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Exploring the Effects of Varied Land Use on Elemental Concentrations Within Streams

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Undergraduate Honors Thesis

Abstract

It is well documented that human activity influences the chemistry of surrounding waters. As such, it is possible that there is a link between land use within a watershed and the chemical composition of the stream. The objectives of this study are to determine if varied land use does affect the concentrations of macronutrients and trace elements present in the streams of Northwest Arkansas, and if so, to determine what extent urban and agricultural development are responsible for these changes. Water samples were collected across 19 streams in the Northwest Arkansas region between January and March of 2022. Water samples were analyzed using inductively coupled plasma optical emissions spectrometry analysis to determine concentrations of aluminum, arsenic, cadmium, barium, boron, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, sodium, titanium, vanadium, and zinc. Watershed land use categories were determined via the Model My Watershed tool (https://modelmywatershed.org/), using the Land Use/Cover 2019 data.

In the selected streams, significant positive correlations were found between urban land use and mean concentrations of boron, copper, calcium, magnesium, and sodium. Significant positive correlations were also found between agricultural land use and mean concentrations of barium and potassium across all stream sites, while negative correlations were found between agricultural land use and mean magnesium and zinc concentrations. No positive correlations between forested land use and any elemental concentration were found, but negative correlations between forested land use and mean concentrations of calcium, copper, potassium, and sodium were found. The data suggests that urban and agricultural development are the primary drivers of these trends.

Introduction

Scientists have documented that human activity influences the chemistry of surrounding waters and watersheds. This is often seen in the form of nutrient runoff, such as excess fertilizer from agricultural operations (Alexander et al., 2000) or heavy metal effluent in industrialized areas (Krishna et al., 2009). However, human development can also impact watershed chemistry through more indirect means, such as how the increasing acidity of rainfall has led to increased weathering of bedrock in certain karst areas (Zhu et al., 2020). From this increased weathering, many nutrients and trace elements make their way through the watersheds, altering the typical chemical composition and equilibrium of streams.

When the chemical balance of a watershed is disturbed, it often has consequences for the downstream aquatic ecosystem at large. Algal blooms, for example, are typically caused by elevated nitrogen (N) and phosphorous (P) concentrations in lakes and streams (Zohdi & Abbaspour, 2019). These blooms not only cause large diurnal swings in dissolved oxygen content (DO), but can also block sunlight from filtering through to the bottoms of lakes and streams. This can lead to large areas of a waterway becoming uninhabitable for native plant and animal life (Beegle, 2013). Elevated nutrient levels are one of the dominant causes of aquatic habitat degradation, and reducing nutrient concentrations can lead to the rapid recovery of affected areas (Lefcheck et al., 2018).

Much like the major nutrients, alterations to the concentrations of trace elements in a waterway can impact the health of the surrounding ecosystem. As such, it is important to be aware of potential sources of trace elements, and where they may end up once in the water. Being one of the primary sources of rock weathering, water carries with it many trace elements derived from the weathering process. The concentrations of these elements are affected by

factors that accelerate natural weathering, such as increased acidity, urban and industrial activity, and chemical runoff (Scudlark et al., 2005). Furthermore, anthropogenic dust and debris often becomes airborne, making atmospheric deposition a potential source of trace elements in lakes and streams several dozen miles from any major sources of pollutants (Child et al., 2018).

Among the anthropogenic sources of trace elements, agricultural runoff is a particularly noteworthy vector. Agricultural runoff is often cited for its role in eutrophication (Alexander et al., 2000), but it often contains metals and other potential pollutants as well. Poultry litter, which is sometimes applied as a crop fertilizer, can contain arsenic (As), copper (Cu), and zinc (Zn) (Toor et al., 2007). Although the application of poultry litter does not substantially increase the concentration of these metals within the soil (Pirani et al., 2006; Toor & Haggard, 2009; Toor et al., 2007), it is possible that runoff from fields receiving poultry litter may carry trace elements into local waterways (DeLaune & Moore Jr, 2016). As such, it is important that any potentially impacted streams be monitored for significant alterations in chemical composition.

Much like agriculture, urban land use is a potential source of trace elements in streams. It has been shown in many cities that traffic and industry are the sources of a large portion of aerial particulate matter (Karagulian et al., 2015), which can contain numerous trace elements, such as lead (Pb), Cu, and As (Contardo et al., 2020). These atmospheric pollutants can then be deposited onto impervious surfaces and carried into waterways via storm runoff (Child et al., 2018). Rooftops, for example, are a common pathway by which airborne particles might settle and then be washed away by rainfall. Not only that, but metal roofs have been shown to be a source of cadmium (Cd) and Zn, and asphalt-shingle roofs a source of Pb (Van Metre & Mahler, 2003). Even debris from tire wear is a major potential source of Zn in urban runoff to streams, rivers, and lakes (Rhodes et al., 2012). Given the many potential sources of trace elements

present in an urban environment, it is entirely possible that waterways near urban centers may have elevated concentrations of trace elements in their water and sediment.

Within the Northwest Arkansas region, there are numerous potential sources of trace elements. There are multiple urban centers in the region, with a combined population of over 525,000 (Bowden & Bernet, 2017), as well as several industries. In terms of agriculture, the region primarily produces livestock and poultry, with poultry litter generally being applied as fertilizer for pastures. Between these urban, agricultural, and industrial sources, it is entirely possible that land use impacts stream chemical concentrations within the region. The objectives of this study are to determine if varied land use does affect the concentrations of macronutrients and trace elements present in the streams of Northwest Arkansas, and if so, to determine what extent urban and agricultural development are responsible for these changes.

Materials and Methods

Sample Collection

Water samples were collected on January 6th, January 28th, and March 2nd, 2022. These samples were taken from 19 different sampling sites spread throughout Northwest Arkansas. The watersheds of each sampling site were delineated using the Model My Watershed tool (https://modelmywatershed.org/), using the Land Use/Cover 2019 data to provide the percentages of land use categories for the delineated areas. The sampling sites were chosen in order to have a spread of land use percentages ranging from less than 10% to greater than 70% in the categories of urban land use (%Urb), agricultural land use (%Ag), and forested land use (%For) (Table 1). Watersheds that are mostly forested (>80 %For) were chosen to provide background chemical concentrations.

