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Factors contributing to pesticide contamination in riverine systems: The role of wastewater and landscape sources

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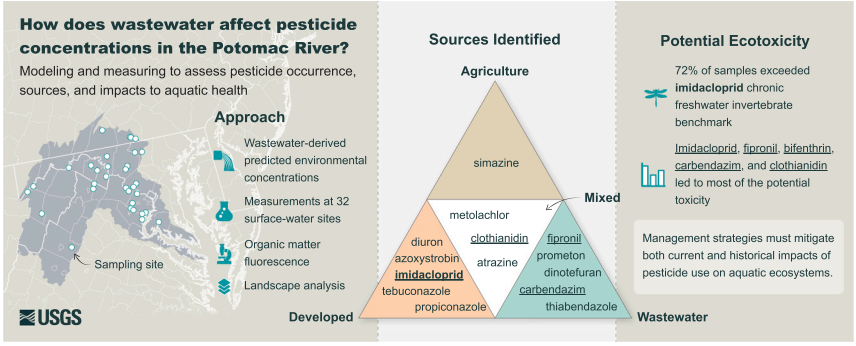
HIGHLIGHTS

- Pesticide concentrations were modeled based on wastewater percentage in stream water.
- Model fit was strongest for insecticides, followed by fungicides and herbicides.
- Organic matter characterization identified wastewater and urban runoff sources.
- Imidacloprid and fipronil led to most of the potential invertebrate toxicity.
- 72 % of samples exceeded the imidacloprid chronic freshwater invertebrate benchmark.

GRAPHICAL ABSTRACT



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ABSTRACT

Wastewater treatment plant (WWTP) discharges can be a source of organic contaminants, including pesticides, to rivers. An integrated model was developed for the Potomac River watershed (PRW) to determine the amount of accumulated wastewater percentage of streamflow (ACCWW) and calculate predicted environmental concentrations (PECs) for 14 pesticides in non-tidal National Hydrography Dataset Plus Version 2.1 stream segments. Predicted environmental concentrations were compared to measured environmental concentrations (MECs) from 32 stream sites that represented a range of ACCWW and land use to evaluate model performance and to assess possible non-WWTP loading sources. Statistical agreement between PECs and MECs was strongest for insecticides, followed by fungicides and herbicides. Principal component analysis utilizing optical fluorescence and ancillary water quality data identified wastewater and urban runoff sources. Pesticides that indicated relatively larger sources from WWTPs included dinotefuran, fipronil, carbendazim, thiabendazole, and prometon whereas imidacloprid, azoxystrobin, propiconazole, tebuconazole, and diuron were more related to urban runoff. In addition, PECs generally comprised a low proportion of MECs, which indicates possible dominant loading sources beyond WWTP discharges. Cumulative potential toxicity was higher for sites with greater ACCWW and/or located in developed areas. Imidacloprid, fipronil, and carbendazim accounted for the largest portion of

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predicted potential toxicity across sites. The chronic aquatic life toxicity benchmarks for freshwater invertebrates were exceeded for 82 % of the imidacloprid detections ($n = 28$) and 47 % of the fipronil detections ($n = 19$). These results highlight the ecological implications of pesticide contamination from WWTP discharges and also the potential legacy effects from accumulated soil and groundwater sources. Pesticide management strategies that mitigate both current and historical impacts may improve the health of aquatic ecosystems.

1. Introduction

Assessing the risk posed to aquatic life and drinking-water quality by sewerage wastewater treatment plant (WWTP) discharges is a global environmental health priority (Brunelle et al., 2024; Glassmeyer et al., 2023, 2017; Malaj et al., 2014; Ramírez-Malule et al., 2020). Wastewater discharges, although treated and in compliance with existing regulations, can be a continuous source of organic contaminants, including pesticides, to rivers worldwide (Berens et al., 2021; Budd et al., 2023; Finckh et al., 2022; Guardian et al., 2021; Kahle et al., 2008; Kolpin et al., 2002; Munz et al., 2017; National Research Council, 2012; Overdahl et al., 2021; Pandey et al., 2023; Rice and Westerhoff, 2015; Sadaria et al., 2016; Sutton et al., 2019; Webb et al., 2021). Pesticides can be introduced to WWTPs through down-the-drain sources from households and businesses, including washing and disposal of food, urine/feces (Curwin et al., 2007; Thompson et al., 2020), tap water (Klarich et al., 2017; Klarich Wong et al., 2019; Montiel-Leon et al., 2018; Wan et al., 2019), use on companion animals and pet bathing (Perkins et al., 2024, 2021; Sadaria et al., 2017; Teerlink et al., 2017), and improper disposal (Flint, 2003; Straw et al., 2023; U.S. Environmental Protection Agency, 2005). For WWTPs with combined sewer systems, untreated sewage sometimes contains urban stormwater that may include sources of pesticides from residential lawns and gardens (Blanchoud et al., 2004; Masoner et al., 2019; Md Meftaul et al., 2020), leaky septic systems (Ślósarczyk and Witkowski, 2021), or outdoor pest control, including applications to impervious surfaces (Jiang and Gan, 2016; Jiang et al., 2015). Separate sanitary sewer systems can also contain water sourced from groundwater via infiltration through cracked or broken sewerage pipes (Diem et al., 2022). Frequently, pesticides are transformed or not completely removed during conventional wastewater treatment and are discharged in the effluent to receiving waterbodies (Barber et al., 2022; Gardner et al., 2012; Pal et al., 2014; Petrie et al., 2015; Shah et al., 2020). In addition, some WWTPs receive industrial discharges that could contain pesticides (Hubbard et al., 2022). Although pesticides are frequently introduced to aquatic environments from agricultural and developed land-use nonpoint sources (Kolpin et al., 2004; Masoner et al., 2019; Stone et al., 2014; Wolfand et al., 2019), WWTP-derived pesticides are of particular concern because they are continuously discharged to receiving waters (Webb et al., 2021).

Pesticides are designed for their potency on biological pathways and are known to elicit adverse effects in non-target organisms following exposures even at trace concentrations (Barber et al., 2022). The potential toxicological impacts are complex and there is limited information available regarding the ecosystem-level effects of these exposures (Nilsen et al., 2019). Documented effects include a loss in taxa abundance and richness, disrupted adult emergence, altered trophodynamics, endocrine disruption, reduced fecundity, mouthpart deformities, immunosuppression, increased mortality, and phytotoxicity (Barber et al., 2019; Bradley et al., 2019; Covert et al., 2020; Iwanowicz et al., 2009; Lal, 2007; Oliver et al., 2023; Schmidt et al., 2022). Dietary and environmental exposures to pesticides may additionally result in bioaccumulation in animal tissues and biomagnification through higher trophic level species and humans (Chopra et al., 2011). The presence of these contaminants in the environment as chemical mixtures may result in further complex synergistic or additive effects (Barber et al., 2022; De Zwart and Posthuma, 2005; Loken et al., 2023; Schmidt et al., 2022).

A broad range of pesticides are not widely regulated or monitored in surface waters despite proven acute and chronic ecotoxicological effects in multiple aquatic taxa (Nowell et al., 2024). Pesticides have been identified as key stressors impairing benthic communities in the United States (Waite et al., 2021), 'are likely' under-represented in stressor identification assessments in the Potomac River watershed (PRW; Fanelli et al., 2022), and are a contaminant class of global concern beyond the PRW (Maggi et al., 2023; Tang et al., 2021). To fully assess the aquatic health impacts of pesticide exposures, it is essential to understand the exposure concentrations that occur in aquatic environments. Monitoring is the one of the most accurate methods to achieve this understanding but is faced with several challenges. Although the characterization of pesticide exposure at low concentrations has improved due to the increased availability of sensitive analytic instrumentation, many pesticides (that are of toxicological concern) occur in trace amounts that can be difficult to detect using standard analytical procedures. Sampling and laboratory evaluation are costly and time-consuming endeavors, limiting the availability of monitoring and trend data (Faunce et al., 2023).

Modeling approaches to prioritize stream segments with greater percentages of accumulated treated WWTP effluent to target sampling and assessments, and to estimate predicted environmental concentrations (PECs) of priority contaminants provide useful tools for researchers and water managers. A number of studies have used these approaches to provide insight on water quality, potential contaminant occurrence, and environmental risk across different scales (Barber et al., 2022, 2019; Faunce et al., 2023; Rice and Westerhoff, 2015; Rice et al., 2013; Weisman et al., 2021, 2019). However, research gaps remain in accurately predicting the exposure and potential ecotoxicity of contemporary pesticides in stream water.

The present study is an expansion of wastewater modeling previously applied to the PRW (Faunce et al., 2023) and the Shenandoah River watershed, a PRW subbasin (Barber et al., 2022, 2019; Weisman et al., 2021, 2019). Faunce et al. (2023) used historical measured environmental concentrations (MECs) at sample sites across the PRW compiled from U.S. Environmental Protection Agency (USEPA) and U.S. Geological Survey (USGS) databases to calculate and evaluate PECs using 2016 effluent discharge data. Predicted environmental concentrations indicated strong relations with MECs for pharmaceuticals and consumer product chemicals, but weaker correlations for pesticides indicated other important sources of pesticides beyond WWTP effluent (Faunce et al., 2023). Because the PEC model is based only on the presence of accumulated wastewater, PECs may represent only a portion of the MECs; therefore, differences between MECs and PECs can occur when other pesticide sources are present.

The MEC values compiled from online databases by Faunce et al. (2023) were reported over a 50-year period and may represent the level of a constituent that predated the construction of a WWTP or different pesticide usage that occurred at the time the sample was collected. The objective of this study was to obtain contemporary pesticide MECs across a gradient of 32 wastewater-impacted rivers in the PRW during low-flow conditions to: (1) characterize pesticide exposures in PRW streams; (2) re-evaluate PEC and MEC comparisons to refine model performance and infer possible landscape sources of pesticides beyond WWTPs; and (3) compare MECs to published aquatic life benchmarks to evaluate potential ecotoxicological risk. In addition, a goal of this study was to increase the number of pesticides modeled from accumulated wastewater beyond the initial three compounds (imidacloprid, clothianidin, and N,N-Diethyl-meta-toluamide) reported in (Faunce et al.,

2023) to include fourteen current-use pesticides previously not well documented in the literature but commonly occurring in WWTP effluent.

2. Methods

2.1. Study area

The PRW is the second largest watershed (36,750 km^2) within the Chesapeake Bay watershed and contributes about 15 % of the total streamflow to the Bay (Blomquist et al., 1996). The mainstem of the Potomac River has minimal flow regulation and contains freshwater upstream from Washington, D.C. Between Washington, D.C. and Point Lookout, Md., the Potomac River becomes tidal and progressively more saline (Blomquist et al., 1996). Population in the PRW more than doubled from 1970 (3.2 million) to 2020 (6.9 million). The majority of development during this period occurred in the Washington, D.C. metropolitan area, where about 84 % of the PRW's population resided as of 2020 (Interstate Commision on the Potomac River Basin, 2023). To accommodate population growth, forest and agricultural lands have been reduced and public water supply and wastewater treatment systems have been expanded. A majority of public-supply withdrawals (80 %) in the PRW are from surface water (Dieter et al., 2018).

The PRW contains a varied landscape (Fig. 1) consisting of steep mountains, rolling hills, broad valleys, and plains. The majority (53 %) of the basin is forested, 23 % is agricultural, and 13 % is developed whereas smaller remaining portions contain water, wetlands, and barren land cover (Chesapeake Bay Program, 2023). The PRW was previously divided into eight topographically and geologically distinct subunits for the purpose of water-quality assessment (Blomquist et al., 1996) and are presented in Supplemental Information (SI) Part A.1 (Fig. A.1). The subunits are primarily divided by physiographic province (Fenneman,

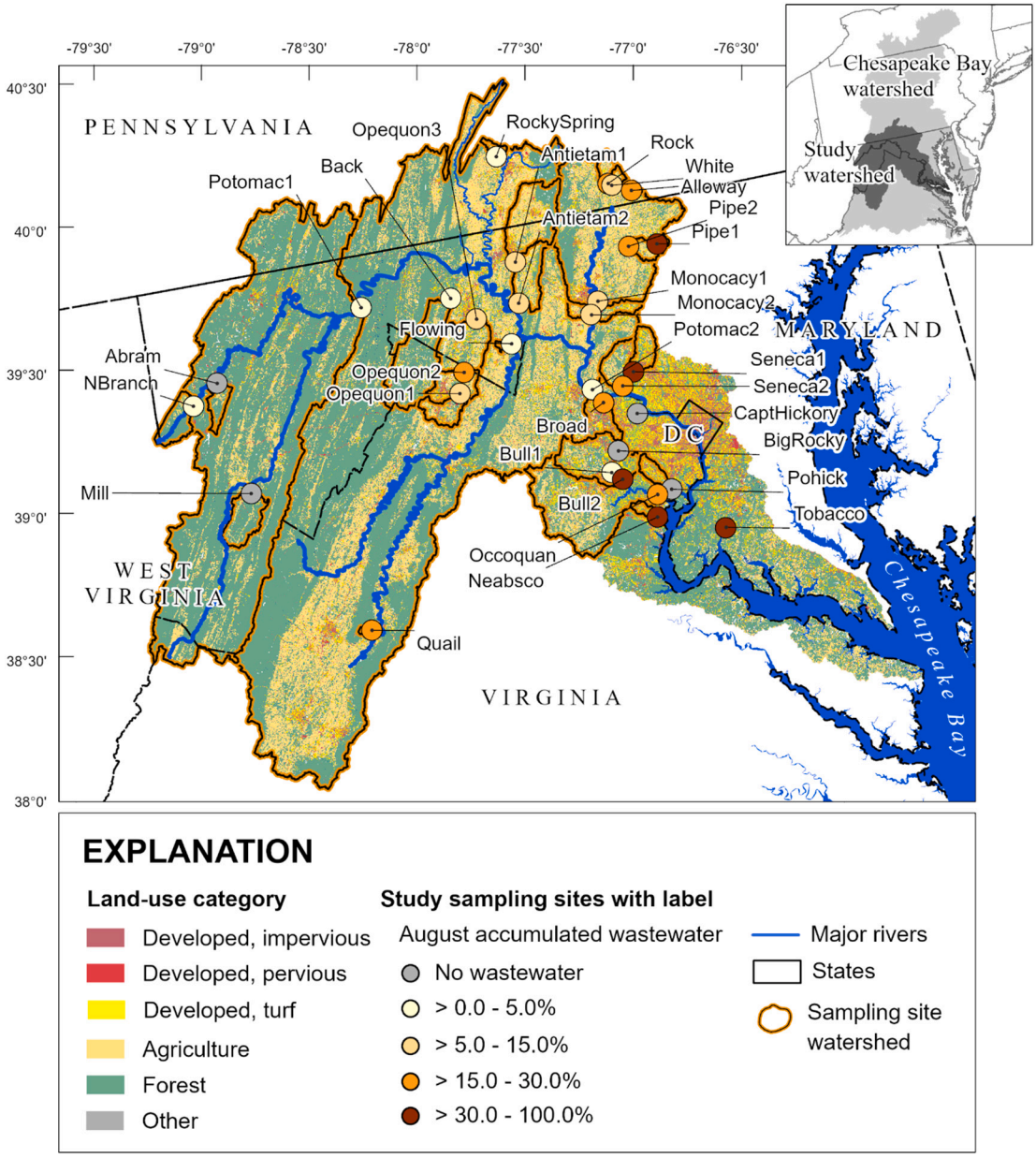

Fig. 1. Sampling locations for 32 sites within the Potomac River watershed and major land-use categories. Study sampling locations are colored by the August accumulated wastewater percentage (percent of total streamflow). Land-use data from Chesapeake Bay Program (2023) aggregated to dominant categories. August accumulated wastewater from Table 1.

1946), and lithology is used as a secondary basis. These distinctions have influenced human development throughout the basin over time and subsequently impacted pesticide and water use, wastewater discharges, and water-quality patterns from the natural background conditions (Blomquist et al., 1996). The dominant subunit, by watershed area, was determined for each study location to assess pesticide concentration patterns (Table 1; Fig. A.1).

Watershed area was delineated for each sampling site using the USGS streamgage coordinates from the StreamStats (https://streamstats.usgs.gov/ss/) web application, and land cover was obtained from the Chesapeake Bay Program and summarized for each study watershed (Chesapeake Bay Program, 2023). Study watersheds were grouped into four broad land-use categories to evaluate pesticide concentration variation: agriculture, developed, forest, and mixed. Agriculture watersheds had at least 40 % land cover devoted to combined cropland and pasture/hay lands and <30 % developed land use. Developed watersheds had at least 50 % from all combined impervious, turfgrass, and other pervious developed categories. Forest watersheds had at least 50 % combined forest, natural succession, harvested forest, and other tree canopy classes. Remaining watersheds that did not fall into these categories were classified as mixed land use. Pesticide concentrations and detections were compared among the land use categories using Tukey's HSD test (de Mendiburu, 2023) and the Wilcoxon rank-sum test (R Core Team, 2024) where significant differences were determined when $p < 0.05$.

Additional landscape metrics from the StreamCat dataset (Hill et al., 2016) and potential contaminant sources (Gordon et al., 2017) for each study watershed were obtained and joined to each site location by National Hydrography Dataset Version 2.1 (NHDPlus V2), common identifier (COMID). The StreamCat dataset contains over 600 metrics that represent both natural (e.g. soils and hydrology) and anthropogenic (e.g. agriculture and urban areas) landscape information that were used in statistical analyses. County-level agricultural pesticide-use data from 2017, the closest year available to the time of sampling, were aggregated for each study watershed (Wieben, 2021).

2.2. Data collection and analytical methods

Water samples were collected once from 32 surface-water sites during low-flow conditions between August and September of 2022 encompassing a range of drainage areas, accumulated wastewater, geology, and land use to better understand how these factors influence stream water pesticide concentrations (Fig. 1; Table 1). Field sampling methods used for this study followed published USGS protocols and procedures (U.S. Geological Survey, 2015). Field parameters (pH, water temperature, dissolved oxygen, turbidity, and specific conductance) were recorded during each sampling event at each site. Blank, replicate, and pesticide matrix spike samples were collected at three randomly selected sites for quality assurance. In addition, for each sample, mass-labeled surrogate standards were each spiked with 50 µL of a 1 ng/µL recovery surrogate solution containing atrazine-$^{13}C_3$, fipronil-$^{13}C_4$, $^{15}N_2$, imidacloprid-d_4, metolachlor-$^{13}C_6$, cis-permethrin-$^{13}C_6$, p,p′-DDE-$^{13}C_{12}$, tebuconazole-$^{13}C_3$, and trifluralin-d_{14}. Samples were collected daily and stored in coolers on ice. All samples were shipped the same day as collected using priority overnight shipping. Samples were shipped in coolers with ice at 4 °C. All water-quality data are available from Miller et al. (2024).

Laboratory analyses were run with standard curves, procedural blanks, and reference materials as available and appropriate (Miller et al., 2024). For pesticide analyses, unfiltered water samples were collected in pre-cleaned 1 L amber-glass bottles filled to the shoulder and stored at 4 °C. Samples for dissolved organic carbon analysis and

Table 1
Site information, including abbreviated name, U.S. Geological Survey station number, drainage area (https://streamstats.usgs.gov/ss/), August accumulated wastewater percentage (ACCWW%; Table A.7), dominant physiographic subunit described in SI part A.1 (Blomquist et al., 1996), and land use (Chesapeake Bay Program, 2023). [AP = Appalachian Plateau; TR = Triassic Lowlands; GVC = Great Valley Carbonate; VR = Valley and Ridge; PD = Piedmont; GVNC = Great Valley Noncarbonate; CP = Coastal Plain.]

