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Distribution and Seasonal Variation of Total Metals in Surface Water of the Tennessee River Basin

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Abstract

Heavy metals in surface water were measured to determine their distribution and seasonal variations in Flint Creek and Flint River watersheds. Bi-weekly stream water samples were collected from six selected sites within the watersheds. The samples were digested using an approved EPA method SW 846-3015 in a closed vessel microwave and analyzed for total recoverable metals of some selected elements of concern (Al, Co, Ni, Cu, Fe, Mn, Cd, As, Se, Zn, Pb, and P), using ICP-OES (Perkin-Elmer Optima 2100 DV series). Heavy metal concentrations ranged from undetectable to 123 µg l^{-1} (Pb), 409 µg l^{-1} (Al), and 453 µg l^{-1} (Zn). Physical and chemical water quality parameters including heavy metal concentrations were also measured. The concentration ranges of all the metals measured were mostly below the EPA guidelines for acceptable concentrations for drinking water, except Al, Pb, Fe and P. The water quality parameter shows that the dissolved oxygen (DO) concentrations in three of the sites are very low (<5 mg l^{-1}) and could affect aquatic organisms. All metals were statistically significant (at $p \leq 0.05$) by watershed. Patterns observed were a steady increment in metal concentrations from upstream to downstream in both watersheds. The seasonal variation was also evident that the rivers had higher heavy metal content (>45%) during winter and spring than summer and fall. Results suggested that agriculture, past and present land use practices, have resulted in significant adverse impacts on the study areas

1. Introduction

The Flint Creek (FC) has at least 40 km of impaired surface water due to nutrients, organic enrichment, and pathogens originating from animal holding and other non-point sources (USEPA, 1994). Most of the surface waters within the FC watershed are designated for F&W use; however, the lower part of FC is also classified PWS, and a 15 km long central segment is classified limited warm-water fishery (LWF) (The Flint Creek Watershed Project, 1995). Most of the Flint River Watershed (FRW) contains productive farmland (predominantly cotton, corn, and soybeans). A specific area of interest exhibiting dramatic changes in Madison County, Alabama is the FRW. In 1984, only 5% of the FRW was developed. By the year 2000, 20% of the watershed had been developed-a four-fold increase within 16 years. Today, the percentage of developed land in the watershed is nearly equal to that of the county as a whole (Laymon, 2005). Heavy metals naturally occur in the water due to geological structure of the region but may also be introduced as a result of human activities including: processing of ores and metals, the industrial use of metal compounds, and leaching from industrial and domestic waste dumps. Heavy metal pollution in Flint River (FR) is partly caused by agriculture and growing urbanization, while heavy metal pollution in FC is partly caused by mining, agriculture and geological structure of the region (Tsegaye et al., 2006). Numerous impoundments along the Tennessee River (TR), upstream from the Huntsville intake, regulate stream-flow and water quality in the river, thus, dampening short-term fluctuations caused by runoff. Studies by Hoos et al. (2000), have reported that during storms, however, the quality of water at the intake is greatly affected by predominantly agricultural FR basin as a result of incomplete mixing at the confluence of the FR and TR. Non-point source contaminants from agricultural activities include pesticides, sediment, nutrients and heavy metals, such as Al and Pb.

It has been suggested that Al may be linked to Alzheimer's disease, although that research has recently been refuted; Al accumulation may be a consequence of the Alzheimer's damage, not the cause. A blood Pb level≥10 µg dl^{-1} is considered to be an elevated blood Pb level by the federal government. Blood Pb level≥10 µg dl^{-1} is associated with harmful effects on children's learning and behavior (EPA's Toxics Release Inventory). Fish kills occur when exposed for a few hours to dissolved oxygen (DO) concentrations below 3 mg l^{-1} (EPA 822-R-94-001, 1994).

This study focused on the determination of the presence, concentration, and the distribution of heavy metals in FC and FR watersheds because the primary drinking water source for Morgan and Madison County, Alabama is surface water, and the city of Huntsville withdraws about 60% of its drinking water from the TR. The result of this study could provide baseline data on heavy metal concentration and data on physical and chemical parameters in surface water of the watersheds and, thus, aid in future prevention and mitigation strategies by decision makers.

The long-term goal of this study is to improve the water quality of these streams in order to sustain aquatic life, spur the growth of fish, maintain the watershed designations, and meet the goal of the Clean Water Act. A comprehensive study to investigate the status of water quality in the FC and FR is necessary.

