

## **Insecticide washoff from concrete surfaces: characterization and prediction**

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### **Abstract**

Pesticide runoff from impervious surfaces is a significant cause of aquatic contamination and ecologic toxicity in urban waterways. Effective mitigation requires better understanding and prediction of off-site transport processes. Presented here is a comprehensive study on pesticide washoff from concrete surfaces, including washoff tests, experimental data analysis, model development and application. Controlled rainfall experiments were conducted to characterize washoff loads of commercially formulated insecticides with eight different active ingredients. Based on the analysis of experimental results, a semi-mechanistic model was developed to predict pesticide buildup and washoff processes on concrete surfaces. Three pesticide product specific parameters and their time dependences were introduced with empirical functions to simulate the persistence, transferability, and exponential characteristics of the pesticide washoff mechanism. The parameters were incorporated using first-order kinetics and Fick's second law to describe pesticide buildup and washoff processes, respectively. The model was applied to data from 21 data sets collected during 38 rainfall events, with parameters calibrated to pesticide products and environmental conditions. The model satisfactorily captured pesticide mass loads and their temporal variations for pesticides with a wide range of chemical properties ( $\log K_{OW}=0.6\sim 6.9$ ) under both single and repeated (1~7 times) rainfall events after varying set times (1.5 hours~238 days after application). Results of this study suggested that, in addition to commonly reported physicochemical properties for the active ingredient of a pesticide product, additional parameters determined from washoff experiments are required for risk assessments of pesticide applications on urban impervious surfaces.

### **Introduction**

Pesticide contamination and toxicity have been frequently detected in urban streams, and linked to pesticide uses in urban and residential areas. Environmental monitoring studies have shown that urban pesticide applications result in potentially toxic surface water runoff in the United

States and other counties (1-10). In a national monitoring study pyrethroids commonly occurred in urban stream sediments in seven metropolitan areas across the United States (11). Based on the multi-area urban monitoring program initiated by the California Department of Pesticide Regulation (CDPR), 50% of water samples contained five or more pesticides, with pyrethroids, imidacloprid, fipronil and its degradates, and malathion detected frequently (12). Concentrations of pesticides in water samples frequently exceeded their lowest USEPA aquatic benchmark. To protect water quality in urban areas, CDPR recently adopted new regulations to restrict pyrethroid applications in urban and residential areas by limiting application amounts and contact areas (13). Pesticide washoff from treated surfaces, which is the source for subsequent transport to receiving water bodies, must be characterized and predicted to evaluate the effectiveness of the regulation and mitigation practices.

Pesticides could be directly applied to impervious surfaces by structural pest control, applications to paved areas, and incidental treatments by overspray and aerial drift. In California, survey data indicated that home owners applied 60% of urban pesticide on hard surfaces around home (14). In the Netherlands, the urban pesticide use on pavements rose from 23% to 50% in the period 1986-2001 (15). With higher runoff generation potentials, impervious surfaces are particularly important contributors to off-site pesticide movement to urban waterways (16,17). Urban environment is associated with multiple landuse types and great spatial variability. Characterization of pesticide off-site movement over a real urban landscape are usually based on the knowledge gleaned from small-scale experiments on individual landscape components. In the USEPA risk assessment of urban pesticide uses, for example, applied pesticides (by broadcast spray, perimeter application, or crack and crevice treatment) are separated evaluated on pervious and impervious surfaces (18,19). Herbicide washoff has been tested on various hard surfaces including asphalt, ballast, concrete, and gravel (20,21). Recent studies also evaluated insecticides and biocides washoff from various building materials (22-24).

Compared to other surfaces such as turf and bare soils, limited knowledge is available for pesticide buildup and washoff on artificial impervious surfaces such as concrete pavements. Since 2005, CDPR has sponsored a series of studies on pesticide washoff from concrete surfaces at both laboratory and urban watershed scales (<http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts.htm>). Experiments were conducted with prepared and prewashed concrete slabs, and expected to conservatively represent pesticide washoff from impervious surfaces in real urban environment. First, tested slabs may represent worse conditions for runoff generation and pesticide washoff compared to that with the existence of cracks and crevices in pavement. In addition, tested slabs may not be coated with atmospherically derived organic films as in field conditions. For pollutants accumulated from the atmosphere, the film facilitates the accumulation and provides a transient sink for mass transfer from air to storm water (25). For intentionally applied chemicals such as insecticides, however, the film may reduce pesticide yields from impervious surfaces during a storm event, since it is associated with high fugacity capacity for hydrophobic organic compounds (26).

