Science of the Total Environment 958 (2025) 177837

Contents lists available at ScienceDirect

Science of the Total Environment

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

The occurrence and persistence of surface water contaminants across different landscapes

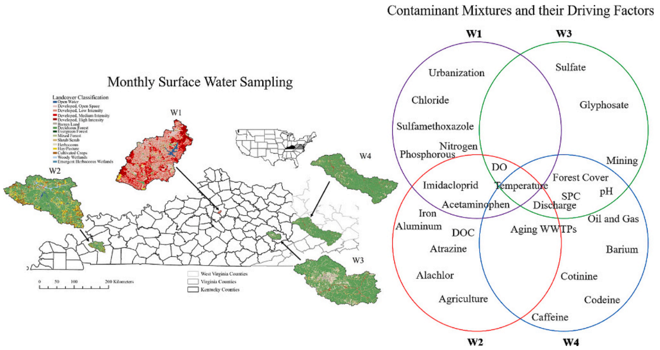
Emily Nottingham Byers [a,*,1], Tiffany L. Messer [a], Jason Unrine [b,c], Christopher Barton [d], Carmen Agouridis [a], Daniel N. Miller [e]

[a] *Department of Biosystems and Agricultural Engineering, University of Kentucky, 128 CE Barnhart, Lexington, KY 40506, USA*
[b] *Department of Plant and Soil Sciences, University of Kentucky, Lexington, KY, USA*
[c] *Kentucky Water Research Institute, University of Kentucky, Lexington, KY, USA*
[d] *Department of Forestry and Natural Resources, University of Kentucky, Lexington, KY, USA*
[e] *United States Department of Agriculture, Agriculture Research Service, University of Nebraska-Lincoln, Lincoln, NE, USA*

HIGHLIGHTS

- Water quality was characterized for urban, agricultural, and forested watersheds.
- Seventy-seven contaminants were detected using POCIS and water grab samples.
- Contaminants varied by location, season, flooding, and physiochemical properties.
- Five contaminants exceeded water quality criteria limits for freshwater organisms.
- Pharmaceuticals identified areas in need of wastewater infrastructure improvements.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jay Gan

Keywords:
Water quality
Contaminants of emerging concern
Non-point source pollution
Pharmaceuticals and personal care products
Ecotoxicity
Pesticides

ABSTRACT

Surface water contaminants, including both conventional contaminants (e.g., nutrients, trace elements) and emerging contaminants (e.g., pesticides, pharmaceuticals) are heavily influenced by urban and rural land use practices. The goal of the study was to characterize the influence of watershed land use practices on surface water quality. Specific objectives were to (1) identify and quantify the type and concentration of nutrients, trace elements, pesticides, pharmaceuticals and personal care products in four watersheds and (2) understand potential sources of contamination based on the watershed's land cover and land use characteristics (i.e., oil and gas, urban, mining, agriculture). Monthly polar organic chemical integrative samples and water grab samples were collected from March–October 2022. The results showed that surface water quality varied by location, season, and flood condition Specifically, aluminum (mean = 758 μg L^{-1}) and iron (mean = 1130 μg L^{-1}) exceeded

---

Abbreviations: PPCP, Pharmaceuticals and personal care products; HSG, Hydrologic soil group; POCIS, Polar organic chemical integrative samplers; TWA, Time-weighted average; HLB, Hydrophilic-lipophilic balanced; SPC, Specific conductivity; DO, Dissolved oxygen; DOC, Dissolved organic carbon; USGS, United States Geological Survey; EPA, United States Environmental Protection Agency; WWTP, Wastewater treatment plant.

[*] Corresponding author.
E-mail address: Emily.Byers@usda.gov (E.N. Byers).
[1] Present address: United States Department of Agriculture, Agricultural Research Service, Columbus, OH, USA.

https://doi.org/10.1016/j.scitotenv.2024.177837
Received 9 August 2024; Received in revised form 27 November 2024; Accepted 27 November 2024
Available online 4 December 2024
0048-9697/Published by Elsevier B.V.

chronic aquatic life water quality criteria in the agricultural watershed, while imidacloprid exceeded the chronic criteria limit for freshwater invertebrates in both the urban (mean = 5.96 ng L^{-1}) and agricultural (mean = 4.72 ng L^{-1}) watersheds. Sulfate concentrations (mean = 666 mg L^{-1}) also exceeded ambient water quality criteria in the watershed with a high activity of mining. This study provides important steps for developing a comprehensive understanding of land use impacts on contaminant presence and concentration in surface waters, improved understanding of the implications to non-target species, and necessary water treatment processes to ensure a safe water supply.

1. Introduction

Non-point source pollution from runoff is a leading cause of surface water impairments (EPA, 2005). Surface runoff can contain a variety of contaminants (e.g., nutrients, suspended sediments, pesticides, trace elements, antibiotics) depending on the land cover (e.g., urban, cropland, forested) and land use practices (e.g., recreation, logging, coal mining, agriculture) within the watershed. If left untreated, contaminants can not only have ecological but also human health effects since approximately 70 % of all freshwater used in the United States comes from surface water of which 20 % is for the public water supply (e.g., drinking water) and 60 % is used for irrigation (Dieter et al., 2017).

A wide range of land use practices can lead to excess nutrients in the environment including, fertilizer applications in both agricultural (Kolenbrander, 2013; Yufen Ren et al., 2014) and urban landscapes (Hobbie et al., 2017), livestock (Szogi et al., 2015), and effluent discharge from water treatment plants (Zhang et al., 2015). Excess loading of nutrients to surface waters also has the potential to impact water quality, lead to harmful algal blooms, and limit recreational activity (Carpenter et al., 1998). Further, while trace elements can occur naturally in the environment, their increase and persistence in waterways have been reported to come from industrial activities (e.g., mining, foundries, smelters, wood preservation and paper processing plants, petroleum combustion, medical use; Tchounwou et al., 2012), agricultural practices (He et al., 2005), domestic effluents (Hassaan et al., 2016), and landfills (Hassaan et al., 2016). Although some trace elements (e.g., manganese, iron, copper, and zinc) are considered macronutrients, they can still cause harm at high enough concentrations, while others (e.g., mercury, cadmium, lead, aluminum, and arsenic) can cause harm to aquatic and human life even at low concentrations (Donadt et al., 2021; Kolarova and Napiórkowski, 2021).

Pesticides, including herbicides, fungicides, and insecticides, are widely used for agricultural production to meet the growing demand for food throughout the world (Atwood and Paisley-Jones, 2016); Roser, 2019). Pesticides are also commonly applied in urban settings (e.g., lawns, parks, golf courses) to manage unwanted pests and weeds (Md Meftaul et al., 2020). Neonicotinoids, a class of insecticides including acetamiprid, clothianidin, imidacloprid, thiacloprid, and thiamethoxam, are an example of pesticides used across both urban and agricultural landscapes for the management of sucking, biting, and chewing pests (Simon-Delso et al., 2015). Neonicotinoids account for approximately 25 % of the global pesticide market due to their high toxicity to pests compared to other insecticides (Simon-Delso et al., 2015); however, they pose threats to pollinator species (Chauzat and Faucon, 2007) along with disrupting human reproductive health and brain development (Bal et al., 2012; Han et al., 2018; Kimura-Kuroda et al., 2012). Chronic exposure to the herbicide atrazine, the most common pesticide found in surface water since its creation in 1958, has been shown to have carcinogenic properties along with links to adverse birth effects (Almberg et al., 2018). The health impacts from glyphosate, another common herbicide in use since 1974, has long been debated with the World Health Organization's International Agency for Research on Cancer (IARC) categorizing the herbicide as a probable human carcinogen (Mesnage and Antoniou, 2017).

Pharmaceuticals and personal care products (PPCPs) are a suite of contaminants found in cosmetics or medications used by humans and in the agribusiness industry to enhance the growth and health of livestock (Daughton, 2006). Depending on the PPCP, only a portion (5–95 %) of the product is absorbed by the body and the remainder is excreted (Okoye et al., 2022). The unused PPCPs can then enter the environment (i.e., groundwater, surface water) through wastewater effluent discharge (Daughton and Ternes, 1999), runoff from large animal farms (Nikolaou et al., 2007), or runoff and leaching from agriculture fields that land apply biosolids (Kinney et al., 2006). The impact of water contamination from domestic wastewater can be exacerbated by aged wastewater infrastructure, direct discharge of untreated sewage into waterways, and improper disposal of PPCPs before ingestion (Freitas and Radis-Baptista, 2021). Left untreated, PPCPs have potential negative effects on humans, aquatic species, and plants by altering their physiology and biochemical processes (Okoye et al., 2022).

Relevant data on fate, transport, and ecotoxicological effects of surface water contaminants on human and environmental health are often scarce or not well understood (Pietrzak et al., 2020). Monitoring monthly loads of conventional and emerging contaminants across varying landscapes can provide important temporal and spatial information that will enhance the overall understanding of the scale and magnitude of the threat such contaminants pose to the environment and downstream surface water users. To date, there have been limited studies to assess mixtures or “cocktails” of water contaminants in rivers with varying watershed types. While many studies have provided monitoring of specific classes of contaminants, this study aimed to provide a seasonal assessment of a suite of contaminants across four watersheds. Therefore, the goal of this study was to characterize trace elements, nutrients, pesticides, and a suite of PPCPs occurring in streams across varying landscapes to determine monthly loads of contaminants and their relationship to watershed characteristics. The study had two main objectives: (1) identify and quantify the type and concentration of contaminants in four watersheds during the growing season and (2) understand potential sources of contamination based on land cover and land use characteristics of the watershed. The overall hypothesis was that the type of contaminants present would be impacted by land cover and land use characteristics within the watershed, where seasonality and precipitation would impact the concentration of contaminants.

2. Materials and methods

2.1. Sampling sites and watershed characteristics

The sampling sites were selected based on land cover and land use characteristics. Four watershed types were selected: urban, agricultural, mining, and oil and gas (Fig. 1). W1 is an urbanized watershed (89.9 % developed; 6.10 % forested) and is the smallest in size at 39 km^2 (Dewitz, 2021). W2 is 660 km^2 and its land use consisted of approximately 8.31 % cultivated cropland (37.2 % corn, 32.5 % soybeans, and 9.20 % winter wheat; USDA-NASS, 2023), 11.7 % hay/pasture, 67.0 % forested (59.8 % deciduous forest), and 4.97 % developed area. There were approximately 40,700 cattle throughout the three counties that W2 spanned (USDA, 2022). Portions of the watershed also lie within the Western Coal Field of Kentucky resulting in approximately 4 % of the area defined as inactive (3.49 %) or reclaimed mine land (0.749 %). W3 was 484 km^2 and defined as 78.4 % forested (71.4 % deciduous forest, 6.90 % mixed forest), 8.50 % herbaceous, 5.17 % developed, and 3.51 %

barren according to the 2019 National Land Cover Dataset. However, 70.3 % of the watershed is defined as active, inactive, or reclaimed surface mining (Horn, 2021) in which native Appalachian forests do not reestablish on most post-mining landscapes, shifting the land cover from a forested ecosystem to grassland/shrubland (Pericak et al., 2018). W3 also had 58 oil and gas wells equating to 0.120 wells km^{-2} (KGS, 2022). The watershed, W4, was the largest in area at 3320 km^2 and extended into Kentucky, Virginia, and West Virginia. The land cover for W4 consisted of 87.1 % forested, 4.86 % developed, and 6.98 % herbaceous, hay/pasture, and shrubs. Additionally, 44.3 % of W4 fell within a permitted mine boundary (Horn, 2021; WVDEP, 2017) with extensive mining and coal processing, and contained the highest number of oil and gas wells (5040) of the studied sites equating to 1.52 wells km^{-2} (KGS, 2022; VaEnergy, 2022; WVDEP, 2016).

The watersheds also varied by geology and topography. W3 and W4 were in the Appalachian Mountain Plateau and had an elevation relief of 378 m and 868 m, respectively (USGS, 2022) whereas W1 and W2 had a relief of 57.9 m and 143 m, respectively, and were located within a karst landscape (Paylor and Current, 2001). The major lithologic constituents for W3 and W4 consisted of approximately 40 % sandstone, 35 % shale, 15 % siltstone, 10 % coal, and < 5 % limestone (Noger, 1988), while W1 was predominantly 90 % limestone and 10 % shale. In contrast, W2 was comprised of 70 % siltstone, 30 % sandstone, and some limestone and coal. As for soil type, W1 was predominantly composed of Bluegrass-Maury Silt Loam along with hydrologic soil group (HSG) B soils with moderate infiltration rates consisting of sandy loam or loam soils and HSG C soils with low infiltration rates consistent with sandy clay loams (NRCS, 2023). W2 was approximately 50 % HSG C (sandy clay loam) soils, 23 % HSG C/D (clay loam, silty clay loam, sandy clay loam) soils, and 17 % HSG B (sandy loam and loam) soils. The main soil classification was Zanesville Silt Loam. W3 was comprised of 40 % HSG A with high infiltration rates consistent with sand and loamy sand soil types, 35 % HSG B (silt loam and loam), and 25 % HSG C (sandy clay loam). The main soil classification for W3 was Shelocta-Highsplint-Gilpin complex in pre-mined or un-mined areas and Kaymine, Fairpoint, and Fiveblock soils in mined regions of the watershed (Williamson and Barton, 2020).

The soil type for W4 was defined as 40 % HSG A (sand and loamy sand) soils and 55 % HSG B (silt loam and loam) soils with the main soil classification being Pineville-Berks association.

The average temperatures during the growing season for the study region were 7.20 to 24.4 °C, peaking in July (NOAA, 2023). The average annual precipitation total for Kentucky was 1190 mm and the most amount of precipitation occurred in July with an average of 135 mm (PRISM, 2022). W2 received an annual average of 1300 to 1372 mm of precipitation while the other three watersheds received 1220 to 1300 mm (PRISM, 2022).

2.2. Field sampling procedures

Field sampling took place from March to October 2022 to analyze monthly contaminant signatures during the growing season and capture runoff associated with pesticide and fertilizer applications. Polar organic chemical integrative samplers (POCIS) and grab samples were used to collect water samples. POCIS is a type of passive sampler that can be used to determine a time-weighted average (TWA) of concentrations at a given sampling point by binding water-soluble polar organic compounds moving through the water column (Alvarez et al., 2004; Satiroff et al., 2020). The POCIS utilized in this study were hydrophilic-lipophilic balanced (HLB). POCIS canisters were deployed monthly at each site and placed perpendicular to stream flow in the middle of the channel and secured in the stream by chaining to a bridge or a nearby tree. Each sampling period lasted approximately one month (26–35 days, Table 1S). At the conclusion of each sampling period, the POCIS were retrieved and a new set was installed at the same locations. The POCIS were deployed seven times to determine monthly concentrations of neonicotinoids and strobilurin pesticides along with PPCPs (EPA 1694 Group 1). After retrieving the POCIS from the field, membranes were wrapped in aluminum foil to limit photodegradation that could occur post-sampling. To limit the membranes from drying out and further contaminant degradation, the membranes were placed on ice in a cooler and then stored at <0 °C until they were shipped for analysis. Sample holding time was <60 day from collection to analysis.

