Pesticide Runoff from Concrete Surfaces

-- A Field-Scale Study & Environmental Implications

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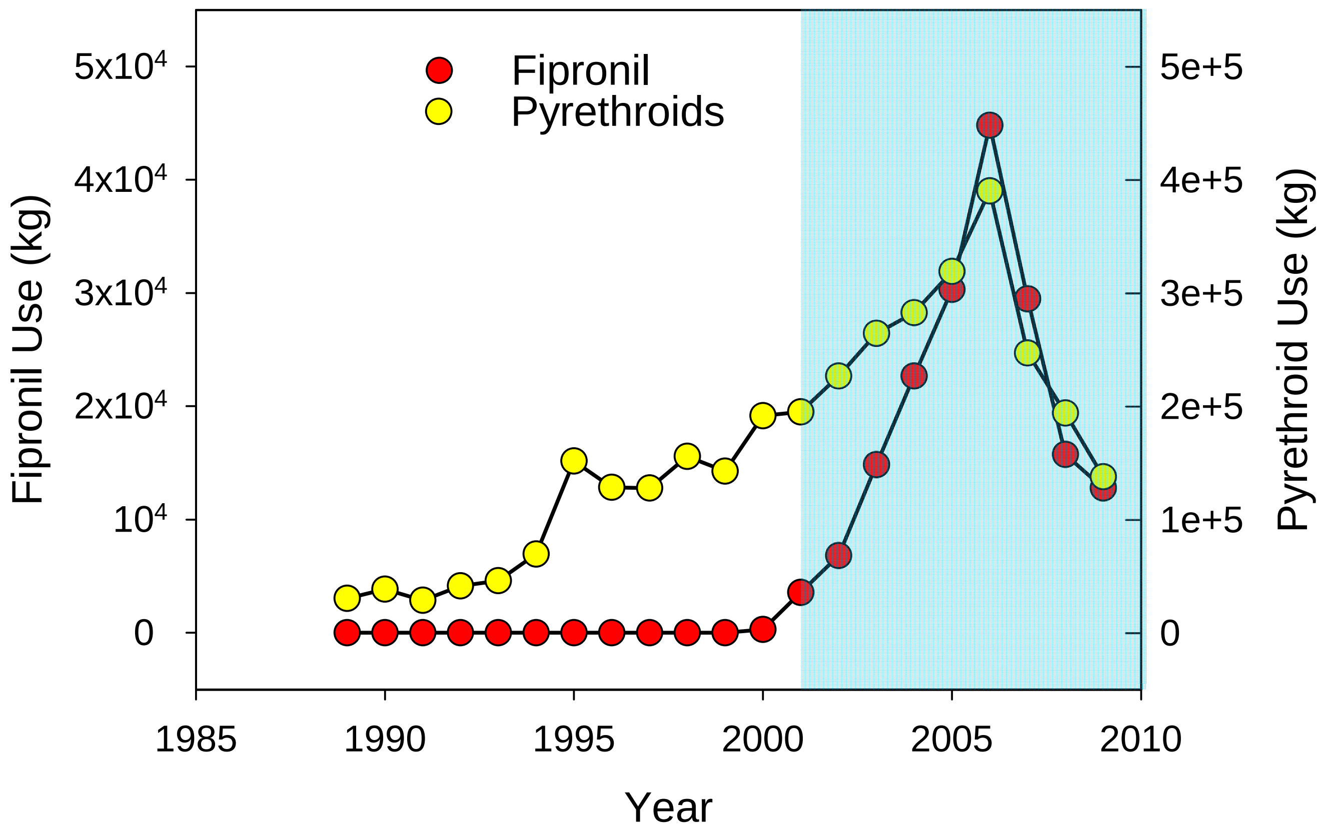
Pesticide Use in Urban and Residential Areas

- **Pyrethroid and fipronil use by licensed applicators for structural pest control and landscape maintenance in California**



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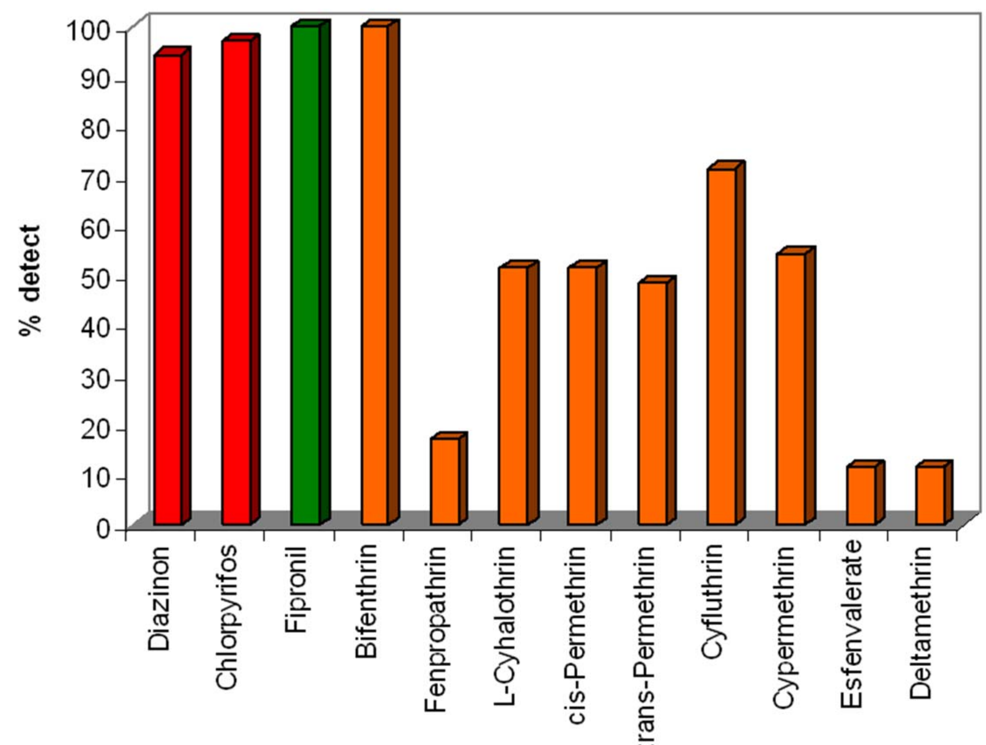
Pesticide Contamination in Urban Areas

class[a]	insecticide name	N[b]	detection frequency (%)
PP	fipronil	478	40
OC	γ-chlordane	478	74
OC	α-chlordane	478	69
OC	p,p′-DDT	422	41
OC	p,p′-DDE	478	33
OC	heptachlor	478	13
OP	chlorpyrifos	479	78
OP	diazinon	480	35
OP	malathion	480	15
PY	*cis*-permethrin	459	89
PY	*trans*-permethrin	448	88
PY	cypermethrin	480	46
PY	bifenthrin	466	33
PY	deltamethrin	468	27
PY	sumithrin	468	22
PY	λ-cyhalothrin	467	21
PY	cyfluthrin	480	17
PY	esfenvalerate	468	15
PY	tetramethrin	480	15
PY	allethrin	468	7
PY	pyrethrin I	467	5
PY	fenpropathrin	479	4
PY	imiprothrin	468	3
PY	pyrethrin II	468	2
PY	prallethrin	468	1
PY	resmethrin	467	0.4
SYN	PBO[d]	475	52

Pesticides on indoor surfaces



Southern California

Pesticides in Urban Runoff

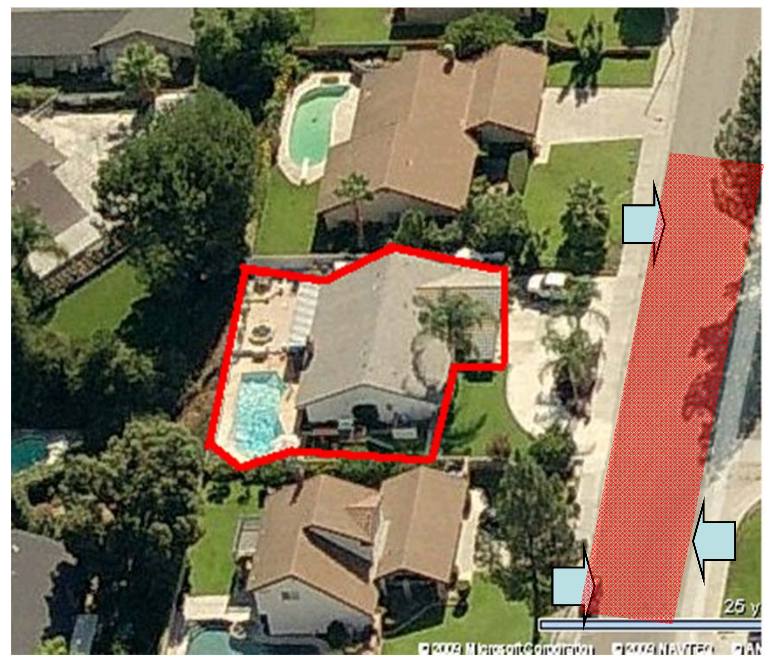
Stout et al., *Environ Sci Technol*, 2009; unpublished data

Hard Surfaces in Urban Areas

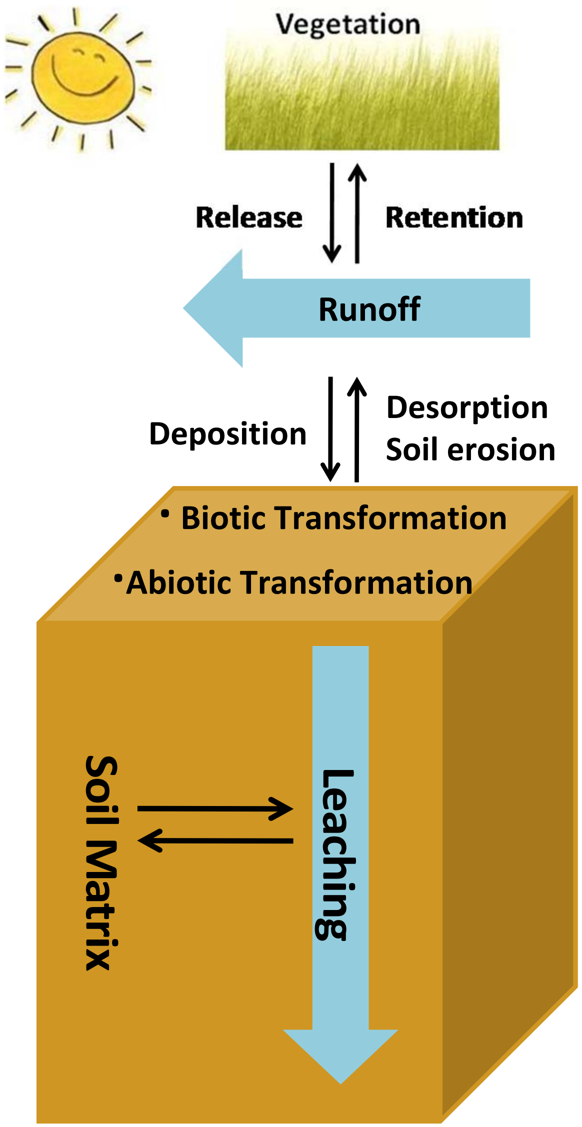
- **Impermeability**
  - **Low** water penetration rate
  - To facilitate **rapid** urban surface drainage

- **Up to 90 % of urban surface areas**

- **Pesticide deposition on hard surfaces**
  - **Direct** application
  - Wind/water facilitated transport



Fate of Insecticides in Soils



- **Impervious surfaces**
  - Larger runoff flow
  - Higher pressure to neighboring soils
- **No vegetation growth**
  - Higher insecticide runoff potential
- **Different environment for insecticides**
  - Different persistence and runoff potential than soil
- **Highly populated areas**
  - Fragile water bodies
  - Higher ecological/environmental importance

Highlights from Some Pilot Studies

Environ. Sci. Technol. 2011, 45, 602–607

Sorption and Desorption of Pyrethroid Insecticide Permethrin on Concrete

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Use of pesticides around residential homes is linked to contamination of urban waterways, where impervious surfaces like concrete are considered as sources or facilitators of the contamination. However, the fate of pesticides on urban hard surfaces is poorly understood. We characterized sorption and desorption of permethrin, the most used pyrethroid insecticide, on concrete surfaces, to understand its availability for contaminating runoff water. Sorption of ^{14}C-permethrin to concrete was rapid, and the surface area-normalized K_d ...

California, with bifenthrin and permethrin as the most frequently detected (3). In California, the total amount of pyrethroids used by licensed applicators for structural pest control and landscape maintenance increased from 30 730 kg in 1989 to 247 300 kg in 2007, and over 48% of the use was permethrin, an active ingredient found in numerous commercial formulations (7).

Although direct evidence is absent, impervious hard surfaces are considered a primary factor in urban contaminant transport. Urbanized areas are characterized by artificial impervious surfaces, such as concrete that may account for up to 90% of the total urban area in ...

