

A new modeling approach for estimating first flush metal mass loading

L.-H. Kim*, M. Kayhanian**, S.-L. Lau*** and M.K. Stenstrom***

*Dept. of Civil and Environmental Engineering, Kongju National University, 182 Shinkwan-dong, Kongju-si, Chungnam-do, 314-701, Korea

**Center for Environmental and Water Resources Engineering, Dept. of Civil and Environmental Engineering, University of California, Davis, California, 95616, USA

***Dept. of Civil and Environmental Engineering, University of California, Los Angeles, California, 90095-1593, USA

Abstract The purpose of this study was to investigate pollutant mass loading from major highways in Southern California, with emphasis on interpretation of event mean concentrations and first flush effects. The results of monitoring eight sites during the 1999-2002 storm seasons found that metal contaminants had higher concentrations at the early stages of storm events compared with other stages of rain storms. A new washoff model was developed to predict the event mean concentrations of metal contaminants taking first flush effect into account. Model variable parameters included average daily traffic, antecedent dry period, rain intensity, total runoff volume, and runoff coefficient. The results obtained using the washoff model were compared with measured values and found to fit well for heavy metals with R^2 ranging from 0.8 to 0.95.

Keywords Event mean concentration (EMC); first flush; mass loading; metal contaminants; washoff model

Introduction

Large amounts of heavy metals in road surfaces are from wear and tear of various vehicle components such as tires, engine parts, brake pads; auto body rusting; lubricants; and fuel combustion (USEPA, 1995). In general, metals accumulate during dry days and wash from highways during storm events, usually absorbed by soil particles and move to receiving waters. The California Department of Transportation engaged in various storm water characterization studies throughout the state (Kayhanian *et al.*, 2001). One of these was first flush (FF) characterization, carried out jointly by the Department of Civil and Environmental Engineering at the University of California, Davis (UCD) and Los Angeles (UCLA) campuses. The FF characterization study has been ongoing since 1998 and several aspects of FF characterization have been published in Ma *et al.* (2002); Lau *et al.* (2002); Kayhanian *et al.* (2002).

Often the pollutant concentrations decline over time, which tends to create greater emission rates 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 (BMPs). The existence of first flush is debated and many defining criteria exist. It is most often observed in small watersheds, particularly if the amount of imperviousness area is proportionally high.

Models are often used to predict pollutant concentrations. Different models have been used, including regression, stochastic, and deterministic simulation (Irish Jr. *et al.*, 1998). The main difference between these 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, etc. Generally, it is difficult to consider all factors because many different site-specific conditions exist, such as the presence or absence of street

sweeping, soil saturation, wind direction, etc. Regression models have been criticized as poor predictors of future events or for different regions (Driscoll *et al.*, 1990). No model, however, is available to take first flush into account as part of the mass loading computation. This paper will provide a new approach defining first flush criteria and its application for EMCs and mass loading calculations.

Methods

All eight monitoring were selected to include primarily highway runoff. Samples have been collected since the 1999 rainy season. Table 1 summarizes the monitoring periods and partial characteristics of each site. Monitoring was performed by collecting 4L grab samples. Generally, five 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 the runoff. Rainfall and runoff rates were also measured with automated monitoring equipment. Additional information on sample collection, equipment, analytical constituents and other related items can be found in Kayhanian *et al.* (2002) and Ma *et al.* (2002).

Washoff model development

Because of random characteristics of runoff quality and quantity, the EMCs cannot be determined by simple statistical averages of measured pollutant concentrations in stormwater runoff. The sources of uncertainty are generally caused by uncertainties in magnitude of rainfall intensity, experimental errors, and lack of sufficient data. Gupta and Saul (1996) used multiple linear regression analysis for data interpolation and Larsen *et al.* (1998) calculated EMCs using the medium point method. Many researchers (Charbeneau and Barrett, 1998; Deletic and Mahsimovic, 1998; Irish Jr. *et al.*, 1998; Osuch-Pajdzinska and Zawilski, 1998; Deletic *et al.*, 2000) used mass emission rates from the exponential washoff model to estimate EMCs.

The exponential model ignores many different trends in concentrations normally observed during monitoring. For instance, it is not possible to predict dilution 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 washoff 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 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 create the opposite trend, continuously adding to the washoff mass.

