Progress Report

Source Evaluation and Mitigation of Off-site Movement of Pesticides from Residential Homes

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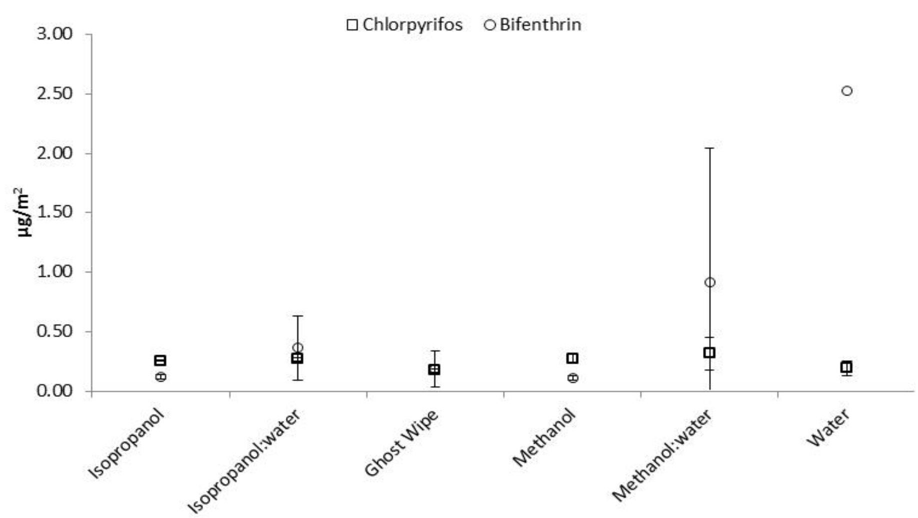
Task 1. Optimization of surface wipe method for predicting runoff potential

Different wipe materials and wetting agents have been traditionally used to collect pesticide residues from indoor surfaces in human exposure assessments. Such methods were developed to estimate human pesticide exposure through skin contact. From an environmental point of view, wiping methods may be also applied to predict the runoff potential of pesticides on urban impervious surfaces. Since loose particles contribute the most to the pesticide levels found in the runoff water, a quantitative surface wipe method should be able to recover transferable pesticide residues either sorbed on concrete or attached to particles, with the aim to quantitatively estimate the pesticide runoff potential from concrete surfaces.

In a previous study, a piece of 10 cm ×10 cm Versalon sponge pre-wetted with 10 mL isopropanol was tested on small concrete slabs that were treated with different pesticide formulations at different times. There was consistently a good agreement between the amount of pesticides detected in the simulated runoff water and those found on the sponge wipes.

This task focuses on the optimization of the surface wipe method. First, a different type of wipe, the ghost wipe, was included in the testing. The ghost wipe is a polyvinyl alcohol wipe readily available. Since it is pre-packaged and ready to use, its implementation in a large-scale study should be highly feasible. The Versalon sponge was also tested with different solvents (methanol, isopropanol and water) or solvent-water mixtures (1:1). Concrete slabs were used for these experiments. To simulate pesticide contamination, dust collected from urban environments was uniformly spread onto the slabs.