Environ. Sci. Technol. 2010, 44, 4951

Formulation Effects and the Off-Target Transport of Pyrethroid Insecticides from Urban Hard Surfaces

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Received January 21, 2010. Revised manuscript received April 5, 2010. Accepted May 18, 2010.

Controlled rainfall experiments utilizing drop-forming rainfall simulators were conducted to study various factors contributing to off-target transport of off-the-shelf formulated pyrethroid insecticides from concrete surfaces. Factors evaluated included active ingredient, product formulation, time between application and rainfall (set time), and rainfall intensity. As much as 60% and as little as 0.8% of pyrethroid applied could be recovered in surface runoff depending primarily on product formulation, and to a lesser extent on product set time. Resulting wash-off profiles during one-hour storm simulations could be categorized based on formulation, with formulations utilizing emulsifying surfactants rather than organic solvents resulting in unique wash-off profiles with overall higher wash-off efficiency. These higher wash-off efficiency profiles were qualitatively replicated by applying formulation-free neat pyrethroid in the presence of independently applied linear alkyl benzene sulfonate (LAS) surfactant, suggesting that the surfactant component of some formulated products may be influential in pyrethroid wash-off from urban hard surfaces.

Introduction

Studies conducted throughout the nation have documented pyrethroid insecticide concentrations in urban waterways that exceed known toxicity thresholds for the protection of aquatic life (1–3). In a specific urban watershed study conducted in the Central Valley of California, pyrethroid insecticides detected in urban creek sediments were found to significantly correlate with acute mortality in amphipod-based toxicity bioassays, with a strong proximal relationship to residential development and associated stormwater outfalls (1). Pyrethroid-related sediment toxicity has similarly been observed from single-family home dominated urban watersheds in central Texas (3). In a targeted urban monitoring study, chemical analysis of both dry- and wet-weather runoff from single-family homes in California's central valley consistently detected pyrethroid insecticides, with frequent detections of bifenthrin, permethrin, and cyfluthrin (4). These studies point to applications on residential landscapes and structures as likely sources of pyrethroid insecticides in urban streams.

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Urban Pesticides Risk Assessment and Management

WASH-OFF POTENTIAL OF URBAN USE INSECTICIDES ON CONCRETE SURFACES

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(Submitted 17 March 2009; Returned for Revision 19 May 2009; Accepted 18 June 2009)

Abstract—Contamination of surface aquatic systems by insecticides is an emerging concern in urban watersheds, but sources of contamination are poorly understood, hindering development of regulatory or mitigation strategies. Hardscapes such as concrete surfaces are considered an important facilitator for pesticide runoff following applications around homes. However, pesticide behavior on concrete has seldom been studied, and standardized evaluation methods are nonexistent. In the present study, a simple batch method for measuring pesticide wash-off potential from concrete surfaces was developed, and the dependence of washable pesticide residues was evaluated on pesticide types, formulations, time exposed to outdoor conditions, and number of washing cycles. After application to concrete, the washable fraction of four pyrethroids (bifenthrin, permethrin, cyfluthrin, and cyhalothrin) and fipronil rapidly decreased, with half-lives ≤3 d, likely due to irreversible retention in micropores below the concrete surface. The initial fast decrease was followed by a much slower declining phase with half-lives ranging from one week to two months, and detectable residues were still found in the wash-off solution for most treatments after 112 d. The slow decrease may be attributed to a fraction of pesticides being isolated from degradation or volatilization after retention below the concrete surface. Wash-off potential was consistently higher for solid formulations than for liquid formulations, implying an increased runoff contamination risk for granular and powder formulations. Trace levels of pyrethroids were detected in the wash-off solution even after 14 washing–drying cycles over 42 d under outdoor conditions. Results from the present study suggest that pesticide residues remain on concrete and are available for contaminating runoff for a prolonged time. Mechanisms for the long persistence were not clearly known from the present study and merit further investigation. Environ. Toxicol. Chem. 2010;29:1203–1208. © 2010 SETAC

Keywords—Urban pesticides, Pyrethroids, Fipronil, Hardscapes, Pesticide runoff

INTRODUCTION

Insecticides are widely used in urban areas for control of vector, structural, and other insects. Owing to potential adverse health or ecological effects, many historically important pesticides, including many organochlorines and some organophosphates (e.g., diazinon and chlorpyrifos) have been discontinued for residential use in the United States [1,2]. Consequently, the use of replacement insecticides such as pyrethroids and fipronil has increased in recent years. For example, most insecticides sold in retail stores for residential use in California, USA, contain pyrethroids as active ingredients ([3,4]; http://www.up3project.org/documents/Final2005ShelfSurvey.pdf). The total amounts of pyrethroids and fipronil reported by licensed applicators for structural pest control and landscape maintenance in California increased from 195,360 kg and 3,560 kg, respectively, in 2001 to 247,295 kg and 29,478 kg, respectively, in 2007 ([5]; http://www.cdpr.ca.gov/docs/pur/purs07rep/07_pur.htm). In addition, surveys show that home owners also use significant amounts of pesticides, although the use is very poorly tracked or understood ([6]; http://www.tdcenvironmental.com/UP3%20Use%20Report%202006.pdf).

The widespread use of insecticides in urban areas has apparently contributed to contamination of urban streams, estuaries, and other surface water bodies, and resulted in sediment and water-column toxicities. Recent monitoring studies show almost ubiquitous contamination of urban bed sediments by pyrethroids in California, often at concentrations acutely toxic to benthic invertebrates [2,7,8]. For instance, sediments and water sampled from mouths of urban drains verified the presence of various pyrethroids, and the concentrations were generally far beyond acutely toxic thresholds for aquatic invertebrates [9]. Residues of pyrethroids were found in sediments of various urban creeks in other studies [1]. In addition, fipronil and its metabolites have also been detected in urban streams [10].

Urbanized areas are distinguished by hardscapes, especially concrete surfaces that are generally termed *impervious surfaces* [11]. Such hard surfaces are estimated to account for 20 to 90% of urban surfaces areas, depending on the site design ([11,12]; http://www.cpesc.org/reference/tr55.pdf, [13]; http://www.ci.olympia.wa.us/en/city-utilities/storm-and-surface-water/science-and-innovations.aspx). For instance, impervious surfaces comprise 25 to 60% of surfaces in a typical medium-density, single-family home residential area [13]. Urban hardscapes have low infiltration rates and are designed to facilitate surface runoff that may contain pollutants [11,14–16]. Pesticides may be applied directly to concrete or similar hard surfaces, such as in treatments for ant trail eradication. A survey shows that 60% of residential outdoor pesticides used in regions such as California are for treatments on hard surfaces [3]. In addition, drift during application and wind/water-facilitated transport may also cause pesticides to deposit on hard surfaces [16–18].

Although pesticide fate and transport have been well studied in soil, very little is known about pesticide behavior on hardscapes such as concrete. Basic methods for evaluating pesticide persistence or runoff potentials on hard surfaces are lacking. The general paucity of research on pesticide fate and transport

* To whom correspondence may be addressed (jgan@ucr.edu).
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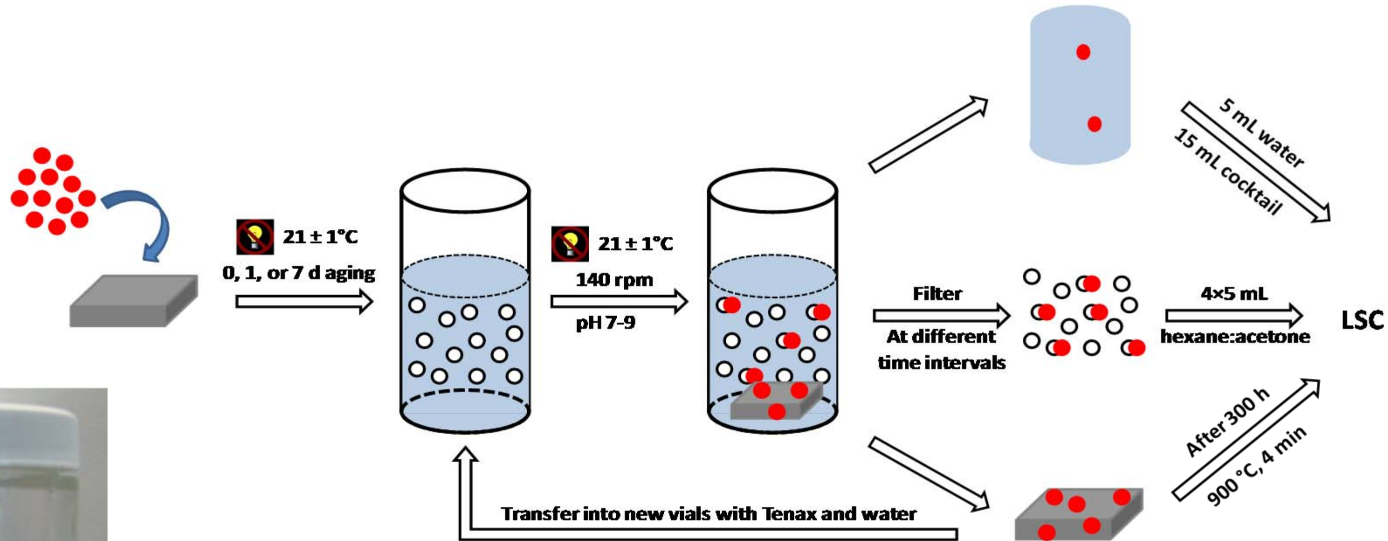
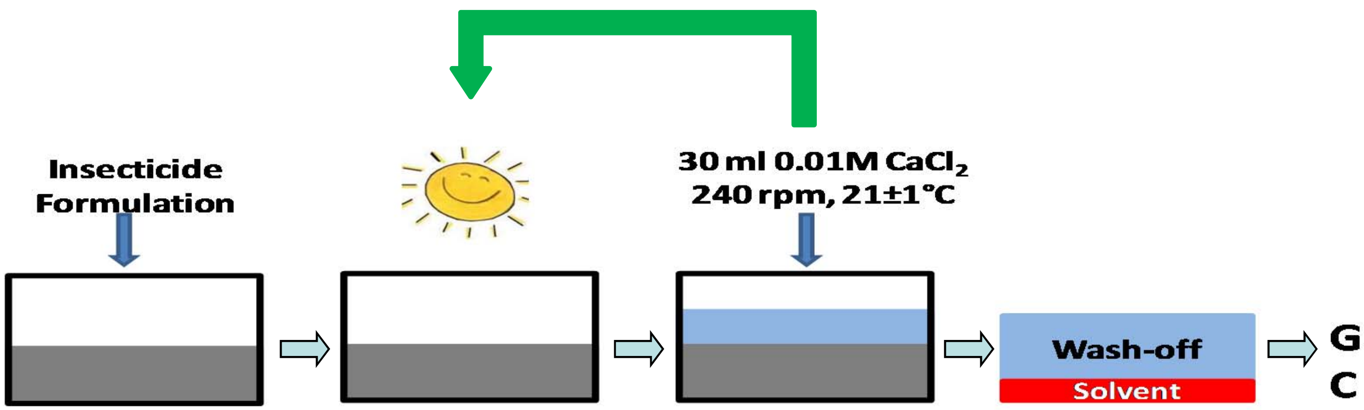

21 ± 1°C
0, 1, or 7 d aging
21 ± 1°C
140 rpm
pH 7-9
Filter
At different time intervals
5 mL water
15 mL cocktail
4×5 mL
hexane:acetone
LSC
After 300 h
900 °C, 4 min
Transfer into new vials with Tenax and water


Insecticide Formulation
30 ml 0.01M $CaCl_2$
240 rpm, 21±1°C
Wash-off
Solvent
G
C

- **Persistent wash-off of pyrethroids and fipronil from concrete**
  - 112 d exposure to hot and dry outdoor conditions
  - >10-time repeated wash-offs

(results published at ***Environ. Toxicol. Chem***., 2010, 1203-1208)

- **Continuous pyrethroid desorption from concrete for over 300 h.**

(results published at ***Environ. Sci. Technol.***, 2011, 602-607)

- **Effects of pesticide formulations on pyrethroid runoff patterns during a continuous runoff event**

(Jorgenson et al., ***Environ. Sci. Technol.***, 2010, 4951-4957)