Table 1 Monitoring site descriptions

Site name	Freeway location	ADT (cars/day)	Watershed area (m ²)	Monitoring period
UCLA 1	101	328,000	12,800	1999-current
UCLA 2	405	260,000	16,900	1999-current
UCLA 3	405	322,000	3,900	1999-current
CDM7-10	210	176,000	48,100	1999-2000
CDM7-185	91 & 605	220,000	2,300	1999-2000
URS23	210	122,000	29,100	2000-current
URS6-20F	60	216,600	1,700	2000-current
URS8-23C	605	229,000	2,500	2000-current

The washoff rate can be described such as Eq. (1).

$$\frac{d[C(t)]}{dt} = -\alpha \cdot \frac{Q_{Ru}(t) \cdot C(t)}{V_{TRu}} \quad (1)$$

where

α = washoff rate coefficient

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

Q_{RU} = Runoff volumetric rate (m^3/s)

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

Rearranging and integrating Eq. (1), we can obtain:

$$C(t) = \beta \cdot \exp[-\alpha \cdot V_{nRu}(t)] \quad (2)$$

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

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

$$C(t) = \beta \cdot \exp[-\alpha \cdot V_{nRu}(t)] + \gamma \quad (3)$$

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

$$M(t) = C(t) \cdot Q_{Ru}(t) \quad (4)$$

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

$$C(t) = \frac{\Delta M(t)}{\Delta Q_{Ru}(t)} = \frac{\int_{t-1}^t M(t)dt}{\int_{t-1}^t Q_{Ru}(t)dt} = \frac{\int_{t-1}^t M(t)dt}{\int_0^t Q_{Ru}(t)dt - \int_0^{t-1} Q_{Ru}(t)dt} \quad (5)$$

from which can be obtained

$$C(t) = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot \frac{\int_{t-1}^t M(t)dt}{V_{TRu}} \quad (6)$$

The right side of Eq. (6) has units of mass/volume or concentration. This new concentration term is a key premise of the model. Let $\int_{t-1}^t M(t)dt/V_{TRu} = C^*[V_{nRu}(t)]$, where C^* is defined as new concentration.

Equation 6 now can be expressed as follows:

$$C(t) = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot C^*[V_{nRu}(t)] \quad (7)$$

By equating Eqs. (3) and (7), we obtain:

$$\beta \cdot \exp[-\alpha \cdot V_{nRu}(t)] + \gamma = \frac{1}{\beta_1 \cdot V_{nRu}(t)} \cdot C^*[V_{nRu}(t)] \quad (8)$$

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

$$C^*[V_{nRu}(t)] = \beta^* \cdot V_{nRu}(t) \cdot \exp[-\alpha \cdot V_{nRu}(t)] + \gamma^* \cdot V_{nRu}(t) \quad (9)$$

In Eq. (9), a parameter is needed to describe the initial condition (δ), which ideally should be related to antecedent dry periods. The new washoff model is finally expressed as follows:

$$C^*[V_{nRu}(t)] = \delta + V_{nRu}(t) \cdot \{\gamma^* + \beta^* \cdot \exp[-\alpha \cdot V_{nRu}(t)]\} \quad (10)$$

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. Eq. (10) 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.

Results and conclusions

Runoff coefficient

The runoff coefficients are shown in Figure 1 as a function of total rainfall. The average is 0.87. Events with less rainfall have lower runoff coefficients, and lie below the regression line. This phenomenon is well established in the literature and is related to saturation of the site.