Name	USGS station number	Drainage area (km^2)	August ACCWW%	Subunit	Land use
Abram	01595300	110.6	0.0	AP	Forest
Alloway	01638985	10.5	26.8	TR	Mixed
Antietam1	01619270	479.1	11.3	GVC	Agriculture
Antietam2	01619500	725.0	6.2	GVC	Agriculture
Back	01614000	608.2	0.3	VR	Forest
BigRocky	0165694286	8.8	0.0	PD	Developed
Broad	01644280	197.2	25.2	TR	Developed
Bull1	01656978	378.1	0.02	TR	Mixed
Bull2	01657415	478.4	35.5	TR	Mixed
CaptHickory	01645940	3.6	0.0	PD	Developed
Flowing	391733077471001	21.5	1.6	GVC	Mixed
Mill	385740079065201	244.6	0.0	VR	Forest
Monocacy1	01643000	2112.6	6.3	TR	Agriculture
Monocacy2	01643128	2265.5	9.0	TR	Agriculture
NBranch	01595000	189.6	0.02	AP	Forest
Neabsco	01657859	40.6	54.1	PD	Developed
Occoquan	01657700	1538.3	19.0	TR	Mixed
Opequon1	01615000	150.6	11.2	GVNC	Mixed
Opequon2	01616258	346.9	19.9	GVC	Mixed
Opequon3	01616500	704.6	10.3	GVC	Agriculture
Pipe1	01640000	20.4	59.5	PD	Developed
Pipe2	01640150	104.3	28.6	PD	Agriculture
Pohick	01655400	82.7	0.0	PD	Developed
Potomac1	01610000	8060.6	1.7	VR	Forest
Potomac2	01644148	28,816.8	3.6	VR	Forest
Quail	01629070	9.8	28.1	GVNC	Forest
Rock	01638890	60.9	16.7	TR	Agriculture
RockySpring	395830077420701	40.4	1.3	GVNC	Forest
Seneca1	01644600	139.3	47.0	PD	Developed
Seneca2	01645080	332.6	22.3	PD	Mixed
Tobacco	383138076593701	1.6	73.9	CP	Developed
White	01638900	32.0	9.2	TR	Agriculture

ultraviolet light absorbance at 254 nm were filtered in the field through 0.45 μm capsule filters, collected in pre-cleaned 125 mL (dissolved organic carbon) and two 40 mL (excitation-emission matrix spectra) amber-glass vials filled to the shoulder, and stored at 4 °C.

The chemical concentrations of 183 pesticides (including metabolites and transformation products) were assessed (Gross et al., 2024; Miller et al., 2024). Prior to analysis, samples for pesticide analysis were filtered in the lab (0.7 μm glass fiber filters) and analyzed via solid-phase extraction and liquid chromatography-tandem mass spectrometry using an electrospray ionization source in positive and negative modes and analyzed by gas chromatography-tandem mass spectrometry using an advanced electron ionization source in positive mode at the USGS Organic Chemistry Research Laboratory in Sacramento, Calif. (Gross et al., 2024). Instrument parameters were optimized for the highest sensitivity, and at least two transitions were monitored for each analyte. Method detection limits ranged from 0.5 to 10.6 ng L^{-1} and reporting limits ranged from 1.1 to 21.1 ng L^{-1} (Table A.1). Surrogate recoveries for eight mass-labeled pesticides were evaluated for each sample and were within the acceptable range of 73–123 % (median = 92 %) (Table A.2). There was good agreement between quality-assurance replicate samples (Table A.3) and regular samples with relative percent differences <5.7 % (median = 1.6 %), and blank samples had no detected pesticide concentrations, indicating no contamination from sampling equipment, the field environment, or laboratory handling (Miller et al., 2024). Three pesticide matrix spike quality assurance samples also had acceptable recoveries (median = 86 %, range = 70–119 %) (Table A.3). These quality assurance results confirmed that the pesticide samples were properly collected, handled, processed, and maintained at all stages.

In addition to pesticides, samples were analyzed for fluorescence excitation-emission matrix spectra (EEMs), pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), consumer product chemicals, major elements/ions, and trace elements (Miller et al., 2024). Optical characterization was performed at the USGS's Organic Matter Research Laboratory (OMRL) in Sacramento, Calif. Simultaneous absorbance, transmission, and fluorescence EEMs spectra were measured according to a previously published method (Hansen et al., 2018) that was modified for the newer Horiba Scientific (Irvine, California) Aqualog® 800 instrument. Blank samples analyzed for optical characterization indicated no contamination from sampling or laboratory equipment (Miller et al., 2024). Replicate samples had acceptable agreement with relative percent differences <9.6 % (median = 0.3 %) confirming that samples collected for optical characterization were properly collected, handled, processed, and maintained at all stages (Miller et al., 2024). Fluorescence spectroscopy data have been used in other studies to compare to pesticide MECs, validate WWTP locations, and characterize wastewater quality (Booth et al., 2023; Corsi et al., 2021).

2.3. Wastewater modeling

Accumulated wastewater (ACCWW, as a percent of total streamflow) and PECs (ng L^{-1}) were calculated for each non-tidal NHDPlus V2 (U.S. Environmental Protection Agency, 2012) stream segment in the PRW. Analyses were conducted using the open-source Python (Python Software Foundation, 2023) and R (R Core Team, 2024) scripting languages following methods described by Faunce et al. (2023). The wastewater discharge input dataset was obtained using the R package 'echoR' (Schramm, 2023) and consisted of WWTP effluent discharges for National Pollutant Discharge Elimination System (NPDES)-permitted sewerage system facilities (Standard Industrial Classification [SIC] code of 4952) discharging to surface-water bodies (Miller et al., 2024; Table A.4). Locations for each permitted outfall were obtained from the literature (Williams et al., 2021).

Effluent discharges are the median monthly average effluent discharge rates for each permitted facility obtained from discharge monitoring reports (DMRs) from August 2021 to September 2022 to align with the sampling period. This analysis of the results uses a smaller number of WWTP facilities compared to the analysis by Faunce et al. (2023), reflecting differences in dataset compilation. The dataset used in the present analysis and PEC calculations represents data compiled during the sampling period, uses DMRs rather than the Chesapeake Bay Model Phase 6 (Chesapeake Bay Program, 2020) to obtain effluent flows, and includes only NPDES permits with an assigned SIC code of 4952 for PEC calculations. These changes were made to align the effluent discharges with the water-quality sampling period and reduce uncertainties in the dataset but does exclude several smaller facilities in the PWR that are not required to submit DMRs but are also considered potential sources of pesticides. Because WWTP data are catalogued from a variety of systems and sources (including self-reporting), discrepancies and uncertainties are inherent in the data (https://echo.epa.gov/resources/echo-data/known-data-problems).

Mean-monthly and mean-annual streamflow for each NHDPlus V2 stream segment were obtained from the gage-adjusted Enhanced Runoff Method (EROM; U.S. Environmental Protection Agency, 2012). The monthly and annual ACCWW for each NHDPlus V2 stream segment was calculated as the percentage of accumulated wastewater to total streamflow:

$$\mathrm{ACCWW} = \left[\left(\frac{\Sigma\,\text{upstream and incoming WWTP discharge}}{\text{EROM streamflow} + \Sigma\,\text{upstream WWTP discharge}}\right)\right] \times 100.$$

Concentrations from literature-derived WWTP effluent data were used to estimate pesticide effluent loads for 14 'target' pesticides representing compounds with detection frequencies ≥50 % from PRW samples collected in this study and had loading input data from multiple studies to calculate PECs (Tables A.5 & A.6). Studies were included in the compiled input dataset if treated effluent concentrations were provided for each sample along with the sampling date and detection limit which led to the exclusion of studies that only reported summary statistics of effluent concentrations. In addition, we compiled data from the USGS National Water Information System (NWIS; U.S. Geological Survey, 2024) from wastewater facility outfalls (Site Type Code FA-OF). We constrained all compiled data to samples collected from 2013 to 2023 to represent current use pesticides. Many studies only reported effluent concentrations; therefore, to include as many pesticide PECs as possible, treatment techniques were assumed to be representative of the WWTP treatment techniques within the PRW. Following these assumptions, pesticide loads (ng d^{-1}) were modeled from each WWTP using:

$$\mathrm{WWTP}_{Load} = (Q_{WWTP} \times C_{Median})$$

where Q_{WWTP} represents the median effluent discharge from each WWTP reported from DMRs (L d^{-1}) and C_{Median} represents the median WWTP effluent pesticide concentration (ng L^{-1}) obtained from the literature and adjusted for non-detected values using the Kaplan-Meier method (Lee, 2020). In addition to modeling PECs using C_{Median}, PECs were also modeled using the 5th and 95th percentile, adjusted for non-detected values, to represent a range of scenarios where WWTP effluent may have relatively lower or higher pesticide concentrations. Mean-monthly and mean-annual PECs (ng L^{-1}) were estimated for each NHDPlus V2 stream segment:

$$\mathrm{PEC} = \frac{\mathrm{WWTP}_{Load}}{Q_{Stream} + Q_{WWTP}}$$

where Q_{Stream} represents the EROM streamflow (L d^{-1}) for each NHDPlus V2 stream segment. In-stream attenuation beyond dilution was not considered because many of the target pesticides lack comprehensive studies that analyze other forms of in-stream attenuation.

2.4. Stream water pesticide characterization

Pesticide MECs were compared to field parameters, fluorescence

spectroscopy data, and spatial watershed variables using Spearman's rank correlation coefficient (ρ) and principal component analysis (PCA; R Core Team, 2024) to identify potential pesticide sources beyond wastewater. Statistically significant correlations were determined when $p \leq 0.05$ unless otherwise noted. In addition, pesticide MECs greater than the method reporting limit were summed overall ($\sum$ pesticide) and by class ($\sum$ fungicide, $\sum$ herbicide, $\sum$ insecticide) to determine the total concentration, and the number of detections for each class at each site.

Fluorescence spectroscopy data were used to discriminate sources of stream water based on dissolved organic matter characteristics using PCA with the R function *prcomp* from the 'stats' package (R Core Team, 2024). Data were normalized by subtracting the mean of each variable from the observed value and dividing by the standard deviation. Concentrations below the detection limit were replaced with values half of the detection limit (Olsen et al., 2012). Fluorescence ratios and absorption slopes were calculated from the optical spectra to remove concentration effects on collinearity (Miller et al., 2024). Regions of fluorescence associated with natural organic matter and anthropogenic components, such as optical brighteners and refined hydrocarbons, were assessed as indicators of water sources. In total, 14 fluorescence ratios related to the properties of various organic substances were included for source discrimination (Hansen et al., 2018; Miller et al., 2024). The various indicator ratios were merged with upstream land-use, August ACCWW, and pesticide concentrations. Initially, all indicator ratios were included in the PCA, but ratios that contributed the least to explaining the variability in the principal components were subsequently removed to avoid variables that were prone to multicollinearity and overfitting the model (Sergeant et al., 2016).

Pesticide PECs (both individual and grouped by class) and MECs were compared using ρ to evaluate model agreement excluding non-detected MECs from analysis. Wastewater from treated sewerage effluent represents only one pathway of pesticide loading to rivers; therefore, sources other than sewerage WWTPs were inferred by: (1) dividing individual pesticide and class PECs by MECs to determine the proportion of the MEC contributed from WWTPs, and (2) subtracting PECs from MECs ('corrected MECs'), which were then compared to spatial watershed variables and agricultural pesticide use data (Wieben, 2021).

Pesticide MECs were compared to the U.S. Environmental Protection Agency's Aquatic Life Benchmarks (U.S. Environmental Protection Agency, 2024) for chronic and acute toxicity to freshwater vertebrates and invertebrates to determine the potential effects on the aquatic organisms living in the sampled stream water. Toxicity quotients were calculated by dividing the MECs by the chronic and acute benchmarks for freshwater vertebrates and invertebrates.

3. Results and discussion

3.1. Accumulated wastewater and target pesticide inputs

The WWTP dataset used to derive PECs included 228 permitted features from 212 sewerage WWTPs actively discharging a total of 748 million L d^{-1} to non-tidal PRW stream segments (Miller et al., 2024; Fig. A.2; Table A.4). Fourteen percent, or 2151 of the 14,885 non-tidal PRW stream segments received direct or accumulated effluent from sewerage WWTPs (Fig. A.2). The percentage of accumulated wastewater is presented for mean-August conditions, which are representative of when the samples were collected and when streamflow typically is lowest and has the greatest ACCWW due to reduced dilution. The total flow volume and percentage of ACCWW data are available for all months and annually (Miller et al., 2024; Table A.7). Among the 32 study watersheds, mean-August ACCWW ranged from 0 % (Abram, BigRocky, CaptHickory, Mill, Pohick) to 74 % (Tobacco), with a median of 10 % (Fig. 1; Table 1).

Twelve WWTP effluent datasets with pesticide input loading data were compiled from the literature, representing 14 analytes from 236 samples from 128 WWTPs (for a total of 1965 data points) spanning a range of locations and sampling dates (Table A.5). Pesticides with greater detection frequencies and ample literature on WWTP effluent concentrations were identified as targets for PEC modeling. The target compounds selected for detailed assessment consisted of 5 fungicides (azoxystrobin, carbendazim, propiconazole, tebuconazole, and thiabendazole), 5 herbicides (atrazine, diuron, metolachlor, prometon, and simazine), and 4 insecticides (clothianidin, dinotefuran, fipronil, and imidacloprid) (Fig. 2).

Effluent concentrations spanned several orders of magnitude for most target pesticides and may be influenced by many factors including the pesticide use patterns and regulations for a specific location, unique wastewater treatment processes, seasonal application patterns, different analytical methods, and industrial activities. However, for most target pesticides we did not observe large differences between the ranges of concentrations reported from WWTPs in the United States compared to Europe. By including as many samples as possible, the median value represented in the PEC model helps reduce some of variability in reported WWTP effluent pesticide concentrations. In addition, PECs modeled using lower (5th percentile) and higher (95th percentile) concentrations from the compiled dataset represent a broader range of possible concentrations discharged from WWTPs.

The number of samples analyzed for a given target pesticide ranged from 16 (dinotefuran) to 213 (imidacloprid), with a median of 162 (Table A.6). Detection frequencies among the target pesticides ranged from 32 % (clothianidin) to 100 % (dinotefuran), with a median of 64 % (Fig. 2). Median detected WWTP effluent concentrations among the target pesticides ranged from 3.5 ng L^{-1} (metolachlor) to 28.9 ng L^{-1} (diuron), with a median of 10.0 ng L^{-1}. Detection frequencies among all fungicides (70 %) were slightly greater than herbicides (63 %) or insecticides (61 %). The median concentration among detected insecticides in WWTP effluent (15.0 ng L^{-1}) was slightly greater than herbicides (12.0 ng L^{-1}) or fungicides (11.3 ng L^{-1}). However, target pesticide concentrations assigned to WWTP effluent used during PEC modeling incorporated non-detected results using the Kaplan-Meier method and ranged from 0.77 ng L^{-1} (clothianidin) to 22.80 ng L^{-1} (diuron) (Table A.6).

3.2. Sample pesticide exposure and characterization

Forty-nine of the 183 pesticides and transformation products (27 %;

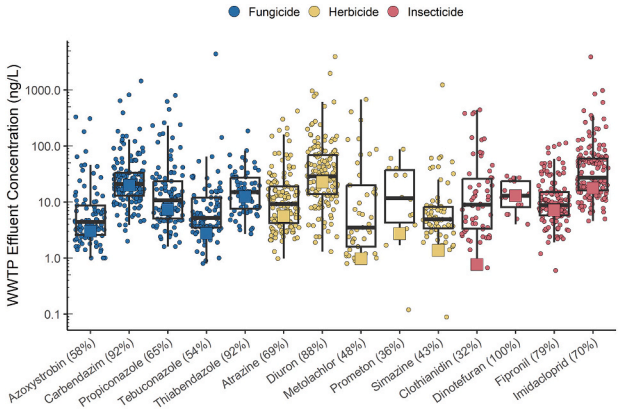

Fig. 2. WWTP effluent pesticide concentrations used for model input parameters (Berens et al., 2021; Brunelle et al., 2024; Finckh et al., 2022; Guardian et al., 2021; Munz et al., 2017; Overdahl et al., 2021; Pandey et al., 2023; Sadaria et al., 2016, 2017; U.S. Geological Survey, 2024; Vatovec et al., 2016; Webb et al., 2021). Number in parentheses refers to the detection frequency, censored data are omitted from this figure. [Data sources and summaries are presented in Tables A.5 and A.6; large squares denote the input parameter concentration used for the PEC model which incorporates non-detected values.]

referred to collectively as pesticides) measured were detected in at least one stream sample (Miller et al., 2024; Fig. 3; Table A.2). Of these, 16 were fungicides, 16 were herbicides, and 17 were insecticides. The 14 target pesticides used for ACCWW modeling in this study were often detected at greater concentrations and frequencies compared to the other detected pesticides (Fig. 3).

Principal component analysis revealed several groupings of the pesticide data (Fig. 4). Principal component one represented 34.49 % of the variability and described a gradient from less to more urban developed, with herbicides occurring toward the rural end of the gradient and insecticides occurring toward the urban end. Principal component two represented 20.6 % of the variation and was dominated by optical indicators drawing a gradient from relatively simple and labile organic matter associated with wastewater effluent and herbaceous vegetation to more complex, recalcitrant organic matter structures associated with hydrocarbons and humic acids. Combined, these components separated pesticides associated with developed areas not strongly associated with sewerage wastewater effluent (azoxystrobin, diuron, imidacloprid, propiconazole, tebuconazole), a suite of pesticides associated with sewerage wastewater effluent (carbendazim, dinotefuran, fipronil, prometon, and thiabendazole), and the herbicides occurring in the agricultural landscape (atrazine, metolachlor, and simazine).

The fluorescence ratio that was most closely related to the developed PCA signal was the ratio of refined fuels (RF): fluorescent dissolved organic matter (fDOM) in which higher values indicate more anthropogenic hydrocarbon fluorescence relative to fulvic DOM. The sum of all measured *per-* and polyfluoroalkyl substances (PFAS) and perfluoropentanoic acid (PFPeA) also plotted in this region of the PCA which may indicate sources from developed areas. Wastewater-derived pesticides inferred from the PCA were supported by multiple lines of evidence that infer greater wastewater contribution including the ratio of optical brightener (OBc): fDOM, fluorescence index (FI), the sum of pharmaceuticals (Pharm), gadolinium, boron, and Aug ACCWW. A higher FI is indicative of greater relative contribution of microbial versus plant-derived organic matter to the DOM pool (McKnight et al., 2001). Forest and agricultural study watersheds plotted in the lower left PCA quadrant and indicated relations with common agricultural herbicides (atrazine, metolachlor, and simazine); however, shorter arrows in Fig. 4 indicated lower contribution to the variability in the dataset which may be confounded by similar usage rates across different land uses in the PRW and less distinct sources. Agricultural study watersheds tended to be associated with a greater F:C fluorescence ratio which is indicative of more reduced humic DOM structures compared to oxidized forms, whereas forested watersheds had greater D:C ratios which indicates more terrestrial soil fulvic DOM relative to background humic DOM (Lochmueller and Saavedra, 1986; Miller et al., 2009).