Results of the CDPR-sponsored studies suggested that the transport of pesticides from concrete may not be adequately characterized by simple exponential or power-law functions as conventionally used for other urban pollutants (e.g., chlorides, heavy metals, hydrocarbons, nutrients, and suspended solids) (27-30). For example, application rate and chemical properties

could not sufficiently explain the differences in total washoff loads among pesticides (16). While the surfactant component of some formulated products may be influential in washoff from concrete surfaces, effects of environmental settings such as rainfall intensity and concrete surface conditions were not statistically significant (16,31). In addition, while rapid initial washoff was observed for most pesticides, in later stages extended “tailing” or slow release from concrete surfaces was typical. This latter behavior suggests the potential for sustained contamination (16,31,32).

The principal objectives of the present study were to mathematically characterize the transport of pesticides from concrete surfaces and interpret the results mechanistically. Eight popular commercial insecticide products were selected in this study, containing the active ingredients bifenthrin, beta-cyfluthrin, carbaryl, esfenvalerate, fipronil, imidacloprid, lambda-cyhalothrin, and malathion. Experimental data was analyzed to quantify pesticide washoff masses and their dependences on factors such as chemical properties, product formulation, set time, rainfall duration, and repetition of rainfall. In addition, a mathematical model was developed based on the observed characteristics and underlying physical mechanisms. The model was parameterized to simulate the experimental data. By evaluating model performance and interpreting model parameters, this study provides one of the first comprehensive approaches for the numerical prediction of pesticide washoff from concrete surfaces. The results contribute to the quantification of pesticide risks in urban environmental settings and inform appropriate mitigation practices to control those risks.

## **Experimental Section**

### **Washoff tests and chemical analysis**

Insecticide products containing eight active ingredients (bifenthrin, beta-cyfluthrin, carbaryl, esfenvalerate, fipronil, imidacloprid, lambda-cyhalothrin, and malathion) were tested in this study based on their aquatic toxicity, use amounts, and detection frequency in urban and residential areas of California (Table 1). Experimental washoff data for all tested insecticides were obtained by similar methods. In summary, prepared concrete surfaces were treated with commercially available formulated products diluted to product label specifications. Treated concrete surfaces were subject to simulated rainfall after a prescribed set time (i.e., period between application and simulated wash-off), most typically 1.5 hours after application (1.5HAA), one day after application (1DAA), and seven days after application (7DAA). In addition, repeated rainfall was applied to the treated surfaces after various time intervals (Table 2). Simulated runoff from the treated surfaces was collected in volume intervals and analyzed by various analytical techniques for insecticide active ingredient residue. Detailed experimental and analytical measurement procedures can be found in Jorgenson and Young (16) for pyrethroid insecticides, in Thuyet et al. (33) for imidacloprid and fipronil, and are described below for malathion and carbaryl.

Multiple 80cm×80cm concrete test surfaces were prepared and aged as described in Jorgenson and Young (2010). Prior to each product application, concrete surfaces were washed with high pressure water to remove settled material then allowed to dry. Treated slabs were stored outdoors where they were exposed to natural sunlight. Commercially available general-use formulated

products of malathion and carbaryl were used for experimentation (Table 1). Products were diluted and applied to concrete surfaces per label specification. Labels did not indicate a specific rate of application, but provided a qualitative suggestion such as “wet the surface with a coarse spray but without soaking”. The entire concrete surface was treated and the application rate was recorded. Application utilized an aftermarket pump action hand sprayer (Delta Industries, King of Prussia, PA). Application rates are 440 mg (with a relative standard deviation of 2.6%) for carbaryl, and 91 mg (10.8%) for malathion.

Drop forming rainfall simulators identical to those described in Jorgenson and Young (16) and Thuyet et al. (33) were used to provide 60 minutes of simulated rainfall in experimental duplicate format. Simulators used a local treated groundwater supply (average total dissolved solids: 340 mg/L, average pH: 8.4) which was dechlorinated by granulated activated carbon filtration. Temperature of simulated rainfall averaged 17°C over the course of the study. Rainfall intensity was controlled at 25 mm/hr for all experiments, while a higher intensity (50 mm/hr) was also tested in some cases. Experiments with 25 mm/hr rainfall were selected in this study for data analysis and modeling. For the first rainfall, experimental set times were usually 1.5HAA, 1DAA or 7DAA. On some surfaces, a second successive simulation was conducted following the 1DAA simulation without an intervening product application (7DAA, 2<sup>nd</sup> rainfall). Runoff samples were collected every 6 minutes, so there were 10 samples during the 60-min rainfall duration in each experiment, which further allowed plotting of the experimental washoff profile.

Neat standards of carbaryl, malathion, and diazinon (surrogate) were obtained from ChemService, Inc. (West Chester, PA). An Agilent 6890 gas chromatograph equipped with a J&D Scientific DB-5 column (30 m × 0.25 mm × 0.25 μm), and Agilent nitrogen phosphorus detector was used for the quantitative determination of carbaryl and malathion in simulated runoff samples. The following thermal gradient was used: 100 °C to 250 °C at 15 °C/min after an initial 0.5 minute hold at 100 °C and a concluding hold of 1.5 minutes at 250 °C. The inlet was set to 290 °C and the detector set to 310 °C. Detector gasses were set to 3.0 ml/min for hydrogen, 60 mL/min for air, and 7 mL/min for nitrogen.

