Chemosphere 209 (2018) 496–507

Contents lists available at ScienceDirect

Chemosphere

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

Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA

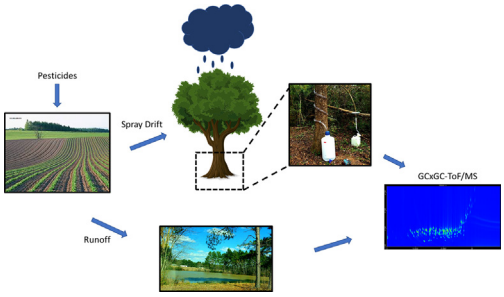
Donna A. Glinski [a, b, *, 1], S. Thomas Purucker [c], Robin J. Van Meter [d], Marsha C. Black [b], W. Matthew Henderson [c]

[a] Grantee to U.S. Environmental Protection Agency via Oak Ridge Institute of Science and Education, Athens, GA, 30605, USA
[b] University of Georgia, Department of Environmental Health Science, Interdisciplinary Toxicology Program, Athens, GA, 30602, USA
[c] U.S. Environmental Protection Agency, ORD/NERL, Athens, GA, 30605, USA
[d] Washington College, Departments of Biology and Environmental Science/Studies, Chestertown, MD, 21620, USA

HIGHLIGHTS

- Pesticide concentrations in surface water, stemflow and throughfall were analyzed.
- Metolachlor and tebuconazole were the most frequently detected pesticides.
- Higher concentrations were observed in throughfall compared to stemflow samples.
- Understanding migration of pesticides will help estimate risk to non-target species.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 March 2018
Received in revised form
10 June 2018
Accepted 16 June 2018
Available online 18 June 2018

Handling Editor: Klaus Kümmerer

Keywords:
Surface water
Stemflow
Throughfall
Pesticides
GCxGC-ToF/MS

ABSTRACT

To study spray drift contributions to non-targeted habitats, pesticide concentrations in stemflow (water flowing down the trunk of a tree during a rain event), throughfall (water from tree canopy only), and surface water in an agriculturally impacted wetland area near Tifton, Georgia, USA were measured (2015–2016). Agricultural fields and sampling locations were on the University of Georgia's Gibbs Research Farm, Tifton, GA. Samples were screened for more than 160 pesticides, and cumulatively, 32 different pesticides were detected across matrices. Data indicate that herbicides and fungicides were present in all types of environmental samples analyzed while insecticides were only detected in surface water samples. The highest pesticide concentration observed was 10.50 μg/L of metolachlor in an August 2015 surface water sample. Metolachlor, tebuconazole, and fipronil were the most frequently detected herbicide, fungicide, and insecticide, respectively, regardless of sample origin. The most frequently detected pesticide in surface water and stemflow samples was metolachlor (0.09–10.5 μg/L), however, the most commonly detected pesticide in throughfall samples was biphenyl (0.02–0.07 μg/L). These data help determine the importance of indirect chemical exposures to non-targeted habitats by assessing inputs from stemflow and throughfall into surface waters.

* Corresponding author. Grantee to U.S. Environmental Protection Agency via Oak Ridge Institute of Science and Education, Athens, GA, 30605, USA.
E-mail address: donna.glinski@dcu.ie (D.A. Glinski).
[1] Current address: Dublin City University, School of Chemical Sciences, Dublin, Ireland.

https://doi.org/10.1016/j.chemosphere.2018.06.116
0045-6535/

1. Introduction

In 2007, approximately 5.2 billion pounds of pesticides were used worldwide; of that amount, 1.1 billion pounds were applied on U.S. soils (Grube et al., 2011). Along with detect concentrations of pesticides in surface waters, pesticides have also been found globally in rainwater (Hüskes and Levsen, 1997; Ahmed et al., 1998; McConnell et al., 1998; Coupe et al., 2000; Dubus et al., 2000; Goel et al., 2005; Sauret et al., 2009; Zhang et al., 2011; Potter et al., 2014; Rice et al., 2016; Potter and Coffin, 2017). Many researchers have monitored pesticides in rainfall, where concentrations have reached 22.9 μg/L of methyl parathion near agricultural sites (Coupe et al., 2000). In rainwater, herbicides were frequently found to be more prevalent, based on detection frequency, (46–61%) and at higher concentrations than insecticides and fungicides (Trevisan et al., 1993; Goel et al., 2005).

Spray drift is the process whereby, during application, an amount of pesticide does not reach the intended application zone due to wind transportation (Briand et al., 2002; Vischetti et al., 2008). Pesticide spray drift often contributes to contamination of nearby surface waters and other non-agriculturally targeted areas. Many parameters can affect spray drift such as climatic conditions and land topography, as well as spray characteristics (i.e. droplet diameter, viscosity of the formulation, and spraying technique) (Briand et al., 2002; Vischetti et al., 2008). Due to variations in climatic conditions, pesticide spray drift may contaminate areas 10–100 m from the intended application site (de Snoo and de Wit, 1998). Even with the presence of a 20-m buffer zone surrounding agricultural fields, spray drift can significantly pollute the surrounding area (Cunha et al., 2012).

Throughout the world, 40% of applied pesticides are herbicides, 33% are insecticides, while 10% are fungicides and 17% are classified as others. Many of these compounds can be readily volatilized after application due to their physical properties (Stokstad and Grullón, 2013). Volatilization coupled with spray drift likely causes many agriculturally-applied pesticides to be transported to the atmosphere, resulting in quantifiable amounts in rainwater far from application sites (Hüskes and Levsen, 1997; Ahmed et al., 1998; Coupe et al., 2000). Gish et al. (2011) determined that volatilization of herbicides occurred immediately after application and measurable concentrations were detected more than 5 days later. It has been estimated that, on average, 23–65% of applied metolachlor can volatilize under certain climatic conditions, within a few days of application (Gish et al., 2011). For other current-use pesticides, up to 90% of the total mass applied can volatilize during and following agricultural application (LeNoir et al., 1999).

Due to volatilization, long-range atmospheric transport of pesticides can occur; compounds can traverse many miles and have been found in remote regions such as the Arctic (Cotham and Bidleman, 1991; Rice and Chernyak, 1997). Conveyance of pesticides to the atmosphere can be caused by spray drift, volatilization, runoff, and wind erosion of soil (Briand et al., 2002). Both runoff and volatilization, as previously discussed, have been investigated for sources of pesticide loss. It was found that runoff accounts for less than 3% loss, while volatilization accounts for approximately 2–25% total loss (Gish et al., 2011). Atmospheric transport has also been shown to deposit pesticides to nearby pristine areas and it is well-documented that pesticides applied in the agriculturally intensive Central Valley of California have been transported and deposited to the Sierra Nevada mountain range (McConnell et al., 1998; LeNoir et al., 1999). Of note: tebuthiuron, a herbicide, was detected at concentrations four times higher in a Brazilian riparian forest compared to other areas, possibly due to air pollution concentrating the pesticide in the tree canopy and then releasing into the soil during rain events (Bicalho et al., 2010).

Pesticide residues may enter the ecosystem through precipitation, leaching, spray drift, discharge of wastewater and other routes (Griffini et al., 1997; Konstantinou et al., 2006; Rice et al., 2016). During a rain event, contaminating pesticides are often washed off trees and surrounding foliage which results in stemflow (precipitation that flows down along the tree trunk) and throughfall (rain that passes through the tree canopy). These routes of environmental release have been well-studied and higher concentrations of pesticides are often detected in stemflow and throughfall samples when compared to open-field rainfall (Bernhardt and Ruck, 2004; Rice et al., 2016). Further, stemflow encounters more arboreal surface area for a longer period of time than throughfall, resulting in higher pesticide concentrations in stemflow than in throughfall (Rice et al., 2016). Pesticides studied by Bernhardt and Ruck (2004) were detected in stemflow samples for a longer period of time than rainfall samples due to the trees acting as filters and concentrating contaminants from the atmosphere. Large pulses of pesticides have also been shown to flow into rivers or surface waters after spray application that coincides with a rain event (Thurman et al., 1991; Griffini et al., 1997; Konstantinou et al., 2006; Rice et al., 2016). Understanding how concentrations of pesticides enter aquatic habitats is paramount in quantifying the cumulative environmental exposure and risk associated with spray drift.

In a recent survey that analyzed pesticide concentrations in streams throughout the U.S., the occurrence rate of detecting one or more pesticides in agricultural, urban or mixed use watershed matrices was over 90% (Gilliom et al., 2006). The most frequently detected herbicides in these waters were atrazine, glyphosate, aminomethylphosphonic acid (AMPA; a metabolite of glyphosate) and metolachlor (Gilliom et al., 2006; Battaglin et al., 2016). In agreement, Smalling et al. (2012) detected 24 pesticides in pond water samples collected from several states throughout the U.S. The most frequently detected pesticides were, again, herbicides, mainly atrazine, glyphosate and AMPA. Battaglin et al. (2016), however, reported that fungicides were more frequently detected in water samples collected throughout the U.S. compared to insecticides and herbicides, likely due to their more frequent, intensive application schedules even with lower application rates. Overall, concentrations of pesticides in surface waters tend to follow seasonal trends with higher detectable concentrations observed during periods of heavy use (such as in spring and summer due to preparation for planting) and lower concentrations in winter and after crop harvesting (Konstantinou et al., 2006).

