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Review of Modeling Approaches for Pesticide Washoff from Impervious Surfaces

Yuzhou Luo

Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA 95812, USA, yluo@cdpr.ca.gov

Abstract

Pesticide uses on impervious surfaces and subsequent offsite transport significantly contribute to pesticide detection and aquatic toxicity in urban watersheds. This review evaluates the various methods that currently exist to model pesticide washoff from impervious surfaces. Empirical equations successfully describe pesticide washoff by calibration to a single rainfall event, but lack consistent parameterization with varying set time and repeated rainfall. Partitioning coefficients determined from experimental data could significantly improve PRZM capability in predicting pesticide washoff from impervious surfaces. Highlighted in this review is a new semi-mechanistic approach which incorporates the time-dependence of washoff potential during the dry period after application and washoff dynamics during a runoff event. This review aims to provide information to guide model selection and model development for pesticide registration, regulation, and mitigation for urban pesticide uses.

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Introduction

Pesticide transport in urban watersheds is a function of stormwater hydrology, various processes that control transport in watercourses, and the dynamics of pesticide release and washoff from treated surfaces. While stormwater modeling and pesticide transport in runoff have been extensively investigated, relatively few studies have evaluated pesticide washoff from urban landscapes, especially from impervious surfaces. Impervious surfaces are primary sources of overland flow generation in the urban environment. Impervious surfaces are often directly treated with pesticides in structural pest control applications, paved area applications, and incidental overspray or drift (*1*, *2*). Previous studies suggest that impervious surfaces are the dominant contributors to pesticide movement off-site in urban areas (*3*-*5*). Compared to other surfaces such as turf and bare soils, limited knowledge is available on the dynamics of pesticide buildup and washoff on impervious surfaces. The California Department of Pesticide Regulation (CDPR) recently adopted new regulations to protect water quality in urban areas by restricting pyrethroid application amounts and certain contact areas (*6*). Thus, there is an emerging research need for improved washoff modeling capabilities to evaluate the effectiveness of the regulations and extrapolate the effect of mitigation practices to different conditions.

The physical processes and modeling approaches of urban pollutant washoff and runoff have been reviewed in previous studies (*7*-*13*). Most of the reviews focus on pesticide transport in overland flow, concentrated flow and/or pipe flow over urban landscapes. This chapter reviews existing modeling approaches for simulating pesticide washoff from impervious surfaces, and introduces a semi-mechanistic model developed based on washoff experiments data. The models discussed here are classified as empirical or mechanistic (or semi-mechanistic) approaches. The empirical models are based on statistical analysis and data fitting and do not explicitly simulate mass transfer from pesticide-treated surfaces to the overlying water layer. These models use regression equations to mimic the observed washoff loading curves as function of time or runoff volume. The mechanistic models formulate pesticide mass fluxes based on the concentration gradients across the boundary layer of treated surface and runoff water. These models also explicitly describe the dynamics of water runoff and degradation on pesticide washoff loss.

Characterization of Pesticide Washoff

Most studies investigating pesticide washoff from impervious surfaces are small-scale experiments, such as those on concrete cubes and slabs, with pesticide spikes and simulated or natural rainfall (*3, 4, 14-17*). Runoff water samples are analyzed for pesticides (active ingredients and/or degradates) to estimate mass flux and persistence for off-site transport. The amount of pesticide available to runoff extraction is defined as "washoff potential", M_P (kg/m^2, or user-defined unit of mass/area), at a given time after application referred to as "set time" or "incubation period" (Figure 1a). In addition to degradation, the decrease in washoff potential over time may be associated with transport to inaccessible domains of the concrete matrix, called irreversible adsorption (*14*). Washoff potential is unlikely to be directly measured; instead, it is operationally indicated by "washoff load", i.e., cumulative mass of pesticide released to water over the duration of a rainfall event, M_W (mass/area). Washoff load is determined by experiments with flowing water (runoff induced by natural or artificial rainfall) or static water (immersion for a given equilibration period). Washoff load can be measured at given time intervals during a washoff event, M_W(t), or only at the end of the event as "total washoff load". For the former case, washoff load is usually plotted with cumulative time or runoff, referred as a "washoff profile" (*3*) or "load characteristic curve" (*18*) for a pesticide in a given experimental configuration (Figure 1b). Two time systems are presented in Figure 1: t_d accounts for the duration of the dry period since the last pesticide application, and t describes the washing time.