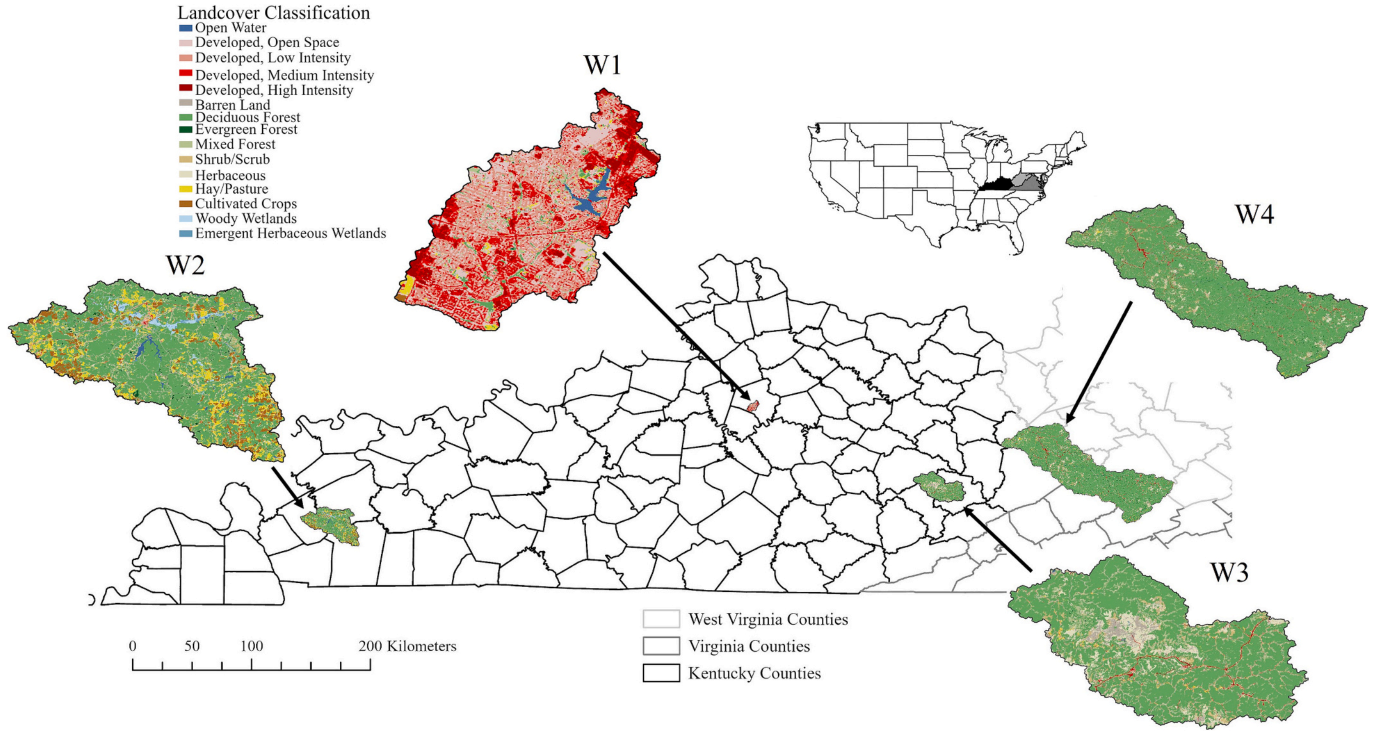


Fig. 1. Field sites with the dominant land cover and land use practices (Dewitz, 2021).

Grab samples were utilized to determine concentrations of glyphosate, trace elements, dissolved organic carbon (DOC), and nutrients (i.e., ammonia (NH_3), nitrate-N (NO_3-N), total nitrogen (TN), orthophosphate (PO_4-P), total phosphorous (TP), sulfate (SO_4^{2-}), bromide (Br^-), chloride (Cl^-)). Grab samples were taken at the beginning and end of each sampling period for a total of eight sample points. Additional grab samples were also taken if a POCIS canister was missing or damaged to help determine the concentrations of neonicotinoids and PPCPs at the time of sampling (Table 1S). Table 1 outlines the sample container, preservation, storage method, laboratory, and analysis used for each contaminant.

Additional stream characteristics (e.g., pH, dissolved oxygen, specific conductance, discharge, depth, water temperature, stream profile) were also measured at each sampling point. Specific conductance (SPC), pH, and dissolved oxygen (DO) concentrations were measured monthly at each site using a YSI handheld multimeter (YSI Incorporated, Yellow Springs, OH). United States Geological Station (USGS) gauge stations were located at W1, W2, and W4 sites and were utilized to determine continuous discharge and water depth. W3 did not have a nearby USGS monitoring gauge; therefore, a HOBO® U20L04 Water Level Logger (Onset, Cape Cod, MA) was installed to collect continuous water depth measurements and site surveys using a SonTek River Surveyor® M9 ADCP (Xylem, Washington D.C.) was used to determine stream morphology and velocity. Additionally, HOBO® Pendant® Temp/Light MX2202 (Onset, Cape Cod, MA) Loggers were installed at all monitoring locations to determine continuous water temperature and measure light fluxes on the POCIS to account for potential implications for photodegradation on the membranes.

2.3. *Water quality analysis*

Four POCIS membranes were deployed each sampling period at the four sites. Two membranes were composited and analyzed for neonicotinoids and strobilurin pesticides and the remaining two membranes were composited and analyzed for PPCPs. Pesticides and PPCPs samples were processed and analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS; Snow et al., 2020). Isotopically labeled internal standards were used for calibration based on availability of compounds. Surrogates were added at the beginning of the processing to evaluate effects of ion suppression or enhancement from sample matrices. Fortified blanks, fortified matrix, and reagent blanks were run at a frequency ≥ 5 % each (1 for every 20 field samples). Compound recovery for the spiked standards (Table 3S) along with method detection limits (MDL; Table 2S) for each analyte are presented in the supplementary materials.

The water grab samples were either shipped or hand-delivered to the appropriate laboratories for analysis within two days of collection. The analysis method for each contaminant is listed in Table 1. Briefly, nutrients were analyzed using ion chromatography and followed methods SM 4500 for NH_3 and TN, EPA Method 365.3 for TP, and EPA Method 9056A for NO_3-N, PO_4-P, SO_4^{2-} and Cl^- analysis. Dissolved organic carbon was analyzed with high temperature combustion using a total organic carbon analyzer and EPA Method 415.1. Trace elements were digested according to EPA Method 3015 A (SW-846) and analyzed for total recoverable element concentrations with an inductively coupled plasma-mass spectrometry (ICP-MS) based on EPA Method 200.8. Glyphosate was analyzed using ICP-MS following Guo et al. (2005). The remaining pesticides and PPCPs grab samples were analyzed using a high performance liquid chromatography and tandem mass spectrometry (HPLC/MS/MS) when samples were collected (Table 1S).

2.4. *Estimated concentrations for POCIS*

The analysis of the POCIS extracts resulted in a measured mass for each analyte per membrane. The TWA concentrations were determined using the recovered mass from extracts and experimentally determined uptake rates for each analyte:

$$C_w = \frac{N}{R_s * t} \tag{1}$$

where C_w was the ambient chemical concentration (ng L^{-1}), N was the mass accumulation (ng), R_s was the experimentally determined uptake rates for POCIS (L d^{-1}), and t was the exposure time in days (d; Ahrens et al., 2015; Noro et al., 2020). Experimentally determined uptake rates were based on published values in the literature (Table 4S).

2.5. *Statistical analysis*

A statistical assessment was completed to determine relationships between sites, sampling date, and individual contaminant. All data were log-transformed and analyzed with R studio (RStudio, 2021) using one-way analysis of variance (ANOVA) with post hoc Tukey honest significance difference (HSD). Principal component analysis (PCA) was performed to describe the relationship between the land cover, physiochemical, and contaminant properties of the four watersheds. The log-transformed variables were standardized by subtracting each of the values by its mean and dividing them by the standard deviation to ensure each variable had the same level of contribution to the analysis. Then the covariance matrix, eigenvectors, and eigenvalues were calculated. The top two principal components were selected for data analysis. The square cosine value (cos2) for each variable concerning the first two

Table 1
Sampling and analysis procedures for grab samples.

Contaminant	Sample container	Preservation and storage methods	Analysis laboratory	Analysis reference
Nutrients and Inorganic Ions	250 mL polypropylene bottle	Stored at 4 °C	Kentucky Geological Survey (Lexington, KY)	APHA et al., 2017; EPA, 1978, 2007c
Dissolved Organic Carbon (DOC)	250 mL polypropylene bottle	Filtered, Acidified with Sulfuric Acid and stored at 4 °C	Biosystems and Agricultural Engineering Water Quality Laboratory (Lexington, KY)	EPA, 1999
Trace Elements	50 mL metal-free polypropylene vial	Acidified with Nitric Acid and stored at 4 °C	Analytical Chemistry Core for Environmental Sciences, University of Kentucky (Lexington, KY)	Samples were digested (EPA, 2007b) and then analyzed for total recoverable element concentrations (EPA, 1994)
Glyphosate	125 mL polypropylene bottle	Stored at <6 °C	Nebraska Water Sciences Laboratory (Lincoln, NE)	Guo et al., 2005
Herbicide[a]	1 L amber glass jar	Stored at < 6 °C	Nebraska Water Sciences Laboratory (Lincoln, NE)	Cassada et al., 1994
Neonicotinoids[a]	250 mL amber glass bottle	Stored at < 6 °C	Nebraska Water Sciences Laboratory (Lincoln, NE)	Magalhaes et al., 2009
Human pharmaceuticals[a]	250 mL amber glass bottle	Stored at < 6 °C	Nebraska Water Sciences Laboratory (Lincoln, NE)	EPA, 2007a

[a] Collected only if the POCIS was missing for the sampling period.

principal components was used to compare the contribution of each variable.

3. Results and discussion

3.1. Stream physiochemical characteristics

Over the sampling period, the physiochemical characteristics of the stream (e.g., temperature, discharge, pH, SPC, DO) changed between each site. Overall, W4 had the largest discharge and W1 had the smallest discharge (Table 2), which was unsurprising given their differences in watershed areas (Galster, 2007). It is important to note several flooding events, during March, April, and August when W2 experienced high-water conditions where stream waters were in the floodplain during the sampling events. A major flooding event occurred during July 25th to 30th where an unprecedented 35 to 40 cm of rain fell over W3 (Table 2), equating to a 1 in 1000-year rainfall event (Kohli, 2022). Due to the flood, sampling during August at W3 and W4 did not occur due to limitations in access to the sites and concerns about safety. The POCIS and depth logger for W3 were lost in the flood, resulting in missing discharge and contaminant data for July.

Mean water temperature values for all the sites ranged from 10.6°C in the early spring to 28.7°C in mid-summer (Table 3). Water pH values also remained consistent throughout the sampling period ranging from 6.73 in March for W2 to 8.17 in July for W3. Overall, W1 and W2 had the lowest DO values throughout the sampling period ($Sep_{W2} = 1.78$ mg L^{-1}; $Oct_{W1} = 3.61$ mg L^{-1}) which were below a freshwater criteria limit (>5 mg L^{-1}; NREPC, n.d.). W3 had the highest DO values ($Oct_{W3} = 14.01$ mg L^{-1}) whereas larger and faster-moving mountain streams tend to have higher DO with increased mixing and movement of the water (Canadell et al., 2020). There was an inverse relationship between DO and SPC and temperature where increased temperatures and SPC values resulted in lower DO levels. Morosanu et al. (2016) found similar results and concluded that the increases in DO resulted from the elimination of pollutants that cause turbidity, as shown by the decreased SPC values. As for temperature, cold water can hold more dissolved oxygen than warmer water driving seasonal variations (Rajwa-Kuligiewicz et al., 2015).

The SPC for W3 had significantly ($\alpha < 0.05$) higher values for all sampling periods. Surface mining operations in the Appalachian Mountains have been linked to increased salinity resulting in SPC values ranging from 68.0 μs cm^{-1} to 3050 μs cm^{-1}, with the major ionic constituents in surface water receiving mining discharge being SO_4^{2-}, alkalinity, magnesium (Mg^{2+}), calcium (Ca^{2+}), Cl^-, and sodium (Na^+; Armstead et al., 2016). Additionally, in the Central Appalachians, an SPC threshold of 300 μS cm^{-1} is deemed protective of aquatic biota (EPA, 2011), and all the samples collected in W3 and W4 were well above that level. As for W2, dramatic changes in SPC in October can be an indicator of anthropogenic pollution such as agricultural fertilizer runoff with increases in NO_3^- and PO_4^{3-} or wastewater pollution with increases in Cl^- (de Sousa et al., 2014; Harwell et al., 2008) however, this was not the case. Rather, the site's high conductivity in October could have been due to low water levels (0.029 m^3 s^{-1}) concentrating ions in the stream.

3.2. Nutrients

Nitrogen (i.e., NO_3-N) and phosphorous (i.e., PO_4-P, TP) species were significantly ($\alpha < 0.05$) higher in W1 (89.9 % urban, 2.21 % agriculture) and second highest in W2 (4.97 % urban, 22.5 % agriculture; Fig. 2). While TN (0.900–1.82 mg N L^{-1}) was highest for W1, there was not a significant difference between the urbanized (W1) and agricultural (W2; 0.480–2.00 mg N L^{-1}) watersheds. Additionally, W2 had the highest concentrations of NH_3^+ (0.036–0.292 mg NH_3^+ L^{-1}) but was not significantly different from W1 (0.011–0.109 mg NH_3^+ L^{-1}). However, both sites detected concentrations of NH_3^+ that were above a chronic criterion for freshwater organisms (0.05 mg L^{-1}) except for May (0.036 mg NH_3^+ L^{-1}) for W2 and March (0.011 mg NH_3^+ L^{-1}), May (0.02 mg NH_3^+ L^{-1}), September (0.049 mg NH_3^+ L^{-1}) and October (0.049 mg NH_3^+ L^{-1}) for W1 (EPA, 2014).

A wastewater treatment plant (WWTP) is present downstream of the W1 site, indicating that effluent discharge may not be contributing to nutrient concentrations in the urban stream, however, leaky sewage pipes and overflows with combined stormwater and wastewater networks have been shown to result in elevated levels of nutrients in the environment (Ellis and Butler, 2015). For all other sampling sites, a WWTP was upstream of the site (Table 1S). Increased nutrient concentrations in W1 are also due to non-point sources such as fertilizer applications to lawns, gardens, and recreational areas. The increased nutrient loads in W2 may also be attributed to fertilizer, livestock, and land-applied manure within the watershed (Gu et al., 2022) as well as point source discharge from wastewater treatment and septic systems (Katz et al., 2010).

W1 had significantly ($\alpha < 0.05$) higher concentrations of Cl^- (April

Table 2
Discharge values (Q; m^3 s^{-1}) and monthly precipitation totals (P; mm) for each site over the study period.

