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THE ASSESSMENT OF HEAVY METAL POLLUTION IN SURFICIAL SEDIMENTS OF THE FLINT CREEK AND FLINT RIVER WATERSHEDS: AN INDEX ANALYSIS APPROACH

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ABSTRACT

Sedimentation is a significant problem in Alabama's rivers and other water bodies in watersheds impacted by erosion from farmland, urban areas, and stream banks and beds. Accumulation of sediment reduces water depth and quality and impacts such uses as water supply, fish and benthic habitats. An Index Analysis approach was used to assess the heavy metal pollution in surficial sediments of the Flint Creek and Flint River Watersheds in Northern, Alabama. The soil / sediment samples were analyzed using the EPA analytical method SW-6010B for total recoverable elements that are environmental contaminants of concern (such as Al, Fe, Mn, As, and Pb). The concentration of metals showed significant variability, 3300-25800 mg kg^{-1} for Aℓ; 3300-51700 mg kg^{-1} for Fe; 56.40-2010 mg kg^{-1} for Mn; 1.21-15.20 mg kg^{-1} for As; and, 4.83-57.90 mg kg^{-1} for Pb respectively. All metals analyzed for this study at both watersheds were statistically significant (at $P \leq 0.05$). The indexes used in this study were Geo-accumulation Index (*I*geo), Enrichment Factor (EF), Pollution Load Index (PLI) and Ecotoxicological Risk Assessment for sediment dwelling organisms using consensus-based sediment quality guidelines. Different indexes gave diverse status of FC and FR watershed's soil/sediment quality. The selected heavy metals were studied to determine the presence of contaminants and extent of anthropogenic and lithogenic inputs from urban and rural activities. Comparison of the metal levels in the sediments from different areas of the watersheds indicates that there is a significant anthropogenic input to the watersheds. The enrichment factor, geo-accumulation index (*I*geo), contamination factor (CF), and Pollution Load Index has been calculated to assess the degree of pollution in sediments. The geo-accumulation index shows that Aℓ, Fe, Mn, As, and Pb moderately polluted the sediments at all sites of the two watersheds. Flint Creek sediments appear to have higher levels of environmental contaminants than Flint River, however, the concentrations of most of the elements appeared to be below, and some are above biologically significant threshold levels. Nevertheless, long-term bioaccumulation of these contaminants can result in impacts on benthic organisms and it should be cause for concern.

KEYWORDS: Total recoverable metals; surficial sediment; anthropogenic input; lithogenic; Index of geo-accumulation; sediment quality guidelines (SQGs).

1. INTRODUCTION

The Flint Creek watershed (FC), in Morgan County, and Flint River (FR) watershed, in Madison County, of which are both in Northern Alabama, and its hydrological characteristics, are governed by the sub-tropic and humid climate. The water channels of the FR are used for fishing and canoeing for most of the year. The FC watershed is part of the Tennessee River basin and has a total drainage area of 600 km^2, covering approximately 291,000 acres. The FC is used for fishing and boating. Most of the FC watershed is in Morgan County with portions in Cullman and Lawrence Counties and flows in a northwesterly direction until it reaches the impounded waters of Wheeler Reservoir on the Tennessee River. The overall surface water quality within the FC watershed has been designated “fair” to “poor”, biological assessments have indicated areas of poor fish health.[1] Heavy metal concentrations in watershed sediments at these watersheds are usually high due to significant anthropogenic metal loadings carried by the upstream of the rivers.[2] The sediments in rivers serve as a metal pool that can release metals to the overlying water, via, natural or anthropogenic processes, causing potential adverse health effects to the ecosystems or benthic dwellers.[3] Moreover, the benthic-dwelling organisms can uptake metals, which, in turn, enhance the potential of some metals entering the food chain.

Heavy metals have toxic properties, leading to adverse effects on human and ecosystem health even in small doses,[4] Another problem-causing property is their non-degradability. Once they enter the watersheds, it is hard to get rid of them. Metals tend to accumulate in soils and sediments, and immobilization only occurs through geological; therefore, extremely slow, processes. Accumulation in the food chain may lead to an increased stock in biota, thereby magnifying the human dose. According to Ming-Ho Yu,[5] the concentration or dosage of any toxicant to which an organism or human is exposed is often the most important factor affecting the toxicity.

