# PESTICIDE WASHOFF FROM IMPERVIOUS SURFACES: CHARACTERIZATION AND PREDICTION

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# Outline

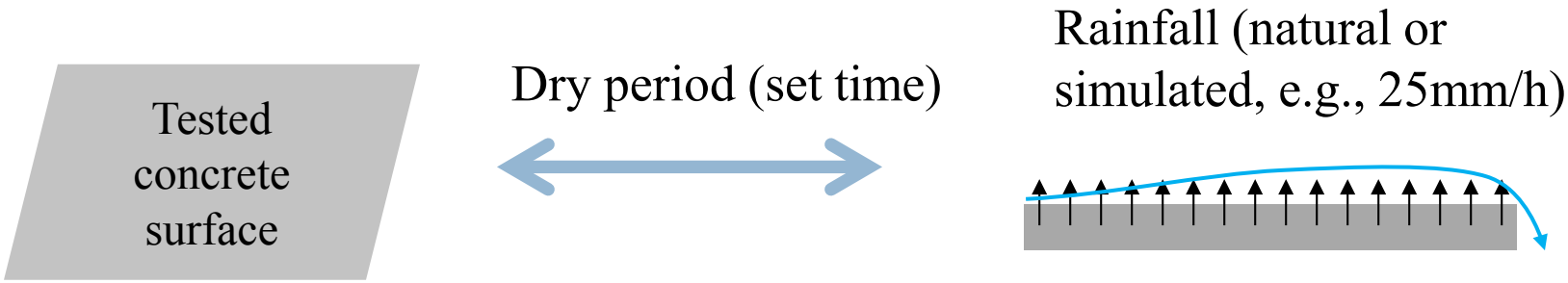


- Washoff tests and implications
- Empirical functions to fit experimental data
- Effective $K_d$ approach
- Development & application of a semi-mechanistic model

# Washoff tests on impervious surface



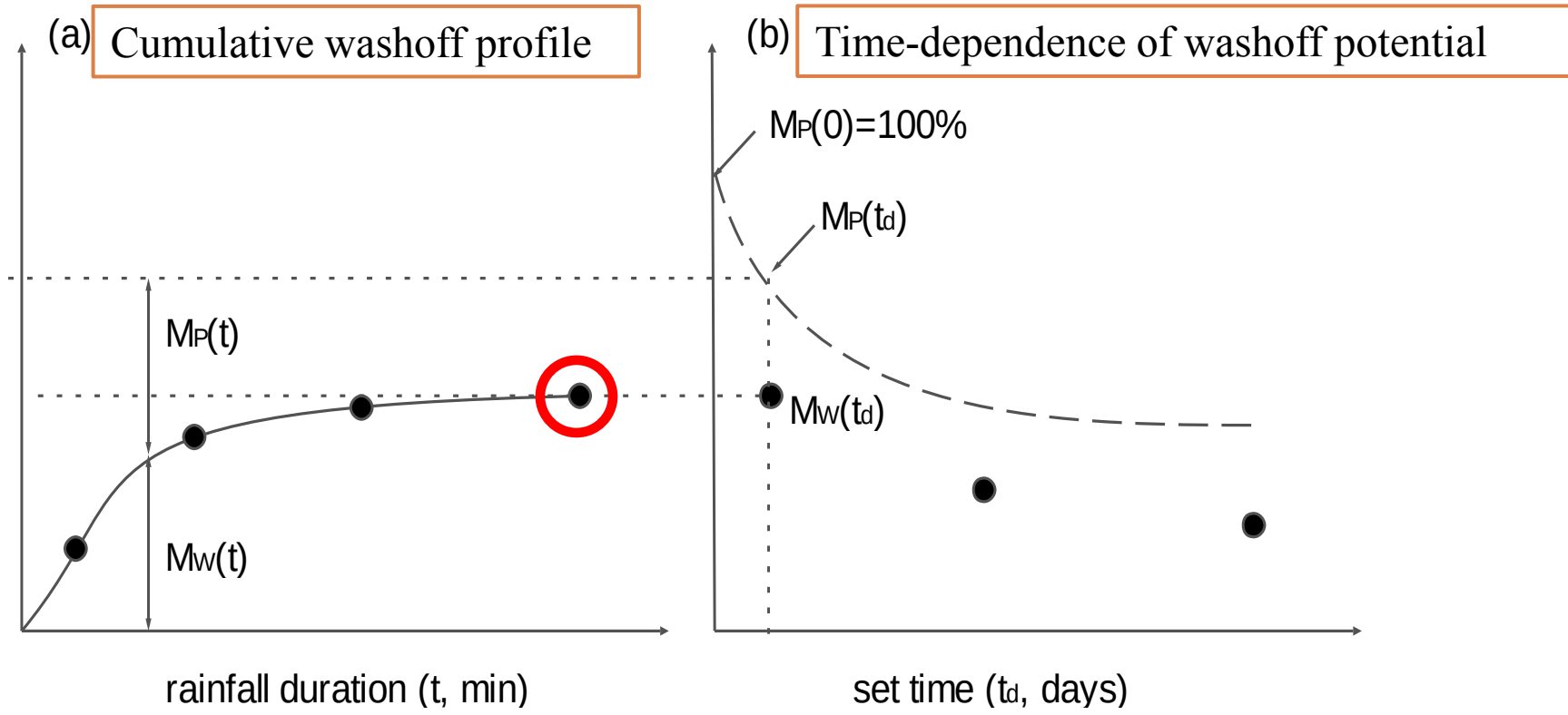
1. Pesticide application
2. Dry period
3. Runoff test