Month[a]	Variable		W1	W2	W3	W4
Mar	Q	Range	0.310–4.08	5.60–75.0	0.00–5.78	24.1–88.9
	(m^3 s^{-1})	Mean	0.700	34.7	1.99	50.4
	P (mm)	Total	102	131	40.1	57.7
Apr	Q	Range	0.660–11.3	6.14–115	0.00–8.59	25.4–52.9
	(m^3 s^{-1})	Mean	0.830	44.9	2.50	36.3
	P (mm)	Total	94.0	117	80.3	65.3
May	Q	Range	0.150–17.9	0.220–14.2	0.030–34.7	19.3–237
	(m^3 s^{-1})	Mean	0.510	2.66	3.24	48.8
	P (mm)	Total	102	102	153	166
Jun	Q	Range	0.050–7.16	0.060–15.1	0.00–1.24	12.6–42.7
	(m^3 s^{-1})	Mean	0.190	1.71	0.470	19.4
	P (mm)	Total	43.2	51.5	52.8	88.7
Jul	Q	Range	0.050–30.6	0.080–24.9	–	11.3–577
	(m^3 s^{-1})	Mean	0.560	1.56		86.8
	P (mm)	Total	185	175	441	337
Aug	Q	Range	0.070–17.1	0.540–44.7	–	16.0–65.9
	(m^3 s^{-1})	Mean	0.580	6.78		56.4
	P (mm)	Total	109	129	74.9	147
Sep	Q	Range	0.070–14.3	0.030–0.870	0.00–5.37	8.69–33.1
	(m^3 s^{-1})	Mean	0.230	0.290	1.32	14.4
	P (mm)	Total	17.8	32.8	97.8	62.2

[a] Mar: March; Apr: April; Jun: June; Jul: July; Aug: August; Sep: September.

Table 3
Stream physiochemical characteristics for each sampling event.[a]

Variable	Site	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
T (°C)	W1	14.4	14.1	21.5	26.3	27.9	26.8	24.7	15.0
	W2	10.6	12.1	20.6	26.9	25.0	25.6	25.8	16.0
	W3	17.3	17.0	20.7	28.8	25.9	–	28.0	15.9
	W4	12.1	13.8	20.3	22.4	25.1	–	25.4	15.5
pH	W1	7.90	7.85	8.20	7.73	7.85	8.00	7.74	7.61
	W2	6.73	8.05	7.50	7.67	7.31	7.25	6.86	6.97
	W3	7.33	8.02	7.80	7.97	8.17	–	8.16	8.01
	W4	6.79	7.61	7.80	7.85	8.07	–	8.16	8.02
SPC (μs cm^{-1})	W1	727	744	745	762	707	671	712	596
	W2	135	200	308	352	551	625	396	**807**
	W3	**726**	**1320**	**789**	**1010**	**1550**	–	**1760**	**2270**
	W4	**477**	**659**	**557**	**387**	**703**	**–**	**783**	**834**
DO (mg L^{-1})	W1	8.23	9.69	**4.50**	8.70	9.60	**4.94**	**4.43**	**3.61**
	W2	8.20	8.20	7.30	6.00	**4.00**	**3.68**	**1.78**	7.27
	W3	11.4	6.68	9.00	9.00	10.0	–	5.50	14.0
	W4	13.1	7.22	8.50	7.40	7.80	–	**4.91**	12.1

[a] The bolded values indicate that criteria limits for Kentucky surface waters were exceeded with criteria limits stated in Supplementary Materials. T: Temperature; SPC: Specific Conductivity; DO; Dissolved Oxygen; Mar: March; Apr: April; Jun: June; Jul: July; Aug: August; Sep: September; Oct: October.

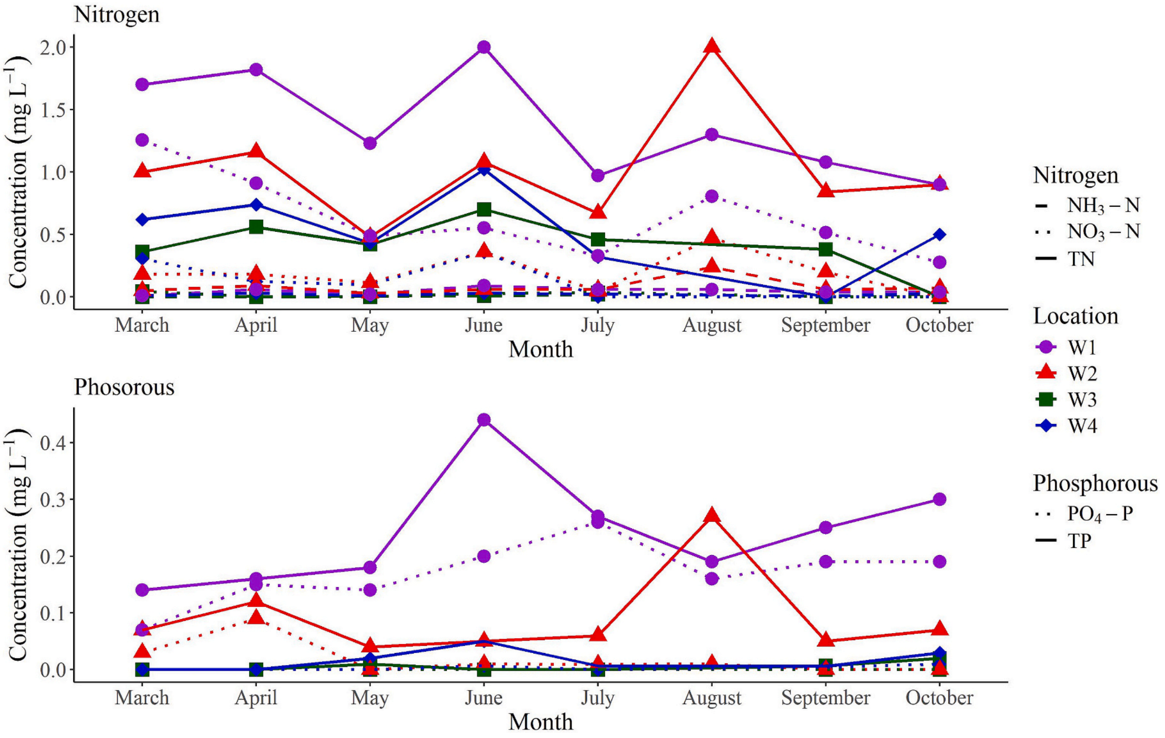


Fig. 2. Mean nitrogen (N) and phosphorous (P) concentrations (mg L^{-1}) for all site.

=126 mg L^{-1}) compared to the other sampled watersheds throughout the entire study period (Fig. 3). Chloride is commonly found in highly urbanized systems and can occur from road salts, wastewater, fertilizer, animal waste, irrigation, energy production wastes, and landfill leachates (Granato et al., 2015). However, it is likely that elevated levels of Cl$^-$ in the more urban watershed (W1) are mainly due to the dissolution of Cl$^-$ from the limestone geology in the region (Krawczyk and Ford, 2005; Lang et al., 2006).

The watershed with the highest activity of mining had significantly ($\alpha < 0.05$) greater concentrations of SO$_4^{2-}$ and exceeded an ambient water quality criterion for freshwater of 500 mg L^{-1} in 4 of the 8 months sampled (DEP, 2012; Fig. 4). In freshwater, SO$_4^{2-}$ is typically considered non-toxic, but at high concentrations, it can induce osmoregulatory stress in organisms (Soucek and Kennedy, 2005) while also contributing to the salinization of water bodies (Cañedo-Argüelles et al., 2013) and impact the biogeochemical processes of C, N, and P (Zak et al., 2021). Sulfate has also been found to increase Cl$^-$ induced corrosion of water pipes, leading to the release of metals in a drinking system (Sun et al., 2017). The higher SPC values for W3 also corresponded to the variation in SO$_4^{2-}$, indicating SO$_4^{2-}$ is the major ion driving the conductance of the stream. Elevated levels of SO$_4^{2-}$ in freshwater occur commonly in anthropogenically impacted waters and may be attributed to intensive mining and weathering of sulfide minerals and gypsum (Arkoc et al., 2016; Niu et al., 2018; Runtti et al., 2018). Several studies have reported high SO$_4^{2-}$ and SPC levels from mining activities in the same mined watershed examined in this study (Hutton et al., 2020; Hutton et al., 2021; Muncy et al., 2014; Price et al., 2018) and noted declines in salamander species abundance and occupancy within streams. Arkoc et al. (2016) measured SO$_4^{2-}$ ranging from 4 to 756 mg L^{-1} in surface waters downstream of coal mining in Turkey. Niu et al. (2018) found that SO$_4^{2-}$

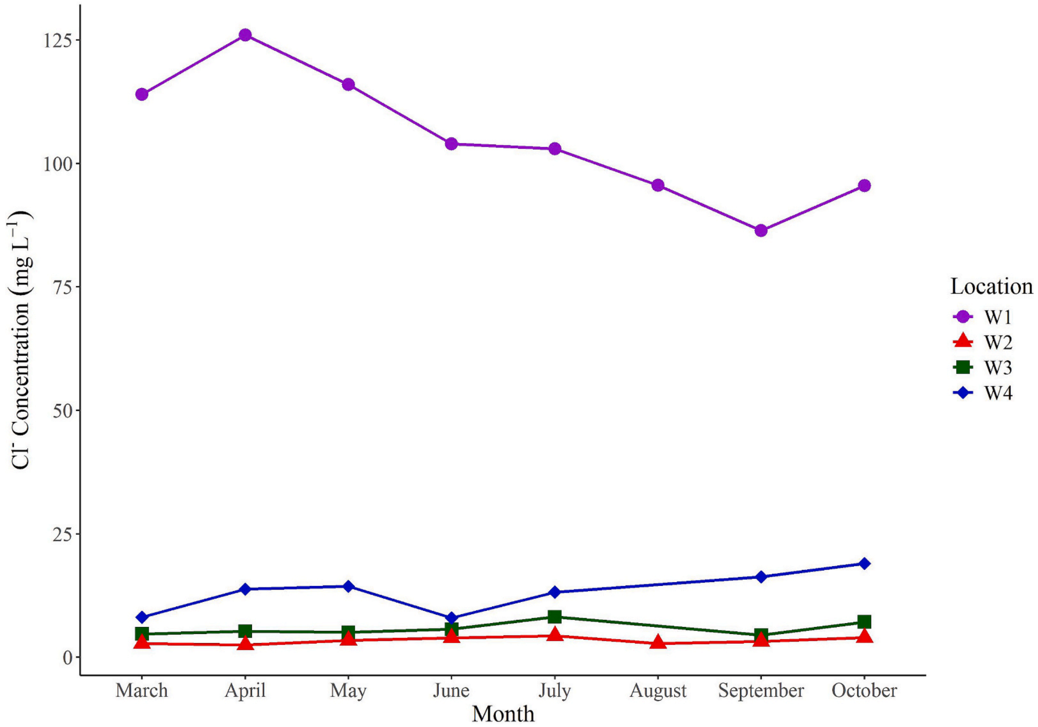


Fig. 3. Chloride (Cl^-) Concentrations in mg L^{-1} for all sites over the study period.

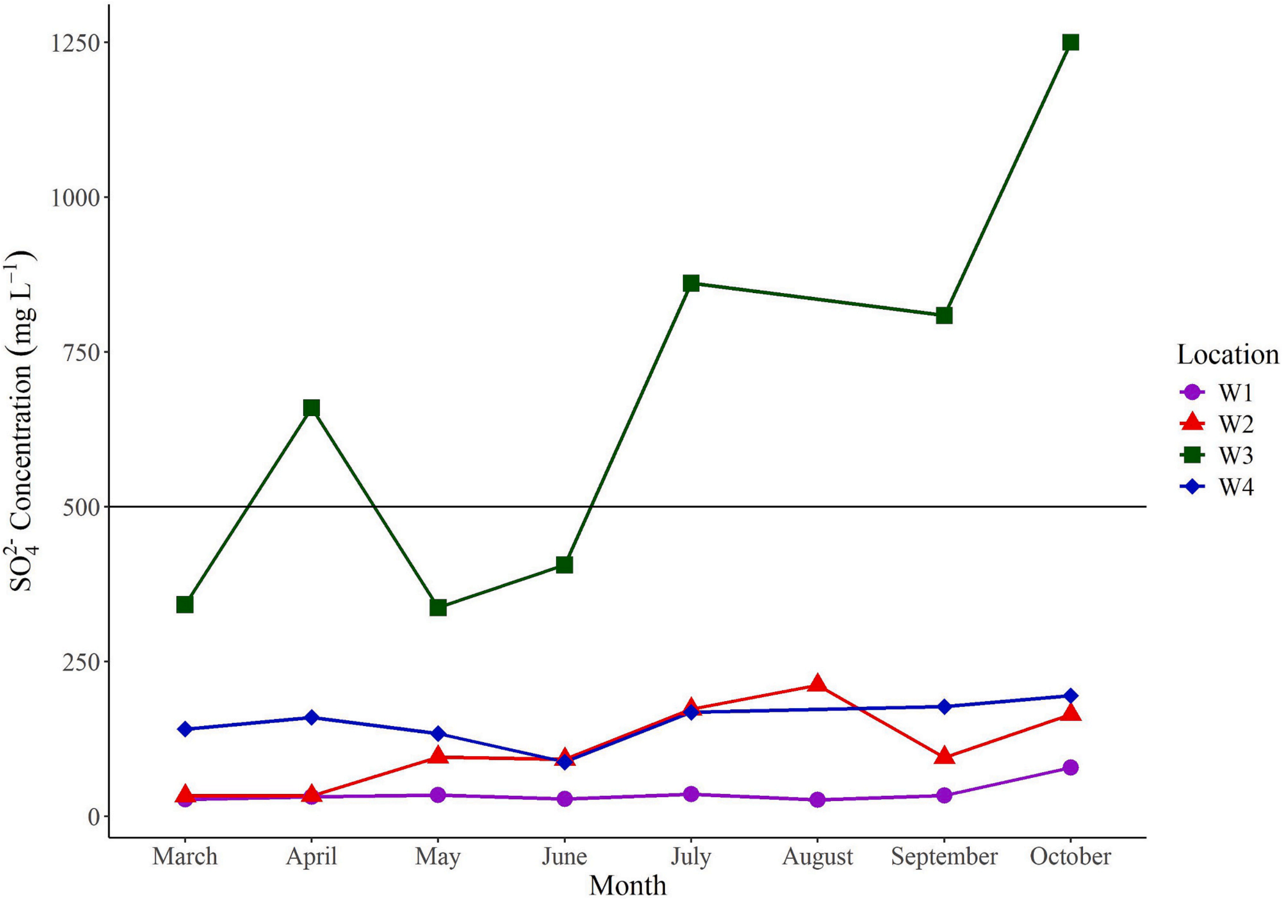


Fig. 4. Sulfate (SO_4^{2-}) concentrations (mg L^{-1}) for all sites over the study period. The solid horizontal line denotes the ambient water quality criterion for SO_4^{2-} in freshwater (500 mg L^{-1}).

increased above baseline levels in areas where there was intensive coal mining in Pennsylvania, peaking at 90,100 mg L^{-1} and median values of 100 mg L^{-1}.