2. Materials and Methods

2.1. Study site and sampling

The study areas were FC and FR. The FC watershed is in Morgan County at 34°30' north latitude and 86°57' west longitude. The FR watershed is located in Southern Tennessee and in Madison County, Alabama at 34°30' north latitude and 86°28' west longitude, both rivers are in northern Alabama. Six sampling sites, representative of the two river reaches, were chosen at key locations within the overall river systems (Figure 1 and 2). The areas surrounding the FC watersheds are primarily agricultural/rural, and FR is mixture of urbanized/agricultural land. The FC and the FR watersheds make up most of the Wheeler Lake (WL) basin.

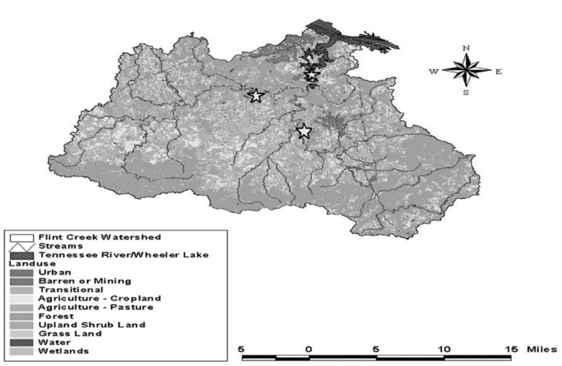

Figure 1: Flint Creek watershed study sites

Water sampling (20 cm in depth) was carried out between 2009 and 2011. Collected samples were stored in polyethylene bottles and transported to Alabama A&M University laboratory for subsequent preparation and analyses. Polyethylene bottles were rinsed at least five times with a double-distilled water and 1:1 HNO_3:H_2O. Water samples were passed through Whatman glass micro-fiber filters. The samples were acidified with (0.2 v/v) ultra pure nitric acid to pH<2 as acidification minimizes to absorption of metals into the wall of the containers and stored approximately at 4°C.

The study design of the FC and FR watersheds incorporated grab surface-water samples to help understand water-quality conditions and issues affecting the FC and FR watersheds (Table 1). A selected number of contaminants were sampled once a week, over a three years period (2009, 2010 and 2011) at fixed sites on the two watersheds and some of its tributaries. This period covered the (winter, spring, summer and fall). For two to three year studies, fixed-period, and semi-monthly sampling provided not only the least biased, but also the most precise loads (Robertson et al., 2000).

2.2. Analytical techniques and quality control

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin-Elmer Optima 2100 DV series) was used for heavy metal analysis. The 6600EDS Sonde probe was used for physical and chemical parameter determinations of: DO, turbidity, pH, temperature, water conductivity and chlorophyll. Shinn and Reich (1999) in their study have demonstrated the use of ICP-OES as a rapid, low-cost method for obtaining accurate data for about 30 elements. ICP-OES is based on the principle that sample material is introduced into an argon-based, high-temperature radio-frequency plasma, usually by pneumatic nebulization. Energy transfer from the plasma to the sample stream causes desolvation, atomization, and ionization of target elements. Ions generated by these energy-transfer processes are extracted from the plasma through a differential vacuum interface, and separated on the basis of their mass-to-charge ratio by an optical emission spectrometer (OES).

The analytical calibrations were established with reference and

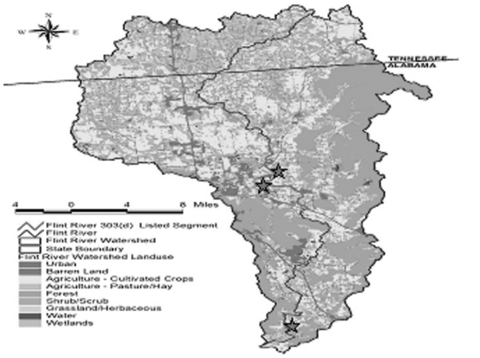

Figure 2: Flint River watershed study sites

prepared concentration solutions. The linear dynamic range; resulting analytical curves exhibited linearity over four (0, 0.5, 1, and 2.5 mg l^{-1}) concentration points. The relative standard deviations determined over an extended period of time ranged from 0.01 to 0.08. The inductively coupled plasma (ICP) exhibited good sensitivity, i.e. the functional relationship between emission intensity and concentration. Duplicate samples were processed on a routine basis. A quality-control sample was processed with every ten samples and the r^2 for calibration for each element was maintained at ≥0.99. Blank samples were also prepared using the same reagents and quantities used in sample preparation, placed in vessels of the same type, and processed with the samples (Patnaik, 1997). Chemical analysis for target elements including Al, Co, Ni, Cu, Fe, Mn, Cd, As, Se, Zn, Pb and P (nutrient) were analyzed using the ICP-OES.