This research is focused on total recoverable metals in sediments; because, sediments act as sources, sinks, and major reservoir for metals and contaminants in aquatic environments because of their variable physical and chemical properties. A study of the presence of the metals of concern, enrichment, and accumulation of heavy metals due to industrialization and urbanization in the FR and FC watersheds sediments is important to the assessment of the possible influence of anthropogenic activities on river waters,[6,7] and risk to sediment dwelling organisms. The study of metal contents from anthropogenic and lithogenic activities are particularly important for the assessment of water quality and protection. In this study, we determined the physical and chemical properties of the two watershed sediments for pH, salinity, electron conductivity (EC), total dissolved solids (TDSs), organic matter (OM) and soil texture (clay, silt and, sand). Physicochemical parameters of the soil and sediment at reference sites were measured to assist us in the interpretation of the data. We also examined the distribution of heavy metals such as Aℓ, Fe, Mn, As, and Pb in the sediments at the six sites (Figures 1a and 1b) in winter/spring of 2017. The extent of metal contamination was assessed using the geo-accumulation index (I_{geo}) developed by Muller,[8] enrichment factor (EF), Pollution Load Index (PLI), and Ecotoxicological Risk Assessment. A reliable scheme of the preliminary risk assessment of metal contamination in surface sediments approved by the USEPA which comprise: 1) comparisons of concentrations with datasets from un-impacted or background sediments, and 2) comparisons with threshold values of sediment quality guidelines[9,10,11] was used for the assessments.

A Pearson correlation analysis between pertinent sediment characteristics and sediment metal concentration was performed to determine the relationship between the variables for possible factors controlling the total metal concentration in the FC and FR sediments. The overall objectives of this study were: 1) to perform a sediment quality assessment in order to evaluate the conditions of the sediment in the FC and FR watersheds and 2) to provide base-line information necessary for developing strategies for pollution control and sediment remediation of the watersheds.

2. MATERIAL AND METHODS

2.1 Study area

Flint Creek and Flint River receives industrial, mining, agricultural, urban, wastes from water treatment plants, as well as domestic wastes from various drains of Morgan and Madison Counties. In the process, the water and sediment of the two rivers get contaminated with heavy metals and other pollutants. Flint Creek and Flint River watersheds are in the Lower Tennessee River Basin in Northern Alabama.

Based on the drainage systems and effective sampling location, three sampling sites per watershed were chosen for soil/sediment samples collection. Sampling locations were geo-referenced utilizing Garvin GPS map 76 CS GPS unit as shown in Figures 1 a and 1b.

Table 1: Description of sampling Locations and Their codes. geographic coordinate points of sampling locations at the FC and FR Watersheds.

FR Watershed (Huntsville, Alabama)				
Sites	**Stream**	**Codes**	**Coordinate Points**	**Elevation**
1	Winchester Road	WR-FR	N34^{o}30'12.50"/W86o28'00.4"	721.5 +/ 19"
2	Briar Fork Rd	BF-FR	N34^{o} 47'23.15"/W86^{o} 29'05.4"	751.5 +/ 36"
3	Hobbs Island Road	HR-FR	N34^{o}32'19.50"/W 86^{o} 55'52.6"	660.5 +/ 30"
FC Watershed (Decatur, Hartselle, Alabama)				
Sites	Stream	Codes	Coordinate Points	Elevation
4	Red Bank Rd	RB-FC	N34^{o}30’22.50"/W 86^{o}57'20.8"	788.5 +/ 50"
5	Means Bridge	MB-FC	N34^{o}29’37.80"/W 87^{o}01'34.9"	602.5 +/ 42"
6	Vaughn Bridge Rd	VB-FC	N34^{o}27’48.15"/W86^{o}57'52.4"	521.5 +/ 56"