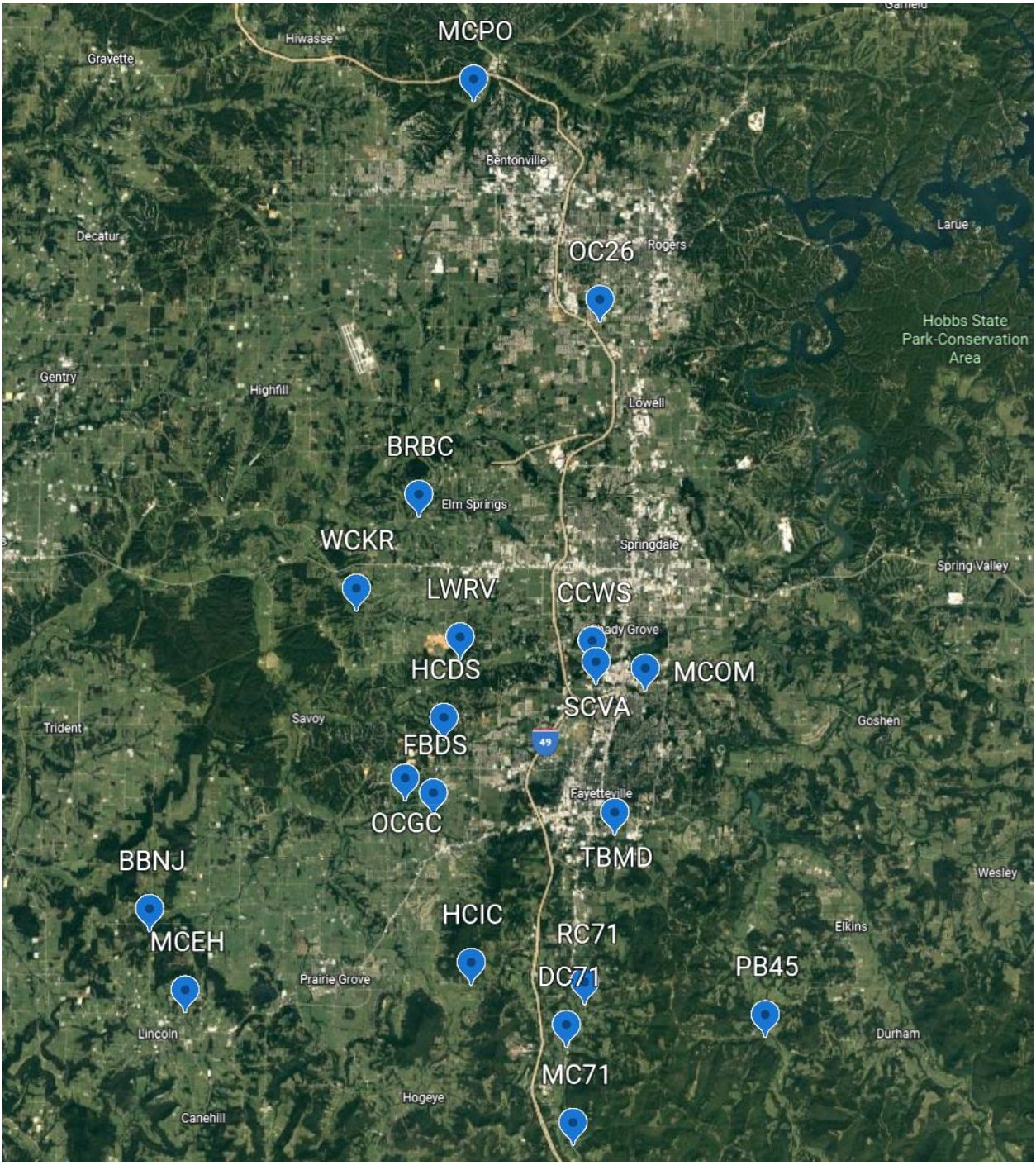

Figure 1: Sampling Sites Within Northwest Arkansas

%Urb was defined as the sum of developed open, low, medium, and high intensity land use, as given by the Model My Watershed tool. %Ag was defined as the sum of grassland, cultivated crop, and pasture/hay land use. %For was defined as the sum of deciduous, evergreen, and mixed forest land use. Additionally, prior studies in the area have found that nutrient concentrations often increase with both agricultural and urban development (Giovannetti et al., 2013; Haggard et al., 2003). Though these studies focused on nutrients rather than trace elements, it is not unreasonable to assume the same would be true for trace elements. Another category, Human Development Index (%HDI), was added to account for this, and %HDI was calculated as the sum of both %Urb and %Ag land use values for each watershed.

Samples were collected from the vertical centroid of the stream, either by using an Alpha-style horizontal sampler from a bridge or by grab sample where conditions allowed. Water samples were delivered to the Arkansas Water Resources Center Water Quality Lab (AWRC WQL). Filtered water samples were then analyzed for dissolved elements, including aluminum (Al), As, barium (Ba), boron (B), Cd, calcium (Ca), chromium (Cr), cobalt (Co), Cu, iron (Fe), Pb, magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), potassium (K), selenium (Se), sodium (Na), titanium(Ti), vanadium (V), and Zn, using inductively coupled plasma optical emissions spectrometry (ICP-OES). Additional information is available at: https://arkansas-water-center. uark.edu/water-quality-lab.php.

During the second round of sample analysis, it was found that the containers used to store the acidified filtrate were borosilicate glass, which contaminated the filtrate with B. Because of this, the results of the analysis returned a very high concentration of B, ranging from 0.8 to 1.4 mg/L. It is also possible that this excess B concentration masked other elements within the analysis, as several trace elements were not detected in this round of sampling. Fortunately, there

was enough water left in the sample containers, and additional samples were processed for ICP-OES analysis. This data was used in the data analysis.