To date, few studies have attempted to quantify pesticides in stemflow and throughfall and determine how these concentrations impact surface water concentrations (Trevisan et al., 1993; Bernhardt and Ruck, 2004; Zhang et al., 2011; Rice et al., 2016). The overall objective of this study was to identify and quantify pesticides in surface water, stemflow and throughfall, adjacent to agricultural fields, over the course of a year (February 2015 through January 2016). We also compared stemflow to throughfall concentrations after rain events at three paired sites. This research will ultimately inform regulatory aspects of pesticide application such as environmental residence time in rainwater, surface waters/rivers, and surrounding foliage as a result of spray drift and its impact on non-target organisms inhabiting the areas.

2. Materials and methods

2.1. Chemicals

In total, we screened for 160 pesticides by combining those commercially available in the gas chromatography (GC) multi-residue pesticide kit from Restek ($n > 150$); Bellefonte, PA) and supplementing additional pesticides that were obtained from the

U.S. EPA National Pesticides Standard Repository (Fort Meade, MD). All solvents and analytical reagents used were of highest purity (≥HPLC grade) and obtained from Fisher Scientific (Pittsburgh, PA).

2.2. Surface water collection

Monthly surface water samples were collected from ten different locations on Gibbs Research Farm in Tifton, GA from February 2015–January 2016 (Fig. 1). Sites 4, 5, 8, 9 and 10 were classified as "ponds" while the other sites were "streams". However, all of these sites are interconnected to each other through small streams, ponds and a weir. Gibbs Farm is an agricultural research facility used by the University of Georgia (UGA) and the U.S. Department of Agriculture (USDA). In southwest Georgia, the most prominent crops are cotton and peanuts, although corn and soybeans are also frequently farmed (personal communication, Thomas Potter, USDA). Corn, peanuts, and cotton were visually identified in the fields where water samples were collected. After three pre-rinses, 1 L of surface water was obtained from each site in glass amber jars. Duplicate 4 L samples were collected at sites 4, 5 and 8 to afford the additional detection of pesticides due to their proximity to application and cropped fields. All samples were immediately capped, labeled and placed in a cooler on ice. Back at the U.S. EPA lab in Athens, GA, all samples were placed in the refrigerator at 4 °C until processed before two weeks elapsed as described below.

2.3. Stemflow and throughfall collection

Stemflow and throughfall samples were collected on a rain-event basis at the Gibbs Farm in Tifton, GA from March 2015–January 2016, when rainfall was greater than 0.5 mm (100 mL). For stemflow collection, PVC clear vinyl tubing was wrapped ~2.5 times around a tree at three different locations on Gibbs Farm (adapted from Williams, 2004). These setups were adjacent to sites 3, 4, and 7, and selected trees had a diameter at breast height (DBH) of 29.11, 29.11 and 33.15 cm, respectively (see Fig. 1). Trees were selected based on distance to field (i.e. closest), DBH, and the absence of overlapping tree canopies. Tubing, with the top half removed, was attached to the tree using nails and silica adhesive glue, allowing the top portion to remain open for water collection and transport (adapted from Williams, 2004). Stemflow was collected in 25 L carboys to minimize environmental/animal interactions with samples.

Throughfall was collected under the same tree canopy used for stemflow collection, using a large funnel attached to PVC pipe and tubing connected to a 20 L carboy (adapted from Williams, 2004). The funnel was covered with screen mesh to eliminate large debris such as leaves and sticks. After each rain event, 1 L of thoroughly mixed stemflow and throughfall subsamples were transferred to pre-labeled amber jars with date and volume recorded, then stored in a refrigerator at 4 °C until processed as described below. Samples were collected as soon as possible and all stemflow and throughfall concentrations were normalized to 1 L.

2.4. Extraction procedure

All water samples were filtered through a 0.45 μm GF/F filter paper using a glass filtration apparatus. The entire 1 L sample was passed through a pre-conditioned C18 solid phase extraction (SPE) cartridge (Oasis HLB 6 cc, 500 mg), that was attached to a vacuum manifold, at a rate of 10 mL min^{-1}. The SPE was dried under vacuum for 45 min and then eluted sequentially with 6 mL each of methanol and dichloromethane into a glass disposable cell culture tube. The sample was gently evaporated under nitrogen gas and then reconstituted in 1 mL of ethyl acetate and transferred to a 2 mL GC/MS vial. All samples were analyzed on a 4D gas chromatograph by gas chromatograph time of flight mass spectrometer (GCxGC-ToF/MS) as described below.

2.5. GCxGC-ToF/MS analysis

All water samples were analyzed on a LECO Pegasus® 4D GCxGC-ToF/MS equipped with a Rtx-CLPesticides II (30 m, 0.25 μm thickness, and 0.32 mm ID; Restek, Bellefonte, PA) primary column, and a Rxi-17Sil MS (2 m, 0.15 μm thickness, and 0.15 mm ID; Restek,

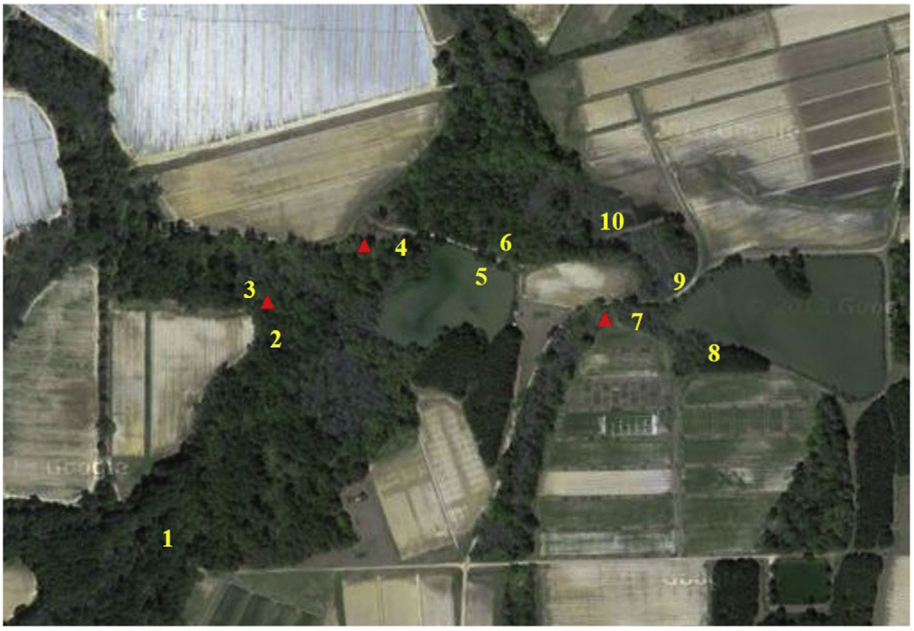


Fig. 1. Location of study sites in Tifton, GA at the University of Georgia's Gibbs Research Farm. Triangles represent the locations of the paired stemflow and throughfall collectors located at sites 3, 4 and 7.

Bellefonte, PA) secondary column, following the method in de Koning and Gumpendobler (2007). GCxGC enables two compounds to separate out based on a second varying phase column. While a time of flight mass spectrometer (ToF/MS) was utilized because it can detect all ions that hit the detector at any given time, instead of scanning for a specific *m/z* value. Therefore, this instrumentation allowed us to maximize our efforts in identifying pesticides within these environmental matrices. All injections (4 μL) were made in splitless mode. The inlet, transfer line and source temperatures were 275 °C, 250 °C and 225 °C, respectively. Helium was the carrier gas and maintained at a constant pressure of 26 psi during the analytical run. The primary oven's initial temperature was 95 °C and held for 5 min, then ramped 10 °C min^{-1} to 200 °C, followed by a ramp of 7 °C min^{-1} to 270 °C, with a final ramp of 10 °C min^{-1} to 320 °C held for 10.5 min. The secondary oven's initial temperature was 105 °C for 6 min, ramped from 10 °C min^{-1} to 360 °C and held for 15 min. The modulator offset was 30 °C higher than the primary oven, and the modulation period for liquid nitrogen was 5 s with a hot pulse of 0.6 s. A prepared standard mix was analyzed to develop a data processing method and calibration method for comparison to all field samples based on protocols supplied by the GCxGC-ToF/MS manufacturer. The standards were all reprocessed using the final data processing method to obtain concentrations for the corresponding pesticides against the calibration curve (Tables S1 and Table S2).

