Science of the Total Environment 580 (2017) 158–167

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Assessing pesticide wet deposition risk within a small agricultural watershed in the Southeastern Coastal Plain (USA)☆

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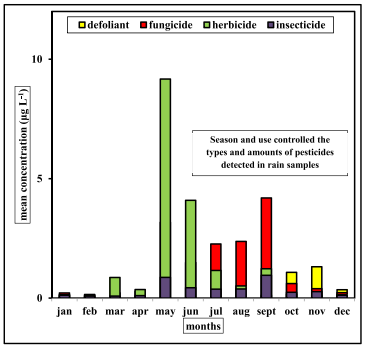
HIGHLIGHTS

- Current use pesticides were monitored in rainfall in a small watershed for 3 years.
- A fungicide and an insecticide were detected in nearly all samples.
- Their concentration frequently exceeded harm to aquatic life benchmarks.
- Wet deposition of an herbicide, metolachlor, exceeded runoff from nearby fields.
- Study supports inclusion of wet deposition in pesticide risk and fate assessments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 September 2016
Received in revised form 2 November 2016
Accepted 3 November 2016
Available online 24 December 2016

Editor: J Jay Gan

Keywords:
Rainfall
Endosulfan
Chlorothalonil
Metolachlor
Ecological risk assessment

ABSTRACT

Pesticide volatilization and deposition with precipitation is widely documented and has been connected to adverse ecological impact. Here we describe a 3-yr study of current use and legacy pesticides in event-based rain samples within a 123-ha agricultural watershed. Crops in farm fields were documented quarterly with data used to estimate target compound use. The median number of pesticide detections in samples was 6. The fungicide, chlorothalonil which was used most intensively was detected in nearly all samples. It had the highest mean and peak concentrations with total deposition ≈0.1% of the estimated amount applied. The insecticide endosulfan also had relatively high use with behavior mirroring chlorothalonil. There was strong seasonal variation in concentration and depositional dynamics with the highest values measured during growing seasons. Similar behavior was observed with other compounds detected in rain samples with a general decrease in deposition and mean concentrations as use decreased. Comparison of measured concentrations to values associated with toxic impact on aquatic organisms indicated that chlorothalonil, endosulfan, chlorpyrifos, malathion and atrazine may contribute to adverse impact. The number of samples exceeding risk endpoints ranged from 1 to 77%. The highest value was for endosulfan; however its on-going phase-out is expected to reduce risks. Another finding was that the wet deposition of the herbicide, metolachlor exceeded measured runoff rates in the watershed by 5-fold. The study has demonstrated that localized pesticide wet deposition may present ecological risks and that volatilization and wet deposition is an important pesticide transport pathway at the local scale. Findings point to the need to include wet deposition in assessments of pesticide ecological risk and environmental fate.

Published by Elsevier B.V.

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http://dx.doi.org/10.1016/j.scitotenv.2016.11.020
0048-9697/Published by Elsevier B.V.

1. Introduction

Evaporation from soil, plant, and other treated surfaces results in pesticide transfer in the gas phase into the atmosphere. As a process this is commonly termed volatilization and can occur during or post-application. The topic has been investigated for >50 years and periodically reviewed (Abbott et al., 1965; Bedos et al., 2002; Majewski and Capel, 1995; Spencer et al., 1973; Van Den Berg et al., 1998). Studies have indicated that post application volatilization losses span a broad range, from 0.2% to >90% of the amount applied (Barbash, 2007; Van Pul et al., 1999). The magnitude of losses was linked to pesticide physical chemical properties including: vapor pressure; Henry's Law constants; potential to sorb to soil, plant, and other treated surfaces; and diffusion coefficients. Volatilization losses were also linked to climatic conditions, soil water status, mode of application including spray characteristics and formulation, plant uptake, and management practices, such as soil incorporation and conservation tillage (Alletto et al., 2009; Barbash, 2007; Bedos et al., 2002, 2010; Woodrow et al., 1997).

Once in the atmosphere, gas phase pesticides are subject to advective and diffusive transport, photochemical oxidation and degradation, sorption on aerosols and particulate matter, and wet and dry deposition. Transport distances from areas of application and emission vary from meters to 1000s of kilometers depending on rates of atmospheric degradation and depositional fluxes (Van Pul et al., 1999).

Most studies that have evaluated deposition have focussed on collection and analysis of rain. Generally this is relatively simple compared to dry deposition measurements that involve both pesticides in the gas phase and those sorbed to particulate matter and aerosols. Wania et al. (1998), have described the process of pesticide scavenging from air by rainfall. Equilibrium partitioning between vapor-phase pesticides and raindrops is typically assumed, with Henry's Law constants and temperature governing the process.

Like pesticide volatilization, the occurrence and deposition of pesticides in rain has been the focus of a very large number of published investigations spanning more than 5 decades. They have included reports of detection of legacy pesticides, like DDT, as well as numerous products in current use (Wheatley and Hardman, 1965; Dubus et al., 2000). Monitoring was conducted in remote areas, approximately 1000 km away from pesticide sources, at stations at intermediate distance (1 to 100 km), and within areas <1 km where the pesticides were applied (Dubus et al., 2000; Potter et al., 2014a; Van Dijk and Guicherit, 1999).