The DOC ranged from 1.78 to 10.8 mg C L^{-1} (average = 4.41 mg C L^{-1}) for W4, BDL to 14.9 mg C L^{-1} (average = 6.27 mg C L^{-1}) W3, 2.93 to 15.7 mg C L^{-1} (average = 6.05 mg C L^{-1}) for W1 and 5.40 to13.4 mg C L^{-1} (average = 6.23 mg C L^{-1}) for W2. DOC concentrations were similar to or slightly higher than what has been reported for Kentucky surface waters (Hoppe-Jones et al., 2010; Lei et al., 2020; Yurista et al., 2001). For all locations, the DOC was highest during summer (July; $\alpha < 0.05$) and lowest during spring (March and April) and fall (October). DOC concentrations in streams have been shown to vary by land cover, stream slope, temperature, and precipitation (Cool et al., 2014). The results indicated a negative correlation between DOC and the 5-day rainfall totals for W1 (−0.29) and W2 (−0.52) and a positive correlation for W3 (0.11) and W4 (0.59). While there is often a positive correlation between precipitation and DOC, it has also been shown that precipitation events can also have a dilution effect where the amount of precipitation added to the stream exceeds the increasing levels of DOC from sediment and tree litter during rainfall events (Liu and Wang, 2022; Ruckhaus et al., 2023). Temperatures positively impact the production of DOC since it is a microbial-meditated process where warmer temperatures increase the activity of organic matter degrading enzymes (Gillooly et al., 2001; Wallenstein and Weintraub, 2008). Deciduous forests are associated with lower DOC concentrations (Cool et al., 2014), and in our study, the lowest DOC concentrations were found in W4 (83.7 % deciduous forest cover). DOC plays an important role in freshwater ecosystems, regulates carbon and energy cycling, and can alter aquatic chemistry by contributing to acidification and the formation of complexes with trace elements (Toming et al., 2020).

3.3. *Trace elements*

Sixteen trace elements were measured in water grab samples (Table 4). Trace elements can result from soil parent material and geologic formations and anthropogenic activities. For W2, iron (Fe) concentrations exceeded the chronic criterion for aquatic organisms (1000 μg L^{-}1) during March, July, and August and aluminum (Al) concentrations exceeded their chronic criterion for aquatic organisms (350–1400 μg L^{-1}) in March, April, August, and September (EPA, 2023b). The chronic criterion for aquatic organisms for Al depends on pH, alkalinity, and DOC and was calculated each month using the EPA's Aluminum Criteria Calculator (EPA, 2018). The discharge values at the time of sampling were 70.5 m^{3} s^{-1}, 44.9 m^{3} s^{-1}, 24.8 m^{3} s^{-1}, and 0.290 m^{3} s^{-1} respectively, and the mean annual flow for the stream is 9.00 m^{3} s^{-1} (Martin, 2002). During high streamflow events, sediments were likely washed into the stream due to erosion. Metals bind to sediments and suspend with the solids during the high flow and reducing conditions (Ekström et al., 2016). Iron and Al are naturally occurring throughout the region due to the rock and soil types present with mean ambient background soil concentrations of 11,000 mg Al kg^{-1} and 22,500 mg Fe kg^{-1} (EEC, 2004). Additionally, W2 is predominantly silty clay loams (68 % silt, 17 % clay, 3.6 % organic matter) where metals tend to bind with clay soils rich in organic matter. Elevated levels of trace elements beyond natural sources can also occur from industrial, agricultural (e.g., commercial fertilizers, liming materials, sewage sludges, irrigation, agrochemicals), and mining activities (He et al., 2005; Shan et al., 2019). W2 was located within the Western Kentucky Coal Fields which has been shown to contribute elevated levels of Fe, particularly in groundwater (Fisher and Davidson, 2007). The watershed also had the highest concentrations of manganese (Mn; $\alpha < 0.05$) peaking in July along with zinc (Zn) and lead (Pb) peaking in March.

W1 exceeded the chronic criteria for aquatic organisms for Al and Fe in July (932 μg Al L^{-1}; 1530 μg Fe L^{-1}) and September (582 μg Al L^{-1}; 1040 μg Fe L^{-1}). The elevated levels of Al and Fe in the watershed were likely due to residential runoff (e.g., roadways, vehicle traffic, roof runoff; Joshi and Balasubramanian, 2010; Reeves et al., 2018). W3 had the highest concentrations of strontium (Sr), a metal associated with mining activity, which was significantly ($\alpha < 0.05$) different from the concentrations detected in W1 and W2 (Clark et al., 2018; Clark et al., 2023). It was expected that W3 would also have elevated levels of Fe from the extensive mining activity in the watershed, however, the solubility and speciation are impacted by pH, which was between 7.3 and 8.2 resulting in lower concentrations of Fe in W3 (Tusher et al., 2015). Cadmium (Cd) was highest both in W3 and W4 and is often associated with mining and oil and gas activities (Clark et al., 2018; Johnston et al., 2019). Barium (Ba) was the highest in W4 and is used in drilling muds for oil and gas production (Ebrahimi and Vilcaez, 2018).

Table 4
Summarized trace element concentrations (μg L^{-1}) for each site over the study period. The bolded values indicate concentrations that exceeded ambient water quality criteria.[a]

Variable		W1	W2	W3	W4
Al	Range	67.2–**932**	108–**1440**	BDL - 87.7	46.7–476
	Mean	301	**758**	49.70	165
Cr	Range	BDL - 4.35	BDL - 5.14	BDL - 0.620	BDL - 2.53
	Mean	1.26	1.70	0.160	0.700
Mn	Range	35.6–253	72.1–1440	48.9–169	22.8–55.7
	Mean	120	660	88.1	35.4
Fe	Range	117–**1530**	379–**1820**	BDL - 261	165–738
	Mean	523	**1130**	166	333
Co	Range	0.205–1.25	0.597–3.25	0.323–0.867	BDL - 0.593
	Mean	0.573	1.46	0.593	0.346
Ni	Range	0.850–2.30	2.58–6.09	BDL - 3.41	BDL - 2.02
	Mean	1.42	3.80	2.17	1.13
Cu	Range	BDL - 10.6	BDL - 8.68	BDL - 1.61	BDL - 4.43
	Mean	3.55	3.00	0.390	2.50
Zn	Range	BDL - 18.2	6.87–37.4	BDL - 11.6	4.83–11.7
	Mean	8.84	13.7	5.95	7.92
As	Range	0.369–1.15	0.549–1.62	0.145–0.301	BDL - 0.690
	Mean	0.790	1.05	0.232	0.372
Se	Range	0.103–1.37	BDL - 0.108	0.197–0.658	BDL - 1.36
	Mean	0.430	0.103	0.356	0.792
Sr	Range	123–180	59.0–210	495–2000	374–810
	Mean	146	134	1060	653
Cd	Range	BDL - 0.036	BDL - 0.241	BDL - 0.031	BDL - 0.010
	Mean	0.011	0.068	0.011	0.012
Ba	Range	22.2–39.4	32.8–66.7	26.6–65.5	46.9–75.8
	Mean	30.4	50.1	41.5	61.3
Hg	Range	BDL - 0.048	BDL - 0.091	BDL - 0.153	BDL - 0.080
	Mean	0.018	0.031	0.063	0.034
Pb	Range	0.300–2.84	0.479–4.28	0.124–0.327	BDL - 1.03
	Mean	1.23	1.80	0.220	0.479
U	Range	0.214–1.27	0.116–0.697	0.124–2.73	0.000–1.03
	Mean	0.482	0.421	1.17	0.488

[a] BDL: below detection limit. The bolded values indicate concentrations that exceeded ambient water quality criteria.

3.4. *Pesticides*

In total, 38 pesticides or pesticide by-products were analyzed, 35 were analyzed using the POCIS and 3 pesticides, glyphosate, AMPA, and glufosinate, were collected via grab sampling. Of the pesticides sampled, only seven (i.e., 6-chloronicotinic aldehyde, 6-chloro-*N*-methylnicotinamide, dimethoate, sulfoxaflor, thiacloprid, tefluthrin, trifloxystrobin), were not detected (Tables 5 and 6).

Watersheds W1 (89.9 % urban; 2.21 % agriculture) and W2 (3.97 % urban; 22.5 % agriculture) had the highest concentrations of imidacloprid and its by-products throughout the sampling period compared to the other sites (Table 5). All imidacloprid formations and by-products peaked in July (Fig. 5; $\alpha < 0.05$). Imidacloprid is a widespread neonicotinoid insecticide commonly found in both urban and agricultural watersheds (Satiroff et al., 2020). In urban settings, imidacloprid is used to manage pests in grassy areas such as parks, golf courses, and lawns (Mourikes et al., 2023) and is also used in flea and tick medicine where

Table 5

Summarized concentrations of the sampled insecticides (ng L^{-1}). The bolded values indicate concentrations that exceeded ambient water quality criteria.[a]

Variable		W1	W2	W3	W4
6-Chloronicotinic acid	Range	BDL	BDL - 0.751	BDL	BDL
	Mean	BDL	BDL	BDL	BDL
6-Hydroxynicotinic acid	Range	49.1–225	60.7–643	61.1–145	30.2–43.5
	Mean	119	279	115	38.9
Azoxystrobin	Range	0.325–1.46	0.078–3.10	BDL	BDL
	Mean	0.760	0.880	BDL	BDL
Clothianidin	Range	0.800–6.94	2.38–45.0	BDL - 0.354	BDL - 0.234
	Mean	2.06	11.3	0.270	0.090
Dinotefuran	Range	0.300–5.78	BDL - 6.61	BDL	BDL - 0.137
	Mean	3.58	1.28	BDL	0.030
Imidacloprid	Range	1.73–**17.8**	1.37–**22.7**	BDL	0.034–0.460
	Mean	7.78	6.06	BDL	0.170
Imidacloprid desnitro	Range	14.4–83.3	4.54–66.0	BDL	0.150–1.34
	Mean	51.5	30.4	BDL	0.640
Imidacloprid olefin	Range	BDL	BDL	BDL - 0.090	BDL
	Mean	BDL	BDL	BDL	BDL
Imidacloprid urea	Range	12.1–82.2	3.78–62.4	BDL	BDL
	Mean	47.3	28.6	BDL	BDL
Metalaxyl	Range	0.210–4.00	0.150–7.65	BDL	BDL
	Mean	1.11	2.21	BDL	BDL
Picoxystrobin	Range	BDL - 0.650	BDL - 0.170	BDL	BDL
	Mean	0.110	0.050	BDL	BDL
Pyraclostrobin	Range	BDL - 0.180	BDL –1.03	BDL	BDL
	Mean	0.060	0.180	BDL	BDL
Thiamethoxam	Range	0.113–1.70	0.604–14.2	BDL	BDL - 0.074
	Mean	0.660	3.40	BDL	0.030
Thiamethoxam urea	Range	BDL	BDL - 0.717	BDL - BDL	BDL
	Mean	BDL	0.140	BDL	BDL

[a] BDL: below detection limit.

urban systems often have a larger density of domesticated household pets and dog parks. More recently, imidacloprid was used as a soil drench to treat emerald ash borer, a common infestation in trees in W1 (Larson and Crocker, 2022). Due to common detection in urban streams, imidacloprid is listed as an urban signature pesticide with increasing toxicity related to an increase in urbanization (Nowell et al., 2021).

The loading of imidacloprid in the environment has increased approximately 50 times in the past 20 years and has been linked to the killing of non-target insects like pollinators (Motaung, 2020). While the nicotinic agonist of the acetylcholine receptor (nAChR) for the target species is assumed to be specific to insects, some studies have shown toxicity implications for mammals (Kimura-Kuroda et al., 2012) including humans (Loser et al., 2021). An aquatic life benchmark for imidacloprid is set as the chronic criterion for freshwater invertebrates is 0.01 μg L^{-1} (EPA, 2023a). W1 exceeded the criterion during May, June, and July, and W2 exceeded the criteria in June. Even more, imidacloprid metabolites (e.g., imidacloprid desnitro, imidacloprid urea, imidacloprid olefin) are often more toxic than the parent compound and can increase the potency in mammals compared to insects (Chao and Casida, 1997; Huang et al., 2021; Liu et al., 1993; Tomizawa and Casida, 2000). The main pathway for the degradation of imidacloprid into its byproducts is through photodegradation with a half-life of 0.2 days in water with light exposure, but can also occur through hydrolysis, chlorination, and biological processes (e.g., microbial, fungal, plant; Loser et al., 2021).

The herbicides, alachlor and atrazine, were found in larger concentrations (2190 ng atrazine L^{-1}; 823 ng alachlor L^{-1}) in W2, peaking in June, compared to the other sampled sites. Atrazine is the most common pesticide found in agricultural surface waters due to its widespread use for controlling certain annual broadleaf and grass weeds and is primarily used for corn, but also applied to sorghum, sugarcane, and other crops. Alachlor has similar uses but is predominately used on corn and soybean fields, the most common crops grown in the watershed (USDA-NASS, 2023). Because of the herbicides' water solubility and association with the pre-emergent application, the high concentrations are likely attributable to the spring flush (Battaglin et al., 2003; Hansen et al., 2019; Mottim et al., 2021; Rinsky et al., 2012; Thurman et al., 1991). For example, Battaglin et al. (2003) found concentrations of 4070 ng atrazine L^{-1} and 50 ng alachlor L^{-1} in agricultural streams after the first precipitation event following application where low-flow conditions produced 170 ng atrazine L^{-1} and <50 ng alachlor L^{-1}. Additionally, Hansen et al. (2019) detected mean atrazine concentrations of 1.29 μg L^{-1} with a maximum concentration of 175 μg L^{-1} predominately in the early growing season in watersheds with a high amount of corn production and heavy precipitation in the United States. Both herbicides can be a threat to non-target aquatic species (Graymore et al., 2001; Hayes et al., 2010; Pereira et al., 2021). However, all concentrations detected throughout the sampling period were below the EPA's chronic aquatic life benchmarks of 5 μg L^{-1} and 187 μg L^{-1} for fish and 60 μg L^{-1} and 100 μg L^{-1} for invertebrates for atrazine and alachlor, respectively (EPA, 2023a).

Glyphosate, used to manage unwanted weeds in agriculture but can also be used in pastureland, forestry, lawn care, gardens, and paved areas (Hébert et al., 2018), was also detected. It was hypothesized that all herbicides would peak in the early summer months following the first rainfall event post application and would be highest in W2, since it had the most agricultural land cover. However, the largest glyphosate concentrations were detected during August through September in W3, a watershed with little agricultural activity (0.9 % hay/pasture; Dewitz, 2021). As mentioned previously, a 1 in 1000-year rainfall event occurred over W3 from July 25th to 30th, corresponding with the peak glyphosate concentrations. A report written by the Ohio River Valley Institute and Appalachian Citizens' Law Center (Dixon and Shelton, 2023), estimated that approximately 9000 homes were damaged by the flood. Entire homes and garages were swept away by flood waters, and it is likely that chemicals stored in those buildings were spilled and led to the high concentrations detected.