2.6. Statistical analysis

We tested whether field observations of stemflow concentrations were greater than throughfall concentrations. Samples were paired across three locations and 18 different sampling dates, resulting in 54 observations for each of the 32 pesticides detected. Many samples were non-detects in both stemflow and throughfall samples, therefore a non-parametric Wilcoxon Rank Sum test was implemented. Other tests requiring distribution assumptions such as t-tests were considered impractical due to non-detects and resulting data skewness. The method used to calculate the signed-rank test by Wilcoxon (1945), discards any tied data and then calculates the signed ranks. We used the wilcox.test with ties (paired = TRUE, alternative = 'two.sided', exact = FALSE) from the R stats package R Core Team (2017), run on pooled pair-wise comparisons across all chemicals, date and sample locations.

3. Results and discussion

3.1. Pesticide concentration in surface water, stemflow and throughfall

Our in house standard mixture of pesticides was analyzed at the beginning of each set of samples and these daily runs were used to process all field samples (Table S2). In total, 32 different pesticides were identified and quantified in all three environmental matrices (surface water, stemflow, and throughfall). Overall, ten herbicides, eleven fungicides, five insecticides, five pesticide degradates, and one bird repellent were detected in at least one water sample (Table 1). In this study, metolachlor was the most frequently detected herbicide, with a detection frequency of 86% in surface water, 90% in stemflow, and 78.8% in throughfall (Table 1). The highest measured concentration of metolachlor was 10.50 μg/L observed in surface water in August collected at site 3. Metolachlor is applied in south Georgia as a pre-emergent herbicide on peanuts and cotton via tractor boom pivot from late April to early May (personal communication, Thomas Potter, USDA). Tebuconazole was the second most frequently detected pesticide, as well as the most frequently detected fungicide, with detection frequencies of 62% in surface water, 30% in stemflow, and 83% in throughfall samples (Table 1). The highest concentration detected for tebuconazole was 1.8 μg/L in an August throughfall sample. Tebuconazole is one of the most commonly applied fungicides in south Georgia with application beginning in mid-June, approximately one month after planting, and can be applied 7–8 times using tractor boom pivots (personal communication, Thomas Potter, USDA). Data was not available for the exact timing of pesticide application(s) at the sampling sites. Furthermore, vapor pressure values in Pa were obtained from EPI Suite™ (U.S. EPA, 2012), however, they did not appear to be a predictor of concentrations (Table 1).

Presence of multiple pesticides in a given water sample was frequently observed with more than one pesticide present in more than 80% of surface water and stemflow samples. More than 94% of the throughfall samples contained at least two pesticides. Similar to our data, Gilliom et al. (2006) also detected two or more pesticides more than 90% of the time in urban, agricultural and mixed-use streams. These results demonstrate that mixtures of pesticides are constantly present in the environment. Furthermore, in this study, the occurrence of more than 5 pesticides in surface water was observed more than 35% of the time; this trend also occurred 8% and 55% of the time for stemflow and throughfall, respectively. Dubus et al. (2000) reported that, in Europe, two or more pesticides were detected in rainwater samples on average. Potter and Coffin (2017), reported that the median number of pesticide detections in rainwater near Tifton, GA from 2007 to 2009 was 6, which was higher than our stemflow (3) and throughfall (5) maximum number detects. These results demonstrate that pesticide mixtures are present in several different matrices, making it difficult to determine the potential adverse effects these compounds will have on non-target species.

3.2. Surface water samples

Metolachlor was detected the most frequently, in nine of ten surface water sites, the exception was site 7, where 2-phenylphenol and flutolanil were the most abundant pesticides. For eight of the twelve months studied, metolachlor was detected at a higher concentration relative to all other pesticides. For the months of September and January, metalaxyl was detected at the highest concentration, while atrazine and ethalfluralin (both herbicides) were measured highest in May and December, respectively. Interestingly, the fungicide metalaxyl, is not known to be used on crops located at our collection sites; its detection may arise from agricultural use on adjacent fields.

At sites 1 and 7 the highest pesticide concentration detected was 0.29 μg/L and 0.34 μg/L for flutolanil (a fungicide) in July and August, respectively. Metolachlor had the highest concentrations at 8 sites ranging from 0.32 to 10.50 μg/L in April to September. Sites and months were ranked by total concentrations per site and month, with site 10 and the month of August having the highest total pesticide concentrations of 39.62 μg/L and 39.67 μg/L, respectively. August had the highest pesticide concentration possibly due to the highest amount of rainfall being observed between the July and August sampling dates, this would cause a spike in water concentrations due to runoff. January and site 2, had the fewest detections and lowest overall pesticide concentration from cumulative ranked data (5.28 μg/L) and location (1.48 μg/L).

Metolachlor and tebuconazole, which had the highest frequencies of detection and concentrations were plotted over time for each site (Fig. 2) to investigate temporal trends. Initial application time for metolachlor at our research location, appears to be in April with high concentrations at sites 3 and 10 emerging; however, surface water samples were only collected monthly so estimating the exact application date is difficult. A second 'spike' in

Table 1
Pesticide type, vapor pressure, detection frequency and maximum concentration in surface water, stemflow and throughfall samples. ND = not detected; LOD = limit of detection.

Compound	Type	Vapor Pressure (Pa)[b]	Detection Frequency (%)			Maximum Concentrations		
			Surface water (n = 114)	Stemflow (n = 50)	Throughfall (n = 52)	Surface water µg/L	Stemflow µg/L	Throughfall µg/L
2-Phenylphenol	Fungicide	9.41E-02	28.1	30.0	44.2	0.28	0.68	0.55
Acetochlor	Herbicide	3.74E-03	6.1	10.0	34.6	0.46	0.95	3.05
Alachlor	Herbicide	2.73E-03	25.4	nd	nd	1.40	<LOD	<LOD
Anthraquinone	Bird Repellent	5.10E-06	14.0	8.0	9.6	0.29	2.88	0.26
Atrazine	Herbicide	3.81E-03	10.5	20.0	32.7	1.65	3.65	7.09
DEA	Degradate	1.24E-02	3.5	22.0	5.8	1.25	9.54	1.55
Benfluralin	Herbicide	2.42E-03	0.9	nd	nd	0.11	<LOD	<LOD
Bifenthrin	Insecticide	5.22E-05	1.8	2.0	nd	0.14	0.08	<LOD
Biphenyl	Fungicide	9.99E-01	nd	26.0	84.6	<LOD	1.34	0.07
Chlorothalonil[a]	Fungicide	6.29E-05	4.4	nd	nd	0.33	<LOD	<LOD
Cyprodinil	Fungicide	5.31E-03	10.5	nd	nd	0.38	<LOD	<LOD
Diazinon	Insecticide	7.24E-03	0.9	nd	nd	0.18	<LOD	<LOD
Diphenylamine	Fungicide	1.29E-01	1.8	6.0	nd	0.16	0.21	<LOD
Endosulfan Ether	Degradate	2.83E-02	14.9	nd	nd	0.14	<LOD	<LOD
Endosulfan Lactone	Degradate	5.55E-04	21.1	nd	1.9	0.83	<LOD	0.07
Endosulfan Sulfate	Degradate	1.55E-05	1.8	nd	nd	0.19	<LOD	<LOD
Ethalfluralin	Herbicide	1.96E-03	1.8	nd	nd	0.74	<LOD	<LOD
Fipronil	Insecticide	1.51E-07	4.4	nd	nd	0.19	<LOD	<LOD
Fludioxonil	Fungicide	4.19E-05	nd	2.0	3.8	<LOD	0.40	0.56
Flutolanil	Fungicide	5.44E-05	20.2	30.0	53.8	0.35	0.38	0.63
Malathion	Insecticide	1.65E-02	0.9	nd	nd	0.11	<LOD	<LOD
Metalaxyl	Fungicide	3.80E-03	33.3	nd	1.9	5.76	<LOD	0.42
Metolachlor[a]	Herbicide	5.05E-03	86.0	90.0	78.8	10.50	2.63	2.98
Myclobutanil[a]	Fungicide	3.11E-04	4.4	nd	nd	0.23	<LOD	<LOD
Oxadiazon	Herbicide	4.50E-05	nd	nd	1.9	<LOD	<LOD	0.04
Oxyfluorfen	Herbicide	3.06E-03	4.4	nd	nd	0.35	<LOD	<LOD
Pendimethalin[a]	Herbicide	2.69E-02	1.8	nd	nd	0.20	<LOD	<LOD
Piperonyl butoxide	Insecticide, synergist	6.96E-04	1	nd	nd	0.23	<LOD	<LOD
Propyzamide	Herbicide	1.05E-06	1	nd	nd	0.15	<LOD	<LOD
Tebuconazole	Fungicide	6.14E-06	62	30	83	0.48	1.64	1.80
Tetrahydrophthalimide	Degradate	1.58E-05	1	nd	nd	0.16	<LOD	<LOD
Triadimefon	Fungicide	1.16E-03	8	nd	nd	0.20	<LOD	<LOD

[a] Pesticides known to be applied in adjacent agricultural field (personal communication with Tom Potter).
[b] Values were obtained from EPI Suite (U.S. EPA, 2012).

metolachlor concentration was observed in August, the month with the largest amount of rainfall. This was followed by a steady decline in pesticide concentration at each site, and total metolachlor concentrations diminished over remaining collection period. Since all the sites were hydrologically connected, this could lead to pesticide concentrations being observed in sites that, earlier, had no detectable levels due to water moving from one site to the next through weirs and drainage pipes.

