Human Exposure to Surface Pesticide Residues: Dislodgeable Foliar Residues and Pilot Studies to Predict Bioavailability

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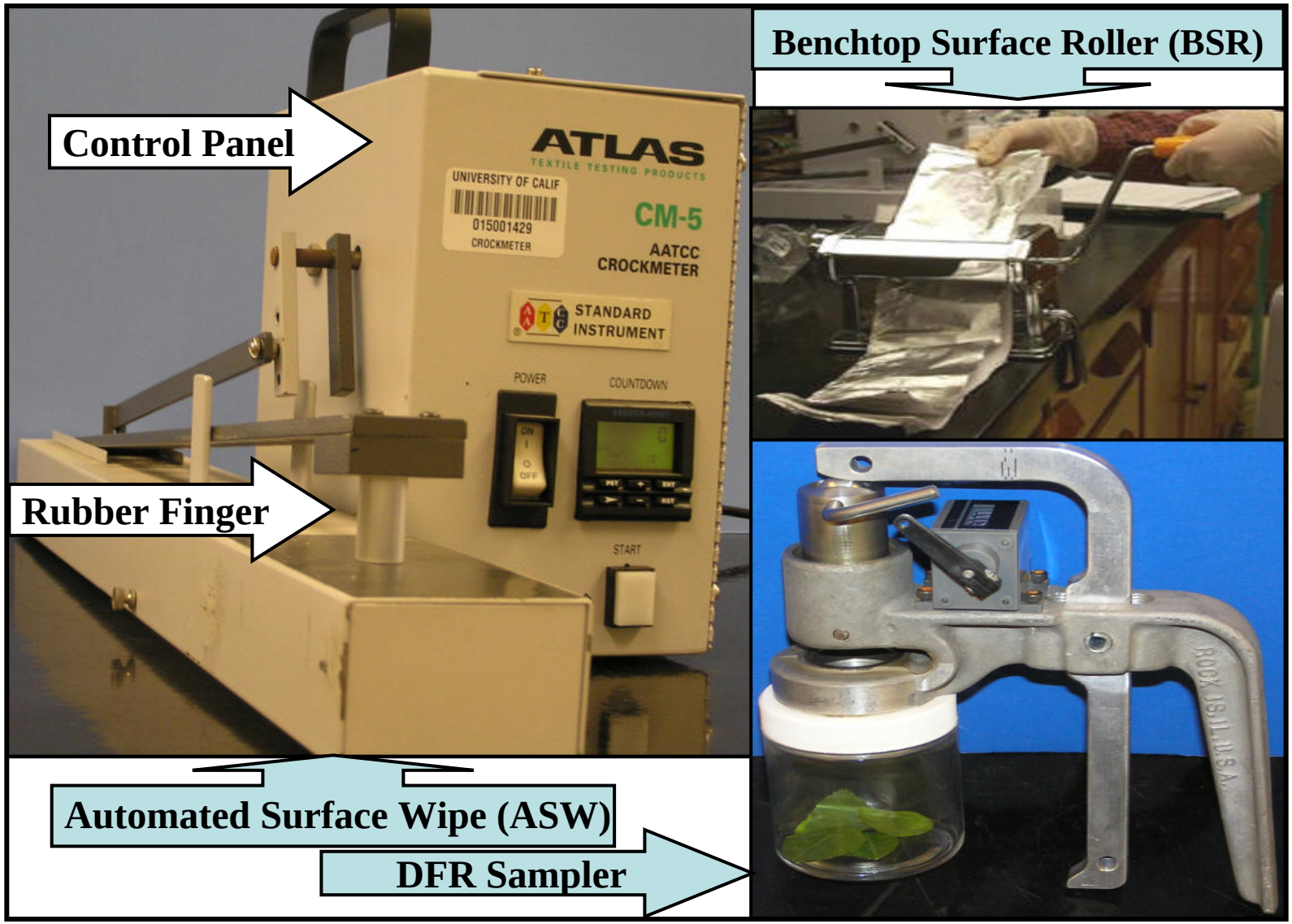
Abstract

