Suspect Screening for Pesticides in Rain and Snow Using Liquid Chromatography High-Resolution Mass Spectrometry

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Abstract

Pesticides are one of the only chemical contaminants that are purposefully introduced to the environment in large quantities. After application to crops, pesticides can be volatilized into the atmosphere and undergo medium to long-range transport. Through wet deposition, pesticides can be removed from the atmosphere far from their initial application site, posing a variety of environmental and health hazards, such as toxicity to terrestrial and aquatic species, crop damage, and poor air quality. Identifying pesticides and their degradation products in wet deposition is crucial to understanding how they are transported in the atmosphere. High-resolution mass spectrometry is a useful tool to carry out suspect screening on complex mixtures. However, suspect screening for pesticides in atmospheric waters is lacking. In this work, liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (LC-QToF-MS) is used for the first time to screen for suspect pesticides in wet deposition. The composition of precipitation samples collected in the central United States from 2018 to 2021 was screened against a library of thousands of compounds, and the presence of 23 pesticides was confirmed using reference standards, including common herbicides such as atrazine, metolachlor, and alachlor, as well as three species that had never before been quantified in wet deposition: diphenamid, octhilinone,

and desthio-prothioconazole. A significant increase in the deposition flux of many pesticides was observed at the start of planting season, suggesting local agricultural sources to the atmosphere. In addition, pesticides not commonly used locally were also detected, suggesting regional atmospheric transport. Using statistical analyses and air mass back trajectory calculations, the seasonal trends, physicochemical properties, and potential origins of pesticides were examined. Overall, this work highlights the power of liquid chromatography high-resolution mass spectrometry for identifying both known and unexpected pesticides in precipitation, allowing for more accurate modeling of the atmospheric transport and fate of these compounds.

Keywords

High-resolution mass spectrometry, pesticides, wet deposition, precipitation, suspect screening

1. Introduction

Agriculture is one of the largest contributors to pesticide use, accounting for approximately 85% of all pesticides applied (Kim et al., 2017). For example, in 2018 in the U.S. state of Ohio alone, 100% of corn fields were treated with herbicides, 19% with insecticides, and 12% with fungicides, accounting for over 10.5 million pounds of pesticides (National Agricultural Statistics Service, 2019). After crop application, pesticides enter the atmosphere through spray drift, volatilization, and wind erosion of soil (Gil and Sinfort, 2005; Socorro et al., 2016; Unsworth et al., 1999). Once in the atmosphere, pesticides can undergo long-range transport and be deposited through wet or dry deposition far from their initial application site. Pesticides have been found in remote locations, including the Swiss Alps (Jakobi et al., 2015) and the high Artic (Unsworth et al., 1999; Van Dijk and Guicherit, 1999). Transport of pesticides through the atmosphere to secondary locations can contaminate waterways and drinking sources (Albuquerque et al., 2016; Derbalah et al., 2019; Ippolito et al., 2015; Pehkonen and Zhang, 2002; Rosic et al., 2020; Shoda et al., 2016), as well as pose dangers to wildlife and aquatic life (DeLorenzo et al., 2001; Katagi, 2004; Kohler and Triebskorn, 2013; Zubrod et al., 2019). Pesticides, often in significant

quantities, have been detected throughout the environment, including in tissues of aquatic species and sediment (Abrantes et al., 2010), ambient air (Nascimento et al., 2018; Socorro et al., 2016), various bodies of water (Metcalfe et al., 2019; Stackpoole et al., 2021), and groundwater and drinking water (Bexfield et al., 2021), yet measurements of current-use pesticides on atmospheric aerosol particles and in wet deposition remain sporadic (Degrendele et al., 2016; Wang et al., 2021; H. Zhang et al., 2018). Indeed, the most recently reported deposition fluxes of herbicides in the Midwestern United States, a region of high agricultural activity, date all the way back to 2004 (Vogel et al., 2008). More widespread monitoring of pesticides in the atmosphere is needed to better model their fate and transport (Li et al., 2011). While these processes are well-characterized in terrestrial and aquatic environments (de Souza et al., 2020; Rice et al., 2007; Wauchope et al., 2002), sources and sinks of pesticides in the troposphere remain largely unexplored.

Advances in high-resolution mass spectrometry (HRMS) have allowed this technique to become a valuable tool for identifying a variety of atmospheric and environmental contaminants, including pesticides, in a wide array of matrices. With HRMS, several analytical approaches can be applied, including targeted analysis, suspect screening, and non-targeted analysis. Targeted analysis is common when monitoring the presence of specific, known pesticides, whereas non-targeted analysis is discovery of “unknown unknowns” (Aceña et al., 2015; González-Gaya et al., 2021). The suspect screening approach compares experimental data to databases with thousands of compounds in an attempt to identify species in a sample. With the availability of multiple HRMS instruments such as time-of flight (TOF), quadrupole time-of-flight (QTOF), and Orbitrap, many methods have been developed to identify pollutants, including pesticides, in water matrices (Du et al., 2022; Leendert et al., 2015).

While many water matrices have been extensively studied for the presence of pesticides, the analysis of atmospheric samples, such as precipitation, using HRMS is surprisingly lacking. Gas chromatography (GC)-HRMS has been used to study organochlorine pesticides in precipitation in

Tanzania (Mahugija et al., 2015) and in the Alps (Jakobi et al., 2015); however, these studies employed targeted analysis. While targeted analysis is a useful approach, prior knowledge of the likely sample composition is required, and many pesticides may remain unidentified. In 2021, Mazur et al. used GC-HRMS to conduct non-targeted analysis and suspect screening of snow samples collected in Moscow. Over 500 compounds were identified, including organochlorine pesticides (Mazur et al., 2021). While this work provides a wealth of information about the composition of snow, the pesticides identified were confirmed using knowledge of fragmentation pathways and retention indices from NIST. Without the use of reference standards, the compound assignments are low confidence. Several other studies have employed two-dimensional gas chromatography (GC × GC) coupled with HRMS to analyze unknown organic compounds in rainwater and snow (Cottrell et al., 2013; Lebedev et al., 2020; Mazur et al., 2020; Polyakova et al., 2018), but none identified pesticides. Notably, the use of GC as the separation technique limits the compounds detected to those with appropriate volatilities and thermal stabilities (Moschet et al., 2017). A complementary technique, such as liquid chromatography (LC)-HRMS, can expand the chemical space analyzed. However, the analysis of precipitation using LC-HRMS has only been reported recently and focuses on non-targeted analysis of complexing agents in atmospheric waters rather than unknown pollutants (Beck et al., 2022). LC-HRMS also has the potential to provide insights into a variety of environmental contaminants, such as pesticides, present in the atmosphere.

Here we present the first application of LC-HRMS for suspect screening of environmental contaminants, specifically pesticides, in precipitation. Accurate identification of pesticides in precipitation can assist in modeling pesticide transport through the atmosphere. This work develops a LC-QToF-MS/MS method with a suspect screening workflow to accurately and confidently identify pesticides in precipitation. Seasonal trends, relationships with physicochemical properties, and air mass back trajectory analysis provide insights into potential sources of pesticide contamination in wet deposition.