An analytical method was used for the detection and quantification of desired metal species present in the sample. The analytical procedure was also tested for both measurement precision and accuracy in order to assess the degree of reliability which can be allocated to the data generated by this study. The recovery percentages were near 100%. Level of accuracy was determined by recovery test results. ICP-OES was used for this study because it is more suitable for elements with high concentration, and it may not be affected by mass-spectral interference.

2.3. *Digestion of sample*

There is a need for proper preparation of the materials to be used for digestion of samples (Kingston et al., 1998). The laboratory glasswares were soaked in nitric acid bath and were rinsed thoroughly using pure de-ionized water to avoid contamination of metal. The materials used were 50 ml florence flask, glass cover, graduated cylinder (10 ml, 50 ml), microwave-digestion plastic vessels, plugs, and cover for the sample. The working area was cleaned as much as possible to eliminate contamination of the sample to be analyzed since it will affect the result. Total recoverable metals were analyzed which includes all metals, organically and inorganically bound, both dissolved and particulate (APHA, 1992). Most surface water samples will require digestion before analysis to reduce organic matter interference and to convert metal to a form (free metal) that can be analyzed by ICP-OES. An EPA approved, SW846-3015 method using Microwave Accelerated Reaction System (MARS) oven was used for the sample digestion. A 25 ml sample placed inside each Teflon transparent digestion vessel with a 5 ml solution of (70% nitric acid) was subjected to rapid heating in a sealed vessel, elevated pressures, causing the sample to digest in a short time.

Table 1: Sampling site: geographic coordinate points of sampling locations at the FC and FR watersheds

Flint River watershed (Huntsville, Alabama)

Sites	Stream	Codes	Coordinate points	Elevation
1	Winchester Road	WR-FR	N 34o30’12.5” W 86o28’00.4”	721.5±19”
2	Briar Fork Road	BF-FR	N 34o47’23.15” W 86o29’05.4”	751.5±36”
3	Hobbs Island Road	HR-FR	N 34o32’19.5” W 86o55’52.6”	660.5±30”

Flint Creek watershed (Decatur, Hartselle, Alabama)

Sites	Stream	Codes	Coordinate points	Elevation
4	Red Bank Road	RB-FC	N 34o30’22.5” W 86o57’20.8”	788.5±50”
5	Means Bridge	MB-FC	N 34o29’37.8” W 87o01’34.9”	602.5±42”
6	Vaughn Bridge Road	VB-FC	N 34o27’48.15” W 86o57’52.4”	521.5±56”

2.4. *Statistical analysis*

The concentration of the heavy metals was statistically analyzed using statistical analysis system (SAS) (SAS 9.1, 1999). The data was tested using analysis of variance (ANOVA) with sampling sites (location) and seasons as the major sources of variation. Mean comparisons were conducted using Tukey statistical tests. The ANOVA and Tukey analysis provided results for each segment of 96 samples by sampling locations and seasons. Table of mean concentrations of heavy metals of concern were observed to describe changes in metal concentrations with changes in season and by location.

3. Results and Discussion

Results of ANOVA showed that there were significant differences ($p<0.05$) among the four sampling seasons (winter, spring, summer, and fall) and locations (WR-FR, BF-FR, HR-FR, RB-FC, MB-FC, and VB-FC) **(Tables 2a and 2b).** The HR-FR and VB-FC showed the highest concentration for all the heavy metals. The two sites are the tributaries of the FR and FC, respectively. The remaining sites had lower metal concentrations. From the result of the concentrations, there are a few trends that are apparent from this analysis:

1. Surface water concentrations for heavy metals are less in most cases than the Maximum Contaminant Level (MCL) set by EPA guidelines for drinking water, and
2. Concentrations generally increased in an upper to lower reaches across the watersheds.