3.5. *Human use pharmaceuticals and personal care products*

The last class of contaminants analyzed was PPCPs. In total 47 PPCPs were analyzed using the POCIS samples and 29 analytes were not

Table 6
Summarized concentrations of the sampled herbicides (ng L^{-1}).[a]

Variable		W1	W2	W3	W4
Alachlor	Range	1.15–41.2	BDL - 823	0.169–3.99	BDL - 0.373
	Mean	11.6	169	0.737	0.112
Atrazine	Range	3.06–110	BDL - 2190	0.450–10.6	BDL - 0.99
	Mean	30.8	450	1.96	0.300
Butylate	Range	BDL - 5.58	BDL - 2.37	BDL - 4.54	BDL
	Mean	2.31	1.26	0.649	BDL
Cyanazine	Range	BDL - 3.79	BDL	BDL	BDL
	Mean	0.560	BDL	BDL	BDL
DEA	Range	BDL - 13.1	BDL - 3.60	BDL - 0.734	BDL
	Mean	3.26	0.93	0.217	BDL
Dimethenamid	Range	BDL - 5.76	BDL - 13.6	BDL - 4.21	BDL - 4.11
	Mean	3.86	3.94	0.601	0.720
EPTC	Range	BDL - 14.7	BDL - 2.62	BDL - 2.50	BDL - 1.04
	Mean	3.06	0.460	0.602	0.210
Metolachlor	Range	BDL - 42.8	BDL - 537	BDL - 6.05	BDL - 4.08
	Mean	12.0	105	0.865	0.700
Metribuzin	Range	BDL - 2.54	BDL	BDL	BDL
	Mean	0.380	BDL	BDL	BDL
Norflurazon	Range	BDL	BDL	BDL	BDL - 6.81
	Mean	BDL	BDL	BDL	1.16
Pendimethalin	Range	BDL	BDL - 0.580	BDL	BDL
	Mean	0.990	0.200	BDL	BDL
Prometon	Range	BDL - 8.76	BDL - 3.06	BDL	BDL - 3.84
	Mean	5.02	0.540	BDL	0.970
Propachlor	Range	BDL	BDL - 4.08	BDL	BDL
	Mean	BDL	0.71	BDL	BDL
Propazine	Range	BDL - 2.26	BDL - 26.7	BDL	BDL - 1.02
	Mean	0.410	5.51	BDL	0.362
Glyphosate	Range	BDL	BDL	BDL - 91,700	BDL
	Mean	BDL	BDL	19,900	BDL
AMPA	Range	BDL	BDL	BDL - 34,100	BDL
	Mean	BDL	BDL	10,600	BDL
Glufosinate	Range	BDL	BDL	BDL - 121,000	BDL
	Mean	BDL	BDL	28,700	BDL

[a] BDL: below detection limit.

detected or BDL. The largest detection of PPCPs was caffeine observed in March at 553 ng L^{-1} in W4 (4.86 % urban) and the second highest (260 ng L^{-1}) in W2 (4.97 % urban; Table 7). The peak concentration in March is likely due to the cooler water temperatures throughout the month since caffeine degrades quicker in warmer environments resulting in lower concentrations of caffeine observed throughout the summer (Table 3; Hillebrand et al., 2012a). Hillebrand et al. (2012a) detected mean caffeine concentrations in freshwater of 10.3 ng L^{-1} with higher concentrations occurring during the winter months and after a precipitation event. In general, caffeine is removed efficiently during wastewater treatment; however, at times the amount of caffeine that enters the water is greater than what can be degraded during treatment (Zhu et al., 2013). The half-life of caffeine is also shown to be stable in the aquatic environment with 100 to 240 d (Hillebrand et al., 2012b). Another study detected caffeine concentrations ranging from 118 to 735 ng L^{-1} in August and September in the United Kingdom resulting from untreated or poorly treated wastewater (Nakada et al., 2017).

Acetaminophen (18.6 ng L^{-1}) and cotinine (29.1 ng L^{-1}; $\alpha < 0.05$) were also highest in W2 during March. Sulfamethoxazole was the only PPCP detected that was highest for W1 (89.9 % urban), peaking in July at 10.9 ng L^{-1} ($\alpha < 0.05$). Sulfamethoxazole is persistent in sediments, potentially limiting its detection in water bodies (Conkle et al., 2012). The two most predominant PPCPs found at elevated concentrations in the environment are caffeine and acetaminophen attributed to their high consumption (Osuoha et al., 2023).

All four of the PPCPs discussed are efficiently removed (>70 %) by WWTP (Buerge et al., 2008; Osuoha et al., 2023; Wu et al., 2023; Zhu et al., 2013). A high proportion of caffeine in the environment is evidence of untreated sewage (Daneshvar et al., 2012) and can be an indicator for the presence of other PPCPs (Hillebrand et al., 2012a). Katz et al. (2010) analyzed groundwater samples in a karst environment, similar to the geology of W1 and W2, and observed that septic systems resulted in the detection of caffeine, acetaminophen, and sulfamethoxazole. The study region has had a long history of wastewater problems and unpermitted sewage discharge, leading to environmental harm (EPA, 2002). An estimated 40 % of Kentucky households are not connected to a centralized sewer system with approximately 33 % of rivers and streams in Kentucky impaired with high levels of pathogens (EPA, 2002). For W4, approximately 11 % of the households in the sampled county are on a public sewer system compared to 97 % of households in W1 (KIA, 2015). Additionally, both W3 and W2 have 90 % and 95 % of the wastewater lines over 20 years old respectively (KIA, 2015). While PPCPs are efficiently removed during water treatment, the use of non-centralized sewer systems and aging infrastructure could be leading to the detection of PPCPs in these rural watersheds.

Furthermore, the only PPCP that occurred at just one of the sites was codeine, an opioid pain reliever, and was only detected in W4. Rodayan et al. (2016) detected codeine in surface (25–100 ng L^{-1}), wastewater effluent (350 ng L^{-1}), and drinking water samples (50 ng L^{-1}) linking drug abuse and the impact on downstream water sources. Among the counties in W4, there is an elevated rate of overdoses from drug abuse with an opioid overdose morality rate of 414.2 (deaths per 100 k population) compared to the national rate of 27.3 from 2018 to 2021 (NORC, 2024). Thus, not only can measuring PPCP in surface waters help to target areas for wastewater infrastructure improvements, but the presence of codeine in this rural Appalachian watershed highlights the potential use to target areas for public health and community resources related to drug abuse.

3.6. *The impact of land use and land cover practices on contaminant mixtures*

A PCA analysis was conducted to understand the relationship between land cover, water chemistry, and water quality. The PCA analysis was first conducted utilizing the entire dataset including land cover (i.e., percent urbanized area, percent agricultural area, percent mining area, density of oil and gas wells), physiochemical properties, and contaminant concentrations. Analysis was completed using the top two components which explained 65.1 % and 10.4 % of the variance respectively. The analysis showed that the top contributing variables were percent mining area, imidacloprid and its degradation byproducts (i.e., imidacloprid desnitro, imidacloprid urea), azoxystrobin, Sr, metalaxyl, TP, thiamethoxam, and dinotefuran (Table 6S). The top contributing variables were grouped together, showing that they are all positively correlated to each other, except for mining and Sr which are grouped together opposite of the other variables. Imidacloprid olefin showed a negative correlation with imidacloprid and its other byproducts, likely due to the very low concentrations of imidacloprid olefin that were BDL for all site and events excluding W3 in September. The land cover seemed to have a larger influence than the water's physiochemical properties where most of the fungicides and insecticides positively correlated with the percent agricultural area. The PPCPs also were more positively correlated with the percent urbanized area and density of oil and gas wells. Discharge was positively correlated with glyphosate and percent mining areas, which aligns with the high concentrations of glyphosate following the flooding event in W3.

The PCA analysis was also run with the top four contaminants that

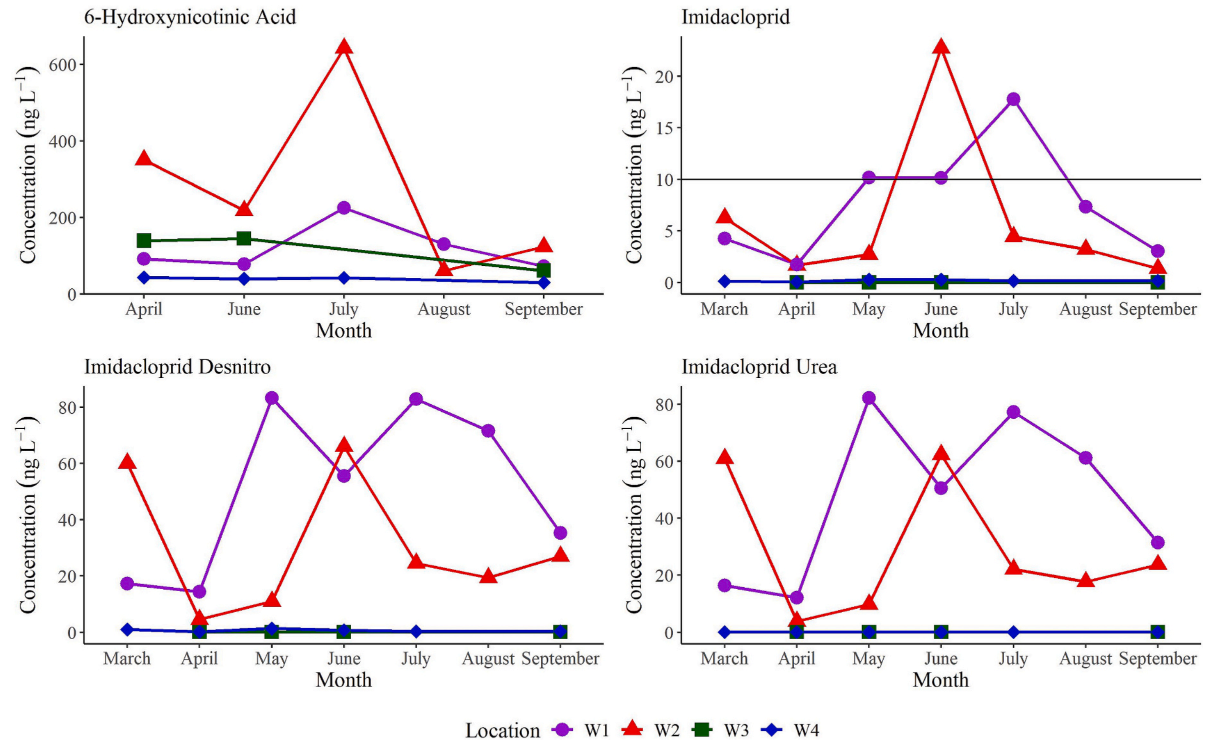


Fig. 5. POCIS-derived estimated concentrations of imidacloprid and its by-product over the study period for each site. The horizontal black line denotes the EPA's aquatic life benchmark for the chronic toxicity limit for freshwater invertebrates of 10 ng L^{-1} for imidacloprid (EPA, 2023a).

Table 7
Observed concentrations of human use pharmaceuticals and personal care products (PPCPs; ng L^{-1}) for each sampling location over the study period.[a]

Variable		W1	W2	W3	W4
1–7-Dimethylxanthine	Range	2.94–8.86	BDL - 9.52	BDL - 3.32	1.38–4.93
	Mean	4.58	2.74	1.98	2.65
Acetaminophen	Range	BDL - 1.70	BDL - 18.8	BDL - 5.13	BDL - 16.8
	Mean	0.278	2.84	2.08	4.61
Azithromycin	Range	BDL - 2.01	BDL	BDL - 0.130	BDL - 0.152
	Mean	0.400	BDL	0.048	0.060
Caffeine	Range	19.2–169	5.30–260	18.6–31.6	7.11–553
	Mean	103	48.1	24.7	131
Carbamazepine	Range	0.283–0.515	0.120–1.88	0.430–2.49	0.750–2.26
	Mean	0.390	0.717	1.13	1.29
Clarithromycin	Range	BDL - 1.38	BDL - 0.057	0.023–0.111	BDL - 0.236
	Mean	0.294	0.020	0.063	0.072
Codeine	Range	BDL	BDL	BDL	BDL - 0.598
	Mean	BDL	BDL	BDL	0.236
Cotinine	Range	6.99–15.6	3.07–29.1	1.05–3.28	0.960–7.39
	Mean	12.1	9.02	2.48	3.90
Diltiazem	Range	BDL - 0.123	BDL	BDL	BDL
	Mean	0.053	BDL	BDL	BDL
Diphenhydramine	Range	BDL - 0.060	BDL	BDL - 0.020	BDL - 0.182
	Mean	0.030	BDL	0.017	0.085
Erythromycin	Range	BDL - 0.120	BDL - 0.040	BDL - 0.030	0.016–0.044
	Mean	0.050	0.027	0.015	0.029
Fluoxetine	Range	BDL - 0.600	BDL	BDL	BDL - 1.08
	Mean	0.220	BDL	BDL	0.476
Lincomycin	Range	BDL - 0.430	BDL - 1.90	BDL - 0.060	BDL - 0.069
	Mean	0.090	0.325	BDL	BDL
Sulfadimethoxine	Range	BDL - 0.516	BDL - 0.196	BDL - 0.080	BDL - 0.233
	Mean	0.110	0.060	0.050	0.068
Sulfamethazine	Range	BDL	BDL - 0.040	BDL - 0.080	BDL
	Mean	BDL	0.022	0.025	BDL
Sulfamethoxazole	Range	0.200–10.9	BDL - 2.66	0.720–2.17	0.092–4.13
	Mean	4.76	0.606	1.43	2.23
Thiabendazole	Range	0.060–0.276	0.052–0.205	BDL - 1.83	0.022–0.088
	Mean	0.210	0.128	0.484	0.053
Trimethoprim	Range	BDL - 0.173	BDL	BDL - 0.190	BDL - 0.242
	Mean	0.042	BDL	0.068	0.129

[a] BDL: below detection limit.

had the highest concentrations in each category (i.e., nutrients, trace elements, pesticides, PPCPs) to reduce the number of variables and gain a better understanding of the relationship between land cover and contaminant concentrations (Fig. 6). The results of the analysis identified DOC had a positive correlation with the nutrients, Al, Fe, Mn, imidacloprid, atrazine, alachlor, and cotinine, while temperature (T) had a positive correlation with Cl^-, caffeine, and sulfamethoxazole. Both pH and SPC had a negative correlation with Al and Fe and a positive correlation with Sr, Cl^-, and sulfamethoxazole. DO and discharge both had a positive correlation with SO_4^{2-}, glyphosate, and acetaminophen.

4. Conclusion

Surface water sampling took place over eight months during the growing season to capture the seasonal variations in water conditions throughout four watersheds with varying land cover and land use practices (i.e., urban, agricultural, mining, oil and gas). In total, 77 different contaminants were detected throughout the sampling period in at least one of the watersheds. The contaminants ranged from commonly detected contaminants such as nutrients and trace elements to more emerging contaminants such as PPCPs and neonicotinoid insecticides.