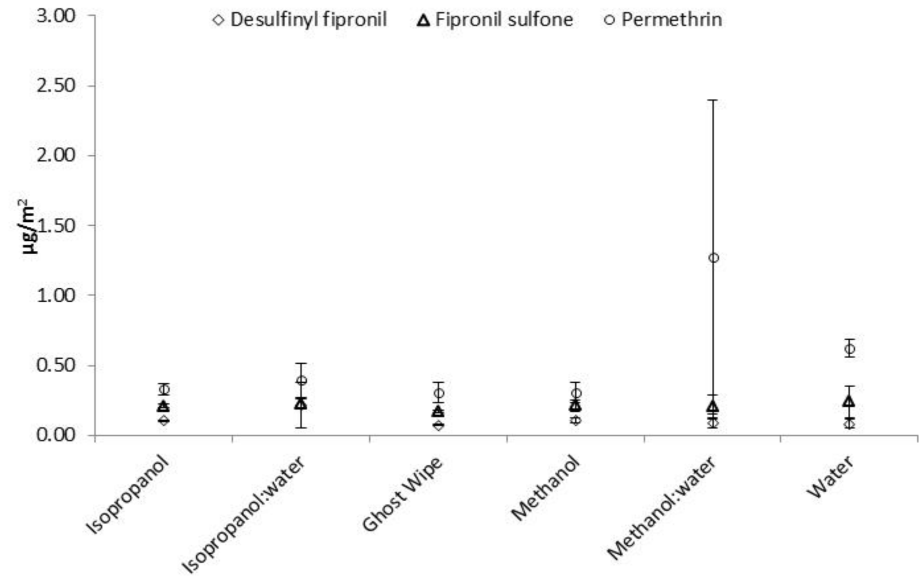


Figure 1. Pesticide residues collected from the slabs using different types of wipes and solvents.

From the levels found in the different treatments (Figure 1), the different variables did not greatly affect the amount of pesticides recovered. The use of water or water-solvent mixture appeared to result in increased variability.

Task 2. Relationships between loose particles and pesticide runoff from concrete surfaces

In outdoor environments, hard surfaces such as concrete from driveway, sidewalk or street are covered with dust particles. The runoff potential or transferability of pesticides accumulated on such particles to runoff during rainfall or irrigation events is still unclear and may be influenced by different factors, such as the particle size distribution. In this task, pesticides were extracted and analyzed from fractionated dust samples collected from the driveway of different houses in Southern California.

Three pesticides (bifenthrin, chlorpyrifos and permethrin) and one degradate from the oxidation of fipronil (fipronil sulfone) were consistently found in the different dust samples. Pesticides detected at higher concentrations were bifenthrin (maximum concentration of 199 µg/kg), permethrin (55 µg/kg) and fipronil sulfone (15 µg/kg). The largest (>250 µm) and smallest (<53 µm) particle size fractions contained higher amounts of pesticides (Figure 2). For example, 77% of the total fipronil sulfone in a dust sample was found in those fractions. This information may have implications for understanding the sources and transport of pesticides in urban environments, and for the development of mitigation strategies.

Additionally, experiments will be carried out in 2015 to determine the mechanisms by which particles become contaminated and contribute to offsite transport. In the first experiment, the sorption/desorption of pesticides to urban dust will be investigated. Since the urban dust may have a different composition than soil due to a blending of sources (soil, weathered concrete, weathered asphalt, and deposition from automobile exhaust), the sorption/desorption and Kd values may be different for urban dust than for soil. Similarly, the sorption of pesticides from the concrete surface to urban dust will be examined in order to determine its relative importance as a mechanism of dust contamination. The results of this experiment will be compared to the sorption/desorption of pesticides on concrete surfaces which was previously carried out by Jiang.

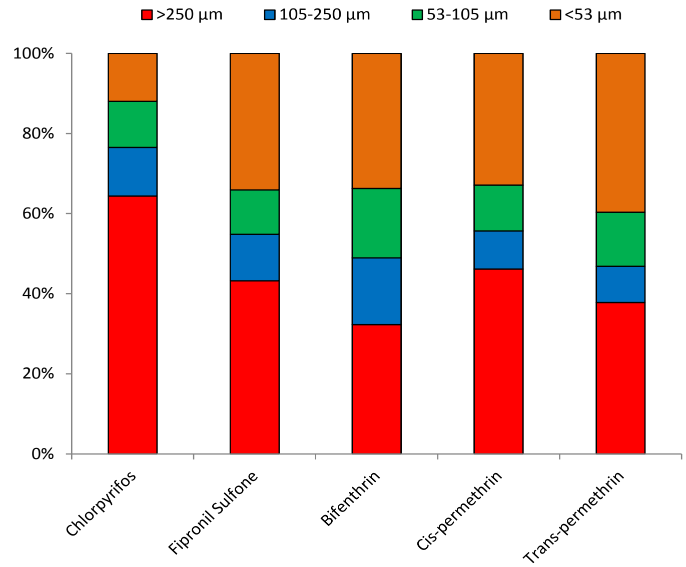


Figure 2. Pesticide distribution among different fractions as % of the total chemical mass

The second experiment will be a field scale experiment utilizing the 60 x 40 cm concrete slabs. All the concrete slabs will be cleaned thoroughly before the experiment. One set of the slabs will then be treated with bifenthrin, permethrin, and fipronil and then covered so no dust particles can be deposited onto the surfaces. The second set will be treated with pesticides, and then dust will be applied to the surface. Another set of slabs will have dust applied to the concrete surfaces first, followed by pesticide application. Lastly, a set of concrete slabs will receive no pesticide treatment to act as the control. Simulated rainfalls will then be conducted 1, 7, 21, 48, and 90 days after the treatment. Runoff samples will be collected and pesticide concentrations among treatments will be compared. Immediately prior to each simulated rainfall event, a portion of the surface of each slab will be vacuumed and the solid particles collected will be extracted and analyzed to determine the fraction of pesticides in runoff that are associated with solid particles.