In some studies measured deposition was related to the mass of pesticides used in contributing areas. For example, Vogel et al. (2008), reported that total pesticide wet deposition measurements made in 4 agricultural watersheds ranged from 0.06 to 1.73% of the amount applied. The highest deposition rate was in the local-scale area where the pesticides were applied to agricultural fields. This value is comparable to surface runoff rates that are commonly observed, ≈1% of the amount applied (Wauchope et al., 1995). Potter et al. (2014a) estimated that about 0.1% of the insecticide endosulfan applied to farm fields in Southern Florida was deposited locally in rainfall. In another investigation that linked surface runoff to volatilization, Gish et al. (2011), found that the volatilization mass loss of the herbicides atrazine and metolachlor when applied preemergence to bare soils was 2 to >130 and 10 and >150 times the mass loss in runoff; however deposition was not measured.

Findings that volatilization of some active ingredients may greatly exceed runoff rates and that wet deposition of pesticides at least at the local scale may be comparable, suggests that pesticide volatilization and wet deposition may need to be considered in risk assessments of pesticide use. The human and ecological risks of pesticide volatilization and deposition were discussed in detail at an international symposium in 1998 (Guicherit et al., 1999). The symposium included recommendations for approaches that may be used to incorporate volatilization and deposition into regulatory risk assessments (Bakker et al., 1999; Gilbert, 1999). However these processes are not currently an integral part of risk assessment processes. For example, in USA pesticide release into the atmosphere is evaluated, but the focus is on drift and post-volatilization transport of fumigants (USEPA, 2016a). Wet deposition is not considered.

We measured wet deposition of 14 current-use and 2 legacy pesticide active ingredients and 1 degradate within a small farm scale (123 ha) watershed in south central Georgia (USA) for 3 years. The watershed is intensively farmed with >50% of the land in mixed crop production (Lowrance et al., 2007). We hypothesized that frequent rainfall during growing seasons and high rates of pesticide use in the watershed would contribute to relatively high rates of pesticide wet deposition. Wet deposition measurements were used to support first-tier risk assessments and to identify the upper bounds of pesticide wet deposition in watersheds in the region.

2. Materials and methods

2.1. Study area and sample collection location

The study was conducted within a 123-ha drainage basin near Tifton, GA (Fig. 1) that forms a headwater for a stream flowing into the Little River, a tributary of the Suwannee River. The bowl-like basin is typical of low-order streams in this landscape with dense riparian forests on stream banks and well-drained soils in uplands that are intensively cropped (Lowrance et al., 2007). In 2007–09, land cover was vegetable and row crops (50%) and adjacent grassed areas (6%), mixed deciduous and evergreen forest (33%), irrigation ponds (4%), and low intensity "urban" development, including roads (7%). These values differed slightly from the surrounding county, where proportions of row crop/pasture and open water covers were lower (48% and 2%, respectively), and urban and forested land cover proportions were higher (11% and 37%, respectively). Cropped areas included fields located on the University of Georgia Gibbs research farm and nearby areas in intensive commercial vegetable production (Fig. 1). Vegetable crops were: cucumber (*Cucumis sativus*), squash (*Cucurbita pepo*), green peppers (*Capsicum annuum*), melons (*Cucumis melo*), tomatoes (*Solanum lycopersicum*), eggplant (*Solanum melongena*), green beans (*Phaeolus vulgaris*), collards (*Brassica oleracea* var. *viridis*), and cabbage (*Brassica oleracea* var. *capitata*). They were produced using plastic mulches with drip-irrigation, and in some cases (tomatoes; eggplant) were double cropped. The principal growing season for most crops was March through October. Crops on the research farm were primarily cotton (*Gossypium hirsutum* L.), peanut (*Arachis hypogaea* L.), and field corn (*Zea mays*). Cotton and peanut growing seasons were May to October and, for corn, March to July. With few exceptions all farm fields were left fallow during winter months (December to February). The pesticide wet deposition collector was located on the research farm (N31°26′16″, W83°35′19″; elevation 99.3 masl) in an open field midway between the lower boundary of research plots in rotational cotton and peanut production and a riparian forest (Fig. 1). The distance between the plots and the trees was about 25 m. A weather station was co-located approximately 50 m east of the sampler (Bosch et al., 2012).

2.2. Rain sample collection

Samples were collected on an event basis using a modified MIC-B® rain sampler (Meteorological Instruments of Canada, Richmond, ONT, Canada) equipped with a covered 0.2 m^2 stainless steel funnel and lid controlled by a moisture activated sensor. A filter cartridge assembly composed (sequentially) of a Teflon® column (12 cm length × 14 mm diameter), a Teflon® filter head containing a 45-mm diameter glass fiber filter (Whatman GF/F, 0.7 μm nominal pore size), and a solid phase extraction (SPE) cartridge containing 500 mg of Oasis® HLB copolymer beads (Waters, USA) was attached to the bottom of the funnel. A peristaltic pump was connected to the cartridge outlet, which was activated when the funnel lid was opened. The pump pulled rainwater