Entry into pesticide treated fields can present significant hazard to harvesters and other agricultural workers. Dislodgeable foliar residues (DFRs) are an important determinant of worker field entry intervals. DFRs are measured by using a weak detergent solution to wash the residues from the surface of leaf samples. This ***chemical*** process contrasts with the predominantly ***physical*** contact-transfer that occurs in the field. We are investigating two new procedures to measure physical TSRs (Transferable Surface Residues): an Automated Surface Wipe (ASW) and Benchtop Surface Roller (BSR). These procedures physically transfer residues from treated surfaces by direct contact. DFRs (chemical) are greater than TSRs (physical), and DFRs decreased with time more sharply than TSRs did. DFRs may not adequately predict longer term exposure. Preliminary spot urine biomonitoring data indicate low exposure of harvesters to treated foliage. In depth exposure studies will follow.

Instruments Used for Analysis



Alternative Methods for Safe Worker Reentry

Introduction

Pesticides are broadly used for pest control in agriculture and residence. Physical contact of exposed skin, gloves, and clothing with pesticide treated surface residues are the major exposure routes for strawberry harvesters. Potential harvester pesticide exposure is determined by leaf surface pesticide residues (DFRs). The existing empirical relationship between worker exposure (E; pesticide on external clothing) and DFR has been used very effectively for defining safe field entry times that keep workers safe from organophosphorous insecticides overexposure. It is also known as the Zweig-Popendorf Equation, where E (μg/h) = DFR (μg/cm^2) × hours × Transfer Coefficient (cm^2/h). DFR is a first approximation of worker exposure potential, but the vast majority of the leaf residue that is removed by the detergent solution is unavailable for human exposure. It is critically important to predict harvester pesticide exposure as accurately as possible. The data are needed to make reasonable and reliable estimates of worker exposure for risk assessment. Physical transfer residue measurements (ASW and BSR, developed by PCEP at UC Riverside) were investigated and may more accurately represent potential worker exposure than DFR.

Materials and Methods

Lab Study at UCR, 2005

1. Chlorpyrifos was applied to strawberry plants by using linear pesticide applicator.
2. Leaf samples were collected on Day 3, Day 6, and Day 10.
3. DFR-LP and TSR (ASW and BSR) were measured.

Field Study in Santa Maria, 2006

1. Malathion was applied with application rate of 2 Pints/Acre in the filed in June and with application rate of 16 oz/Acre in the same field in August.
2. Leaf samples were collected from Day 1 to Day 5, and from Day 13 to Day 17 after the first application; and on Day 8 and Day 11 after the second application.
3. DFR-LP, DFR-WL and TSR (ASW and BSR) were measured.

DFRs: Dislodgeable Foliar Residues (Chemical)

The amount of residues present on the surface of leaves that can be washed from the leaf surface. DFRs are measured by using a weak detergent solution followed liquid-liquid extraction (Iwata et al., 1977)

