52	1.00	-0.25	-0.06	0.01	0.22
γ	0.86	0.04	0.19	0.21	0.01	0.03	0.05	0.21	1.00	0.19	-0.48	-0.42
β	0.57	0.40	0.84	0.14	0.06	0.12	0.98	0.78	0.35	1.00	-0.07	-0.46
α	0.11	0.00	0.78	0.08	0.01	0.00	0.30	0.97	0.01	0.75	1.00	0.30
AVRAINTEN	0.72	0.48	0.56	0.31	0.00	0.00	0.08	0.28	0.03	0.02	0.14	1.00

Appendix 2.2. Correlation Table and Matrix for COD



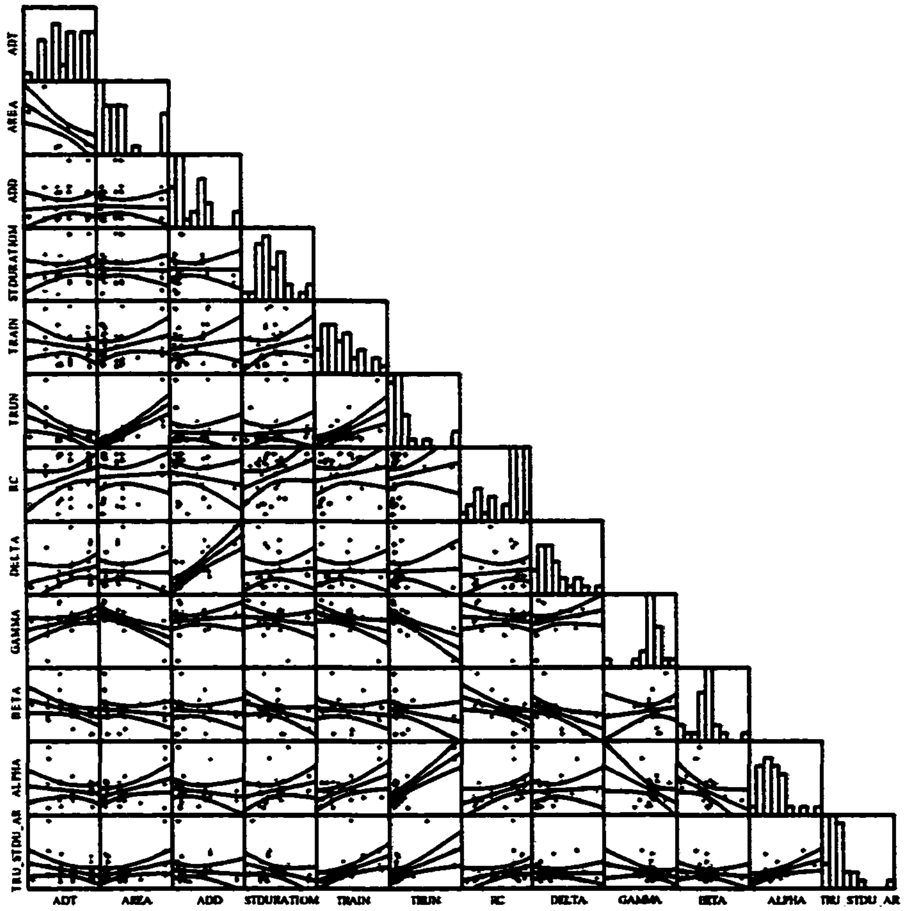
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.51	0.08	0.22	0.19	0.13	0.71	0.06	0.00	-0.16	-0.03	0.46
AREA	0.01	1.00	0.06	-0.01	-0.07	0.45	-0.25	-0.06	-0.49	-0.01	0.50	-0.22
ADD	0.72	0.78	1.00	-0.20	0.14	-0.06	-0.24	0.86	0.30	0.20	-0.04	0.01
STDURATION	0.32	0.95	0.36	1.00	0.27	0.49	0.35	-0.31	-0.47	-0.09	0.46	-0.06
TRAIN	0.38	0.74	0.51	0.21	1.00	0.58	-0.05	-0.06	-0.45	-0.36	0.52	0.75
TRUN	0.57	0.03	0.78	0.02	0.00	1.00	0.18	-0.21	-0.75	-0.19	0.88	0.36
RC	0.00	0.25	0.27	0.10	0.82	0.41	1.00	-0.25	-0.25	-0.19	0.08	0.33
δ	0.79	0.77	0.00	0.14	0.80	0.33	0.25	1.00	0.52	0.19	-0.08	-0.14
γ	0.99	0.02	0.17	0.02	0.03	0.00	0.26	0.01	1.00	0.12	-0.68	-0.33
β	0.46	0.98	0.35	0.67	0.09	0.40	0.38	0.39	0.58	1.00	-0.22	-0.57
α	0.89	0.01	0.86	0.03	0.01	0.00	0.73	0.73	0.00	0.32	1.00	0.23
AVRAINTEN	0.03	0.30	0.98	0.78	0.00	0.10	0.12	0.53	0.13	0.00	0.28	1.00

Appendix 2.3. Correlation Table and Matrix for TOC



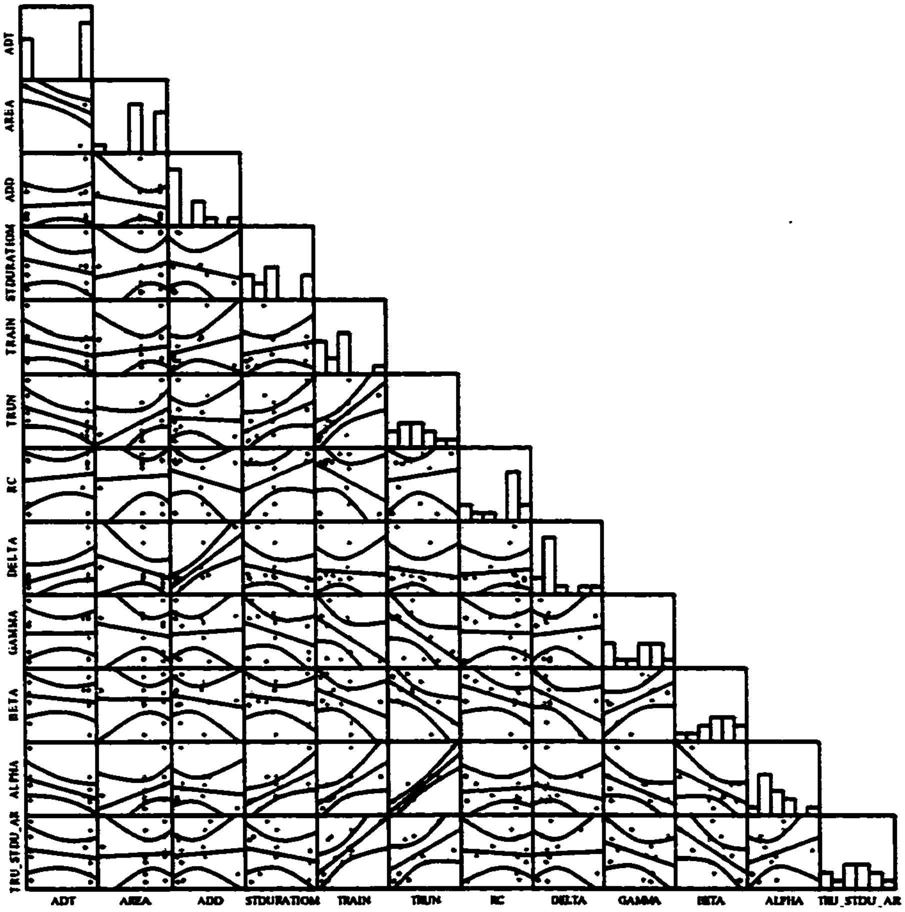
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.71	0.16	-0.08	-0.15	-0.36	0.24	0.31	0.54	-0.24	-0.38	0.08
AREA	0.00	1.00	-0.16	0.20	0.50	0.76	0.20	-0.24	-0.60	0.03	0.66	0.30
ADD	0.53	0.54	1.00	0.12	-0.03	-0.11	-0.21	0.88	0.42	-0.07	-0.03	-0.12
STDURATION	0.76	0.44	0.65	1.00	0.36	0.41	0.08	-0.08	-0.08	-0.02	0.33	-0.43
TRAIN	0.55	0.03	0.92	0.14	1.00	0.87	0.60	0.12	-0.46	-0.35	0.65	0.54
TRUN	0.15	0.00	0.67	0.09	0.00	1.00	0.39	-0.11	-0.42	-0.15	0.73	0.41
RC	0.34	0.42	0.42	0.74	0.01	0.11	1.00	0.04	-0.48	-0.46	0.34	0.54
δ	0.21	0.35	0.00	0.75	0.64	0.67	0.88	1.00	0.27	-0.41	-0.08	0.14
γ	0.02	0.01	0.09	0.77	0.05	0.09	0.05	0.28	1.00	0.37	-0.47	-0.43
β	0.33	0.91	0.79	0.95	0.15	0.56	0.06	0.09	0.13	1.00	0.02	-0.37
α	0.12	0.00	0.92	0.18	0.00	0.00	0.16	0.76	0.05	0.95	1.00	0.27
AVRAINTEN	1.00	0.23	0.63	0.07	0.02	0.09	0.02	0.59	0.08	0.13	0.29	1.00