Tested concrete surfaces (40cm*60cm or 80*80cm), uniformly treated with pesticide

# Washoff profile and potential






- $M_W(t)$: measured washoff mass under experiment settings
- $M_P(t_d)$: washoff potential (a theoretical value of mass available for washing)
- Two systems of time: t (rainfall duration), $t_d$ (dry period)

# Data sources & Acknowledgements

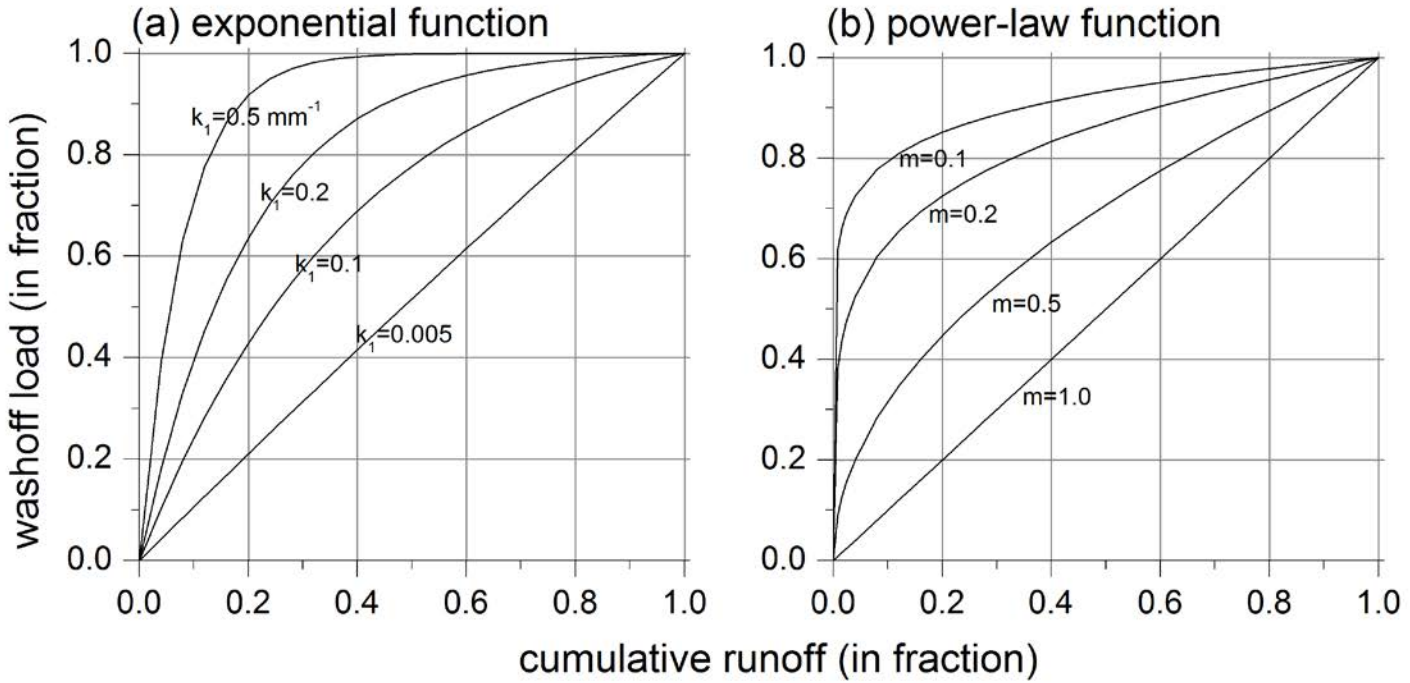


- CDPR research contracts on urban pesticide transport (http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts.htm)
  - 13-0052; 13-0002; 11-0111; 11-0086; 10-0121; 10-0085; 08-0085; 06-0129; 06-0086; 05-0408