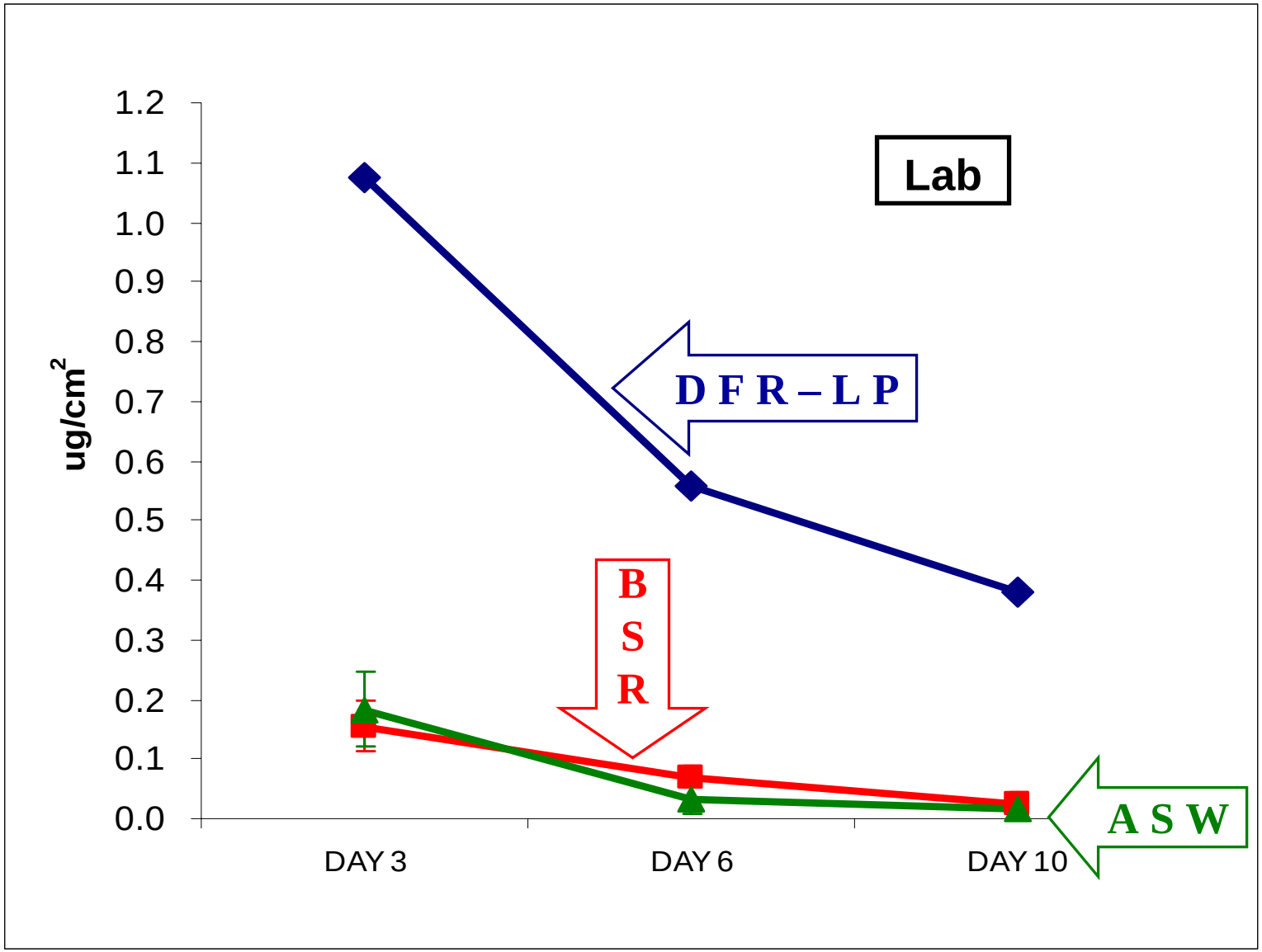
- **DFR-LP**: DFR Leaf Punch Samples
- **DFR-WL**: DFR Whole Leaf Samples

TSRs: Transferable Surface Residues (Physical)