Statistical summaries of measured metal concentrations

Figure 2 shows the box plots of measured concentration for seven metals. The box plots show minimum, median, maximum, standard deviations, upper/lower 95 percent confidence intervals and outliers for each metal. For example, the concentration ranges

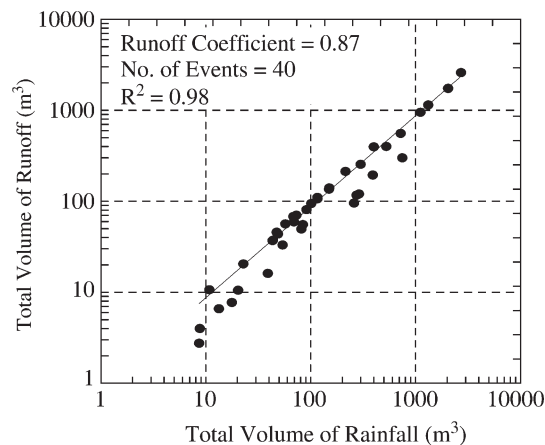


Figure 1 Runoff coefficient plot

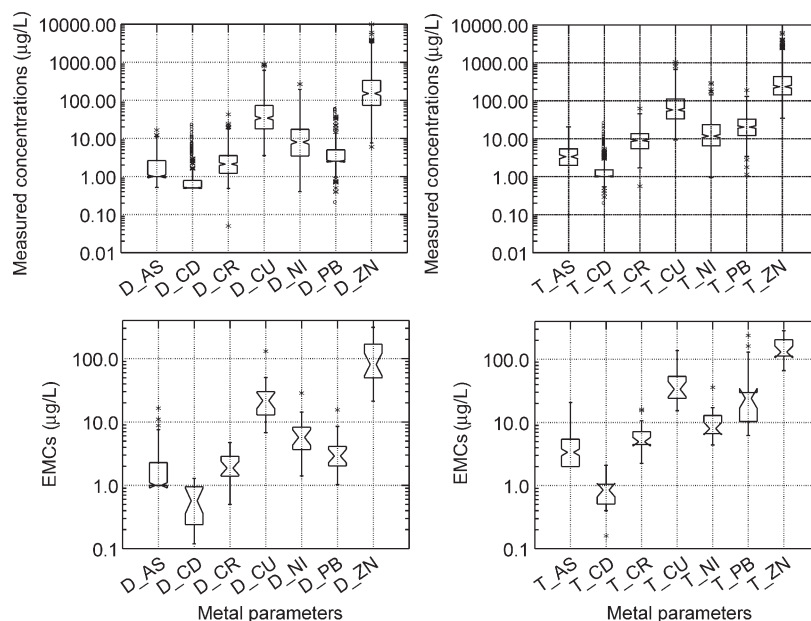


Figure 2 Box plots for dissolved and total concentrations and related EMCs for seven metals

0.7–1.2 $\mu\text{g/L}$, 27.3–51.7 $\mu\text{g/L}$, 15.6–70.1 $\mu\text{g/L}$, 126–208.6 $\mu\text{g/L}$ for total Cd, Cu, Pb, and Zn, respectively under 95 percent confidence intervals. These plots clearly showed that there are large differences between minimum and maximum concentrations. These differences are assumed to be partially due to variations in rainfall intensity and antecedent dry periods. In most cases it was determined that large fraction of metal contaminants is in dissolved phase. However, the ratios of total to dissolved fraction for all metal contaminants were not the same. For example, as shown in Figure 2, the ratio of T-Pb and D-Pb is substantially higher than other metal pollutants.

Because of these extreme variations of pollutant concentrations from event to event, the use of medium concentration in modeling effort can introduce large error, particularly when only a few samples are collected. Similarly, because the EMC values are affected by rainfall and antecedent dry periods the exponential model may not fit the observed data and that can result in large errors. The new modeling approach introduced in this paper will delineate some of these errors.

First flush criteria

It is important to know the probabilities and magnitude of the first flush. True estimation of the first flush magnitude is difficult, due to random characteristics of runoff quality and quantity, uncertainties in rainfall intensity and magnitude, experimental errors, and lack of sufficient data. Models to predict first flush of metal pollutants are rare. Therefore, the existence and importance of first flush has been debated. If first flush exists, it is more practical and cost effective to capture and treat more of the earlier runoff volume and bypass the remaining runoff volume.

Figure 3 shows the example of displaying first flush in the case of total Zn. The results were obtained by fitting the model to each storm event and then using the model results to calculate mass emission rates. The left side of Figure 3 shows total Zn mass emission rates for successive normalized runoff volumes ranging from 10 to 100 percent with the increment of 10 percent. This method of plotting shows that the first 10 percent of the normalized volume carries the greatest mass of pollutants. The right side of Figure 3 shows mass first flush ratio (MFF). For example the MFF_{10} for total Zn is 2.2, which means that 22 percent of the normalized total Zn mass is washed off in the first 10 percent of normalized runoff. The MFF ratio declines as the storm proceeds and the MFF_{20} and MFF_{30} decline to 1.6 and 1.4, respectively.