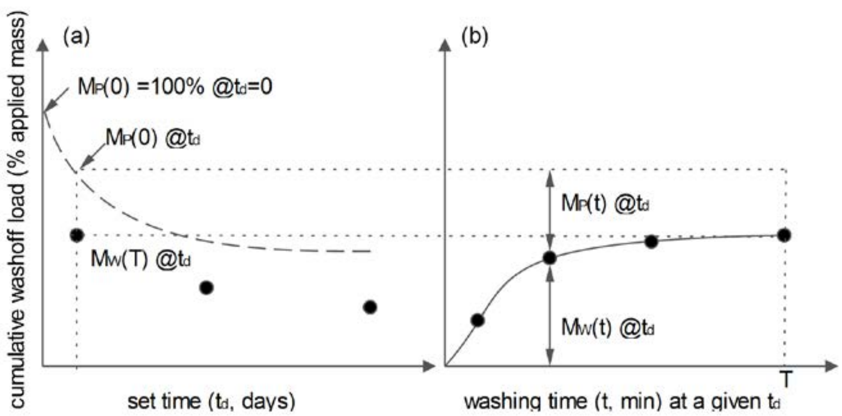


Figure 1. (a) Washoff potential, $M_P(0)$ (dashed line) and total washoff load, M_W(T) (dots) are presented at a given set time t_d. (b) Cumulative washoff loads, $M_W(t)$ (dots) and washoff profile (solid line) measured during washing time t (t=0~T). Note: Dotted lines included to connect M_P(0) and M_W(T) in the two panels.

Published washoff experiments for pesticides from impervious surfaces have been reviewed previously (*19, 20*). According to measure washoff loads, $M_W(T)$, usually only a small portion of applied mass could be detected in the runoff, even with a short set time, suggesting a rapid initial dissipation. With a longer set time, however, extended "tailing" or slow release from concrete surfaces was also typically observed. This behavior suggests the potential for further transport to non-target areas (Figure 1a). The surfactant components of some formulated pesticide products are influential in washoff from concrete surfaces. The effects of chemical properties (such as soil partitioning coefficient and soil metabolism half-lives) and environmental settings (including rainfall intensity and surface conditions of concrete and other media such as asphalt, vinyl siding, stucco, wood siding, etc.) were inconsistent. Pesticide washoff profiles generally follow a convex, advanced-type curve (Figure 1b), and thus can be characterized by a steep initial washoff rate followed by a steadier rate.

In summary, pesticide buildup and washoff, as demonstrated in Figure 1(a) and 1(b), respectively, should be considered in model development for simulating pesticide washoff loads from impervious surfaces. The term of "buildup" is taken from early studies of urban non-point source loads of suspended solids, heavy metals, chlorides, nutrients, and hydrocarbons. In those studies, buildup is considered as a natural accumulation of pollutant available for washoff. More recent modeling studies typically included model implementation for degradation and application of chemicals in buildup simulation.

Empirical Equations for Washoff Profiles

The most popular modeling approaches for predicting pesticide washoff from impervious surfaces are based on empirical equations, including exponential functions or power-law functions of runoff volume. Since the empirical equations are applied to each individual rainfall event with a given set time (t_d), the associated washoff potential and washoff load are only dependent on the washing time (t). Therefore, t_d does not appear in the following equations.

The exponential function follows from the assumption that the rate of pollutant washoff is proportional to the washoff potential during a rainfall event (*18*),

$$\frac{dM_P(t)}{dt} = -k_1 \cdot r \cdot M_P(t) \tag{1}$$

$$M_P(t) = M_P(0)\exp(-k_1 \cdot r \cdot t) = M_P(0)\exp(-k_1 R)]$$

$$M_W(t) = M_P(0) - M_P(t) = M_P(0)[1 - \exp(-k_1 R)] \tag{2}$$

Where

k_1 = the washoff coefficient (mm^{-1})

r = the runoff rate (mm/hr)

R = the cumulative runoff depth (R=r*t, mm)

Eq. (2) is the integrated form of Eq.(1), where a constant runoff rate is assumed. A similar exponential relationship is obtained for time-dependent rates. The exponential function for washoff prediction has been used in the hydrological simulation program – FORTRAN (HSPF) (*21*), early versions of the storm water management model (SWMM) (*22*), the storage, treatment, overflow, runoff model (STORM) (*23*), and site-specific modeling studies (*24*-*27*). The washoff coefficient k_1 is related to pollutant characteristics and the shear stress at the flume bottom (*28, 29*). The coefficient value determines the shape of washoff profile predicted by the exponential function (Figure 2). In the early version of SWMM, for example, the default k_1 value was set as 0.18 mm^{-1} (*18*), indicating 90% washoff under 12.7 mm (or 0.5 inch) runoff, i.e., 1-exp(-0.18*12.7)=0.9.