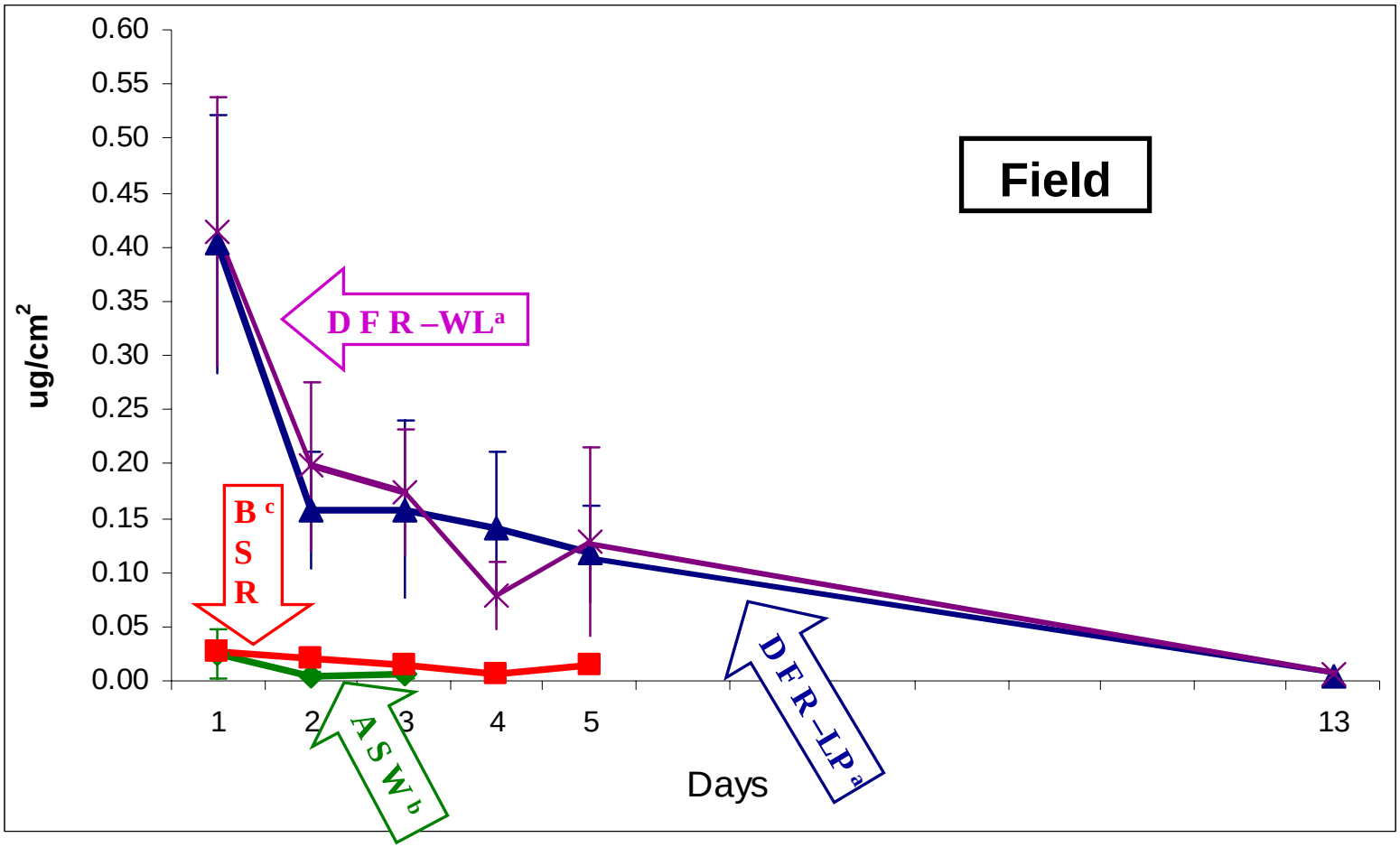
The amount of residues that are available for dermal absorption through physical contact.

- **ASW,** Automated Surface Wipe, is a new device we developed to simulate field workers' physical contact with pesticide treated leaf surfaces. This machine, intended to test color-fastness of textiles, automatically wipes the leaf surface with an attachment covered by cotton cloth and foil.
- **BSR,** Benchtop Surface Roller, is another device we developed for physical surface sampling. This machine, intended to make pasta, simulates direct worker contact with treated foliage. A cotton cloth and foil containing leaf samples is used to obtain residue.