The results supported the studies hypothesis, that the type of contaminants present would be impacted by land cover and land use

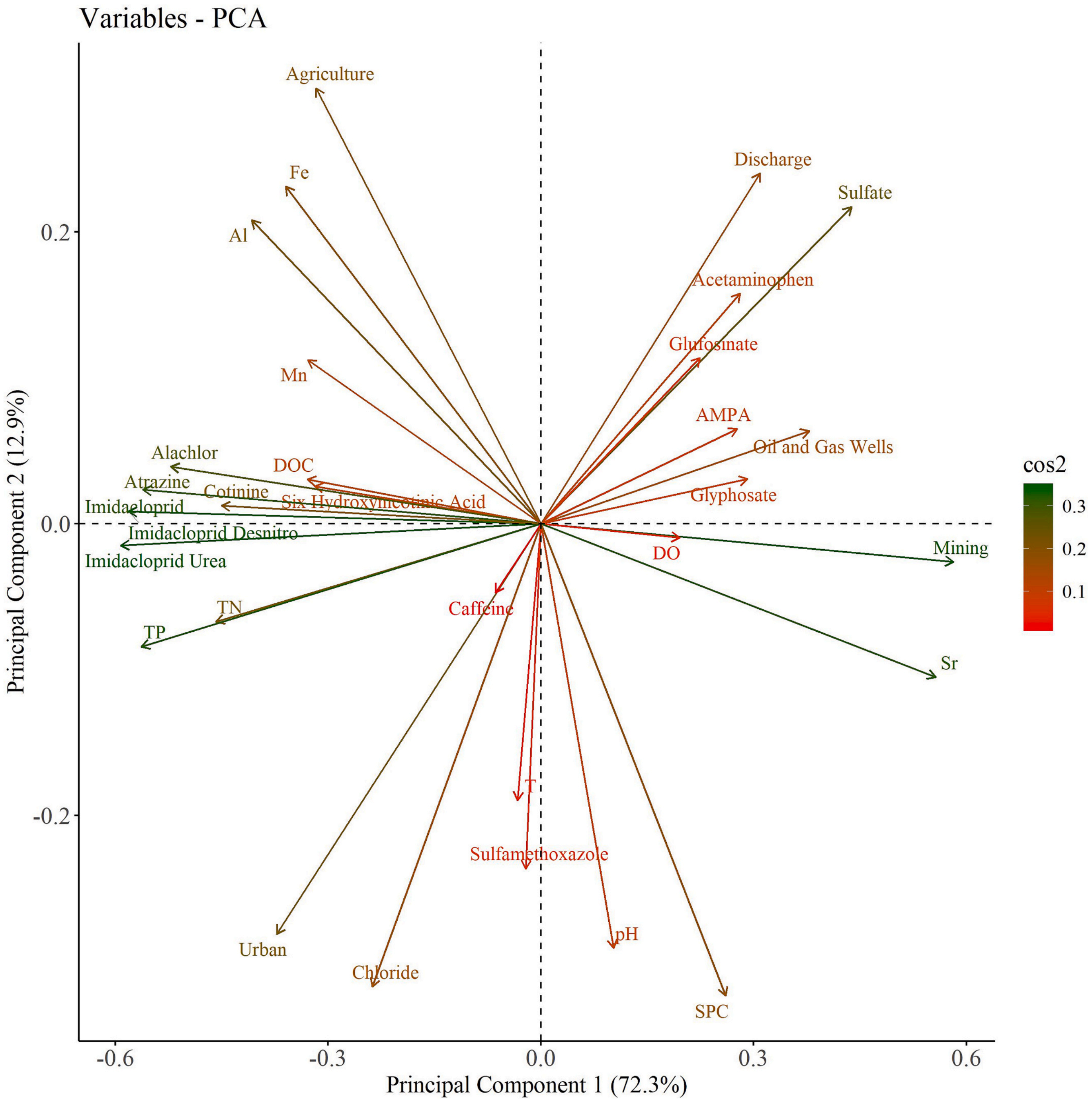


Fig. 6. A biplot for the principal component analysis (PCA) of the top four contaminants with the highest concentrations in each category (e.g., nutrients, trace elements, pesticides, PPCPs).

characteristics where seasonality and precipitation would impact the concentration of contaminants. Overall, W1 had the highest concentrations of nutrients (e.g., NO_3-N, PO_4-P, Cl^-) and the insecticide, imidacloprid. W2 had high concentrations of trace elements (e.g., Fe, Al) during high flow conditions in the stream along with the highest concentrations of herbicides like atrazine and alachlor during the early summer months. The site with the most oil and gas wells showed the highest concentrations of PPCPs like caffeine due to older wastewater infrastructure. W3 (70.3 % mining) had the highest concentrations of SO_4^{2-} throughout the entire sampling period along with glyphosate occurring after a major flooding event. These observations were further supported by the PCA which highlighted the impact of land cover and land use on contaminant presence and concentrations. Most fungicides, insecticides, and herbicides were positively correlated with agriculture and insecticides also had a positive correlation with the amount of urbanization. PPCPs were positively correlated with urbanization but also had a positive correlation to the density of oil and gas wells, highlighting the impact of older wastewater infrastructure on the presence of PPCPs in rural areas as well. Glyphosate and SO_4^{2-} were also positively correlated with W3 along with discharge values, highlighting the impact of flooding on the presence of these contaminants.

Regulatory limits for chronic exposure to aquatic organisms in freshwater exceeded SPC (300 μS cm^{-1}) in all watersheds but were exceeded throughout the entire sampling period in both W3 and W4. Ammonia ecotoxicity limits (0.05 mg NH_3^+ L^{-1}) were exceeded for both W1 and W2. The chronic aquatic life water quality criteria for Al (550 μg L^{-1}) and Fe (1000 μg L^{-1}) were exceeded during March, July, and August. The chronic criterion for freshwater invertebrates for imidacloprid (10 ng L^{-1}) was also exceeded in the urban (W1; June and July) and agricultural (W2; June) watersheds. Lastly, SO_4^{2-} concentrations were above the ambient water quality criterion (500 mg L^{-1}; April, July, September, October) in W3. The other detected contaminants were either below regulatory limits or a federal or state limit had not been determined (Table 5S).

This study provides important first steps for developing a comprehensive understanding of land use impacts on contaminant presence and concentration in surface waters. With over 100 different contaminants analyzed across 4 distinct landscapes, this research identified common contaminant mixtures found throughout the various landscapes while addressing their implications to aquatic organisms. Furthermore, the detection of PPCPs in rural communities provided evidence for the use of these contaminants to track sources and target communities in need of improved wastewater infrastructure as well as areas to target public health initiatives for drug abuse. These findings will be critical for providing guidance for adaptive management strategies to treat contaminated surface waters while also helping to target areas for increased water quality monitoring. Future work should investigate the use of best management practices with the goal of treating the contaminant mixtures detected and reduce the impact of land use practices on surface water quality.

Funding sources

This project was supported by UK-CARES through Grant P30 ES026529, National Science Foundation Grant No. 2042761, National Science Foundation Grant No. 1922695, U.S. Hatch Multistate Capacity funding grant No. W-4045, and the Southeast Center for Agricultural Health and Injury Prevention Grant No. 5U54OH007547. Its contents are solely the responsibility of the authors and do not necessarily represent the official views of the NIEHS, USDA, or NSF. Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture (USDA). USDA is an equal opportunity provider and employer.

CRediT authorship contribution statement

Emily Nottingham Byers: Writing – original draft, Visualization, Project administration, Investigation, Formal analysis, Data curation. **Tiffany L. Messer:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Jason Unrine:** Writing – review & editing, Validation, Resources. **Christopher Barton:** Writing – review & editing, Validation. **Carmen Agouridis:** Writing – review & editing, Validation. **Daniel N. Miller:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Tiffany L Messer reports financial support was provided by National Science Foundation. Tiffany L Messer reports financial support was provided by University of Kentucky Center for Appalachian Research in Environmental Sciences. Emily Nottingham Byers reports financial support was provided by National Science Foundation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

A special thank you to Matthew Russell, Dayana Nayelly Rodriguez Jimenez, Jacob Richardson, Kyra Sigler, Alexis McFadden, William Rud, Shristi Shrestha, Tami Smith, and the Water Sciences Laboratory with the Nebraska Research Initiative for their support throughout the project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.177837.

Data availability

Data will be made available on request.

References

Ahrens, L., Daneshvar, A., Lau, A.E., Kreuger, J., 2015. Characterization of five passive sampling devices for monitoring of pesticides in water. J. Chromat. A 1405, 1–11. https://doi.org/10.1016/j.chroma.2015.05.044.

Almberg, K.S., Turyk, M.E., Jones, R.M., Rankin, K., Freels, S., Stayner, L.T., 2018. Atrazine contamination of drinking water and adverse birth outcomes in community water systems with elevated atrazine in Ohio, 2006(−)2008. Int. J. Environ. Res. Public Health 15 (9). https://doi.org/10.3390/ijerph15091889.

Alvarez, D.A., Petty, J.D., Huckins, J.N., Jones-Lepp, T.L., Getting, D.T., Gooddard, J.P., Manahan, S.E., 2004. Development of a passive, in situ, integrative sampler for hydrophilic organic contaminants in aquatic environments. Environ. Toxicol. Chem. 23 (7), 1640–1648. https://doi.org/10.2134/jeq2006.0463.

APHA, AWWA, WEF, 2017. 4500-NH3 Nitrogen (Ammonia) Standard Methods For the Examination of Water and Wastewater, 23rd. In Standard Methods For the Examination of Water and Wastewater. American Public Health Association.

Arkoc, O., Ucar, S., Ozcan, C., 2016. Assessment of impact of coal mining on ground and surface waters in Tozaklı coal field, Kırklareli, northeast of Thrace, Turkey. Environ. Earth Sci. 75 (6). https://doi.org/10.1007/s12665-015-5120-1.

Armstead, M.Y., Bitzer-Creathers, L., Wilson, M., 2016. The effects of elevated specific conductivity on the chronic toxicity of mining influenced streams using Ceriodaphnia dubia. PLoS One 11 (11). https://doi.org/10.1371/journal.pone.0165683.

Atwood, D., Paisley-Jones, C., 2016. Pesticides Industry Sales and Usage, 2008-2012 Market Estimates. Retrieved September, 9 from. https://www.epa.gov/pesticides/pesticides-industry-sales-and-usage-2008-2012-market-estimates.

Bal, R., Türk, G., Tuzcu, M., Yilmaz, O., Kuloglu, T., Gundogdu, R., Gür, S., Agca, A., Ulas, M., Çambay, Z., Tuzcu, Z., Gencoglu, H., Guvenc, M., Ozsahin, A.D., Kocaman, N., Aslan, A., Etem, E., 2012. Assessment of imidacloprid toxicity on reproductive organ system of adult male rats. J. Environ. Sci. Health B 47 (5), 434–444. https://doi.org/10.1080/03601234.2012.663311.

Battaglin, W.A., Thurman, E.M., Kalkhoff, S.J., Porter, S.D., 2003. Herbicides and transformation products in surface waters of the Midwestern United States. JAWRA J. Am. Water Res. Assoc. 39 (4), 743–756. https://doi.org/10.1111/j.1752-1688.2003.tb04402.x.

Buerge, I.J., Kahle, M., Buser, H.R., Müller, M.D., Poiger, T., 2008. Nicotine derivatives in wastewater and surface waters: application as chemical markers for domestic wastewater. Environ. Sci. Technol. 42 (17), 6354–6360. https://doi.org/10.1021/es800455q.

Canadell, M.B., Gómez-Gener, L., Clémençon, M., Lane, S.N., Battin, T.J., 2020. Daily entropy of dissolved oxygen reveals different energetic regimes and drivers among high-mountain stream types. Limnol. Oceanogr. 66 (4), 1594–1610. https://doi.org/10.1002/lno.11670.

Cañedo-Argüelles, M., Kefford, C., Piscart, N., Prat, R.B., Schäfer, C.-J., Schulz, C.J., 2013. Salinization of rivers: an urgent ecological issue. Environ. Pollut. 173, 157–167. https://doi.org/10.1016/j.envpol.2012.10.011.

Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen, 8(3), pp. 559–568. https://doi.org/10.1890/1051-0761(1998)008.

Cassada, D.A., Spalding, R.F., Cai, Z., Gross, M.L., 1994. Determination of atrazine, deethylatrazine and deisopropylatrazine in water and sediment by isotope dilution gas chromatography–mass spectrometry. Anal. Chim. Acta 287 (1), 7–15. https://doi.org/10.1016/0003-2670(94)85095-X.

Chao, S.L., Casida, J.E., 1997. Interaction of imidacloprid metabolites and analogs with the nicotinic acetylcholine receptor of mouse brain in relation to toxicity. Pestic. Biochem. Physiol. 58 (1), 77–88. https://doi.org/10.1006/pest.1997.2284.

Chauzat, M.P., Faucon, J.P., 2007. Pesticide residues in beeswax samples collected from honey bee colonies (Apis mellifera L.) in France. Pest Manag. Sci. 63 (11), 1100–1106. https://doi.org/10.1002/ps.1451.

Clark, E.V., Daniels, W.L., Zipper, C.E., Eriksson, K., 2018. Mineralogical influences on water quality from weathering of surface coal mine spoils. Appl. Geochem. 91, 97–106. https://doi.org/10.1016/j.apgeochem.2018.02.001.

Clark, E.V., Soucek, D.J., Schoenholtz, S.H., Whitmore, K.M., Zipper, C.E., 2023. Trace elements and consequent ecological risks in mining-influenced streams of Appalachia. Environ. Toxicol. Chem. 42 (12), 2651–2665. https://doi.org/10.1002/etc.5734.

Conkle, J.L., Gan, J., Anderson, M.A., 2012. Degradation and sorption of commonly detected PPCPs in wetland sediments under aerobic and anaerobic conditions. J. Soils Sediments 12 (7), 1164–1173. https://doi.org/10.1007/s11368-012-0535-8.

Cool, G., Lebel, A., Sadiq, R., Rodriguez, M.J., 2014. Impact of catchment geophysical characteristics and climate on the regional variability of dissolved organic carbon (DOC) in surface water. Sci. Total Environ. 490, 947–956. https://doi.org/10.1016/j.scitotenv.2014.05.091.

Daneshvar, A., Aboulfadl, K., Viglino, L., Broseus, R., Sauve, S., Madoux-Humery, A.S., Weyhenmeyer, G.A., Prevost, M., 2012. Evaluating pharmaceuticals and caffeine as indicators of fecal contamination in drinking water sources of the Greater Montreal region. Chemosphere 88 (1), 131–139. https://doi.org/10.1016/j.chemosphere.2012.03.016.

Daughton, C.G., 2006. PPCPS: Overview of sources, environmental impacts, and solutions.

Daughton, C.G., Ternes, T.A., 1999. Pharmaceuticals and personal care products in the environment: agents of subtle change? Environ. Health Perspect. 107 (6). https://doi.org/10.1289/ehp.99107s6907.

de Sousa, D.N., Mozeto, A.A., Carneiro, R.L., Fadini, P.S., 2014. Electrical conductivity and emerging contaminant as markers of surface freshwater contamination by wastewater. Sci. Total Environ. 484, 19–26. https://doi.org/10.1016/j.scitotenv.2014.02.135.

DEP, 2012. Rationale for the development of ambient water quality criteria for sulfate: Protection of aquatic life use. Commonwealth of Pennsylvania Department of Environmental Protection Bureau of Point And Non-Point Source Management.

Dewitz, J., 2021. National Land Cover Database (NLCD) 2019 Products (ver. 2.0, June 2021): U.S. Geological Survey data release.