Table 1: Sampling Sites, GPS Coordinates, Catchment Area, Land Use Percentages, and Level 3 Ecoregion, where %Urb is

Stream Name	Site Code	Latitude	Longitude	Area (km^2)	%Urb	%Ag	%For	%HDI	Level 3 Ecoregion
Dye Creek	DC71	35.94198	-94.17844	8.6	4.0	26.0	69.8	30.0	Boston
Hickory Creek	HCIC	35.97202	-94.23541	20.6	4.9	38.9	56.1	43.8	Boston
Mill Creek	MC71	35.89483	-94.17424	19.0	2.8	14.7	82.2	17.4	Boston
Mud Creek	MCOM	36.11473	-94.13096	24.3	53.0	25.6	21.1	78.6	Boston
Parker Branch	PB45	35.94665	-94.05945	11.0	2.7	17.2	80.2	19.8	Boston
Rock Creek	RC71	35.96267	-94.16714	14.9	2.9	33.5	63.4	36.5	Boston
Scull Creek	SCVA	36.07248	-94.16496	12.0	77.4	10.7	11.5	88.1	Boston
Town Branch	TBMD	36.04477	-94.14938	27.4	51.5	13.8	34.3	65.3	Boston
Beatty Branch	BBNJ	35.99777	-94.42836	10.7	5.7	59.2	34.7	64.9	Ozark
Brush Creek	BRBC	36.19851	-94.26714	45.0	37.7	53.0	7.8	90.7	Ozark
Clear Creek	CCWS	36.12776	-94.16279	26.6	39.7	47.0	9.5	86.7	Ozark
Farmington Branch	FBDS	36.05407	-94.25821	14.2	28.7	32.4	38.6	61.1	Ozark
Hamestring Creek	HCDS	36.09065	-94.25193	29.1	42.4	37.7	19.0	80.1	Ozark
Little Wildcat	LWRV	36.12968	-94.24221	21.9	14.2	72.1	13.1	86.2	Ozark
McKisic Creek	MCPO	36.40013	-94.23423	11.6	36.3	43.8	19.6	80.2	Ozark
Moores Creek	MCEH	35.95860	-94.40677	8.7	18.5	70.3	8.6	88.8	Ozark
Osage Creek	OC26	36.29338	-94.15818	17.1	69.6	26.6	2.5	96.2	Ozark
Owl Creek	OCGC	36.06115	-94.27548	10.8	29.5	50.9	19.5	80.4	Ozark
Wildcat Creek	WCKR	36.15328	-94.30478	18.3	6.1	79.0	14.9	85.1	Ozark

Percent Urban Landuse, %Ag is Percent Agricultural Landuse, %For is Percent Forested Landuse, and %HDI is the Percent Human Development Index.

Data Analysis

The mean concentrations of each element were calculated at each site to be used in linear regression with the land use percentages. Concentrations of each element were compared to %Urb, %Ag, and %For present in the watershed from which the sample was retrieved. A relation between mean elemental concentrations and land use percentages would suggest that watershed land use influences stream chemistry. Regression analysis was performed in MS Excel using the Analysis Toolpack with an alpha of 0.05 to determine significance.

To compare variance between level 3 ecoregions, mean concentrations of each element in samples from Boston Mountains sites were compared to mean elemental concentrations in samples from Ozark Mountains sites. This was done via the t-Test: Two-Sample Assuming Equal Variances function of the MS Excel Analysis Toolpak with an alpha of 0.05 to determine significance. In these tests, a significant result would suggest that the level 3 eco-region that a stream is in influences the chemistry of said stream.

Correlations between mean elemental concentrations across sites were evaluated using a Pearson Correlation Table. The table was created using the Correlation function of the MS Excel Data Analysis Toolpak. The Pearson Correlation Table provides the coefficient of correlation between the elements in question. A positive value indicates the two elemental concentrations increase with each other, and a negative value indicates that one decreases as the other increases. Squaring the coefficient of correlation provides the R^2 value between the two, which can be used in conjunction with a linear regression to determine if the correlation is significant.

Toxicity levels were based on Arkansas Water Quality Standards (Pollution Control and Ecology Commission, 2020), and on the EPA National Drinking Water Regulations (EPA, 2009). This study was performed on surface water streams over the course of multiple months, and therefore used the chronic criteria for aquatic life to determine if any elements were present at toxic levels. The majority limits are based on water hardness, which was found by adding the mean calcium and magnesium concentrations for each stream, expressed as $CaCO_3$. The water hardness of each stream was then run through the equations provided by the state to determine the toxicity limits for each stream. These limits were then compared to the mean elemental concentrations for each stream.

Results

Land Use

For the elements Cd, Pb, Mo, Ni, Ti, and V, mean concentrations were below 0.001 mg/L across the majority of sampling sites and much less than reported method detection limits (MDL) for the ICP-OES analysis at the certified lab. This means that there was not a measurable concentration of these elements in the majority of samples. As such, the relation between their mean concentrations and varying land use within the sample watersheds was not able to be evaluated.

For the elements Al, As, Cr, Co, Fe, Mn, and Se, the mean elemental concentrations were not related to watershed land use percent ($P>0.05$). For As, Cr, Co, and Se, all mean concentrations were less than their respective MDLs, but elemental mean concentrations are reported as measured (Table 2). For Al, Fe, and Mn, mean concentrations both above and below the MDLs were reported at various stream sites. Mean Al concentrations (MDL 0.017 mg/L) ranged from <0.001 mg/L at numerous locations to 0.033 mg/L at the Moores Creek site (MCEH). Mean Fe concentrations (MDL 0.023 mg/L) in the streams ranged from 0.004 mg/L at the Little Wildcat Creek site (LWRV) to 0.126 mg/L at the MCEH site. Mean Mn concentrations (MDL 0.011 mg/L) ranged from <0.001 mg/L at multiple sites to 0.048 mg/L at the McKisic Creek site (MCPO).