Dislodgeable Foliar Residue and Transferable Surface Residue: Chlorpyrifos, Strawberry



Dislodgeable Foliar Residue and Transferable Surface Residue: Malathion, Strawberry

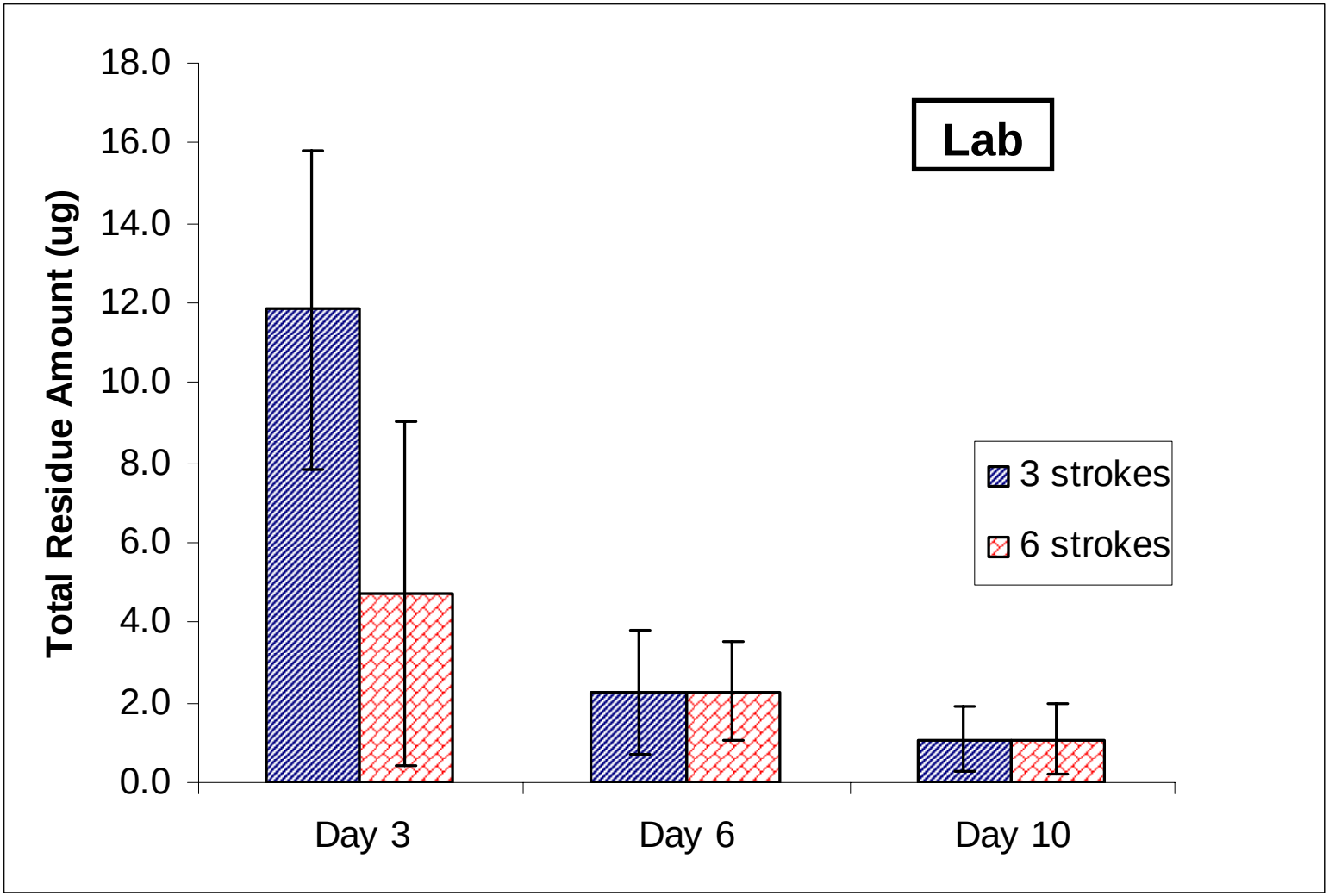


[a] DFR-LP and DFR-WL: Malathion detected on Day 13 under detection limit of 1 ppm, considered as ½ of detection limit.