The exponential function in Eq. (1) implies the independence of predicted pollutant concentration on the runoff rate,

$$C(t) = -\frac{dM_P(t)}{A \cdot r \cdot dt} = \frac{k_1}{A} M_P(t) \tag{3}$$

Where

A = the area of study surface, and A*r*dt is the total runoff volume in the corresponding units.

The result is referred to as an event-mean-concentration (EMC). EMCs are widely used in watershed-scale transport modeling, especially for total maximum daily load (TMDL) projects. Concentrations in urban runoff may vary with runoff rate, as observed in previous studies (*12, 30*). The standard adjustment to overcome this limitation is to introduce a power (n, dimensionless) of runoff intensity to Eq. (1),

$$\frac{dM_P(t)}{dt} = (k_2 \cdot r^n) M_P(t) \tag{4}$$

with k_2 as a new washoff coefficient which has different units and values than k_1 in Eq. (1). In this case, the resultant concentration will also be proportional to $r^{(n-1)}$, so the concentration may increase or decrease with runoff rate according to the value of n.

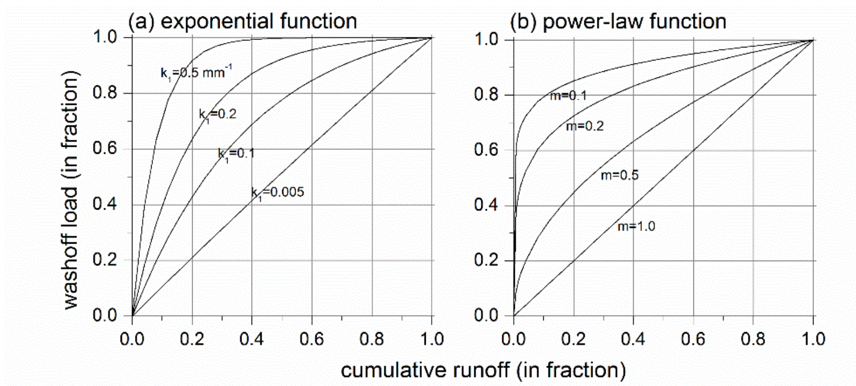


Figure 2. Demonstration of washoff profiles based on (a) exponential function, Eq. (2); and (b) power-law function, Eq. (6) with k_4=1

The mechanism of the power-law model is associated with the simulation of a diffusion process for a planar system. The early portion of the washoff profile could be formulated as,

$$M_W(t) = (k_3 \cdot t^m) M_P(0) \tag{5}$$

where k_3 and m are the linear and exponent characteristics of the diffusion process, respectively (Figure 2). A value of m=0.5 suggests a diffusion process that follows Fick's laws. With m<1, the power-law function generates convex, advanced-type washoff profiles consistent with those observed for pesticide washoff from concrete surfaces (Figure 1). With m close to 0, the profile suggests rapid initial washoff followed by a more steady state, or "type A" profile (*3*), while large m values indicate "type B" profile with relative steady washoff rate over the duration of the experiment. Again the simple relationship of R=r*t can be introduced to Eq. (6) for the prediction of pollutant washoff by runoff depth,

$$M_W(t) = (k_3 \cdot r^{-m} R^m) M_P(0) = (k_4 R^m) M_P(0) \tag{6}$$

Eq. (6) has been widely used in the urban pollutant runoff models such as SWMM and more recent modeling studies (*31, 32*). Similar functions have also been successfully used to predict in-stream pollutant loadings, including pesticides at watershed scale (*33, 34*). Model efforts were applied to estimate the exponents (m) from commonly available properties. In HardSPEC, a first-tier model for estimating aquatic exposure resulting from herbicides applied to hard surface developed by the UK Pesticide Safety Directorate (*35*), for example, the exponents in power-law function are formulated as functions of pesticide solubility (for soluble mass) or specific gravity (non-soluble mass).