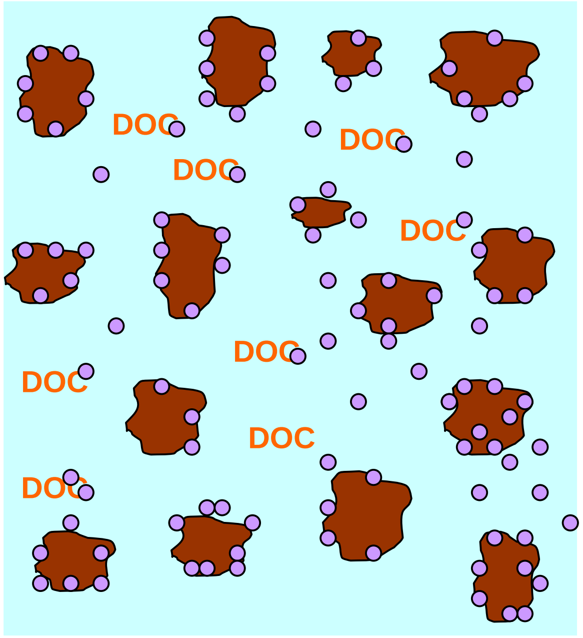
Gap of Knowledge


Sorption and Desorption of Pyrethroid Insecticide Permethrin on Concrete

Formulation Effects and the Off-Target Transport of Pyrethroid Insecticides from Urban Hard Surfaces

WASH-OFF POTENTIAL OF URBAN USE INSECTICIDES ON CONCRETE SURFACES

- Relatively **small** scale of the experiment setup;
- Many **environmental** and **application** factors were not evaluated;
- Non-identified **transport pathway**
  - ✓ **Phase-distribution** of pesticides in the runoff
  - ✓ Contributions of **particles** on pesticide transport
- Methods for pesticide **runoff prediction**
- **Pest control efficacy**
- Occurrence of **degradates** in the runoff



Study objective:

Persistence and runoff transferability of current-use pesticides on concrete surfaces

Specifically,

- **Pesticide runoff pattern**
- **Different application/environmental factors**
- **Runoff prediction**
- **Pest control efficacy**
- **Occurrence of degradates**

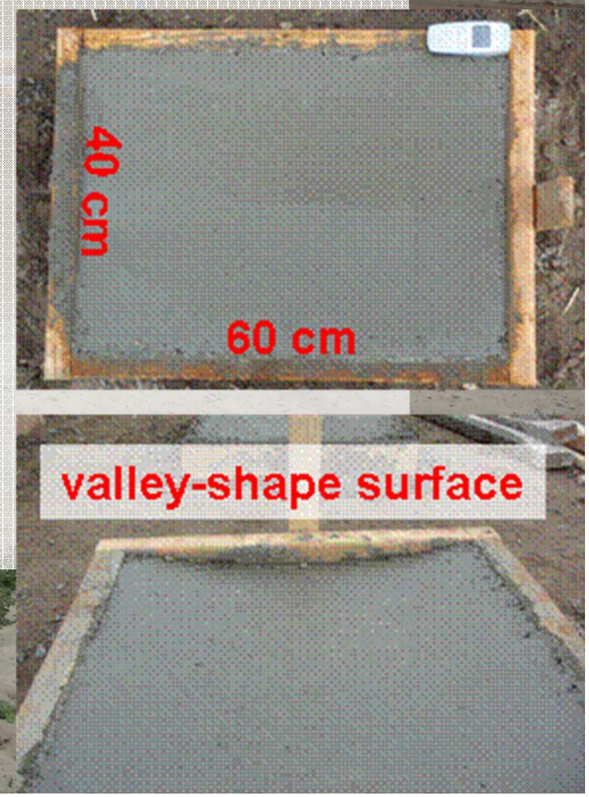
Work of 2010-2011: Field-scale study
Pesticide Runoff from Concrete Surfaces

Experiment Setup & Selection of Pesticides

- Preparation **of concrete slabs**

- **Selection of Pesticides**
  - **Pyrethroids**
    - ✓ **Bifenthrin:** found most frequently in the environment
    - ✓ **Permethrin:** most intensively used
      - *cis*-permethrin
      - *trans*-permethrin
  - **Fipronil**

- **Formulations**
  - Homeowners: Ready-to-use (RTU)
    - ✓ RTU solid
    - ✓ RTU liquid
  - Professional

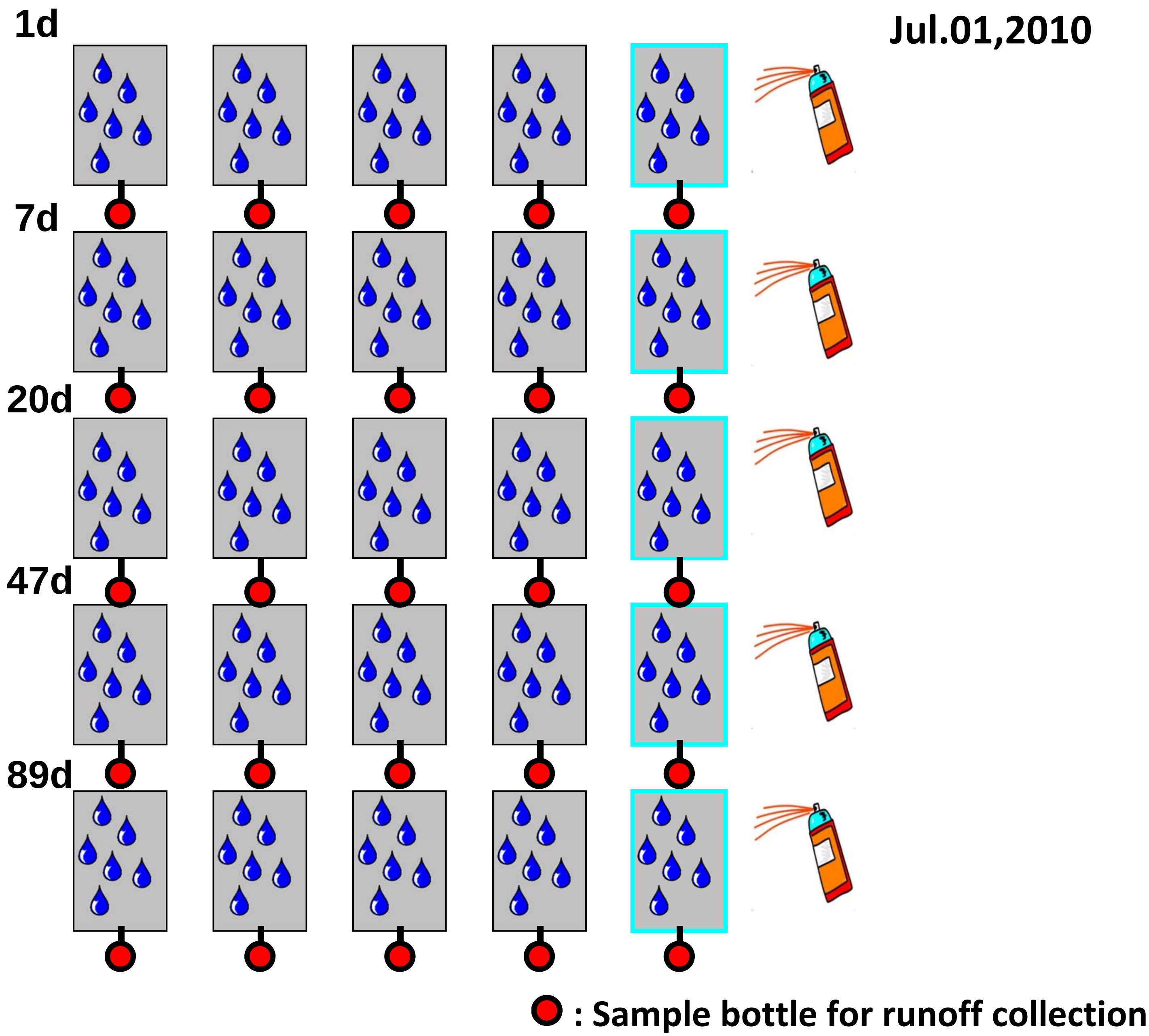


Active Ingredient	Formulation	Application Rate (µg/cm^2)	Trade name
Bifenthrin	RTU granule	3.8	Ortho Home Defense Max, Ortho, Marysville, OH
	RTU liquid	3.5	Ortho Home Defense Max, Ortho, Marysville, OH
	professional	3.2	Talstar® professional, FMC, Philadelphia, PA
Permethrin	RTU dust	175.5	Ortho Ant B GON Dust, Ortho, Marysville, OH
	RTU liquid	248.3	Hot Shot Bedbug and flea home insect killer, Spectrum, St. Louis, MO
	professional	233.3	Tengard® SFR-One shot, United Phosphorus, Inc., King of Prussia, PA
Fipronil	professional	9.47	Termidor®, BASF, Research Triangle Park, NC

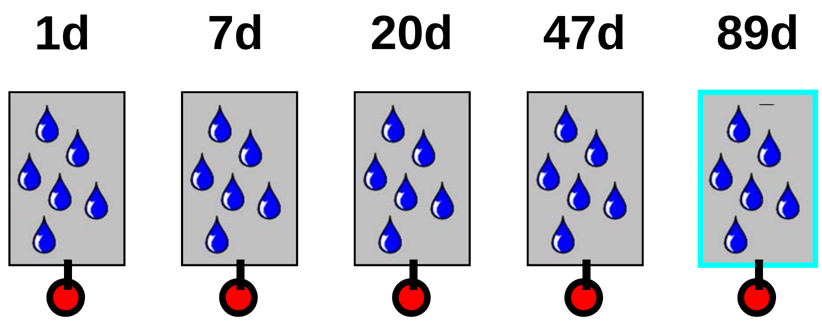
Objective I: Pesticide Runoff Pattern

- **Different types of precipitations**
  - **Simulated**
    - Single-time
    - Repeated
  - **Natural rainfalls**