Appendix 2.4. Correlation Table and Matrix for Oil & Grease



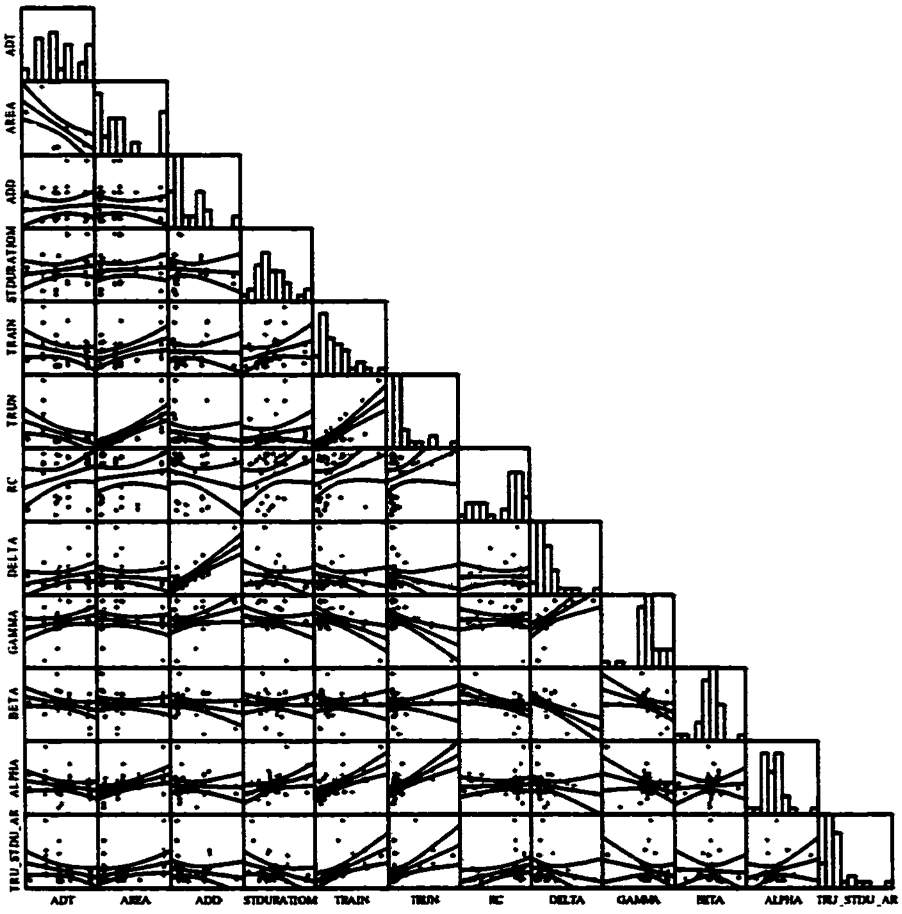
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.59	0.11	0.17	-0.26	-0.47	0.30	0.27	0.37	-0.31	-0.18	-0.28
AREA	0.00	1.00	0.01	0.06	0.32	0.79	-0.04	-0.03	-0.75	-0.16	0.35	0.19
ADD	0.60	0.98	1.00	-0.11	0.17	0.02	-0.09	0.80	0.13	-0.16	-0.14	0.09
STDURATION	0.43	0.78	0.61	1.00	0.29	0.17	0.45	0.07	-0.15	-0.37	0.24	-0.16
TRAIN	0.21	0.12	0.43	0.16	1.00	0.66	0.14	0.03	-0.46	-0.22	0.53	0.72
TRUN	0.02	0.00	0.93	0.41	0.00	1.00	0.14	0.05	-0.72	-0.25	0.77	0.54
RC	0.15	0.85	0.68	0.02	0.50	0.51	1.00	0.11	-0.13	-0.47	0.40	0.33
δ	0.19	0.90	0.00	0.73	0.90	0.82	0.61	1.00	0.28	-0.50	0.06	-0.02
γ	0.07	0.00	0.54	0.46	0.02	0.00	0.54	0.17	1.00	0.12	-0.42	-0.28
β	0.13	0.44	0.43	0.07	0.30	0.23	0.02	0.01	0.56	1.00	-0.40	-0.13
α	0.38	0.09	0.49	0.25	0.01	0.00	0.05	0.76	0.04	0.05	1.00	0.52
AVRAINTEN	0.17	0.36	0.68	0.44	0.00	0.01	0.11	0.94	0.17	0.53	0.01	1.00

Appendix 2.5. Correlation Table and Matrix for Alkalinity



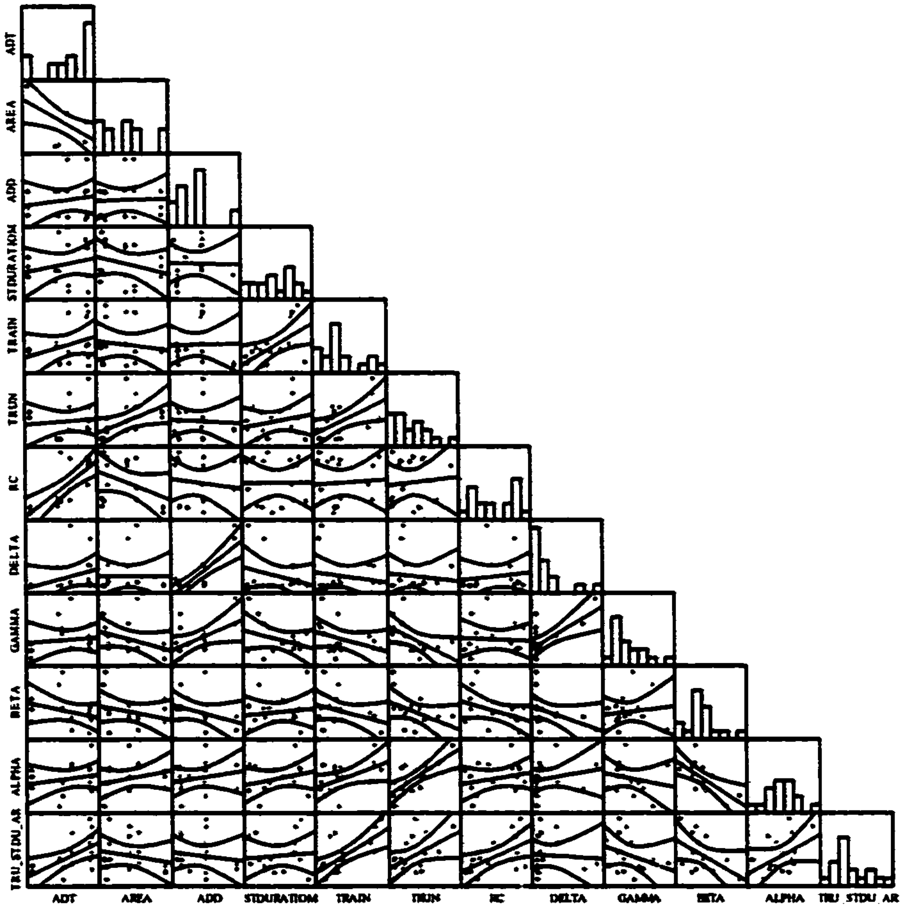
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.71	0.07	-0.28	-0.40	-0.50	0.13	0.49	0.01	-0.17	-0.54	-0.20
AREA	0.01	1.00	-0.16	0.16	0.12	0.49	0.05	-0.32	-0.16	-0.01	0.40	0.04
ADD	0.82	0.62	1.00	-0.19	0.27	-0.05	-0.24	0.80	0.06	-0.18	-0.12	0.09
STDURATION	0.38	0.62	0.56	1.00	0.23	0.53	0.41	-0.28	-0.35	-0.15	0.66	-0.22
TRAIN	0.20	0.71	0.40	0.47	1.00	0.73	-0.40	-0.06	-0.51	-0.38	0.62	0.69
TRUN	0.10	0.11	0.89	0.08	0.01	1.00	0.12	-0.15	-0.57	-0.63	0.90	0.52
RC	0.68	0.89	0.45	0.18	0.20	0.71	1.00	0.10	-0.03	-0.38	0.09	-0.09
δ	0.11	0.32	0.00	0.38	0.85	0.65	0.76	1.00	0.11	-0.47	-0.22	0.04
γ	0.98	0.63	0.85	0.27	0.09	0.05	0.92	0.74	1.00	0.52	-0.51	-0.35
β	0.60	0.98	0.59	0.64	0.23	0.03	0.22	0.13	0.08	1.00	-0.51	-0.58
α	0.07	0.20	0.71	0.02	0.03	0.00	0.79	0.49	0.09	0.09	1.00	0.30
AVRAINTEN	0.54	0.91	0.79	0.50	0.01	0.08	0.79	0.89	0.26	0.05	0.34	1.00