Fluorescence data indicated that specific regions of the EEMs spectra were strongly related to certain pesticides (Figs. 5 and A.3). For example, carbendazim, fipronil, thiabendazole, dinotefuran, and 3,4-dichloroanaline concentrations showed significant positive relations with fluorescence intensities in the refined fuels and tryptophan-like (Flr_T) fluorescence regions. When aggregated by class, fungicide and insecticide fluorescence intensities were significantly positively related to the refined fuels and optical brightener regions, but similar patterns

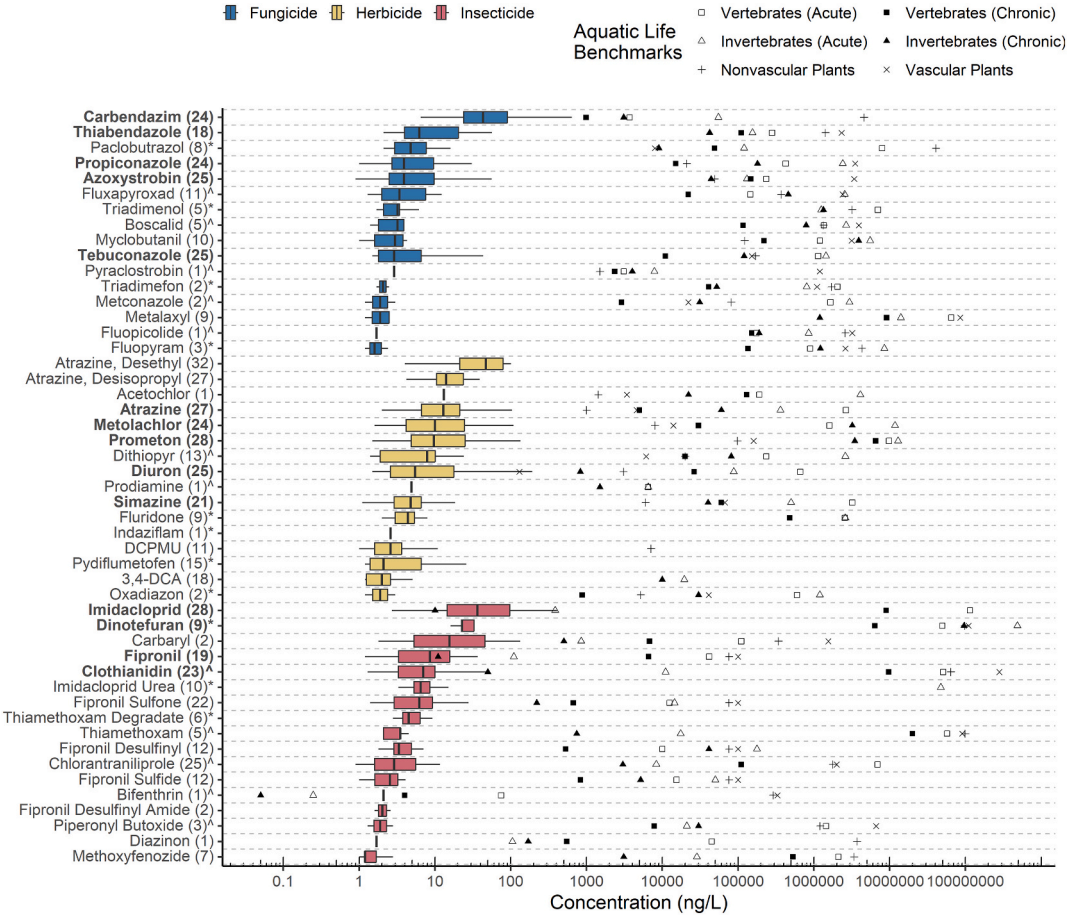

Fig. 3. Sample pesticide concentrations, colored by class, with the number of detections in parentheses (Miller et al., 2024). Diamond and plus symbols show the U.S. Environmental Protection Agency aquatic life chronic benchmark concentrations for freshwater invertebrates and vertebrates, respectively (U.S. Environmental Protection Agency, 2024). Bold values indicate target pesticides. Symbols * and ^ next to pesticide names indicate pesticides previously undetected or detected fewer than 10 times in Potomac River watershed samples and reported to the National Water Information System (NWIS; U.S. Geological Survey, 2024).

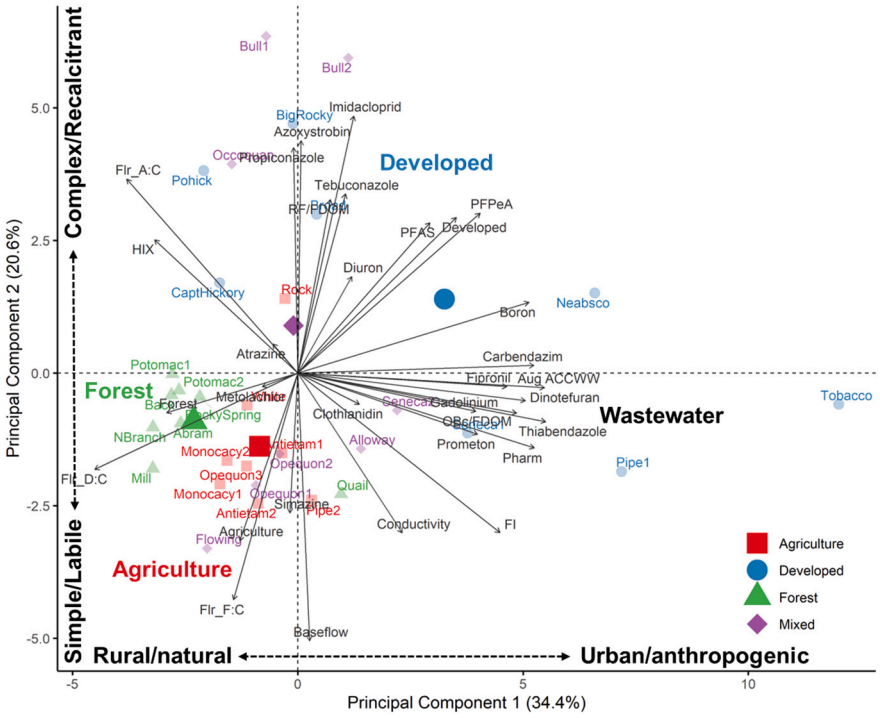

Fig. 4. Principal component analysis using target pesticide measured environmental concentrations (Table A.2), dissolved organic matter properties, landscape characteristics, and ancillary water-quality data (Table A.8).

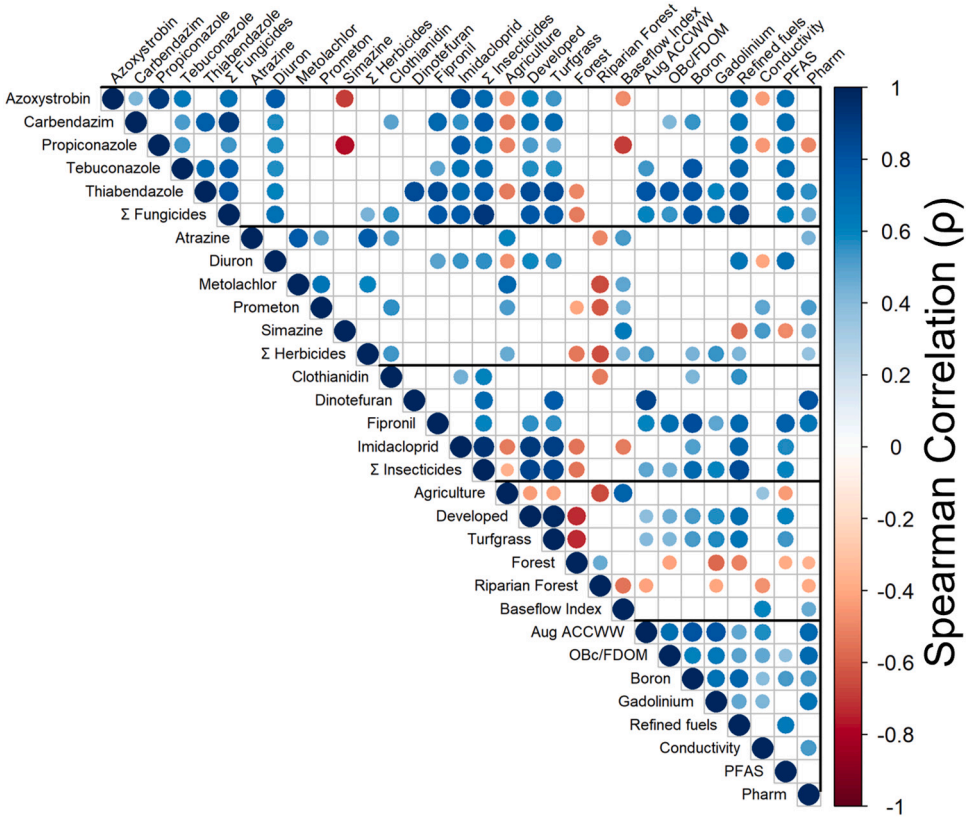

Fig. 5. Spearman correlation matrix between target pesticide MECs (Azoxystrobin-∑ Insecticides) and select landscape variables (Agriculture – Baseflow Index), and wastewater fluorescence indicators and ancillary water quality data (Aug ACCWW – Pharm) denoted by color and circle size. Only significant relations are shown ($p < 0.05$). Data are provided in Table A.8 and Miller et al. (2024).

were not evident for herbicides (Figs. 5 and A.3). These two fluorescence regions are indicative of greater population densities and developed land use (Beisner et al., 2024) and support other lines of evidence that imply sources for target fungicides and insecticides are associated with urban stormwater runoff and wastewater discharge from developed areas (Kahle et al., 2008; Masoner et al., 2019; Stehle et al., 2019).

All target fungicides, diuron, fipronil, and imidacloprid were significantly positively correlated with the total PFAS measured (Fig. 5). The co-occurring presence of these chemicals in stream water could present challenges for both human and aquatic health. Recent studies have detected PFAS directly in insecticide formulations (Lasee et al., 2022) and from rinsate leached from fluorinated high density polyethylene containers that were used to store pesticides (Nguyen, 2022, 2021; Whitehead and Peaslee, 2023), therefore pesticide applications may be a source of PFAS to the environment. In addition, ten of the detected pesticides in this study (bifenthrin, dithiopyr, fipronil, fipronil desulfinyl, fipronil desulfinyl amide, fipronil sulfide, fipronil sulfone, fluopicolide, fluridone, prodiamine) have chemical structures with at least one fully fluorinated carbon atom which would classify these pesticides as PFAS under the PFAS Action Act of 2019 (116th Congress, 2020; Hammel et al., 2022).

Of the 14 target pesticides, only atrazine, fipronil, metolachlor, prometon, and simazine have routinely been sampled and detected within the PRW prior to 2010 (Fig. A.4) based on data from the USGS (U.S. Geological Survey, 2024). A review of 506 surface-water samples collected from 1972 to 1990 (Zappia and Fisher, 1997) found only 13 pesticide detections (of 49 analyzed) across 138 sites, whereas this study detected 49 pesticides (of 183 analyzed) across 32 samples and sites. Of the 13 detected pesticides in Zappia and Fisher (1997), only the herbicides atrazine, prometon, and simazine were detected in the present study. However, 11 of the pesticides detected in the present study represent the first time they have been reported by the USGS from PRW stream water, and 12 other pesticides had been reported <10 times (Fig. 3).

3.3. Predicted and measured data comparisons

Comparisons between MECs and PECs are presented for August

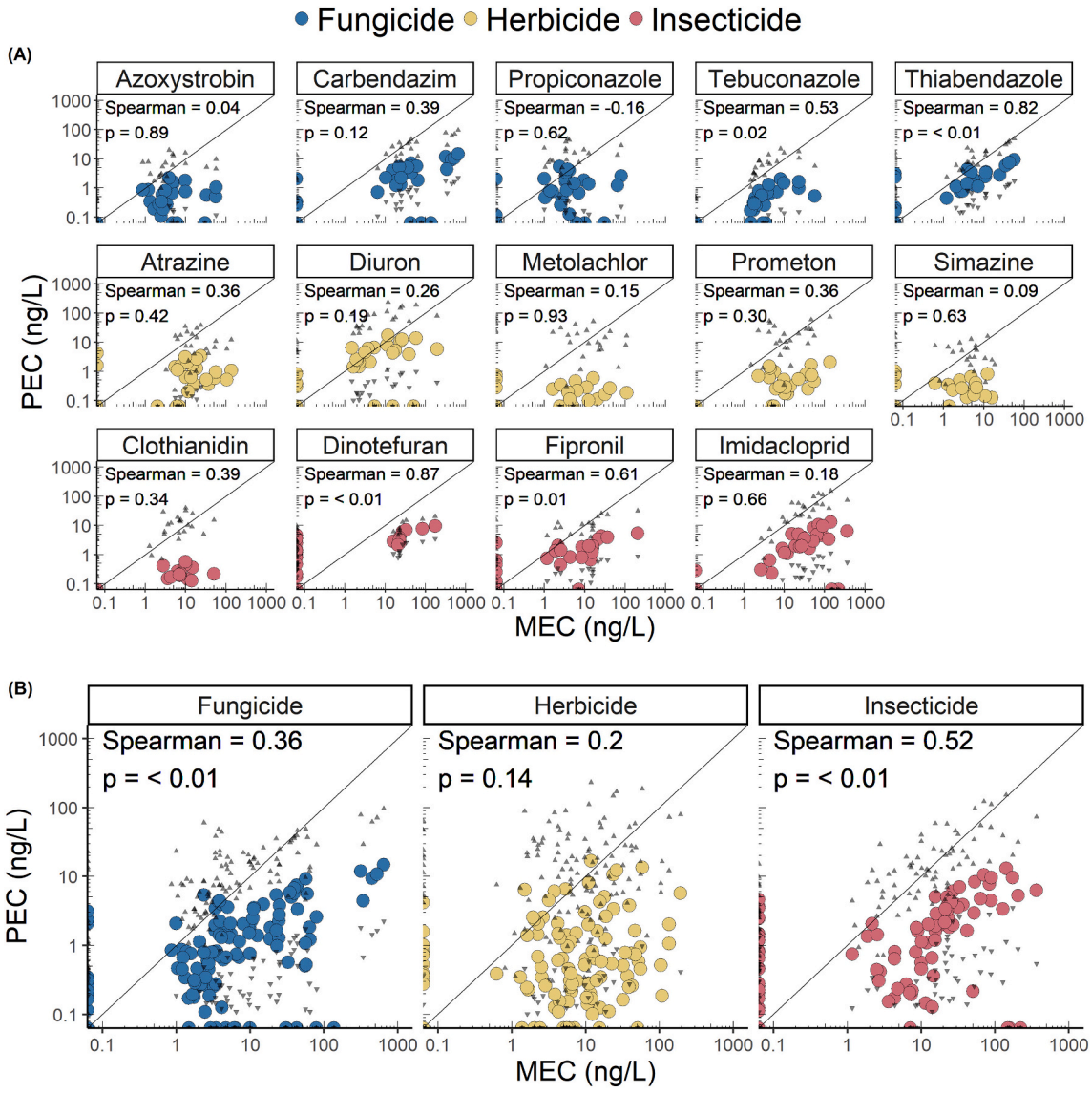

Fig. 6. Comparison between predicted (PEC) and measured environmental concentrations (MEC) for the modeled target pesticides. Spearman correlation coefficient between PECs and MECs and associated *p*-values indicated for each individual pesticide and grouped pesticide classes. Colored symbols represent PECs modeled with the median of effluent concentrations from compiled literature whereas the small black triangles that point up and down (▼, ▲) depict PECs modeled with the 5th and 95th percentile of compiled effluent concentrations, respectively. PECs below 0.1 ng L^{-1} not shown.

conditions to align with the period of sample collection, but PECs for all months and mean-annual conditions are available in Table A.9 and Miller et al. (2024). Among the target pesticides, PECs generally had the best agreement with MECs (Fig. 6) for insecticides ($\rho = 0.52$, $p < 0.01$), followed by fungicides ($\rho = 0.36$, $p < 0.01$) and herbicides ($\rho = 0.20$, $p = 0.14$). Individual pesticides with significant correlations between PECs and MECs included dinotefuran ($\rho = 0.87$, $p < 0.01$), thiabendazole ($\rho = 0.82$, $p < 0.01$), fipronil ($\rho = 0.61$, $p < 0.01$), and tebuconazole ($\rho = 0.53$, $p = 0.02$). Significant correlations were found between these individual pesticide concentrations and water quality indicators of wastewater presence including the optical brightener-to-fluorescein ratio, and boron concentrations, confirming that WWTP effluent likely is a source for these pesticides (Fig. 5).

Pesticides that plot on the x-axis in Fig. 6 occurred in watersheds without upstream WWTPs, indicating loading sources other than sewage effluent may be present. These detected pesticides were commonly collected in three highly developed watersheds with no upstream sewerage WWTP discharge: BigRocky, CaptHickory, and Pohick. In contrast, non-detected MECs with PECs >0 that plot on the y-axis in Fig. 6 indicate in-stream attenuation processes may be occurring that were not accounted for, pesticides may be present but below detection limits (Table A.1), or that they may not be continuously discharged from upstream sewerage WWTPs. For example, detection frequencies in the literature-derived input dataset ranged from 32 % (clothianidin) to 100 % (dinotefuran), indicating not all sewerage WWTPs are continuous sources of pesticides to stream water or that WWTP-derived sources could vary seasonally. The colored circles in Fig. 6, representing median effluent concentrations from the compiled effluent dataset modeled for each WWTP in the study area, generally plot below the one-to-one line which indicates other sources of pesticides beyond WWTP effluent may be important. However, there may be substantial variability in the effluent pesticide concentrations among the 212 modeled WWTPs which are represented with the small black triangles in Fig. 6 to depict the possible range of PECs using the 5th and 95th percentiles of compiled literature effluent concentrations.

Median target pesticide PECs that accounted for the greatest percentage of MECs, indicating greater relative loading from WWTPs, included diuron (50 %), thiabendazole (30 %), propiconazole (23 %), fipronil (16 %), dinotefuran (15 %), tebuconazole (14 %), and azoxystrobin (13 %) (Fig. A.5). These pesticides were also generally detected at relatively higher frequencies compared to other target pesticides in the compiled input WWTP effluent dataset (Table A.5; Fig. 2). Median target pesticide PECs that contributed to the lowest percentage of MECs, indicating greater relative loading from non-WWTP sources, included metolachlor (0.6 %), prometon (2 %), clothianidin (2 %), simazine (3 %), atrazine (5 %), carbendazim (7 %), and imidacloprid (8 %) (Fig. A.5). These calculated percentages were much smaller (0.006 % - 6 %) or larger (20 % - 692 %) if PECs were modeled using the 5th or 95th percentile of compiled effluent concentration data, respectively (Fig. A.5). The median PEC contribution to MEC summarized by class, was greatest for fungicides (14 %), followed by insecticides (12 %) and herbicides (3.5 %).