These analyses were performed on seven metal parameters and we concluded that metal first flush peaked at about 30 percent of the normalized flow. This means that the first flush usually occurred in the first 30 percent of total runoff volume.

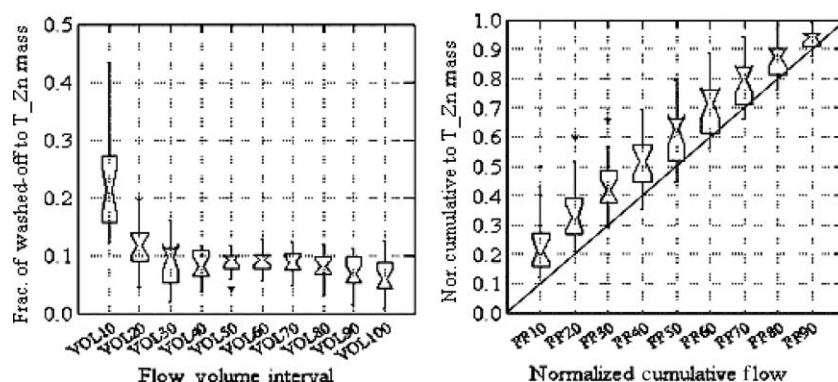


Figure 3 Washoff pollutant mass and volume

Metal pollutographs

Figure 4 shows the measured metal concentration profiles against time and rainfall and flow rate in the background (this type of plot is known as a pollutograph). As shown, the concentrations of Cu and Zn were consistently greater than Ni and Pb.

The concentrations of both dissolved and total Cu and Zn also showed a general declining pattern as storms progress. As previously discussed, the monitoring results also showed that Cu and Zn are predominantly present in the dissolved phase. This observation was consistent during the entire monitoring periods. For example, the dissolved Cu concentration for storm event 1/8/01 was approximately 10 times greater than those present in the particulate phase. For the same storm event, the concentration of dissolved Zn was approximately 36 times more than the particulate Zn concentration. Contrary to Zn, the concentration of dissolved Pb in most of the 2000-2001 samples was below the detection limits ($5 \mu\text{g/L}$) and most of the Pb concentration in runoff samples was found to be in the particulate phase. This phenomenon was also observed in studies performed by Sansalone and Buchberger (1997), and Legret and Pagotto (1999). Unlike Pb, the amount of dissolved Ni found in runoff samples was approximately the same as those found in the particulate phase.

Factors affecting EMCs and mass loadings

Table 2 shows the effects of parameters such as average daily traffic (ADT), watershed area, antecedent dry days (ADD), storm duration (STORM-DUR), volume of total rainfall (T-RAIN), volume of total runoff (T-RUN), runoff coefficient (RC) and average rainfall intensity (ARI) on total Pb mass loadings. The constant value for each predictor is summarized in Table 2. As indicated, average daily traffic, antecedent dry periods, total rainfall, and average rainfall intensity are among the parameters that affect total Pb mass