In several countries throughout Europe, pesticides were detected at higher concentrations in surface water samples after rain events (Griffini et al., 1997; Konstantinou et al., 2006). This pattern was also observed in the U.S. throughout the midwestern states by Thurman et al. (1991) and, more recently, in Maryland by Rice et al. (2016). In the current study, surface water samples were only collected once a month, so it is not feasible to observe the effect of each rainfall event on pesticide concentration at each site. On the other hand, total precipitation between each sampling date was calculated, and the highest amount of precipitation was between July and August (6.05 inches, Fig. 4). This also corresponds to the highest total summed concentration of metolachlor being observed in August (32.2 µg/L), compared to July (5.03 µg/L) or September (10.99 µg/L). Therefore, after summation of all rain events, the highest amount of metolachlor was observed in surface waters for the wettest month (August), which agrees with previous studies. Griffini et al. (1997) observed the highest concentration of metolachlor (3.68 µg/L) after an intense rainfall event. It is possible that metolachlor application as a pre-emergent herbicide from April to May can lead to spray drift and possible runoff into nearby surface waters leading to a spike in concentration levels.

In addition to collecting 1 L surface water samples, 4 L samples were collected at sites 4, 5 and 8 to aid in detecting pesticides at lower concentrations. Compared to the 1 L surface water samples, 19 pesticides were detected in 4 L samples, with biphenyl being the only additional pesticide detected. Cumulative concentrations of pesticides were plotted over time for each month and site with an increase in concentration and number of pesticides detected from June to August (Fig. 3). The highest number of pesticide detects was at site 4 in July with eight pesticides, while sites 5 and 8 had the highest number of pesticides detected in June, with 12 and 9 detects, respectively. This same trend was observed for 1 L surface water samples, with a spike in pesticide concentration during pesticide application followed by a gradual decline over the winter months. The most prominent pesticide was metolachlor which was detected in 34 of 35 samples, with the highest concentration observed in August (10.50 µg/L). Due to sampling error; no sample was collected in July at site 8. Tebuconazole had the second highest frequency of detects similar to 1 L surface water samples with concentrations that initially appear in April and reach a maximum level in August (1.1 µg/L), followed by a gradual decline in winter months.

3.3. Stemflow samples

Stemflow is rainwater that travels down a tree trunk and results from canopy wash. This action can lead to pesticide accumulation by rainwater as it washes the tree surfaces that are potentially

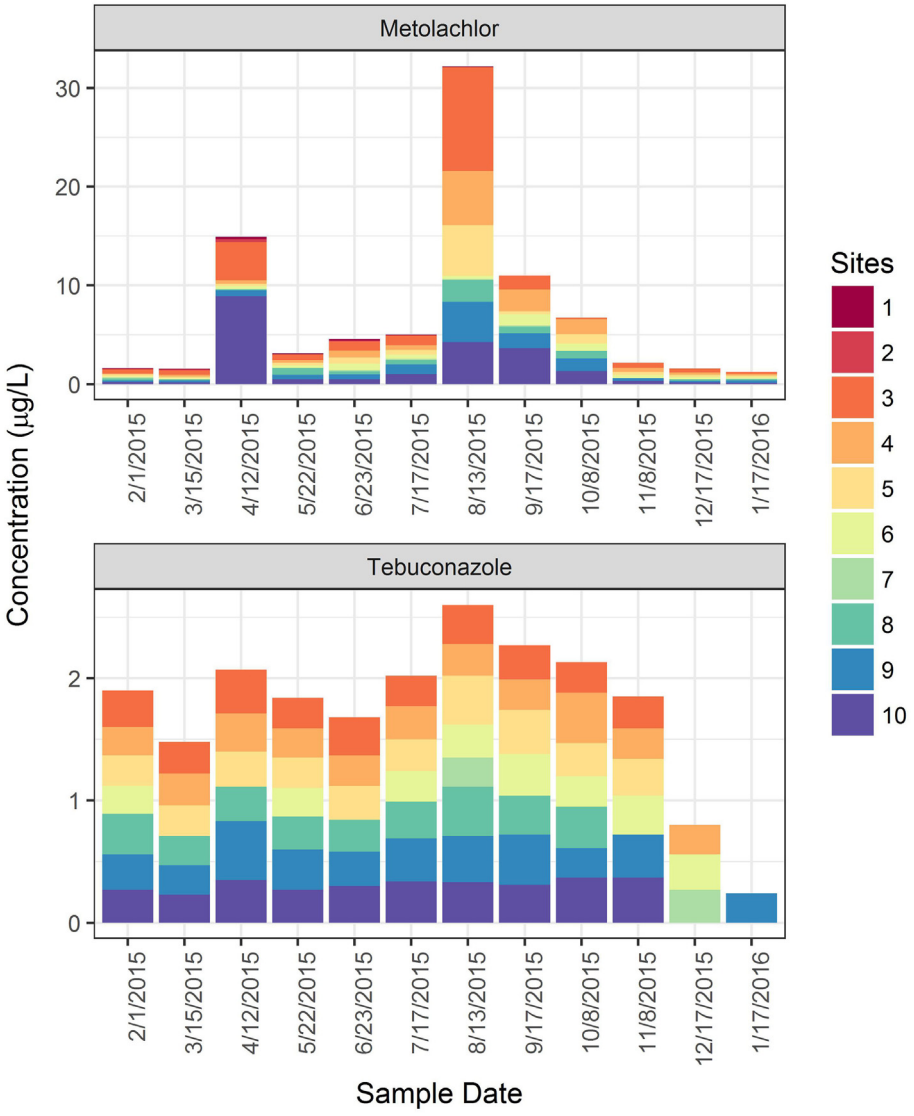


Fig. 2. Surface water concentration (µg/L) of metolachlor and tebuconazole at each site (1–10) during the sample month.

impacted by pesticide spray drift. Desethyl atrazine (DEA), a metabolite of atrazine, had the concentration quantified at 9.54 µg/L in a stemflow sample from May 2015 (Table 1). Of the two most common metabolites of atrazine, DEA and deisopropyl atrazine (DIA), DIA was not detected in the present study, while DEA was detected frequently in accordance with other studies that also detected higher concentrations of DEA in surface waters, subwatersheds, surface runoff, stream, and groundwater samples (Thurman et al., 1991; Shipitalo and Owens, 2003; Gilliom et al., 2006; Hively et al., 2011). This trend is likely due to DIA being more labile than DEA (Thurman et al., 1991). Bacteria, mosses, and fungi on leaf and stem surfaces can biodegrade pesticides (Brinkmann, 1983) which would explain the appearance of the metabolite DEA and why it had higher concentrations and frequencies of detection.

At site 3, the rain event with the highest combined concentration of pesticides was in June (3.92 µg/L), and at site 7 in September (3.03 µg/L). Several studies have investigated pesticide concentration in stemflow, with varying results. Trevisan et al. (1993) found pesticides in nine of the 25 stemflow samples analyzed, including four different herbicides and one organophosphate. Atrazine was found in five stemflow samples, with the highest concentration detected being 1.99 µg/L (Trevisan et al., 1993). Out of the five compounds in the current study, only atrazine was detected (nine times), with the highest concentration at 3.65 µg/L. In Bernhardt and Ruck (2004) metolachlor had the highest concentration (48 ng/L) in a May sample which is 54 times lower than the current study which observed the highest stemflow concentration in September (2.63 µg/L). Overall, stemflow concentrations were 4–64 times higher in the current study than in Trevisan et al. (1993) and Bernhardt and Ruck (2004). On the other hand, both atrazine and metolachlor were observed to have similar concentrations as "Year 1" data from Rice et al. (2016); subsequent years had concentrations 2–4 times higher than the current study. These concentrations could be different due to the fact that the Trevisan et al. (1993) and Bernhardt and Ruck (2004) studies analyzed samples in forests, while this study and Rice et al. (2016) were conducted at agricultural fields.