Task 3. Survey of pesticides in loose particles in Orange County

In this task, 20 homes were randomly selected in the Orange County. Three sampling campaigns (August 2013, October 2013, and February 2014) were carried out. For loose particle collection, vacuum samples were taken in triplicate from the driveway, gutter, and street of each house. Pesticide residues in loose particles are being analyzed, with the aim to estimate their potential runoff loading. Statistical analysis will be performed on the data to understand the seasonal and spatial patterns of accumulation of loose particles and pesticides.

During the third sampling campaign, dust collection was accomplished using both methods: surface wiping and vacuuming. The results obtained will be compared to validate the wiping method for future pesticide surveys in urban environments.

To date, 477 dust samples have been collected from the three sampling events. Of these, 333 have been extracted and 225 have been analyzed. During the last sampling event 180 wipe samples were also collected. Additionally, four composite bulk dust samples were collected in order to collect enough urban dust for characterization purposes. The four bulk dust samples have been separated based upon particle size (2 mm-425 µm, 425-250 µm, 250-149 µm, 149-45 µm, 45-38 µm, and <38 µm.), and pesticide concentrations in each size fraction have been determined for one of the bulk dust samples.

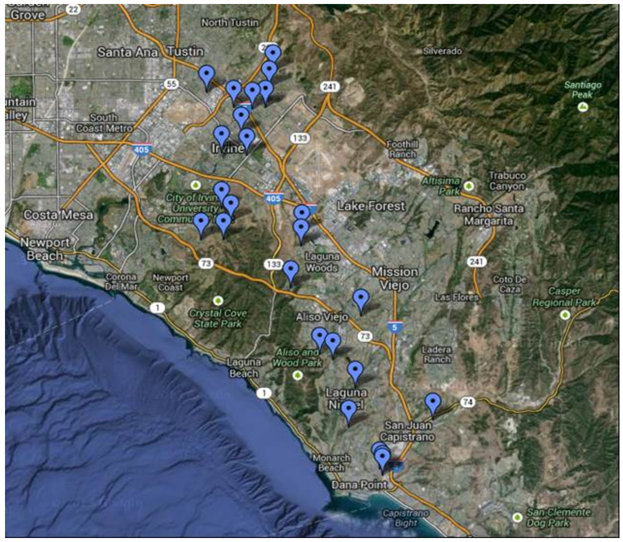


Figure 3. Houses selected for dust sampling in Orange County

Occurrence of Particle Bound Pesticides

Particle-bound pesticides were frequently detected in outdoor dust samples taken during February 2014 (Table 3). Pyrethroids were found to be widespread. Permethrin and bifenthrin were the most commonly detected pesticides with detection frequencies of 94.4 and 92.8%, respectively. The other pyrethroids were detected less frequently, but of the 8 pyrethroids investigated, 5 had detection frequencies over 50%.

Table 1. Occurrence of particle-bound pesticides on outdoor surfaces in residential areas of Orange County, CA.

Pesticide	**DF***	**Median**	**Max**
Pyrethroids	%	ng g^{-1}	ng g^{-1}
Fenpropathrin	50.6	1.3	2383.9
Lambda-cyhalothrin	51.7	1.1	62.9
Bifenthrin	92.8	22.4	2354.1
Permethrin	94.4	20.8	2780.7
Cyfluthrin	41.1	<RL†	133.2
Cypermethrin	25.0	<RL	73.0
Esfenvalerate	37.8	<RL	303.6
Deltamethrin	63.3	7.5	6172.8
Organophosphates			
Diazinon	8.9	<RL	11.3
Chlorpyrifos	21.7	<RL	52.4
Phenylpyrazoles			
Fipronil	36.3	<RL	3663.9
Desulfinyl fipronil	54.4	1.3	2682.0
Fipronil sulfide	16.7	<RL	252.0
Fipronil sulfone	47.8	<RL	2572.3