Single-Time Simulated Rainfall



Repeated Precipitations



Natural Winter Rainfalls

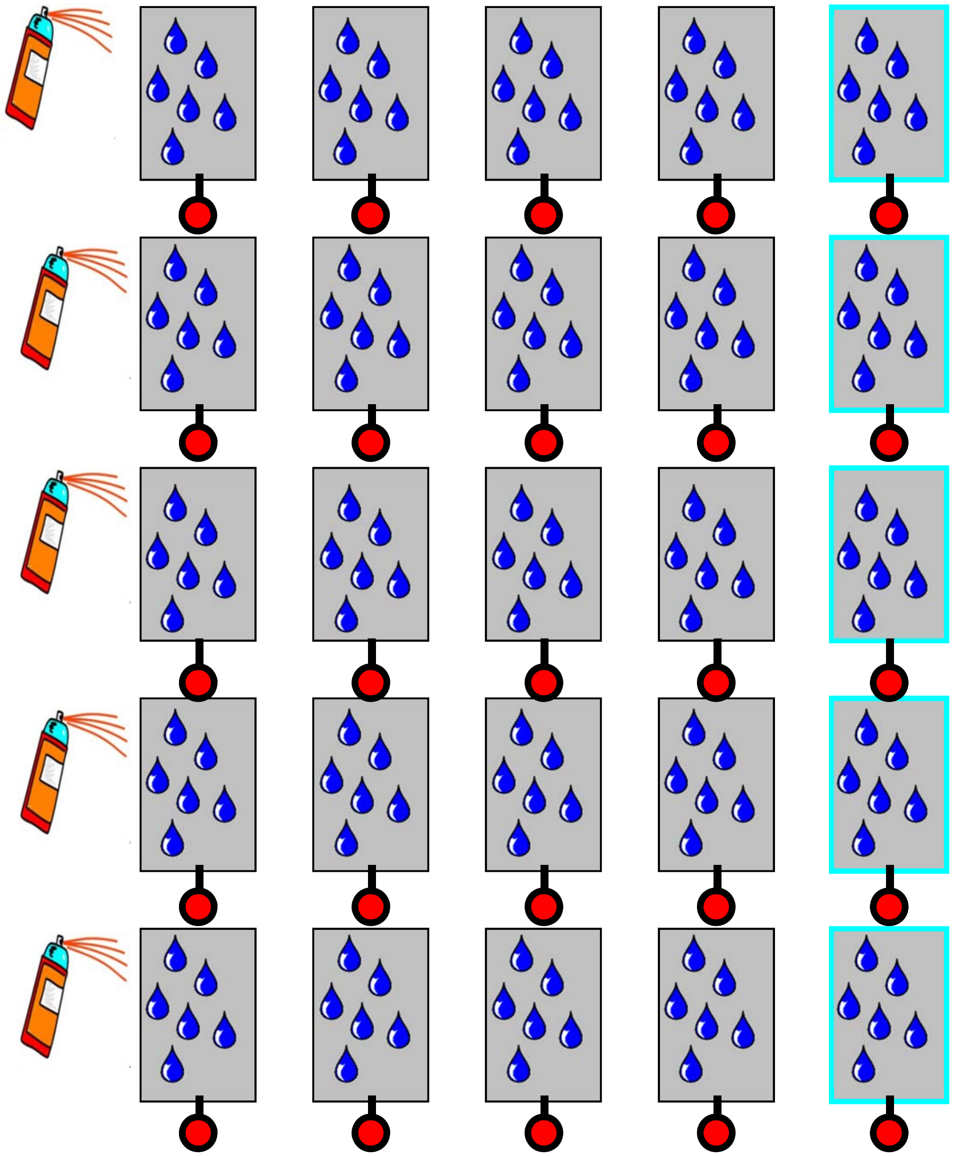
Apr.01, 2010

Jul.01, 2010

Aug.16, 2010

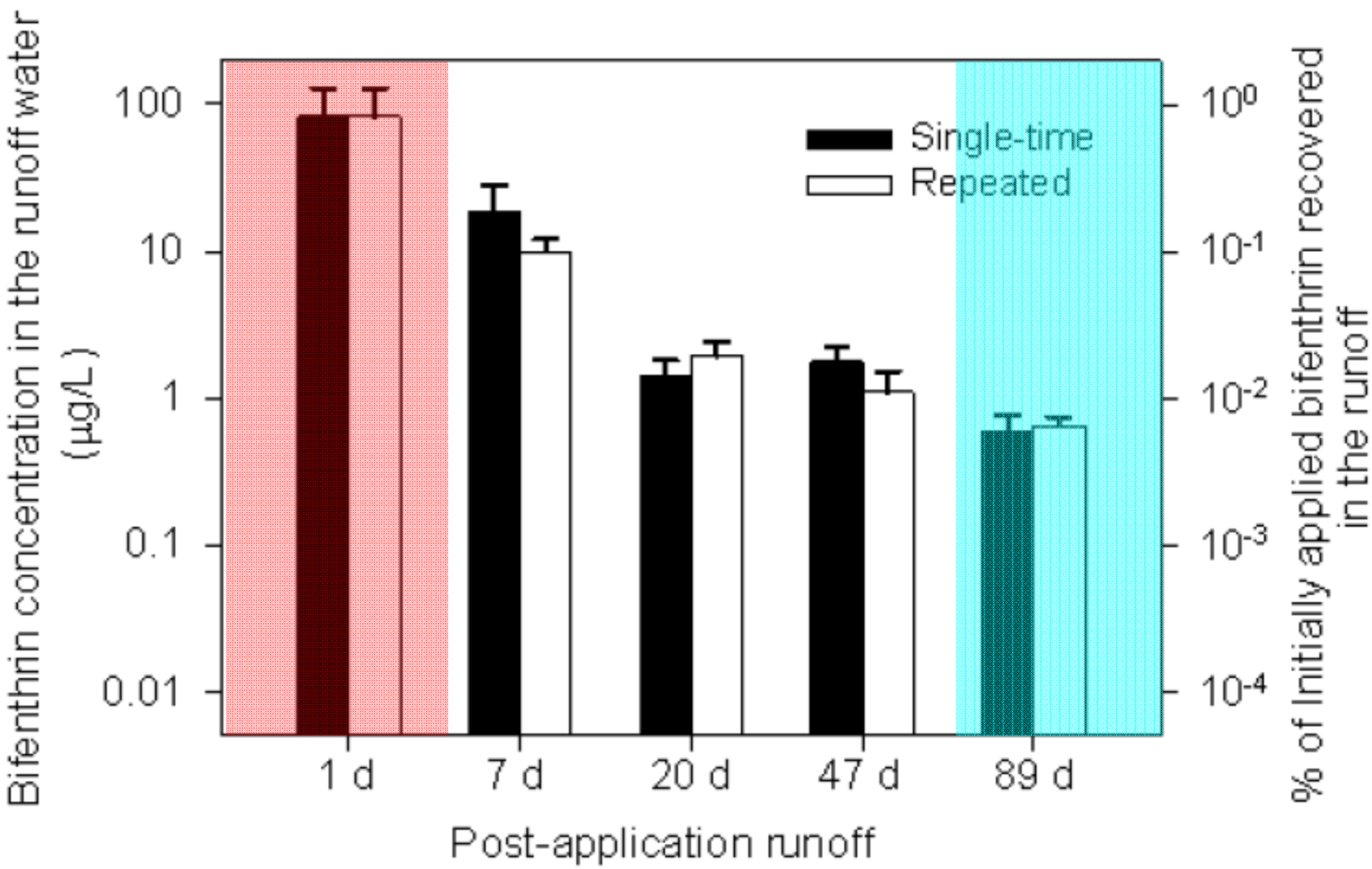
Sept.28, 2010

Nov.01, 2010

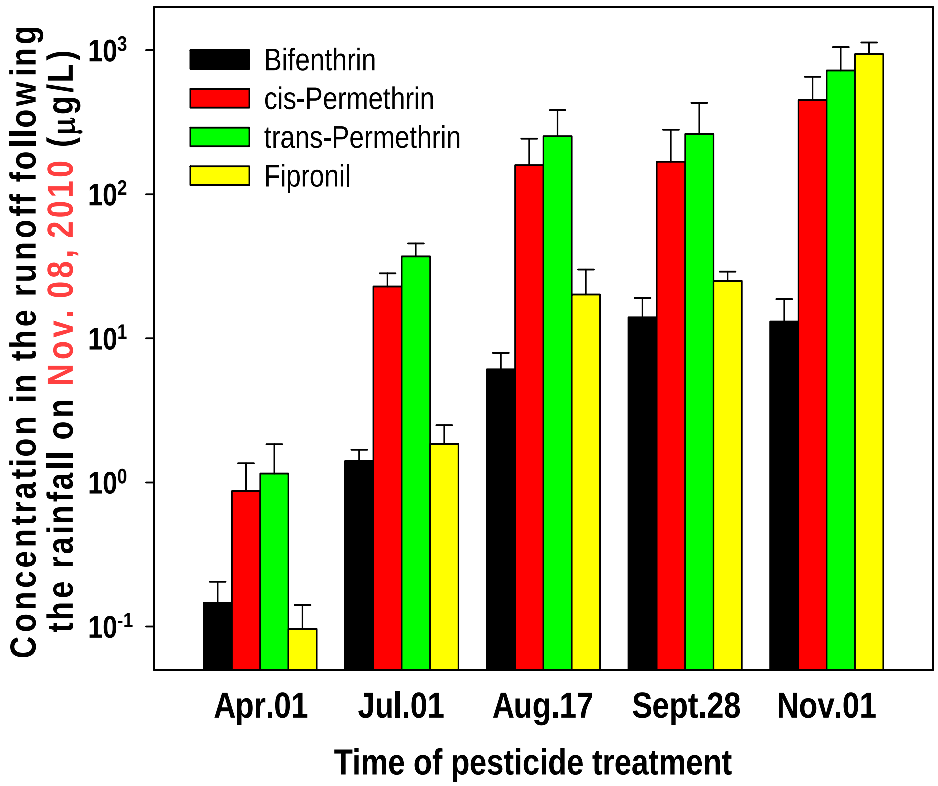


Bifenthrin Runoff from Concrete

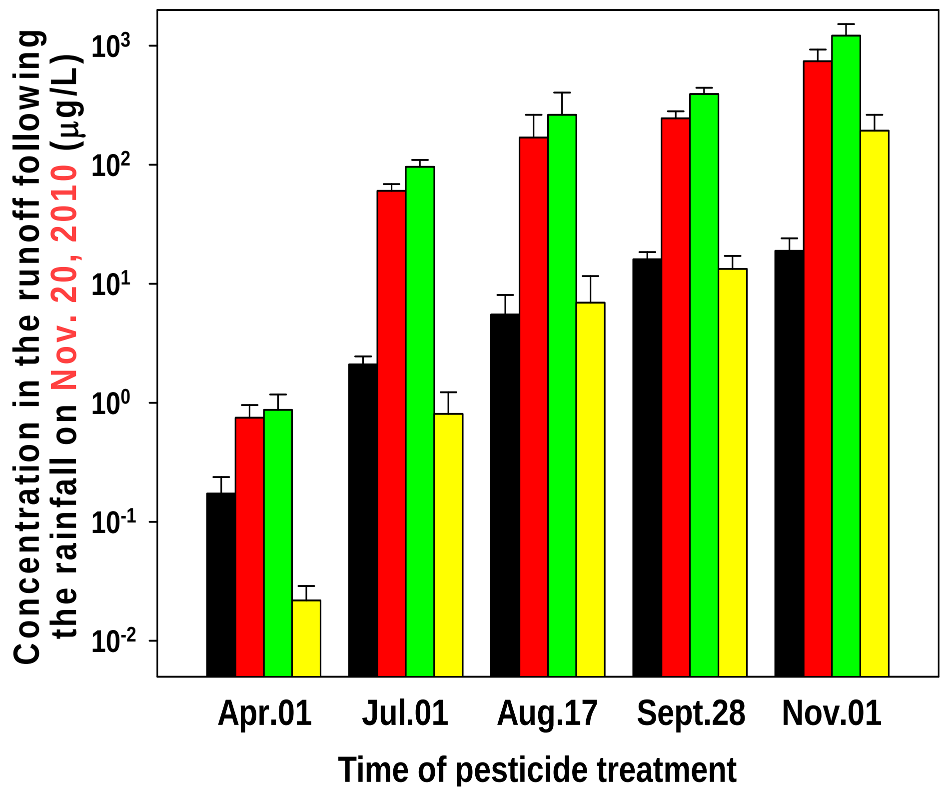
- Treatment conditions:
  - ✓ **Professional formulations**
  - ✓ **26.2 ± 2.7 mm/h, 15min**



Runoff During Winter Rainfalls



Nov.08, 2010



Nov.20, 2010

Loading Patterns through Repeated Precipitations

- First runoff after pesticide treatments, or first flush, contributed **>80%** of total pesticide loadings into the water during the entire study.

Runoff	Post-application exposure (d)	% of the total runoff			
		Bifenthrin	*cis*-Permethrin	*trans*-Permethrin	Fipronil
1st	1	83.29 (5.75)	93.10 (2.94)	90.10 (2.94)	94.85 (2.35)
2nd	7	12.08 (3.88)	4.81 (2.11)	6.29 (2.54)	4.24 (1.88)
3rd	20	2.32 (0.75)	1.25 (0.51)	1.80 (0.67)	0.76 (0.51)
4th	47	1.43 (1.10)	0.53 (0.32)	0.71 (0.46)	0.12 (0.06)
5th	89	0.88 (0.46)	0.30 (0.18)	0.44 (0.24)	0.04 (0.02)

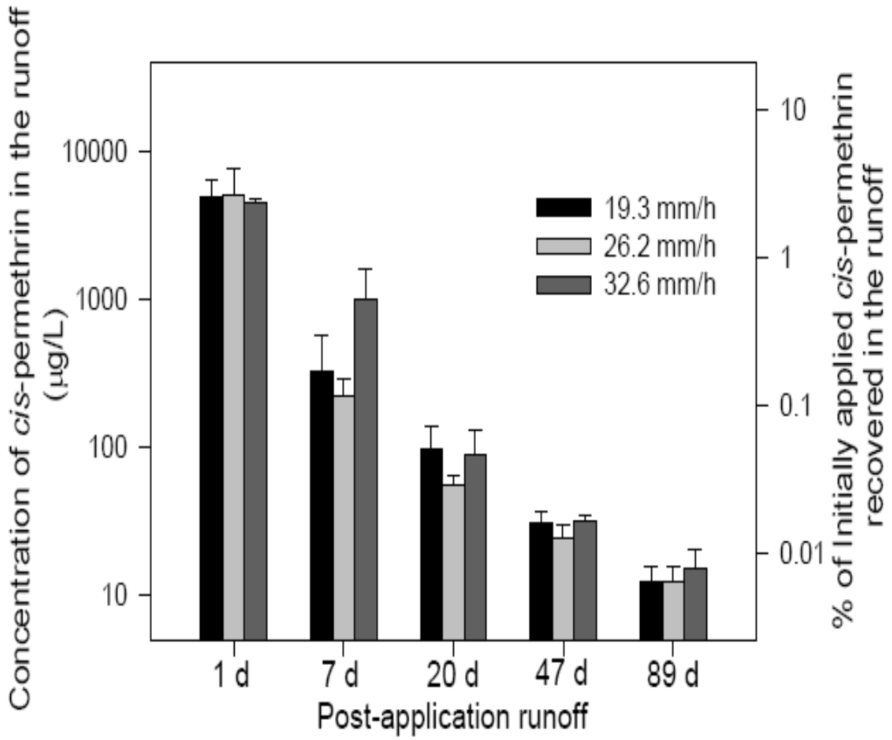
Objective II: Environmental/Application Factors

	Simulated		Natural
	Single-time	Repeated	rainfall
Formulation		X	
Precipitation Intensity		X	X
Concrete modification		X	