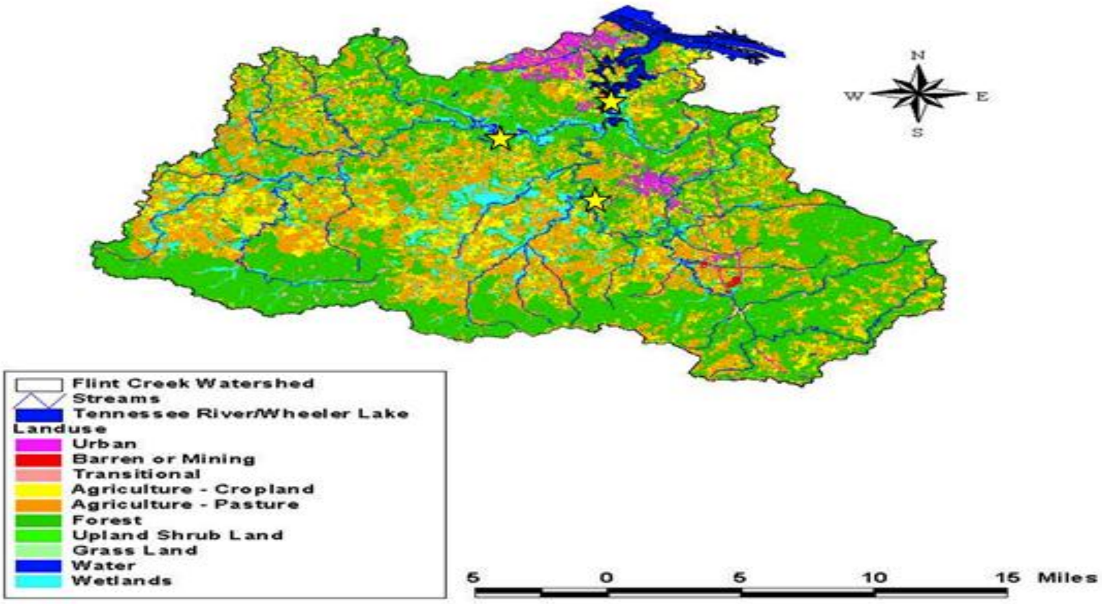

Figure 1a: FC Watershed and Sampling Locations.

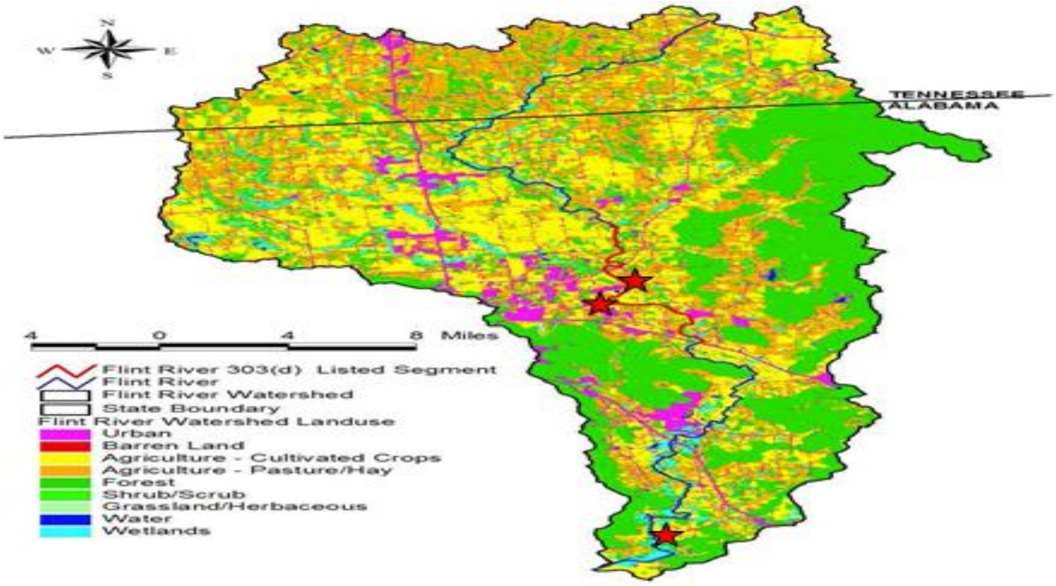

Figure 1b: FR Watershed and Sampling locations.