Diuron was present in 88 % of the input dataset WWTP effluent samples (Fig. 2) and accounted for a large proportion of pesticide loads measured in WWTP effluent (Kock-Schulmeyer et al., 2013; Nitschke and Schussler, 1998). In addition to agricultural applications, diuron has many non-agricultural uses including maintenance of roadsides, commercial areas, lawns, and gardens in developed areas, is commonly found in urban streams (U.S. Geological Survey, 1999), and has been determined to contribute to the largest share of potential toxicity to plants in urban streams (Nowell et al., 2021). The relatively high percentage of diuron detections from the compiled WWTP effluent literature may indicate that infiltration through broken or cracked pipes is a pathway in which groundwater containing pesticides could be transported to WWTPs (Giacomazzi and Cochet, 2004). Thiabendazole was detected in 92 % of the input dataset WWTP effluent samples (Fig. 2). Thiabendazole is a benzimidazole fungicide registered to control fungal diseases in a wide variety of food and non-food crops and is also used as a pharmaceutical product because of its anthelmintic properties to treat infections caused by certain parasitic worms (National Institute of Diabetes and Digestive and Kidney Diseases, 2012) which may explain the relatively high percentage of detections in WWTP effluent, and PECs attributed to MECs. Propiconazole and tebuconazole were detected in 65 % and 54 % of the input dataset WWTP effluent samples, respectively (Fig. 2). These two triazole fungicides are widely used in agriculture and used for several biocidal product types, including wood or coating preservatives (Toda et al., 2021; Woo et al., 2010). Previous analysis of propiconazole and tebuconazole concentrations in WWTP influent and effluent indicated that loads were largely unaffected by wastewater treatment and that loads tended to increase with wastewater throughput, indicating these fungicides may be leached from treated materials during rain events (Kahle et al., 2008). Fipronil was detected in 79 % of the input dataset WWTP effluent samples (Fig. 2). Fipronil is commonly used as a topical spot-on or spray product for flea and tick control or other urban pest control (Sutton et al., 2019), and has been found to be a substantial down-the-drain loading source (Budd et al., 2023; Sadaria et al., 2019; Teerlink et al., 2017). In North Carolina, fipronil concentrations were found to be substantially elevated near WWTP outfalls (McMahen et al., 2016).

3.4. Influence of land use on stream water pesticide concentrations in the Potomac River watershed

Stream water pesticide concentrations within the PRW are influenced by natural and human factors including climate, physiography, geology, hydrology, land use, population, water use, and wastewater discharges, as well as the chemical properties of the compounds (Ator et al., 1998). Numerous combinations of these factors exist throughout the PRW, yielding a complex environmental setting with different pesticide patterns. The existence of diverse loading sources within the PRW is supported by: (1) the detection of at least one pesticide at all 32 stations, including those in primarily forested watersheds or not impacted by upstream WWTP discharges, and (2) the detection of diverse pesticides across a broad range of pesticide classes (fungicides, $n = 16$; herbicides, $n = 16$; insecticides, $n = 17$).

3.4.1. Forest

Forested watersheds in this study generally had the lowest $\sum$ pesticide concentrations (Fig. A.6) and significantly fewer number of unique pesticide detections (Fig. A.7). These watersheds are primarily contained within the Appalachian Plateau and Valley and Ridge subunits located in the western part of the PRW. The larger forested watersheds (Back, Potomac1, and Potomac2) had 10–15 detections in which the agricultural herbicides (atrazine, metolachlor, prometon, and simazine) that have been used for decades were commonly detected as well as two more recent use insecticides (clothianidin and imidacloprid). The drainage area for the Potomac2 study watershed (28,817 km^2) accounts for over 90 % of the drainage area from all 32 study watersheds and drains 18 upstream study watersheds, thus integrating pesticide sources from different physiographic provinces and states that regulate pesticide products differently. The 15 pesticides detected at this station were among the most frequently detected pesticides across all study watersheds, (atrazine, desethyl atrazine, desisopropyl atrazine, azoxystrobin, carbendazim, chlorantraniliprole, clothianidin, imidacloprid, metolachlor, prometon, propiconazole, simazine, tebuconazole, thiabendazole, thiamethoxam degradate) indicating relatively uniform use across the PRW.

The smallest forested study watershed (Quail; 10 km^2), had much greater developed land use (29.0 %) and ACCWW (28.1 %) compared to the other forested study watersheds; the average developed land use and ACCWW for the remaining seven forested study were 7.0 % and 1.0 %, respectively. Despite the relatively low agricultural land use in Quail

(14 %), this watershed had the greatest total animal density (17,514 animal headcounts per square kilometer) among the study watersheds (Gordon et al., 2017), of which all were poultry operations. This site also had greater $\sum$ pesticide concentration compared to the other forested study watersheds including the highest concentration of clothianidin (50.1 ng L^{-1}) among all study watersheds, which was the only sample to exceed the chronic aquatic life benchmark for freshwater invertebrates (50 ng L^{-1}; U.S. Environmental Protection Agency, 2024). Although the largest agricultural use for clothianidin has been in the form of seed treatments, applications also are made to poultry litter manure for Tenebrionidae (Darkling beetles) and other poultry house pests (U.S. Environmental Protection Agency, 2020a).

Quail is a small rural watershed that drains a resort, and the golf course area percentage of the drainage area (7 %) was the greatest among the study watersheds. Many types of pesticides are applied on golf courses (Baris et al., 2010), including clothianidin (Larson et al., 2014), and PEC-corrected clothianidin concentrations normalized by agricultural input showed a significant correlation (Fig. A.8) with golf course area percentage among study locations ($\rho = 0.65$, $p < 0.01$) despite no significant relation between clothianidin MECs and golf course area ($\rho = 0.24$, $p = 0.26$). The Quail study watershed also had the highest concentrations for boscalid (22 ng L^{-1}), chlorantraniliprole (40 ng L^{-1}), and fluxapyroxad (12 ng L^{-1}), pesticides commonly used on turfgrass (Daniels and Latin, 2013; Larson et al., 2012; Ou and Latin, 2018). However, these concentrations were several orders of magnitude below aquatic life benchmarks (Table A.6). Turfgrass, agriculture, and WWTP discharge all may have contributed to the observed clothianidin concentration at Quail. There are 36 registered products containing clothianidin in Virginia (Virginia Department of Agriculture and Consumer Services, 2023; Table A.10), and combined with a lack of reported applications from non-agricultural areas obscures the ability to attribute the sources. However, the measured concentration exceeding the chronic aquatic life use benchmark for freshwater invertebrates may warrant further examination (U.S. Environmental Protection Agency, 2024). Riparian forest cover was found to be significantly negatively correlated with stream water clothianidin concentrations among the study watersheds, despite no significant relation with overall forest land cover (Fig. 5). Herbicide concentration reductions previously have been observed through riparian forest buffers (Lowrance et al., 1997), increasing riparian forest cover may also reduce in-stream concentrations of other pesticides.

3.4.2. Agriculture

The agricultural study watersheds were located within the Great Valley Carbonate, Great Valley Noncarbonate, Triassic Lowlands, and Piedmont subunits. August ACCWW in these watersheds was generally greater compared to forested watersheds, but less than developed watersheds and ranged from 6.2 % (Antietam2) to 29 % (Pipe2) with an average of 12 %. Similarly, the total pesticide concentrations in the agricultural study watersheds were generally in between those observed in the forested and developed watersheds, but median total herbicide concentration was the greatest among the four land uses, though not significantly different from developed or mixed-use study watersheds (Fig. A.6). The herbicides atrazine, metolachlor, prometon, and simazine were significantly positively correlated with agricultural land cover and baseflow index, the ratio of baseflow volume to total streamflow volume (Fig. 5; Hill et al., 2016), which may indicate an accumulation of these pesticides in groundwater following decades of use (Ator et al., 1998; Debrewer et al., 2008; Hainly and Kahn, 1996). Previous USGS research identified groundwater discharge to river baseflow as the principal source of herbicides in agricultural watersheds (Squillace et al., 1993). Atrazine, metolachlor, and prometon were significantly negatively correlated with riparian forest cover percentage despite no such significant relation with total forest cover percentage (Fig. 5).

During the mid-1990s, over 2.2 million kilograms of pesticide active ingredients, including about 1.3 million kilograms of herbicides, 0.5 million kilograms of insecticides and 0.4 million kilograms of fungicides, were applied to agricultural lands annually within the PRW, with almost half of the total mass being applied to cornfields (Ator et al., 1998). In 2017, the closest year with published available data to when samples were collected, an estimated 3.6 million kilograms of pesticides were applied to agricultural lands, of which about 30 % contained the target pesticides presented in this study (Wieben, 2021).

Only a few of the target pesticide corrected-MECs were significantly correlated with estimated agricultural inputs (atrazine, metolachlor, simazine, and clothianidin), indicating the dominant sources of other target pesticides in the study watersheds may not be from diffuse agricultural runoff (Fig. A.9). However, pesticide-specific seasonal occurrence patterns have been reported in the PRW caused by different application periods often resulting in highest occurrence probabilities during the spring and summer months (McClure et al., 2020; Smalling et al., 2021). Therefore, pesticide samples collected during different months may result in different occurrence patterns.

Samples in this study were collected in late summer to target low-flow periods when ACCWW was greatest. Target pesticide corrected-MECs that were significantly correlated with estimated agricultural use included atrazine ($\rho = 0.54$, $p < 0.01$), clothianidin ($\rho = 0.35$, $p = 0.05$), metolachlor ($\rho = 0.62$, $p < 0.01$), and simazine ($\rho = 0.70$, $p < 0.01$). There was no reported estimated use on agricultural land in the study watersheds for thiabendazole, prometon, and fipronil, thus they were omitted in Fig. A.9. The lack of agreement between corrected-MECs and estimated pesticide use on agricultural land for the remaining target pesticides indicates there may be sources beyond WWTP effluent and agriculture during stream base flow conditions. Pesticides are commonly used within the PRW for non-agricultural purposes, such as: (1) maintenance of lawns, gardens, and golf courses, (2) defoliation of rights-of-way, and (3) structural pest control (Ator et al., 1998). Pesticides have also been documented in both wet and dry atmospheric deposition near the PRW (Goel et al., 2010; Harman-Fetcho et al., 2000; Kuang et al., 2003). Pesticide usage rates are not well documented for these categories, which makes source identification difficult.

3.4.3. Developed

Developed study watersheds were in the Piedmont, Triassic Lowlands, or Coastal Plain subunits. Average August ACCWW was greatest among developed watersheds (33 %) and ranged from 0 % (BigRocky, CaptHickory, Pohick) to 74 % (Tobacco). Pesticide concentrations, especially fungicides and insecticides, typically were greater in these watersheds (Fig. A.6) but not necessarily related to the presence of wastewater (Fig. 4). Previous USGS studies have documented a positive relation between pesticide concentrations in low-flow stream water and the degree of urbanization in U.S. metropolitan areas (Sprague et al., 2007; Sprague and Nowell, 2008). In addition, pesticides frequently are detected in urban stormwater (Masoner et al., 2019).

Although the estimated use of individual pesticides for non-agricultural purposes is not well documented, the U.S. Fish and Wildlife Service estimated that homeowners use up to 10 times more chemical pesticides per acre on their lawns than farmers use on crops (U.S. Fish and Wildlife Service, 2000). The U.S. Environmental Protection Agency estimated in 2012 that more money was spent on insecticides used in home and gardens ($2,650,000,000) than in agriculture ($1,499,000,000) and industry ($700,000,000) combined, and overall, 27 million kilograms of pesticides were applied to home and garden areas (Atwood and Paisley-Jones, 2017). Measured biocide loads from urban watersheds were found to be similar to loads from agricultural watersheds in Switzerland (Wittmer et al., 2011). Homeowners frequently apply high rates of pesticides beyond the recommended doses that unintentionally leave residues that pose a variety of human and ecological health threats (Md Meftaul et al., 2020). Among the study watersheds, turfgrass percentage of drainage area was found to be significantly correlated with all target fungicides, insecticides, and diuron (Fig. 5).

Pesticide application in developed areas by homeowners and pest control professionals use a more diversified variety of pesticides to protect properties, maintain aesthetics, and minimize pest and disease threats compared to agricultural areas, which often target specific crops (Wittmer et al., 2010). The developed watersheds in this study generally had a greater number of unique detections compared to forested or agricultural watersheds (Fig. A.7). Although individual pesticides rarely exceeded chronic toxicity thresholds for aquatic life, except for imidacloprid and fipronil, pesticides almost always occur as mixtures in which the synergistic toxicological effects on human and aquatic life are largely unknown (Barber et al., 2022; Bradley et al., 2017; Hernandez et al., 2013).

3.4.4. *Mixed use*

Mixed use study watersheds contained roughly equal proportions of agriculture and developed land. Unlike the developed study watersheds that were primarily located in the Washington D.C. metropolitan area, the mixed-use sites spanned a greater geographic area within the PRW and included smaller municipalities. The $\sum$ pesticide concentration from these watersheds was generally greater compared to agricultural study watersheds and less than developed study watersheds (Fig. A.6). However, the number of unique pesticide detections from mixed use study watersheds was comparable to developed study watersheds (Fig. A.7). Average August ACCWW from these sites was 17 % and ranged from 0.02 % (Bull1) to 36 % (Bull2).

The large difference in ACCWW between the two sites on Bull Run (Bull1 and Bull2) is due to the discharge from the largest WWTP in the study area, which is one of the largest indirect potable water reuse sources in the world (Jeffrey et al., 2022). Previous effluent sampling at this WWTP and on locations upstream and downstream of the WWTP indicated neonicotinoid insecticide (clothianidin, dinotefuran, and imidacloprid) and triazine herbicide (atrazine, prometon, and simazine) loads in Bull Run were increased by the presence of the large WWTP (Flanery, 2020). However, the neonicotinoid load from the WWTP was

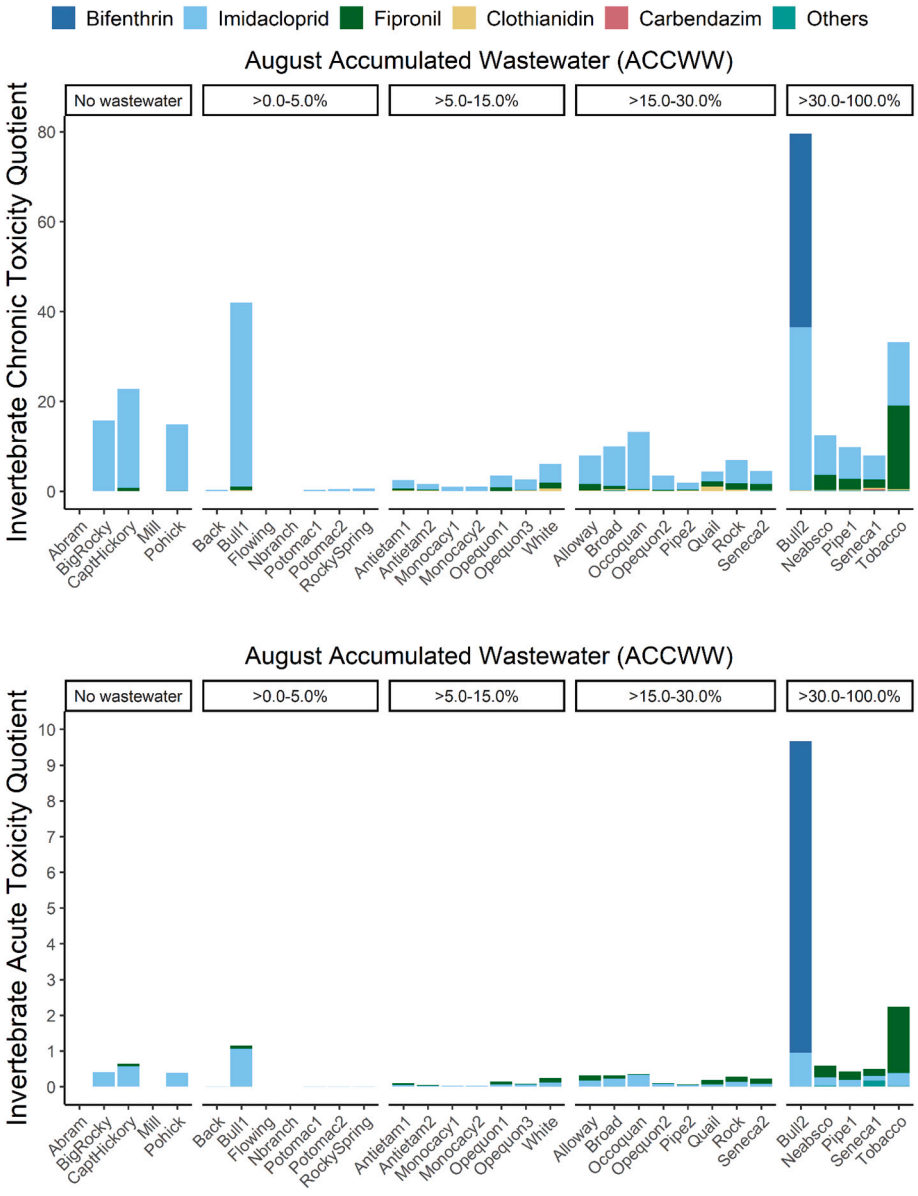

Fig. 7. Chronic (top) and acute (bottom) toxicity quotients for invertebrates at each of the study watersheds, located in the Potomac River watershed, grouped by August accumulated wastewater. Toxicity quotients were calculated by dividing the MECs by the chronic and acute benchmarks for freshwater invertebrates (U.S. Environmental Protection Agency, 2024). Others refer to the sum of remaining compounds. Refer to Fig. 1 for site locations. Sites are arranged in order of increasing August accumulated wastewater percentage.

lower than the measured upstream load on Bull Run, and the triazine loads from the WWTP effluent and upstream source were similar with atrazine having the largest relative loading from the WWTP. The largest downstream pesticide concentration increase between Bull1 and Bull2 in the present study data were atrazine (5.0 ng L^{-1} – Bull1; 11 ng L^{-1} – Bull2) and diuron (4.3 ng L^{-1} – Bull1; 11 ng L^{-1} – Bull2). However, there was also a modest downstream concentration increase of prometon between the two sites (3.7 ng L^{-1} – Bull1; 5.7 ng L^{-1} – Bull2) and simazine was not detected at Bull1 but was detected at Bull2 (2.5 ng L^{-1}). These concentration increases support evidence that WWTPs can be sources of triazines (Barber et al., 2022; Flanery, 2020). In contrast, concentrations of clothianidin (8.9 ng L^{-1} – Bull1; 6.3 ng L^{-1} – Bull2) and imidacloprid (410 ng L^{-1} – Bull1; 360 ng L^{-1} – Bull2) decreased downstream (dinotefuran was not detected at either site). Bull1 and Bull2 had the two highest imidacloprid concentrations among the study watersheds and were nearly twice as high as the third highest concentration. However, the measured imidacloprid concentrations at Bull1 and Bull2 were much greater than the maximum concentration measured in the WWTP effluent (42 ng L^{-1}, $n = 9$) by Flanery (2020), indicating there are other dominant sources of imidacloprid to Bull Run beyond WWTP effluent.