Dieter, C.A., Maupin, M.A., Caldwell, R.R., Harris, M.A., Ivahnenko, T.I., Lovelace, J.K., Barber, N.L., Linsey, K.S., 2017. Estimated use of water in the United States in 2015. United States Geological Survey.

Dixon, E., Shelton, R., 2023. Housing Damage from the 2022 Kentucky Flood. 1–10.

Donadt, C., Cooke, C.A., Graydon, J.A., Poesch, M.S., 2021. Mercury bioaccumulation in stream fish from an agriculturally-dominated watershed. Chemosphere 262, 128059. https://doi.org/10.1016/j.chemosphere.2020.128059.

Ebrahimi, P., Vilcaez, J., 2018. Petroleum produced water disposal: Mobility and transport of barium in sandstone and dolomite rocks. Sci. Total Environ. 634, 1054–1063. https://doi.org/10.1016/j.scitotenv.2018.04.067.

EEC, 2004. Kentucky Guidance for Ambient Background Assessment. Natural Resources and Environmental Protection Cabinet.

Ekström, S.M., Regnell, O., Reader, H.E., Nilsson, P.A., Löfgren, S., Kritzberg, E.S., 2016. Increasing concentrations of iron in surface waters as a consequence of reducing conditions in the catchment area. J. Geophys. Res. Biogeo. 121 (2), 479–493. https://doi.org/10.1002/2015jg003141.

Ellis, J.B., Butler, D., 2015. Surface water sewer misconnections in England and Wales: Pollution sources and impacts. Sci. Total Environ. 526, 98–109. https://doi.org/10.1016/j.scitotenv.2015.04.042.

EPA, 1978. Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Two Reagent). United States Environmental Protection Agency.

EPA, 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry. United States Environmental Protection Agency, Cincinnati, OH.

EPA, 1999. Total Organic Carbon in Water EPA Method 415.1. United States Environmental Protection Agency.

EPA, 2002. Kentucky Straight Pipes Report: Harlan, Martin, and Bath Counties. 1–17. US. EPA. R. 4, ed.

EPA, 2005. Protecting Water Quality from Agricultural Runoff. Available at. https://nepis.epa.gov/Exe/ZyPDF.cgi/P10039OH.PDF?Dockey=P10039OH.PDF.

EPA, 2007a. EPA 1694 Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS. United States Environmental Protection Agency.

EPA, 2007b. EPA Method 3015A (SW-846): Microwave Assisted Acid Digestion of Aqueous Samples and Extracts. United States Environmental Protection Agency.

EPA, 2007c. Method 9056A Determination of Inorgainc Anions by Ion Chromatography. United States Environmental Protection Agency.

EPA, 2011. A field-based aquatic life benchmark for conductivity in Central Appalachian streams. Office of Research and Development, United States Environmental Protection Agency Technical Report.

EPA, 2014. Kentucky Water Quality Standards. U. S. E. P. Agency, ed.

EPA, 2018. Final Aquatic Life Criteria for Aluminum in Freshwater. United States Environmental Protection Agency.

EPA, 2023a. Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides. United States Environmental Protection Agency.

EPA, 2023b. National Recommended Water Quality Criteria - Aquatic Life Criteria Table. United States Environmental Protection Agency.

Fisher, R.S., Davidson, B., 2007. Groundwater quality in Kentucky: Iron. Kentucky Geological Survey.

Freitas, L.A.A., Radis-Baptista, G., 2021. Pharmaceutical pollution and disposal of expired, unused, and unwanted medicines in the Brazilian Context. J. Xenobiot. 11 (2), 61–76. https://doi.org/10.3390/jox11020005.

Galster, J.C., 2007. Natural and anthropogenic influences on the scaling of discharge with drainage area for multiple watersheds. Geosphere 3 (4). https://doi.org/10.1130/ges00065.1.

Gillooly, J.F., Brown, J.H., West, G.B., Savage, V.M., Charnov, E.L., 2001. Effects of size and temperature on metabolic rate. Science 293 (5538), 2248–2251.

Granato, G.E., DeSimone, L.A., Barbaro, J.R., Jeznach, L.C., 2015. Methods for evaluating potential sources of chloride in surface waters and groundwaters of the conterminous United States. U.S. Geological Survey Open-File Report 2015. https://doi.org/10.3133/ofr20151080.

Graymore, M., Stagnitti, F., Allinson, G., 2001. Impacts of atrazine in aquatic ecosystems. Environ. Int. 26 (7), 483–495. https://doi.org/10.1016/S0160-4120(01)00031-9.

Gu, M.N., Pan, Y.P., Sun, Q., Walters, W.W., Song, L.L., Fang, Y.T., 2022. Is fertilization the dominant source of ammonia in the urban atmosphere? Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2022.155890.

Guo, Z.X., Cai, Q., Yang, Z., 2005. Determination of glyphosate and phosphate in water by ion chromatography–inductively coupled plasma mass spectrometry detection. J. Chromatogr. A 1100 (2), 160–167. https://doi.org/10.1016/j.chroma.2005.09.034.

Han, W., Tian, Y., Shen, X., 2018. Human exposure to neonicotinoid insecticides and the evaluation of their potential toxicity: An overview. Chemosphere 192, 59–65. https://doi.org/10.1016/j.chemosphere.2017.10.149.

Hansen, S.P., Messer, T.L., Mittelstat, A.R., 2019. Mitigating the risk of atrazine exposure: Identifying hot spots and hot times in surface waters across Nebraska, USA. J. Environ. Manag. 250. https://doi.org/10.1016/j.jenvman.2019.109424.

Harwell, M.C., Surratt, D.D., Barone, D.M., Aumen, N.G., 2008. Conductivity as a tracer of agricultural and urban runoff to delineate water quality impacts in the northern Everglades. Environ. Monit. Assess. 147 (1–3), 445–462. https://doi.org/10.1007/s10661-007-0131-3.

Hassaan, M.A., Nemr, A.E., Madkour, F.F., 2016. Environmental assessment of heavy metal pollution and human health risk. Am. J. Water Sci. Eng. 2 (3), 14–19. https://doi.org/10.11648/j.ajwse.20160203.11.

Hayes, T.B., Khoury, V., Narayan, A., Nazir, M., Park, A., Brown, T., Adame, L., Chan, E., Buchholz, D., Stueve, T., Gallipeau, S., 2010. Atrazine induces complete feminization and chemical castration in male African clawed frogs (Xenopus laevis). Proc. Nat. Acad. Sci. USA 107 (10), 4612–4617. https://doi.org/10.1073/pnas.0909519107.

He, Z.L., Yang, X.E., Stoffella, P.J., 2005. Trace elements in agroecosystems and impacts on the environment. J. Trace Elem. Med. Biol. Organ Soc. Min. Trace Elem. (GMS) 19 (2–3), 125–140. https://doi.org/10.1016/j.jtemb.2005.02.010.

Hébert, M.P., Fugère, V., Gonzalez, A., 2018. The overlooked impact of rising glyphosate use on phosphorus loading in agricultural watersheds. Front. Ecol. Environ. 17 (1), 48–56. https://doi.org/10.1002/fee.1985.

Hillebrand, O., Nodler, K., Licha, T., Sauter, M., Geyer, T., 2012a. Caffeine as an indicator for the quantification of untreated wastewater in karst systems. Water Res. 46 (2), 395–402. https://doi.org/10.1016/j.watres.2011.11.003.

Hillebrand, O., Nodler, K., Licha, T., Sauter, M., Geyer, T., 2012b. Identification of the attenuation potential of a karst aquifer by an artificial dualtracer experiment with caffeine. Water Res. 46 (16), 5381–5388. https://doi.org/10.1016/j.watres.2012.07.032.

Hobbie, S.E., Finlay, J.C., Janke, B.D., Nidzgorski, D.A., Millet, D.B., Baker, L.A., 2017. Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. Proc. Nat. Acad. Sci. USA 114 (16), 4177–4182. https://doi.org/10.1073/pnas.1618536114.

Hoppe-Jones, C., Oldham, G., Drewes, J.E., 2010. Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems. Water Res. 44 (15), 4643–4659. https://doi.org/10.1016/j.watres.2010.06.022.

Horn, I., 2021. Ky Permited Mine Boundaries. K. D. o. M. P. (DMP), ed. Kentucky Division of Mine Permits (DMP): Kentucky Division of Mine Permits (DMP).

Huang, A., van den Brink, N.W., Buijse, L., Roessink, I., van den Brink, P.J., 2021. The toxicity and toxicokinetics of imidacloprid and a bioactive metabolite to two aquatic arthropod species. Aquat. Toxicol. 235, 105837. https://doi.org/10.1016/j.aquatox.2021.105837.

Hutton, J.M., Price, S.J., Bonner, S.J., Richter, S.C., Barton, C.D., 2020. Occupancy and abundance of stream salamanders along a specific conductance gradient. Freshw. Sci. 39 (3), 433–446. https://doi.org/10.1086/709688.

Hutton, J.M., Price, S.J., Richter, S.C., Barton, C.D., 2021. Diet composition: A proximate mechanism explaining stream salamander declines in surface waters with elevated specific conductivity. Glob. Ecol. Conserv. https://doi.org/10.1016/j.gecco.2021.e01719.

Johnston, J.E., Lim, E., Roh, H., 2019. Impact of upstream oil extraction and environmental public health: A review of the evidence. Sci. Total Environ. 657, 187–199. https://doi.org/10.1016/j.scitotenv.2018.11.483.

Joshi, U.M., Balasubramanian, R., 2010. Characteristics and environmental mobility of trace elements in urban runoff. Chemosphere 80 (3), 310–318. https://doi.org/10.1016/j.chemosphere.2010.03.059.

Katz, B.G., Griffin, D.W., McMahon, P.B., Harden, H.S., Wade, E., Hicks, R.W., Chanton, J.P., 2010. Fate of effluent-borne contaminants beneath septic tank drainfields overlying a karst aquifer. J. Environ. Qual. 39 (4), 1181–1195. https://doi.org/10.2134/jeq2009.0244.

KGS, 2022. Kentucky Oil and Gas Well Location. K. G. Survey, ed. Kentucky Geological Survey Kentucky Geological Survey.

KIA, 2015. Kentucky Wastewater Management Plan. Kentucky Infrastructure Authority, ed.

Kimura-Kuroda, J., Komuta, Y., Kuroda, Y., Hayashi, M., Kawano, H., 2012. Nicotine-like effects of the neonicotinoid insecticides acetamiprid and imidacloprid on cerebellar neurons from neonatal rats. PLoS One 7 (2), e32432. https://doi.org/10.1371/journal.pone.0032432.

Kinney, C.A., Furlong, S.L., Werner, J.D., Cahill, J.D., 2006. Presence and distribution of wastewater-derived pharmaceuticals in soil irrigated with reclaimed water. Environ. Toxicol. Chem. 25 (2), 317–326. https://doi.org/10.1897/05-187r.1.

Kohli, A., 2022. Kentucky Floods Destroyed Homes That Had Been Safe for Generations. Nobody's Sure What to Do Next. In TIME.

Kolarova, N., Napiórkowski, P., 2021. Trace elements in aquatic environment. Origin, distribution, assessment and toxicity effect for the aquatic biota. Ecohydrol. Hydrobiol. 21 (4), 655–668. https://doi.org/10.1016/j.ecohyd.2021.02.002.

Kolenbrander, G.J., 2013. Nitrogen in organic matter and fertilizer as a source of pollution. In Proceedings of the Conference on Nitrogen As a Water Pollutant, 67–84. S. H. Jenkins, ed.: Pergamon.

Krawczyk, W.E., Ford, D.C., 2005. Correlating specific conductivity with total hardness in limestone and dolomite karst waters. Earth Surf. Process. Landf. 31 (2), 221–234. https://doi.org/10.1002/esp.1232.

Lang, Y.-C., Liu, C.-Q., Zhao, Z.-Q., Li, S.-L., Han, G.-L., 2006. Geochemistry of surface and ground water in Guiyang, China: Water/rock interaction and pollution in a karst hydrological system. Appl. Geochem. 21 (6), 887–903. https://doi.org/10.1016/j.apgeochem.2006.03.005.

Larson, J., Crocker, E., 2022. Emerald Ash Borer (EAB) FAQs for Kentuckians. University of Kentucky Cooperative Extension Entfact-453.

Lei, L., Thompson, J.A., McDonald, L.M., 2020. Assessment of dissolved organic carbon and iron effects on water color between a forest and pasture-dominated fine-scale catchment in a Central Appalachian region, West Virginia. Environ. Sci. Pollut. Res. Int. 27 (23), 29464–29474. https://doi.org/10.1007/s11356-020-09251-9.

Liu, F., Wang, D., 2022. Dissolved organic carbon concentration and biodegradability across the global rivers: A meta-analysis. Sci. Total Environ. 818, 151828. https://doi.org/10.1016/j.scitotenv.2021.151828.

Liu, M.Y., Lanford, J., Casida, J.E., 1993. Relevance of [3H]Imidacloprid Binding Site in House Fly Head Acetylcholine Receptor to Insecticidal Activity of 2-Nitromethylene-and 2-Nitroimino-imidazolidines. Pestic. Biochem. Physiol. 46 (3), 200–206. https://doi.org/10.1006/pest.1993.1051.

Loser, D., Grillberger, K., Hinojosa, M.G., Blum, J., Haufe, Y., Danker, T., Johansson, Y., Moller, C., Nicke, A., Bennekou, S.H., Gardner, I., Bauch, C., Walker, P., Forsby, A., Ecker, G.F., Kraushaar, U., Leist, M., 2021. Acute effects of the imidacloprid metabolite desnitro-imidacloprid on human nACh receptors relevant for neuronal signaling. Arch. Toxicol. 95 (12), 3695–3716. https://doi.org/10.1007/s00204-021-03168-z.

Magalhaes, L.C., Hunt, B.D., Siegfried, B.D., 2009. Efficacy of neonicotinoid seed treatments to reduce soybean aphid populations under field and controlled conditions in Nebraska. J. Econ. Entomol. 102 (1), 187–195. https://doi.org/10.1603/029.102.0127.

Martin, G.R., 2002. Estimating mean annual streamflow of rural streams in Kentucky. U. S. Geological Survey Water-Resources Investigations.

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.

Mesnage, R., Antoniou, M.N., 2017. Facts and fallacies in the debate on glyphosate toxicity. Front. Public Health 5, 316. https://doi.org/10.3389/fpubh.2017.00316.

Morosanu, G.A., Dontu, S., Copacenaru, O., Gavril, V., Zaharia, F., Carstea, E.M., 2016. Evaluation of the Anthropogenic Impact on the Water Quality of Dambovita River. Limnol. Proc. 91–98.

Motaung, T.E., 2020. Chloronicotinyl insecticide imidacloprid: Agricultural relevance, pitfalls and emerging opportunities. Crop Prot. https://doi.org/10.1016/j.cropro.2020.105097.

Mottim, F.d.S.B., Bernardelli, J.K.B., Schnitzler, D.C., 2021. Assessment of persistence and presence of alachlor pesticide residues in surface water. Rev. Virtual Quím. 13 (6), 1338–1344. https://doi.org/10.21577/1984-6835.20210070.