Sample extraction occurred within 24 hours following sample collection. Extraction of malathion and carbaryl was accomplished using an octadecyl (C-18) solid phase extraction cartridge (Supelco ENVI-C18, St. Louis, MO) with a 500 mg sorbent bed. Insecticides were eluted with 10 mL of hexane/ethyl acetate (50/50 v/v; Fisher, Optima, Waltham, MA) and concentrated to 1 mL by nitrogen evaporation, or diluted if necessary to be within the range of calibration standards. Aliquots of sample used for extraction were obtained in the laboratory by shaking the container and drawing sample from mid-depth through a large-bore graduated pipette. Batch method blank analysis confirmed absence of contamination in the analytical system. Batch diazinon matrix spike surrogate recoveries averaged 90%, with relative standard deviation between matrix spike duplicates of 11%. Measurements are reported without surrogate correction.

## **Experimental data analysis and results**

Data analysis was designed to characterize the variability and dynamics in pesticide washoff from concrete surfaces. The following variables were defined to better quantify the washoff processes (Figure 1).

[1] Washoff potentials and loads. The amount of pesticide available to runoff extraction is defined as “washoff potential”,  $M_P$  (kg/m<sup>2</sup>, or user-defined unit of mass/area), at a given set time. Washoff potential is unlikely to be directly measured; instead, it’s operationally indicated by “washoff load”, i.e., total mass of pesticide released to water during a specific runoff event,  $M_W$  (mass/area). Results of first-flush tests, i.e., the first rainfall after application, were investigated to characterize the relationship between washoff potential of pesticides from concrete surfaces and their chemical properties and set time.

[2] Washoff profile. Cumulative washoff loads measured at timed intervals,  $M_W(t)$ , are usually plotted with runoff time or runoff volume, referred as a “washoff profile” (16) or “load characteristic curve” (29) for a pesticide in a given experimental configuration. The shape of a washoff profile reflects the relative release rates of pesticide from concrete surfaces. The variations of washoff profiles on the tested pesticides and set time were evaluated in this study.

In this study, all pesticide masses including washoff load and washoff potential were normalized by the initial application rate and reported as dimensionless values between 0 and 1. The only exception is in the plots of washoff profile where washoff loads measured at timed intervals within a storm event following a set time of  $t_d$  were further normalized by the total washoff load in the rainfall event,  $M_W(t_d, t)/M_W(t_d, T)$ .

### ***Washoff loads***

Except for the long-term test on bifenthrin (“1R” in Table 2), all experiments were conducted in duplicates which allowed calculation of mean and variance. In terms of total washoff mass,  $M_W(t_d, T)$ , in each rainfall event, the relative standard deviation of two replicates ranged from 0.4% to 46.6% with a median value of 10.4% over the 31 experiments with replicates (Table 2). High variances were mainly observed for repeated rainfall events for beta-cyfluthrin especially at 1.5 hours (46.6%) and 7 days (30.0%) after applications. According to the experiment design, more resources were allocated to numerous time interval measurements for the collection of well-defined washoff profile, rather than the variance of the total washoff mass as in other studies (31,32,34). For the development and application of the washoff model, we assumed that the limited replications in this study captured central tendency and dispersion of washoff profile in each experiment.

Washoff loads were reported as averages of two experimental replicates in each washoff test, except for the experiment 1R. For the first simulated rainfall events at 1.5HAA, washoff loads of the tested pesticides ranged from 1.4% (esfenvalerate) to 84.6% (carbaryl). Washoff loads decreased quickly with set time. At 7DAA, washoff loads of less than 10% (median = 3%) were reported for the tested pesticides. Negative correlations between washoff loads and logK<sub>OW</sub> of active ingredients were observed for individual set times, but the correlation was only statistically significant at 1.5HAA ( $r=-0.79$ ,  $p=0.03$  at 1.5HAA;  $r=-0.42$ ,  $p=0.31$  at 1DAA; and  $r=-0.12$ ,  $p=0.79$  at 7DAA) (Figure 2).

To account for washoff potential dynamics, we defined an effective first-order average “dissipation” rate constant  $K_W$ , day<sup>-1</sup> (or half-life  $HL_W=\ln2/K_W$ ) over the set time. This dissipation

rate constant includes pesticide losses due to actual degradation and irreversible sorption. The average  $K_W$  is calculated by applying first-order kinetics to the measured loads for the first simulated rainfall event after application (Table 3). For example, the total washoff load of bifenthrin was 1.5% ( $M_W=0.015$  of applied mass) at  $t_d = 1\text{DAA}$ , and the corresponding average  $K_W$  was calculated as  $-\ln(M_W)/t_d = \ln(0.015)/1 = 4.2 \text{ day}^{-1}$ . The concept of  $K_W$  as a “lumped” rate constant representing both degradation and irreversible sorption was used in previous studies (31,32,34). During the first 1.5 hours after application, quick dissipation was observed for all pesticides on concrete surfaces. The effective  $HL_W$  were less than 7 hours. In addition to degradation, the “loss” of washoff potential may be associated with transport to inaccessible domains of the concrete matrix, called irreversible adsorption (34).