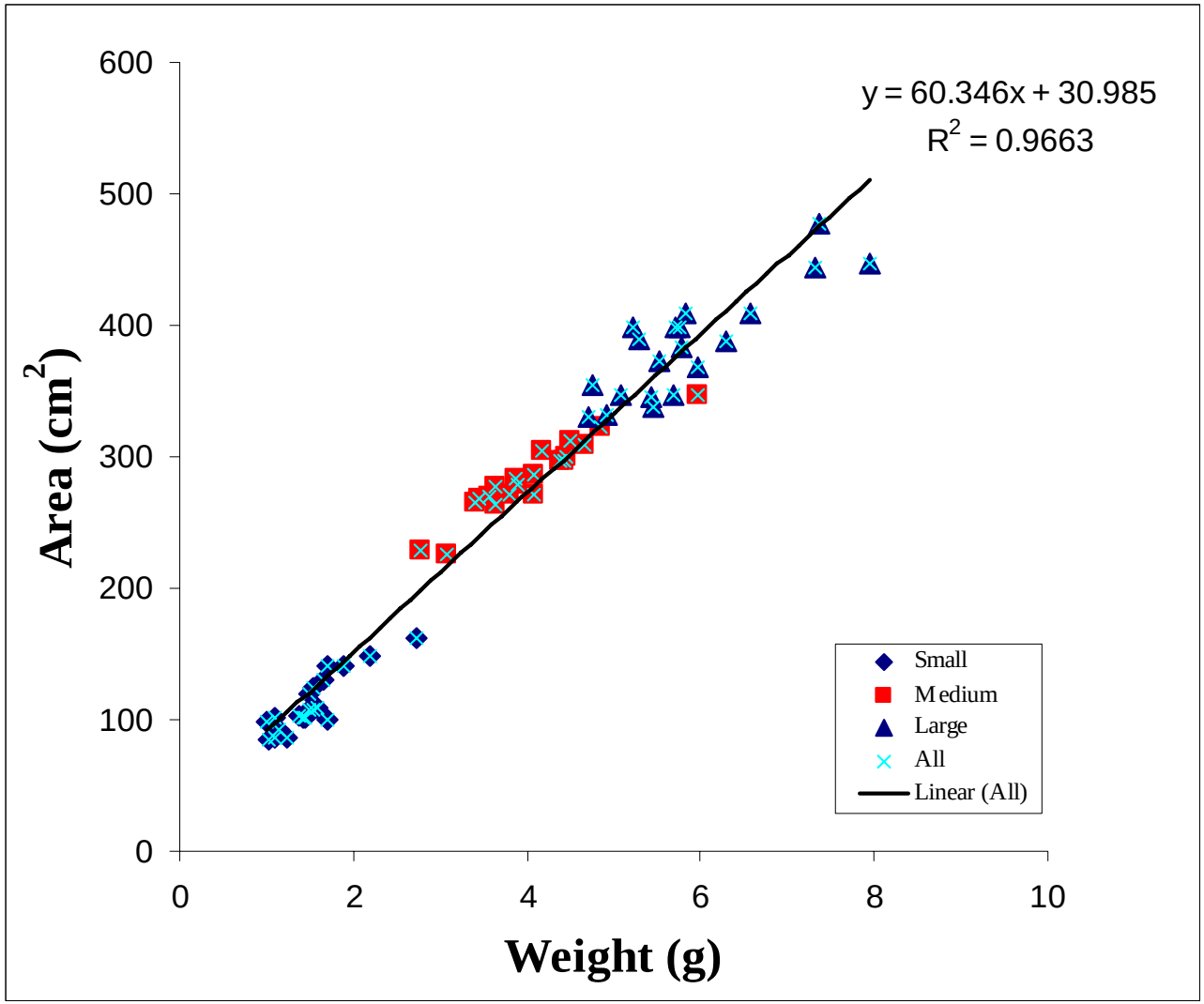
[b] ASW: Malathion detected from Day 1 to Day 3 is far lower than the lowest concentration (5 ppm) of the standard curve. These are estimates. Malathion was not detectable on Day 4.

[c] BSR: Malathion was not detectable on Day 13.