- Washoff data for insecticide from impervious surfaces: bifenthrin, beta-cyfluthrin, carbaryl, esfenvalerate, fipronil, imidacloprid, lambda-cyhalothrin, permethrin, and malathion (Jorgenson and Young, 2010, Thuyet et al., 2012, Jiang et al., 2012, Luo et al., 2014)
- Collaborators: Drs. Brant Jorgenson, Dang Q Thuyet, Thomas Young (UC Davis), Tim Jiang, Jay Gan (UC Riverside)

# Empirical functions



- Exponential function: $M_W=M_P*[1-\exp(-\mathbf{k_1}R)]$
- Power-law function: $M_W=M_P*R^{\mathbf{m}}$

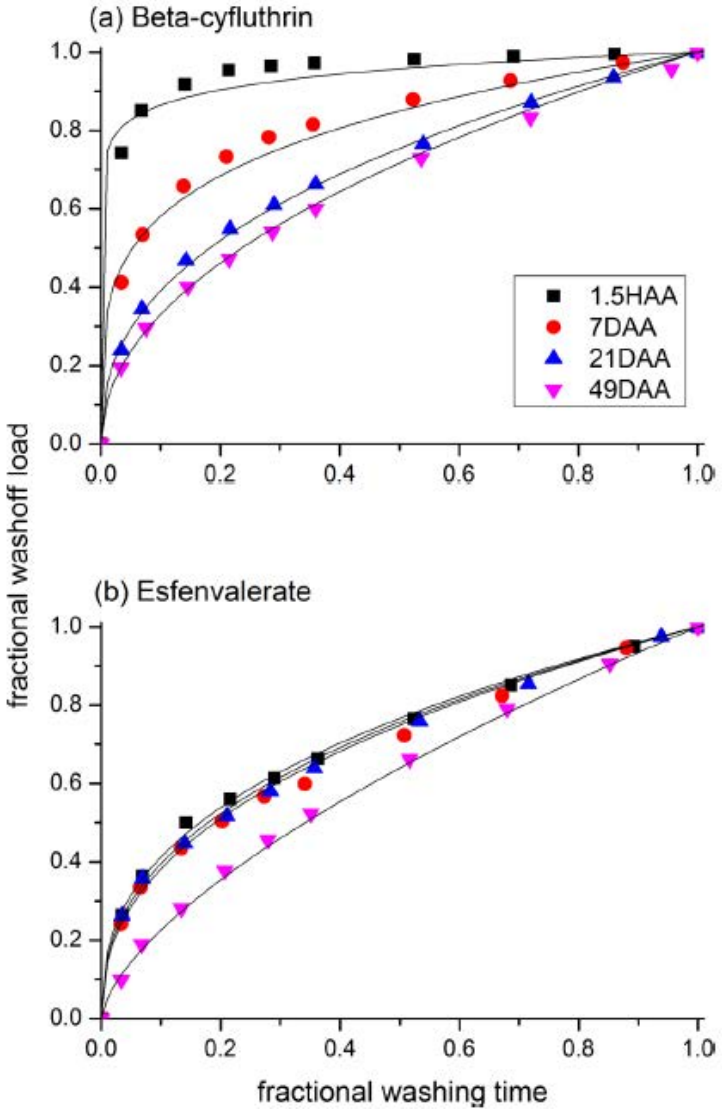



*Notes: $M_W$=cumulative washoff mass, $M_P$=washoff potential, R=cumulative runoff (m), $k_1$ & m =coefficients (Luo, in press)*