Appendix 2.6. Correlation Table and Matrix for Hardness



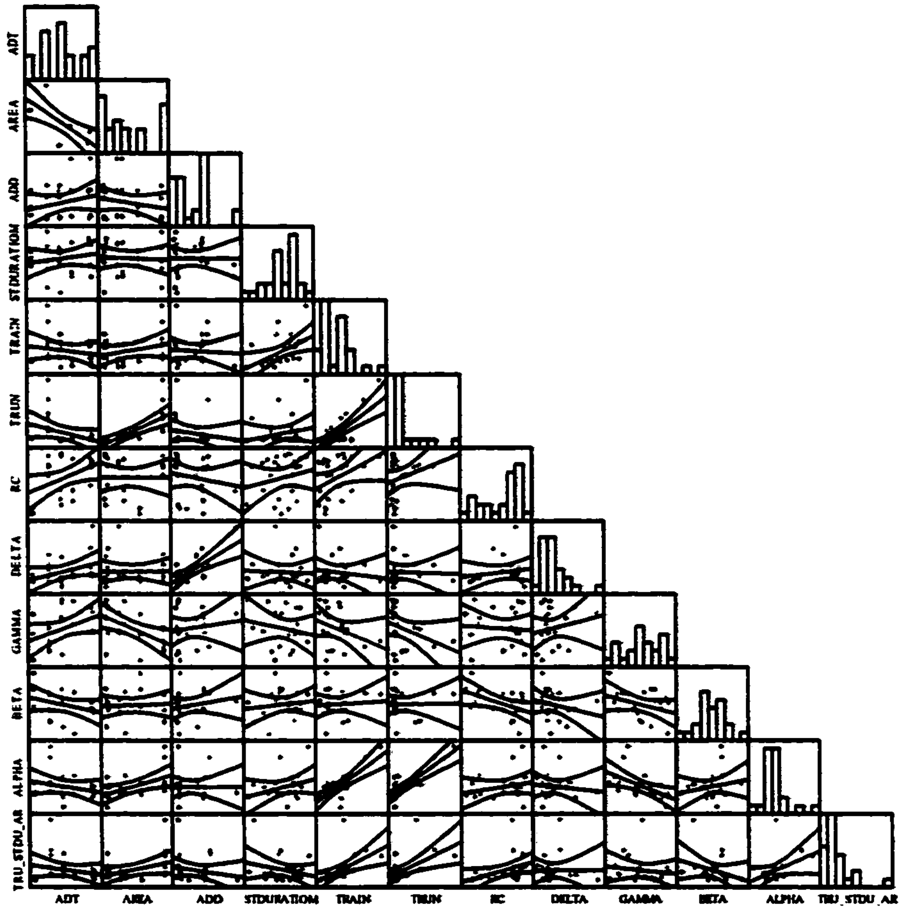
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.59	0.15	0.14	-0.21	-0.41	0.28	0.25	0.29	-0.30	-0.22	-0.26
AREA	0.00	1.00	-0.17	0.07	0.39	0.75	0.04	-0.11	-0.30	-0.03	0.48	0.27
ADD	0.43	0.38	1.00	-0.07	-0.09	-0.27	-0.24	0.83	0.48	-0.32	-0.07	-0.24
STDURATION	0.47	0.71	0.72	1.00	0.29	0.22	0.26	-0.17	-0.23	0.06	0.41	-0.32
TRAIN	0.26	0.03	0.64	0.12	1.00	0.74	0.28	-0.22	-0.55	-0.04	0.62	0.49
TRUN	0.03	0.00	0.15	0.24	0.00	1.00	0.25	-0.22	-0.62	0.01	0.68	0.40
RC	0.14	0.82	0.20	0.16	0.14	0.18	1.00	0.00	-0.09	-0.45	0.04	0.35
δ	0.18	0.56	0.00	0.38	0.25	0.25	0.98	1.00	0.64	-0.64	-0.20	-0.20
γ	0.12	0.11	0.01	0.22	0.00	0.00	0.65	0.00	1.00	-0.39	-0.52	-0.21
β	0.11	0.89	0.09	0.77	0.86	0.95	0.01	0.00	0.04	1.00	0.07	-0.04
α	0.24	0.01	0.71	0.02	0.00	0.00	0.82	0.29	0.00	0.70	1.00	0.16
AVRAINTEN	0.17	0.15	0.20	0.08	0.01	0.03	0.06	0.28	0.26	0.83	0.40	1.00

Appendix 2.7 Correlation Table and Matrix for TKN



	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.64	0.17	0.22	0.33	0.07	0.76	0.33	0.11	-0.30	0.21	0.60
AREA	0.01	1.00	0.06	-0.31	-0.15	0.48	-0.47	0.00	-0.37	-0.27	0.26	-0.24
ADD	0.53	0.83	1.00	-0.01	0.02	-0.03	-0.10	0.83	0.53	-0.33	0.21	-0.13
STDURATION	0.42	0.24	0.99	1.00	0.59	0.20	-0.01	-0.28	-0.32	0.13	0.27	0.09
TRAIN	0.21	0.59	0.94	0.02	1.00	0.59	0.06	-0.16	-0.36	-0.34	0.50	0.69
TRUN	0.81	0.06	0.92	0.47	0.02	1.00	0.04	-0.10	-0.52	-0.42	0.73	0.51
RC	0.00	0.07	0.72	0.98	0.83	0.88	1.00	0.13	-0.06	-0.41	0.24	0.56
δ	0.21	0.99	0.00	0.30	0.56	0.71	0.63	1.00	0.68	-0.41	0.21	-0.07
γ	0.69	0.16	0.04	0.23	0.18	0.04	0.84	0.00	1.00	0.12	-0.21	-0.31
β	0.26	0.32	0.22	0.64	0.19	0.10	0.12	0.12	0.66	1.00	-0.67	-0.49
α	0.44	0.33	0.45	0.31	0.05	0.00	0.37	0.44	0.44	0.01	1.00	0.45
AVRAINTEN	0.01	0.38	0.64	0.75	0.00	0.04	0.03	0.81	0.24	0.06	0.08	1.00