3.5. Aquatic ecotoxicity and management implications

Measured pesticide concentrations were generally several orders of magnitude below potential acute and chronic U.S. Environmental Protection Agency aquatic ecotoxicity benchmarks for freshwater vertebrates and invertebrates as well as benchmarks for nonvascular and vascular plants (U.S. Environmental Protection Agency, 2024), with some exceptions (Figs. 3 and 7). Chronic freshwater invertebrate aquatic life benchmarks were exceeded for: (1) the one detection of bifenthrin (site = Bull2; concentration = 2.2 ng L^{-1}; chronic benchmark = 0.5 ng L^{-1}); (2) 23 samples where imidacloprid was detected (range = 10.1–409.5 ng L^{-1}; chronic benchmark = 10 ng L^{-1}); 9 samples where fipronil was detected (range = 12.5–204.7 ng L^{-1}; chronic benchmark = 11 ng L^{-1}); and (3) one sample where clothianidin was detected (site = Quail; detected concentration = 50.1 ng L^{-1}; chronic benchmark = 50 ng L^{-1}). Acute freshwater invertebrate aquatic life benchmarks were exceeded for: (1) one sample where bifenthrin was detected (site = Bull2; acute benchmark = 75 ng L^{-1}); (2) one sample where imidacloprid was detected (site = Bull1; concentration = 410 ng L^{-1}; acute benchmark = 390 ng L^{-1}); and (3) one sample where fipronil was detected (site = Tobacco; concentration = 210 ng L^{-1}; acute benchmark = 110 ng L^{-1}). The remaining pesticide detections were generally several orders of magnitude below the acute and chronic benchmarks for freshwater invertebrates (Fig. 3); however, some concentrations of carbendazim and diuron were within one order of magnitude of the chronic benchmarks. Although none of the measured pesticide concentrations exceeded the acute or chronic aquatic life benchmarks for freshwater vertebrates, the one detection of bifenthrin was close to the benchmark (acute benchmark = 75 ng L^{-1}; chronic benchmark =4.0 ng L^{-1}) and some carbendazim concentrations were within an order of magnitude of the benchmark (range = 6.5–644.1 ng L^{-1}; acute benchmark = 3700 ng L^{-1}; chronic benchmark = 990 ng L^{-1}). One diuron detection exceeded the benchmark for vascular plants (site = Broad; concentration = 192.7 ng L^{-1}; vascular plants benchmark = 130 ng L^{-1}).

The presence of multiple different pesticides in stream water can have cumulative impacts on potential aquatic ecotoxicity (Bradley et al., 2019; Covert et al., 2020; Nowell et al., 2021, 2018; Schreiner et al., 2016) which were evaluated through toxicity quotients for aquatic invertebrates and vertebrates at chronic and acute thresholds (Figs. 7 & A.10). Twenty-three sites (72 %) had an invertebrate chronic toxicity quotient >1 indicating there is a potential for chronic toxicity, and three sites (Bull2, Tobacco, Bull1) had an invertebrate acute toxicity quotient >1. The greatest invertebrate chronic toxicity quotient occurred at Bull2, partially due to this site having the only bifenthrin detection in this study (Fig. 7). Bifenthrin is a hydrophobic pyrethroid insecticide that partitions to streambed sediments and has been shown to cause toxicity to non-target organisms (Hladik and Kuivila, 2012). Pyrethroid insecticides previously have been identified as a main driver of benchmark exceedances in both water and sediment in non-agricultural surface waters (Stehle et al., 2019). No sites had vertebrate chronic or acute toxicity quotients >1 (Fig. A.10).

Imidacloprid contributed most of the potential toxicity to freshwater invertebrates at all sites followed by fipronil (Fig. 7); a finding documented in other studies (Covert et al., 2020; Macaulay et al., 2021; Nowell et al., 2021, 2018). Potential toxicity was evaluated by comparing measured pesticide concentrations to published aquatic life benchmarks (U.S. Environmental Protection Agency, 2024) but recent mesocosm experiments determined that many stream taxa are sensitive to a lower concentration of fipronil and its degradates (Miller et al., 2020). In comparison, a previous study sampled 17 urban areas in the US (Nowell et al., 2018), where the median cumulative chronic toxicity quotient was greatest for Washington D.C. area sites, primarily because of observed imidacloprid and fipronil concentrations in stream water. Clothianidin, carbendazim, carbaryl, and diuron also contributed to invertebrate toxicity, but generally concentrations were below the aquatic life benchmarks (Nowell et al., 2018).

Sites with greater mean-August ACCWW generally had higher chronic toxicity quotients. However, four of the top six study watersheds in terms of total toxicity quotient were developed sites with little-to-no upstream WWTPs (BigRocky, Bull1, CaptHickory, Pohick). Surrounding these watersheds is a high density of septic systems (Webber et al., 2023) that are not incorporated in the modeling framework represented in this study. Septic system density has been shown to be positively correlated with elevated nitrate concentrations (Porter et al., 2020), indicating that leachate from septic systems could be hydrologically and chemically altering downstream receiving waters (Hyer et al., 2016). Septic systems are known sources of many contaminants associated with domestic use (Conn et al., 2006, 2010; Swartz et al., 2006).

There were no usage estimates for fipronil on agricultural lands in the PRW (Wieben, 2021), and imidacloprid-corrected MECs did not show a positive relation with agricultural use (Fig. A.9). Fipronil was found to be significantly positively related to August ACCWW ($\rho = 0.6$, p-value <0.01); however, the median PEC percentage of the MEC for fipronil (16 %) indicates other important sources. Imidacloprid was not significantly related to August ACCWW and some of the highest detected concentrations were found at developed sites with little-to-no sewerage wastewater discharge (BigRocky, Bull1, CaptHickory, Pohick). Although imidacloprid was detected at 28 of 32 sites, median concentrations among the developed (115 ng L^{-1}) and mixed-use watersheds (48 ng L^{-1}) were significantly greater compared to the agricultural (16 ng L^{-1}) or forested watersheds (4.3 ng L^{-1}) according to the Wilcoxon rank-sum test. Imidacloprid detections also have been found to be significantly positively related to developed land use in the Great Lakes region of the US (Hladik et al., 2018a) and across the entire US (Hladik and Kolpin, 2015). The median fipronil concentration among developed study watersheds (23.5 ng L^{-1}) was also greater compared to agricultural (4.4 ng L^{-1}), forested (12 ng L^{-1}), or mixed-use watersheds (8.4 ng L^{-1}), though not statistically different according to the Wilcoxon rank-sum test.

Among the target pesticides, imidacloprid and fipronil have a much greater number of registered pesticide products in the PRW, and the number of products ranged for each state (Virginia Department of Agriculture and Consumer Services, 2023). For example, there were 244, 379, and 330 registered pesticide products containing imidacloprid in Maryland, Pennsylvania, and Virginia, respectively (Table A.10). The large number of products containing these two pesticides makes it difficult to attribute the dominant sources to the observed stream water concentrations. Imidacloprid and fipronil are common active ingredients in many popular topical pet flea and tick treatments (Sutton et al., 2019) and previous studies have indicated these products may be the primary source for WWTP-derived loads through multiple pathways,

including bathing of treated pets, washing human hands after pet contact, and washing pet bedding (Budd et al., 2023; Sadaria et al., 2017). Imidacloprid and fipronil have been detected in pet hair and urine samples (Diepens et al., 2023), therefore it is possible that these products contribute to non-WWTP derived pesticide loads, such as wash-off during rain or swimming, and through urine and feces. However, pet ownership in Virginia, Maryland, and Washington D.C. is similar to or below the national average (AVMA, 2018). Therefore, pet ownership does not explain why Nowell et al. (2021) observed much greater concentrations of imidacloprid in the Washington D.C. area compared to other urban areas in the US, which indicates other possible dominant sources in the watersheds.

Imidacloprid also is commonly used in pest management to treat *Adelges tsugae* (hemlock woolly adelgid) (Benton et al., 2016; Crayton et al., 2020), *Agrilus planipennis* (emerald ash borer) (Kreutzweiser et al., 2007), and *Reticulitermes* (subterranean termites) in urban trees (Zorzenon and Campos, 2015). Treatment typically involves soil and/or trunk injection and/or drenching. Studies from nearby regions have shown positive relations between the amount of applied imidacloprid and stream water concentrations (Benton et al., 2016) and that chronic leaching of imidacloprid from treated hemlock stands has potential to negatively affect aquatic organisms and impact higher trophic levels (Crayton et al., 2020). The PRW is located within the current extent for both the hemlock woolly adelgid and the emerald ash borer, and eastern hemlock and ash trees are native to the Washington D.C. metropolitan area (MacFarlane and Meyer, 2005; National Park Service, 2020), which may possibly explain why Nowell et al. (2021) observed greater imidacloprid concentrations. Eastern hemlock and ash trees often grow along streams or riparian areas, therefore pest management for these species have the potential to affect non-target organisms.

Imidacloprid use in the US has increased in recent decades despite research that indicates pollinators (Hladik et al., 2018b; Krupke and Long, 2015; Tapparo et al., 2012), aquatic insects (Roessink et al., 2013; Van Dijk et al., 2013), and amphibians (Crayton et al., 2020; Sweeney et al., 2021) are susceptible to chronic sublethal effects which can be exacerbated by shorter hydroperiods (Thompson et al., 2022). Imidacloprid is a neonicotinoid insecticide which, as an insecticide class, provides both contact and residual control for a variety of sucking and piercing pests over an extended period and is comparatively less expensive and more effective than some alternatives (U.S. Environmental Protection Agency, 2020b). However, neonicotinoid pesticides present risks to freshwater invertebrates on a chronic basis (U.S. Environmental Protection Agency, 2020b) and commonly occur as mixtures in streams that have synergistic effects that pose greater than expected risks to stream health (Schmidt et al., 2022). All detections of clothianidin, dinotefuran, and thiamethoxam from our study co-occurred with imidacloprid detections and the majority of imidacloprid detections (24 of 28) co-occurred with other neonicotinoid detections. Neonicotinoids have been detected throughout the US in surface water, groundwater, drinking water, and food (Bradford et al., 2018; Bradley et al., 2023; Hladik and Kolpin, 2015; Klarich et al., 2017; Silvanima et al., 2022; Thompson et al., 2020), and the Centers for Disease Control estimates that half of the US population is exposed to neonicotinoids (Ospina et al., 2019). Imidacloprid has been detected in groundwater samples within our study watersheds at concentrations up to 197 ng L^{-1} (U.S. Geological Survey, 2024, site identification number 383944077184901). Imidacloprid accounted for the majority of insecticide concentrations in groundwater samples collected on Long Island, N.Y. where the highest concentrations (350–5320 ng L^{-1}) occurred near greenhouses and golf courses (Fisher et al., 2021). More studies are needed to fully assess the impact of neonicotinoids on human health (Cimino et al., 2016; Thompson et al., 2020).

The European Food Safety Authority determined there were high acute risks to honey bees from exposure via dust drift and residues (European Food Safety Authority, 2013) leading the European Commission to place a moratorium on the use of imidacloprid, thiamethoxam, and clothianidin (Rondeau et al., 2014). Imidacloprid use on agricultural lands in the US has risen exponentially in recent years (Wieben, 2021) where seed coatings are the primary delivery method despite uncertain crop-yield benefits (Hladik et al., 2018b; Mourtzinis et al., 2019). However, results from this study and others (Hladik et al., 2018a; Hladik and Kolpin, 2015; Weston et al., 2015) indicate greater imidacloprid concentrations among streams draining developed areas compared to agricultural areas, but non-agricultural pesticide use and sales information are poorly documented (U.S. Environmental Protection Agency, 2020b), which limits the ability to better understand dominant sources.

Recently, in efforts to protect environmental resources, including pollinators, New Jersey and New York have amended laws to classify certain imidacloprid products as 'restricted use,' which requires a pesticide-applicator license, requires sales and use data to be annually reported, and further prohibits certain non-agricultural use (State of New Jersey, 2020; State of New York, 2023; State of New York Assembly, 2023). Reductions in imidacloprid applications may reduce imidacloprid concentrations in streams draining non-agricultural areas within the PRW and assist local and state agencies in protecting environmental resources. For example, previous monitoring on ten urban streams in Ontario, Canada reported concentration declines of herbicides 2,4-D, dicamba, and mecoprop from 16 % to 92 % following a ban on the sale and use of pesticides for cosmetic (non-essential) purposes (Todd and Struger, 2014). Previous USGS research found rapid declines in diazinon and chlorpyrifos concentrations in urban streams in the northeastern and midwestern United States following a federally mandated phaseout for the use of these organophosphorus insecticides in outdoor urban settings (Denver and Ator, 2007; Phillips et al., 2007). However, reductions in groundwater pesticide concentrations following reductions in use may take several decades and has been previously shown to be influenced by the polarity of the parent compound and soil-specific retardation factors (Kim et al., 2022).

3.6. Limitations and future research

Water-quality samples were collected from 32 streams within the PRW during low-flow conditions to represent periods with the greatest effects from ACCWW and legacy pesticide sources. This study did not assess variability in results over time, which may be important at some sites based on local conditions. Pesticide-use patterns are often crop, pest, or region-specific and can change considerably over time as compounds are banned or replaced by others (Chow et al., 2020). For example, neonicotinoids have replaced many carbamate and organophosphate pesticides frequently detected between the 1970s and 1990s (Donnelly and Ferrari, 1998; Ferrari and Denis, 1999; Zappia and Fisher, 1997) and more recently replaced pyrethroid insecticides over benthic macroinvertebrate toxicity concerns.

Although samples were collected during low-flow conditions, numerous studies from developed areas indicate imidacloprid and fipronil generally follow a first-flush pattern, where maximum concentrations are observed during initial runoff from turf and concrete surfaces (Armbrust and Peeler, 2002; Batikian et al., 2019; Carpenter et al., 2016; Thuyet et al., 2012). This observation indicates that aquatic toxicity could be greater during storm events within the PRW. Neonicotinoids are highly water soluble and persistent and the half-lives can exceed 1000 days in soil; thus, repeated applications of imidacloprid can accumulate in soils (Bonmatin et al., 2015). Additional sampling across a range of seasons and streamflow conditions would help better elucidate potential ecotoxicological effects of pesticide use within the PRW.

The PEC estimates do not account for in-stream attenuation factors beyond dilution, which may be important for select pesticides examined in this study. In general, the PEC estimates may reflect the upper bound, because in-stream attenuation factors beyond dilution were not accounted for, advanced treatment at some PRW WWTPs may remove pesticides more effectively than the WWTPs compiled in the input

dataset, and detection frequencies observed in the compiled input dataset (Fig. 2) indicate that the target pesticides may not be detected in every PRW WWTP's effluent sample. The presence of pesticides in sewerage WWTP effluent may vary spatially and temporally, as many pesticide products are designed to target specific fungi, plants, and insects that may not be present throughout the entire PRW year-round. Although some of the studies compiled in the input dataset were from WWTPs within the PRW, others outside of the watershed may not accurately reflect pesticides that are routinely used within the watershed. Inclusion of these studies outside of the PRW, however, allows for an understanding of typical pesticide occurrence and concentration ranges in WWTP effluent. Modeled pesticide inputs from WWTP effluent were limited to sewerage systems (SIC code 4952); however, pesticides may also enter waterbodies through industrial discharge point sources, but pesticide concentrations from these types of effluent are poorly documented. There were no wastewater facilities in the study area with SIC codes that could be additional sources of pesticides, for example SIC code 2879 (Pesticides and Agricultural Chemicals, Not Elsewhere Classified), SIC code 5191 (Farm Supplies), or SIC code 5261 (Retail Nurseries, Lawn and Garden Supply Stores).

Source identification of pesticides is complicated by the lack of comprehensive monitoring data, changes in pesticide usage and analytical capabilities over time, and a lack of documentation required for non-agricultural applications and seed treatments. In addition, states within the PRW regulate pesticide products differently. For example, triadimenol was detected at five Virginia sites despite there being no registered products in the state containing this active ingredient, further complicating source identification (Virginia Department of Agriculture and Consumer Services, 2023). This fungicide is commonly used as seed treatment compounds therefore seeds may have been coated outside of Virginia which could explain their occurrence. Seed treatments can contain a wide variety of fungicidal, insecticidal, nematicidal, and growth-regulating active ingredients and have increased in major field crops over the last several decades (Hitaj et al., 2020). In 2008, neonicotinoid insecticides accounted for 80 % of the total insecticidal seed treatment market (Jeschke et al., 2011). However, publicly available pesticide use data on seed treatments are not currently available in the US making it difficult to assess the effects of pesticides on environmental health (Hitaj et al., 2020). Previous research has documented that <2 % of neonicotinoids used in seed treatment were translocated into plant tissues throughout the growing season (Alford and Krupke, 2017) and numerous studies have found widespread detections of neonicotinoids in streams or groundwater located in corn and soybean regions (Bradford et al., 2018; Chrétien et al., 2017; Hladik et al., 2014; Raby et al., 2022; Schaafsma et al., 2019).

4. Conclusions

Discharge of effluent from sewerage WWTPs, although treated and in compliance with existing regulations, can be a continuous source of organic contaminants, including pesticides, to rivers. Statistical agreement between measured and predicted pesticide concentrations was strongest for insecticides, followed by fungicides and herbicides. Although herbicides commonly used in agriculture were significantly correlated with agricultural land use and estimated pesticide use on agricultural lands, target fungicides and insecticides generally exhibited significant positive relations with developed land cover, including both indications of urban runoff and wastewater discharge. Multiple lines of evidence were used to distinguish pesticides that indicated relatively larger sources from WWTPs (dinotefuran, fipronil, carbendazim, thiabendazole, and prometon) from those more commonly associated with urban runoff (imidacloprid, azoxystrobin, propiconazole, tebuconazole, and diuron). Most of the detected pesticides were below acute and chronic U.S. Environmental Protection Agency aquatic ecotoxicity benchmarks for freshwater vertebrates and invertebrates (U.S. Environmental Protection Agency, 2024). However, fipronil and imidacloprid detections exceeded the chronic freshwater invertebrate aquatic life benchmark 47 %, and 82 % of the time, respectively. Chronic potential ecotoxicity was generally higher for sites with greater ACCWW and/or located in developed watersheds. Our model can be used as a screening-level assessment to identify stream segments within the Potomac River watershed that are susceptible to cumulative WWTP discharges and potential associated risks to aquatic life from contaminants of emerging concern, including contemporary pesticides. Results from this study could support development of management strategies to mitigate both current and historical impacts of pesticide use on aquatic ecosystems and public health.

CRediT authorship contribution statement

Samuel A. Miller: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kaycee E. Faunce:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Larry B. Barber:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Jacob A. Fleck:** Writing – review & editing, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Daniel W. Burns:** Writing – review & editing, Methodology, Data curation, Conceptualization. **Jeramy R. Jasmann:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Michelle L. Hladik:** Writing – review & editing, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data are available in the Supplementary Information.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174939.

References

116th Congress, 2020. H.R.535 - PFAS Action Act of 2019. https://www.congress.gov/bill/116th-congress/house-bill/535/text. (Accessed 1 July 2024).

Alford, A., Krupke, C.H., 2017. Translocation of the neonicotinoid seed treatment clothianidin in maize. PLoS One 12, e0173836. https://doi.org/10.1371/journal.pone.0173836.