2. Materials and Methods

2.1. Chemicals and Standards

Solvents used include LC-MS grade methanol (OmniSolv, Sigma Aldrich, St. Louis, MO), LC-MS grade ethyl acetate (Riedel-de-Haën, Seelze, Germany), LC-MS grade formic acid (>98.0%, TCI America, Portland, OR), and Nanopure water (18.2 MΩ-cm). Ammonium fluoride (>98.0%) was purchased from Sigma Aldrich. Isotopically labeled pesticides were used as surrogates and internal standards. The surrogates include atrazine-d5, diuron-d6 (Restek, Bellefonte, PA, USA); metolachlor-d6, N-methyl metribuzin-d3, and DEET-d10 (TRC, Toronto, ON, Canada). Simazine-d5 (LGC, Teddington, UK) was used as an internal standard. Pesticide standard mixtures were purchased from Restek. Table S1 includes compounds found in the Restek standard mixtures, as well as 19 other pesticide reference standards purchased separately from VWR International, Sigma Aldrich, LGC Standards USA (Manchester, NH), Santa Cruz Biotechnology (Dallas, TX), Riedel-de-Haën, and TCI America.

2.2. Sample Handling

2.2.1. Glassware Preparation

Pyrex bowls for sample collection and amber glass bottles for storage were cleaned using Fenton solution (1.0 mmol L^{-1} Fe^{2+} and 100 mmol L^{-1} H_2O_2, acidified to pH 2.5 with HCl) (Campos et al., 2007). The Fenton solution was added to the bowl or bottle and irradiated with shortwave UV light (λ = 254 nm, UVP Mercury Pen-Ray lamps for the bottles and UVP Mineralight Lamps for collection bowls) for 30 minutes. The container was then rinsed with copious Nanopure water.

2.2.2. Sample Collection and Storage

Precipitation was collected on the College of Wooster campus in Wooster, Ohio (40.81° N, 81.94° W) from March 2018 to April 2021, for a total of 53 samples. This site was selected because of its proximity to a combination of agricultural, industrial, and residential sources of volatile organic compounds to the atmosphere. When precipitation was expected to be 6 mm or greater, a clean Pyrex

bowl was placed on the roof of the chemistry building, and the bowl was retrieved following the end of the precipitation event. Frozen samples were allowed to melt in a cold room at 4 °C prior to storage. Samples were stored in clean 1-L amber glass bottles at 4 °C until further preparation.

2.3. Sample Preparation

2.3.1. Filtration

All samples were filtered to remove particulate matter. Precipitation samples from 2018 were filtered using 0.45 µm cellulose acetate syringe filters. Precipitation samples from 2019-2021 were filtered using vacuum filtration with 0.2 µm polyethersulfone (PES) membranes. The change of filter type was due to aims not associated with this work. It should be noted that PES membranes often bind organic compounds, particularly those with high log K_{ow} values. (Vermeirssen et al., 2012) Therefore, losses of pesticides with high log K_{ow} values may have occurred. Percent recoveries for these filtration techniques are incorporated in Table S2. Based on the surrogates analyzed, there is minimal difference between the cellulose acetate and PES filters.

2.3.2. Solid Phase Extraction

A Visiprep vacuum manifold (Sigma Aldrich, St. Louis, MO) was used with Oasis HLB cartridges (Waters, 6 cc, 200 mg, 30 µm) to conduct solid phase extraction (SPE). Prior to extraction, transfer lines were rinsed using Nanopure water, and each sample was spiked with 20 ng of each isotopically labeled surrogate, apart from DEET-d10, which was spiked at 10 ng. The sorbent was conditioned with 5 mL of LC-grade ethyl acetate, two additions of 5 mL of LC-grade methanol, followed by two additions of 5 mL of Nanopure water. The sorbent soaked in each solvent for approximately one minute and was never allowed to fully dry. Each 1-L sample bottle was then connected to the transfer lines and extracted at a rate of 1-2 drops per second. After the sample was added to the cartridge, the bottle was rinsed with 5-10 mL of Nanopure water, which was then pulled through the cartridge. The bottle rinse was repeated twice. The cartridge was then allowed to dry under vacuum for approximately one hour. Analytes were

first eluted with two 5-mL additions of LC-grade ethyl acetate and set aside for GC analysis (not discussed here). Two 5-mL additions of LC-grade methanol were then used as the eluent for LC analysis.

2.3.3. Evaporation

Following solid phase extraction, methanol was evaporated under a gentle stream of nitrogen gas and medium heat using an Organomation Nitrogen Evaporator (Berlin, MA) to a volume of 200 µL, then reconstituted by adding 800 µL of Nanopure water. In addition, 10 ng of an internal standard (simazine-d5) was added, and the entire volume was transferred to an HPLC vial. Vials were stored in a -20 °C freezer until analysis.

2.4. LC-QToF-MS

An Agilent 1260 Infinity II liquid chromatograph equipped with an Agilent C18 Poroshell 120 column (2.1 x 100 mm, 2.7 µm) and an Agilent 6545 electrospray ionization quadrupole time-of-flight mass spectrometer were used for sample analysis. Both positive and negative ion mode were employed. All operating parameters for the LC-QToF method and the batch order are listed in the Excel SI.

2.5. Data Analysis

2.5.1. Feature Reduction

An open-source software, MS-DIAL (version 4.60), was used for feature annotation (Tsugawa et al., 2015). Parameters used for positive and negative mode analysis in MS-DIAL are listed in the Excel SI. A series of criteria was established to reduce the number of features to the most prominent. These criteria include: (1) the ratio of the sample maximum to deposition blank median was greater than 10 (see section 2.5.5), (2) features appeared in three or more samples with a peak height of at least 3000, (3) the sum of the peak heights across all samples was greater than 100,000, and (4) the feature was named after comparison to the imported libraries. Features that met all four criteria were considered significant and evaluated further.

2.5.2. Feature Confirmation

Features that fit all the criteria outlined in section 2.5.1. were manually annotated to confidence according to the Schymanski levels (Schymanski et al., 2014). Experimental MS/MS spectra were manually compared to spectral libraries, including Toxicology PCDL, Pesticides PCDL, and Water Screening PCDL (Agilent). A good spectral match met all of the following criteria: (1) at least one of the largest three product ion peaks matched the library in terms of m/z and relative intensity, (2) at least three times as many peaks matched as remained unmatched (excluding the precursor ion), and (3) the accurate mass similarity score was at least 80%. If a quality spectral match was present, the feature was annotated as Level 2. Standards of pesticides identified as Level 2 were purchased and analyzed using the same LC-QToF methodology as the samples. Retention times and MS/MS spectra for the Level 2 features were compared for both the sample and standard. Features were annotated as Level 1 if the retention times matched within 0.2 minutes.