# Data fitting

(1) **Different** initial coefficients
(2) General trend with set time, but with **different** slopes






*Parameterization of first-flush events by power-law functions:* $M_W = M_P * R^m$

| | "m" @ set time of | | |
|---|---|---|---|
| | 1.5h | 1d | 7d |
| bifenthrin | .066 | .214 | - |
| β-cyfluthrin | .078 | .118 | .181 |
| carbaryl | .184 | .512 | .726 |
| Esfenvalerate | .381 | .485 | .452 |
| Imidacloprid | .353 | .509 | .503 |
| λ-cyhalothrin | .330 | .440 | .531 |
| malathion | .388 | .354 | .714 |

(Luo et al., 2014)

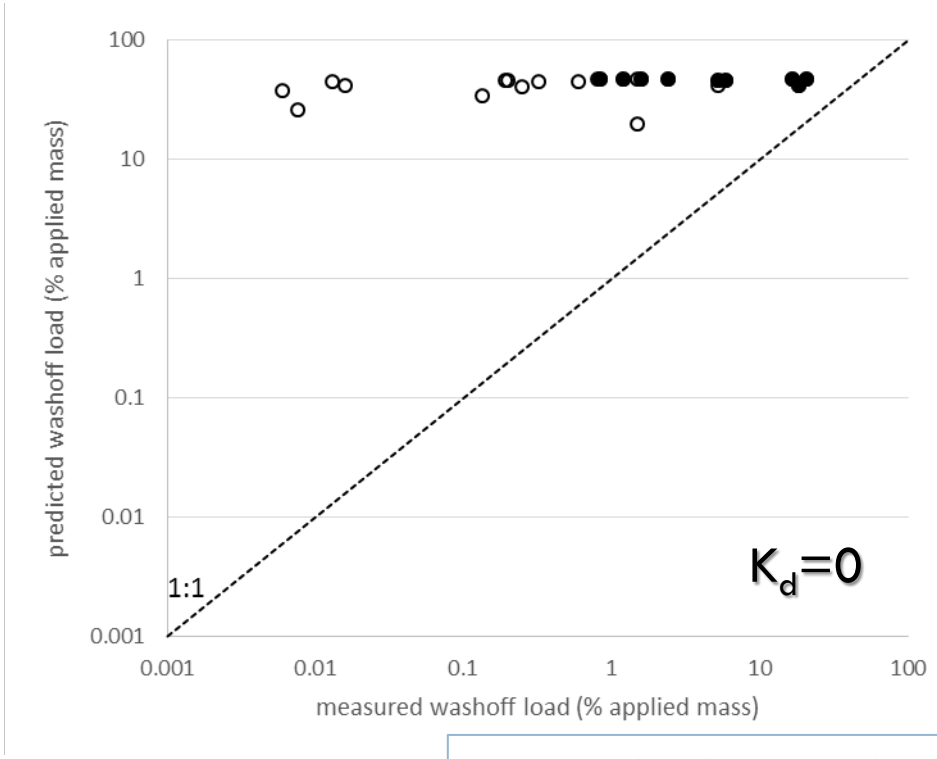
# Approach with "effective" $K_d$



- Extension of modeling approaches for pervious surfaces (i.e., ag. fields) to impervious surfaces
- Tested model: USEPA regulatory model PRZM (Pesticide Root-Zone Model) and its modeling scenario for "*San Francisco impervious surface*"
- Transferability settings
  1) Partitioning coefficient $K_d$=0 (extremely mobile)
  2) Reported soil $K_d$
  3) Calibrated $K_d$ from washoff experimental data