Transport Modeling with Impervious Scenarios

In addition to empirical equations, physically-based modeling approaches have also been used to predict pesticide washoff over impervious surfaces. Model equations were originally developed based on transport mechanisms in soils. For example, USEPA developed Tier 2 modeling scenarios for its regulatory model PRZM (Pesticide Root-Zone Model) for applications on impervious surfaces (*36*). PRZM assumes instantaneous chemical equilibrium between water, air, and soil/concrete matrix during a rainfall event. When applied to impervious surfaces, PRZM transport equation can be simplified,

$$\frac{\partial}{\partial t}[C_w(\theta + K_d\rho_s + \alpha K_H)] = -C_w[K_s(\theta + K_P\rho_s) + \frac{Q}{A_w \cdot z} + \frac{X_e K_d}{A_w \cdot z}] \qquad (7)$$

Where

z = the interaction depth of the impervious surface layer containing pesticide potentially available to water extraction and all the following variables are defined within this depth

C_w = the dissolved concentration (g/cm^3)

θ = the volumetric water in the soil (dimensionless)

α = the volumetric air contents in the soil (dimensionless)

ρ_s = the bulk density (g/cm^3)

K_H = the dimensionless Henry's constant

K_P = the lumped, first-order decay constant (d^{-1}) for the solid phase

K_d = the lumped, first-order decay constant (d^{-1}) for the dissolved phases

Q = the total runoff volume (cm^3/day)

A_w = the drainage area (cm^2)

X_e = the erosion loss (g/day)

In addition to the processes presented in Eq. (7), PRZM also simulates dispersion and diffusion in dissolved and vapor phases as well as degradation in the vapor phase. The washoff flux was adjusted according to the availability of chemical residues in the dissolved phase for runoff extraction, which is assumed to be decreasing with the interaction depth z. Soil-related properties (soil adsorption coefficient, soil aerobic metabolism half-life, and soil photolysis half-life) are applied to a hypothetical impervious surface characterized by high curve number (CN2=98), small incorporation depth (0.1 cm) and zero partitioning coefficient to concrete (K_d=0).

The PRZM-based modeling approach for impervious surfaces can be further improved by introducing an effective pesticide partition coefficient for impervious surfaces (K_d^*) to replace the soil K_d in Eq. (7). Values of K_d^* can be directly incorporated in PRZM simulations. For other models, K_d^* can be expressed as the product of K_{OC} (soil partitioning coefficient normalized by organic carbon, OC, content) and a "surface coefficient" representing the OC content equivalent for each impervious surface. This was also accepted by the HardSPEC model with a "surface coefficient" of 0.02% for concrete and 1% for asphalt based on herbicide washoff experiments (*35*).

For demonstrating the model capability, PRZM with USEPA impervious modeling scenario was tested for nine pesticides commonly used in urban areas (Table 1). Washoff measurements were taken from CDPR-supported experiments under controlled rainfall of approximately 25mm/hr for 1 hour (*3, 4, 16, 20*). Pesticide washoff loads were measured from pre-washed concrete surfaces at various set times. The following three simulation settings were involved in the test, [1] K_d=0 as suggested by USEPA, [2] reported K_d values from soil adsorption studies, and [3] K_d calibrated to the measured washoff loads at 1 day after application (DAA), and applied to data with a longer set time. Input parameters were mainly retrieved from registration data (*37*) (Table 1). Pesticide degradation on the impervious surfaces during dry periods was simulated with soil photolysis half-life (SPHOT) (*38*). It's worthy to note that K_d and other physiochemical properties are retrieved for the active ingredients, while K_d^* were determined for the pesticide products with formulations specified in the experimental documentations. Even with the same active ingredient, pesticide products with different formations could be associated with different K_d^* values. As expected, the simulations with K_d=0 significantly overestimated the measured data of all tested pesticides. Predicted mass losses were up to 46% of applied mass, while the measured data ranged from 0.006% to 20.8%. By using reported K_d values in soils, PRZM generally underestimated washoff loadings measured at 1DAA (Figure 3a), except for two chemicals with relatively high mobility (imidacloprid and malathion, K_d<2 mL/g for both). With a longer set time, conservative estimates were obtained for some pesticides, mainly due to their persistence as indicated by large SPHOT values used in PRZM for representing terrestrial dissipation.