2.5.3. Semi-Quantitation

Calibration curves were created for each Level 1 pesticide using Agilent MS Quantification (version 10.1) and the method of isotopic dilution. Equation 1 shows the general form for the line of best fit, where *F* is the response factor:

$$\frac{\text{Area of Target}}{\text{Area of Surrogate}} = F\,\frac{\text{Conc of Target}}{\text{Conc of Surrogate}} \qquad \text{(Equation 1)}$$

An appropriate surrogate for comparison was selected on proximity of retention time to the target compound (Table S3). Average response factors, instrument and method limits of detection (LOD), and linear range for each Level 1 pesticide can be found in Table S3. Comparing signals from analytes to signals from isotopically labelled surrogates, which are added prior to SPE, minimizes error due to loss during sample preparation.

2.5.4. Deposition Flux

The mass of pesticides per unit area, or deposition fluxes, are reported instead of concentrations to account for scavenging and washout of pesticides in the atmosphere during

precipitation events (Goolsby et al., 1997). Deposition flux, in ng m^{-2}, was calculated using Equation 2, where *c* is the concentration of pesticide in precipitation in ng L^{-1}, and *f* is the total amount of precipitation in meters. Here, multiplying by 1000 serves as a conversion factor (1 L = 1000 m^3).

$$\text{Flux} = 1000cf \qquad \text{(Equation 2)}$$

2.5.5. QA/QC

Several types of blanks were prepared to monitor sources of contamination. Deposition blanks were collected by placing a clean Pyrex bowl with approximately one liter of Nanopure water at the collection site when precipitation was not expected to capture dry deposition. In addition, lab reagent and lab fortified blanks were prepared to monitor contamination from the extraction process, assess matrix effects, and determine percent recovery of the method (Table S2). Lab reagent blanks consisted of 20 ng of isotopically labeled surrogates spiked into approximately one liter of Nanopure water prior to SPE. The lab fortified blanks (LFB) included 20 ng of the Restek standard mixtures and 20 ng of surrogates spiked into approximately one liter of Nanopure water prior to SPE. All blanks were stored and analyzed in the same manner as precipitation samples.

Instrument performance and consistency were monitored across batches during LC-QToF-MS measurements. Sets of calibration solutions ranging from 0.05 to 100 ng mL^{-1} for positive mode and 1 ng mL^{-1} to 200 ng mL^{-1} for negative mode were analyzed multiple times in a batch. A QA sample containing 50 ng mL^{-1} of each surrogate and 10 ng mL^{-1} of the internal standard, simazine-d5, was injected every 10-15 samples. Accuracy and precision of QA injections can be found in Table S4. The Non-Targeted Analysis (NTA) Study Reporting Tool (SRT) was used in the preparation of this manuscript (BP4NTA, 2022; Peter et al., 2021).

2.6. HYSPLIT

Version 5 of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT; (Stein et al., 2015) model from the National Oceanic and Atmospheric Administration (NOAA) is widely used to

estimate moisture sources for precipitation-producing air masses (Bershaw et al., 2012; Criscitiello et al., 2016; Kostrova et al., 2019). Here, we calculate air mass back trajectories for each precipitation event using HYSPLIT and the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis meteorological data with 2.5° x 2.5° spatial resolution and 6-hour temporal resolution (Kalnay et al., 1996). All trajectories were started in Wooster, Ohio (40.81 N, 81.94 W) at altitudes of 500, 1000, and 3000 meters above ground level and were traced backwards 120 hours. A total of 36 trajectories were created starting at each simulated altitude for each precipitation event, starting six days before the precipitation event and adding another trajectory every four hours until sample collection. An altitude of 1000 meters is used to summarize the HYSPLIT analysis as the results are largely similar between different elevations.

2.7. Statistics

Analyses and visualization were carried out using RStudio (version 4.1.2) (R Core Team, 2021). Packages used include ggplot2 (Wickham, 2016), NADA2 (Julian and Helsel, 2021), and various base R functions. Statistical analyses performed include ANOVA, multiple linear regression, Kendall's tau correlation, and principal component analysis (PCA). For multiple linear regression, co-linearity between the independent variables was examined prior to analysis. The Kendall's tau correlation analysis and PCA were carried out with consideration that the data is left-censored. However, PCA does not have an adaptation to account for censored data in the NADA2 package. For ANOVA and PCA, any data below the limit of detection was replaced with a random value below the detection limit as determined by a random number generator in R. For seasonal comparisons, winter was defined as December, January, and February; spring was defined as March, April, May; summer was defined as June, July, August; and fall was defined as September, October, November.

3. Results and Discussion

3.1. Feature Annotation

246 3.1.1. Positive Mode

247 Initially, MS-DIAL identified 36,847 features in the precipitation samples analyzed in positive
248 ionization mode. By implementing the filters described in Section 2.5.1, the number of features to be
249 manually examined was reduced to 5,346. Of these 5,346 features, 625 were annotated as Level 2. A
250 total of 32 Level 2 features were suspected pesticides (Table S5). Reference standards of the Level 2
251 pesticides were used to confirm their presence and increase the assigned confidence to Level 1. If the
252 retention time of the feature and the reference standard did not match, then the confidence was
253 decreased to Level 3. Table 1 lists the 21 pesticides that were assigned Level 1 confidence using positive
254 ionization mode. Overall, the suspect screening workflow provided a positive identification rate of 66%.

Table 1: Pesticides annotated as Level 1

Ionization Mode	Compound*	Use	Percent of Samples > LOD
Positive	**alachlor**	Herbicide	18.9
	ametryn	Herbicide	0.0
	atraton	Herbicide (obsolete)	0.0
	atrazine	Herbicide	35.8
	atrazine-desethyl	Degradation product of atrazine	26.4
	atrazine-desisopropyl	Degradation product of atrazine	7.5
	cyanazine	Herbicide	3.8
	cycloate	Herbicide	1.9
	DEET	Insect repellant	100
	desthio-prothioconazole	Degradation product of prothioconazole (fungicide)	18.9
	flutriafol	Fungicide	9.4
	hexazinone	Herbicide	30.2
	metolachlor	Herbicide	37.7
	metribuzin	Herbicide	3.8
	octhilinone	Fungicide	28.3
	propazine	Herbicide	3.8
	simazine	Herbicide	7.5
	simetryn	Herbicide	0.0
	dichlorvos	Insecticide	1.9
	diphenamid	Herbicide	11.3
	triadimefon	Fungicide	0.0
Negative	diuron	Herbicide	1.9
	fomesafen	Herbicide	0.0

*Bolded entries denote compounds where three or more samples had concentrations greater than the limit of detection (LOD).

255

256 3.1.2. Negative Mode

257 Using negative mode ionization, 27,425 features were identified. Following the implementation
258 of the filters described in Section 2.5.1, the number of features was reduced to 1,995. Of the 1,995
259 features, 73 were annotated as Level 2. Two Level 2 features were identified as pesticides (Table S6).
260 Following a comparison to reference standards, these two pesticides were annotated as Level 1 (Table
261 1).