# Results for various $K_d$ settings

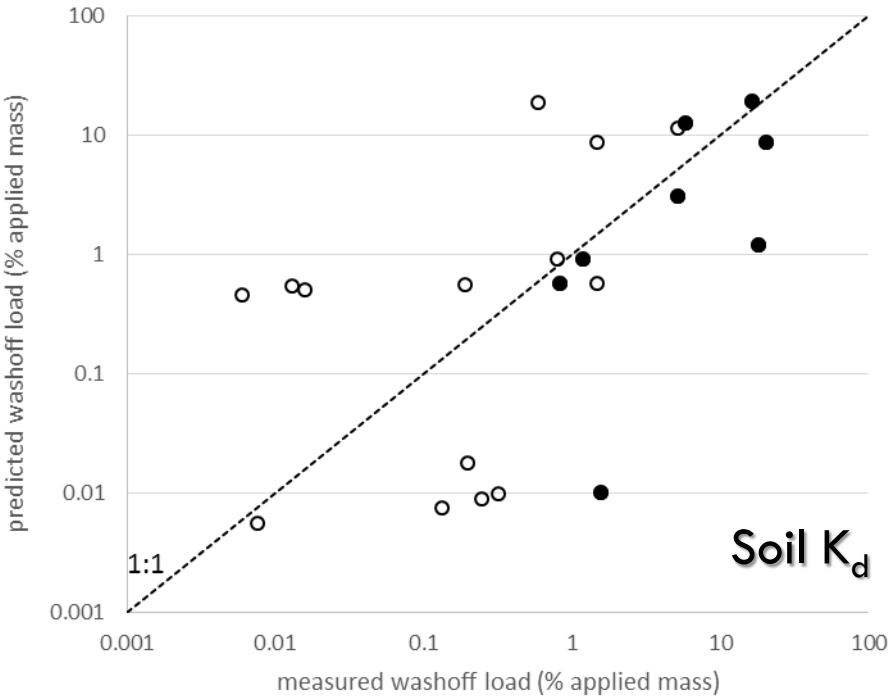





9 insecticides, set time of 1~89 days

- ● data at 1DAA (day after application)
- o >= 7DAA

(Luo, in press)

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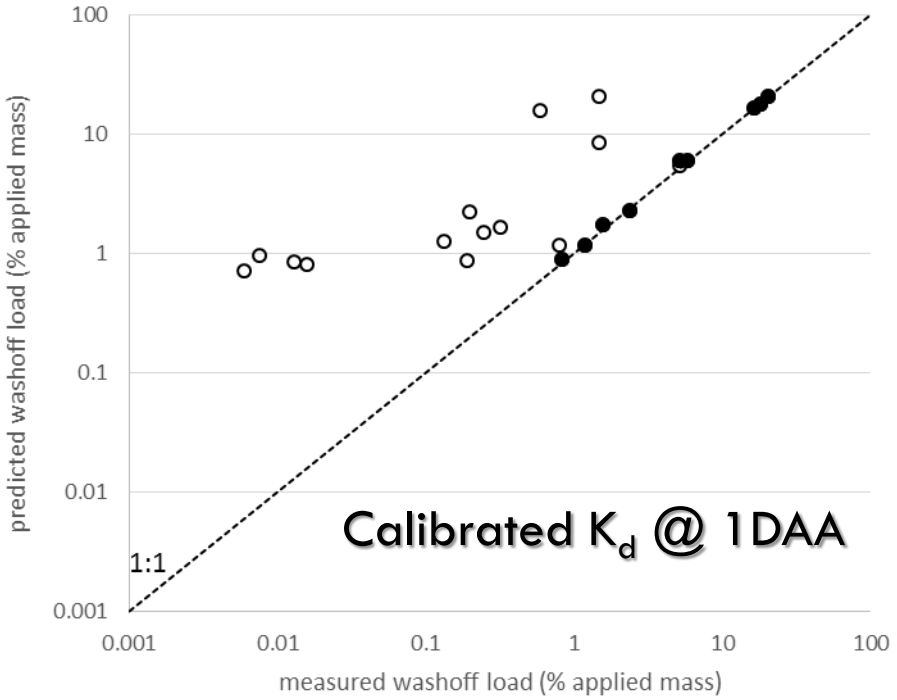