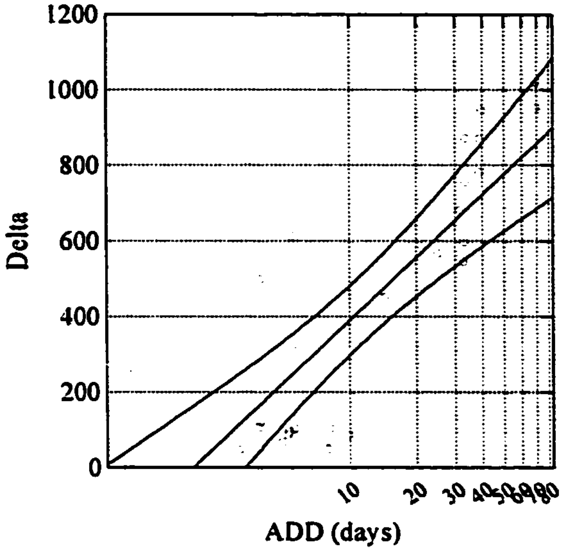
Appendix 2.8. Correlation Table and Matrix for TP

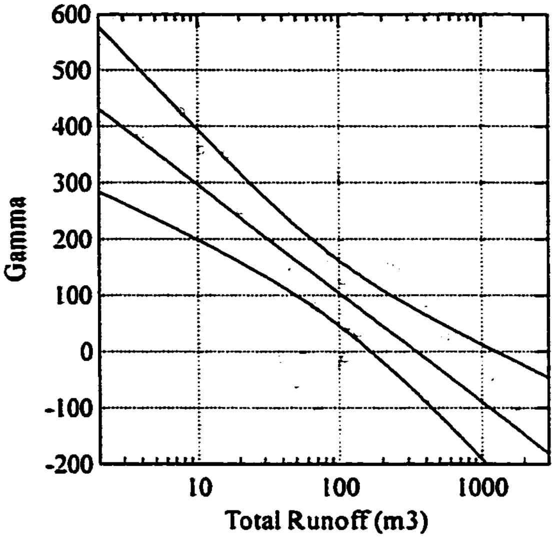


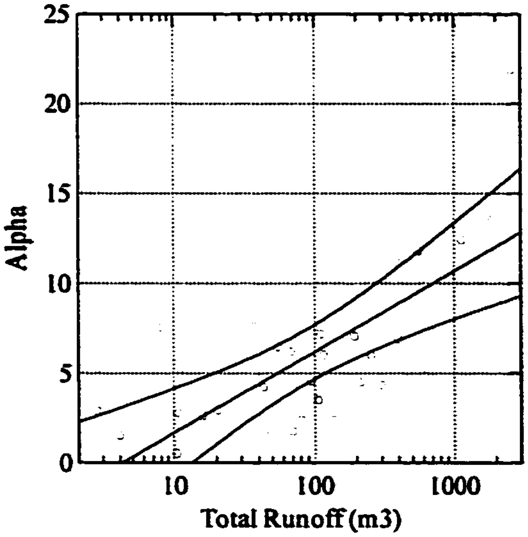
	ADT	AREA	ADD	STDURATION	TRAIN	TRUN	RC	δ	γ*	β*	α	AVRAINTEN
ADT	1.00	-0.64	0.21	0.16	-0.18	-0.36	0.46	0.39	0.41	-0.34	-0.25	-0.20
AREA	0.00	1.00	-0.11	-0.04	0.41	0.72	0.02	0.06	-0.55	-0.02	0.54	0.45
ADD	0.37	0.64	1.00	0.12	-0.06	-0.11	-0.18	0.72	0.13	0.25	0.00	-0.23
STDURATION	0.48	0.87	0.60	1.00	0.49	0.21	0.21	-0.05	-0.19	0.14	0.30	-0.27
TRAIN	0.43	0.06	0.80	0.03	1.00	0.86	0.40	-0.14	-0.33	0.07	0.80	0.55
TRUN	0.11	0.00	0.63	0.36	0.00	1.00	0.31	-0.04	-0.36	0.02	0.84	0.59
RC	0.04	0.95	0.43	0.37	0.08	0.17	1.00	0.17	-0.07	-0.49	0.23	0.38
δ	0.08	0.81	0.00	0.85	0.55	0.87	0.46	1.00	0.17	-0.17	-0.10	0.01
γ	0.06	0.01	0.59	0.42	0.15	0.11	0.76	0.46	1.00	-0.32	-0.55	-0.14
β	0.13	0.94	0.28	0.56	0.76	0.93	0.03	0.46	0.16	1.00	0.21	-0.29
α	0.28	0.01	0.99	0.18	0.00	0.00	0.32	0.65	0.01	0.36	1.00	0.42
AVRAINTEN	0.38	0.04	0.32	0.23	0.01	0.01	0.09	0.98	0.54	0.21	0.06	1.00

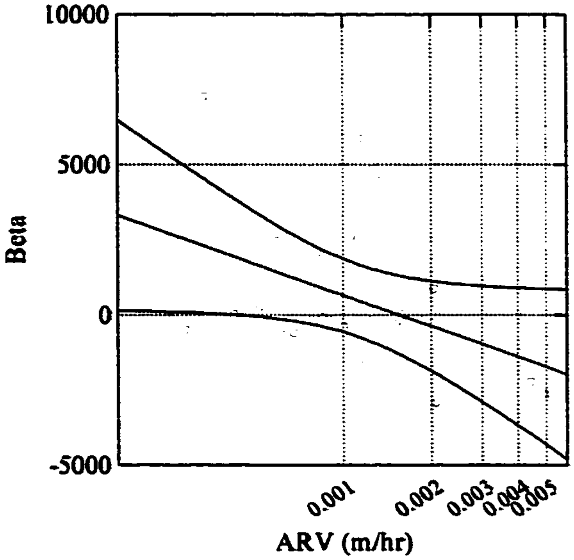
Appendix 3. Relationships between Model Parameters and Affecting Factors