Table 1. Tested pesticide products with PRZM inputs

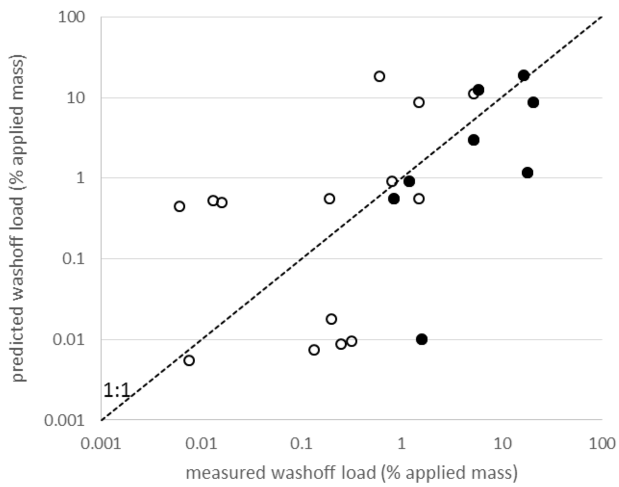
Pesticide	MW	HENRY	VP	SOL	SPHOT	K_d	K_d^*
Bifenthrin	422.9	7.2E-3	1.4E-7	0.001	104	3925	20
Beta-	434.3	5.3E-7	1.6E-8	0.0012	5.6	23	0.8

cyfluthrin							
Carbaryl	201.2	2.7E-9	1.2E-6	11.3	3421	3.2	0.9
Esfenvalerate	419.9	6.3E-7	1.5E-9	0.001	1391	38.8	30
Fipronil	437.2	8.5E-11	2.8E-9	1.9	34	10.7	5
Imidacloprid	255.7	6.5E-11	1.0E-7	514	39	1.9	5
Lambda-cyhalothrin	449.8	1.8E-7	1.6E-9	0.01	274	1960	15
Malathion	330.4	1.2E-8	3.4E-6	125	118	1.0	1.3
Permethrin	391.3	7.5E-8	4.5E-8	0.07	289	63.3	40

Parameters:
MW = molecular weight (g/mol)
HENRY = Henry's law constant (Pa m^3/mol)
VP = vapor pressure (mPa)
SOL = water solubility (ppm)
SPHOT = soil photolysis half-life (day)
K_d = soil partitioning coefficient (mL/g)
K_d^* = calibrated partitioning coefficient on impervious surfaces (mL/g).

Notes: Chemical properties are mainly taken from CDPR Pesticide Chemistry Database (*37*). For data not reported in the CDPR database, other data sources are used: SOL of bifenthrin, beta-cyfluthrin, and esfenvalerate from the IUPAC FOOTPRINT pesticide properties database (*39*), and SPHOT of beta-cyfluthrin from a USEPA publication (*40*).

(a)



(b)

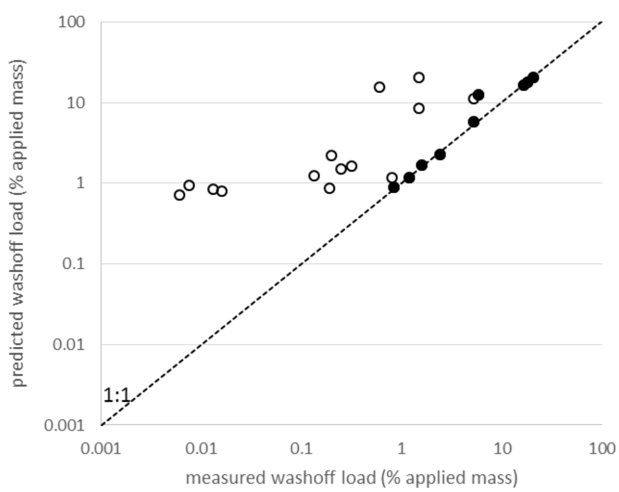


Figure 3. PRZM-predicted pesticide washoff loads from impervious surfaces relative to measurements (*3, 4, 16, 20*), (a) with repeated soil K_d (partitioning coefficient), and (b) with K_d calibrated to measurements at 1DAA (days after application). Open circles for data at 1DAA (days after application) and closed circles for those >1DAA

Simulation results with calibrated K_d values (Figure 3a) were between those with K_d=0 and reported soil K_d: predictions overestimated observations at >1DAA within 1 magnitude for most of the tested pesticides. Except for imidacloprid and malathion, which are associated with relatively high mobility, calibrated K_d^* values (Table 1) were smaller than the corresponding soil K_d. This finding was consistent with previous studies for pyrethroids (*38, 41, 42*). This suggests that adjustments are required before using a K_d value measured in soil adsorption studies to transport modeling on impervious surfaces. Based on the data in Table 1, the ratio of K_d/K_d* showed an increasing trend with the corresponding K_d value ($p<0.001$).