*DF=Detection Frequency, N=180

†RL= Reporting Limit: 1.0 ng/g for all compounds except for bifenthrin and diazinon where RL = 0.50 ng g^{-1}

The organophosphates diazinon and chlorpyrifos were not detected frequently, and the median concentrations were below the reporting level of 0.5 and 1.0 ng g^{-1}, respectively. Even the maximum observed concentrations were two orders of magnitude smaller than the maximum concentrations of permethrin and bifenthrin. These results coincided well with the use patterns, as residential use of diazinon and chlorpyrifos was discontinued about 10 years ago in California.

Occurrence of particle-bound fipronil was observed to be less widespread than pyrethroids. Fipronil was detected in 36.3% of the 180 dust samples collected, which is less than the detection frequencies of its photolysis (desulfinyl fipronil 54.4%) and oxidation (fipronil sulfone 47.8%) degradation products. This highlights the importance of measuring degradation products as well as the parent compound. Although widespread detection of fipronil and its degradation products occurred, only desulfinyl fipronil had a median concentration above the reporting limit.

Spatial Distribution

In order to determine which areas around a residential home may contribute more particle-bound pesticides to runoff contamination, the spatial distribution of particle-bound pesticides was evaluated. During the February 2014 sampling event, significantly larger ($p<0.05$) concentrations of fipronil and fipronil metabolites were found in samples taken from the driveway than from gutter or street surfaces (Figure 4). These results may be attributed to the fact that the driveway is the closest to the perimeter of houses where pesticide application usually occurs. In fact, it is a common practice for licensed applicators to spray along garage doors for ant control. However, no significant spatial differences were observed in the distribution of pyrethroids or Ops in dust particles. These results were unexpected and may suggest that movement of dust caused by wind or traffic helps redistribute pyrethroids within a neighborhood. This finding also suggests that surfaces other than the driveway should be sampled in order to predict pyrethroid runoff loadings. However, these results are only from one sampling event and the spatial distribution patterns will be validated with more samples.

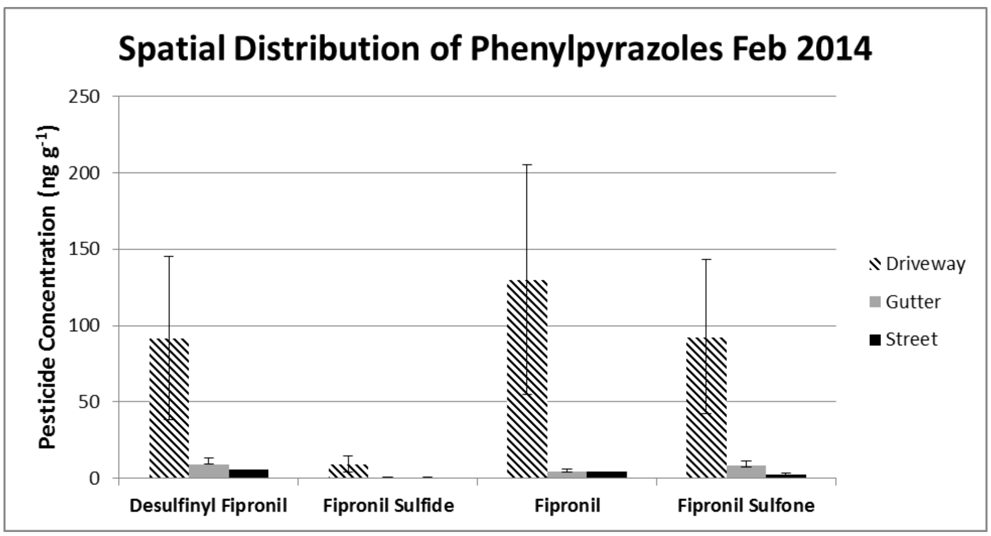


Figure 4. Concentrations of fipronil and its degradates in dust samples collected from driveways, gutters, and streets of Orange County, CA.