The southward trend is commensurate with a north to south increase in urbanization and industrialization in Madison and Morgan counties. A preliminary statistical cluster analysis showed that Zn, P, and Cu clustered strongly with Al and Fe at site 4, which are often associated with high clay content. The

Table 2a: Distribution of total heavy metals in FR surface water*

Sites	Al	Fe	Mn	As	Pb
Heavy Metals in Surface Water (n=96) (mg kg^{-1})					
WR-FR					
Average	48.55	59.89	6.501	1.75	5.14
Maximum	93.6	91.0	10.1	5.0	20.3
Minimum	8.0	20.0	4.0	ND	ND
BF-FR					
Average	164.91	130.33	9.3	1.74	11.95
Maximum	409.0	276.8	15.0	5.0	32.6
Minimum	28.0	32.0	7.0	ND	ND
HR-FR					
Average	131.31	167.1	20.84	3.3	29.91
Maximum	200.7	330.5	29.0	8.0	123.0
Minimum	80.0	45.0	13.0	ND	ND

*Means are only given where all samples are above detection limits ND=Not detected (below detection limit)

Table 2b: Distribution of total heavy metals in FC surface water*

Sites	Al	Fe	Mn	As	Pb
Heavy Metals in Surface Water (n=96) (mg kg-1)					
RB-FC					
Average	142.85	193.16	27.045	1.85	7.79
Maximum	221.3	340.2	47.6	4.5	34.1
Minimum	41.0	51	10.3	ND	ND
MB-FC					
Average	122.65	185.94	46.96	0.85	9.26
Maximum	171.8	230.9	84.6	2.4	37.9
Minimum	63.0	169.01	13.6	ND	ND
VB-FC					
Average	150.81	155.09	45.83	0.8	4.08
Maximum	329.8	310.1	90.0	2.2	17.3
Minimum	86.0	9.0	19.6	ND	ND

*Means are only given where all samples are above detection limits; Pearson Correlation Coefficients (SAS Proc Corr); N=96, Probability>[r] under H0: Rho=0; ND=Not detected (below detection limit)

silty clay soil in FC watershed suggests a terrigenous source. FC watershed interestingly is in Limestone County.

Factors other than heavy metal that can impact aquatic organisms' populations and diversity in surface water include: changes in habitat, low DO, temperature, pH, and turbidity. The targeted DO criterion for summer low flow conditions in FC is a minimum of 5 mg l^{-1} in the reaches classified as F&W or PWS and 3 mg l^{-1} in the reaches classified as LWF. Most of the surface waters within the FC watershed are designated F&W use classification, however, the lower part of FC is also classified PWS, and a nine mile long central segment is classified LWF. Fish kills occur when exposed for a few hours to DO concentrations below 3 mg l^{-1} (EPA 822-R-94-001, 1994). As **Table 3** shows, the DO concentrations for sites 3, 5, and 6 are definitely below the targeted criterion for these watersheds. The low DO in VB-FC (site 6) may be due to heavy concentration of organic matter (dead leaves and tree limbs) in the stream that may depress the oxygen concentration below that required level to support fish life. Oxygen deficiency is fatal to fish, and many types of aerobic bacteria (Tan, 1998). Furthermore, water circulation at these sites is more restricted than at other sites in the study area, implying longer residence times for the contaminants. Also, under oxygen deficient conditions, there will be decreased redox potential and this will change the composition of metal complexes and release the metal ions into the overlying water. Site 6, on FC, is definitely in poor state and these findings raise significant ecological and public concerns. The average of the temperature and pH remains about the same at all sites, but a closer look at the data shows very low pH and somewhat acidic surface water in winter and spring seasons (pH: 6.2-6.4). Conductivity in rivers is affected by geology of the area through which the water flows. As shown in Table 3, sites 1 and 2 are low in conductivity which may be probably due to the stream running through areas with granite bedrock that does not dissolve into ionic components when washed into the water. Sites 3, 4, 5, and 6 are high in conductivity and this may be due to the streams at

Table 3: Results of the physicochemical parameters measured in the sampling sites