3.4. Throughfall samples

Throughfall is rainwater that comes in contact with leaf surfaces of the tree canopy only (i.e., foliage capture of pesticides predominantly from spray drift). Atrazine was detected at the highest

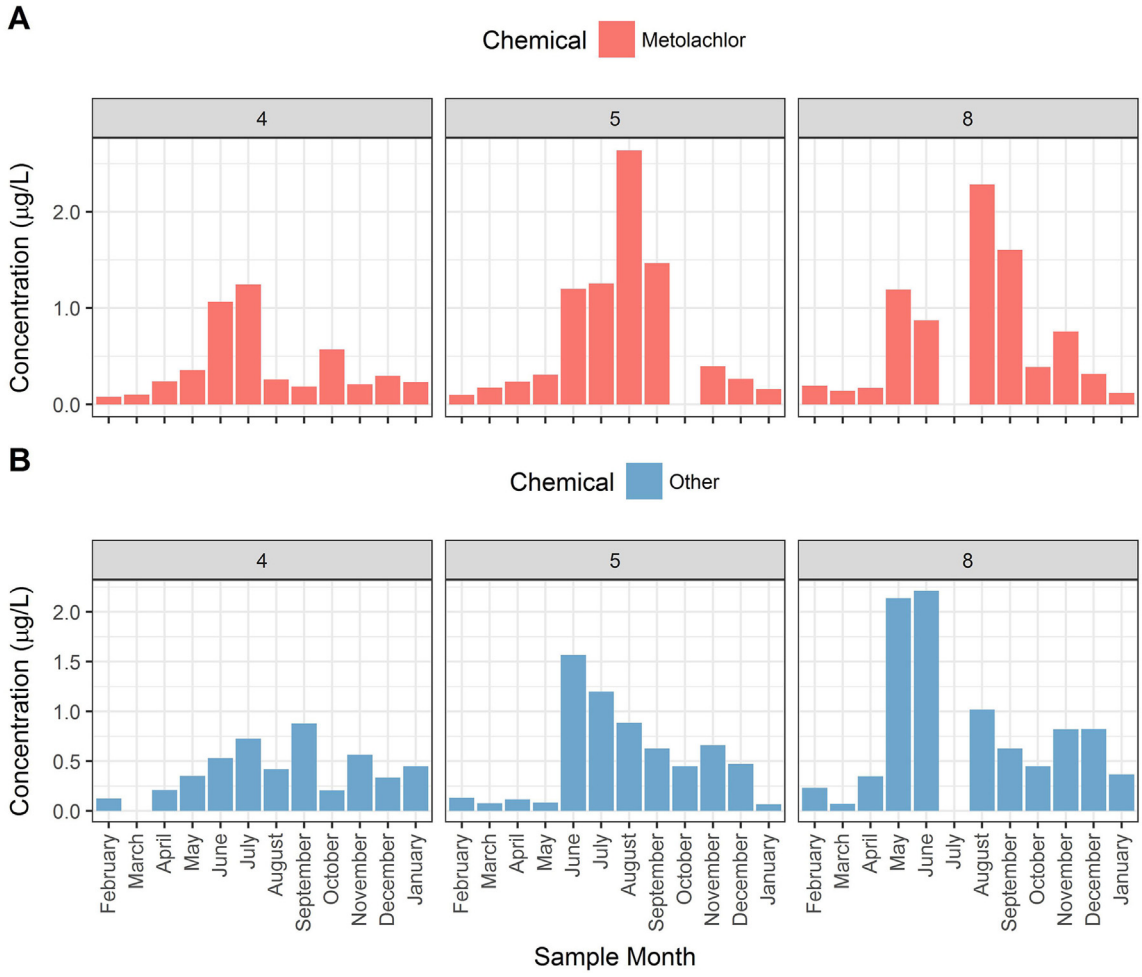


Fig. 3. Metolachlor (A) and cumulative concentrations (B) in (µg/L) for all pesticides quantified in 4 L surface water samples for sites 4, 5 and 8 at each month. For site 8 in July, no sample was collected.

concentration in throughfall samples (7.09 µg/L) in May 2015 (Table 1). May data contained the highest summed concentration for throughfall at sites 3 (9.38 µg/L) and 4 (4.25 µg/L), while site 7 (5.01 µg/L) was the highest summed pesticide concentration in July. In the current study, thirteen pesticides were detected in throughfall (Table 1). Trevisan et al. (1993) detected ten pesticides in twenty different samples in Italian forests, with diazinon detected most frequently. In Bernhardt and Ruck (2004), two herbicides, prosulfocarb and isoproturon, were quantified in throughfall from three separate rain events in a beech forest in Germany. Zhang et al. (2011) measured organochlorine fluxes for hexachlorobenzenes, hexachlorocyclohexanes, and DDT (with metabolites) in a metropolitan area and concluded that throughfall accounted for 10% of the mass in runoff. Even though organochlorines were not detected in our study, throughfall could result in other detectable pesticides in runoff and thus higher concentrations in surface water. Rice et al. (2016) analyzed throughfall samples for the herbicides atrazine and metolachlor for four years after a single application each year near a corn field. Higher concentrations of metolachlor, compared to atrazine, were presumably due to its higher K_{oc} (organic carbon adsorption coefficient), which resulted in its retention in the tree canopy during days without rain (Rice et al., 2016). This was not observed in our study where atrazine and its metabolite DEA were detected, on average, at higher concentrations than metolachlor; potentially due to different application rates of the two pesticides in south Georgia. Furthermore, not all of these past studies were done in an agricultural setting, which can result in various pesticides being identified in different countries, moreover, not all pesticides are used equally throughout the world.

3.5. Stemflow vs throughfall

Due to stemflow and throughfall collectors being paired up at three different sites, comparison between pesticide concentrations for each matrix and rain event were conducted. Concentrations for metolachlor and tebuconazole in stemflow and throughfall were plotted against time (Fig. 4). Stemflow samples of metolachlor were higher than throughfall samples for most samples. This phenomenon was also observed by Rice et al. (2016) who noted that the tree canopy acted as a filtering mechanism for the pesticides. Due to the higher surface area and longer period of time that rainwater is in contact with a tree to create stemflow, higher concentrations are expected (Rice et al., 2016). This was also observed by Bicalho et al. (2010) who noted that air pollution was being concentrated in the tree canopy and then released during rain events. Also Bernhardt and Ruck (2004) stated that higher concentrations were found in stemflow due to the trees acting as filters. This phenomenon is not specifically limited to pesticides; heavy metals and ions, especially nitrates, exhibited higher concentrations (up to 4 times greater) in soil impacted by stemflow rainwater around trees, compared to distal areas (Marchionni et al., 1999; Chang and Matzner, 2000;