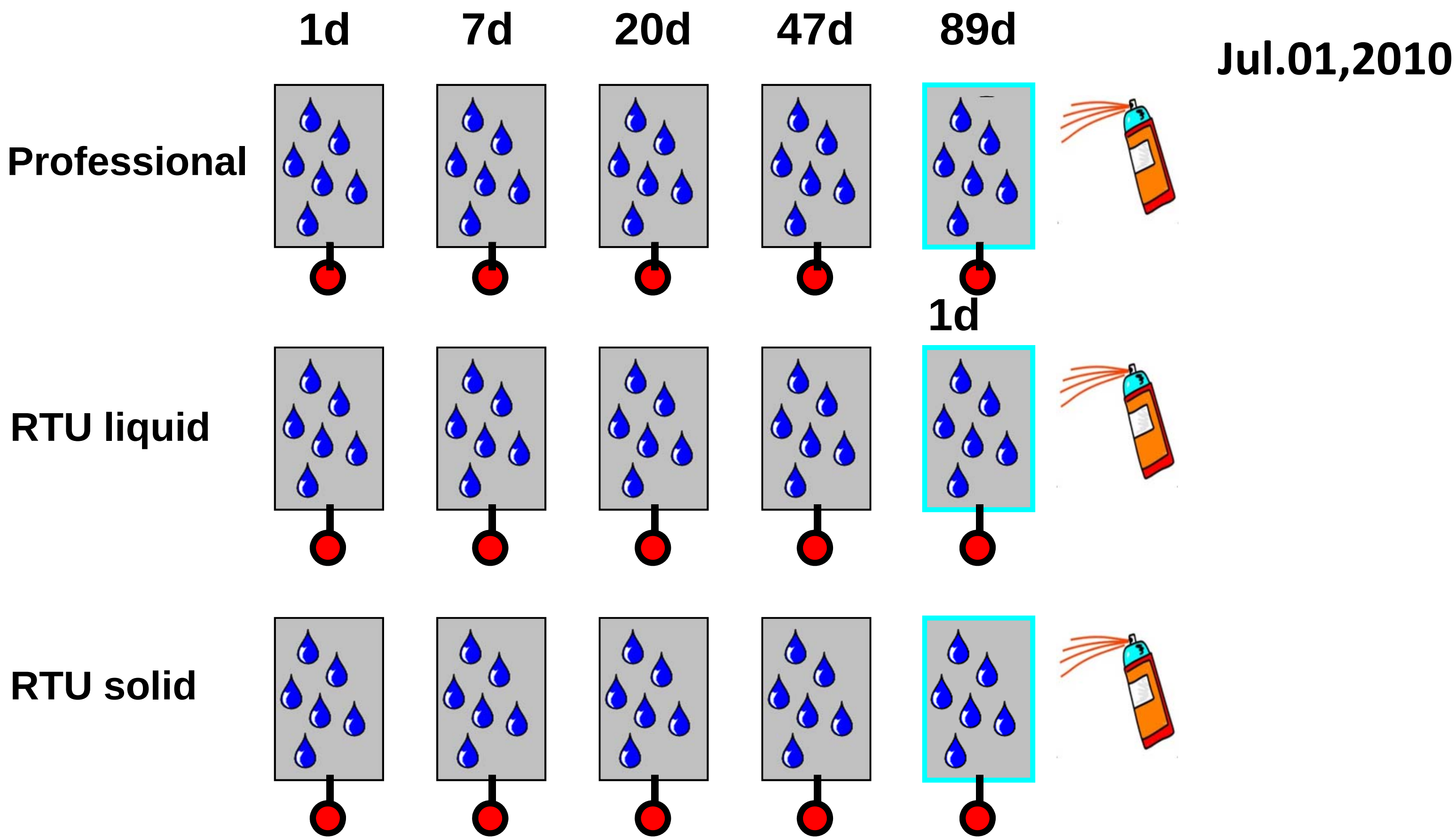
Different Environmental Factors

- Precipitation intensity:
  - **19.3 mm/h, 20 min**
  - **26.2 mm/h, 15 min**
  - **32.6 mm/h, 10 min**

- Concrete surface:
  - **Regular**
  - **Acid wash**
  - **Silicone sealing**
  - **Texture stamping**
  - **Microsilica addition**

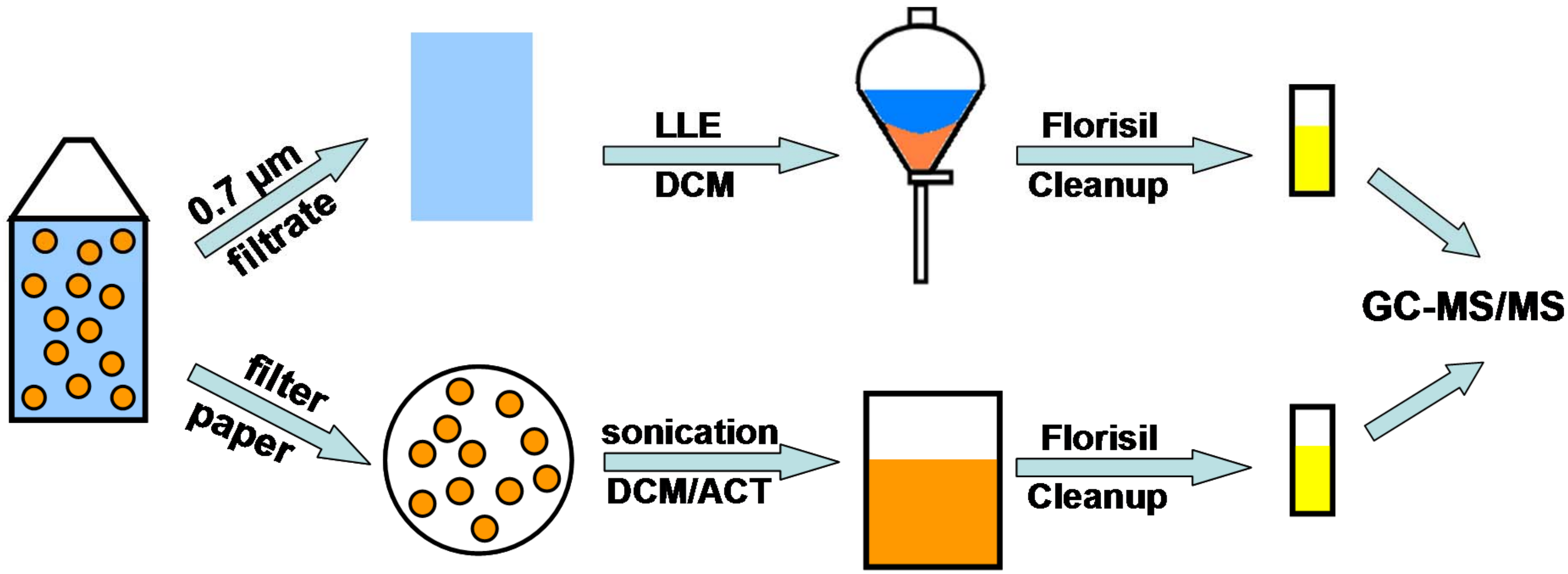


Formulation Effects

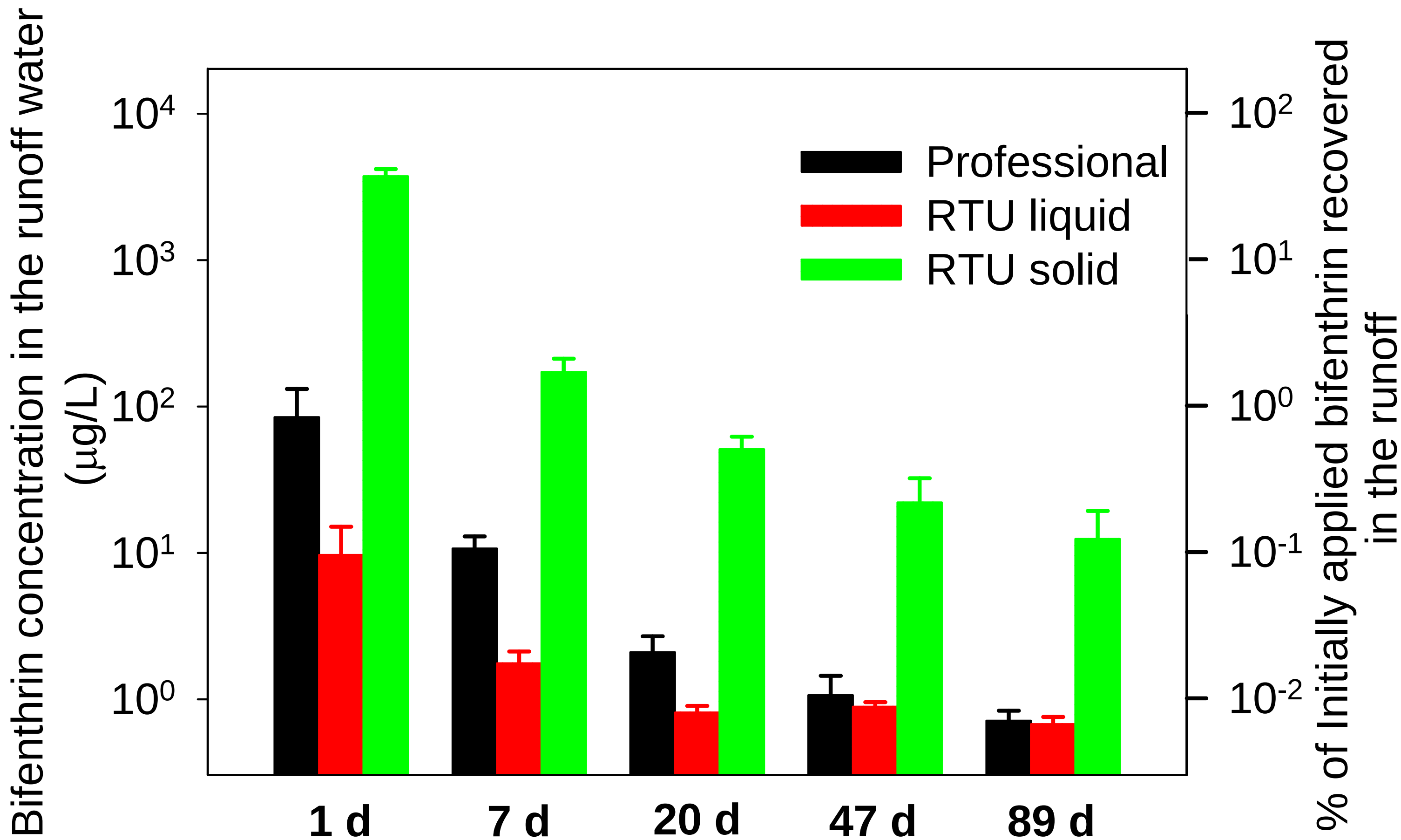


Analysis of Pesticides in the Runoff Water

- **Runoff water**
  - 0.7µm glass-fiber filter paper



Pyrethroid Runoff during Repeated Precipitations



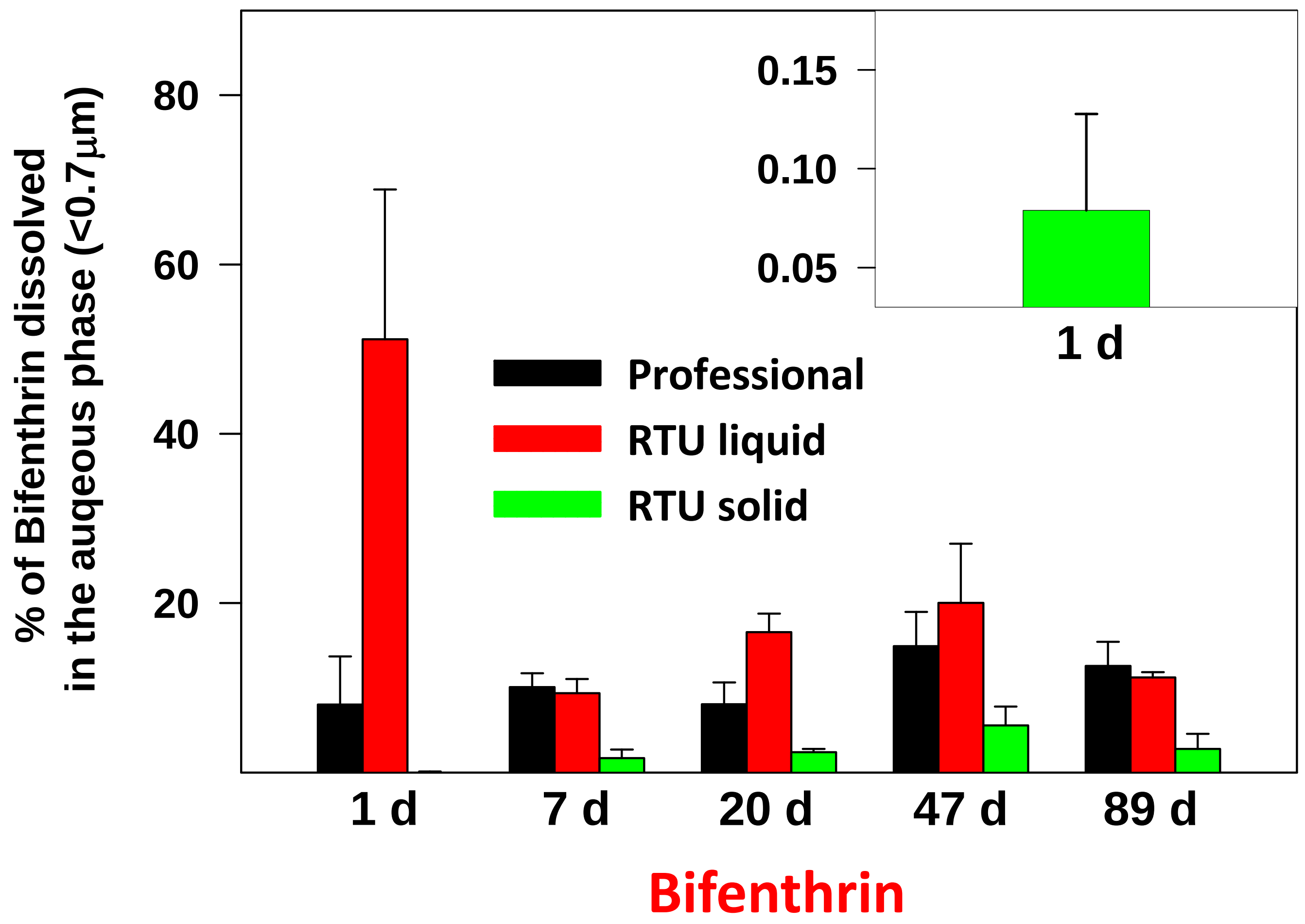
Formulation	Professional C_{runoff} (µg/L)	RTU liquid C_{runoff} (µg/L)	RTU solid C_{runoff} (µg/L)
Bifenthrin	0.64 ± 0.10	0.76 ± 0.07	15.50 ± 7.35
cis -Permethrin	12.44 ± 2.98	22.87 ± 6.70	215.15 ± 76.09
trans -Permethrin	19.98 ± 4.51	22.36 ± 3.44	358.10 ± 136.59