262 3.1.3. Comparison to Blanks and Detection Limit

263 Samples were compared to various blanks to ensure the pesticides originated from the
264 precipitation. The concentration of each pesticide in lab reagent blanks was compared to the
265 concentration in the samples using a one-tailed *t*-test. If results of the *t*-test indicated that there was no
266 statistically significant difference in the concentrations of the sample and lab reagent blank ($p > 0.05$),
267 these pesticides were removed from consideration. Lab reagent blanks did not contain significant
268 amounts of any of the pesticides detected; therefore, we conclude that the experimental method did
269 not contribute contamination. In addition, deposition blanks were analyzed to determine the relative
270 contributions from wet and dry deposition. The presence of DEET in the deposition blanks was typically
271 greater than the limit of detection but less than the concentrations found in most samples. Therefore, it
272 was concluded that the presence of DEET arose from both dry and wet deposition. All other relevant
273 Level 1 pesticides yielded concentrations less than the limit of detection in the deposition blanks. This
274 suggests that the presence of these pesticides was due primarily to wet deposition.

275 Of the 23 pesticides identified in the precipitation samples, the 12 bolded compounds in Table 1
276 were most frequently detected, including six herbicides, two fungicides, one insect repellent, as well as
277 three degradation products. Four of the herbicides—alachlor, atrazine, metolachlor, and simazine—have
278 been detected in rainwater in the Midwestern region of the United States from the mid-1980s through

279 the mid-2000s (Goolsby et al., 1997; Majewski et al., 2000; Miller et al., 2000; Nations and Hallberg,
280 1992; Richards et al., 1987; Steinheimer and Scoggin, 2001; Thurman and Scribner, 2008; Vogel et al.,
281 2008), and the degradates atrazine-desethyl and atrazine-desisopropyl have also been detected in
282 Midwestern precipitation previously (Goolsby et al., 1997; Vogel et al., 2008). To the best of our
283 knowledge, no new measurements have been published for the wet deposition of any of these
284 herbicides or degradates in the Midwest since the work of Vogel et al. in 2008, though the insecticide
285 DEET was detected in Minnesota precipitation in 2015 (Ferrey et al., 2018). In addition, atrazine and
286 metolachlor have been recently detected in ambient air in the Great Lakes region (Wang et al., 2021,
287 2018); however, the concentrations are much lower than presented here. Similarly, low concentrations
288 of alachlor (Hayward et al., 2010), simazine, atrazine-desethyl (Yao et al., 2008), and atrazine-
289 desisopropyl (Peck and Hornbuckle, 2005) in airborne particulate matter were also detected throughout
290 the United States and globally. Furthermore, our work marks the first quantitation of diphenamid,
291 desthio-prothioconazole, and octhilinone in wet deposition samples anywhere, as well as the first
292 quantitation of hexazinone (Santos et al., 2017) and flutriafol (Casara et al., 2012; Nogueira et al., 2012)
293 in wet deposition outside of Brazil. Diphenamid, octhilinone, hexazinone have also not been identified
294 via air sampling; however, desthio-prothioconazole has been found in ambient air in Austria (Zaller et
295 al., 2022) and Canada (Raina and Smith, 2012), and flutriafol has been detected in atmospheric
296 particulate matter in Vietnam (Duong et al., 2021). The concentrations of these pesticides are
297 significantly lower in air than in wet deposition found in this work. These novel findings reinforce that
298 suspect screening by LC-QToF-MS is a useful strategy to identify unexpected pesticides in wet
299 deposition.

300 *3.2. Pesticide Deposition Fluxes*

301 Event-based deposition fluxes of pesticides in Wooster, Ohio varied greatly, from less than one
302 ng m^{-2} to greater than 30,000 ng m^{-2} (Figure 1). Larger quantities of pesticides, such as atrazine (and its

degradation products), alachlor, and metolachlor, deposited give rise to potential field and surface water contamination. In agreement with prior studies (Charizopoulos and Papadopoulou-Mourkidou, 1999; De Rossi et al., 2003; Goolsby et al., 1997; Majewski et al., 2014; Scheyer et al., 2007; Vogel et al., 2008), significant seasonal trends are observed for a subset of herbicides detected: alachlor, metolachlor, and atrazine and its degradation products (atrazine-desisopropyl and atrazine-desethyl) have large increases in deposition flux in the months of May and June each year (Figure 1a). These herbicides, as well as simazine, have statistically significant differences in deposition fluxes in May and June compared to other months (Figure 2). These months correspond to the start of planting season in Ohio when pre-emergent herbicides are applied. Alachlor, metolachlor, atrazine, and simazine are all pre-emergent herbicides most commonly used on corn and soybeans (Wieben, 2019). In Wayne County, Ohio, where Wooster is located, over 55,000 acres of corn and 53,000 acres of soybeans were planted in 2017 (Census of Agriculture, 2017). Therefore, heavy use of these pesticides in Wayne County is likely. According to the United States Geological Survey (USGS), between 2017 and 2019 the average masses of metolachlor, atrazine, and simazine used in Wayne County were 1.258×10^4 kg, 1.212×10^4 kg, and 2.476×10^3 kg, respectively (Wieben, 2019). The heavy use of these pesticides in proximity to Wooster in conjunction with a clear seasonal trend suggests local atmospheric origins of these pesticides. In contrast, alachlor is not widely used in Wayne County (approximately 1,776 kg in 2017, with no data available for 2018 onwards) (Wieben, 2019). The use of alachlor nationally has been steadily declining since the early 2000's. This trend suggests that alachlor may be transported from other regions to Wooster, Ohio, as supported by HYSPLIT trajectories, discussed in section 3.6.

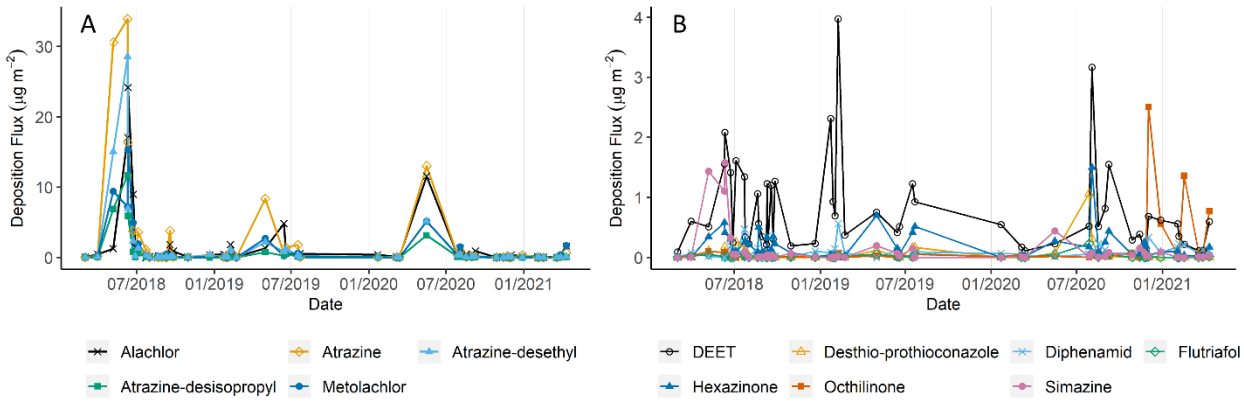

Figure 1: Deposition flux (ng m^{-2}) of (a) pesticides that have a strong seasonal trend and (b) pesticides that do not display seasonal trends.