Appendix 3.1. Parameter Generation for TSS

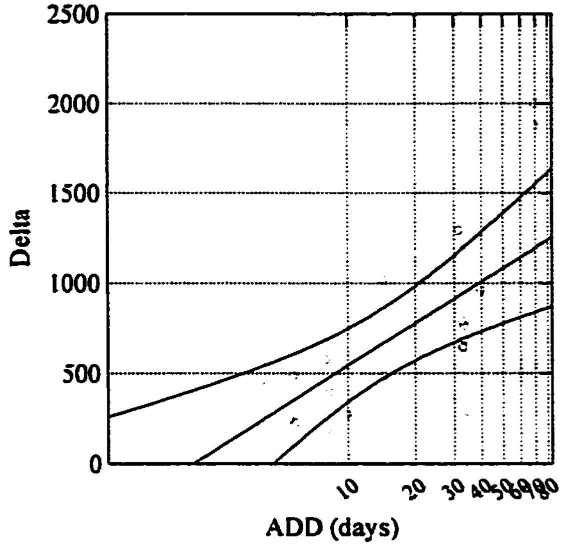


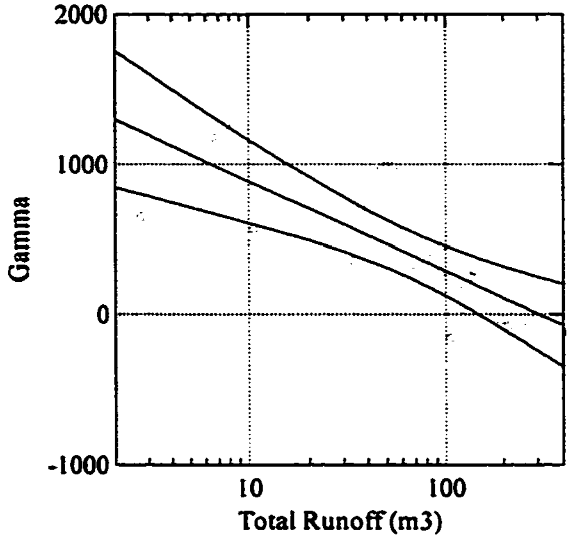


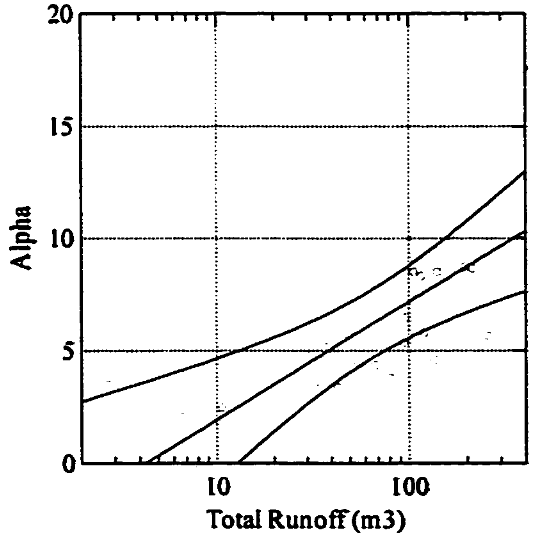


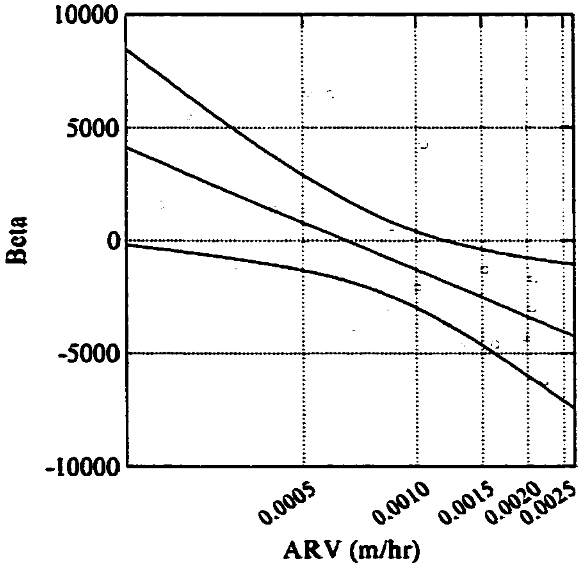


Appendix 3.2. Parameter Generation for COD

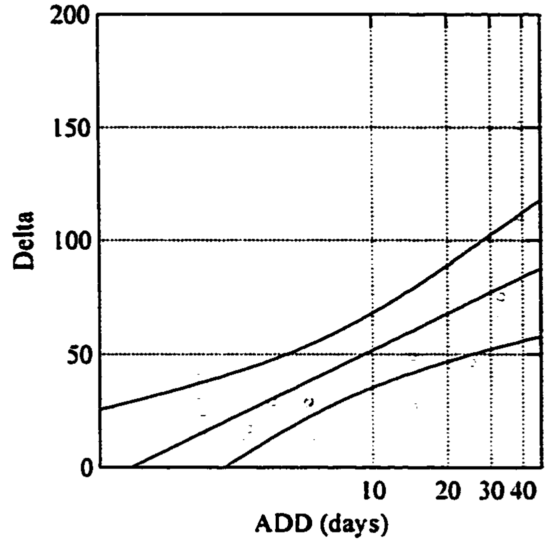


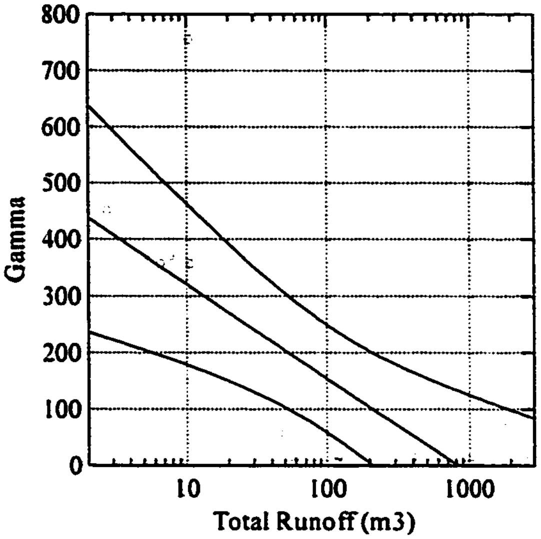


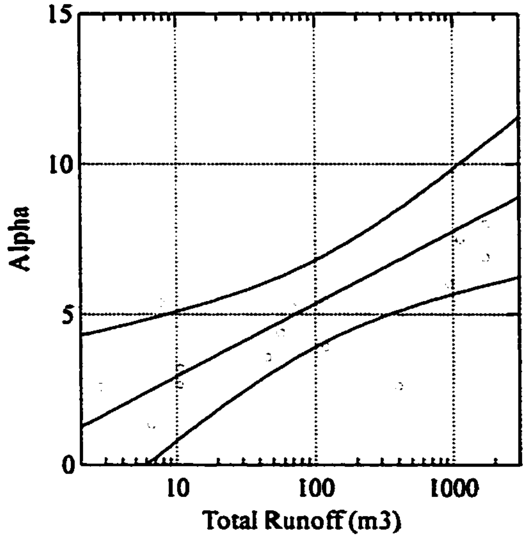


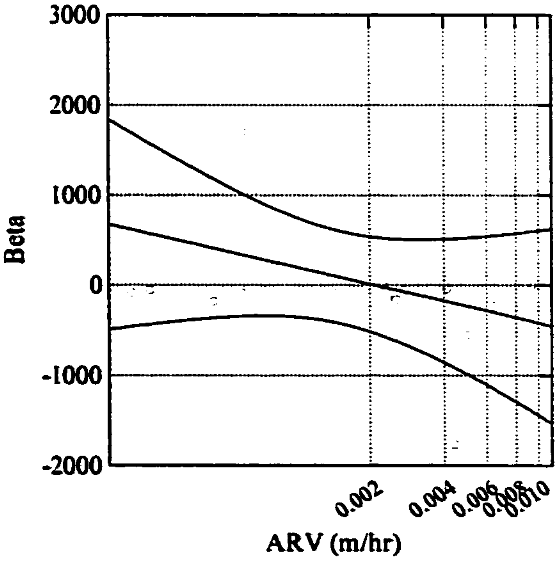


Appendix 3.3. Parameter Generation for TOC