Across all stream sites, mean Ba concentrations were greater than the MDL (0.011 mg/L, Table 2). The least mean concentration, 0.083 mg/L, occurred at the TBMD site, while the greatest, 0.210 mg/L, occurred at the Brush Creek site (BRBC). Mean Ba concentrations were not significantly related to %Urb ($P=0.86$) or %For ($P=0.12$) across these streams and their

respective watersheds. However, mean Ba concentrations increased with increasing agricultural land usage (%Ag) across all stream watersheds (Figure 2). After performing a t-test analysis, Ba showed significant differences (P=0.03) in mean concentration between watersheds in the Boston (0.140 mg/L) and Ozark Mountain ecoregions (0.172 mg/L).

Table 2: Mean Elemental Concentrations and Method Detection Limits (MDL) by Sample Site for Water Samples Collected from December 2021 through March 2022.

Site Code	Al (mg/L)	As (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Cr (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	K (mg/L)	Se (mg/L)	Na (mg/L)	Zn (mg/L)
MDL	**0.017**	**0.017**	**0.011**	**0.036**	**0.090**	**0.016**	**0.012**	**0.015**	**0.023**	**0.030**	**0.011**	**0.210**	**0.020**	**0.217**	**0.016**
BBNJ	0.024	0.001	0.153	0.030	8.27	0.003	0.002	0.003	0.040	2.30	0.000	2.51	0.004	6.32	0.029
BRBC	0.000	0.005	0.210	0.024	48.41	0.003	0.002	0.008	0.007	2.03	0.010	1.87	0.003	7.62	0.035
CCWS	0.006	0.004	0.188	0.049	43.91	0.003	0.002	0.006	0.021	2.02	0.003	1.87	0.004	6.75	0.036
DC71	0.001	0.004	0.169	0.022	35.58	0.003	0.002	0.001	0.015	2.30	0.000	0.70	0.000	4.60	0.038
FBDS	0.000	0.007	0.122	0.074	70.01	0.006	0.005	0.007	0.015	4.03	0.004	1.06	0.005	10.18	0.032
HCDS	0.000	0.003	0.147	0.021	61.90	0.003	0.002	0.006	0.008	2.94	0.001	1.44	0.000	12.72	0.029
HCIC	0.004	0.004	0.130	0.028	37.63	0.003	0.002	0.002	0.033	4.75	0.003	1.39	0.000	9.21	0.034
LWRV	0.002	0.004	0.190	0.027	43.87	0.003	0.002	0.006	0.004	1.99	0.000	2.17	0.002	8.28	0.034
MC71	0.014	0.001	0.170	0.022	12.74	0.003	0.002	0.001	0.035	2.03	0.001	0.52	0.005	3.33	0.035
MCEH	0.033	0.001	0.178	0.030	19.70	0.003	0.002	0.003	0.126	2.51	0.026	2.65	0.006	7.26	0.035
MCOM	0.000	0.003	0.153	0.042	46.53	0.003	0.002	0.005	0.017	4.36	0.048	1.43	0.008	12.01	0.036
MCPO	0.000	0.003	0.172	0.027	70.83	0.003	0.002	0.005	0.004	2.51	0.000	1.54	0.005	9.62	0.036
OC26	0.000	0.005	0.210	0.026	44.17	0.003	0.002	0.006	0.008	2.33	0.002	1.59	0.009	11.17	0.037
OCGC	0.000	0.007	0.131	0.036	67.19	0.003	0.002	0.002	0.004	3.96	0.001	1.57	0.002	13.22	0.037
PB45	0.006	0.002	0.142	0.016	18.43	0.003	0.002	0.001	0.030	1.61	0.000	0.42	0.000	23.00	0.034
RC71	0.002	0.004	0.141	0.019	30.77	0.003	0.002	0.001	0.019	2.68	0.000	0.81	0.009	4.58	0.033
SCVA	0.000	0.003	0.131	0.059	68.64	0.004	0.002	0.007	0.010	5.89	0.004	1.89	0.003	24.22	0.040
TBMD	0.000	0.003	0.083	0.036	53.62	0.003	0.002	0.006	0.021	9.56	0.030	2.40	0.004	22.96	0.063
WCKR	0.000	0.000	0.190	0.018	38.80	0.003	0.002	0.003	0.006	1.90	0.000	2.46	0.005	10.34	0.030

Of the 19 sample sites, only 5 had mean B concentrations greater than the MDL (0.036 mg/L, Table 2); however, all means are reported as measured. Across these 19 watersheds, mean B concentrations increased significantly with increasing %Urb across all watersheds (Figure 2). They were not related to %Ag (P=0.39) or %For (P=0.23). The least mean B concentration,

0.016 mg/L, occurred at the Parker Branch site (PB45), and the greatest, 0.074 mg/L, occurred at the Farmington Branch site (FBDS).

