Distribution of pesticides in dust particles in urban environments☆

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ABSTRACT

In regions with a mild climate, pesticides are often used around homes for pest control. Recent monitoring studies have linked pesticide use in residential areas to aquatic toxicity in urban surface water ecosystems, and suggested dust particles on paved surfaces as an important source of pesticides. To test the hypothesis that dust on hard surfaces is a significant source of pesticides, we evaluated spatial and temporal patterns of current-use insecticides in Southern California, and further explored their distribution as a function of particle sizes. Pyrethroid insecticides were detected in dust from the driveway, curb gutter and street at 53.5—94.8%, with median concentrations of 1—46 ng g^{-1}. Pyrethroid residues were uniformly distributed in areas adjacent to a house, suggesting significant redistribution. The total levels of pyrethroids in dust significantly (p < 0.01) decreased from October to February, suggesting rainfalls as a major mechanism to move pesticide residues offsite. Fipronil as well as its degradation products, were detected at 50.6—75.5%, and spatial and temporal patterns of fipronil residues suggested rapid transformations of fipronil to its biologically active intermediates. Moreover, pyrethroids were found to be enriched in fine particles that have a higher mobility in runoff than coarse particles. Results from this study highlight the widespread occurrence of pesticides in outdoor dust around homes and the potential contribution to downstream surface water contamination via rain-induced runoff.

1. Introduction

Pesticides are used in urban environments to control undesirable pests such as ants, termites, and spiders. The most intensive urban pesticide use occurs in regions such as California that have highly urbanized populations and a conducive climate for pest activity year-round. For example, it was estimated that over 1.6 million kilograms of pesticide active ingredients were applied by professional applicators in urban settings in California in 2012 (CDPR, 2012). The actual pesticide consumption could be significantly larger if applications by homeowners are also considered (Budd et al., 2007).

Many studies in recent years have shown the occurrence of urban-use insecticides such as synthetic pyrethroids and fipronil in irrigation and rain-induced runoff and in urban streams (Gan et al., 2005; Amweg et al., 2006; Budd et al., 2007; Holmes et al., 2008; Hintzen et al., 2009; Weston et al., 2009; Ding et al., 2010; Lao et al., 2010; Gan et al., 2012; Jiang et al., 2012; Ensminger et al., 2013). In some cases, pesticide levels in the sediment or water of urban waterbodies exceed their acute toxicity thresholds for sensitive species such as Hyallela azteca (Holmes et al., 2008).

Due to their strong affinity for solid surfaces, it may be expected that after application, pesticides can contaminate surface soil in landscaped areas and dust on pavement. Wind, water or traffic may cause further movement and redistribution of these contaminated loose solids, depositing them onto paved surfaces. Irrigation or rain-induced surface runoff may subsequently carry these particles, along with the pesticide residues, to downstream water bodies. Due to the fact that up to 90% of the urban surface area may be comprised of impervious surfaces (e.g., pavement, roofs), pesticide-contaminated dust on hard surfaces can be a primary source for pesticide contamination of urban streams (USDA., 1986; Jiang et al., 2015). A recent study showed that concentrations of chlorpyrifos, cypermethrin, and permethrin in dust in an urban area of southern China varied seasonally based upon application and were within the same range as those seen near agricultural areas in the US, Malaysia, and Japan (Li et al., 2014). Mahler et al. (2009) measured concentrations of fipronil, fipronil sulfide, and fipronil desulfinyl in

indoor and outdoor dust associated with an apartment complex in Texas and found that 100% of the samples contained at least one of the target compounds with outdoor concentrations ranging from <0.5–300, <0.5–8.42, and <0.5–120 µg kg^{-1}, respectively. A recent study by Jiang et al. (2015), found that 75.8% of outdoor dust samples contained 7 or more pesticides, and that pesticide concentrations in outdoor dust can be used to predict concentrations in runoff. These studies provide initial evidence of pesticide association with outdoor dust in urban residential areas. However, to date little effort has focused on identifying dust particles on urban pavement as a major contributor to pesticide contamination of urban surface water.

The main objectives of this study were to quantify the types and levels of pesticides in dust particles on urban pavement, determine whether spatial, temporal, or particle size distribution patterns exist, and evaluate contributions of urban pavement dust to off-site pesticide transport and surface water contamination in urban watersheds. This information may be used to improve the prediction of pesticide loadings to urban surface water bodies and to design more targeted mitigation measures to reduce the offsite transport of urban-use insecticides.