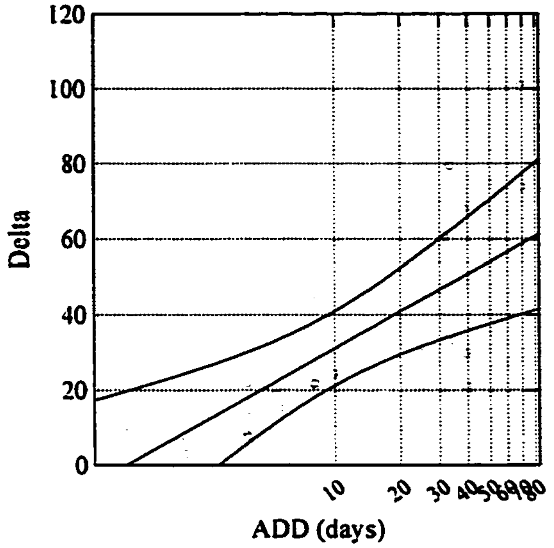


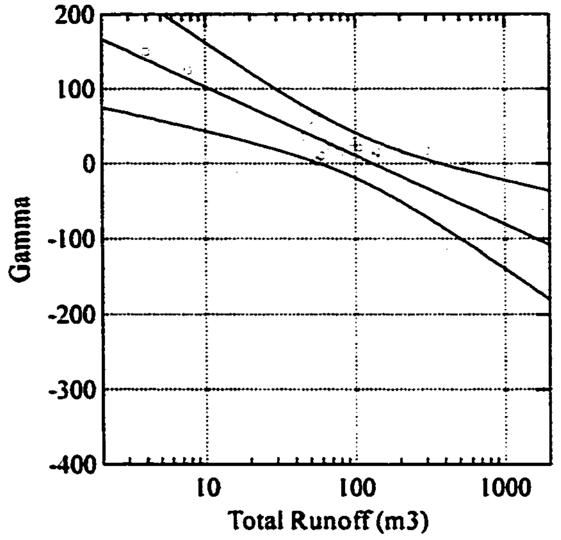


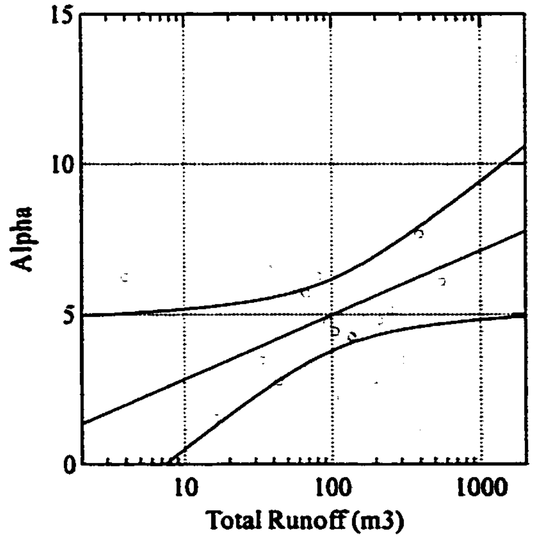


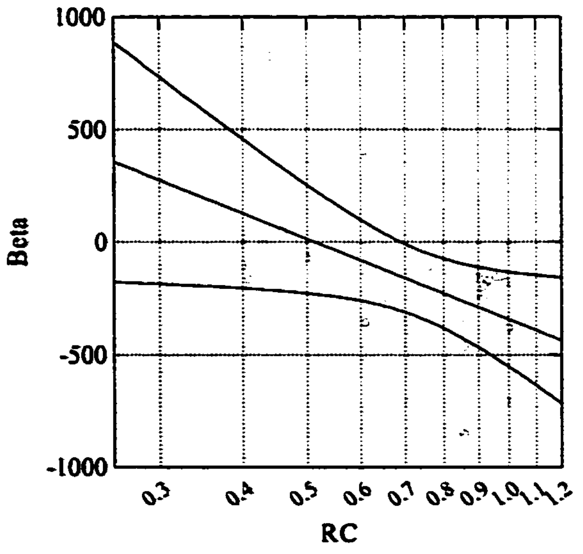


Appendix 3.4. Parameter Generation for Oil & Grease

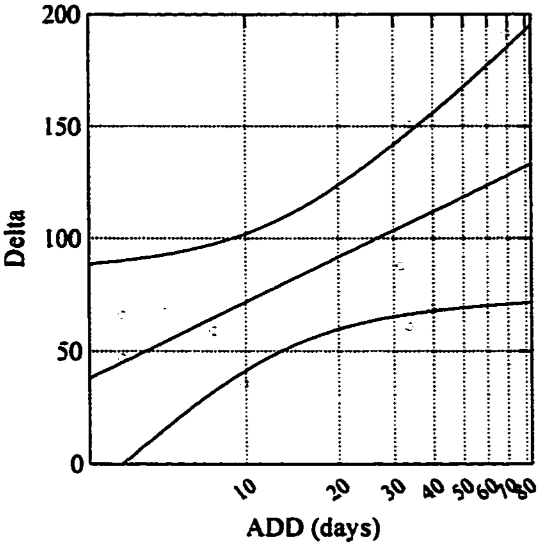


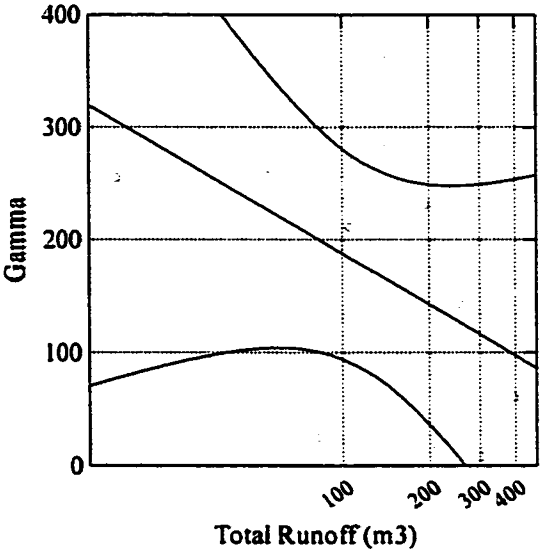


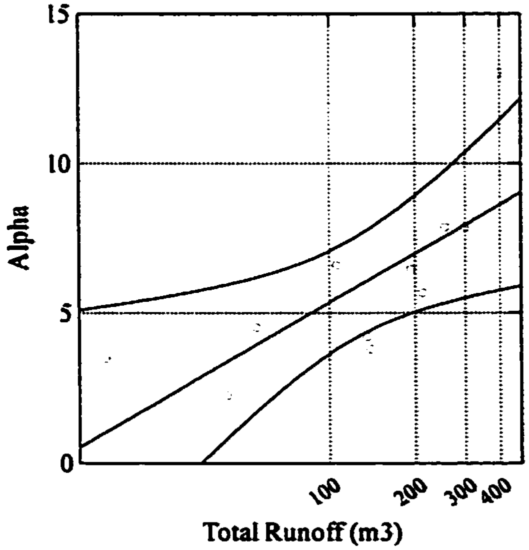


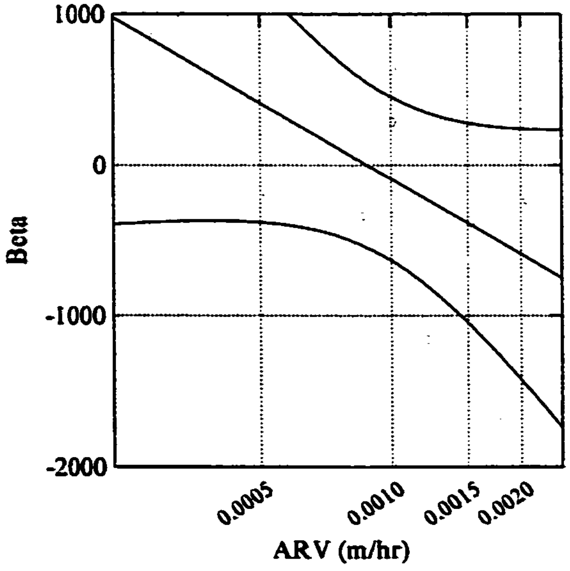


Appendix 3.5. Parameter Generation for Alkalinity

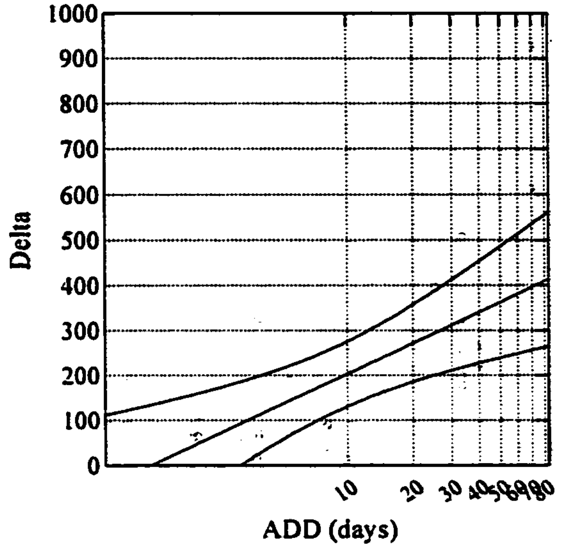