Temporal Distribution

We have completed the analysis of all 180 samples from the February 2014 sampling event and 45 samples from the August 2013 event. Therefore, the following temporal comparisons can only be made between samples taken from the same 5 houses in August 2013 and February 2014.

During both sampling events, particle-bound permethrin had the highest average concentration (Figure 5). This agrees well with the monitoring data in which permethrin was the most commonly detected pesticide and also had the second highest median concentration during the February 2014 sampling event. Desulfinyl fipronil, fipronil sulfone, bifenthrin, permethrin, and deltamethrin all displayed larger concentrations in August 2013 than February 2014. These concentration differences may be due to the fact that Orange County received 8.79 cm of rainfall between the August 2013 and February 2014 (CIMIS data). However, differences in concentrations between the two sampling time points were not significant at the p=0.05 level. The lack of significance is probably due to the small sample size (n=45 for each sampling event). Temporal distributions should become more distinct once the data are available for all 20 houses and all 3 sampling events.

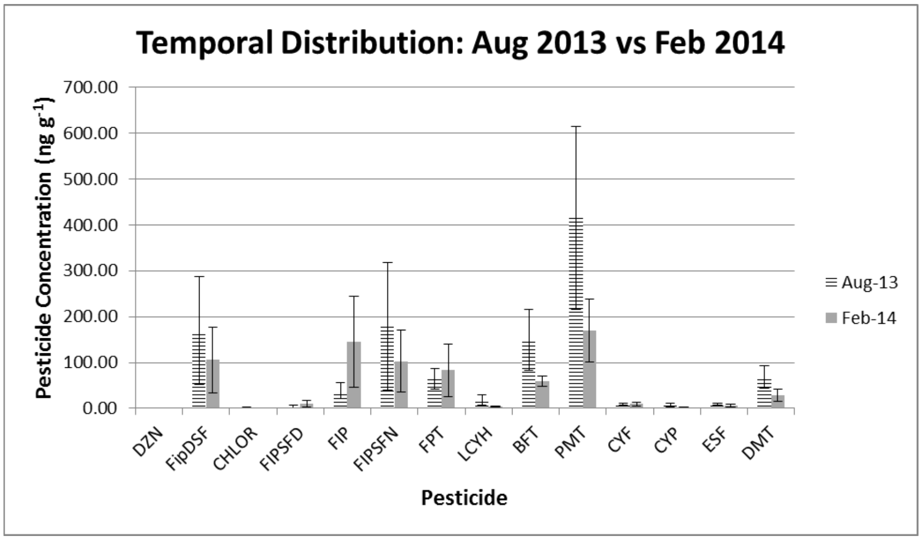


Figure 5. Concentrations of particle-bound pesticides in samples collected from 5 houses in Orange County, CA during August 2013 and February 2014 n = 45 for each sampling event

Particle Characteristics

Bulk dust collection was conducted in July 2014 from 4 houses in Orange County, CA. To date, all four of the bulk dust samples have been separated into different size groups, and the pesticide concentrations associated with each particle size (2,000-425 µm, 425-250 µm, 250-149 µm, 149-45 µm, 45-38 µm, and < 38 µm) have been analyzed in triplicate for one of the bulk dust samples (Figure 6). Significantly higher ($p<0.01$) concentrations of diazinon, fipronil sulfone, esfenvalerate, and deltamethrin were observed in the 45-38 µm and <38 µm size fractions. Similarly, the <38 µm size fraction had a significantly higher ($p<0.01$) concentration of cyfluthrin than any of the other size fractions. These results are probably due to the fact that the smaller particle sizes have a larger surface area for sorption when compared to larger particle sizes. Therefore, the compounds with larger Log Kow values should be present in the smaller size fractions in greater concentrations. However, similar patterns were not found for permethrin and fenpropathrin, for which the highest concentrations are associated with the 250-149 µm size fraction (Figure 6C). These results may be due to the use of a granular formulation of pesticides that contained relatively large particles. In addition, organic carbon content may also influence the size-dependent distribution and should be considered in future analysis. A conclusion may become more evident when all samples have been analyzed and the data pooled for analysis.

If the majority of particle-bound pesticides are associated with the fine fractions, off-site transport by wind or runoff water may carry pesticide residues over long distances as settling of suspended particles is known to be proportional to particle size. By understanding this distribution, more targeted mitigation practices may be developed to control offsite pesticide movement. This information will also aid in the predicative capabilities of models.