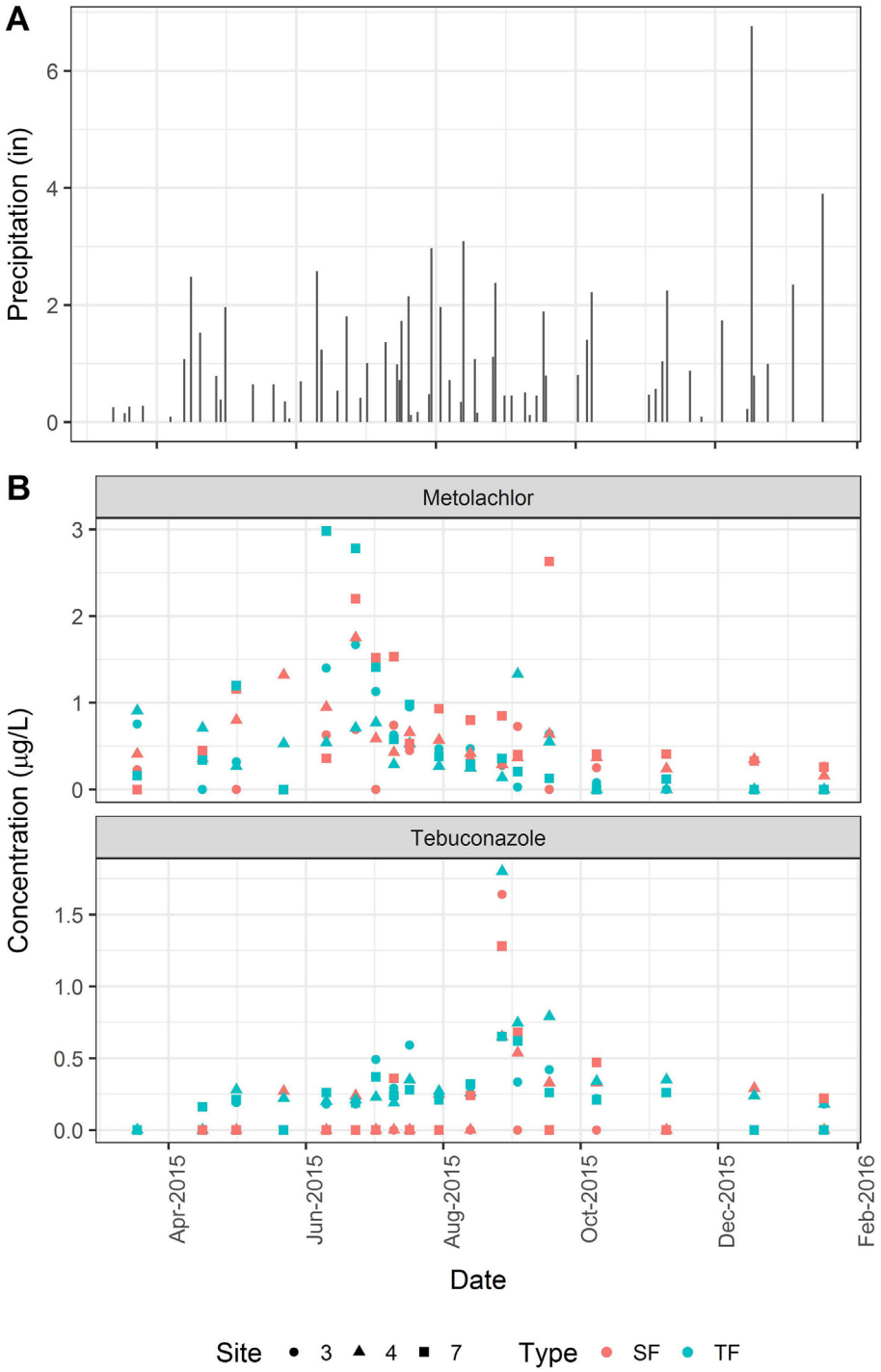


Fig. 4. Measured precipitation of rainwater (inches) over time (A) and plot of concentration (µg/L) versus time (B) for stemflow (SF) and (TF) at sites 3, 4 and 7 for metolachlor and tebuconazole.

Morselli et al., 2004). Furthermore, metolachlor was still detectable in stemflow samples weeks to months post-application in the current study, compared to throughfall samples. When examining all pesticides detected in throughfall and stemflow samples, however, throughfall samples had higher concentrations than its corresponding stemflow sample 172 times ($p = 0.0013$; Fig. 5). This is contrary to Rice et al. (2016) where, directly after application, higher concentrations were observed in stemflow than throughfall. In the current study, stemflow and throughfall samples were collected for an entire year, including during pre-application rain events. These pre-application rain events could skew the results so that throughfall samples appear higher than stemflow, while directly after application, stemflow could have higher concentrations. Furthermore, it was quite possible for the first rain event after pesticide application produced a spike of pesticides in stemflow samples, resulting in an initial flush and higher concentrations, followed by a large volume of rainfall with low, diluted concentrations. This contrasts with a corresponding throughfall sample

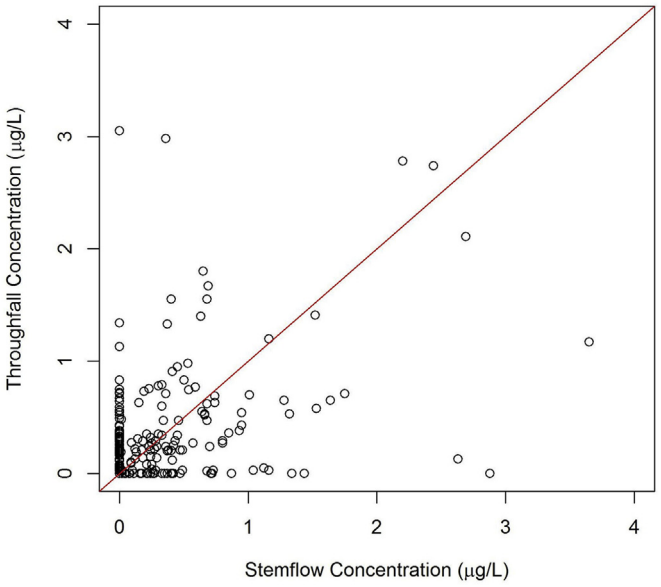


Fig. 5. Comparison of throughfall concentration (µg/L) versus stemflow concentration (µg/L) for all pesticides that were detected in these matrices.

where rainwater would still interact with foliage and have elevated pesticide concentrations.

3.6. Toxicity values

During rain events, atmospheric water is known to rinse pesticides from leaves and stems and further contaminate the surrounding soil or aquatic systems. Pesticides are also known to migrate through the atmosphere, post-application, and contaminate pristine areas. However, this influx of pesticides can be harmful to non-target organisms either due to the additional pulses of pesticides being released or environmental transformation of the pesticides that form metabolites that are often more toxic than parent pesticides (Boone et al., 2001; Relyea and Diecks, 2008). Additionally, pesticide application and the drying up of these small streams and ponds during the summer can lead to higher concentrations of pesticides concentrating in these aquatic systems, which will result in more adverse effects being expressed in non-target organisms (Boone and James, 2003; Relyea, 2005; Boone, 2008; Smalling et al., 2012; Battaglin et al., 2016; Potter and Coffin, 2017).

Even though there are measurable concentrations of pesticides in different environmental matrices, this does not necessarily mean that these levels will be toxic to aquatic life (Gilliom et al., 2006; Potter and Coffin, 2017). Therefore, in the current study, determined stemflow, throughfall and surface water concentrations were compared against aquatic life benchmarks and environmental water screening values to determine if adverse effects would occur for non-targeted organisms (Table 2). Over 80 percent of the time mixtures are present in the different matrices and thus it is difficult to determine the potential adverse effects that these compounds will have on aquatic life, due to the fact that the pesticides could cause additive, synergistic or antagonist effects.

To assess the possible risk that agricultural pesticides have on non-target organisms, samples from surface water, stemflow, and throughfall were collected and analyzed. Using the U.S. EPA's aquatic life benchmark data for freshwater, a table was compiled

Table 2
The most sensitive aquatic freshwater benchmark values (µg/L) and their endpoint type for pesticides that were detected in surface water (SW), stemflow (SF) and throughfall (TF) along with the number of samples that exceeded the benchmark value. (NR = not reported).[a]

Pesticide	Value (µg/L)	Endpoint Type	Matrix Found In	Number of Samples that Exceeded Value
2-Phenylphenol	NR	NR	SW, SF, TF	0
Acetochlor	1.43	Nonvascular Plants – Acute	SW, SF, TF	1 (1 – TF)
Alachlor	1.64	Nonvascular Plants – Acute	SW	0
Anthraquinone	NR	NR	SW, SF, TF	0
Atrazine	<1	Nonvascular Plants – Acute	SW, SF, TF	11 (1 – SW, 5 – SF, 5 -TF)
DEA	NR	NR	SW, SF, TF	0
Benfluralin	1.9	Fish – Chronic	SW	0
Bifenthrin	0.0013	Aquatic Invertebrates – Chronic	SW, SF	3 (2 – SW, 1 – SF)
Biphenyl	NR	NR	SF, TF	0
Chlorothalonil	0.6	Aquatic Invertebrates – Chronic	SW	0
Cyprodinil	8	Aquatic Invertebrates – Chronic	SW	0
Diazinon	0.105	Aquatic Invertebrates – Acute	SW	1 (1 – SW)
Diphenylamine	NR	NR	SW, SF	0
Endosulfan Ether	NR	NR	SW	0
Endosulfan Lactone	NR	NR	SW, TF	0
Endosulfan sulfate	1.9	Fish – Acute	SW	0
Ethalfluralin	0.4	Fish – Chronic	SW	2 (2 – SW)
Fipronil	0.011	Aquatic Invertebrates – Chronic	SW	5 (5 – SW)
Fludioxonil	19	Fish – Chronic	SF, TF	0
Flutolanil	220	Fish – Chronic	SW, SF, TF	0
Malathion	0.035	Aquatic Invertebrates – Chronic	SW	1 (1 – SW)
Metalaxyl	100	Aquatic Invertebrates – Chronic	SW, TF	0
Metolachlor	8	Nonvascular Plants – Acute	SW, SF, TF	2 (2 – SW)
Myclobutanil	830	Nonvascular Plants – Acute	SW	0
Oxadiazon	5.2	Nonvascular Plants – Acute	TF	0
Oxyfluorfen	1.1	Nonvascular Plants – Acute	SW	0
Pendimethalin	5.2	Nonvascular Plants – Acute	SW	0
Piperonyl Butoxide	30	Aquatic Invertebrates – Chronic	SW	0
Propyzamide	NR	NR	SW	0
Tebuconazole	12	Fish – Chronic	SW, SF, TF	0
Tetrahydrophthalimide	>56500	Aquatic Invertebrates – Acute	SW	0
Triadimefon	41	Fish – Chronic	SW	0

[a] OPP Aquatic Life Benchmark values for freshwater (U.S. EPA, 2016a).

that included the most sensitive values to be evaluated against the pesticides detected in these matrices similar to Potter and Coffin (2017) (U.S. EPA, 2016a). Of the 32 pesticides detected, only seven had concentration values that exceeded the aquatic life benchmark value. These pesticides were acetochlor, atrazine, bifenthrin, diazinon, ethalfluralin, fipronil, and malathion. Acetochlor and atrazine were two pesticides that exceeded benchmark values for throughfall samples, where these pesticide levels pose a risk to many organisms that live under tree canopies. Two pesticides, atrazine and bifenthrin had stemflow values that exceeded the benchmark level. These values place many amphibians, especially treefrogs, at risk for hazardous adverse effects because they reside on trees. Since stemflow samples comprise of rainwater that washes down the tree trunk, it is a composite of all the pesticides, both parents and metabolites, impacted by spray drift. Furthermore, six pesticides were detected in surface water samples which could directly cause harm to non-target organism, that are returning to the ponds to breed or tadpoles that are growing. Several of these pesticides were detected in colder months, which would be harmful to aquatic organisms that overwinter in these areas.