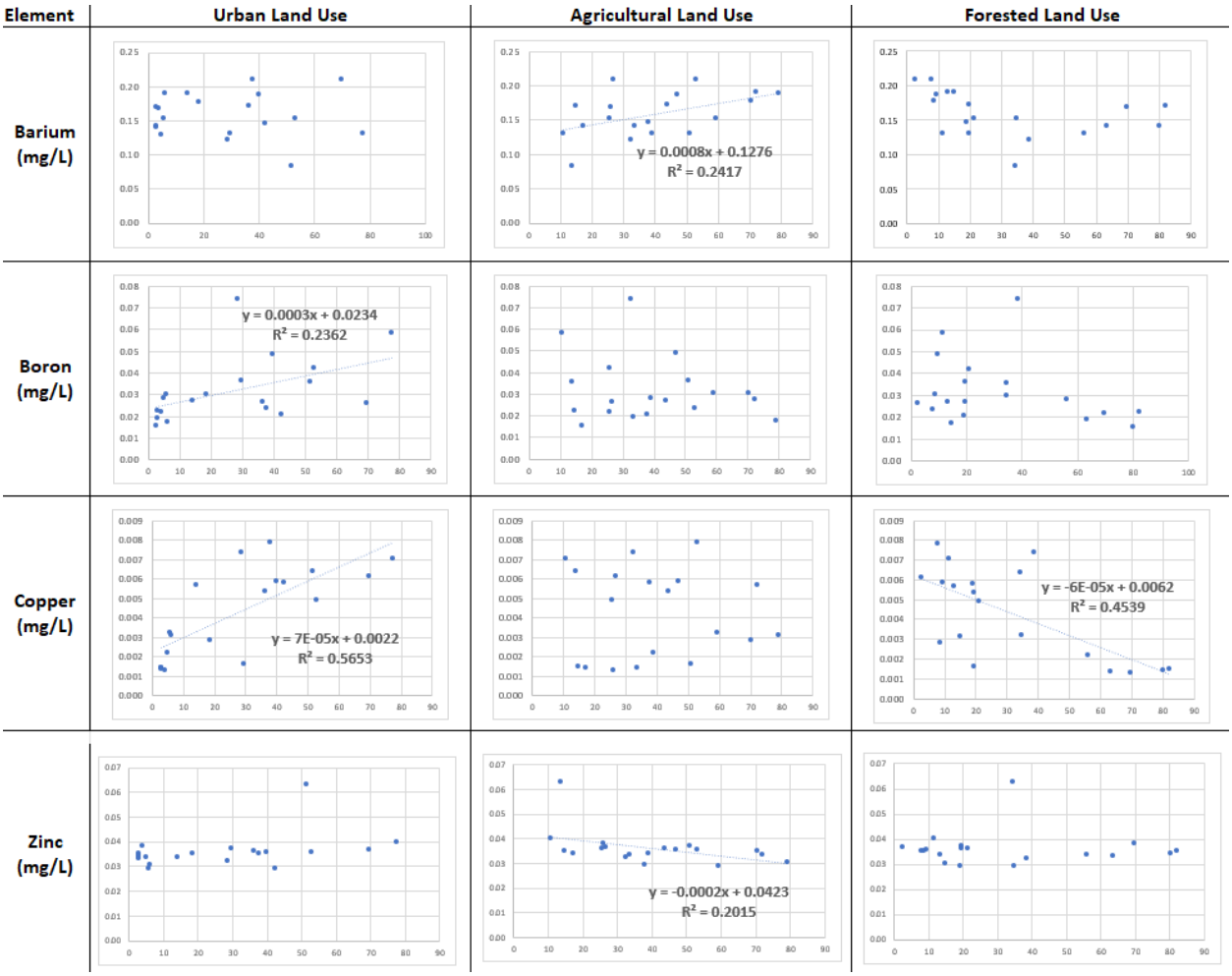

Figure 2: Relationships Between the Trace Elements Barium, Boron, Copper, and Zinc and Varying Land Usages in the Stream's Watershed (based on 2019 Land Use Land Cover, modelmywatershed.org)

Mean Cu concentrations across all sites were less than the MDL (0.015 mg/L, Table 2), ranging from 0.001 mg/L at numerous locations to 0.008 mg/L at the BRBC site. Despite all means being less than the MDL, mean Cu concentrations across these sites were significantly related to watershed land use, except for %Ag (P=0.89) (Figure 2). Mean Cu concentrations decreased with increased %For across all stream sites (P<0.01), while concentrations increased with %Urb (P<0.01).