### ***Washoff profiles***

Washoff profiles, or plots of cumulative pesticide washoff load versus washing time generally yielded convex, advanced-type curves (Figure 3), which can be described with a power-law function,

$$M_W(t_d, t) = a \cdot t^m \quad (1)$$

where  $M_W(t_d, t)$  is the cumulative washoff load during the washing time  $t=0\sim T$  measured at a set time of  $t_d$ , and  $a$  and  $m$  are the linear and exponent characteristics of the power-law function, respectively. Normalizations on  $M_W$  and  $t$  were applied in our previous studies (16,33) to generate washoff profile plots with both axes within 0 and 1,

$$\frac{M_W(t_d, t)}{M_W(t_d, T)} = \left(\frac{t}{T}\right)^m \quad (2)$$

where  $M_W(t_d, T)$  and  $T$  are the same as defined in Figure 1. The mechanism of the power-law model is associated with the simulation of diffusion-like process for a planar system (35). A value of  $m=0.5$  is consistent with a diffusion process that follows Fick’s laws, while other exponents suggest non-Fickian processes. With  $m$  close to 0, the profile suggests rapid initial washoff followed by a more steady state, or “type A” profile as described in our previous study (16), while large  $m$  values indicate “type B” profile with relative steady washoff rate over the duration of the experiment. The power-law function has been widely used in environmental modeling for pollutant washoff from hard surfaces (30,33,36,37). Demonstrated in Figure 3 are washoff profiles for beta-cyfluthrin and esfenvalerate, which were selected as representative chemicals with “type A” and “type B” profiles, respectively.

Table 4 shows the power-law exponents estimated using regression for experimental data collected during the first rainfall events for all tested pesticides. Generally, the power-law function fit the observed washoff profiles well with  $R^2$  ranging from 0.86 to 1.00. Results suggested the time-dependence of the effective diffusivity of tested pesticides on concrete surfaces. With a short set time (1.5 hours in this study), small  $m$  values were observed for all pesticides ( $m<0.1$  for bifenthrin and beta-cyfluthrin; and  $m<0.4$  for other pesticides), suggesting a high effective diffusivity from concrete at the initial stage of a rainfall event. This might be related to the enhancement of effective diffusivity by surfactants in the pesticide products.

Results of previous experiments with LAS (linear alkylbenzene sulfonate)/bifenthrin treated concrete surface showed that the initial LAS concentrations in the first 5L of runoff were sufficient to enhance the dissolution and solubilization of bifenthrin (16). There was a general trend toward increasing  $m$  values with increasing set time and with repeated rainfall for all tested pesticides. For relatively soluble chemicals (carbaryl, imidacloprid, fipronil, and malathion), resultant  $m$  values were close to or larger than 0.5 after 1DAA, suggesting an invariant or increasing effective diffusivity during the rainfall event.

## Modeling Section

### Model development

Based on the experimental data analysis we developed a model for pesticide washoff by describing washoff potential dynamics during dry periods and washoff profiles during rainfall events. The conceptual model in our previous study (17) was applied in the development with two modeled pesticide pools of washoff potential in concrete and washed mass in overland flow. As shown in Figure 1, two time systems were involved:  $t_d$  accounted for the duration of the dry period since the pesticide application (or since the last rainfall event in repeated washoff tests,  $t_d$  up to 111 days, Table 2), and  $t$  described the washing time ( $t=0\sim 60$  min in this study).

Pesticide washoff potential as a function of set time was simulated with the pseudo-first-order kinetics with time-varying rate constant,

$$\frac{dM_P(t_d,0)}{dt_d} = -K_P(t_d) \cdot M_P(t_d,0) \quad (3)$$

where  $M_P(t_d,0)$  is the washoff potential immediately before the rainfall event to be modeled at set time  $t_d$ , and  $K_P$  ( $d^{-1}$ ) is the effective rate constant of the overall loss of pesticide washoff potential. As mentioned previously, the loss of washoff potential during dry period after application is attributed to pesticide degradation and irreversible adsorption to concrete matrix. The definition of  $K_P$  is similar to that of  $K_W$  in Table 3 but  $K_P$  is an instantaneous rate constant for the decline in washoff potential with set time, while  $K_W$  is an average rate constant for the first-order decay determined from the measured washoff loads.