Atrazine exceeded the most sensitive aquatic benchmark value for eleven samples (5% detection frequency). Atrazine is a herbicide, that has been shown to elicit neuroendocrine effects in mammals, in addition to, effecting developmental and reproductive systems by altering hormone levels in rats (U.S. EPA, 2016b). Six of these eleven samples were collected on the same date in May 2015, one surface and six stemflow and throughfall sites. Therefore, atrazine application most likely occurred in April between the two collection dates. This would agree with time of application for atrazine because it is applied as a pre-emergent. Additionally, pesticide concentrations in stemflow and to a lesser extent, in throughfall were still detectable even at lower concentrations, however, they were still above the benchmark value.

In contrast, fipronil was detected in five surface water samples in the beginning of the year. This could have resulted from application in the previous year and residues remained over the winter, or early application of the insecticide in spring which resided for several weeks (Greenberg et al., 2010, 2014). Fipronil is known to affect the GABA receptors in the central nervous system, by blocking the GABA-gated chloride channels (Das et al., 2006). Therefore, detecting concentrations that are above benchmark values will be hazardous for aquatic organisms that overwinter in ponds. Furthermore, the metabolites of fipronil are known for being more toxic than the parent, which can also pose a risk to these non-target organisms (U.S. EPA, 1996; Baird et al., 2013).

Metolachlor was the most frequently detected pesticide in both surface water and stemflow samples, in particular, the concentration in two samples (8.92 and 10.5 μg/L) exceeded the aquatic benchmark value. This preemergent herbicide is mainly used on corn, and interestingly, site 3 is adjacent to a corn field at Gibbs Research Farm.

Bifenthrin is an insecticide that affects the central nervous system and exceeded the aquatic benchmark value in at least 3 samples, in two surface water and one stemflow samples. The herbicide ethalfluralin exceeded the limit twice in surface water samples collected in December. While malathion and diazinon both organophosphate insecticides were above the limit once each in surface water samples. Even though these compounds were detected above the aquatic benchmark value once, they can still pose a potential risk to aquatic life considering other pesticides were detected in the water samples at the same time. For the malathion sample that exceeded the aquatic benchmark value atrazine was also detected in the same sample. This is problematic considering several studies have demonstrated that atrazine can increase the toxicity of organophosphates when present in mixtures (Pape-Lindstrom and Lydy, 1997; Wacksman et al., 2006).

Furthermore, mixtures present at concentrations lower than benchmark values can still have adverse effects on non-targeted organisms. Moreover, the average number of pesticides detected in a stemflow samples was 2.6, throughfall was 4.4, while surface waters detection percents were 3.6 pesticides per collected date and site. While concentrations of these pesticides were below the aquatic benchmark values for each individual compound, it is possible for the summation of pesticide type (i.e. herbicides, fungicides, and insecticides) or specific mode of action to have a major impact on non-target organisms.

4. Conclusions

Out of the 160 pesticides that were targeted for this study, 32 were quantified either in surface water, stemflow or throughfall samples. Overall, metolachlor was the most frequently detected pesticide in all surface water and stemflow samples, while biphenyl was more prevalent in throughfall. Tebuconazole and metolachlor were the most frequently detected fungicide and herbicide, respectively, in all matrices analyzed. Stemflow samples had lower concentrations than throughfall samples for most pesticides analyzed in this study, potentially due to higher volumes of water collected at stemflow samplers which resulted in a dilution effect.

Pesticides from spray drift accumulate on trees in buffer zones producing high concentrations of both parent and metabolites in stemflow and throughfall. Spray drift can result in subsequent rain events washing pesticides off trees in buffer zones leading to higher concentrations in nearby streams and wetlands where non-targeted habitats become contaminated. Thus, most surface water samples contained pesticides due to pesticides moving through the interconnected forested wetlands. This study shows that examining various environmental matrices can aid in identifying different pesticides or metabolites while analyzing for a whole suite of pesticides would be beneficial because in addition to analyzing known pesticides that were applied during our sampling, additional pesticides were detected and quantified demonstrating that these processes contribute to environmental exposure and need to be considered for pesticide risk assessment. This research can aid in informing regulatory aspects of pesticide application and concentrations in surface waters, rainwater as stemflow and throughfall due to spray drift and its impact on non-target species inhabiting the areas.

Conflicts of interest

The authors declare no conflict of interest.

Data accessibility

The R code and data that implements the analyses and generates the figures for the manuscript are available from a GitHub repository located at https://github.com/puruckertom/glinski_stemflow.

Acknowledgments

Thanks to Thomas Potter and Margie Whittle of the USDA for support and to Sephus Willis and the University of Georgia Tifton Campus for access to the Gibbs Farm. Thanks to Fran Rauschenberg, Jonathon Mosley and Jack Jones for manuscript review and comments. Many hours of field assistance were given by Jacob Veiga, Linda George, Carolyn McDermott, Carmen Kuan, Madison

Hamilton, Marcia Snyder, Mike Cyterski and Kurt Wolfe. This research was supported in part by an appointment to the Research Participation Program for the U.S. Environmental Protection Agency, Office of Research and Development, administered by the Oak Ridge Institute for Science and Education through interagency agreement between the U.S. Department of Energy and EPA. Additionally, funding was supported by the Interdisciplinary Toxicology Program at the University of Georgia to D.A.G. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.06.116.