Site #	pH	Turb (NTU)	Temperature (°C)	DO (mg l-1)	Conductivity (µmhos cm^{-1})	P (nutrient)
1	7.73	8.07	16.01	17.42	148.60**	27.20**
2	7.52	5.66	15.82	19.74	167.33**	34.23**
3	7.42	12.11	16.42	4.27***	207.22*	49.00**
4	7.22	7.43	16.21	11.74	235.56*	31.15**
5	7.29	8.03	15.86	3.16****	250.06*	43.95**
6	7.35	31.16****	16.93	2.81****	205.62*	193.10**

alicized=Normal level

*Significantly above maximum contaminate level

**Moderately above maximum contaminate level

***Below acceptable level

****Significantly below acceptable level those sites running through areas with clay soils with presence of materials that ionize when washed into the water. Streams within the WLB support good mixed fisheries. They typically have a conductivity range between a low of 150 and a very high of 500 µhos cm^{-1}. The MCL for phosphorous is 10 µg l^{-1}, the highest concentration average for phosphorous for the two years was 193 µg l^{-1} at VB-FC and this shows about 20 folds in phosphorous average concentration with maximum at this site reaching 450 µm l^{-1}. There are animal farms along VB and animal wastes littered on open-fields. This may be the source of so much P in the river water.

The t Test shows that the variation between mean concentrations of the metals is significant (Table 4). The results for heavy metals in this study did not follow a *generally accepted pattern*. Al, Zn, and Fe reached their maximum at HR-FR and VB-FC; these are the FR and FC tributaries to TR. Ni, Cd, and As were low, even absent, at most of the sites. There were substantial variations of metal concentration along the length of the rivers by season.

Co, Ni, Cu and Cd remained low at all sites. All the metals showed high concentration in winter and spring instead of summer and fall, which is the general pattern. This may be due to precipitation as shown in FR at Hobbs Road site (Figure 3**)**. It has been reported that the behavior of most metals in acidic water is strongly controlled by precipitation (Dinelli et al., 2001). This behavior is due to salt efflorescence as the majority of metals form depositions (Gray, 1998; Lopez-Pamo et al., 1999). In summer, evaporation of acidic waters produced a layer of efflorescent salts mainly made up of hydrated metal sulfates (Keith et al., 2001) and the dissolved metal content, therefore, dropped. Early rainfall in late winter dissolved efflorescence and the salts returned to the river bed, so metal content increased.

Table 4: The results of heavy metal analysis

Simple Statistics					T test
Metals	Mean	SD	Minimum	Maximum	Probability>[t]
Al	126.9	93.15	8	409	<0.0001
Co	2.925	9.446	0	42	0.0371
Ni	1.508	1.123	0	4.1	<0.0001
Cu	1.385	1.790	0	7.5	<0.0001
Fe	2.833	2.263	1	9	<0.0001
Mn	26.07	23.43	4	96	<0.0001
Cd	0.873	0.762	0	4	<0.0001
As	1.715	2.033	0	8	<0.0001
Se	3.844	7.948	0	40	0.0016
Zn	65.15	98.92	0	453	<0.0001
Pb	11.35	25.67	0	123	0.0036

Pearson correlation of the mean concentrations showed significantly positive correlation among the metals (Table 5). There was highly significant correlation between Fe and Al (0.77), Pb and Zn (0.73), Cd and Mn (0.72). There was also, significant correlation between Zn, Pb with Co (0.65). The highly significant correlations between metals indicated that these metals probably had similar sources.

The groupings by location showed that all the heavy metals were present at all the sites except, Co. Al was present at a concentration higher than the MCL allowable for drinking water at all the sites, and the concentration of Pb was present at the BF-FR and HR-FR higher than the MCL. The groupings by season shows similar pattern except that Co, As, Se, Zn, and Pb are below the detection limit for fall. The concentration of the metals are higher in winter>spring>summer>fall. Al is

Table 5: Pearson Correlation Coefficients between the heavy metals

	Al	Co	Ni	Cu	Fe	Mn	Cd	As	Se	Zn	Pb
Al	1.0										
Co	Ns	1.0									
Ni	*	Ns	1.0								
Cu	0.52^{***}	Ns	***	1.0							
Fe	0.77^{***}	Ns	ns	*	1.0						
Mn	Ns	Ns	0.50^{***}	ns	Ns	1.0					
Cd	**	*	*	ns	*	0.72^{***}	1.0				
As	**	Ns	ns	ns	*	*	*	1.0			
Se	Ns	Ns	ns	ns	ns	ns	ns	0.66^{***}	1.0		
Zn	*	0.65^{***}	ns	**	ns	*	0.47	ns	ns	1.0	
Pb	*	0.65^{***}	*	0.57	ns	ns	ns	ns	ns	0.73^{***}	1.0

*0.90 *0.95 ***0.99 significant level, ns=Not significant

Figure 3: Dry Hobbs Road (Flint River) in winter/spring

higher than the MCL in all the seasons. Pb is higher than the MCL in winter and fall, and all the other metals are below the maximum contaminant level for all seasons (Table 6 and 7).