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- o >= 7DAA

# A semi-mechanistic model



- Washoff potential: First-order kinetics with a time-variable dissipation rate constant
  - Initial value, K(0)
  - Time-dependence: $K(t_d)=K(0)*M_P(t_d)$
- Washoff profile: 1D diffusion equation with a time-variable mass transfer coefficient (MTC)
  - Initial value: D(0)
  - Time-dependence: $D(t)=D(0)*t^{[1-s*M_P(t_d)]}$

Note: parameters are defined for a product (not AI) AND a set of environmental configurations

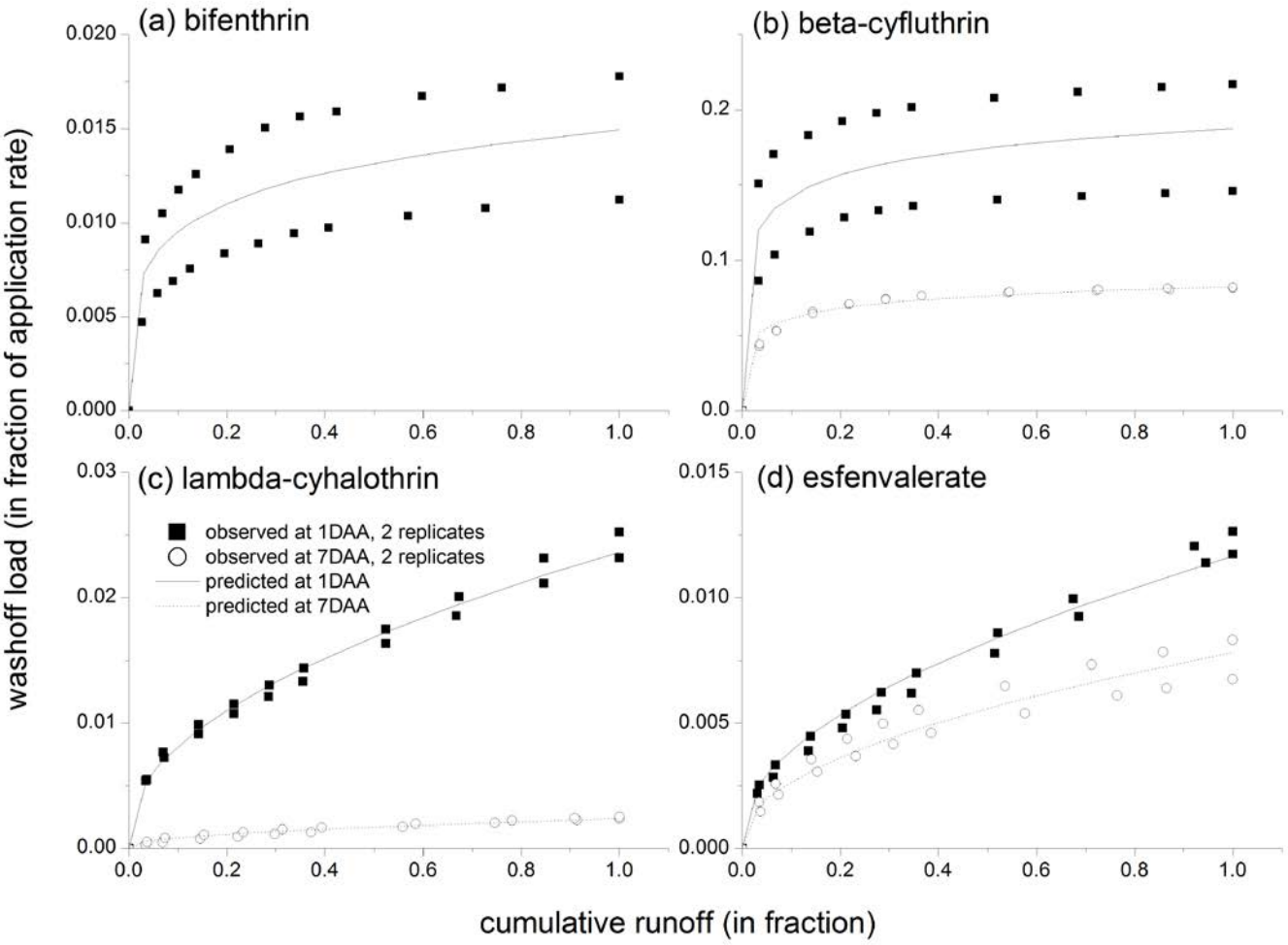
# Model applications



- Insecticides: bifenthrin, beta-cyfluthrin, carbaryl, esfenvalerate, fipronil, imidacloprid, lambda-cyhalothrin, permethrin, and malathion ($\log K_{OW}$=0.6~6.9)
- Settings: 100+ rainfall events (@25mm/h for 1h), under single and repeated (1~7 times) rainfall events with set time of 1.5h~238d after application.