References

Ahmed, M.T., Ismail, S.M.M., Mabrouk, S.S., 1998. Residues of some chlorinated hydrocarbon pesticides in rain water, soil and ground water, and their influence on some soil microorganisms. Environ. Int. 24, 665–670.
Baird, S., Garrison, A., Jones, J., Avants, J., Bringolf, R., Black, M., 2013. Enantioselective toxicity and bioaccumulation of fipronil in fathead minnows (*Pimephales promelas*) following water and sediment exposures. Environ. Toxicol. Chem. 32, 222–227.
Battaglin, W., Smalling, K., Anderson, C., Calhoun, D., Chestnut, T., Muths, E., 2016. Potential interactions among disease, pesticides, water quality and adjacent land cover in amphibian habitats in the United States. Sci. Total Environ. 566, 320–332.
Bernhardt, A., Ruck, W., 2004. Determination of herbicides in stemflow and throughfall of beeches (*Fagus sylvatica* L.) and in rainfall. Chemosphere 57, 1563–1570.
Bicalho, S., Langenbach, T., Rodrigues, R., Correia, F., Hagler, A., Matallo, M., Luchini, L., 2010. Herbicide distribution in soils of a riparian forest and neighboring sugar cane field. Geoderma 158, 392–397.
Boone, M.D., 2008. Examining the single and interactive effects of three insecticides on amphibian metamorphosis. Environ. Toxicol. Chem. 27, 1561–1568.
Boone, M.D., Bridges, C.M., Rothermel, B.B., 2001. Growth and development of larval green frogs (*Rana clamitans*) exposed to multiple doses of an insecticide. Oecologia 129, 518–524.
Boone, M.D., James, S.M., 2003. Interactions of an insecticide, herbicide, and natural stressors in amphibian community mesocosms. Ecol. Appl. 13, 829–841.
Briand, O., Bertrand, F., Seux, R., Millet, M., 2002. Comparison of different sampling techniques for the evaluation of pesticide spray drift in apple orchards. Sci. Total Environ. 288, 199–213.
Brinkmann, W., 1983. Nutrient Balance of a Central Amazonian Rainforest: Comparison of Natural and Man-managed Systems. Hydrology of Humid Tropical Regions IAHS Publication, p. 140.
Chang, S.C., Matzner, E., 2000. Soil nitrogen turnover in proximal and distal stem areas of European beech trees. Plant Soil 218, 117–125.
Cotham, W.E., Bidleman, T.F., 1991. Estimating the atmospheric deposition of organochlorine contaminants to the arctic. Chemosphere 22, 165–188.
Coupe, R.H., Manning, M.A., Foreman, W.T., Goolsby, D.A., Majewski, M.S., 2000. Occurrence of pesticides in rain and air in urban and agricultural areas of Mississippi, April-September 1995. Sci. Total Environ. 248, 227–240.
Cunha, J.P., Chueca, P., Garcerá, C., Moltó, E., 2012. Risk assessment of pesticide spray drift from citrus applications with air-blast sprayers in Spain. Crop Protect. 42, 116–123.
Das, P.C., Cao, Y., Cherrington, N., Hodgson, E., Rose, R.L., 2006. Fipronil induces CYP isoforms and cytotoxicity in human hepatocytes. Chem. Biol. Interact. 164, 200–214.
de Koning, S., Gumpendobler, M., 2007. Determination of 287 pesticides at trace levels by GCxGC-TOFMS. Life Science and Chemical Analysis Solutions. Leco, Corporation. Form No. 203-821-327.
de Snoo, G.R., de Wit, P.J., 1998. Buffer zones for reducing pesticide drift to ditches and risks to aquatic organisms. Ecotoxicol. Environ. Saf. 41, 112–118.
Dubus, I.G., Hollis, J.M., Brown, C.D., 2000. Pesticides in rainfall in Europe. Environ. Pollut. 110, 331–344.
Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., 2006. Pesticides in the Nation's Streams and Ground Water, 1992–2001. Geological Survey, US.
Gish, T.J., Prueger, J.H., Daughtry, C.S., Kustas, W.P., McKee, L.G., Russ, A.L., Hatfield, J.L., 2011. Comparison of field-scale herbicide runoff and volatilization losses: an eight-year field investigation. J. Environ. Qual. 40, 1432–1442.
Goel, A., McConnell, L.L., Torrents, A., 2005. Wet deposition of current use pesticides at a rural location on the Delmarva Peninsula: impact of rainfall patterns and agricultural activity. J. Agric. Food Chem. 53, 7915–7924.
Greenberg, L., Rust, M.K., Klotz, J.H., Haver, D., Kabashima, J.N., Bondarenko, S., Gan, J., 2010. Impact of ant control technologies on insecticide runoff and efficacy. Pest Manag. Sci. 66, 980–987.
Greenberg, L., Rust, M.K., Richards, J., Wu, X., Kabashima, J., Wilen, C., Gan, J., Choe, D.-H., 2014. Practical pest management strategies to reduce pesticide runoff for argentine ant (Hymenoptera: Formicidae) control. J. Econ. Entomol. 107, 2147–2153.
Griffini, O., Bao, M.L., Barbieri, C., Burrini, D., Pantani, F., 1997. Occurrence of pesticides in the Arno River and in potable water - a survey of the period 1992–1995. Bull. Environ. Contam. Toxicol. 59, 202–209.
Grube, A., Donaldson, D., Kiely, T., Wu, L., 2011. Pesticides Industry Sales and Usage. US EPA, Washington, DC.
Hively, W.D., Hapeman, C.J., McConnell, L.L., Fisher, T.R., Rice, C.P., McCarty, G.W., Sadeghi, A.M., Whitall, D.R., Downey, P.M., de Guzmán, G.T.N., 2011. Relating nutrient and herbicide fate with landscape features and characteristics of 15 subwatersheds in the Choptank River watershed. Sci. Total Environ. 409, 3866–3878.
Hüskes, R., Levsen, K., 1997. Pesticides in rain. Chemosphere 35, 3013–3024.
Konstantinou, I.K., Hela, D.G., Albanis, T.A., 2006. The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environ. Pollut. 141, 555–570.
LeNoir, J.S., McConnell, L.L., Fellers, G.M., Cahill, T.M., Seiber, J.N., 1999. Summertime transport of current-use pesticides from California's Central Valley to the Sierra Nevada mountain range, USA. Environ. Toxicol. Chem. 18, 2715–2722.
Marchionni, M., Benedetti, A., Riccardi, C., Villarini, M., 1999. Model for the study of the impact of atmospheric heavy metals on soil microbial biomass. Ann. Chim. 90, 715–721.
McConnell, L.L., LeNoir, J.S., Datta, S., Seiber, J.N., 1998. Wet deposition of current-use pesticides in the Sierra Nevada mountain range, California, USA. Environ. Toxicol. Chem. 17, 1908–1916.
Morselli, L., Brusori, B., Passarini, F., Bernardi, E., Francaviglia, R., Gataleta, L., Marchionni, M., Aromolo, R., Benedetti, A., Olivieri, P., 2004. Heavy metals monitoring at a Mediterranean natural ecosystem of Central Italy. Trends in different environmental matrixes. Environ. Int. 30, 173–181.
Pape-Lindstrom, P.A., Lydy, M.J., 1997. Synergistic toxicity of atrazine and organophosphate insecticides contravenes the response addition mixture model. Environ. Toxicol. Chem. 16, 2415–2420.
Potter, T.L., Coffin, A.W., 2017. Assessing pesticide wet deposition risk within a small agricultural watershed in the Southeastern Coastal Plain (USA). Sci. Total Environ. 580, 158–167.
Potter, T.L., Hapeman, C.J., McConnell, L.L., Harman-Fetcho, J.A., Schmidt, W.F., Rice, C.P., Schaffer, B., 2014. Endosulfan wet deposition in Southern Florida (USA). Sci. Total Environ. 468–469, 505–513.
R Core Team, 2017. R: a Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. https://www.R-project.org/.
Relyea, R.A., 2005. The impact of insecticides and herbicides on the biodiversity and productivity of aquatic communities. Ecol. Appl. 15, 618–627.
Relyea, R.A., Diecks, N., 2008. An unforeseen chain of events: lethal effects of pesticides on frogs at sublethal concentrations. Ecol. Appl. 18, 1728–1742.
Rice, C.P., Bialek, K., Hapeman, C.J., McCarty, G.W., 2016. Role of riparian areas in atmospheric pesticide deposition and its potential effect on water quality. J. Am. Water Resour. Assoc. 52, 1109–1120.
Rice, C.P., Chernyak, S.M., 1997. Marine arctic fog: an accumulator of currently used pesticide. Chemosphere 35, 867–878.
Sauret, N., Wortham, H., Strekowski, R., Herckes, P., Nieto, L.I., 2009. Comparison of annual dry and wet deposition fluxes of selected pesticides in Strasbourg, France. Environ. Pollut. 157, 303–312.
Shipitalo, M.J., Owens, L.B., 2003. Atrazine, deethylatrazine, and deisopropylatrazine in surface runoff from conservation tilled watersheds. Environ. Sci. Technol. 37, 944–950.
Smalling, K.L., Orlando, J.L., Calhoun, D., Battaglin, W.A., Kuivila, K.M., 2012. Occurrence of Pesticides in Water and Sediment Collected from Amphibian Habitats Located throughout the United States, 2009–2010, p. 36. US Geological Survey Data Series 707.
Stokstad, E., Grullón, G., 2013. Infographic: pesticide planet. Science 341, 730–731.
Thurman, E.M., Goolsby, D.A., Meyer, M.T., Kolpin, D.W., 1991. Herbicides in surface waters of the midwestern United States: the effect of spring flush. Environ. Sci. Technol. 25, 1794–1196.
Trevisan, M., Montepiani, C., Ragozza, L., Bartoletti, C., Ioannilli, E., Delre, A.A.M., 1993. Pesticides in rainfall and air in Italy. Environ. Pollut. 80, 31–39.
U.S. EPA, 1996. Fipronil Pesticide Fact Sheet: Washington, DC. Report no.: EPA 737-F-96–9005.
U.S. EPA, 2012. Estimation Programs Interface Suite™ for Microsoft® Windows. United States Environmental Protection Agency, Washington, DC, USA, v. 4.11.
U.S. EPA, 2016a. Aquatic Life Benchmarks for Pesticide Registration. US Environmental Protection Agency Office of Pesticide Programs, Washington, DC, USA. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarkspesticideregistration#use. (Accessed 9 October 2016).
U.S. EPA, 2016b. Refined Ecological Risk Assessment for Atrazine. U.S. Environmental Protection Agency Office of Pesticide Programs, Washington, DC. https://www.regulations.gov/document?D=EPA-HQ-OPP-2013-0266-0315. (Accessed 22 January 2017).
Vischetti, C., Cardinali, A., Monaci, E., Nicelli, M., Ferrari, F., Trevisan, M., Capri, E., 2008. Measures to reduce pesticide spray drift in a small aquatic ecosystem in vineyard estate. Sci. Total Environ. 389, 497–502.
Wacksman, M., Maul, J., Lydy, M., 2006. Impact of atrazine on chlorpyrifos toxicity

in four aquatic vertebrates. Arch. Environ. Contam. Toxicol. 51, 681–689.
Wilcoxon, F., 1945. Individual comparisons by ranking methods. Biometrics Bull. 1, 80–83.
Williams, M.B., 2004. Investigating the Contribution of Stemflow to the Hydrology of a Forest Catchment. University of Southampton.
Zhang, W., Ye, Y., Tong, Y., Ou, L., Hu, D., Wang, X., 2011. Contribution and loading estimation of organochlorine pesticides from rain and canopy throughfall to runoff in an urban environment. J. Hazard Mater. 185, 801–806.