Other pesticides, such as DEET, desthio-prothioconazole, diphenamid, flutriafol, hexazinone, and octhilinone, did not show a significant seasonal trend (Figure 1b). These pesticides were present in precipitation at low levels year-round. Use of pesticides such as DEET and octhilinone are not reported by the USGS, likely due to the inability to effectively track their use. DEET is the active ingredient in commercial insect repellents, making personal use much more significant than agricultural use. Similarly, octhilinone is largely used as a biocide for materials preservation for coatings, sealants, and plastics (United States Environmental Protection Agency, 2007a). Diphenamid, flutriafol, and hexazinone have not been heavily applied in Wayne County, although flutriafol and hexazinone have been used in other portions of the Midwest; thus, regional transport may have contributed to their presence in precipitation. Air mass back trajectories (section 3.6) support this hypothesis. An average of 174 kg per year of prothioconazole, the parent compound of desthio-prothioconazole, has been applied in Wayne County from 2017-2019. While prothioconazole was not detected, its degradation product was found in approximately 19% of samples. The lack of the parent compound is not unexpected as its degradation occurs rapidly (Z. Zhang et al., 2018).

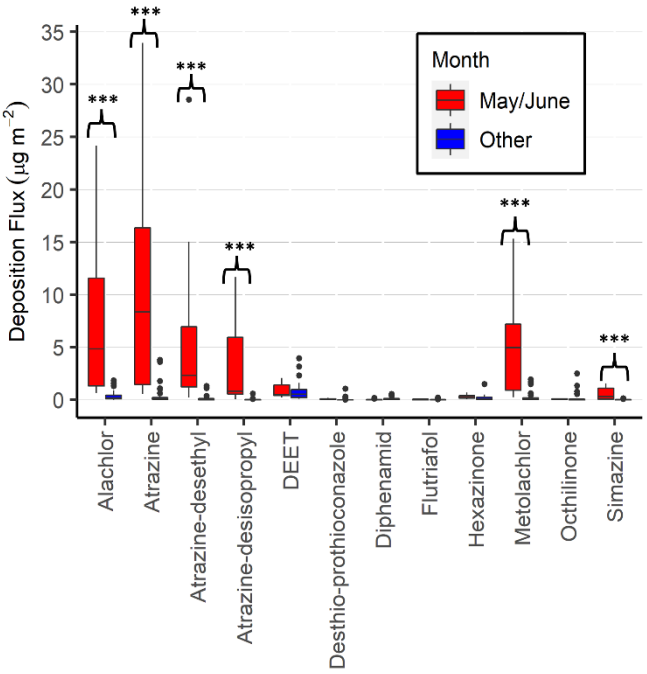

Figure 2: Pesticide deposition flux in May and June compared to all other months. *** denotes a statistically significant difference ($p < 0.05$).

Annual wet deposition fluxes (Table 2) were estimated from the average monthly pesticide concentrations measured over March 2018 to April 2021 and the monthly precipitation amounts from the NOAA 2006-2020 U.S. Climate Normals for Wooster, Ohio (NOAA, 2022). A broader climate normal is utilized here instead of monthly precipitation totals in Wooster to account for not collecting samples during every precipitation event. This estimate will allow for comparison of annual deposition flux from previous literature reports. The estimated annual deposition flux for all quantified pesticides is approximately 590 µg m^{-2} yr^{-1}.

Table 2. Minimum, maximum, median concentrations and estimated annual and seasonal deposition fluxes for each pesticide

	Concentration (ng L^{-1})			Annual Deposition Flux	% Annual Flux
Compound	Min	Max	Median	(µg m^{-2} yr^{-1})	from April-Oct
alachlor	N.D.	792	14.5	100	96%
atrazine	0.3	2316	6.9	192	99%
atrazine-desethyl	N.D.	1138	3.2	95	99%
atrazine-desisopropyl	N.D.	523	0.8	45	100%
diphenamid	N.D.	52.4	3.1	6.0	46%
hexazinone	N.D.	34.3	5.8	9.6	86%
metolachlor	0.5	713	4.0	81	98%

simazine	N.D.	109	1.3	9.7	91%
Σ Herbicides	*8.3*	*4921*	*53.6*	*538*	*97%*
desthio-prothioconazole	N.D.	56.6	0.1	3.1	99%
flutriafol	N.D.	12.2	0.5	1.2	88%
octhilinone	N.D.	87.8	0.8	9.7	52%
Σ Fungicides	*0.5*	*88.1*	*3.1*	*14*	*66%*
DEET (*Insecticide*)	3.7	228	0.8	37	67%
Σ Pesticides	*13.1*	*4979*	*93.1*	*590*	*95%*

N.D. = not detected

Herbicides make up roughly 91% of the total estimated annual deposition flux of pesticides in Wooster, Ohio. Agriculture, which uses substantial quantities of herbicides, is a large industry in areas surrounding Wooster, and 97% of the estimated annual deposition flux for herbicides occurs during the growing season (April to October). The exception to the seasonal herbicide trend is diphenamid, which is not in common use locally and has never before been measured in precipitation. The herbicide with the greatest estimated deposition flux in Wooster, Ohio is atrazine (192 μg m^{-2} yr^{-1}). Such levels are comparable to wet deposition fluxes across the Midwest in 1990-1991 (Goolsby et al., 1997) and in Indiana in 2003-2004 (Vogel et al., 2008). As seen in the early Midwestern measurements by Goolsby et al. (Goolsby et al., 1997), the ratio of atrazine-desethyl to atrazine measured here was approximately 2:1, providing support for desethylation occurring in the environment. We observed a greater deposition flux of atrazine-desethyl than of atrazine-desisopropyl; this finding is consistent with prior measurements (Goolsby et al., 1997; Thurman et al., 2000) and is reasonable given that atrazine-desethyl is more readily formed and is longer-lived than atrazine-desisopropyl (Thurman and Scribner, 2008). Outside the Midwest, the most recently reported seasonal deposition fluxes for atrazine and its degradates are from 2011 in Winnipeg, Manitoba: 5 μg m^{-2} for atrazine, 1 μg m^{-2} for atrazine-desethyl, and 0 μg m^{-2} for atrazine-desisopropyl (Farenhorst et al., 2015). However, because atrazine is applied

much more broadly in the Wooster, Ohio area than in the Winnipeg, Manitoba area, it is reasonable for the deposition fluxes reported here to be significantly higher.

The estimated annual deposition flux of alachlor (100 μg m^{-2} yr^{-1}) was on the order of annual deposition fluxes measured in the Midwest in 1990-1991 (Goolsby et al., 1997). However, application of alachlor in the U.S. dropped sharply beginning in 1994 (Wieben, 2019), and the seasonal deposition flux of alachlor was only 3 μg m^{-2} in 2004 in Indiana (Vogel et al., 2008). The most recently available deposition flux measurement for alachlor in rainwater was even lower: 0.15 μg m^{-2} during the 2007 growing season in the Mississippi Delta (Majewski et al., 2014). No new flux measurements for alachlor have been reported in the past 15 years. Possible sources of the high alachlor levels observed in Wooster precipitation over 2018-2021 are discussed in section 3.6.