A Semi-Mechanistic Model Based on Experimental Data

Implication and research gap based on model/data review

The review and investigation of existing modeling approaches and experimental data suggest that the basic concepts of fate and transport processes and their modeling implementations, such as chemical dissipation half-lives and mass transfer coefficients (MTC's) (as a function of portioning coefficient and boundary layer depth), are also mathematically applicable for predicting pesticide washoff from impervious surfaces. However, adjustments are required to better predict measured washoff data. First, pesticide washoff from impervious surfaces cannot be simulated with the commonly reported chemical properties for pesticides such as soil partitioning coefficient and soil metabolism half-lives. New parameters should be defined and determined from measured data. The effective partitioning coefficient value of a pesticide on concrete could be significantly lower than that in soils (Table 1). Secondly, the effective dissipation rate of washoff potential shows a decreasing trend with set time. As mentioned previously, the loss of washoff potential during the dry period after application is attributed to pesticide degradation and irreversible adsorption to concrete matrix. This is further confirmed by fitting the total washoff losses into a pseudo-first-order kinetics (*15, 20*), and suggests that the transferability of a pesticide from impervious surfaces to runoff water after application is initially high, but decreases quickly over time. Systematical simulations for the time-dependence of the effective dissipation rate constant are not available in modeling approaches by empirical equations or by PRZM.

Finally, the effective MTC also changes during a rainfall event. Using the power-law function as an example, most experiments reported a non-Fickian washoff profile ($m\neq0.5$) (*20*), indicating a varying MTC with washing time. The major challenge in applying empirical equations is that the calibrated model parameters (k_1 in Eq. (2) and m in Eq. (6)) vary with set time to reproduce measured data. Washoff profiles must be described as bi-phasic or multi-phasic processes (*14, 16, 26, 27, 43*). For example, Thuyet et al. (*16*) applied power-law functions to fit washoff profiles of imidacloprid from concrete surfaces, and the results indicated that the regression coefficients must be calibrated separately for each of the washoff profiles with various set times. Similarly, power-law exponents (m values) were estimated for measured washoff data of commonly used insecticides from 21 controlled rainfall events with R^2 ranging from 0.86 to 1.00 (*20*). Small m values were observed with a short set time for all tested pesticides. There was a general trend toward increasing m values with increasing set time and with repeated rainfall.

In summary, new model development will address the above implications and research gaps in predicting pesticide washoff from impervious surfaces. This can be realized by formulating new parameters for pesticide dissipation rate constant, mass transfer coefficient, and their time dependence.

Model equations and evaluation

A semi-mechanistic model was developed for pesticide washoff from impervious surfaces by describing washoff potential dynamics during dry periods and washoff profiles during rainfall events. Detailed information on model development and applications were documented in the previous publications (*19, 20*). This review highlights the key equations and features in the model.

Pesticide washoff potential as a function of set time was simulated by pseudo-first-order kinetics with a time-varying parameter, $K_P(t_d)$ (d^{-1}), as the effective rate constant of the overall loss of pesticide washoff potential. Analysis of experimental data suggested that K_P is associated with the washoff potential for each rainfall event. A linear relationship between K_P and the washoff potential was assumed,

$$K_P(t_d) = K_P(0) \cdot M_P(0)\,|_{t_d} \tag{8}$$

where $K_P(0)$ is the initial rate constant immediately after pesticide application. Eq. (8) demonstrates that the rate of decline of washoff potential decreases over time, which was consistent with the results from the experimental data analysis.