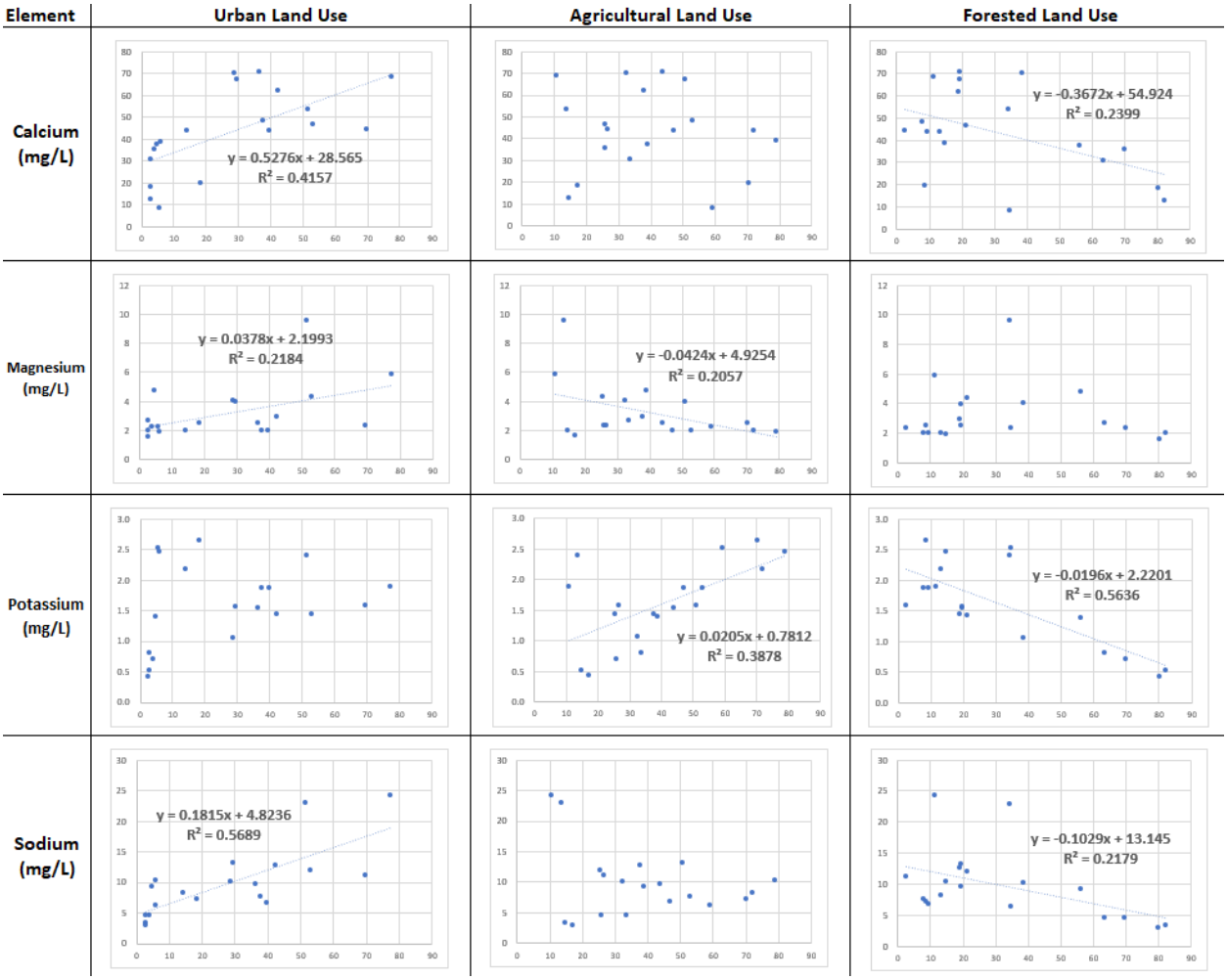

Figure 3: Relationships between the Macro-Elements Calcium, Magnesium, Potassium, and Sodium, and Varying Land Uses in the Stream's Watershed (Based On 2012 Land Use Land Cover, modelmywatershed.org)

Interestingly, mean Zn concentrations decreased with increasing %Ag (P=0.05) across sampled streams. Mean Zn concentrations were above the MDL (0.016 mg/L) across all stream sites, and ranged from 0.029 mg/L at the Beatty Branch site (BBNJ) to 0.063 mg/L at the Town Branch site (TBMD). There was not a significant relationship between mean Zn concentrations and %Urb (P=0.09), nor was there a relationship between mean Zn concentrations and %For (P=0.97).

Unsurprisingly, mean concentrations for the macro-elements included in ICP-OES analysis were well above their respective MDLs (Table 2) across all 19 sampled streams. These

macro-elements include Ca, Mg, K, and Na. For all of these macro-elements, there was a significant relationship between their respective mean concentrations and varying land usage within the sampled streams and their respective watersheds (Figure 3). Mean Ca concentrations significantly increased with increasing %Urb ($P<0.01$) and decreased with increasing %For ($P<0.05$), but were not significantly related to %Ag ($P=0.61$). Mean Ca concentrations ranged from 8.27 mg/L at the BBNJ site to 70.83 mg/L at the MCPO site. Mean Mg concentrations significantly increased with increased %Urb ($P=0.04$), decreased with increased %Ag ($P=0.05$), and were not significantly related to %For ($P=0.81$). The greatest mean Mg concentration was 9.56 mg/L at the TBMD site, and the least was 1.61 mg/L at the PB45 site.

Moving on to the monovalent cations, K was the only macro-element for which mean concentrations increased with increasing %Ag ($P<0.01$) across all sites. Mean K concentrations also decreased with increasing %For ($P<0.01$), although there was no relation between mean K concentrations and %Urb ($P=0.27$). Mean K concentrations ranged from 0.42 mg/L at the PB45 site to 2.65 at the MCEH site. There was also a significant difference ($P=0.02$) between mean K concentrations and their variance across level 3 ecoregions. Na behaved similarly to Ca, with mean Na concentrations increasing with %Urb ($P<0.01$) and decreasing with increasing %For ($P=0.04$) across all sites. There was not a significant relationship between mean Na concentrations and %Ag ($P=0.25$). The least mean Na concentration was 3.33 mg/L at Mill Creek (MC71), and the greatest was 24.22 mg/L at Scull Creek (SCVA).

Elemental Correlations

Table 3: Pearson Correlation Table for Various Elements, Where Bolded Cells Represent Significant Correlations

	Al (mg/L)	As (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Cr (mg/L)	Co (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Mn (mg/L)	K (mg/L)	Se (mg/L)	Na (mg/L)
As (mg/L)	**-0.57**													
Ba (mg/L)	0.12	-0.12												
B (mg/L)	-0.11	0.42	-0.36											
Ca (mg/L)	**-0.70**	**0.62**	-0.24	**0.52**										
Cr (mg/L)	-0.13	0.37	-0.31	**0.67**	0.42									
Co (mg/L)	-0.07	0.39	-0.26	**0.69**	0.32	**0.94**								
Cu (mg/L)	-0.35	0.34	0.09	**0.54**	**0.62**	0.29	0.22							
Fe (mg/L)	**0.90**	**-0.49**	0.01	-0.05	**-0.56**	-0.01	0.05	-0.32						
Mg (mg/L)	-0.25	0.17	**-0.78**	0.43	0.42	0.13	0.08	0.30	-0.06					
Mn (mg/L)	0.12	-0.12	-0.21	0.20	0.01	-0.15	-0.08	0.20	0.33	**0.48**				
K (mg/L)	0.31	-0.27	0.13	0.12	0.07	-0.20	-0.19	0.39	0.25	0.23	0.28			
Se (mg/L)	0.12	-0.06	0.25	0.12	-0.07	0.05	0.03	0.16	0.13	-0.07	0.31	0.12		
Na (mg/L)	-0.37	0.14	**-0.49**	**0.47**	**0.65**	0.07	0.00	**0.54**	-0.24	**0.83**	0.33	0.43	-0.03	
Zn (mg/L)	-0.20	0.11	**-0.49**	0.15	0.23	-0.12	-0.13	0.23	-0.03	**0.81**	**0.45**	0.19	-0.03	**0.61**

Across all sampled streams, numerous elemental concentrations were significantly correlated with one another ($P<0.05$, Table 3). The positive correlations observed included:

- Al was correlated with Fe (r=0.90)
- As was correlated with Ca (r=0.62)
- B was correlated with Ca (r=0.52), Cr (r=0.67). Co (r=0.69), Cu (r=0.54), and Na (r=0.47)
- Ca was correlated with Cu (r=0.62) and Na (r=0.65)
- Cr was correlated with Co (r=0.94)
- Cu was correlated with Na (r=0.54)
- Mg was correlated with Mn (r=0.48), Na (r=0.830, and Zn (r=0.81)
- Mn was correlated with Zn (r=0.45)
- Na was correlated with Zn (r=0.61)