The estimated annual deposition fluxes of metolachlor (81 μg m^{-2} yr^{-1}) and simazine (9.7 μg m^{-2} yr^{-1}) also exceeded amounts from elsewhere. The metolachlor and simazine deposition fluxes in Indiana were 21 μg m^{-2} and 2 μg m^{-2}, respectively, during the 2004 growing season (Vogel et al., 2008). Farther afield, the seasonal deposition flux of metolachlor was 17 μg m^{-2} during the 2007 growing season in the Mississippi delta (Majewski et al., 2014) and 0.3 μg m^{-2} during the 2011 growing season in Winnipeg, Manitoba (Farenhorst et al., 2015). To the best of our knowledge, there have been no new direct reports of the deposition flux of simazine since 2004. While one study identified hexazinone in rainwater in Brazil (Santos et al., 2017), there have been no reports of its deposition fluxes anywhere in the literature. Clearly there is a wide gap in field measurements of wet deposition of atmospheric pesticides.

DEET, the sole insecticide identified in precipitation from Wooster, contributes 6% of the total annual deposition flux of all pesticides quantified in this study. The use of DEET primarily comes from personal insect repellents. Elsewhere, DEET has been reported at concentrations up to 14.5 ng L^{-1} in wet deposition from Minnesota (Ferrey et al., 2018) and between 1.66 – 94.8 ng L^{-1} in precipitation from Singapore (H. Zhang et al., 2018). For comparison, our detected concentrations ranged from 3.7 – 228

ng L^{-1}. Ferrey et al. proposed that DEET could enter the atmosphere from wastewater emissions (Ferrey et al., 2018). A similar process could be occurring in Wooster, though its population of 26,000 is small in comparison to urban collection sites like Minneapolis/St. Paul and Singapore.

The remaining 3% of the annual pesticide deposition flux in Wooster, Ohio arises from fungicide use. The growing season accounts for 99% and 88% of the annual deposition fluxes of desthio-prothioconazole and flutriafol, respectively, but only 52% of the annual deposition flux of octhilinone. As noted above, octhilinone is used primarily in construction materials, so its concentration in the atmosphere is unlikely to depend on agricultural activity. Neither desthio-prothioconazole nor its parent compound has been detected previously in precipitation. Flutriafol was found in rainwater from Mato Grosso, Brazil at concentrations of 50-120 ng L^{-1} (Casara et al., 2012); these values exceed the maximum concentration detected in rainwater from Wooster, Ohio. However, deposition fluxes of flutriafol were not reported in the Brazilian study to allow a more direct comparison.

In summary, our results show that pesticides applied locally can be detected in significant amounts, particularly in early summer (May and June) when crops are being planted and the use of pesticides is high. The estimated deposition fluxes for the eight herbicides, three fungicides, and one insecticide identified are 538 µg m^{-2} yr^{-1}, 14 µg m^{-2} yr^{-1}, and 37 µg m^{-2} yr^{-1}, respectively. Based on the sampling period of this study, approximately 590 µg m^{-2} yr^{-1} of pesticides were deposited through precipitation. The identification and semi-quantification of these pesticides suggest local transport within the Wooster area. In addition, pesticides that are not heavily used in northeastern Ohio have also been detected, which suggests regional atmospheric transport from other locations.

3.3. Physical and Chemical Properties

A multiple linear regression was carried out to investigate whether physicochemical properties, including water solubility (*WS*), vapor pressure (P_{vap}), Henry's Law constant (K_H), and octanol-water partition coefficient (K_{ow}), of pesticides could predict pesticide detection frequency in precipitation.

Values for all physicochemical properties (Table S7) were collected from the EPA CompTox database (Williams et al., 2017). Co-linearity between all independent variables was examined prior to carrying out the regression model. It was determined that no co-linearity between any variables exists. The relationship between the detection frequency and each independent variable was nonlinear, therefore the log of all components was taken to improve the linearity. Variables that did not significantly contribute to the model (i.e. *p*-values > 0.1) were removed. The results of the regression following the removal of insignificant variables indicated that vapor pressure is the only significant predictor for detection frequency in precipitation (Table 3). Based on the log-transformed regression model, for every 1% increase in vapor pressure, we expect the detection frequency to increase by approximately 0.13%.

Table 3. Results of multiple linear regression of physical and chemical properties

Explanatory Variable	Coefficient	Standard Error	*p*-value
Constant	0.305	0.565	0.602
Vapor pressure	0.132	0.0381	0.007
R^2_{adj} = 0.524 (N = 11, F = 12.0, p = 0.007)			

Overall, the vapor pressure of a pesticide is the only significant indicator of pesticide detection in precipitation in Wooster, Ohio. Pesticides have multiple avenues for entering the atmosphere such as volatilization, spray drift, and wind erosion of soil. Volatilization appears to be the primary path for pesticides entering the atmosphere in this study based on the strong relationship between vapor pressure and detection frequency. Compounds with higher vapor pressures more easily enter the gas phase and can be transported through the atmosphere (Messing et al., 2013). Surprisingly, the other properties studied here do not exhibit a significant relationship with frequency of detection. Pesticides with high water solubilities and high K_H values should readily partition into cloud droplets and undergo scavenging into precipitation; however, these pesticides are less likely to be volatilized into the atmosphere in the first place if they remain dissolved in water on the surface of plants and soil (Unsworth et al., 1999). Furthermore, pesticides with a propensity to adsorb to soil (high K_{ow} values) that

441 enter the atmosphere through wind erosion would be filtered out during sample preparation for this
442 analysis, and thus not be considered. Finally, our simplistic model does not account for the temperature
443 dependence of any of these physicochemical properties (Bidleman, 1999).

444 Another limitation of the regression model is that pesticide usage is not considered. Average
445 application amounts of each pesticide in Wayne County, Ohio during the sampling period were collected
446 from the USGS (Wieben, 2019). These data show no significant relationship to the frequency of
447 detection (Figure S1). While local sources are suspected to contribute to the detection of atrazine and
448 several other pesticides, regional transport may also play a critical role; therefore it is difficult to
449 pinpoint which counties to include in the regression model. Furthermore, different formulations and
450 different application methods for each pesticide hinder a straightforward comparison between amount
451 applied and amount in the atmosphere (Unsworth et al., 1999). In addition, only 11 pesticides were
452 analyzed in this regression, which typically requires a larger data set to yield significant results. Despite
453 the small sample size, significant results were obtained for vapor pressure. The correlation between
454 vapor pressure and detection frequency is moderately strong (correlation = 0.756), further supporting
455 the results of the multiple linear regression.