# Modeling results, first flush





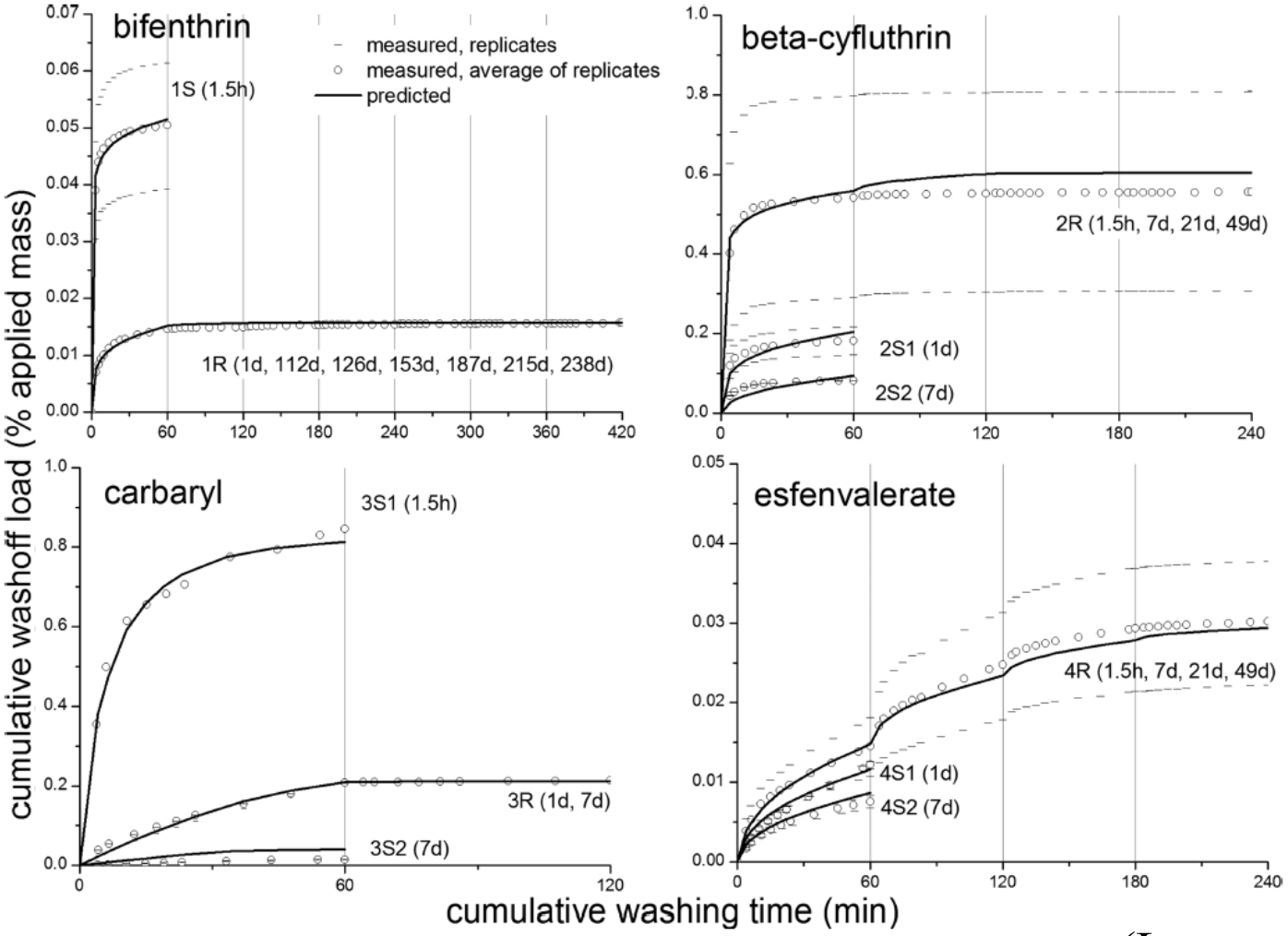

(Luo et al., 2013)