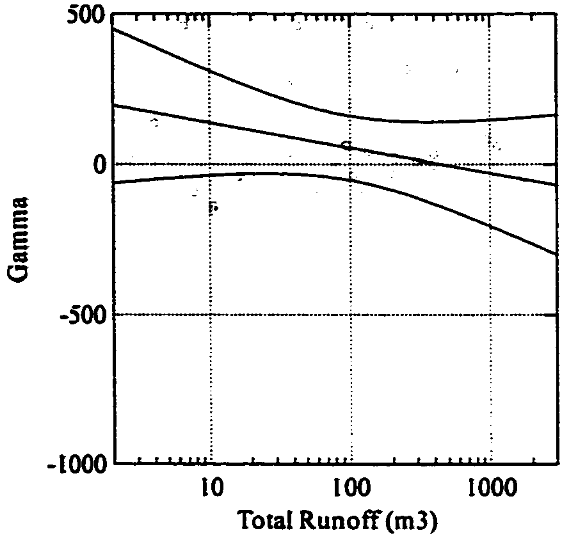


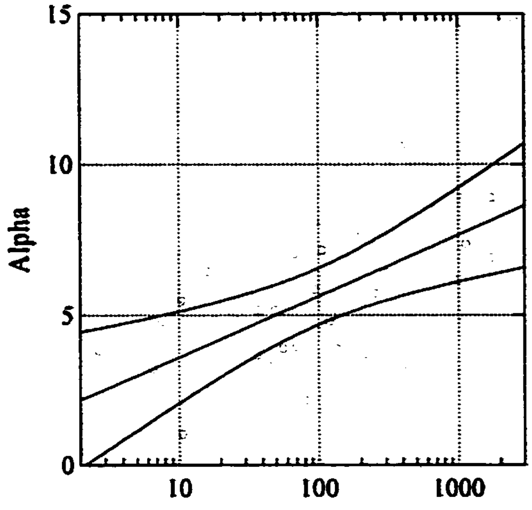


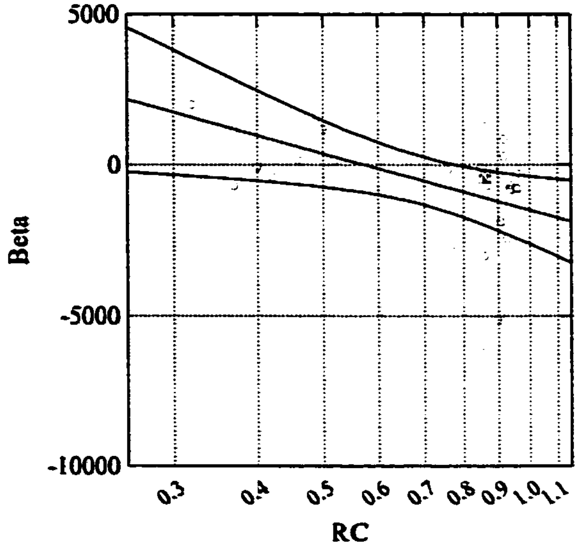


Appendix 3.6. Parameter Generation for Hardness

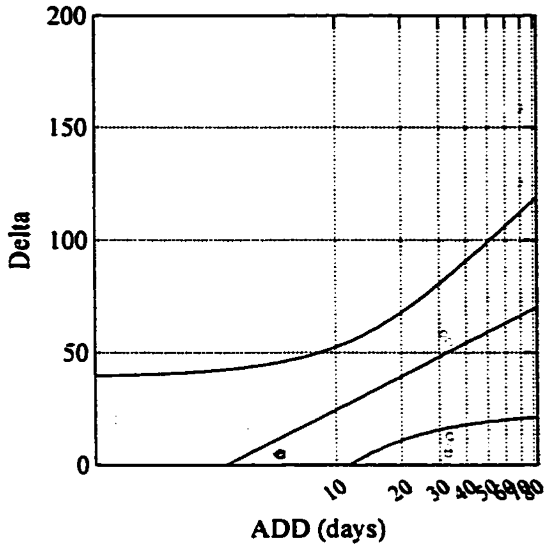


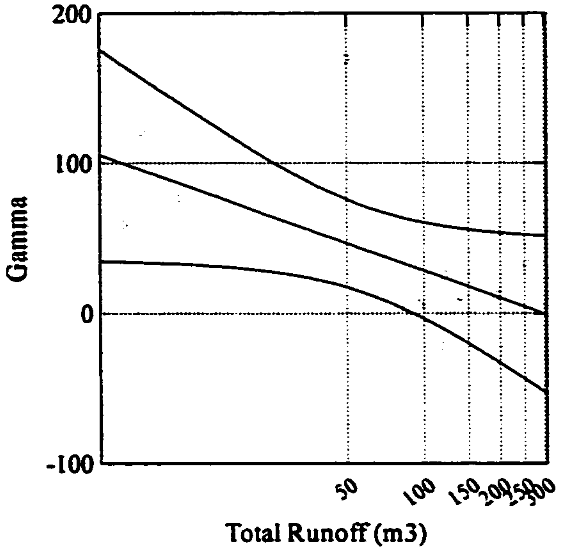


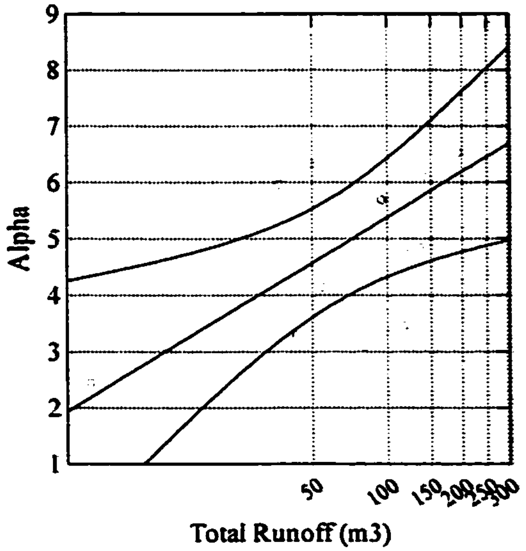


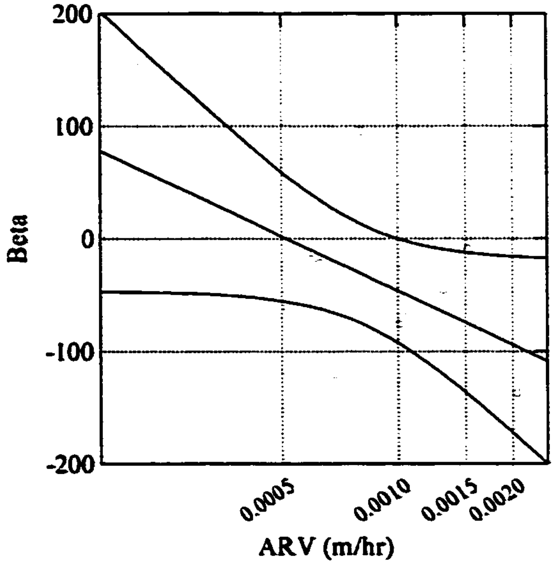


Appendix 3.7. Parameter Generation for TKN

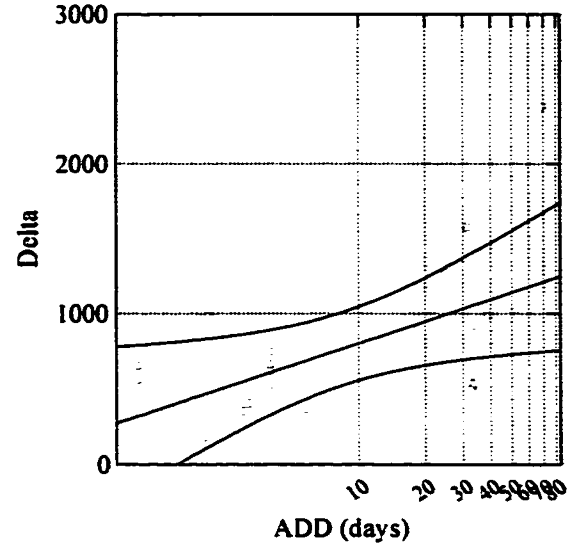


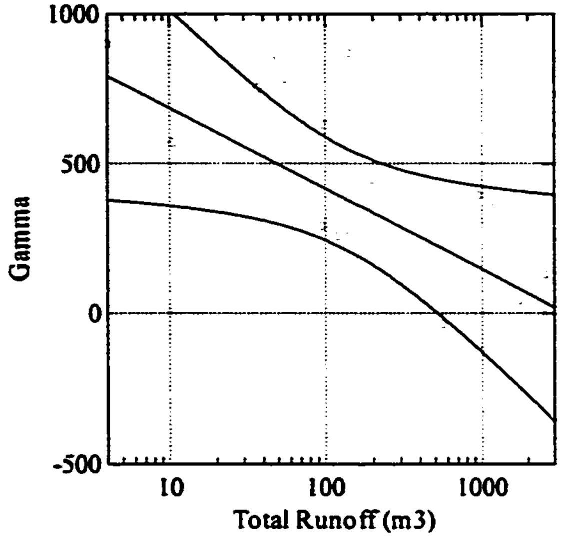