Washoff profiles were simulated using an equation in the form of Fick's second law but with the effective diffusivity varying with time,  $D(t)$  ( $m^2/s$ ),

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial z^2} \quad (4)$$

where  $z$  is the coordinate measured in the direction of pesticide release (Figure 4),  $C$  ( $kg/cm^3$ ), as a function of  $t$  and  $z$ , is the pesticide concentration in the concrete subject to washing by overland flow. An analytical solution can be derived for the washoff load,  $M_W(t_d,t)$ , as fraction of washoff potential ( $F$ ) (38,39),

$$F = \frac{M_w(t_d, t)}{M_p(t_d, 0)} = \begin{cases} \sqrt{\frac{4\tau}{\pi}}, & F \leq 0.52 \\ 1 - \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 \tau}{4}\right), & F > 0.52 \end{cases} \quad (5)$$

where  $\tau$  is a characteristic dimensionless time,

$$\tau = \int_0^t \left(\frac{D}{l^2}\right) dt = \int_0^t [D^*(t)] dt \quad (6)$$

Although the thickness  $l$  cannot be physically measured, it can be calibrated together with  $D$  as a first-order mass transfer coefficient (MTC)  $D^*$  ( $=D/l^2$ ,  $s^{-1}$ ). The concept of  $D^*$  was also used in previous studies in defining the diffusion Deborah number (40). Initial and boundary conditions for Eq. (4) and details in the development of the analytical solution were provided in the Supporting Information section. In addition to the above model equations derived from the first-order kinetics and Fick's second law, two empirical equations were introduced for the time-dependence of the rate constant  $K_p$  in Eq. (3) and the mass transfer coefficient  $D^*$  in Eq. (8). Results of experimental data analysis suggested that both  $K_p$  and  $D^*$  were associated with the set time or the washoff potential for each rainfall event. Specifically, we assumed a linear relationship between  $K_p$  and the washoff potential before a rainfall event, and a power-law function to estimate  $D^*$  from washoff potential and an additional factor for the types of washoff profiles. The Supporting Information section includes more details on the model development. In summary, the developed model requires three input parameters for each pesticide product: the initial rate constant immediately after pesticide application,  $K_p(0)$ , the effective MTC at the beginning of a rainfall event,  $D^*(0)$ , and a shape factor,  $s$ .

## Model applications

The model was applied to the washoff experiments summarized in Table 2. Previous studies indicated insignificant effects of rainfall intensity (in the tested range of 25~50 mm/hour) on pesticide washoff (16,31). In this study, therefore, model testing was only performed for the experiments with simulated rainfall rates of 25 mm/hour. One set of model parameters  $D^*(0)$ ,  $K(0)$ , and  $s$  was assigned to each pesticide product for all experiments with that product. Parameters were estimated by global optimization with the shuffled complex evolution (SCE-UA) method (41). The objective function to be minimized was defined as the coefficient of variation (CV) of root mean square error (RMSE) (i.e., RMSE normalized by the mean of observations) between the predicted and observed washoff loads. Parameter optimization concluded when the change of the objective function for the last 10 evolution loops was less than 0.1%. The Nash-Sutcliffe efficiency (NSE) was also reported for evaluating model performance.

Pesticide washoff shortly after application was usually associated with extremely high fitted values of the effective diffusivity. As mentioned before, for some pesticides their residues (active ingredient and non-volatile formulation components such as surfactants, adjuvants, etc.) are not completely incorporated into concrete during a short time set of 1.5 hours (33). The actual effects of the incomplete incorporation on effective diffusivity were product specific and could not be simulated by the developed model. For the simulation of experiments at 1.5HAA, namely single-



rainfall experiments 1S, 3S1, 7S1, and 8S1; and the first rainfall in the repeated-rainfall experiments 2R, 4R, and 6R (Table 2), therefore, we introduced an artificial amplification factor ( $f_D$ , dimensionless) to the  $D^*(0)$  calibrated from experiments at 1 and 7 DAA. In summary, parameter set  $[D^*(0), K_P(0), s]$  was used in model simulations for experiments with set time  $\geq 1$ DAA, and  $[f_D \times D^*(0), K_P(0), s]$  for 1.5HAA. Model parameters were generally calibrated by experimental data from the first rainfall events (Table 2), and validated with repeated rainfall results. For lambda-cyhalothrin, no model validation was conducted because of the limited data available. Calibrated model parameters and performance are listed in Table 5. Modeling results are illustrated for the cumulative mass loss of tested pesticides (Figure 5).

With appropriate calibration, the model was able to capture the dynamics in repeated rainfall washoff profiles from concrete surfaces for insecticides with a wide range of chemical properties ( $\log K_{OW}=0.6\sim 6.9$ ) over a long period following application (1~238 DAA). Resultant CV[RMSE] were less than 10% and NSE values were larger than 0.95 for most of the washoff experiments (Table 5). For model calibration, the median statistics were reported as 6.6% for CV[RMSE] (ranging from 2.7% to 9.9%) and 0.995 for NSE (0.980 to 0.998). No major differences were detected for model performance between experiments with single rainfall and repeated rainfall experiments. The largest discrepancy was observed for lambda-cyhalothrin, for which predictions significantly overestimated the observations at 7DAA (experiment 7S3) (total mass loss: observed = 0.24% vs. predicted =0.52%).