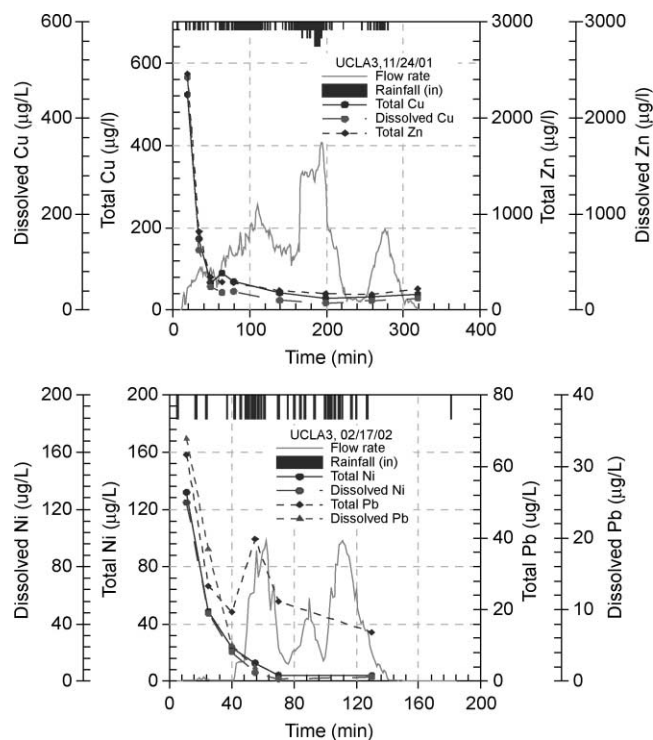


Figure 4 Typical pollutographs for total and dissolved Cu, Pb, Ni, and Zn during two representative storm events

Table 2 Summary of predicting variables used in washoff model to compute total Pb mass loading

Factors	ADT	AREA	ADD	STORM-DUR	T-RAIN	T-RUN	RC	δ	γ^*	β^*	α	ARI
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
STORM-DUR	0.42	0.82	0.61	1.00	0.29	0.12	0.40	−0.16	−0.25	0.30	0.35	−0.21
T-RAIN	0.63	0.19	0.20	0.15	1.00	0.61	0.14	0.40	−0.54	−0.38	0.52	0.67
T-RUN	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
ARI	0.72	0.48	0.56	0.31	0.00	0.00	0.08	0.28	0.03	0.02	0.14	1.00

loading more than the other parameters. It is important to note that δ value is highly dependent on antecedent dry periods, α and γ^* are related to total runoff, and β^* is related to rainfall, runoff coefficient and storm duration. From our collected data, however, no significant correlations among EMCs, mass loading and storm characteristics could be observed.

Model performance and implications

The washoff model is capable of predicting metal concentrations based on linear, exponential, and gamma function using defined parameters. Figure 5(a) shows examples of measured and predicted metal concentrations for total and dissolved Cu and Zn for storm events during 14 December 2001. The predicted results by washoff model agree well with measured results. Figure 5(b) compares the measured and predicted (model) results for total Cu. As shown, a good fit for measured and model results was obtained for total Cu with R^2 ranging from 0.80 to 0.95. The residuals, not shown in the figure, are unbiased.

Metal pollutant concentrations predicted by the washoff model can be used to predict event mean concentrations for different stages of storm events. This new modeling approach will enable engineers to compute metal pollutant mass loadings for a specific portion of a storm event (i.e., early stage) that may be more practical to treat than by treating the entire runoff volume.

Conclusions

A new washoff model was developed to predict mass emission rates of metals from highway runoff during first flush. Several predictor parameters were introduced in this model to estimate rapidly declining concentrations in the early part of the storm as well as slowly declining concentrations in the later part of the storm. This new model can be calibrated based on predicted stormwater runoff using estimated rainfall volume and is not dependent on continuous flow measurement. The model can be used to estimate EMCs and mass loading rates. Major findings of this study were the following.

- Most metal pollutants showed first flush on concentration and mass basis. The range of metal concentrations from early stages of a storm compared to the final stages of the storm can be tenfold. This large variation can introduce rare error that is normally associated with other modeling approaches. Mass first flushes were also observed and classified as: high, medium and non-first flush cases. Approximately 80 percent of the storm events exhibited a high or medium first flush.

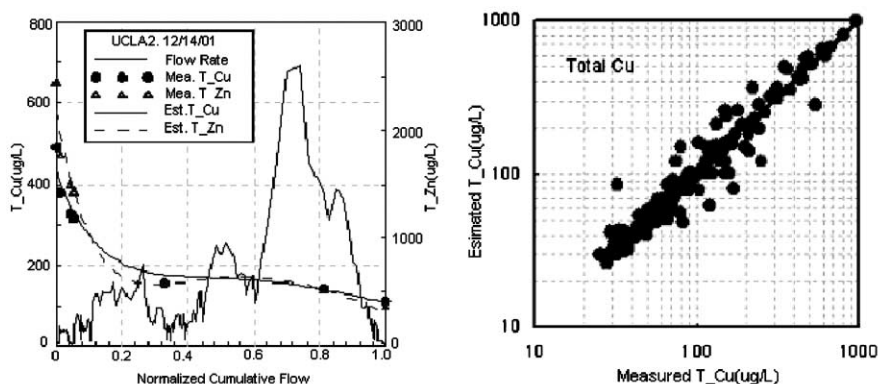


Figure 5 (a) Measured and predicted concentrations of total Cu and Zn versus normalized flow; (b) Correlation between measured and predicted total Cu