Armbrust, K.L., Peeler, H.B., 2002. Effects of formulation on the run-off of imidacloprid from turf. Pest Manag. Sci. 58, 702–706. https://doi.org/10.1002/ps.518.
Ator, S.W., Blomquist, J.D., Brakebill, J.W., Denis, J.M., Ferrari, M.J., Miller, C.V., et al., 1998. Water quality in the Potomac River basin, Maryland, Pennsylvania, Virginia, West Virginia, and the District of Columbia, 1992–96. In: U.S. Geological Survey Circular 1166. https://doi.org/10.3133/cir1166. http://pubs.usgs.gov/publication/cir1166.
Atwood, D., Paisley-Jones, C., 2017. Pesticides industry sales and usage: 2008–2012 market estimates. https://www.epa.gov/sites/default/files/2017-01/documents/pesticides-industry-sales-usage-2016_0.pdf.
AVMA, 2018. AVMA Pet Ownership and Demographic Sourcebook. American Veterinary Medical Association (978-1-882691-53-1).
Barber, L.B., Rapp, J.L., Kandel, C., Keefe, S.H., Rice, J., Westerhoff, P., et al., 2019. Integrated assessment of wastewater reuse, exposure risk, and fish endocrine disruption in the Shenandoah River watershed. Environ. Sci. Technol. 53, 3429–3440. https://doi.org/10.1021/acs.est.8b05655.
Barber, L.B., Faunce, K.E., Bertolatus, D.W., Hladik, M.L., Jasmann, J.R., Keefe, S.H., et al., 2022. Watershed-scale risk to aquatic organisms from complex chemical mixtures in the Shenandoah River. Environ. Sci. Technol. 56, 845–861. https://doi.org/10.1021/acs.est.1c04045.
Baris, R.D., Cohen, S.Z., Barnes, N.L., Lam, J., Ma, Q., 2010. A quantitative analysis of over twenty years of golf course monitoring studies. Environ. Toxicol. Chem. 29, 1224–1236. https://doi.org/10.1002/etc.185.
Batikian, C.M., Lu, A., Watanabe, K., Pitt, J., Gersberg, R.M., 2019. Temporal pattern in levels of the neonicotinoid insecticide, imidacloprid, in an urban stream. Chemosphere 223, 83–90. https://doi.org/10.1016/j.chemosphere.2019.01.165.
Beisner, K.R., Travis, R.E., Alvarez, D.A., Barber, L.B., Fleck, J.A., Jasmann, J.R., 2024. Temporal variability and sources of PFAS in the Rio Grande, New Mexico through an arid urban area using multiple tracers and high-frequency sampling. Emerging Contaminants. 10, 100314. https://doi.org/10.1016/j.emcon.2024.100314.
Benton, E.P., Grant, J.F., Mueller, T.C., Webster, R.J., Nichols, R.J., 2016. Consequences of imidacloprid treatments for hemlock woolly adelgid on stream water quality in the southern Appalachians. For. Ecol. Manag. 360, 152–158. https://doi.org/10.1016/j.foreco.2015.10.028.
Berens, M.J., Capel, P.D., Arnold, W.A., 2021. Neonicotinoid insecticides in surface water, groundwater, and wastewater across land-use gradients and potential effects. Environ. Toxicol. Chem. 40, 1017–1033. https://doi.org/10.1002/etc.4959.
Blanchoud, H., Farrugia, F., Mouchel, J.M., 2004. Pesticide uses and transfers in urbanised catchments. Chemosphere 55, 905–913. https://doi.org/10.1016/j.chemosphere.2003.11.061.
Blomquist, J.D., Fisher, G.T., Denis, J.M., Brakebill, J.W., Werkheiser, W.H., 1996. Water-quality assessment of the Potomac River Basin: basin description and analysis of available nutrient data, 1970–90. In: U.S. Geological Survey Water-Resources Investigations Report 95-4221. https://doi.org/10.3133/wri954221. http://pubs.er.usgs.gov/publication/wri954221.
Bonmatin, J.M., Giorio, C., Girolami, V., Goulson, D., Kreutzweiser, D.P., Krupke, C., et al., 2015. Environmental fate and exposure; neonicotinoids and fipronil. Environ. Sci. Pollut. Res. 22, 35–67. https://doi.org/10.1007/s11356-014-3332-7.
Booth, A., Fleck, J., Pellerin, B.A., Hansen, A., Etheridge, A., Foster, G.M., et al., 2023. Field techniques for fluorescence measurements targeting dissolved organic matter, hydrocarbons, and wastewater in environmental waters: principles and guidelines for instrument selection, operation and maintenance, quality assurance, and data reporting. In: U.S. Geological Survey Techniques and Methods 1-D11. https://doi.org/10.3133/tm1D11. http://pubs.usgs.gov/publication/tm1D11.
Bradford, B.Z., Huseth, A.S., Groves, R.L., 2018. Widespread detections of neonicotinoid contaminants in Central Wisconsin groundwater. PLoS One 13, e0201753. https://doi.org/10.1371/journal.pone.0201753.
Bradley, P.M., Journey, C.A., Romanok, K.M., Barber, L.B., Buxton, H.T., Foreman, W.T., et al., 2017. Expanded target-chemical analysis reveals extensive mixed-organic-contaminant exposure in U.S. streams. Environ. Sci. Technol. 51, 4792–4802. https://doi.org/10.1021/acs.est.7b00012.
Bradley, P.M., Journey, C.A., Berninger, J.P., Button, D.T., Clark, J.M., Corsi, S.R., et al., 2019. Mixed-chemical exposure and predicted effects potential in wadeable southeastern USA streams. Sci. Total Environ. 655, 70–83. https://doi.org/10.1016/j.scitotenv.2018.11.186.
Bradley, P.M., Kolpin, D.W., Thompson, D.A., Romanok, K.M., Smalling, K.L., Breitmeyer, S.E., et al., 2023. Juxtaposition of intensive agriculture, vulnerable aquifers, and mixed chemical/microbial exposures in private-well tapwater in Northeast Iowa. Sci. Total Environ. 868, 161672. https://doi.org/10.1016/j.scitotenv.2023.161672.
Brunelle, L.D., Batt, A.L., Chao, A., Glassmeyer, S.T., Quinete, N., Alvarez, D.A., et al., 2024. De facto water reuse: investigating the fate and transport of chemicals of emerging concern from wastewater discharge through drinking water treatment using non-targeted analysis and suspect screening. Environ. Sci. Technol. 58, 2468–2478. https://doi.org/10.1021/acs.est.3c07514.
Budd, R., Teerlink, J., Alaimo, C., Wong, L., Young, T.M., 2023. Sub-sewershed monitoring to elucidate down-the-drain pesticide sources. Environ. Sci. Technol. 57, 5404–5413. https://doi.org/10.1021/acs.est.2c07443.
Carpenter, K.D., Kuivila, K.M., Hladik, M.L., Haluska, T., Cole, M.B., 2016. Storm-event-transport of urban-use pesticides to streams likely impairs invertebrate assemblages. Environ. Monit. Assess. 188, 345. https://doi.org/10.1007/s10661-016-5215-5.
Chesapeake Bay Program, 2020. Chesapeake Assessment and Scenario Tool (CAST) Version 2019 [dataset]. https://cast.chesapeakebay.net/.
Chesapeake Bay Program, 2023. Chesapeake Bay Land Use and Land Cover (LULC) Database 2022 Edition [Dataset]. U.S. Geological Survey data release. https://doi.org/10.5066/P981GV1L.
Chopra, A.K., Sharma, M.K., Chamoli, S., 2011. Bioaccumulation of organochlorine pesticides in aquatic system—an overview. Environ. Monit. Assess. 173, 905–916. https://doi.org/10.1007/s10661-010-1433-4.
Chow, R., Scheidegger, R., Doppler, T., Dietzel, A., Fenicia, F., Stamm, C., 2020. A review of long-term pesticide monitoring studies to assess surface water quality trends. Water Research X. 9. https://doi.org/10.1016/j.wroa.2020.100064.
Chrétien, F., Giroux, I., Thériault, G., Gagnon, P., Corriveau, J., 2017. Surface runoff and subsurface tile drain losses of neonicotinoids and companion herbicides at edge-of-field. Environ. Pollut. 224, 255–264. https://doi.org/10.1016/j.envpol.2017.02.002.
Cimino, A.M., Boyles, A.L., Thayer, K.A., Perry, M.J., 2016. Effects of neonicotinoid pesticide exposure on human health: a systematic review. National Institute of Environmental Health Sciences. 155–162. https://doi.org/10.1289/EHP515.
Conn, K.E., Barber, L.B., Brown, G.K., Siegrist, R.L., 2006. Occurrence and fate of organic contaminants during onsite wastewater treatment. Environ. Sci. Technol. 40, 7358–7366. https://doi.org/10.1021/es0605117.
Conn, K.E., Siegrist, R.L., Barber, L.B., Meyer, M.T., 2010. Fate of trace organic compounds during vadose zone soil treatment in an onsite wastewater system. Environ. Toxicol. Chem. 29, 285–293. https://doi.org/10.1002/etc.40.
Corsi, S.R., De Cicco, L.A., Hansen, A.M., Lenaker, P.L., Bergamaschi, B.A., Pellerin, B.A., et al., 2021. Optical properties of water for prediction of wastewater contamination, human-associated bacteria, and fecal indicator bacteria in surface water at three watershed scales. Environ. Sci. Technol. 55, 13770–13782. https://doi.org/10.1021/acs.est.1c02644.
Covert, S.A., Shoda, M.E., Stackpoole, S.M., Stone, W.W., 2020. Pesticide mixtures show potential toxicity to aquatic life in U.S. streams, water years 2013-2017. Sci. Total Environ. 745, 141285. https://doi.org/10.1016/j.scitotenv.2020.141285.
Crayton, S.M., Wood, P.B., Brown, D.J., Millikin, A.R., McManus, T.J., Simpson, T.J., et al., 2020. Bioaccumulation of the pesticide imidacloprid in stream organisms and sublethal effects on salamanders. Global Ecology and Conservation. 24, e01292. https://doi.org/10.1016/j.gecco.2020.e01292.
Curwin, B.D., Hein, M.J., Sanderson, W.T., Striley, C., Heederik, D., Kromhout, H., et al., 2007. Urinary pesticide concentrations among children, mothers and fathers living in farm and non-farm households in Iowa. Ann. Occup. Hyg. 51, 53–65. https://doi.org/10.1093/annhyg/mel062.
Daniels, J.P., Latin, R., 2013. Residual efficacy of fungicides for controlling brown patch on creeping Bentgrass fairways. Plant Dis. 97, 1620–1625. https://doi.org/10.1094/PDIS-12-12-1130-RE.
de Mendiburu, F., 2023. agricolae: Statistical Procedures for Agricultural Research. R Package Version 1.3-7. https://CRAN.R-project.org/package=agricolae. (Accessed 30 July 2024).
De Zwart, D., Posthuma, L., 2005. Complex mixture toxicity for single and multiple species: proposed methodologies. Environ. Toxicol. Chem. 24, 2665. https://doi.org/10.1897/04-639r.1.
Debrewer, L.M., Ator, S.W., Denver, J.M., 2008. Temporal trends in nitrate and selected pesticides in mid-Atlantic ground water. J. Environ. Qual. 37, S-296–S-308. https://doi.org/10.2134/jeq2007.0664.
Denver, J.M., Ator, S.W., 2007. Chapter 8: the occurrence of pesticides in the bay watershed. In: Phillips, S.W. (Ed.), Synthesis of U.S. Geological Survey Science for the Chesapeake Bay Ecosystem and Implications for Environmental Management. U.S. Geological Survey Circular 1316. U.S. Geological Survey, Reston, Virginia, p. 71. https://pubs.usgs.gov/circ/circ1316/circular1316.pdf.
Diem, J.E., Pangle, L.A., Milligan, R.A., Adams, E.A., 2022. How much water is stolen by sewers? Estimating watershed-level inflow and infiltration throughout a metropolitan area. J. Hydrol. 614, 128629. https://doi.org/10.1016/j.jhydrol.2022.128629.
Diepens, N.J., Belgers, D., Buijse, L., Roessink, I., 2023. Pet dogs transfer veterinary medicines to the environment. Sci. Total Environ. 858. https://doi.org/10.1016/j.scitotenv.2022.159550.
Dieter, C.A., Maupin, M.A., Caldwell, R.R., Harris, M.A., Ivahnenko, T.I., Lovelace, J.K., et al., 2018. Estimated use of water in the United States in 2015. In: U.S. Geological Survey Circular 1441. https://doi.org/10.3133/cir1441. http://pubs.er.usgs.gov/publication/cir1441.
Donnelly, C.A., Ferrari, M.J., 1998. Summary of pesticide data from streams and wells in the Potomac River Basin, 1993–96. In: U.S. Geological Survey Open-File Report 97-666. https://doi.org/10.3133/ofr97666. http://pubs.er.usgs.gov/publication/ofr97666.
European Food Safety Authority, 2013. Conclusion on the peer review of the pesticide risk assessment for bees for the active substance imidacloprid. EFSA J. 11, 3068. https://doi.org/10.2903/j.efsa.2013.3068.
Fanelli, R., Cashman, M.J., Porter, A.J., 2022. Identifying key stressors driving biological impairment in freshwater streams in the Chesapeake Bay Watershed, USA. Environ. Manag. 70, 926–949. https://doi.org/10.1007/s00267-022-01723-7.
Faunce, K.E., Barber, L.B., Keefe, S.H., Jasmann, J.R., Rapp, J.L., 2023. Wastewater reuse and predicted ecological risk posed by contaminant mixtures in Potomac River watershed streams. JAWRA Journal of the American Water Resources Association. 59, 779–802. https://doi.org/10.1111/1752-1688.13110.
Fenneman, N.M., 1946. Physical divisions of the United States. In: U.S. Geological Survey Report. https://doi.org/10.3133/70207506. http://pubs.er.usgs.gov/publication/70207506.
Ferrari, M.J., Denis, J.M., 1999. Water-quality assessment of the Potomac River Basin: occurrence of pesticides in the Great Valley Carbonate subunit. In: U.S. Geological Survey Water-Resources Investigations Report 98-4054. https://doi.org/10.3133/wri984054. http://pubs.er.usgs.gov/publication/wri984054.
Finckh, S., Beckers, L.-M., Busch, W., Carmona, E., Dulio, V., Kramer, L., et al., 2022. Concentrations of 366 Emerging Chemicals in 56 European Wastewater Treatment