2.2 Sample collection

Soil samples were collected from six sites as seen earlier in Figures 1a and 1b. Four sampling sites were from upstream and midstream (WR-FR, BF-FR, RB-FC, and MB-FC), two remaining sites were from the tributary of the watersheds (HR-FR and VB-FC). About 1 kg of sediment samples were obtained from each site. Samples were transferred into EPA approved plastic bags and placed in a cooler at 4^{o}C and then transported to the Alabama A&M University Laboratory freezers for storage until processing and analysis.

In-situ measurements were taken at the time of soil and sediment sampling. Additional parameters include pH, temperature, DO, turbidity, etc were measured using a recently calibrated YSI 6600 EDS Sonde probe. The soil/sediment-sampling locations from each site includes: 1) in-stream/depositional area, 2) riverbank, and 3) upland in (riparian zone). For soil and sediment sampling, each spot was sampled five times to have a composite and a well-mixed representative sample (see Figures 2). A stainless steel soil probe was used for collecting soils from the banks and upland areas, and an 225-cm. pole sediment sampler-Pakar (patent pending) was used for collecting sediments from in-stream/depositional area across the upper, middle, and lower streams, covering a distance of ~110 km. Twelve composite samples were collected from each site (four samples from upland riparian zone spots, four samples from riverbank, and four samples from the in-stream/depositional areas). Samples were taken from the uppermost layer of the sediment (1 to10 cm) taking care to minimize contamination. Seventy-two soil/sediment-samples were collected from the watersheds. The sediment sampling was carried out in low flow conditions, because trace metal pollution may be highest during this period, and it may be accumulated from water to sediments. Under conditions of high-water discharge, erosion of riverbed takes place. According to Geesey,[12] following peak discharge, the presence of the metals in bed sediments will increase as the water flow again decreases. Therefore, sediment analysis should be carried out in low flow conditions, where the highest accumulation of metal takes place from water to sediments.

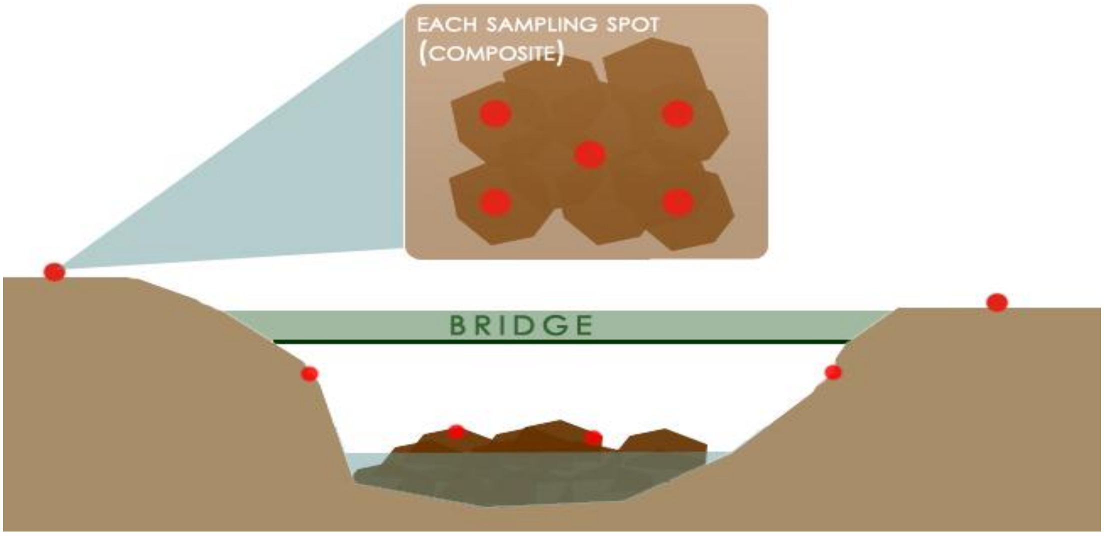

Figure 2: Soil/Sediment-Sampling side Bridge view.