- Among the predictor variables, initial conditions (δ) and runoff coefficient have the strongest influence on the metal washoff mass loading estimation. Other important variables are average daily traffic, antecedent dry period, total runoff volume and average rainfall intensity.
- The results were compared with measured values and fitted well for heavy metals with R^2 ranging from 0.8 to 0.95.

Acknowledgements

Financial support for this study was provided by the California Department of Transportation (Caltrans), Division of Environmental Analysis under contracts 43A0014 and 43A0073.

References

- Charbeneau, R.J. and Barrett, M.E. (1998). Evaluation of methods for estimating stormwater pollutant loads. *J. of Water Environmental Research*, **70**, 1295–1302.
- Deletic, A. (1998). The first flush load of urban surface runoff. *Wat. Res.*, **32**, 2462–2470.
- Deletic, A., Ashley, R. and Rest, D. (2000). Modeling input of fine granular sediment into drainage systems via gully-pots. *Wat. Res.*, **34**, 3836–3844.
- Deletic, A.B. and Mahsimovic, C.T. (1998). Evaluation of water quality factors in storm runoff from paved areas. *J. of Environ. Engineering*, **124**, 869–879.
- Driscoll, E.D., Shelley, P.E. and Strecker, E.W. (1990). *Pollutant loading and impacts from stormwater runoff*. Vol. III, Analytical Investigation and Research Report, FHWA-RD-88-008, Federal Highway Administration, USA.
- 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, L.B., Jr., Barrett, M.E., Malina, J.F., Jr. and Charbeneau, R.J. (1998). Use of regression models for analyzing highway storm-water loads. *J. of Environ. Engineering*, **124**, 987–993.
- Kayhanian, M., Kummerfeldt, S., Kim, L.-H., Gardiner, N. and Tsay, K. (2002). Litter pollutograph and loadgraph, *Proceedings of 9th International Conference on Urban Drainage*, 8–13 September, Portland, Oregon.
- Kayhanian, M., Johnston, J., Yamaguchi, H. and Borroum, S. (2001). Caltrans storm water management program. *Stormwater*, **2**, 52–67.
- Larsen, T., Broch, K. and Andersen, M.R. (1998). First flush effects in an urban catchment area in Aalborg. *Wat. Sci. Tech.*, **37**(1), 251–257.
- Lau, S.L., Ma, M., Kayhanian, M. and Stenstrom, M.K. (2002). First flush of organics in highway runoff, *Proceedings of 9th International Conference on Urban Storm Drainage*, September 8–13, Portland, Oregon.
- Legret, M. and Pagotto, C. (1999). Evaluation of pollutant loadings in the runoff water from a major rural highway. *Sci. Tot. Environ.*, **235**, 143–150.
- Ma, M., Khan, S., Li, S., Kim, L.H., Ha, H., Lau, S.L., 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 Storm Drainage*, September 8–13, Portland, Oregon.
- Osuch-Pajdzinska, E. and Zawilski, M. (1998). Model of storm sewer discharge I: description. *J. of Environ. Engineering*, **124**(7), 593–599.
- 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 Environ. Engineering*, **124**(5), 427–440.
- Shaheen, D.G. (1975). *Contribution of urban roadway usage to water pollution*, EPA 600/2-75-004, US EPA, Washington, D.C.
- USEPA (1995). *Controlling nonpoint source runoff pollution from roads, highways and bridges*, US EPA, Report EPA-841-F-95-008a, USA.
- Vorreiter, L. and Hickey, C. (1994). Incidence of the first flush phenomenon in catchments of the Sydney region. *National Conf. Publication-Institution of Engineers*, Australia, (Vol. 3), pp. 359–364.