456 3.4. *Kendall's tau Correlation Analysis*

457 Kendall's tau correlation coefficients were calculated to determine relationships between pairs
458 of pesticides (Table S8) and are displayed in Figure 3. While most correlations were not strong, several
459 were significant ($p < 0.05$). Alachlor, atrazine, atrazine-desethyl, atrazine-desisopropyl, and metolachlor
460 are moderately correlated with each other (correlations between 0.240 to 0.441). The Kendall's tau
461 correlation is consistent with the seasonal trend previously discussed in section 3.2. These herbicides
462 were all detected in substantial concentrations in the months of May and June each year.

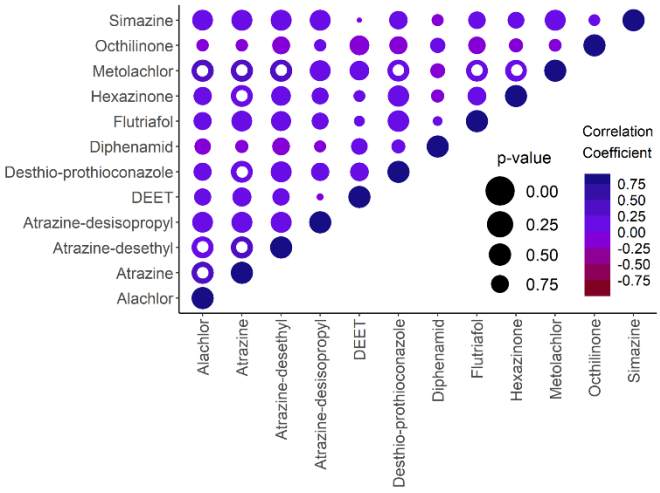

Figure 3: Kendall's tau correlation plot for detected pesticides. Points with a white center correspond to coefficients with a *p*-value < 0.05.

Other significant correlations include desthio-prothioconazole with atrazine (correlation = 0.229) and metolachlor (correlation = 0.218). Metolachlor also displays statistically significant correlations with flutriafol (correlation = 0.190) and hexazinone (correlation = 0.193). This slight correlation suggests that hexazinone (herbicide), desthio-prothioconazole (fungicide degradate), and flutriafol (fungicide) increase along with atrazine and metolachlor, both of which display strong seasonal trends. It is possible that hexazinone, prothioconazole, and flutriafol may be applied to crops at similar times to atrazine and metolachlor. Hexazinone is registered as both a pre-emergent and post-emergence herbicide (United States Environmental Protection Agency, 1994). In addition, it is recommended that prothioconazole and flutriafol be applied preventively or at the first sign of disease, which may occur in the early growth stage of the crop (United States Environmental Protection Agency, 2020, 2007b). Therefore, hexazinone, prothioconazole, and flutriafol application likely occurs in late spring to early summer. However, a strong seasonal trend of these pesticides would not be expected if much less significant quantities were applied.

Kendall's tau correlation analysis was also carried out on seasonal data (Figures S2-5 and Tables S9-12). Spring and summer months (Figures S2 and S3) showed similar profiles to the profile of the

entire data set (Figure 3), emphasizing the seasonal trend for metolachlor, alachlor, atrazine, and its degradation products. Metolachlor and atrazine-desethyl are moderately correlated with desthio-prothioconazole, particularly in the spring months. This correlation suggests that desthio-prothioconazole may also arise from local sources, similar to metolachlor and atrazine.

3.5. Principal Component Analysis

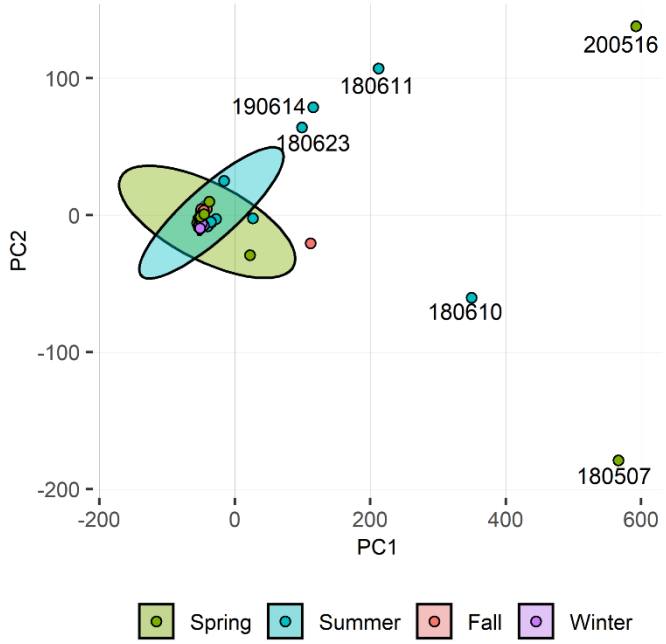

Figure 4: Principal component analysis of all precipitation samples. Labeled dates are in the format YYMMDD.

Principle component analysis was performed on the precipitation samples to visualize similarities between sample composition. The first principal component explains 87% of the variation in the data, while the second principal component accounts for 7% of the variation (Figure S6). The cumulative variation explained by the first two components is 94%. Figure 4 clearly shows that many of the samples have a similar profile; however, the majority of samples from May and June each year are vastly different. The dates labeled in Figure 4 make up 67% of the samples from May and June. Larger values in the first principal component arise from high amounts of metolachlor, simazine, alachlor,

atrazine, and its degradation products (Table S13). As previously discussed, these pesticides are detected in significant amounts in May and June, likely due to local agricultural sources. This analysis also shows the large variation of compositions in the spring and summer months. Figure S7 shows the variation in the fall and winter months, which is significantly narrower than in spring and summer. While pesticides are still found in precipitation in the fall and winter, they are detected in much lower amounts and stay relatively consistent during that time. In summary, PCA clearly illustrates which samples are vastly different in terms of composition and which pesticides differentiate those samples.

3.6. Air Mass Trajectories

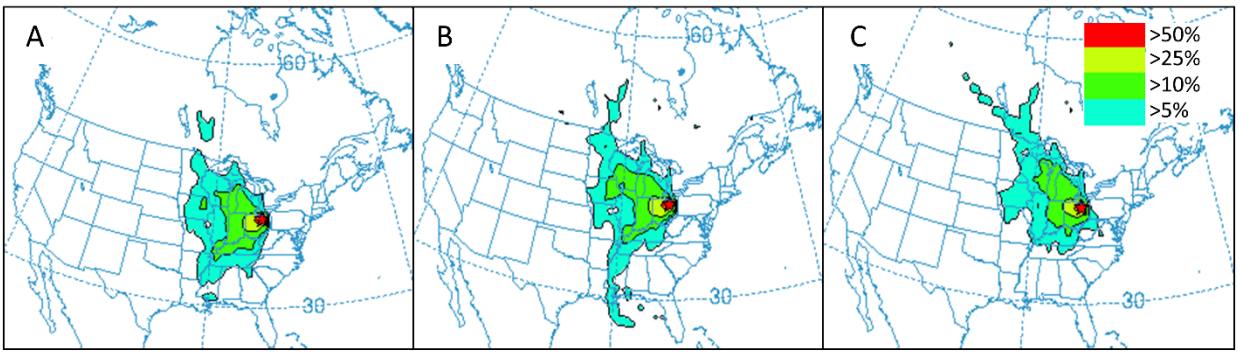

Figure 5: Frequency plot of the air mass back trajectories (percentage of trajectories that intersect each grid cell) for precipitation events where the flux of (A) atrazine, (B) metolachlor, and (C) alachlor is greater than 100 ng mL^{-1} as measured by the instrument. Trajectories start at 1000 m above ground level in Wooster, Ohio.