2.3 Sediment sample processing

The samples were later air dried, and slightly grounded with an agate mortar. Sediment samples were screened with sieve to remove large particles. The screened sediments were air dried in open air of a greenhouse at about 65°C for ~72 hours (3 days), and further dried in the oven for ~24 hours. The dried sediments were disaggregated and ground to powder using an agate mortar and pestle. All soil/sediment samples for heavy metal analysis were sent to a United States Environmental Protection Agency (USEPA), National Environmental Laboratory Accreditation Program (NELAP) and U.S. Army Corps of Engineers (USACE) approved laboratory called Environmental Testing and Consulting Lab, Inc. in Memphis, Tennessee.

2.4 QC/Data Validation

The analyses were performed in accordance with Standard Methods, the Solid Waste Manual SW-846, and EPA Methods for Chemical Analysis of Water and Wastes. Inductively

Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used to measure the analysis. The testing laboratory asserts that the analytical data was validated using standard quality control measures performed as required by the USEPA analytical method 3050B. The method was used to analyze for total recoverable elements (Aℓ, Fe, Mn, As, and Pb) of concern; because they are "environmentally available" for plants and aquatic animals. Moreover, that the Quality Assurance, Instrumentation maintenance and calibration were performed in accordance with guidelines established by the USEPA, NELAP, and the USACE. The instruments were calibrated to eliminate or minimize bias in the overall measurement system.

2.5 Sampling Soils and Sediments for background determination

In order to characterize anthropogenic total metal contamination, local background for the elements' concentrations (i.e., reference conditions) was determined to provide a frame of reference for metal contamination. Marcello, et al.,[13] stated that this is true, no matter what the objective of the soil and sediment monitoring program. It was accomplished by locating area upstream sites which are uncontaminated by the metal of interest and have similar geological and physical characteristics in soil and sediment (e.g., grain size and organic matter content). The degree of contamination of the aquatic environment was compared relative to background soil and sediment.

Data from the samples collected from the upland areas from each site were used as background or reference values. Data from upland area was used because: 1) the reference sites were free of any possible anthropogenic PS contamination, and 2) establishing representative reference sites is critical, because, if reference sites are not highly similar to the areas under study, misleading or inappropriate conclusions may be drawn when making data comparisons.[14]

Soils from upland areas were collected from less disturbed location as to establish a geochemical background or a reference concentration of the metal. Physical characteristics and sampling procedures used in reference areas matched conditions and procedures in contaminated locations sampled (in-stream).[15]

2.6 Data analysis

Descriptive data Analysis and Correlations

Descriptive data analysis (mean, standard deviation, maximum and minimum concentrations) on the total element concentrations was applied accompanied by correlation analysis to determine relationships among different metals. Understanding such relationships may help to clarify sources and transport of individual metals within the aquatic environment. Additionally, correlations between individual heavy metals and the organic matter of the sediment were analyzed to assess its role as scavenger for traces. Descriptive analysis was performed using SAS programs, while the possible associations between different variables were assessed by applying the Spearman's rank correlation analysis.[16]

2.7 Evaluation of the environmental significance of Metals in sediments by Geoaccumulation Index (I_{geo}).

The Index of geoaccumulation (I_{geo}) introduced by Muller[17] is: $I_{geo} = \log_2 (C_n/1.5B_n)$, where C_n is the measured concentration of the examined metal "n" in the sediment and B_n is the geochemical background or reference concentration of the metal "n". The factor 1.5 was used because of possible variations in background values due to lithological variability. The geoaccumulation index for samples from each site were calculated using: 1) the total heavy metal data and metal concentration from reference sites (Upland), 2) the world shale average by Turekian and Wedepohl, [18], and 3) North American Shale Composite (1989) as the background value for a thorough analysis. The I_{geo} is associated with a qualitative scale of pollution intensity, samples may be classified as described in Table 2.

Table 2. I_{geo} Classification.