Mourikes, V.E., Márquez, R. Santacruz, Deviney, A.A., Neff, A.M., Laws, M.J., Flaws, J.A., 2023. Imidacloprid and its bioactive metabolite, desnitro-imidacloprid, differentially affect ovarian antral follicle growth, morphology, and hormone synthesis in vitro. Toxics 11 (4). https://doi.org/10.3390/toxics11040349.

Muncy, B.L., Price, S.J., Bonner, S.J., Barton, C.D., 2014. Mountaintop removal mining reduces stream salamander occupancy and richness in southeastern Kentucky (USA). Biol. Conserv. 180, 115–121. https://doi.org/10.1016/j.biocon.2014.09.040.

Nakada, N., Hanamoto, S., Jurgens, M.D., Johnson, A.C., Bowes, M.J., Tanaka, H., 2017. Assessing the population equivalent and performance of wastewater treatment through the ratios of pharmaceuticals and personal care products present in a river basin: Application to the River Thames basin, UK. Sci. Total Environ. 575, 1100–1108. https://doi.org/10.1016/j.scitotenv.2016.09.180.

Nikolaou, A., Meric, S., Fatta, D., 2007. Occurrence patterns of pharmaceuticals in water and wastewater environments. Anal. Bioanal. Chem. 387 (4), 1225–1234. https://doi.org/10.1007/s00216-006-1035-8.

Niu, X., Wendt, A., Li, Z., Agarwal, A., Xue, L., Gonzales, M., Brantley, S.L., 2018. Detecting the effects of coal mining, acid rain, and natural gas extraction in Appalachian basin streams in Pennsylvania (USA) through analysis of barium and sulfate concentrations. Environ. Geochem. Health 40 (2), 865–885. https://doi.org/10.1007/s10653-017-0031-6.

NOAA, 2023. NOAA Online Weather Data. National Weather Service National Oceanic and Atmospheric Administration.

Noger, M.C., 1988. Geologic map of Kentucky: sesquicenntennial edition of the Kentucky Geological Survey: U.S. Geological Survey and the Kentucky Geological Survey.

NORC, 2024. Drug Overdose Deaths in the United States. NORC at the University of Chicago.

Noro, K., Endo, S., Shikano, Y., Banno, A., Yabuki, Y., 2020. Development and Calibration of the Polar Organic Chemical Integrative Sampler (POCIS) for Neonicotinoid Pesticides. Environ. Toxicol. Chem. 39 (7), 1325–1333. https://doi.org/10.1002/etc.4729.

Nowell, L.H., Moran, P.W., Bexfield, L.M., Mahler, B.J., Van Metre, P.C., Bradley, P.M., Schmidt, T.S., Button, D.T., Qi, S.L., 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.

NRCS, 2023. Soil Survey Geographic (SSURGO) Database. United States Department of Agriculture Natural Resources Conservation Service, ed.

NREPC. n.d. Water Quality Prameters. River Assessment Monitoring Project: Kentucky Natural Resources and Environmental Protection Cabinet.

Okoye, C.O., Okeke, E.S., Okoye, K.C., Echude, D., Andong, F.A., Chukwudozie, K.I., Okoye, H.U., Ezeonyejiaku, C.D., 2022. Occurrence and fate of pharmaceuticals, personal care products (PPCPs) and pesticides in African water systems: A need for timely intervention. Heliyon 8 (3), e09143. https://doi.org/10.1016/j.heliyon.2022.e09143.

Osuoha, J.O., Anyanwu, B.O., Ejileugha, C., 2023. Pharmaceuticals and personal care products as emerging contaminants: Need for combined treatment strategy. J. Hazard. Mater. Adv. https://doi.org/10.1016/j.hazadv.2022.100206.

Paylor, R.L., Current, J.C., 2001. Karst Occurrence in Kentucky. University of Kentucky: Kentucky Geological Survey.

Pereira, S.P., Santos, S.M.A., Fernandes, M.A.S., Deus, C.M., Martins, J.D., de Lima, M.C. Pedroso, Vicente, J.A.F., Videira, R.A., Jurado, A.S., 2021. Improving pollutants environmental risk assessment using a multi model toxicity determination with in vitro, bacterial, animal and plant model systems: The case of the herbicide alachlor. Environ. Pollut. 286, 117239. https://doi.org/10.1016/j.envpol.2021.117239.

Pericak, A.A., Thomas, C.J., Kroodsma, D.A., Wasson, M.F., Ross, M.R.V., Clinton, N.E., Campagna, D.J., Franklin, Y., Bernhardt, E.S., Amos, J.F., 2018. Mapping the yearly extent of surface coal mining in Central Appalachia using Landsat and Google Earth Engine. PLoS One 13 (7), e0197758. https://doi.org/10.1371/journal.pone.0197758.

Pietrzak, D., Kania, J., Kmiecik, E., Malina, G., Wator, K., 2020. Fate of selected neonicotinoid insecticides in soil-water systems: Current state of the art and knowledge gaps. Chemosphere 255, 126981. https://doi.org/10.1016/j.chemosphere.2020.126981.

Price, S.J., Freytag, S.B., Bonner, S.J., Drayer, A.N., Muncy, B.L., Hutton, J.M., Barton, C.D., Brotons, L., 2018. Mountaintop removal mining alters stream salamander population dynamics. Divers. Distrib. 24 (9), 1242–1251. https://doi.org/10.1111/ddi.12760.

PRISM, C.G., 2022. Mean Annual Precipitation: Kentucky. O. S. University, ed.

Rajwa-Kuligiewicz, A., Bialik, R.J., Rowiński, P.M., 2015. Dissolved oxygen and water temperature dynamics in lowland rivers over various timescales. J. Hydrol. Hydromech. 63 (4), 353–363. https://doi.org/10.1515/johh-2015-0041.

Reeves, M.K., Perdue, M., Munk, L.A., Hagedorn, B., 2018. Predicting risk of trace element pollution from municipal roads using site-specific soil samples and remotely sensed data. Sci. Total Environ. 630, 578–586. https://doi.org/10.1016/j.scitotenv.2018.02.171.

Rinsky, J.L., Hopenhayn, C., Golla, V., Browning, S., Bush, H.M., 2012. Atrazine exposure in public drinking water and preterm birth. Public Health Rep. 127 (1), 72–80. https://doi.org/10.1177/003335491212700108.

Rodayan, A., Afana, S., Segura, P.A., Sultana, T., Metcalfe, C.D., Yargeau, V., 2016. Linking drugs of abuse in wastewater to contamination of surface and drinking water. Environ. Toxicol. Chem. 35 (4), 843–849. https://doi.org/10.1002/etc.3085.

Roser, M., 2019. Pesticides- Our World in Data. Available at. https://ourworldindata.org/pesticides.

RStudio, 2021. RStudio: Integrated Development for R. Boston, MA: R Studio Team.

Ruckhaus, M., Seybold, E.C., Underwood, K.L., Stewart, B., Kincaid, D.W., Shanley, J.B., Li, L., Perdrial, J.N., 2023. Disentangling the responses of dissolved organic carbon and nitrogen concentrations to overlapping drivers in a northeastern United States forested watershed. Front. Water. https://doi.org/10.3389/frwa.2023.1065300.

Runtti, H., Tolonen, E.T., Tuomikoski, S., Luukkonen, T., Lassi, U., 2018. How to tackle the stringent sulfate removal requirements in mine water treatment-A review of potential methods. Environ. Res. 167, 207–222. https://doi.org/10.1016/j.envres.2018.07.018.

Satiroff, J.A., Messer, T.L., Mittelstet, A.R., Snow, D.D., 2020. Pesticide occurrence and persistence entering recreational lakes in watersheds of varying land uses. Environ. Pollut. 273, 116399. https://doi.org/10.1016/j.envpol.2020.116399.

Shan, Y., Wang, W., Qin, Y., Gao, L., 2019. Multivariate analysis of trace elements leaching from coal and host rock. Groundw. Sustain. Dev. 8, 402–412. https://doi.org/10.1016/j.gsd.2019.01.001.

Simon-Delso, N., Amaral-Rogers, L.P., Belzunces, J.M., Bonmatin, M., Chagnon, C., Downs, L., Furlan, D.W., L Fau - Gibbons, C. Gibbons Dw Fau - Giorio, V. Giorio C Fau - Girolami, D. Girolami V Fau - Goulson, D. P. Goulson D Fau - Kreutzweiser, C. H. Kreutzweiser Dp Fau - Krupke, M. Krupke Ch Fau - Liess, E. Liess M Fau - Long, M. Long E Fau - McField, P. McField M Fau - Mineau, E. A. D. Mineau P Fau - Mitchell, C. A. Mitchell Ea Fau - Morrissey, D. A. Morrissey Ca Fau- Noome, L. Noome Da Fau - Pisa, J. Pisa L Fau - Settele, J. D. Settele J Fau - Stark, A. Stark Jd Fau - Tapparo, H. Tapparo A Fau - Van Dyck, J. Van Dyck H Fau - Van Praagh, J. P. Van Praagh J Fau - Van der Sluijs, P. R. Van der Sluijs Jp Fau - Whitehorn, M. Whitehorn Pr Fau - Wiemers, and M. Wiemers, 2015. Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites. Environ. Sci. Pollut. Res. 22, 5–34. https://doi.org/10.1007/s11356-014-3470-y.

Snow, D.D., Chakraborty, P., Uralbekov, B., Satybaldiev, B., Sallach, J.B., Hampton, L.M. Thornton, Jeffries, M., Kolok, A.S., Bartelt-Hunt, S.B., 2020. Legacy and current pesticide residues in Syr Darya, Kazakhstan: Contamination status, seasonal variation and preliminary ecological risk assessment. Water Resour. 184, 116141. https://doi.org/10.1016/j.watres.2020.116141.

Soucek, D.J., Kennedy, A.J., 2005. Effects of hardness, chloride, and acclimation on the acute toxicity of sulfate to freshwater invertebrates. Environ. Toxicol. Chem. 24 (5). https://doi.org/10.1897/04-142.1.

Sun, H., Shi, B., Yang, F., Wang, D., 2017. Effects of sulfate on heavy metal release from iron corrosion scales in drinking water distribution system. Water Resour. 114, 69–77. https://doi.org/10.1016/j.watres.2017.02.021.

Szogi, A.A., Vanotti, M.B., Ro, K.S., 2015. Methods for treatment of animal manures to reduce nutrient pollution prior to soil application. Curr. Pollut. Rep. 1 (1), 47–56. https://doi.org/10.1007/s40726-015-0005-1.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy metal toxicity and the environment. Exp. Supp. 101, 133–164. https://doi.org/10.1007/978-3-7643-8340-4_6.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Kolpin, D.W., 1991. Herbicides in surface waters of the midwestern United States: the effect of spring flush. Environ. Sci. Technol. 25 (10), 1794–1796. https://doi.org/10.1021/es00022a018.

Toming, K., Kotta, J., Uuemaa, E., Sobek, S., Kutser, T., Tranvik, L.J., 2020. Predicting lake dissolved organic carbon at a global scale. Sci. Rep. 10 (1), 8471. https://doi.org/10.1038/s41598-020-65,010-3.

Tomizawa, M., Casida, J.E., 2000. Imidacloprid, thiacloprid, and their imine derivatives up-regulate the alpha 4 beta 2 nicotinic acetylcholine receptor in M10 cells. Toxicol. Appl. Pharmacol. 169 (1), 114–120. https://doi.org/10.1006/taap.2000.9057.

Tusher, T.R., Sultana, N., Islam, M.S., Hossain, D., 2015. Assessment of Iron Contamination in Groundwater at Tangail Municipality, Bangladesh. J. Environ. Sci. Natural Resources 6 (1), 117–121. https://doi.org/10.3329/jesnr.v6i1.22051.

USDA, 2022. Cattle County Estimates - January 1, 2022. NASS. United State Department of Agriculture, Kentucky Field Office, ed.

USDA-NASS, 2023. USDA National Agricultural Statistics Service Cropland Data Layer. United States Department of Agriculture. Washington, DC.

USGS, 2022. 1 Arc-second Digital Elevation Models (DEMs) - USGS National Map 3DEP Downloadable Data Collection. United States Geological Survey. Geospatial_Data_Presentation_Form: raster digital data. U. S. G. Survey, ed. Reston, VA.

VaEnergy, 2022. Gas and Oil Data Information System. V. D. o. Energy, ed. Virginia Department of Energy: Virginia Department of Energy.

Wallenstein, M. D., and M. N. Weintraub. 2008. Emerging tools for measuring and modeling the in situ activity of soil extracellular enzymes. Soil Biol. Biochem. 40(9): 2098–2106. doi:10.1016/j.soilbio.2008.01.024.

Williamson, T.N., Barton, C.D., 2020. Hydrologic modeling to examine the influence of the forestry reclamation approach and climate change on mineland hydrology. Sci. Total Environ. 743, 140605. https://doi.org/10.1016/j.scitotenv.2020.140605.

Wu, J.L., Liu, Z.H., Ma, Q.G., Dai, L., Dang, Z., 2023. Occurrence, removal and risk evaluation of ibuprofen and acetaminophen in municipal wastewater treatment plants: A critical review. Sci. Total Environ. 891, 164600. https://doi.org/10.1016/j.scitotenv.2023.164600.

WVDEP, 2016. WVDEP Office of Oil and Gas Well Locations. W. V. D. o. E. Protection, ed. West Virginia Department of Environmental Protection: West Virginia Department of Environmental Protection.

WVDEP, 2017. Permit Boundary: Completely Released. W. V. D. o. E. Protection, ed. West Virginia Department of Environmental Protection: West Virginia Department of Environmental Protection.

Yufen Ren, Z.X., Zhang, Xinyu, Wang, Xiaoke, Sun, Xiaomin, Ballantine, D.J., Wang, Shengzhong, 2014. Nitrogen pollution and source identification of urban ecosystem surface water in Beijing. Front. Environ. Sci. Eng. 8, 106–116. https://doi.org/10.1007/s11783-012-0474-z.

Yurista, P.M., Johnston, K., Rice, G., Kipphut, G.W., White, D.S., 2001. Particulate Organic Carbon Patterns in a Mainstem Reservoir, Kentucky Lake, USA. Lake Reserv. Manag. 17 (4), 330–340. https://doi.org/10.1080/07438140109354139.

Zak, D., Hupfer, M., Cabezas, A., Jurasinski, G., Audet, J., Kleeberg, A., McInnes, R., Kristiansen, S.M., Petersen, R.J., Liu, H., Goldhammer, T., 2021. Sulphate in freshwater ecosystems: A review of sources, biogeochemical cycles, ecotoxicological effects and bioremediation. Earth Sci. Rev. https://doi.org/10.1016/j.earscirev.2020.103446.

Zhang, X., Wu, Y., Gu, B., 2015. Urban rivers as hotspots of regional nitrogen pollution. Environ. Pollut. 205, 139–144. https://doi.org/10.1016/j.envpol.2015.05.031.

Zhu, S., Chen, H., Li, J., 2013. Sources, distribution and potential risks of pharmaceuticals and personal care products in Qingshan Lake basin, Eastern China. Ecotoxicol. Environ. Saf. 96, 154–159. https://doi.org/10.1016/j.ecoenv.2013.06.033.