| Products | Model parameters | | | Model performance | |
|---|---|---|---|---|---|
| | D(0) | K(0) | s | CV[RMSE] | NSE |
| bifenthrin | 5.65E-07 | 0.601 | 0.451 | 0.027 | 0.998 |
| beta-cyfluthrin | 1.04E-04 | 0.694 | 0.436 | 0.069 | 0.994 |
| lambda-cyhalothrin | 8.31E-07 | 1.487 | 0.107 | 0.099 | 0.989 |
| esfenvalerate | 4.53E-08 | 0.070 | 0.052 | 0.085 | 0.980 |

CV[RMSE] = coefficient of variation (CV) of root-mean-square error (RMSE)
NSE = Nash-Sutcliffe model efficiency coefficient

# Modeling results, repeated rainfall





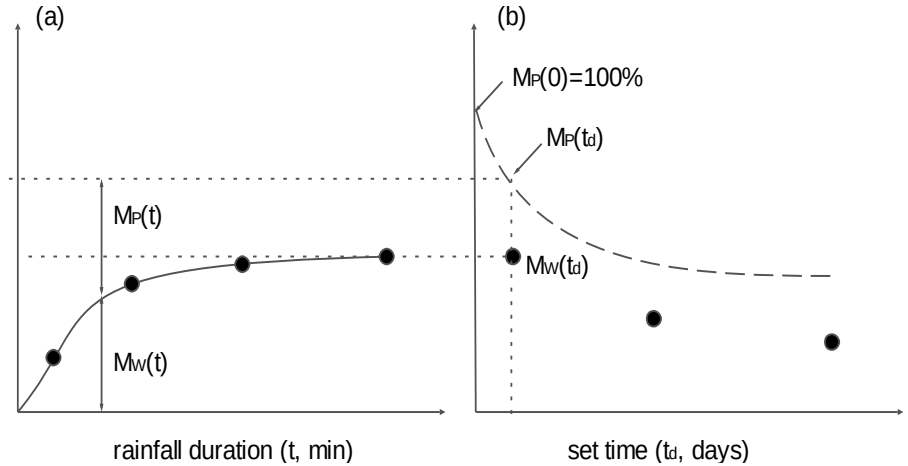

(Luo et al., 2014)

| Pesticide | calibration (first rainfall) | | validation (repeated rainfall) | |
|---|---|---|---|---|
| | CV[RMSE] | NSE | CV[RMSE] | NSE |
| bifenthrin | 0.027 | 0.998 | 0.026 | 0.974 |
| $\beta$-cyfluthrin | 0.069 | 0.994 | 0.075 | 0.782 |
| carbaryl | 0.069 | 0.997 | 0.048 | 0.987 |
| esfenvalerate | 0.085 | 0.980 | 0.047 | 0.986 |
| fipronil | 0.060 | 0.993 | 0.076 | 0.969 |
| imidacloprid | 0.064 | 0.998 | 0.052 | 0.977 |
| $\lambda$-cyhalothrin | 0.099 | 0.989 | NA[c] | NA[c] |
| malathion | 0.063 | 0.997 | 0.078 | 0.942 |

# Summary



- Need more data (in addition to the commonly reported physiochemical properties for pesticides)
- Minimal set of parameters
  - At least one washoff profile shortly (e.g., 1d) after application: conservative estimation of transferability
  - Multiple tests for total washoff mass during a period (e.g., soil photolysis HL), to avoid underestimation by initial, quick dissipation



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  - Thuyet et al., 2012, Sci Total Environ, 414(1): 515-24
  - Jiang et al., 2012, Water Res, 46(3): 645-52
- Modeling work
  - Luo et al., 2013, Water Res, 47(9): 3163-72
  - Luo et al., 2014, ES&T, 48(1): 234-243
  - Luo, ACS Symposium Series Chapter, in press



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