Possible reasons:

- **Facilitated pesticide runoff by sorption on particles in RTU solid formulations**
- **Less interaction with concrete for RTU solid formulations and less pesticide degradation**

Partitioning of Pesticides in the Runoff

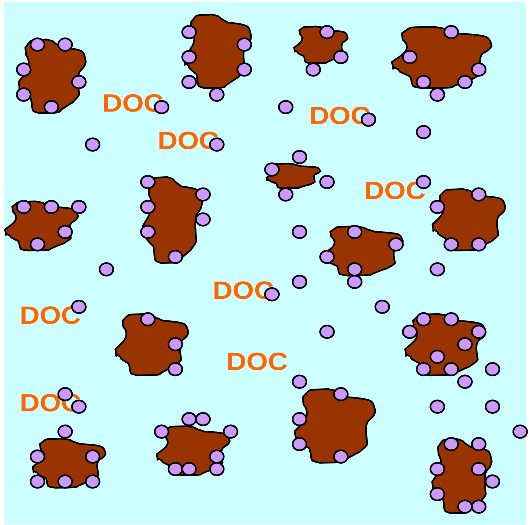
- Dominant role of suspended particles on pyrethroid offsite transport from concrete



Post-application precipitation	Bifenthrin concentrations in the aqueous phase (<0.7µm, µg/L)		
	Professional	RTU liquid	RTU solid
1 d	5.48 ± 2.91	4.28 ± 3.70	2.96 ± 1.66
89 d	0.08 ± 0.02	0.09 ± 0.01	0.41 ± 0.25

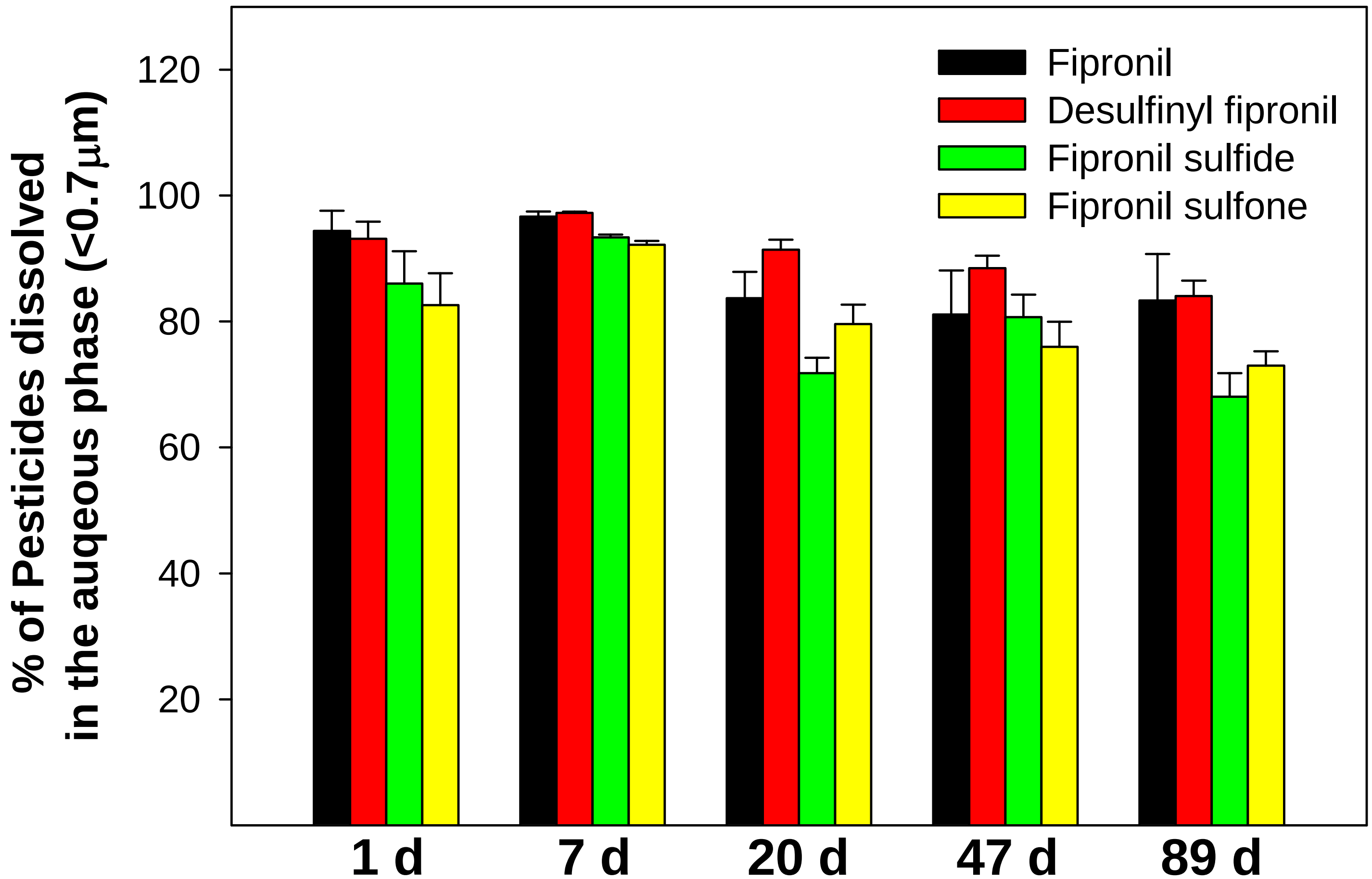
Pesticide Runoff with Particulate Materials

- **Sorption on soil particles** has been proved to be the **primary** pathway for hydrophobic pesticide runoff transport, and many mitigation practices have been proposed to decrease the offsite movement;
- Concrete is bound as an **integrity** and **resists runoff erosion**.
- Sources of particles on concrete:
  - ✓ detached concrete fragments after extended outdoor exposure
  - ✓ deposited dusts from surrounding areas
  - ✓ inert carrier ingredients from pesticide formulations
- Small amounts of particles on concrete (<0.5g) accumulate 80 % of pyrethroids in the runoff.



Partitioning of Fipronil and Degradates in the Runoff

- **Dominant partitioning of fipronil and fipronil degradates in the aqueous phase**



Objective III: Pesticide Runoff Prediction

- **Different parameters for method validation**
  - Different types of precipitations
  - Different pesticide formulations
  - Different periods of outdoor exposure

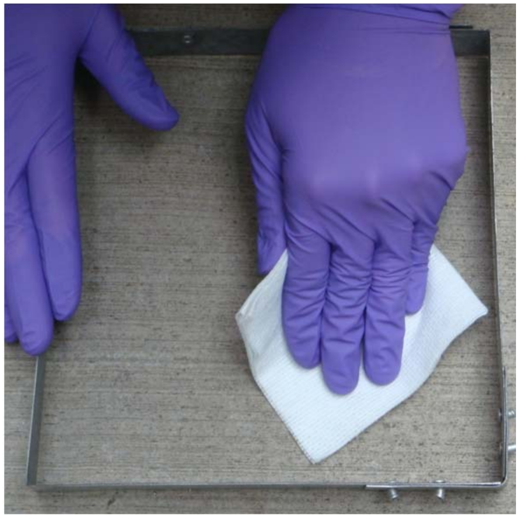
Surface Wiping with Sponges

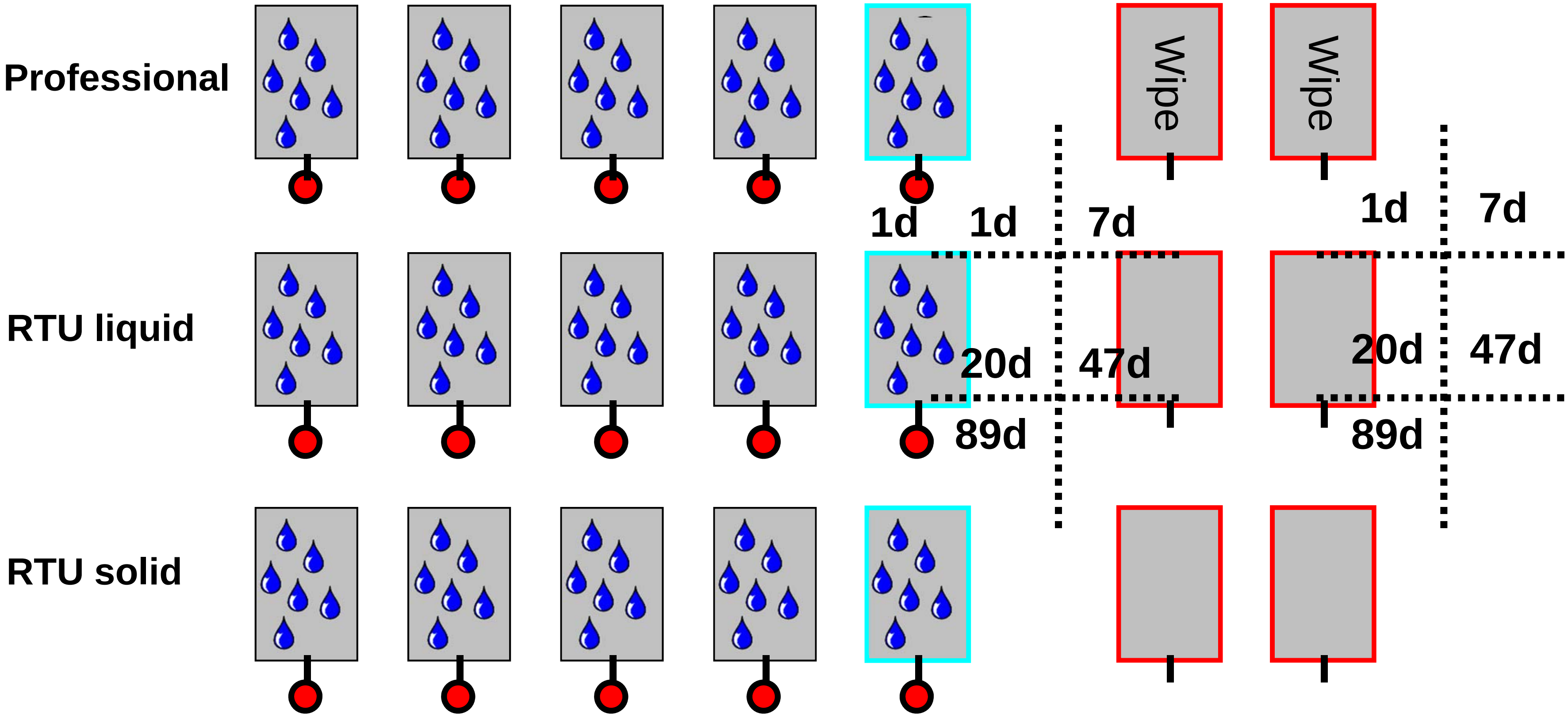
Surface wiping has been used by EPA and other agents to assess human exposure to pesticides on indoor surfaces;

For runoff prediction:

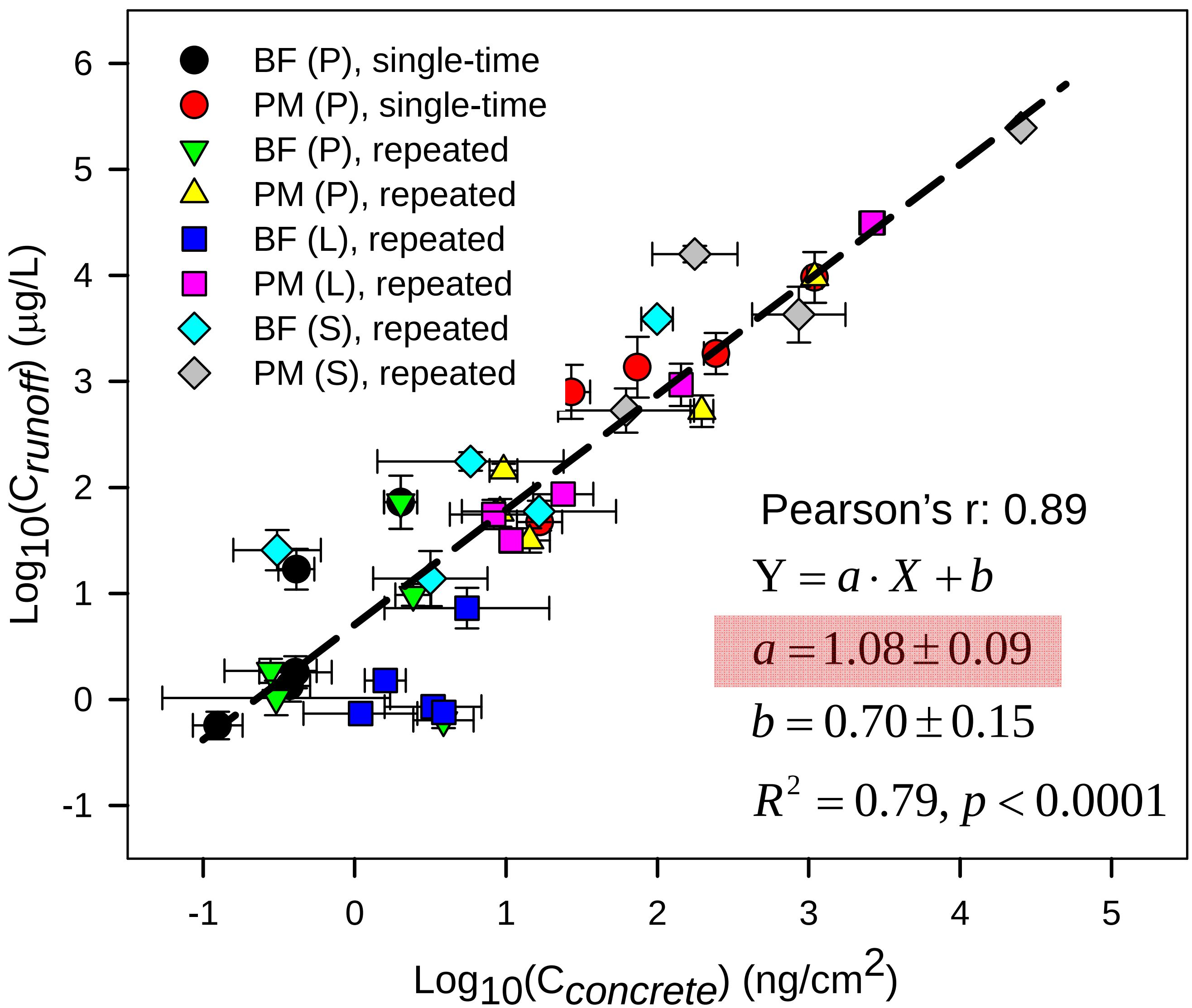
- Used to determine pesticide concentrations on concrete;
- Correlate the results with pesticide concentrations in the runoff water to predict runoff transferability.