Washoff profiles were simulated using an equation similar to Fick's second law, with the effective mass MTC varying with time, D*(t) (s^{-1}). At a given set time t_d, the washoff load as a fraction of the washoff potential (F) was estimated as,

$$F|_{t_d} = \frac{M_W(t)}{M_P(0)} = 1 - \frac{M_P(t)}{M_P(0)} = \begin{cases} \sqrt{\frac{4\tau}{\pi}}, & F \le 0.52 \\ 1 - \frac{8}{\pi^2}\exp(-\frac{\pi^2\tau}{4}), & F > 0.52 \end{cases} \quad (9)$$

where τ is a characteristic dimensionless time,

$$\tau = \int_0^t [D^*(t)]dt \quad (10)$$

According to the analysis of washoff profiles, the early portion of the washoff profiles followed a power-law function and the following equation was assumed for the dynamics of D*,

$$D^*(t) = D^*(0) \cdot t^n \quad (11)$$

$$\text{where } n = -2s \cdot M_P(0)|_{t_d}$$

where s is a slope factor representing the assumed relationship between the exponent n and the washoff potential. The power-law function in Eq. (11) provided a simple mathematical form to describe the dynamics of pesticide release from concrete, which have previously been described as bi-phasic or multi-phasic processes (*14, 16, 26, 27, 43*). Eq. (11) was applied to pyrethroids, suggesting a decreasing trend of the effective mass transfer coefficient during the rainfall event (n<0). For relatively soluble chemicals (carbaryl, imidacloprid, fipronil, and malathion), n was expressed as $1 - 2s \cdot M_P(t_d, 0)$ with a value between -1 and 1. Positive n values indicate that D* increases within a washoff test, as observed in the data analysis on measured washoff profiles with m>0.5 (Figure 2b).

The semi-mechanistic model has been applied to a large set of experimental data with nine insecticides commonly used in urban environment (Table 1). One set of model parameters $D^*(0)$, $K(0)$, and s was assigned to each pesticide product for all experiments with that product. Model parameters were calibrated based on experimental data from the first rainfall events, and validated with data with a longer set time. Calibrated models and their performance in predicting pesticide washoff from impervious surfaces were documented in the previous studies (*19, 20*). Modeling results for selected pesticides are demonstrated in Figure 4. In summary, with appropriate calibration the model was capable to capture the dynamics in washoff profiles from concrete surfaces for insecticides with wide ranges of chemical properties (Table 1) and set time (1.5 hours to 238 days). For overall model performance, resultant relative RMSE (root mean square error) values were less than 10%, and NSE (Nash-Sutcliffe efficiency) coefficients were larger than 0.98 for tested pesticides.