There were fewer significant negative correlations between mean elemental concentrations ($P<0.05$, Table 3), but still several of note. These included:

- Al was correlated with As ($r=-0.57$) and Ca ($r=-0.70$)
- As was correlated with Fe ($r=-0.49$)
- Ba was correlated with Mg ($r=-0.78$), Na ($r=-0.49$), and Zn ($r=-0.49$)
- Ca was correlated with Fe ($r=-0.56$)

Toxicity

Table 4: Toxicity Limits for All Sampled Streams, Based on Arkansas Water Quality Limits for Chronic Aquatic Life Exposure (https://www.epa.gov/sites/default/files/2014-12/documents/arwqs.pdf) and EPA National Drinking Water Regulations (https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations)

Site Code	Hardness (mg/L CaCO3)	As (mg/L)	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Se (mg/L)	Zn (mg/L)
AR Chronic Aquatic Life		N/A						
BBNJ	30	-	<0.001	0.011	0.004	0.001	0.005	0.038
BRBC	129	-	0.001	0.011	0.014	0.003	0.005	0.130
CCWS	118	-	0.001	0.011	0.013	0.003	0.005	0.120
DC71	98	-	0.001	0.011	0.011	0.003	0.005	0.103
FBDS	191	-	0.002	0.011	0.020	0.005	0.005	0.181
HCDS	167	-	0.002	0.011	0.018	0.004	0.005	0.161
HCIC	113	-	0.001	0.011	0.013	0.003	0.005	0.116
LWRV	118	-	0.001	0.011	0.013	0.003	0.005	0.120
MC71	40	-	<0.001	0.011	0.005	0.001	0.005	0.048
MCEH	59	-	0.001	0.011	0.007	0.001	0.005	0.067
MCOM	134	-	0.001	0.011	0.015	0.003	0.005	0.134
MCPO	187	-	0.002	0.011	0.019	0.005	0.005	0.178
OC26	120	-	0.001	0.011	0.013	0.003	0.005	0.122
OCGC	184	-	0.002	0.011	0.019	0.005	0.005	0.175
PB45	53	-	0.001	0.011	0.007	0.001	0.005	0.061
RC71	88	-	0.001	0.011	0.010	0.002	0.005	0.094
SCVA	195	-	0.002	0.011	0.020	0.005	0.005	0.184
TBMD	173	-	0.002	0.011	0.018	0.005	0.005	0.166
WCKR	105	-	0.001	0.011	0.012	0.003	0.005	0.109
EPA Drinking Water Regulations	N/A	0.01	0.005	0.1	1.3	0.015	0.05	5.0 mg/L

Based on Arkansas Water Quality Limits (Pollution Control and Ecology Commission, 2020), several stream sites had mean concentrations of certain elements at levels potentially dangerous for chronically exposed aquatic life. These included:

- Cd at Farmington Branch (FBDS), mean of 0.003 mg/L & limit of 0.0012 mg/L
- Pb at Parker Branch (PB45), mean of 0.002 mg/L & limit of 0.0012 mg/L
- Se (limit of 0.005 mg/L at all sites):
    - Farmington Branch (FBDS), mean of 0.005 mg/L

- Mill Creek (MC71), mean of 0.005 mg/L
- Moores Creek (MCEH), mean of 0.006 mg/L
- Mud Creek (MCOM), mean of 0.008 mg/L
- McKisic Creek (MCPO), mean of 0.005 mg/L
- Osage Creek (OC26), mean of 0.009 mg/L
- Rock Creek (RC71), mean of 0.009 mg/L
- Wildcat Creek (WCKR), mean of 0.005 mg/L

Fortunately, no mean concentrations of any regulated element were above EPA National Primary Drinking Water Regulations at any site.

Discussion

In the United States, level 3 ecoregions are large areas of land defined by similar biotic and abiotic criteria, including the underlying geology (Bailey, 2004). Bedrock influences the hydrochemistry of streams, with even relatively minor differences having a notable impact (Bailey, 2004). The two level 3 ecoregions in this study, the Boston Mountains and Ozark Highlands, have some differences in underlying geology. The Boston Mountains are made up of sandstone and shale, both of which are silicates, while the Ozark Highlands is made primarily of carbonate rocks such as limestone and dolomite (Panfil & Jacobson, 2001).

We might expect to see greater Ca concentrations in streams draining from the Ozarks due to the dissolution of Ca into groundwater (White, 2002). Meanwhile, the weathering of silicate in the Bostons might correspond to increased Na concentrations (Bricker & Rice, 1989). Despite this, there was not a significant difference in mean Ca concentrations for the across watersheds in the two ecoregions, nor was there a difference in Na concentrations, nor indeed for the majority of elements. Instead, dissolved Ca and Na concentrations were the greatest among all elements analyzed (Table 2). This may be explained by the fact that many of the sampled watersheds were not exclusive to one ecoregion, but instead drained mostly from one and partially from the other. In future studies it may be worthwhile to sample from watersheds exclusive to one ecoregion in order to isolate their effects on water chemistry.

The majority of the elements analyzed either did not have measurable concentrations (i.e. >MDLs) and/or did not exhibit any significant relationship with varying land use. However, several of the mean elemental concentrations did trend upwards with increasing human activity, be it agricultural or urban land use. Similarly, no mean elemental concentration increased with increasing forested land use. This is to be expected, as forested land represents the overwhelming

majority of undeveloped land across all of the sampled watersheds. In mostly undeveloped watersheds, geology plays a significant role in stream chemistry (Clow & Sueker, 2000), much more so than human land use. Watersheds with primarily forested land use can therefore be used as a benchmark for natural stream conditions (Martin, 1979).