The effective mass transfer coefficient,  $D^*(0)$ , indicated the transferability of pesticide in the system of concrete matrix and penetrated water. The values of  $D^*(0)$ , or  $D^*(0) \times f_D$  for 1.5HAA, were significantly associated with the washoff loads (Table 3) observed in the early stage after application ( $r=0.88$ ,  $p=0.01$  for 1.5HAA, and  $r=0.77$ ,  $p=0.02$  for 1DAA). No significant correlations were detected between  $D^*(0)$  and chemical properties of the active ingredients (Table 1). Hydrophobic chemicals were not necessarily associated with lower  $D^*(0)$ . For example, the  $D^*(0)$  for the beta-cyfluthrin product used in this study was much higher than those for some products with more soluble active ingredients such as fipronil and imidacloprid. In addition to the active ingredient, other components such as surfactants may have significant effects on the effective diffusivity of a pesticide product, especially during the early period after application (16).

The parameter  $s$  is the exponent that captures changes in the effective MTC and in the washoff profile as set time increases especially during the early stage after application according to Eq. (14). At the set time  $t_d=0$  and  $M_p=1$ , the exponent  $n$  in the  $D^*$  dynamics can be expressed as  $2m_x - 2s - 1$  according to Eq. (14). Smaller  $n$  was observed for bifenthrin (-0.902 @  $t_d=0$ ) and beta-cyfluthrin (-0.872), consistent with the type-A profiles previously identified (16). Larger values of  $s$  indicated a type-B profile, and  $n=0$  suggested a constant effective diffusivity or a Fickian diffusion process. For soluble chemicals, as mentioned before, small  $s$  may result in close-to-zero or even positive  $n$  values, suggesting an increasing trend of effective MTC and a relatively stable rate of washoff load during rainfall event. The enhancement of effective diffusivity might be related to water penetration and further wetting in the concrete matrix. Strong linearity in the cumulative washoff profiles was observed for those chemicals, especially for longer set times (Figure 5). This finding was consistent with Thuyet et al. (33), in which linear functions (rather than exponential functions) were used to fit the cumulative washoff loads of fipronil.

The rate constant  $K_P(0)$  represented the initial loss of washoff potential. Immediately after application, a significant amount of pesticide became unavailable for transfer into runoff, as suggested by  $K_P(0)$  values up to  $5.4 \text{ d}^{-1}$  (for malathion). There was no significant association between  $K_P(0)$  and the typical aerobic soil metabolism half-life (Table 1, converted to the form of a rate constant). The calibrated  $K_P(0)$  values were generally less than the average dissipation rate constants calculated from measured washoff loads at 1.5HAA ( $K_W$ , Table 3), indicating that only a small portion of washoff potential was actually released into the water runoff. Measured washoff loads, as summarized in Table 3, are determined by the two variables of washoff potential (total amount of pesticide available to release, indicated by  $K_P$ ) and washoff rate (by  $D^*$ ). Therefore, the persistence of a pesticide on concrete surfaces, i.e., its remaining washoff potential after a longer set time, might be indicated by considering the parameters  $D^*$  and  $K$ . For example, the ratios of  $D^*(0)/K_P(0)$  were moderately correlated to the washoff loads measured at 7DAA (Table 3,  $r=0.80$ ,  $p=0.05$ ).

Commonly submitted physicochemical properties for pesticide registration and risk assessment, such as  $K_{OW}$ , water solubility, and aerobic soil metabolism half-life, have limitations in characterizing pesticide washoff from concrete surfaces. To predict the dynamics of pesticide washoff potential during dry and wet periods, we introduced a semi-mechanistic modeling framework with three product-specific parameters:  $K_P$  describing the persistence of washoff potential,  $D^*$  for the pesticide transferability from concrete to runoff water, and  $s$  as the diffusional exponent characteristics of the washoff mechanism. This study also demonstrated the required experiments and calibration process to estimate the new parameters. In summary, for each pesticide product at least two washoff profiles, one at 1DAA and another following a longer set time, are needed to estimate for the parameters. Sprayed pesticide is assumed to be fully incorporated with the concrete surface after a minimal set time of 1 day. In addition, predictions at 1-day set time also overestimate pesticide washoff under real field conditions, since it's unusual to apply pesticide on urban landscapes within 1 day of a storm event. For washoff tests shortly after application (e.g., 1.5 hours in this study), amplification factors (Table 5) were required to reflect the elevated transferability for pesticide residue moving to runoff water.