Plant Effluents by LC-HRMS Target Screening. https://doi.org/10.1594/PANGAEA.940755.
Fisher, I.J., Phillips, P.J., Bayraktar, B.N., Chen, S., McCarthy, B.A., Sandstrom, M.W., 2021. Pesticides and their degradates in groundwater reflect past use and current management strategies, Long Island, New York, USA. Sci. Total Environ. 752, 141895. https://doi.org/10.1016/j.scitotenv.2020.141895.
Flanery, A.L., 2020. Impact of Indirect Potable Reuse on Endocrine Disrupting Compounds in the Potomac River Basin. Civil Engineering. Impact of Indirect Potable Reuse on Endocrine Disrupting Compounds in the Potomac River Basin. Civil Engineering. Master of Science. Virginia Polytechnic Institute and State University Falls Church, VA, p. 70. https://vtechworks.lib.vt.edu/server/api/core/bitstreams/d331ec14-6326-48a3-9d3f-166fc1121289/content.
Flint, M.L., 2003. Residential Pesticide Use in California: A Report of Surveys Taken in the Sacramento (Arcade Creek), Stockton (Five-Mile Slough) and San Francisco Bay Areas with Comparisons to the San Diego Creek Watershed of Orange County, California. http://ipm.ucanr.edu/GENERAL/urbanpesticideuse.html.
Gardner, M., Comber, S., Scrimshaw, M.D., Cartmell, E., Lester, J., Ellor, B., 2012. The significance of hazardous chemicals in wastewater treatment works effluents. Sci. Total Environ. 437, 363–372. https://doi.org/10.1016/j.scitotenv.2012.07.086.
Giacomazzi, S., Cochet, N., 2004. Environmental impact of diuron transformation: a review. Chemosphere 56, 1021–1032. https://doi.org/10.1016/j.chemosphere.2004.04.061.
Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Batt, A.L., Benson, R., Boone, J.S., et al., 2017. Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States. Sci. Total Environ. 581-582, 909–922. https://doi.org/10.1016/j.scitotenv.2016.12.004.
Glassmeyer, S.T., Burns, E.E., Focazio, M.J., Furlong, E.T., Gribble, M.O., Jahne, M.A., et al., 2023. Water, water everywhere, but every drop unique: challenges in the science to understand the role of contaminants of emerging concern in the management of drinking water supplies. GeoHealth 7, e2022GH000716. https://doi.org/10.1029/2022GH000716.
Goel, A., McConnell, L.L., Torrents, A., Kuang, Z., Hapeman, C.J., Meritt, D.W., et al., 2010. Environmental factors affecting the levels of legacy pesticides in the airshed of Delaware and Chesapeake Bays, USA. Environ. Toxicol. Chem. 29, 1893–1906. https://doi.org/10.1002/etc.243.
Gordon, S.E., Jones, D.K., Williams, B.H., Wright, C., 2017. Potential contaminant sources and other landscape variables summarized for NHDPlus Version 2.1 catchments within the Chesapeake Bay Watershed (ver. 2.0, June 2021) [dataset]. In: U.S. Geological Survey Data Release. https://doi.org/10.5066/F7SQ8ZB3.
Gross, M.S., Sanders, C.J., De Parsia, M.D., Hladik, M.L., 2024. Methods of analysis—determination of pesticides in filtered water and suspended sediment using liquid chromatography- and gas chromatography-tandem mass spectrometry. In: U.S. Geological Survey Techniques and Methods 5-A12. https://doi.org/10.3133/tm5A12. https://pubs.usgs.gov/publication/tm5A12.
Guardian, M.G.E., He, P., Bermudez, A., Duan, S., Kaushal, S.S., Rosenfeldt, E., et al., 2021. Optimized suspect screening approach for a comprehensive assessment of the impact of best management practices in reducing micropollutants transport in the Potomac River watershed. Water Res X. 11, 100088. https://doi.org/10.1016/j.wroa.2021.100088.
Hainly, R.A., Kahn, J.M., 1996. Factors affecting herbicide yields in the Chesapeake Bay Watershed, June 1994. JAWRA Journal of the American Water Resources Association. 32, 965–984. https://doi.org/10.1111/j.1752-1688.1996.tb04066.x.
Hammel, E., Webster, T.F., Gurney, R., Heiger-Bernays, W., 2022. Implications of PFAS definitions using fluorinated pharmaceuticals. iScience 25, 104020. https://doi.org/10.1016/j.isci.2022.104020.
Hansen, A.M., Fleck, J., Kraus, T.E.C., Downing, B.D., von Dessonneck, T., Bergamaschi, B.A., 2018. Procedures for using the Horiba Scientific Aqualog® fluorometer to measure absorbance and fluorescence from dissolved organic matter. In: U.S. Geological Survey Open-File Report 2018–1096. https://doi.org/10.3133/ofr20181096. https://pubs.usgs.gov/publication/ofr20181096.
Harman-Fetcho, J.A., McConnell, L.L., Rice, C.P., Baker, J.E., 2000. Wet deposition and air−water gas exchange of currently used pesticides to a subestuary of the Chesapeake Bay. Environ. Sci. Technol. 34, 1462–1468. https://doi.org/10.1021/es990955l.
Hernandez, A.F., Parron, T., Tsatsakis, A.M., Requena, M., Alarcon, R., Lopez-Guarnido, O., 2013. Toxic effects of pesticide mixtures at a molecular level: their relevance to human health. Toxicology 307, 136–145. https://doi.org/10.1016/j.tox.2012.06.009.
Hill, R.A., Weber, M.H., Leibowitz, S.G., Olsen, A.R., Thornbrugh, D.J., 2016. The stream-catchment (StreamCat) dataset: a database of watershed metrics for the conterminous United States. JAWRA Journal of the American Water Resources Association. 52, 120–128. https://doi.org/10.1111/1752-1688.12372.
Hitaj, C., Smith, D.J., Code, A., Wechsler, S., Esker, P.D., Douglas, M.R., 2020. Sowing uncertainty: what we do and don't know about the planting of pesticide-treated seed. BioScience 70, 390–403. https://doi.org/10.1093/biosci/biaa019.
Hladik, M.L., Kolpin, D.W., 2015. First national-scale reconnaissance of neonicotinoid insecticides in streams across the USA. Environ. Chem. 13. https://doi.org/10.1071/en15061.
Hladik, M.L., Kuivila, K.M., 2012. Pyrethroid insecticides in bed sediments from urban and agricultural streams across the United States. J. Environ. Monit. 14. https://doi.org/10.1039/C2EM10946H.
Hladik, M.L., Kolpin, D.W., Kuivila, K.M., 2014. Widespread occurrence of neonicotinoid insecticides in streams in a high corn and soybean producing region, USA. Environ. Pollut. 193, 189–196. https://doi.org/10.1016/j.envpol.2014.06.033.
Hladik, M.L., Corsi, S.R., Kolpin, D.W., Baldwin, A.K., Blackwell, B.R., Cavallin, J.E., 2018a. Year-round presence of neonicotinoid insecticides in tributaries to the Great Lakes, USA. Environ. Pollut. 235, 1022–1029. https://doi.org/10.1016/j.envpol.2018.01.013.
Hladik, M.L., Main, A.R., Goulson, D., 2018b. Environmental risks and challenges associated with neonicotinoid insecticides. Environ. Sci. Technol. 52, 3329–3335. https://doi.org/10.1021/acs.est.7b06388.
Hubbard, L.E., Kolpin, D.W., Givens, C.E., Blackwell, B.R., Bradley, P.M., Gray, J.L., et al., 2022. Food, beverage, and feedstock processing facility wastewater: a unique and underappreciated source of contaminants to U.S. streams. Environ. Sci. Technol. 56, 1028–1040. https://doi.org/10.1021/acs.est.1c06821.
Hyer, K.E., Denver, J.M., Langland, M.J., Webber, J.S., Bohlke, J.K., Hively, W.D., et al., 2016. Spatial and temporal variation of stream chemistry associated with contrasting geology and land-use patterns in the Chesapeake Bay watershed—summary of results from Smith Creek, Virginia; Upper Chester River, Maryland; Conewago Creek, Pennsylvania; and Difficult Run, Virginia, 2010–2013. In: U.S. Geological Survey Scientific Investigations Report 2016-5093. https://doi.org/10.3133/sir20165093.
Interstate Commision on the Potomac River Basin, 2023. Potomac basin facts. https://www.potomacriver.org/potomac-basin-facts/. (Accessed 20 September 2023).
Iwanowicz, L.R., Blazer, V.S., Guy, C.P., Pinkney, A.E., Mullican, J.E., Alvarez, D.A., 2009. Reproductive health of bass in the Potomac, USA, drainage: part 1. Exploring the proximity to wastewater treatment plant discharge. Environ. Toxicol. Chem. 28, 1072. https://doi.org/10.1897/08-433.1.
Jeffrey, P., Yang, Z., Judd, S.J., 2022. The status of potable water reuse implementation. Water Res. 214, 118198. https://doi.org/10.1016/j.watres.2022.118198.
Jeschke, P., Nauen, R., Schindler, M., Elbert, A., 2011. Overview of the status and global strategy for neonicotinoids. J. Agric. Food Chem. 59, 2897–2908. https://doi.org/10.1021/jf101303g.
Jiang, W., Gan, J., 2016. Conversion of pesticides to biologically active products on urban hard surfaces. Sci. Total Environ. 556, 63–69. https://doi.org/10.1016/j.scitotenv.2016.02.165.
Jiang, W., Luo, Y., Conkle, J.L., Li, J., Gan, J., 2015. Pesticides on residential outdoor surfaces: environmental impacts and aquatic toxicity. Pest Manag. Sci. 72, 1411–1420. https://doi.org/10.1002/ps.4168.
Kahle, M., Buerge, I.J., Hauser, A., Müller, M.D., Poiger, T., 2008. Azole fungicides: occurrence and fate in wastewater and surface waters. Environ. Sci. Technol. 42, 7193–7200. https://doi.org/10.1021/es8009309.
Kim, H., Voutchkova, D.D., Johnsen, A.R., Albers, C.N., Thorling, L., Hansen, B., 2022. National assessment of long-term groundwater response to pesticide regulation. Environ. Sci. Technol. 56, 14387–14396. https://doi.org/10.1021/acs.est.2c02261.
Klarich Wong, K.L., Webb, D.T., Nagorzanski, M.R., Kolpin, D.W., Hladik, M.L., Cwiertny, D.M., et al., 2019. Chlorinated byproducts of neonicotinoids and their metabolites: an unrecognized human exposure potential? Environ. Sci. Technol. Lett. 6, 98–105. https://doi.org/10.1021/acs.estlett.8b00706.
Klarich, K.L., Pflug, N.C., DeWald, E.M., Hladik, M.L., Kolpin, D.W., Cwiertny, D.M., et al., 2017. Occurrence of neonicotinoid insecticides in finished drinking water and fate during drinking water treatment. Environ. Sci. Technol. Lett. 4, 168–173. https://doi.org/10.1021/acs.estlett.7b00081.
Kock-Schulmeyer, M., Villagrasa, M., Lopez de Alda, M., Cespedes-Sanchez, R., Ventura, F., Barcelo, D., 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. Sci. Total Environ. 458-460, 466–476. https://doi.org/10.1016/j.scitotenv.2013.04.010.
Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., et al., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U. S. streams, 1999-2000: a national reconnaissance. Environ. Sci. Technol. 36, 1202–1211. https://doi.org/10.1021/es011055j.
Kolpin, D.W., Skopec, M., Meyer, M.T., Furlong, E.T., Zaugg, S.D., 2004. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci. Total Environ. 328, 119–130. https://doi.org/10.1016/j.scitotenv.2004.01.015.
Kreutzweiser, D., Good, K., Chartrand, D., Scarr, T., Thompson, D., 2007. Non-target effects on aquatic decomposer organisms of imidacloprid as a systemic insecticide to control emerald ash borer in riparian trees. Ecotoxicol. Environ. Saf. 68, 315–325. https://doi.org/10.1016/j.ecoenv.2007.04.011.
Krupke, C.H., Long, E.Y., 2015. Intersections between neonicotinoid seed treatments and honey bees. Current Opinion in Insect Science 10, 8–13. https://doi.org/10.1016/j.cois.2015.04.005.
Kuang, Z., McConnell, L.L., Torrents, A., Meritt, D., Tobash, S., 2003. Atmospheric deposition of pesticides to an agricultural watershed of the Chesapeake Bay. J. Environ. Qual. 32, 1611–1622. https://doi.org/10.2134/jeq2003.1611.
Lal, B., 2007. Pesticide—induced reproductive dysfunction in Indian fishes. Fish Physiol. Biochem. 33, 455–462. https://doi.org/10.1007/s10695-007-9171-4.
Larson, J.L., Redmond, C.T., Potter, D.A., 2012. Comparative impact of an anthranilic diamide and other insecticidal chemistries on beneficial invertebrates and ecosystem services in turfgrass. Pest Manag. Sci. 68, 740–748. https://doi.org/10.1002/ps.2321.
Larson, J.L., Redmond, C.T., Potter, D.A., 2014. Impacts of a neonicotinoid, neonicotinoid–pyrethroid premix, and anthranilic diamide insecticide on four species of turf-inhabiting beneficial insects. Ecotoxicology 23, 252–259. https://doi.org/10.1007/s10646-013-1168-4.
Lasee, S., McDermett, K., Kumar, N., Guelfo, J., Payton, P., Yang, Z., et al., 2022. Targeted analysis and total oxidizable precursor assay of several insecticides for PFAS. Journal of Hazardous Materials Letters. 3, 100067. https://doi.org/10.1016/j.hazl.2022.100067.
Lee, L., 2020. NADA: Nondetects and Data Analysis for Environmental Data. R Package Version 1.6-1.1. https://CRAN.R-project.org/package=NADA. (Accessed 20 September 2023).

Lochmueller, C.H., Saavedra, S.S., 1986. Conformational changes in a soil fulvic acid measured by time-dependent fluorescence depolarization. Anal. Chem. 58, 1978–1981. https://doi.org/10.1021/ac00122a014.
Loken, L.C., Corsi, S.R., Alvarez, D.A., Ankley, G.T., Baldwin, A.K., Blackwell, B.R., et al., 2023. Prioritizing pesticides of potential concern and identifying potential mixture effects in Great Lakes tributaries using passive samplers. Environ. Toxicol. Chem. 42, 340–366. https://doi.org/10.1002/etc.5491.
Lowrance, R., Vellidis, G., Wauchope, R.D., Gay, P., Bosch, D.D., 1997. Herbicide transport in a managed riparian forest buffer stream. Transactions of the ASAE 40, 1047–1057. https://doi.org/10.13031/2013.21357.
Macaulay, S.J., Hagement, K.J., Piggott, J.J., Matthaei, C.D., 2021. Imidacloprid dominates the combined toxicities of neonicotinoid mixtures to stream mayfly nymphs. Sci. Total Environ. 761. https://doi.org/10.1016/j.scitotenv.2020.143263.
MacFarlane, D.W., Meyer, S.P., 2005. Characteristics and distribution of potential ash tree hosts for emerald ash borer. For. Ecol. Manag. 213, 15–24. https://doi.org/10.1016/j.foreco.2005.03.013.
Maggi, F., Tang, F.H.M., Tubiello, F.N., 2023. Agricultural pesticide land budget and river discharge to oceans. Nature 620, 1013–1017. https://doi.org/10.1038/s41586-023-06296-x.
Malaj, E., von der Ohe, P.C., Grote, M., Kuhne, R., Mondy, C.P., Usseglio-Polatera, P., et al., 2014. Organic chemicals jeopardize the health of freshwater ecosystems on the continental scale. Proc. Natl. Acad. Sci. U. S. A. 111, 9549–9554. https://doi.org/10.1073/pnas.1321082111.
Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., et al., 2019. Urban stormwater: an overlooked pathway of extensive mixed contaminants to surface and groundwaters in the United States. Environ. Sci. Technol. 53, 10070–10081. https://doi.org/10.1021/acs.est.9b02867.
McClure, C.M., Smalling, K.L., Blazer, V.S., Sperry, A.J., Schall, M.K., Kolpin, D.W., et al., 2020. Spatiotemporal variation in occurrence and co-occurrence of pesticides, hormones, and other organic contaminants in rivers in the Chesapeake Bay Watershed, United States. Sci. Total Environ. 728, 138765. https://doi.org/10.1016/j.scitotenv.2020.138765.
McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46, 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.
McMahen, R.L., Strynar, M.J., McMillan, L., DeRose, E., Lindstrom, A.B., 2016. Comparison of fipronil sources in North Carolina surface water and identification of a novel fipronil transformation product in recycled wastewater. Sci. Total Environ. 569-570, 880–887. https://doi.org/10.1016/j.scitotenv.2016.05.085.
Md Meftaul, I., Venkateswarlu, K., Dharmarajan, R., Annamalai, P., Megharaj, M., 2020. Pesticides in the urban environment: a potential threat that knocks at the door. Sci. Total Environ. 711, 134612. https://doi.org/10.1016/j.scitotenv.2019.134612.
Miller, M.P., McKnight, D.M., Chapra, S.C., Williams, M.W., 2009. A model of degradation and production of three pools of dissolved organic matter in an alpine lake. Limnol. Oceanogr. 54, 2213–2227. https://doi.org/10.4319/lo.2009.54.6.2213.
Miller, J.L., Schmidt, T.S., Van Metre, P.C., Mahler, B.J., Sandstrom, M.W., Nowell, L.H., et al., 2020. Common insecticide disrupts aquatic communities: a mesocosm-to-field ecological risk assessment of fipronil and its degradates in U.S. streams. Sci. Adv. 6, 1–12. https://doi.org/10.1126/sciadv.abc1299.
Miller, S.A., Faunce, K.E., Burns, D.W., Barber, L.B., Jasmann, J.R., Fleck, J.A., et al., 2024. Environmental sampling and modeling results to characterize surface-water quality at 32 sites across the Potomac River watershed, 2022 (ver. 2.0, September 2024) [dataset]. In: US Geological Survey Data Release. https://doi.org/10.5066/P9DUC4L1.
Montiel-Leon, J.M., Duy, S.V., Munoz, G., Amyot, M., Sauve, S., 2018. Evaluation of on-line concentration coupled to liquid chromatography tandem mass spectrometry for the quantification of neonicotinoids and fipronil in surface water and tap water. Anal. Bioanal. Chem. 410, 2765–2779. https://doi.org/10.1007/s00216-018-0957-2.
Mourtzinis, S., Krupke, C.H., Esker, P.D., Varenhorst, A., Arneson, N.J., Bradley, C.A., et al., 2019. Neonicotinoid seed treatments of soybean provide negligible benefits to US farmers. Sci. Rep. 9. https://doi.org/10.1038/s41598-019-47442-8.
Munz, N.A., Burdon, F.J., de Zwart, D., Junghans, M., Melo, L., Reyes, M., et al., 2017. Pesticides drive risk of micropollutants in wastewater-impacted streams during low flow conditions. Water Res. 110, 366–377. https://doi.org/10.1016/j.watres.2016.11.001.
National Institute of Diabetes and Digestive and Kidney Diseases, 2012. LiverTox: clinical and research information on drug-induced liver injury. https://www.ncbi.nlm.nih.gov/books/NBK548194/.
National Park Service, 2020. Eastern hemlocks in the national capital region. https://www.nps.gov/articles/eastern-hemlocks-in-capital-region.htm. (Accessed 30 July 2024).
National Research Council. Water Reuse: Potential for Expanding the Nation's Water Supply Through Reuse of Municipal Wastewater. https://nap.nationalacademies.org/catalog/13303/water-reuse-potential-for-expanding-the-nations-water-supply-through.
Nguyen, T., 2021. Rinses from selected fluorinated and non-fluorinated HDPE containers. https://www.epa.gov/sites/default/files/2021-03/documents/results-of-rinsates-samples_03042021.pdf.
Nguyen, D., 2022. Results of EPA's analytical chemistry branch laboratory study of PFAS leaching from fluorinated HDPE containers. https://www.epa.gov/system/files/documents/2022-09/EPA%20PFAS%20Container%20Leaching%20Study%20080122022_0.pdf.
Nilsen, E., Smalling, K.L., Ahrens, L., Gros, M., Miglioranza, K.S.B., Pico, Y., et al., 2019. Critical review: grand challenges in assessing the adverse effects of contaminants of emerging concern on aquatic food webs. Environ. Toxicol. Chem. 38, 46–60. https://doi.org/10.1002/etc.4290.
Nitschke, L., Schussler, W., 1998. Surface water pollution by herbicides from effluents of waste water treatment plants. Chemosphere 36, 35–41. https://doi.org/10.1016/S0045-6535(97)00286-5.
Nowell, L.H., Moran, P.W., Schmidt, T.S., Norman, J.E., Nakagaki, N., Shoda, M.E., et al., 2018. Complex mixtures of dissolved pesticides show potential aquatic toxicity in a synoptic study of Midwestern U.S. streams. Sci. Total Environ. 613-614, 1469–1488. https://doi.org/10.1016/j.scitotenv.2017.06.156.
Nowell, L.H., Moran, P.W., Bexfield, L.M., Mahler, B.J., Van Metre, P.C., Bradley, P.M., et al., 2021. Is there an urban pesticide signature? Urban streams in five U.S. regions share common dissolved-phase pesticides but differ in predicted aquatic toxicity. Sci. Total Environ. 793, 148453. https://doi.org/10.1016/j.scitotenv.2021.148453.
Nowell, L.H., Moran, P.W., Waite, I.R., Schmidt, T.S., Bradley, P.M., Mahler, B.J., et al., 2024. Multiple lines of evidence point to pesticides as stressors affecting invertebrate communities in small streams in five United States regions. Sci. Total Environ. 915, 169634. https://doi.org/10.1016/j.scitotenv.2023.169634.
Oliver, S.K., Corsi, S.R., Baldwin, A.K., Nott, M.A., Ankley, G.T., Blackwell, B.R., et al., 2023. Pesticide prioritization by potential biological effects in tributaries of the Laurentian Great Lakes. Environ. Toxicol. Chem. 42, 367–384. https://doi.org/10.1002/etc.5522.
Olsen, R.L., Chappell, R.W., Loftis, J.C., 2012. Water quality sample collection, data treatment and results presentation for principal components analysis – literature review and Illinois River watershed case study. Water Res. 46, 3110–3122. https://doi.org/10.1016/j.watres.2012.03.028.
Ospina, M., Wong, L., Baker, S.E., Serafim, A.B., Morales-Agudelo, P., Calafat, A.M., 2019. Exposure to neonicotinoid insecticides in the U.S. general population: data from the 2015–2016 national health and nutrition examination survey. Environ. Res. 176. https://doi.org/10.1016/j.envres.2019.108555v.
Ou, L., Latin, R., 2018. Influence of management practices on distribution of fungicides in golf course turf. Agron. J. 110, 2523–2533. https://doi.org/10.2134/agronj2018.02.0115.
Overdahl, K.E., Sutton, R., Sun, J., DeStefano, N.J., Getzinger, G.J., Ferguson, P.L., 2021. Assessment of emerging polar organic pollutants linked to contaminant pathways within an urban estuary using non-targeted analysis. Environ Sci Process Impacts 23, 429–445. https://doi.org/10.1039/D0EM00463D.
Pal, A., He, Y., Jekel, M., Reinhard, M., Gin, K.Y., 2014. Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. Environ. Int. 71, 46–62. https://doi.org/10.1016/j.envint.2014.05.025.
Pandey, A., Kasuga, I., Furumai, H., Kurisu, F., 2023. Concurrent analysis of 84 compounds among emerging contaminants listed by the Ministry of the Environment, Japan, in domestic wastewater treatment plants using liquid chromatography and high-resolution mass spectrometry (LC-HRMS). Journal of Water and Environment Technology. 21, 108–118. https://doi.org/10.2965/jwet.22-076.
Perkins, R., Whitehead, M., Civil, W., Goulson, D., 2021. Potential role of veterinary flea products in widespread pesticide contamination of English rivers. Sci. Total Environ. 755, 143560. https://doi.org/10.1016/j.scitotenv.2020.143560.
Perkins, R., Barron, L., Glauser, G., Whitehead, M., Woodward, G., Goulson, D., 2024. Down-the-drain pathways for fipronil and imidacloprid applied as spot-on parasiticides to dogs: estimating aquatic pollution. Sci. Total Environ. 917, 170175. https://doi.org/10.1016/j.scitotenv.2024.170175.
Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res. 72, 3–27. https://doi.org/10.1016/j.watres.2014.08.053.
Phillips, P.J., Ator, S.W., Nystrom, E.A., 2007. Temporal changes in surface-water insecticide concentrations after the phaseout of diazinon and chlorpyrifos. Environ. Sci. Technol. 41, 4246–4251. https://doi.org/10.1021/es070301.
Porter, A.J., Webber, J.S., Witt, J.W., Jastram, J.D., 2020. Spatial and temporal patterns in streamflow, water chemistry, and aquatic macroinvertebrates of selected streams in Fairfax County, Virginia, 2007–18. In: U.S. Geological Survey Scientific Investigations Report 2020-5061. https://doi.org/10.3133/sir20205061.
Python Software Foundation, 2023. Python v3.9.16 (version 3.9.16) [software]. https://www.python.org/. (Accessed 20 September 2023).
R Core Team, 2024. R: a language and environment for statistical computing. v4.4.1 (Version 4.4.1) [software]. https://www.R-project.org/. (Accessed 30 July 2024).
Raby, M., Lissemore, L., Kaltenecker, G., Beaton, D., Prosser, R.S., 2022. Characterizing the exposure of streams in southern Ontario to agricultural pesticides. Chemosphere 294, 133769. https://doi.org/10.1016/j.chemosphere.2022.133769.
Ramírez-Malule, H., Quiñones-Murillo, D.H., Manotas-Duque, D., 2020. Emerging contaminants as global environmental hazards. A bibliometric analysis. Emerging Contaminants 6, 179–193. https://doi.org/10.1016/j.emcon.2020.05.001.
Rice, J., Westerhoff, P., 2015. Spatial and temporal variation in de facto wastewater reuse in drinking water systems across the U.S.A. Environ. Sci. Technol. 49, 982–989. https://doi.org/10.1021/es5048057.
Rice, J., Wutich, A., Westerhoff, P., 2013. Assessment of De Facto Wastewater Reuse across the US: trends between 1980 and 2008. Environ. Sci. Technol. 47, 11099–11105. https://doi.org/10.1021/es402792s.
Roessink, I., Merga, L.B., Zweers, H.J., Van Den Brink, P.J., 2013. The neonicotinoid imidacloprid shows high chronic toxicity to mayfly nymphs. Environ. Toxicol. Chem. 32, 1096–1100. https://doi.org/10.1002/etc.2201.