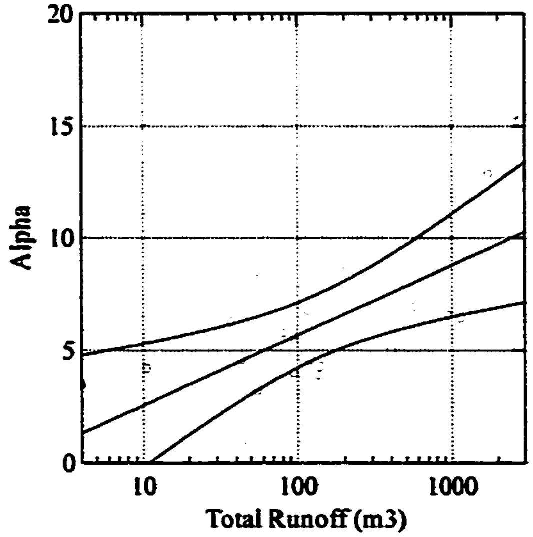


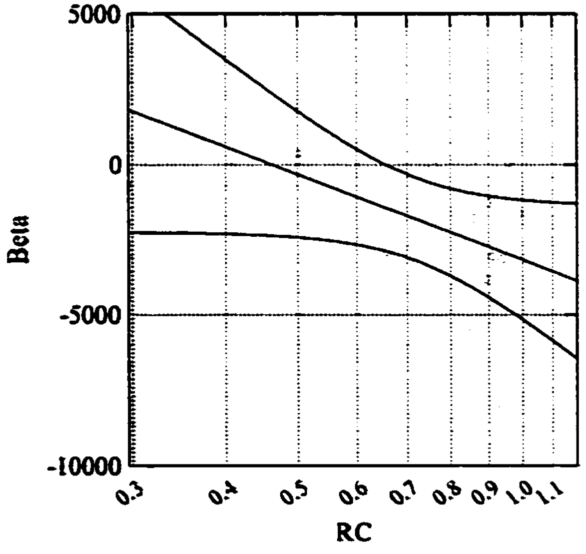


Appendix 3.8. Parameter Generation for TP

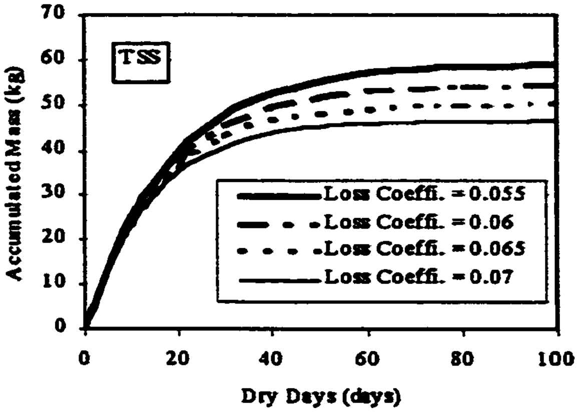


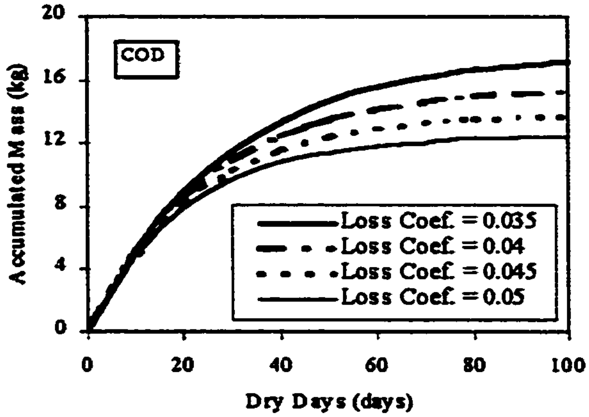


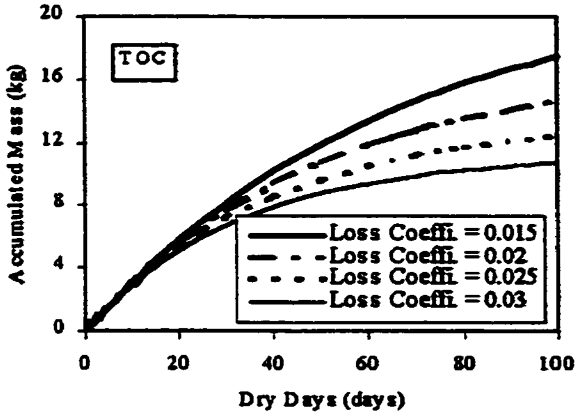


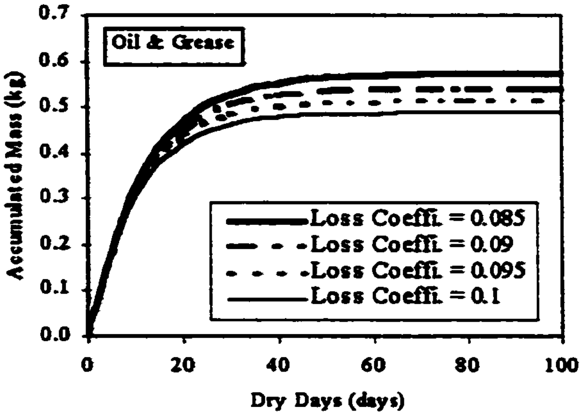


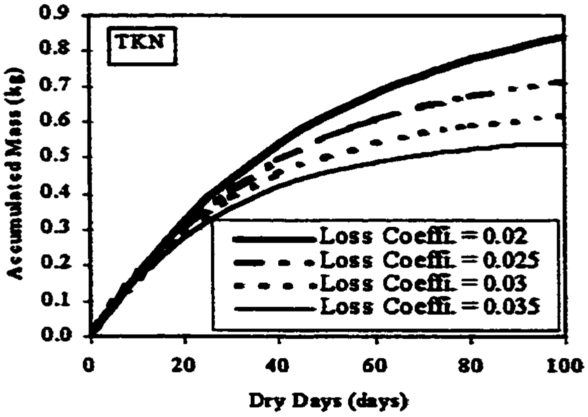
Appendix 4. Sensitivity Analysis with Changes of Loss Coefficient (ψ) at 5000 m^2 Area

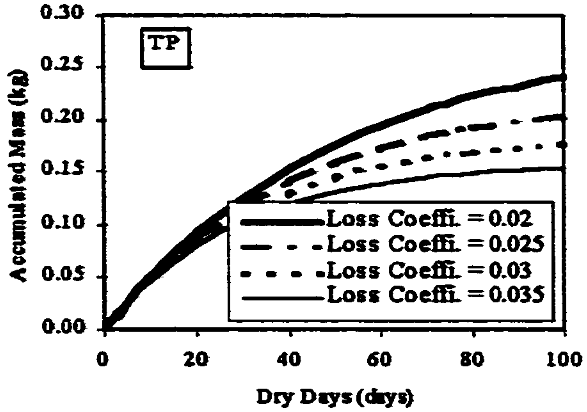












Appendix 5. Litter Analysis