In addition to pesticide product, model parameters in this study were also specific to environmental settings, reflecting integrated effects of product formulation, aging effects, concrete surface conditions, and rainfall on pesticide washoff processes. For model applications for regulation purposes, therefore, further research efforts are needed to develop modeling scenarios according to the local conditions such as representative intensity, duration and frequency of rainfall. For example, rainfall intensity and duration during the simulations in this study, 25 mm/hour for 60 minutes, correspond to a 1-year recurrence interval in Raleigh, North Carolina, and to 5 years in Sacramento, California (33). Modeling scenarios with a typical rainfall pattern and concrete surface condition could be developed as guidelines for the washoff experiments and model application. Based on appropriate modeling scenarios and calibrated parameters, the model developed in this study is anticipated to provide reasonable estimates of pesticide washoff to support risk assessment in urban environmental settings. It's noteworthy that the model and supporting experiments were designed for pesticide release and transport with runoff water within a short distance (less than 80 cm according to the size of the test surface) from a clean concrete surface. For evaluations at urban community scale, the model should be

coupled with other transport mechanisms, such as the effects of loose particles, and pesticide fate and distribution in overland flow. CDPR is supporting multiple projects for field experiments and modeling efforts to characterize pesticide washoff in both dissolved and particle-bound forms and the subsequent transport processes.

## **Acknowledgements**

The experiments described in this paper were supported by funding from the California Department of Pesticide Regulation under contract 06-0086C.

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## Tables

Table 1. Tested pesticide products, their chemical and toxicological properties, and their frequency of detection in urban surface waters.

Pesticide (active ingredient)	Product type	logK <sub>OW</sub>	Solubility (ppm)	AERO (day)	Toxicity (ppb)	Detection frequency (%)
Bifenthrin	CE/RTU	6.60	0.001	26	0.0013	56~84 (0.002)
Beta-cyfluthrin	SC/dilutable	5.90	0.0012	13	NA	NA
Carbaryl	SC/dilutable	2.36	9.1	16	0.5	16~24 (0.05)
Esfenvalerate	EC/RTU	6.24	0.001	44	0.017	NA
Fipronil	SC/dilutable	3.75	3.78	142	0.011	9~71 (0.05)
Imidacloprid	EC/dilutable	0.57	610	191	1.05	51 (0.05)
Lambda-cyhalothrin	EC/dilutable	6.90	0.005	25	0.002	1~2 (0.005)
Malathion	EC/dilutable	2.75	140	0.17	0.035	11~17 (0.04)

Notes: AERO: aerobic soil metabolism half-life; CE: microemulsion; EC: emulsifiable concentrate; SC: suspension concentrate, RTU: ready-to-use. logK<sub>OW</sub>, solubility, and AERO were taken from the IUPAC FOOTPRINT Pesticide Properties DataBase (42). Toxicity values were reported as the lowest USEPA aquatic benchmarks (43). Detection frequency and minimum reporting limit (ppb, in parentheses) are based on California urban monitoring data (12).

Table 2. Design of experiments with single or repeated rainfall events

Insecticide	Experiment set ID	Washoff tests, indexed by time of rainfall after application		
		The first rainfall	The second rainfall	Additional rainfall events
Bifenthrin	1S	1.5h		
	1R	1d	112d	126d, 153d, 187d, 215d, 238d
Beta-cyfluthrin	2R	1.5h	7d	21d, 49d
	2S1	1d		
	2S2	7d		
Carbaryl	3S1	1.5h		
	3R	1d	7d	
	3S2	7d		
Esfenvalerate	4R	1.5h	7d	21d, 49d
	4S1	1d		
	4S2	7d		
Fipronil	5R	1d	7d	14d
Imidacloprid	6R	1.5h	1d	
	6S1	1d		
	6S2	7d		
Lambda-cyhalothrin	7S1	1.5h		
	7S2	1d		
	7S3	7d		
Malathion	8S1	1.5h		
	8R	1d	7d	
	8S2	7d		

Notes: In the experiment ID, “R” is for washoff tests with repeated rainfall and “S” for single rainfall.

Table 3. Total washoff loads of pesticides from concrete surfaces during the first simulated rainfall events after application

Insecticide	Washoff load (% of the applied mass) at			Average dissipation rate constant ( $K_w$ , $d^{-1}$ ) at		
	1.5HAA	1DAA	7DAA	1.5HAA	1DAA	7DAA
Bifenthrin	5.0	1.5	-	47.9	4.2	-
Beta-cyfluthrin	54.2	18.2	8.2	9.8	1.7	0.4
Carbaryl	84.6	20.8	1.5	2.7	1.6	0.6
Esfenvalerate	1.4	1.2	0.8	68.3	4.4	0.7
Fipronil	-	5.2	-	-	3.0	-
Imidacloprid	57.3	5.9	5.2	8.9	2.8	0.4
Lambda-cyhalothrin	4.2	2.4	0.2	50.7	3.7	0.9
Malathion	75.4	16.6	0.6	4.5	1.8	0.7

Table 4. Parameterization and performance of the power-law functions in Eq. (2) during the first simulated rainfall events after application. Total washoff load is presented as % of applied mass.