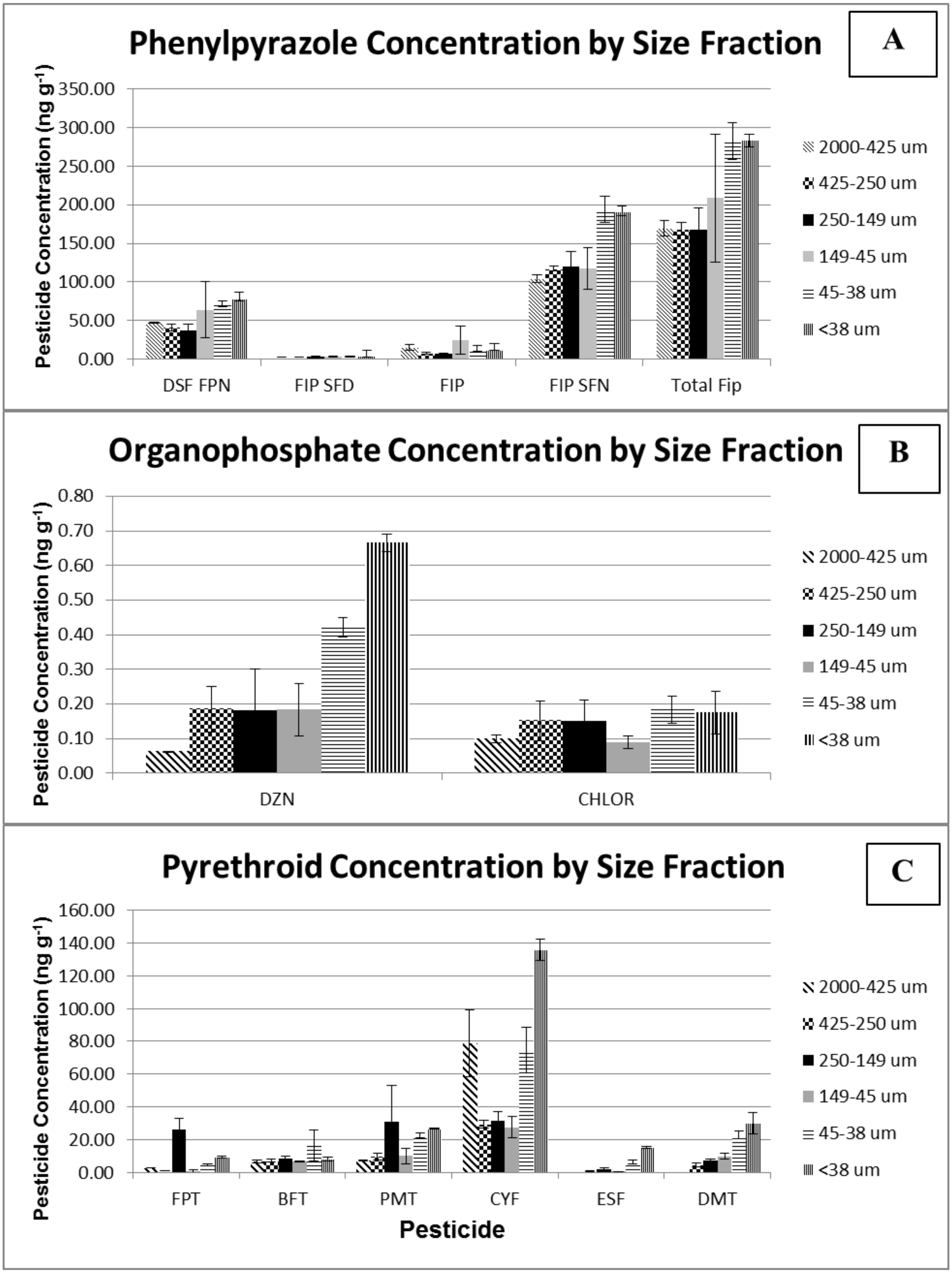


Figure 6. Concentrations of A) phenylpyrazole, B) organophosphate, and C) pyrethroid insecticides in different particle size fractions of one bulk dust sample collected in Orange County, CA