Table 6: Groupings by locations

	WRFR	BFFR	HRFR	RBFC	MBFC	VBFC	EPA-MCL
Al	48.55^{b}	164.91^{a}	131.31^{a}	142.85^{a}	122.65^{ba}	150.80^{a}	50
Co	0.20^{a}	10.24^{a}	6.38^{a}	0.54^{a}	0.20^{a}	0.00^{a}	0
Ni	0.98^{a}	1.59^{a}	1.71^{a}	1.30^{a}	1.50^{a}	1.98^{a}	100
Cu	0.73^{ba}	0.85^{b}a	2.84^{a}	0.66^{b}	1.68^{ba}	1.56^{ba}	1000
Fe	5.50^{a}	2.88^{ba}	2.38^{b}	2.63^{b}	1.25^{b}	2.38^{b}	300
Mn	6.50^{d}	9.30^{dc}	20.84^{dc}	27.04^{bc}	46.96^{a}	45.83^{ba}	50
Cd	0.69^{a}	0.59^{a}	0.68^{a}	0.96^{a}	1.19^{a}	1.14^{a}	5
As	1.75^{ba}	1.74^{ba}	3.30^{a}	1.85^{ba}	0.85^{b}	0.80^{b}	50
Se	4.40^{ba}	1.98^{b}	12.49^{a}	1.19^{b}	1.34^{b}	1.68^{b}	10
Zn	13.28^{b}	117.70^{a}	114.91^{a}	43.41^{ba}	56.65^{ba}	44.95^{ba}	5000
Pb	5.14^{a}	11.95^{a}	29.91^{a}	7.79^{a}	9.26^{a}	4.08^{a}	10

a, b, c, d=Average means (Tukey groupings) with the same letter are not significantly different

Table 7: Groupings by seasons

Pollutants	Winter	Spring	Summer	Fall	EPA-MCL
Al	165.21^{a}	214.45^{a}	51.48^{b}	76.25^{b}	50
Co	11.21^{a}	0.42^{b}	0.08^{b}	0.00^{b}	0
Ni	1.06^{bc}	2.38^{a}	1.84^{ba}	0.76^{c}	100
Cu	1.78b^{a}	2.29^{a}	0.37^{b}	1.10^{ba}	1000
Fe	2.33^{a}	2.92^{a}	3.58^{a}	2.50^{a}	300
Mn	14.32^{b}	25.63^{b}	43.19^{a}	21.17^{b}	50
Cd	0.11^{c}	0.73^{b}	1.58^{a}	1.07^{b}	5
As	1.86^{b}	3.46^{a}	1.54^{b}	0.00^{c}	50
Se	4.13^{ba}	3.45^{ba}	7.79^{a}	0.00^{b}	10
Zn	179.18^{a}	48.01^{b}	33.41^{b}	0.00^{b}	5000
Pb	29.00^{a}	14.04^{ba}	2.38^{b}	0.00^{b}	10

a, b, c, d=Average means (Tukey groupings) with the same letter are not significantly different

4. Conclusion

The temporal distribution of heavy metals and related water quality parameters in the FR and FC watersheds were investigated over time. Our findings indicated that during the winter and spring season some of the metals of concern and physico-chemical parameters had large concentrations that exceeded the EPA standards, and may be having adverse effect on aquatic organisms. As stated earlier, the low DO in VB-FC may be due to heavy concentration of organic matter (dead leaves, tree limbs) in the stream that may depress the oxygen concentration below that required level to support fish life. Results from the study shows that FC tends to be relatively more polluted than FR. The condition of FC at the lower end of the stream may have an adverse effect on the organisms in the water. Statistical analysis revealed that only five heavy metals (Co, As, Cu, Ni and Se) did not show significant differences between sampling sites (p=0.05). On the contrary, Al, Fe, Pb, Zn, and Mn frequently exceeded set standards indicating the widespread presence of these constituents within the stream reaches. This study illustrates the persistence of pollution problems within the FC and FR watersheds. Further analysis and continuous monitoring of these streams is necessary to obtain a clearer conclusion. Integrated approaches are required to deal with the contamination problem and sustainable management of the stream waters of the watersheds and its tributaries.

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