First Touch is Most Important



Strawberry Leaf Area and Weight



Dislodgeable Foliar Residue

Day 16	Leaf Weight (g)	Malathion (µg)	Leaf Area (cm^2)[a]	DFR (µg/cm2)
1	37.10	0.37	2269.8	0.0002
2	37.01	0.37	2264.4	0.0002
3	40.56	0.20[b]	2478.6	0.0001
Average	38.22	0.37	2337.61	0.0001
Std.Ev	2.02	0.00	122.15	0.0000

Primus, Santa Maria

[a] The leaf surface area (including both front side and back side) = Leaf Weight (g) × 60.3 + 31.0

[b] The amount detected under detection limit of 0.01 ppm, considered as 1/2 of detection limit, So the estimate malathion amount = 1/2 × 0.01 ppm × 40.56 g

DFRs and TSRs on Malathion Treated Strawberry Leaves on Day 8 (Second Application[a]) in Field Study, 2006

Samples	BSR	DFR-LP	DFR-WL
	ug/cm^2	ug/cm^2	ug/cm^2
1	/	0.0004[b]	0.001[b]
2	/	0.0004[b]	0.002[b]
3	/	0.0004[b]	0.001[b]
4	/	0.0002[b]	0.001[b]
5	/	0.0105	0.048
6	/	0.0003[b]	0.022
Average	/	0.0020	0.012
STDEV	/	0.0041	0.019

[a] Application rate: 16 oz/Acre

[b] The amount detected under detection limit of 1 ppm, considered as ½ of detection limit

/ Undetectable

Absorbed Daily Dosage[a] of Malathion Equivalent Based on DAP, MCA and DCA in Spot Urinary Specimens

	Collection Day	Alkyl[b]	MCA[c]	DCA[d]
First Application[e]	Day 4	1.19±0.96	1.86±2.46	1.32±1.18
Second Application[e]	Day 10	0.58±0.37	0.81±0.46	0.08±0.06
	Day 11	0.87±0.77	1.14±0.76	0.17±0.26

[a] Absorbed daily dosage, AAD: the unit is ug/day-kg, the bodyweight is assumed as 70kg.

[b] Malathion equivalent was based on DMP, DMTP, DMDTP. The detection limit is 5, 5 and 10 ppm for DMP, DMTP, DMDTP, separately. 4/10, 4/10, 1/10 were detectable for DMP, DMTP and DMDTP on Day 4; 1/10, 2/10, 0/10 on Day 10; 2/10, 1/10, 2/10 on Day 11.
The value is calculated as 1/2 of detection limit when they are undetectable.

[c] Malathion equivalent was based on MCA. MCA was detectable in all of the urine samples.

[d] Malathion equivalent was based on DCA. DCA was detectable in all of the urine samples on Day 4, but only 2/10, 2/10 were detectable in the urine samples on Day 10 and Day 11, separately.

[e] The application rate is 2 pints/Acre for the first one and 16 oz/Acre for the second one.

Discussion

❖ Dislodgeable Foliar Residue (DFR) is higher than Transfer Surface Residue (TSR) in both Lab and Field studies

❖DFR decreased more sharply than TSR did in field studies.

❖DFR was detectable but not measurable on Day 13 (First application, 2 Pints/Acre). Day 16 samples showed two at 0.01ppm and one below detection limit. Malathion degrades quickly in the environment and only trace amounts are present on the leaf surface after a week of application (Malaoxon not detected, 0.01 ppm).

❖Benchtop Surface Roller (BSR) indicated very low level of malathion residues on leaf surface.

❖More leaf samples will be applied for later studies to increase sensitivity.

❖Preliminary spot urine biomonitoring data indicated low malathion exposure level over long term despite inability to detect pesticides with DFR and TSR. Dietary exposure can not be ruled out. In depth exposure studies will be continued to evaluate the availability of leaf surface pesticide residues.

❖We will continue to evaluate the physical transfer of residue to predict long term, low level harvester exposure.