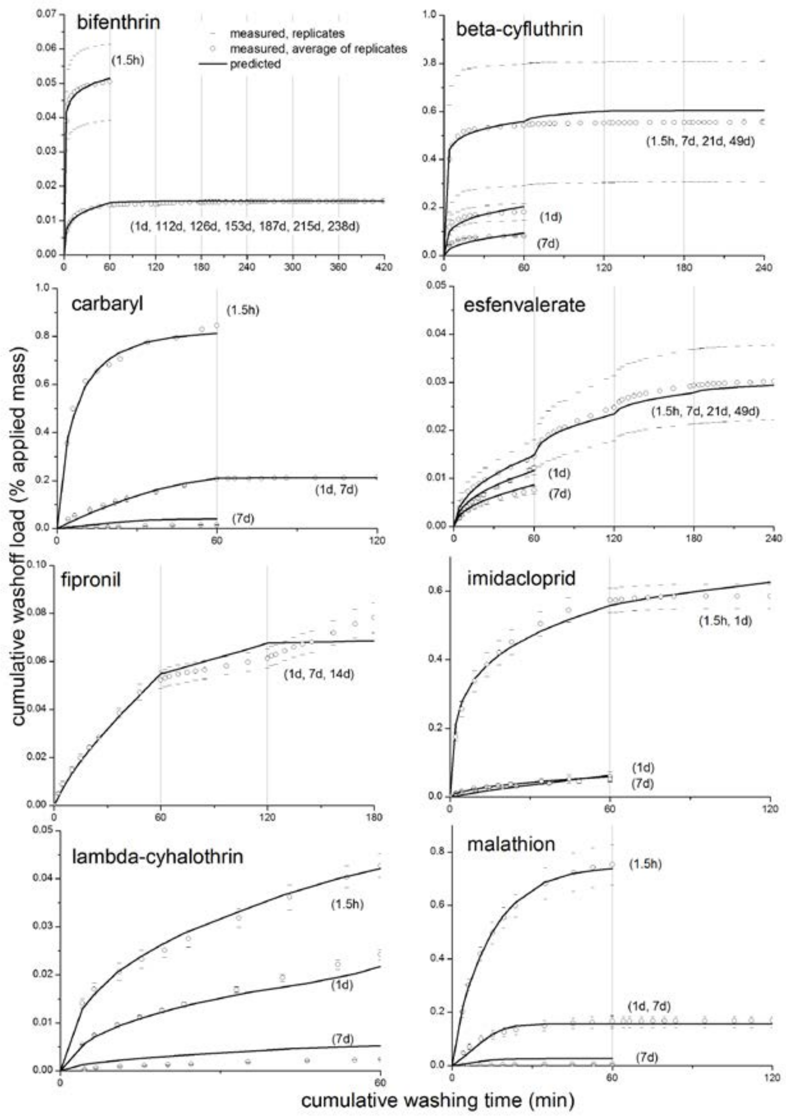


Figure 4. Predicted and observed cumulative washoff loads of selected pesticides. Shown in parentheses are set times (multiple set times indicate related rainfall events). Adapted with permission from reference (*20*). Copyright 2014 ACS Publications.

Summary and Suggestions

This chapter reviewed modeling approaches for predicting pesticide washoff from impervious surfaces, including empirical equations (SWMM as a representative model), a chemical transport model (PRZM), and a semi-mechanistic model. Washoff module in SWMM is based on regression coefficients which are supposed to be parameterized for each individual rainfall events, but do not have direct physical meanings. PRZM and the semi-mechanistic model are designed for more consistent simulations for each pesticide by introducing physically-based processes in washoff simulation. SWMM and the semi-mechanistic model provide sub-daily simulation, while PRZM only reports daily (or event total) results. Since the majority of washoff losses are observed during the early stage of a rainfall event, PRZM parameters calibrated to total washoff loads actually reflect the initial washoff mass flux. Both the empirical equations and the semi-mechanistic model are designed to simulate total (dissolved and adsorbed) pesticide runoff, by incorporating the contribution of particle-bound washoff into the calibrated parameters. PRZM with USEPA impervious modeling scenario only simulates dissolved pesticide. However, the effective K_d value (K_d* in Table 1) were usually calibrated with measured data of total concentrations, so that the predictions would be consistent in terms of total washoff mass.

Both SWMM and PRZM require runoff data supplied by other models, such as the kinematic wave approach for SWMM and SCS curve number method for PRZM. Systematic evaluations on the effects of rainfall intensity and runoff rate on pesticide washoff loads are not available. Increased rainfall intensity may have complicated effects on pesticide washoff loads. However, most of the existing models only simulate one of those effects, i.e., higher runoff rates, and would always predict increased washoff loads under higher rainfall intensity. This is not consistent with recent washoff experiments on insecticides where a significant relationship between rainfall intensity and washoff loads were confirmed (*3, 4*). Therefore, an urban scenario for the semi-mechanistic model is suggested to be developed for regulation evaluation according to the local conditions such as representative weather conditions (intensity, duration and frequency of rainfall) and impervious surface properties (*19, 20*). The scenarios could also serve as guidelines for the washoff experiments and model calibrations to determine the required model input parameters.

SWMM was initially designed for urban pollutants other than pesticides. Applications to urban pesticide evaluation require secondary development, such as the additional module to handle episodic chemical applications. Improved SWMM was applied to California urban community in Orange County, and satisfactorily simulated in-stream pyrethroid concentrations as daily and max 6-hr means (*44*). PRZM with an impervious modeling scenario has been used by USEPA and others in the risk assessment of urban pesticide uses on endangered species (*38, 45, 46*). By incorporating with EXAMS, the model conservatively estimated pesticide concentrations in urban streams. Determination of effective partitioning coefficients for pesticides on impervious surfaces is suggested for future studies. The semi-mechanistic model has been shown to reproduce pesticide washoff profiles for a range of set times and for repeated runoff events with a single calibration (*19, 20*). The model is being incorporated into hydrological simulators of overland flow for pesticide risk assessments at urban community scale. For example, researchers from the Stone Environmental, Inc., have coupled the model into SWMM. More details of their development and applications are provided in other chapters of this book (*47*). In addition, integration with overland flow simulation by kinematic wave equations was also proposed for the development of a spatially high-resolution modeling system for evaluating urban pesticide regulation and mitigation efforts (*48*).

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