Surface Wiping for Runoff Prediction

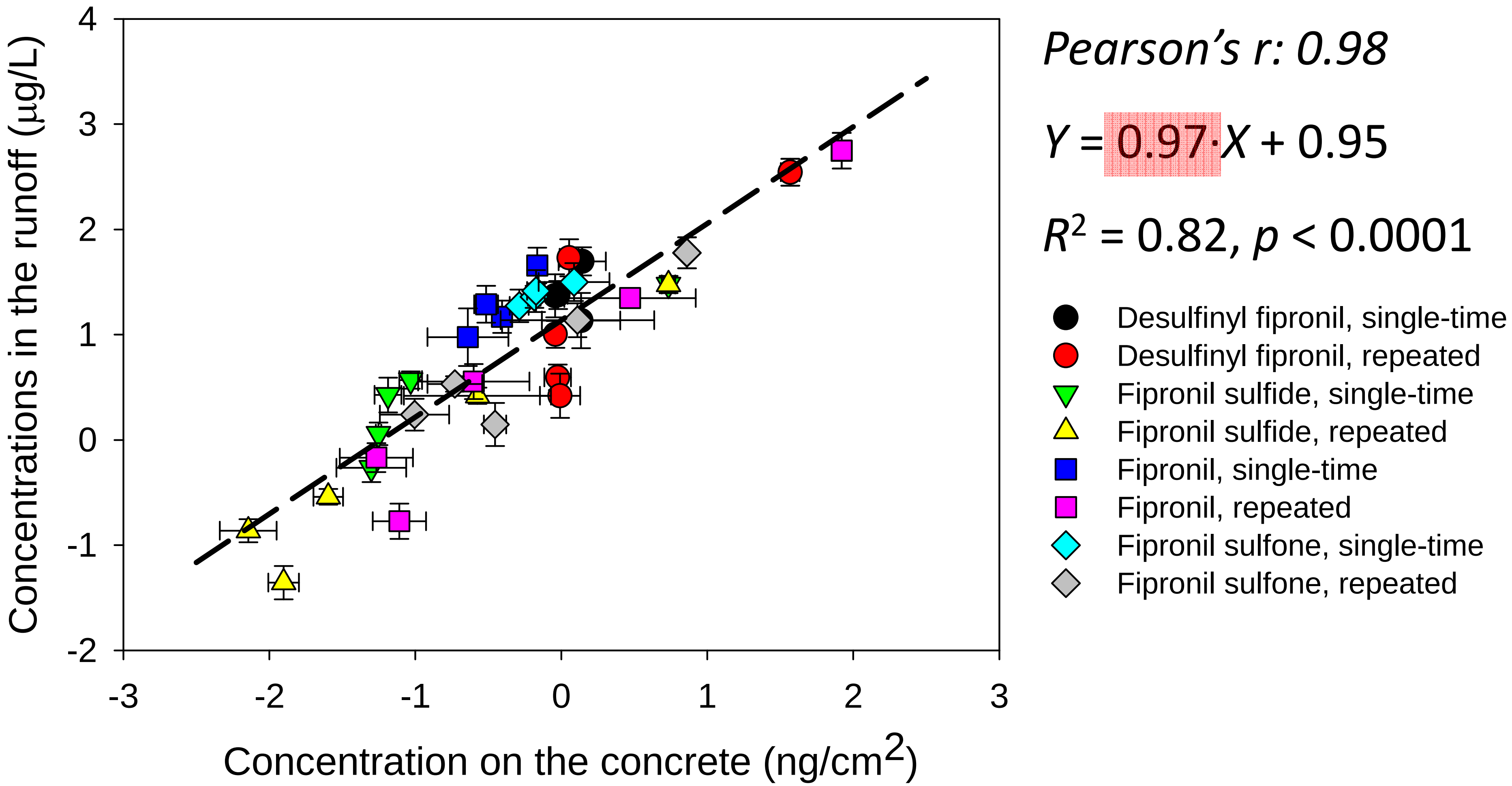




Concrete Wiping for Pyrethroid Runoff Prediction



Concrete Wiping for Fipronil Runoff Prediction

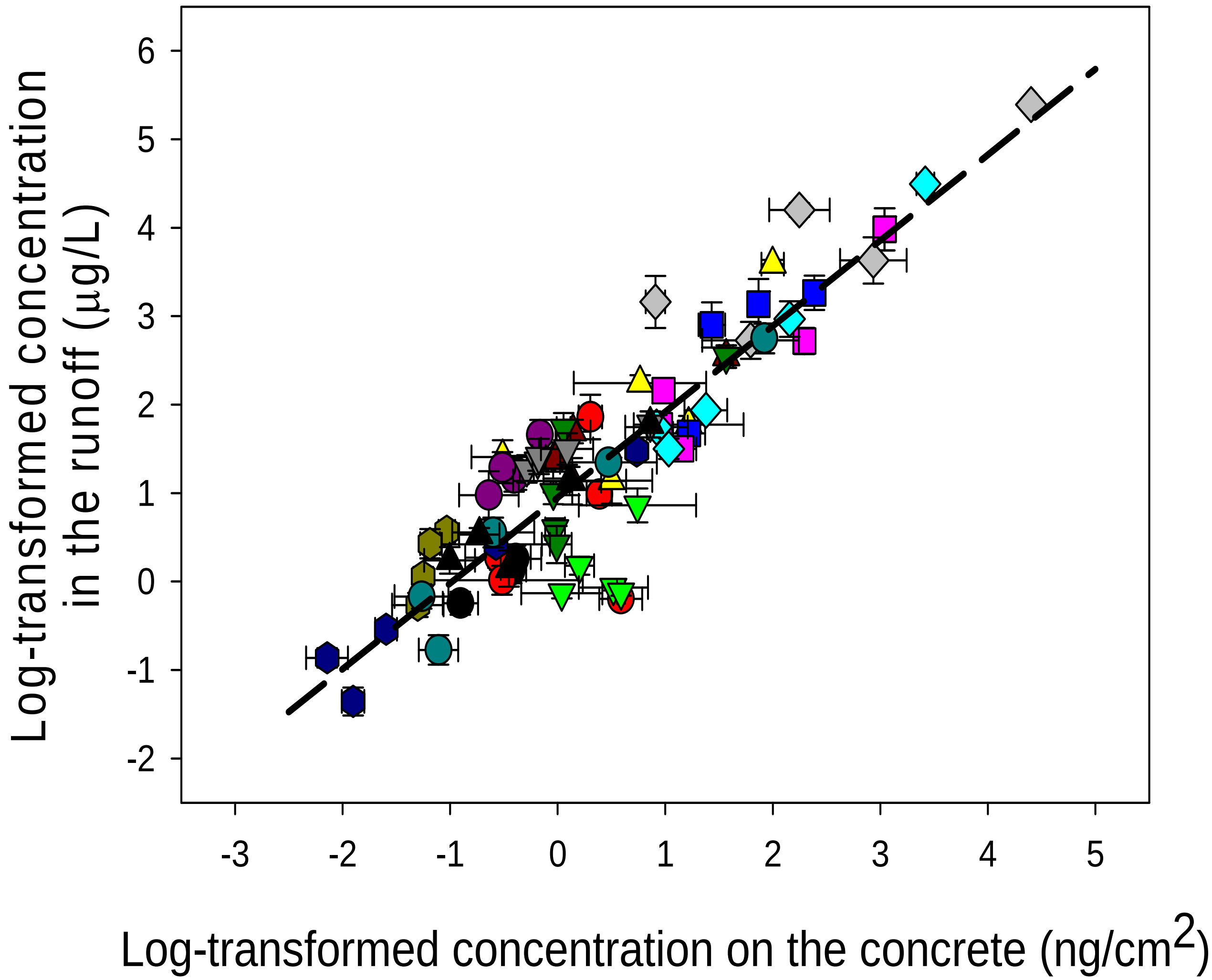


Pearson's r: 0.98

$Y = 0.97 \cdot X + 0.95$

$R^2 = 0.82$, $p < 0.0001$

Correlations for All Tested Pesticides & Degradates



Pearson's r: 0.90

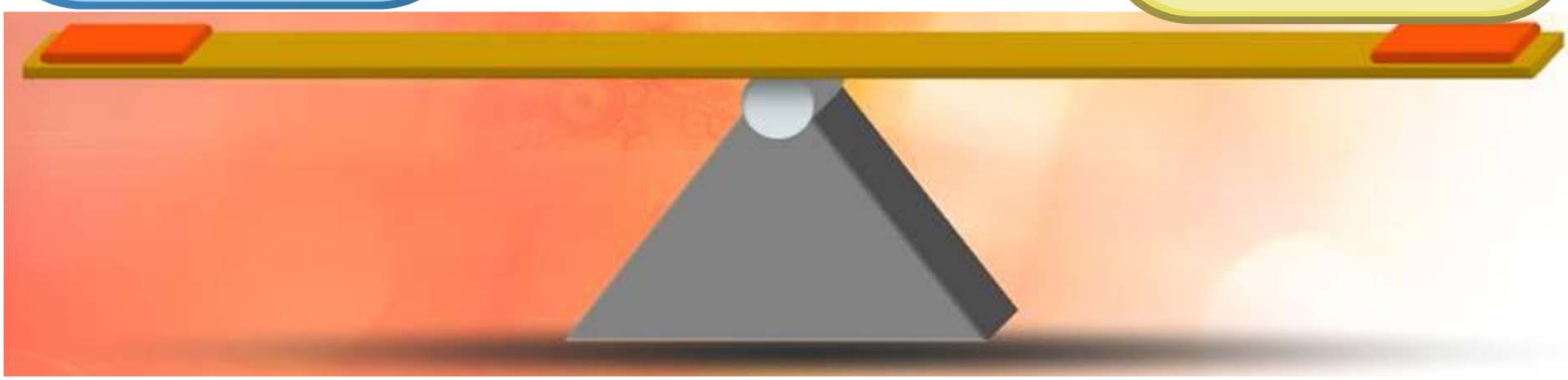
$Y = 0.97 \cdot X + 0.95$

$R^2 = 0.82, p < 0.0001$

Objective IV: Pest Control Efficacy

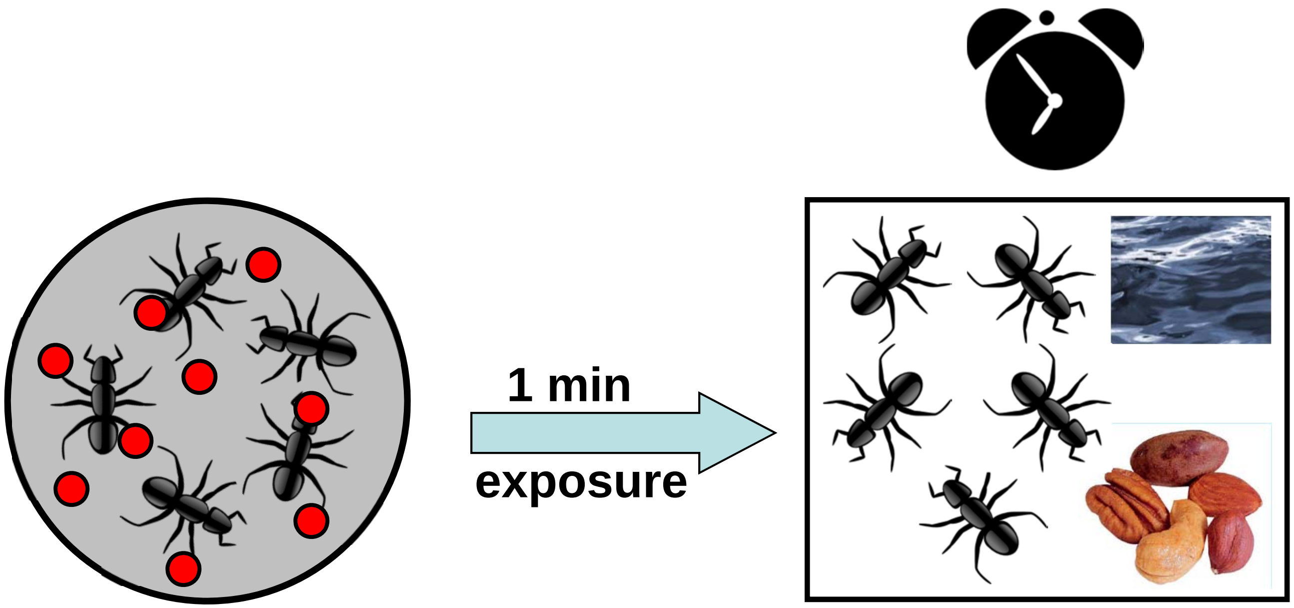
- Active amounts on concrete
- Good pest control efficacy as long as possible

- Less persistence on the concrete
- Runoff from concrete as low as possible



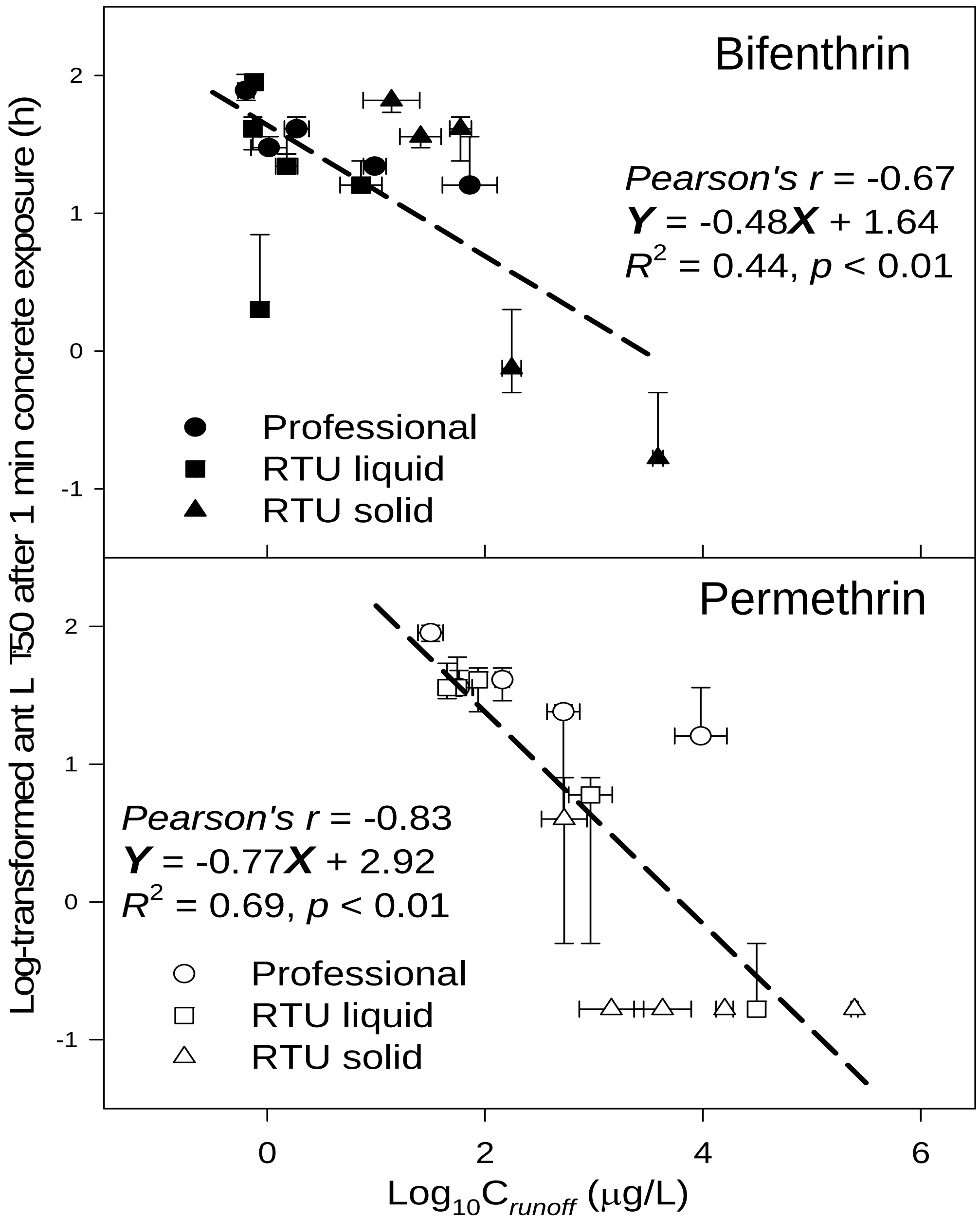
Analysis of Pest Control Efficacy

- **Ant Survivorship Test**



Median lethal time (LT50): average time intervals during which 50% of a given population may be expected to die.

Dissipation of Pest Control Efficacy



Pyrethroids after 89 d Exposure

Pyrethroid	Formulation	LT50 (h)	C_{runoff} (µg/L)	$C_{concrete}$ (µg/cm^2)
Bifenthrin	**RTU solid**	**-**	**15.50 ± 7.35**	**0.63 ± 0.49**
	RTU liquid	**-**	**0.76 ± 0.07**	**0.65 ± 0.05**
	Professional	**-**	**0.64 ± 0.10**	**0.68 ± 0.30**
Permethrin	**RTU solid**	**4 (0.5 - 8)**	**573.25 ± 212.19**	**13.24 ± 11.68**
	RTU liquid	**-**	**45.23 ± 6.53**	**1.80 ± 0.15**
	Professional	**-**	**32.42 ± 7.48**	**2.45 ± 0.74**

Highlights

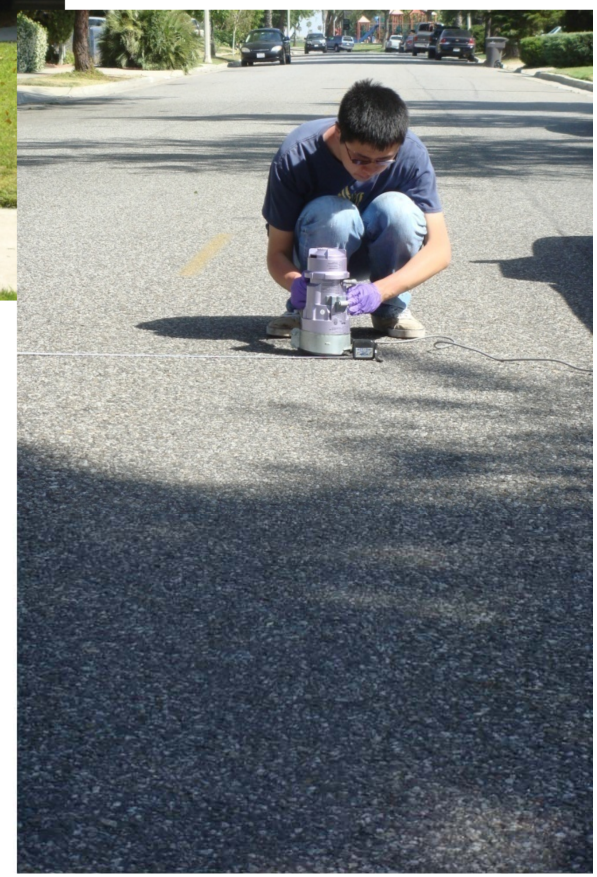
- **Persistence** on concrete and **long-term** runoff potential
  - ✓ **Extended** outdoor exposure
  - ✓ **Repeated** flushes
  - ✓ **Winter** rainfalls/storms
- Dominant contributions of the **first flush**
- Partitioning of pyrethroids on the **suspended particles**
- Partitioning of fipronil and degradates in the **aqueous phase**
- **Surface wiping** for runoff prediction
- **Rapid** dissipation of pest control efficacy over the runoff
- Occurrence of **degradates** in the runoff

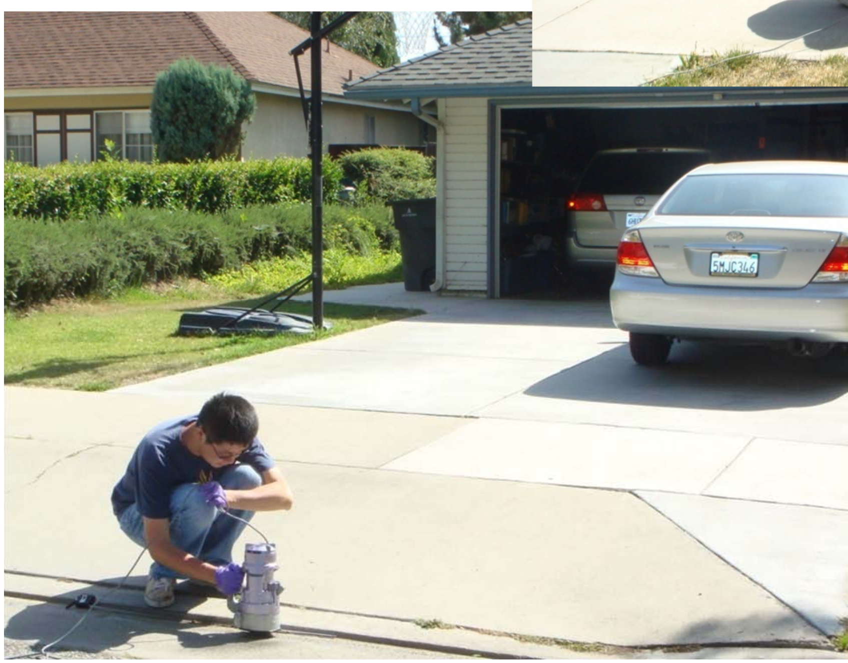
On-going Study:
Pesticides Around Homes

Sampling Site 01: Old House Neighborhood

Sampling Site 02: New House Neighborhood

Vacuum Dust Sampling





Sampling with Surface Wiping

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