2. Materials and methods

2.1. Chemicals

Twelve insecticide compounds in two classes were targeted for analysis in this study. These included 8 pyrethroids, i.e., fenpropathrin, lambda-cyhalothrin, bifenthrin, permethrin, cyfluthrin, cypermethrin, esfenvalerate and deltamethrin; and the phenylpyrazole insecticide fipronil and its three primary transformation products desulfinyl fipronil, fipronil sulfide, and fipronil sulfone. The standards of pyrethroids were obtained from various chemical manufacturers, with purities from 97% to 99.9%. The deuterated bifenthrin (d5-bifenthrin) was provided by Toronto Research Chemicals (Toronto, Ontario, Canada), and phenoxy $^{13}C_6$-labeled *cis*-permethrin (^{13}C-permethrin, 99%) was obtained from Cambridge Isotope Laboratories (Andover, MA). Standards of fipronil (98.9%), desulfinyl fipronil (97.8%), fipronil sulfide (98.8%) and fipronil sulfone (99.7%) were obtained from the U.S. EPA's National Pesticide Standard Repository (Fort Meade, MD). Solvents used were in GC/MS or pesticide grade.

2.2. Sampling locations

Twenty homes distributed throughout Orange County, CA were selected for sample collection. Orange County, CA was chosen because pesticide use records suggested that more urban use pesticides are often used in this area than elsewhere in California (CDPR, 2012). The houses were selected with the help of Dr. Darren Haver of the South Coast Research and Extension Center in Irvine, CA, who had previous contact with the homeowners through the master gardener program. Geographically, the houses selected covered a distance of approximately 44 km from south to north and 17 km from east to west (Fig. S1).

2.3. Sample collection

At each house, triplicate dust samples were collected from the driveway directly against the garage door, curbside gutter, and middle of the street for a total of nine samples per house for each sampling event in August 2013, October 2013, and February 2014. The dust was collected using a handheld vacuum fitted with a metal housing and mesh that contained a pre-weighed 1.6 µm (pore size) Whatman GF/A glass-fiber filter paper (Maidstone, U.K.). The area

vacuumed for each sample was fixed by using a 0.5 m^2 frame. If the amount of dust collected from one frame was small, the frame was moved to an adjacent area and the dust from an additional frame area was collected with the number of frames per sample being recorded. After collecting each sample, the filter paper was carefully removed and sealed in a glass vial for transport to the laboratory. The vacuum and housing were cleaned with isopropanol before collecting the next sample. Samples were transported in insulated containers to the laboratory on the same day of collection. The samples were stored at 4 °C before analysis.

2.4. Sampling and particle size fractionation

Dust samples in larger quantities were collected in April 2014 from three houses to characterize the dependence of pesticide distribution on particle sizes. These bulk dust samples were collected using a handheld vacuum with an attached 0.3 µm pore size vacuum bag and by vacuuming all surfaces (driveway, gutter, and street) at each house to get three representative samples. The bulk dust samples were loaded onto a stack of sieves (with decreasing mesh sizes from top to bottom) and mixed on a mechanical shaker. The fractionation resulted in the following particle size fractions: >2000 µm, 2000–425 µm, 425–250 µm, 250–149 µm, 149–45 µm, 45–38 µm, and <38 µm. The mass of particles in each fraction was weighed to determine the particle size distribution of each dust sample. The fractionated particles were then analyzed individually for the target pesticides.

2.5. Sample preparation

For the driveway, curbside gutter, and street dust samples, each filter paper with the associated particles was weighed again to determine the mass of collected dust particles. Centrifuge tubes containing the filter and dust particles were spiked with a surrogate (d5-bifenthrin) and extracted ultrasonically with 30 mL methylene chloride/acetone (1:1, v/v) for 15 min in a Fisher Scientific FS110H sonication water bath (Waltham, MA). After sonication, the samples were centrifuged at 2000 rpm for 10 min and the extract was passed through a layer of anhydrous sodium sulfate into a 250-mL glass round-bottom flask. The same extraction step was repeated a total of four times, and the organic solvent phase was combined. The extract was then evaporated under a gentle vacuum on a Büchi RE121 Rotavapor (Flawil, Switzerland) at 30 °C to approximately 0.5 mL. The final extract was reconstituted in 5.0 mL of hexane/ethyl ether (7:3, v/v), and cleaned up by passing through a Florisil cartridge and eluting with hexane/ethyl ether (7:3, v/v). The clean extract was evaporated under a gentle nitrogen flow at 40 °C to near dryness and the residue was recovered in 1.0 mL hexane/acetone (9:1, v/v) for analysis.

For the bulk dust samples, a 2.0 g subsample from each size fraction was removed and extracted following the method as described above. The total organic carbon content (TOC) in each particle size fraction was determined by the loss on ignition method described by Gavlak et al. (2003). Briefly, duplicate 2.0 g subsamples from each particle size were removed and dried at 150 °C in a muffle furnace for 2 h. The dried samples were weighed and then heated in the muffle furnace at 425 °C for 2 h. After 2 h, the samples were removed and weighed again. The difference in mass was attributed to organic carbon and was used to calculate TOC. Reagent-grade calcium carbonate was included to determine if any losses of inorganic carbon would occur. Under the used conditions, calcium carbonate showed <0.05% loss.