Pesticide	$t_d=1.5$ hours			1 day			7 days		
	washoff load	$m$	$R^2$	washoff load	$m$	$R^2$	washoff load	$m$	$R^2$
Bifenthrin	5.0	0.066	0.897	1.5	0.214	0.983	-	-	-
Beta-cyfluthrin	54.2	0.078	0.865	18.2	0.118	0.957	8.2	0.181	0.926
Carbaryl	84.6	0.184	0.976	20.8	0.512	1.000	1.5	0.726	0.998
Esfenvalerate	1.4	0.381	0.996	1.2	0.485	0.992	0.8	0.452	0.998
Fipronil	-	-	-	5.2	0.738	0.999	-	-	-
Imidacloprid	57.3	0.353	0.980	5.9	0.509	0.990	5.2	0.503	0.998
Lambda-cyhalothrin	4.2	0.330	0.983	2.4	0.440	0.993	0.2	0.531	0.998
Malathion	75.4	0.388	0.973	16.6	0.354	0.965	0.6	0.714	0.993



Table 5. (a) Calibrated model parameters and (b) model performance for washoff experiments  
(a)

Pesticide	$D^*(0), s^{-1}$	$K_p(0), d^{-1}$	$s$	$f_D$
Bifenthrin	5.65E-07	0.601	0.451	5.0
Beta-cyfluthrin	1.04E-04	0.694	0.436	3.6
Carbaryl	3.04E-05	3.409	0.763	31.9
Esfenvalerate	4.53E-08	0.070	0.052	1.4
Fipronil	6.44E-07	1.229	0.563	NA <sup>[1]</sup>
Imidacloprid	2.00E-06	0.485	0.779	144.3
Lambda-cyhalothrin	8.31E-07	1.487	0.107	1.0
Malathion	1.19E-04	5.392	0.612	3.1

(b)

Pesticide	Calibration (first rainfall)		Validation (repeated rainfall)		Overall (all data)	
	CV[RMSE]	NSE	CV[RMSE]	NSE	CV[RMSE]	NSE
Bifenthrin	0.027	0.998	0.026	0.974	0.027	0.998
Beta-cyfluthrin	0.069	0.994	0.075	0.782	0.087	0.975
Carbaryl	0.069	0.997	0.048	0.987	0.062	0.997
Esfenvalerate	0.085	0.980	0.047	0.986	0.047	0.986
Fipronil	0.060	0.993	0.076	0.969	0.084	0.961
Imidacloprid	0.064	0.998	0.052	0.977	0.074	0.994
Lambda-cyhalothrin	0.099	0.989	NA <sup>[2]</sup>	NA <sup>[2]</sup>	0.099	0.989
Malathion	0.063	0.997	0.078	0.942	0.063	0.997

Notes:  $D^*(0)$  = effective diffusivity before rainfall events ( $t=0$ ),  $K_p(0)$  = effective dissipation rate constant of pesticide washoff potential, initial value immediately after application ( $t_d=0$ ),  $s$  = a shape factor determining the time-dependence of  $D^*$  during rainfall events,  $f_D$  = (applied to experiments at 1.5 hours after application only) an artificial amplification factor for  $D^*(0)$  to reflect the high effective diffusivity due to incomplete incorporation after a short time of application (1.5 hours in this study). CV[RMSE] = coefficient of variation (CV) of root mean square error (RMSE). NSE = Nash-Sutcliffe efficiency coefficient.

[1] for fipronil, no experiment was conducted at 1.5 hours set time (Table 2). Therefore,  $f_D$  is not needed.

[2] for lambda-cyhalothrin, no repeated rainfall test was conducted (Table 2)

## Figure captions

Figure 1. Demonstration of (a) cumulative washoff loads (dots),  $M_W(t_d, t)$ , and washoff profile (solid line) measured during washing time  $t$  ( $t=0\sim T$ ), and (b) washoff potential (dashed line),  $M_P(t_d, t)$ , and total washoff load (dots),  $M_W(t_d, T)$ , at set time  $t_d$ . Dotted lines are added to locate  $M_P(t_d, 0)$  and  $M_W(t_d, T)$  in the two panels.

Figure 2. Relationship between  $K_{OW}$  (Table 1) and total washoff loads (as % of the application rates) of tested pesticides from the first rainfall at 1.5h, 1d, and 7d after application.

Figure 3. Washoff profiles of (a) beta-cyfluthrin and (b) esfenvalerate during repeated rainfall. Model fits to the Eq. (2) were shown as solid lines. “Type A” profiles, i.e., a steep dissipation rate followed by a more steady rate, were observed for beta-cyfluthrin with short set time of 1.5 hours and 1 day.

Figure 4. Numerical schematic of the pesticide washoff model developed in this study.

Figure 5. Predicted and observed cumulative mass losses of tested insecticides. Sets 1R and 3R did not have valid replicates. See Table 2 for experiment set ID.