Rondeau, G., Sánchez-Bayo, F., Tennekes, H.A., Decourtye, A., Ramírez-Romero, R., Desneux, N., 2014. Delayed and time-cumulative toxicity of imidacloprid in bees, ants and termites. Sci. Rep. 4. https://doi.org/10.1038/srep05566.

Sadaria, A.M., Supowit, S.D., Halden, R.U., 2016. Mass balance assessment for six neonicotinoid insecticides during conventional wastewater and wetland treatment: nationwide reconnaissance in United States wastewater. Environ. Sci. Technol. 50, 6199–6206. https://doi.org/10.1021/acs.est.6b01032.

Sadaria, A.M., Sutton, R., Moran, K.D., Teerlink, J., Brown, J.V., Halden, R.U., 2017. Passage of fiproles and imidacloprid from urban pest control uses through wastewater treatment plants in northern California, USA. Environ. Toxicol. Chem. 36, 1473–1482. https://doi.org/10.1002/etc.3673.

Sadaria, A.M., Labban, C.W., Steele, J.C., Maurer, M.M., Halden, R.U., 2019. Retrospective nationwide occurrence of fipronil and its degradates in U.S. wastewater and sewage sludge from 2001–2016. Water Res. 155, 465–473. https://doi.org/10.1016/j.watres.2019.02.045.

Schaafsma, A.W., Limay-Rios, V., Baute, T.S., Smith, J.L., 2019. Neonicotinoid insecticide residues in subsurface drainage and open ditch water around maize fields in southwestern Ontario. PLoS One 14, e0214787. https://doi.org/10.1371/journal.pone.0214787.

Schmidt, T.S., Miller, J.L., Mahler, B.J., VanMetre, P.C., Nowell, L.H., Sandstrom, M.W., et al., 2022. Ecological consequences of neonicotinoid mixtures in streams. Sci. Adv. 8. https://doi.org/10.1126/sciadv.abj8182.

Schramm, M., 2023. Package 'echor': access EPA 'ECHO' data. R package version 0.1.7. https://CRAN.R-project.org/package=echor. (Accessed 1 June 2024).

Schreiner, V.C., Szocs, E., Bhowmik, A.K., Vijver, M.G., Schafer, R.B., 2016. Pesticide mixtures in streams of several European countries and the USA. Sci. Total Environ. 573, 680–689. https://doi.org/10.1016/j.scitotenv.2016.08.163.

Sergeant, C.J., Starkey, E.N., Bartz, K.K., Wilson, M.H., Mueter, F.J., 2016. A practitioner's guide for exploring water quality patterns using principal components analysis and Procrustes. Environ. Monit. Assess. 188, 249. https://doi.org/10.1007/s10661-016-5253-z.

Shah, A.I., Din Dar, M.U., Bhat, R.A., Singh, J.P., Singh, K., Bhat, S.A., 2020. Prospectives and challenges of wastewater treatment technologies to combat contaminants of emerging concerns. Ecol. Eng. 152. https://doi.org/10.1016/j.ecoleng.2020.105882.

Silvanima, J., Sunderman-Barnes, S., Copeland, R., Woeber, A., Miller, E., 2022. Regional extent, environmental relevance, and spatiotemporal variability of neonicotinoid insecticides detected in Florida's ambient flowing waters. Environ. Monit. Assess. 194, 416. https://doi.org/10.1007/s10661-022-10000-3.

Ślósarczyk, K., Witkowski, A.J., 2021. Preliminary evaluation of the possible occurrence of pesticides in groundwater contaminated with nitrates—a case study from southern Poland. Water 13, 3091. https://doi.org/10.3390/w13213091.

Smalling, K.L., Devereux, O.H., Gordon, S.E., Phillips, P.J., Blazer, V.S., Hladik, M.L., et al., 2021. Environmental and anthropogenic drivers of contaminants in agricultural watersheds with implications for land management. Sci. Total Environ. 774, 145687. https://doi.org/10.1016/j.scitotenv.2021.145687.

Sprague, L.A., Nowell, L.H., 2008. Comparison of pesticide concentrations in streams at low flow in six metropolitan areas of the United States. Environ. Toxicol. Chem. 27, 288–298. https://doi.org/10.1897/07-276R.1.

Sprague, L.A., Harned, D.A., Hall, D.W., Nowell, L.H., Bauch, N.J., Richards, K.D., 2007. Response of stream chemistry during base flow to gradients of urbanization in selected locations across the conterminous United States, 2002–04. In: U.S. Geological Survey Scientific Investigations Report 2007–5083. https://pubs.usgs.gov/sir/2007/5083/.

Squillace, P.J., Thurman, E.M., Furlong, E.T., 1993. Groundwater as a nonpoint source of atrazine and deethylatrazine in a river during base flow conditions. Water Resour. Res. 29, 1719–1729. https://doi.org/10.1029/93WR00290.

State of New Jersey, 2020. Senate, No. 1016: restricts use of neonicotinoid pesticides. https://pub.njleg.gov/bills/2020/S1500/1016_R4.HTM. (Accessed 30 July 2024).

State of New York, 2023. S1856A: birds and bees protection act. https://legislation.nysenate.gov/pdf/bills/2023/S1856A. (Accessed 30 July 2024).

State of New York Assembly, 2023. Assembly Bill A7640: birds and bees protection act. https://legislation.nysenate.gov/pdf/bills/2023/A7640. (Accessed 30 July 2024).

Stehle, S., Bline, A., Bub, S., Petschick, L., Wolfram, J., Schulz, R., 2019. Aquatic pesticide exposure in the U.S. as a result of non-agricultural uses. Environ. Int. 133. https://doi.org/10.1016/j.envint.2019.105234.

Stone, W.W., Gilliom, R.J., Ryberg, K.R., 2014. Pesticides in U.S. streams and rivers: occurrence and trends during 1992-2011. Environ. Sci. Technol. 48, 11025–11030. https://doi.org/10.1021/es5025367.

Straw, E.A., Kelly, E., Stanley, D.A., 2023. Self-reported assessment of compliance with pesticide rules. Ecotoxicol. Environ. Saf. 254. https://doi.org/10.1016/j.ecoenv.2023.114692.

Sutton, R., Xie, Y., Moran, K.D., Teerlink, J., 2019. Occurrence and sources of pesticides to urban wastewater and the environment. In: Society, A.C. (Ed.), Pesticides in Surface Water: Monitoring, Modeling, Risk Assessment, and Management, Washington D.C, pp. 63–88. https://pubs.acs.org/doi/abs/10.1021/bk-2019-1308.ch005.

Swartz, C.H., Reddy, S., Benotti, M.J., Yin, H., Barber, L.B., Brownawell, B.J., et al., 2006. Steroid estrogens, nonylphenol ethoxylate metabolites, and other wastewater contaminants in groundwater affected by a residential septic system on Cape Cod, MA. Environ. Sci. Technol. 40, 4894–4902. https://doi.org/10.1021/es052595.

Sweeney, M.R., Thompson, C.M., Popescu, V.D., 2021. Sublethal, behavioral, and developmental effects of the neonicotinoid pesticide imidacloprid on larval wood frogs (Rana sylvatica). Environ. Toxicol. Chem. 40, 1838–1847. https://doi.org/10.1002/etc.5047.

Tang, F.H.M., Lenzen, M., McBratney, A., Maggi, F., 2021. Risk of pesticide pollution at the global scale. Nat. Geosci. 14, 206–210. https://doi.org/10.1038/s41561-021-00712-5.

Tapparo, A., Marton, D., Giorio, C., Zanella, A., Soldà, L., Marzaro, M., et al., 2012. Assessment of the environmental exposure of honeybees to particulate matter containing neonicotinoid insecticides coming from corn coated seeds. Environ. Sci. Technol. 46, 2592–2599. https://doi.org/10.1021/es2035152.

Teerlink, J., Hernandez, J., Budd, R., 2017. Fipronil washoff to municipal wastewater from dogs treated with spot-on products. Sci. Total Environ. 599-600, 960–966. https://doi.org/10.1016/j.scitotenv.2017.04.219.

Thompson, D.A., Lehmler, H.J., Kolpin, D.W., Hladik, M.L., Vargo, J.D., Schilling, K.E., et al., 2020. A critical review on the potential impacts of neonicotinoid insecticide use: current knowledge of environmental fate, toxicity, and implications for human health. Environ Sci Process Impacts 22, 1315–1346. https://doi.org/10.1039/c9em00586b.

Thompson, C.M., Sweeney, M.R., Popescu, V.D., 2022. Carryover effects of pesticide exposure and pond drying on performance, behavior, and sex ratios in a pool breeding amphibian. J. Zool. 317, 229–240. https://doi.org/10.1111/jzo.12975.

Thuyet, D.Q., Jorgenson, B.C., Wissel-Tyson, C., Watanabe, H., Young, T.M., 2012. Wash off of imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. Sci. Total Environ. 414, 515–524. https://doi.org/10.1016/j.scitotenv.2011.10.051.

Toda, M., Beer Karlyn, D., Kuivila Kathryn, M., Chiller Tom, M., Jackson Brendan, R., 2021. Trends in agricultural triazole fungicide use in the United States, 1992–2016 and possible implications for antifungal-resistant fungi in human disease. Environ. Health Perspect. 129, 055001. https://doi.org/10.1289/EHP7484.

Todd, A., Struger, J., 2014. Changes in acid herbicide concentrations in urban streams after a cosmetic pesticides ban. Challenges 5 (1), 138–151. https://doi.org/10.3390/challe5010138.

U.S. Environmental Protection Agency, 2005. National management measures to control nonpoint source pollution from urban areas. https://www.epa.gov/sites/default/files/2015-09/documents/urban_guidance_0.pdf.

U.S. Environmental Protection Agency, 2012. National Hydrography Dataset Plus streams - NHDPlus Ver. 2.1, Vector Digital Data Set [dataset]. https://www.epa.gov/waterdata/get-nhdplus-national-hydrography-dataset-plus-data.

U.S. Environmental Protection Agency, 2020a. Clothianidin and thiamethoxam proposed interim registration review decision. https://www.epa.gov/sites/default/files/2020-01/documents/clothianidin_and_thiamethoxam_pid_final_1.pdf.

U.S. Environmental Protection Agency, 2020b. Imidacloprid proposed interim registration review decision. https://www.epa.gov/sites/default/files/2020-01/documents/imidacloprid_pid_signed_1.22.2020.pdf.

U.S. Environmental Protection Agency, 2024. Aquatic life benchmarks and ecological risk assessments for registered pesticides. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk. (Accessed 16 July 2024).

U.S. Fish & Wildlife Service, 2000. Homeowner's guide to protecting frogs lawn and garden care. https://www.fws.gov/sites/default/files/documents/FW-2003-Homeowners-Guide-to-Protecting-Frogs.pdf.

U.S. Geological Survey, 1999. The quality of our nation's waters: nutrients and pesticides. Circular 1225. https://doi.org/10.3133/cir1225. https://pubs.usgs.gov/publication/cir1225.

U.S. Geological Survey, 2015. National Field Manual for the Collection of Water-Quality Data. U.S. Geological Survey Techniques of Water-Resources Investigations. U.S. Geological Survey Techniques of Water-Resources Investigations 09. https://doi.org/10.3133/twri09.

U.S. Geological Survey, 2024. USGS Water Data for the Nation: U.S. Geological Survey National Water Information System Database. https://doi.org/10.5066/F7P55KJN (accessed September 20, 2023).

Van Dijk, T.C., Van Staalduinen, M.A., Van der Sluijs, J.P., 2013. Macro-invertebrate decline in surface water polluted with imidacloprid. PLoS One 8, e62374. https://doi.org/10.1371/journal.pone.0062374.

Vatovec, C., Phillips, P., Van Wagoner, E., Scott, T.-M., Furlong, E., 2016. Investigating dynamic sources of pharmaceuticals: demographic and seasonal use are more important than down-the-drain disposal in wastewater effluent in a University City setting. Sci. Total Environ. 572, 906–914. https://doi.org/10.1016/j.scitotenv.2016.07.199.

Virginia Department of Agriculture and Consumer Services, 2023. List of registered pesticides. https://www.kelly-products.com/licensing-renewals/. (Accessed 13 October 2023).

Waite, I.R., Van Metre, P.C., Moran, P.W., Konrad, C.P., Nowell, L.H., Meador, M.R., et al., 2021. Multiple in-stream stressors degrade biological assemblages in five U.S. regions. Sci. Total Environ. 800, 149350. https://doi.org/10.1016/j.scitotenv.2021.149350.

Wan, Y., Wang, Y., Xia, W., He, Z., Xu, S., 2019. Neonicotinoids in raw, finished, and tap water from Wuhan, Central China: assessment of human exposure potential. Sci. Total Environ. 675, 513–519. https://doi.org/10.1016/j.scitotenv.2019.04.267.

Webb, D.T., Zhi, H., Kolpin, D.W., Klaper, R.D., Iwanowicz, L.R., LeFevre, G.H., 2021. Emerging investigator series: municipal wastewater as a year-round point source of neonicotinoid insecticides that persist in an effluent-dominated stream. Environ Sci Process Impacts 23, 678–688. https://doi.org/10.1039/d1em00065a.

Webber, J.S., Chanat, J.G., Porter, A.J., Jastram, J.D., 2023. Evaluating drivers of hydrology, water quality, and benthic macroinvertebrates in streams of Fairfax County, Virginia, 2007–18. In: Report. U.S. Geological Survey Scientific Investigations Report 2023-5027. https://doi.org/10.3133/sir20235027. http://pubs.usgs.gov/publication/sir20235027.

Weisman, R.J., Barber, L.B., Rapp, J.L., Ferreira, C.M., 2019. De facto reuse and disinfection by-products in drinking water systems in the Shenandoah River watershed. Environ. Sci.: Water Res. Technol. 5, 1699–1708. https://doi.org/10.1039/C9EW00326F.

Weisman, R.J., Barber, L.B., Faunce, K.E., Rapp, J.L., Ferreira, C.M., 2021. Temporal variations of de facto wastewater reuse and disinfection by-products in public water systems in the Shenandoah River watershed, USA. Water Practice and Technology. 16, 1434–1445. https://doi.org/10.2166/wpt.2021.076.

Weston, D.P., Chen, D., Lydy, M.J., 2015. Stormwater-related transport of the insecticides bifenthrin, fipronil, imidacloprid, and chlorpyrifos into a tidal wetland, San Francisco Bay, California. Sci. Total Environ. 527-528, 18–25. https://doi.org/10.1016/j.scitotenv.2015.04.095.

Whitehead, H.D., Peaslee, G.F., 2023. Directly fluorinated containers as a source of perfluoroalkyl carboxylic acids. Environ. Sci. Technol. Lett. 10, 350–355. https://doi.org/10.1021/acs.estlett.3c00083.

Wieben, C.M., 2021. Preliminary Estimated Annual Agricultural Pesticide Use for Counties of the Conterminous United States, 2019: U.S. Geological Survey data release [dataset]. https://doi.org/10.5066/P9EDTHQL.

Williams, B.M., Gordon, S.E., Putman, A.L., Jones, D.K., 2021. Quality assessed and modified Discharge Monitoring Report (DMR) facility and outfall locations, 2007–2019 [dataset]. In: US Geological Survey Data Release. https://doi.org/10.5066/P9KUSHSE.

Wittmer, I.K., Bader, H.P., Scheidegger, R., Singer, H., Luck, A., Hanke, I., et al., 2010. Significance of urban and agricultural land use for biocide and pesticide dynamics in surface waters. Water Res. 44, 2850–2862. https://doi.org/10.1016/j.watres.2010.01.030.

Wittmer, I.K., Scheidegger, R., Bader, H.-P., Singer, H., Stamm, C., 2011. Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409, 920–932. https://doi.org/10.1016/j.scitotenv.2010.11.031.

Wolfand, J.M., Seller, C., Bell, C.D., Cho, Y.M., Oetjen, K., Hogue, T.S., et al., 2019. Occurrence of urban-use pesticides and management with enhanced Stormwater control measures at the watershed scale. Environ. Sci. Technol. 53, 3634–3644. https://doi.org/10.1021/acs.est.8b05833.

Woo, C., Daniels, B., Stirling, R., Morris, P., 2010. Tebuconazole and propiconazole tolerance and possible degradation by Basidiomycetes: a wood-based bioassay. Int. Biodeterior. Biodegradation 64, 403–408. https://doi.org/10.1016/j.ibiod.2010.01.009.

Zappia, H., Fisher, G.T., 1997. Water-quality assessment of the potomac river basin: analysis of available pesticide data, 1972–1990. In: U.S. Geological Survey Water-Resources Investigations Report 97-4051. https://pubs.usgs.gov/wri/wri97-4051/wri97-4051.pdf.

Zorzenon, F.J., Campos, A.E.C., 2015. Subterranean termites in urban forestry: tree preference and management. Neotrop. Entomol. 44, 180–185. https://doi.org/10.1007/s13744-014-0269-y.