Based upon prior analysis in section 3.2, including a significant seasonal trend corresponding well to time of application, atrazine and metolachlor are thought to come from sources local to Wooster. Air mass back trajectories calculated using HYSPLIT support this hypothesis. Precipitation events with pesticide concentrations greater than 100 ng mL^{-1} as measured by the instrument (corresponding to approximate deposition fluxes of 4000 ng m^{-2}) were considered, and all associated trajectories were combined to create frequency plots. These plots allow for a visual representation of the overlap of air mass trajectories. When deposition fluxes of atrazine and alachlor are above the set

519 threshold, the most common path for air masses arriving in Wooster was from the west, with greater
520 than 25% of air mass trajectories per grid cell in western Ohio (Figure 5). In conjunction with the strong
521 seasonal trend observed for atrazine and metolachlor and widespread use throughout Ohio, this result
522 suggests local transport within Ohio. However, it should also be noted that air mass trajectory frequency
523 was greater than 10% per grid cell in other Midwestern states, primarily Indiana which neighbors Ohio.
524 The use of atrazine and metolachlor in Illinois is also significant. According to the Pesticide National
525 Synthesis Project by the USGS from 2017-2019, greater than 11 kg km^{-2} of atrazine and between 0.5 and
526 3 kg km^{-2} of metolachlor were used in Indiana each year (Wieben, 2019). As previously discussed in
527 section 3.3, there is a mismatch between our measured detection frequency and pesticide use reported
528 in Wayne County, Ohio. The air mass back trajectories suggest that regional transport throughout the
529 Midwest, particularly from regions highlighted in Figure 5, may contribute to this discrepancy; however,
530 future measurements at more sampling sites are needed to examine this hypothesis.
531 Alachlor, while frequently detected with high deposition fluxes in the months of May and June,
532 does not have significant usage in Ohio reported with the USGS. Through air mass back trajectory
533 analysis of the precipitation events with greater than 100 ng mL^{-1} pesticide concentrations as measured
534 by the instrument, it is observed that the air mass trajectory frequency exceeded 25% per grid cell over
535 northern Ohio, and 10% per grid cell over states to the northwest, such as Michigan and parts of
536 Wisconsin (Figure 5). This result suggests transport from regions to the northwest. In 2017 and 2018, the
537 USGS reports that approximately 0.26 to 1.6 kg km^{-2} of alachlor was applied in regions northwest of Ohio
538 (Wieben, 2019). This application may be reflected in the rain collected in Wooster, Ohio if regional
539 atmospheric transport occurs. However, there is also the possibility that although the use of alachlor has
540 been reduced nationwide (Wieben, 2019), it is still in use in Ohio but the reporting is lacking.
541 Other confirmed Level 1 pesticides, such as desthio-prothioconazole, diphenamid, flutriafol,
542 octhilinone, and simazine were also studied using air mass back trajectories. These pesticides were

543 detected less frequently than those previously discussed, and many are not applied in substantial
544 amounts in Ohio. Air mass back trajectories were calculated using precipitation events in which each
545 pesticide was detected above the limit of detection to create frequency plots (Figures S8-12). Similar
546 results were observed as with alachlor. Air masses arriving in Wooster were most likely to have moved
547 through Ohio from the west (over 25% of trajectories per grid cell over western Ohio, and 10-25% of
548 trajectories per grid cell in regions to the west). Greater than 0.09 kg km^{-2} of prothioconazole (the
549 parent compound to desthio-prothioconazole) is used in Ohio and neighboring states, and >0.007 kg
550 km^{-2} of flutriafol has been applied in Ohio and regions west (Wieben, 2019). In addition, greater than
551 0.674 kg km^{-2} of simazine is routinely applied in Ohio and neighboring states, according to the USGS
552 (Wieben, 2019). Application of these less frequently detected pesticides is considerably less than
553 atrazine, metolachlor, and alachlor. Qualitatively, the detection frequency of each pesticide follows the
554 trend of the application fluxes. This correspondence suggests that atmospheric regional transport may
555 play a role in the presence of pesticides in precipitation collected in northeast Ohio.

556 **4. Conclusion**

557 Future directions for our work include further expanding the chemical space analyzed by LC-
558 HRMS. The analytical methods and data processing choices made in this work do not capture the
559 complete composition of precipitation. The use of reversed-phase liquid chromatography as the
560 separation mode hinders the analysis of highly polar compounds. We are currently exploring other
561 separation techniques to enhance detection of highly polar compounds, such as glyphosate (Botero-Coy
562 et al., 2013). The use of other ionization sources may also allow for analysis of different classes of
563 pesticides (Thurman et al., 2001). In addition, the data processing criteria set for this work exclude ultra-
564 trace level compounds, compounds present in only a few samples, and degradation products not
565 present in currently available libraries. Altering the data processing parameters as well as transitioning
566 from suspect screening to non-targeted analysis can expand the chemical space studied. With these

steps, the LC-HRMS method developed in this study will allow for the composition of atmospheric waters to be explored more thoroughly.

Overall, this work emphasizes the important role of high-resolution mass spectrometry as a tool for suspect screening of complex atmospheric water samples, such as precipitation, for the presence of pesticides and other unknown organic species. HRMS allows for highly accurate masses of features, thus allowing for more confident annotation. Coupling this technique with liquid chromatography expands the chemical space that can be sampled in wet deposition compared to previously established GC-HRMS methods. Over 64,000 features were identified in precipitation from the central U.S. using this technique, and 23 pesticides were confirmed with reference standards. Strong seasonal trends in wet deposition were observed for atrazine (and its degradation products), alachlor, and metolachlor. The estimated annual deposition flux of the pesticides detected in precipitation was approximately 590 μg m^{-2} yr^{-1}, allowing for the potential contamination of fields and surface waters. Coupled with air mass back trajectory analysis, it is suggested that these pesticides undergo local atmospheric transport. Other pesticides are less frequently detected and may arise from regional atmospheric transport throughout the Midwest. Using multiple linear regression, pesticides with higher vapor pressures are more frequently detected in precipitation in northeastern Ohio, likely due to their ease of volatilization and gas-phase transport in the atmosphere. In addition, correlation analysis and PCA were employed to emphasize the seasonal trends for primarily atrazine (and its degradation products), alachlor, and metolachlor. In summary, this work develops an LC-HRMS suspect screening method to confidently identify pesticides in atmospheric water samples and provides a valuable assessment of the potential transport of pesticides in the atmosphere.

Competing Interests

The authors have no competing interests to declare.

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