Of the elements which showed significant trends with human activity, most behaved as expected. Mean concentrations of B, Ca, Cu, Mg, and Na all trended upwards with increasing urban land use, and many of these elements were positively correlated with one another. There are many potential sources of these elements in urban areas that might explain these correlations. Road de-icing salts and roadway runoff events can increase major ion concentrations (e.g. Ca, Mg, and Na) in streams (Koryak et al., 2001); the study region had several occurrences of snowfall before and between sampling events. Vehicle traffic in urban areas is a potential source of Cu to steams (Contardo et al., 2020). B is linked to several aspects of urban activity, including glass, cosmetics, and cleaning agents (Vengosh et al., 1994). In fact, B concentrations have been considered a reliable marker of human activity (Guinoiseau et al., 2018), so it is hardly a surprise that it trends upwards with increased urban land use in Northwest Arkansas streams.

Concentrations of several elements were significantly related to agricultural land use, two trending upwards with increased %Ag and two trending downwards. The two elements which significantly increased with increasing %Ag, Ba and K, are often in fertilizer and animal manure (Ahlgren et al., 2012; Korucu et al., 2018). It is well documented that the application of fertilizer and animal manure to agricultural fields influences surface runoff and stream chemistry (Alexander et al., 2000; Conrad et al., 2019). This being the case, it is reasonable to hypothesize that fertilizer and animal manure application within agricultural land use are linked to increased elemental concentrations in these streams.

Also worth noting is that the only two elements that showed a significant difference in mean concentration across level-3 ecoregions were Ba ($P=0.03$) and K ($P=0.02$), with both being greater in the Ozark Highlands. A significant difference was also found in the %Ag of sampled watersheds across the two ecoregions, again being greater in the Ozarks ($P<0.01$). As mean concentrations of both Ba and K trended upwards with increased %Ag, this is the likely cause of the discrepancy. In further studies it would be best to consider sampling such that there is no significant difference in land use across ecoregions. This would make it easier to determine if differences in elemental concentrations are due to changes in ecoregion or in land use.

Mg and Zn showed particularly interesting behavior, being the only elements analyzed which showed decreasing mean concentrations with any form of increased human activity. This is particularly surprising, given that both elements are vital for plant development and thus are prevalent in fertilizers and animal manure (Senbayram et al., 2015; Toor et al., 2007). Studies have shown that Zn concentrations in runoff increase when poultry litter is applied to the landscape (DeLaune & Moore Jr, 2016). Likewise, fertilizer application can lead to Mg leaching from soil and into runoff water (Senbayram et al., 2015). However, these streams did not show the expected relation between these elements and watershed land use. More research into this particular topic may be worthwhile.

There was one site, Town Branch (TBMD), which had a much greater mean concentrations of both Mg (9.56 mg/L) and Zn (0.063 mg/L) than the other streams (Mg: 1.61-5.89 mg/L, Zn: 0.029-0.040 mg/L). This may have been due to runoff from sources within the urban center of the watershed. There is a steel fabrication plant directly upstream of the sample site, which may be responsible for increased Zn and Mg runoff (Odnevall Wallinder & Leygraf,

2017; Sullivan & Worsley, 2002). However, Town Branch (TBMD) did not have elevated concentrations of other trace elements relative to its watershed land use.

The Town Branch (TBMD) site could be considered an outlier for concentrations of both Zn (Z score = 3.8) and Mg (Z score = 3.3). As such, it is valid to remove this site from the land use analysis (Rousseeuw & Hubert, 2011). When this site was removed, mean Zn concentrations no longer displayed a significant relationship with %Ag (R^2=0.2037, P=0.06), nor was there a significant relationship between mean Zn concentrations and %Urb (P=0.06) or %For (P=0.79). Mg concentrations also did not display a significant relationship with %Ag (R^2=0.1342, P=0.13), though the relationship with %Urb persisted. This underscores the potential importance of local sources of trace elements to stream water chemistry.

The Farmington Branch site (FBDS) had much greater mean concentrations of several elements than all other sites. After reviewing the data, it was found that certain elemental concentrations were much greater at the Farmington Branch (FBDS) site during the first round of sampling than during any other round; these elements included As, Cd, Cr, Pb, Mo, V, and Zn. Despite concentrations from the first round of sampling being many times higher than in subsequent samples, none of these values had z-scores (1.0-1.2) large enough to be considered outliers. Having only three data points makes it more difficult to determine if a single sample is an outlier, as the potential outlier will influence both the mean value and standard deviation of the data set (Efstathiou, 2006). More rounds of sampling would be preferrable, as this would reduce the influence of one deviant sample on the overall analysis.

One of the main practical applications for the data collected is that of toxicity. Each state has made its water quality standards publicly available, a section of which pertains to limits for chronic wildlife exposure. The dissolved metals analyzed in this study which are regulated by

Arkansas are Cd, Cr III & VI, Cu, Pb, Ni, Se, and Zn (Pollution Control and Ecology Commission, 2020)(Comission, 2020). For the purposes of this study, the lower limit of the two types of chromium was used, as the ICP-OES analysis does not distinguish between the two.

There were multiple sites with reported mean concentrations of certain elements (Table 2) at levels exceeding Arkansas state regulations (Table 4). It may be necessary to further monitor these sites to ensure that this is not a recurring phenomenon, and for the state to take action if it is. Worth noting, however, is that in many cases the regulatory limits are below the ICP-OES method detection limits. This means that the reported concentrations may not be the actual concentrations of the elements in question. If further monitoring is done, it should utilize a method with lower MDLs to ensure the accuracy of the data. In any case, these are not likely to impact human health as no mean concentration was in excess of EPA National Primary and Secondary Drinking Water Regulations (EPA, 2009).

Conclusions

This study shows that changing land use has a significant impact on mean concentrations of several elements within Northwest Arkansas streams. Watersheds with greater urban land use tended to have streams with greater mean concentrations of B, Cu, Ca, Mg, and Na. Watersheds with greater agricultural land use tended to have increased concentrations of Ba and K, and decreased concentrations of Mg and Zn. Furthermore, no elemental concentrations increased with increasing forested land use, suggesting that human development is the primary driver of these changes.

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