I_{geo}		Code
I_{geo} < or = 0	Practically Uncontaminated	UC
0 <I_{geo} < 1	Uncontaminated to Moderately Contaminated	UMC
1< I_{geo} < 2	Moderately Contaminated	MC
2 < I_{geo} < 3	Moderately to Heavily Contaminated	MHC
3 < I_{geo} < 4	Heavily Contaminated	HC
4 < I_{geo} < 5	Heavily to Very Heavily Contaminated	HVHC
I I_{geo} > or = 5	Very heavily Contaminated	VHC

2.8 Evaluation of the Enrichment Factor (EF).

To assess metal contamination of sediment is complicated, since metals are naturally occurring component of sediment, their concentrations in un-contaminated sediment can vary by orders of magnitude over relatively small spatial scales, and naturally (lithogenic) occurring and anthropogenically (human) introduced metals tend to accumulate in the same areas.[19] To meaningfully interpret sediment metal data, factors affecting metal concentration variability in sediment must first be compensated for before naturally occurring and anthropogenically introduced concentrations can be differentiated. This can be accomplished through the procedure of geochemical normalization. Aluminum (Aℓ) was used for normalizing the concentrations of all other metals, Fe, Mn, As, and Pb. Aℓ has been successfully employed as a reference element to normalize for grain-size differences; because it is a conservative element unaffected by anthropogenic discharges and activities[20] and a main component of the aluminosilicate matrix of clay minerals.[21] The extent of sediment contamination was assessed using the Enrichment Factor (EF). EF is a good tool to differentiate metals between anthropogenic and lithogenic sources.[22] The metal concentrations were normalized to the textural characteristic of sediments. As stated before, the widely used element to normalize the metals in sediments is Aℓ, since it represents the alumina-silicates, the predominant contents of Wheeler Lake basin.

The **EF** in Equation 1 is defined as:

EF = (M conc / Aℓ in sediment) / (M conc/Aℓ earth's crust average). (1)

From Equation (1), EF is the ratio of the heavy metal concentration (M conc) to the Aℓ in sediment and heavy metal concentration to Aℓ in earth's crust or reference average. EF values were interpreted as suggested by Birth[23] for the metal concentrations studied with respect to the crust or background average for each site.[24] Therefore, the EF is the relative abundance of a chemical element in a soil compared to the bedrock.[25] EF is a convenient measure of geochemical trends and is used for comparison between areas. The formula below used by Hernandez, et al[25] has been applied to the heavy metals of concern in this study to assess the anthropogenic and lithogenic contribution **[Equations (1) through (5)]**. Previous studies have also shown that the important geochemical phases for metals in sediments can be deduced by studying the relationship between the concentrations of metals and Aℓ, and, thus, the sources and degree of metal contamination may be inferred.[26,27,28] EF is divided into five contamination categories as shown in Table 3.

Table 3: EF Categories.

EFs					Code
EF	<	2	-	Depletion to Minimal Enrichment	Dep. ME
EF	=	2-5	-	Moderate Enrichment	Mod. E
EF	=	5-20	-	Significant Enrichment	Sig. E

EF	=	20-40	-	Very High Enrichment	VHE
EF	>	40	-	Extremely High Enrichment	EHE

To assess the anthropogenic and lithogenic contribution, the heavy metal concentration can be used to estimate contribution with formulas shown below:

$$[\mathbf{M}]_{\text{Lithogenic}} = [\mathbf{A\ell}]_{\text{Sample}} * ([\mathbf{M}]/[\mathbf{A\ell}])_{\text{Lithogenic}}. \qquad (2)$$

Where ([M] / [Aℓ]) Lithogenic corresponds to the average ratio of the earth crusts

$$[\mathbf{M}]_{\text{Anthropogenic}} = [\mathbf{M}]_{\text{Total}} - [\mathbf{M}]_{\text{Lithogenic}}. \qquad (3)$$

2.9 Evaluation of the Pollution Level Index (PLI).

The PLI is a measure for the overall LEVEL of a set of pollutants, it is a geometric mean of the concentration factor (CF) for a set of pollutants. Tomlinson,[29] who proposed the PLI for sediment samples which were calculated using the total heavy metal data and metal concentration from reference sites (Upland), and the world shale average by Turekian, et al., as the background value. The PLI is obtained as a CF of each metal with respect to the background value in the sediment,[30] by applying Equation (4) below:

CF of the metal (CF_{metal}) = Concentration of the metal in the sample (C_{metal})/
Concentration of metal in the background ($C_{background}$)

$$\mathbf{PLI} = {}^{n}\sqrt{}(\mathbf{CF_1 * CF_2 * \ldots * CF_n}). \qquad (4)$$

The PLI is obtained as CF. This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the site are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals for a site. With the PLI obtained from each site, Equation (5) shows the index is used to compare the pollution status of different sites in a watershed,[31,32]

$CF = C_{metal}/C_{\text{Background value}}$,

$$\mathbf{PLI} = 5\sqrt{}(\mathbf{CF_{A\ell *}\ CF_{Fe *}\ CF_{Mn *}\ CF_{As *}\ CF_{Pb}}), \mathbf{n = number\ of\ metals},$$

PLI varies from 0 (unpolluted) to 10 (highly polluted). (5)

The Tomlinson PLI is calculated as the chemical (heavy metals) product concentrations that are measured in surficial sediments. The PLI standardizes the data by using the quotients obtained by dividing each concentration by a baseline concentration for each chemical, that is, by the lowest concentration of each chemical found in sediments and reference data from each site or listed in the literature. The PLI was proposed as a standardized system for detecting pollution which permits a comparison of pollution levels between different sites.

The PLI represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular site sample.

These indexes evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality.[33] It is also to rank and prioritize the contaminated areas or the chemicals for further investigation.[34]

2.10 Evaluation of the ecological risk to benthic organisms using the SQGs.

Other sediment quality guidelines had been used in the past decade but, Consensus-Based Sediment Quality Guidelines **(CBSQGs)** is used for ecological risk assessment in this study because increasing importance is given to the consensus-based threshold effect concentration **(TEC)** and the probable effect concentration **(PEC)** guidelines proposed by McDonald, et al., for freshwater sediment quality assessment. The two sets of quality guidelines effects-based SQGs that related contaminant concentrations to harmful effects on benthic-dwelling organisms or were intended to be predictive of effects on the same organisms.[35] The predictive abilities of these guidelines proved to be particularly efficient, especially in the case of the priority heavy metals. (See Table 4.)

Table 4: Consensus-Based SQGs (MacDonald et al., 2000) Showing Concentrations Below or Above which Adverse Effects are Probably or "Frequently" Expected to Occur.

Level of Concern	Threshold Effect Concentration (TEC)	Level of Concern	Midpoint Effect Concentration (MEC)	Level of Concern	Probable Effect Concentration (PEC)	Level of Concern
Level 1	From CBSQGs	Level 2	TEC + PEC / 2 = MEC	Level 3	From CBSQGs	Level 4
≤ TEC		> TEC ≤ MEC		> MEC ≤ PEC		> PEC

The metal concentrations at each site were compared with the CBSQG values referred to as the TEC and the PEC proposed by McDonald, et al. The SQGs are based on numerous studies and tests relating concentrations to measured biological effects on benthic organisms. According to the Canadian Council of Ministers of the Environment, [36], PEC represents the concentration above which adverse effects are probable or "frequently" expected to occur. These guidelines have been selected for comparison because various evaluations have demonstrated that the CBSQGs provide a unifying synthesis of the existing SQGs, and reflect causal rather than correlative, effects. According to MacDonald and Long, the analysis of both freshwater sediments based on these quotients has demonstrated an increased probability of toxicity as the mean quotient increases. The use of the CBSQGs as benchmarks for toxicity screening serves to: 1) estimate the likelihood that a particular ecological risk exists, 2) helps identify the need for site-specific data collection efforts, and 3) helps to focus site-specific baseline ecological risk assessments. (See Table 5 below.)

Table 5: Consensus-Based Concentrations for Heavy Metals of Interest.

Dry Wt (mg/kg)	**Level 1 Concern**		**Level 2 Concern**		**Level 3 Concern**		**Level 4 Concern**	**Sources of SQG Effect-Based Concentrations**
	≤ TEC		**> TEC ≤ MEC**		**> MEC ≤ PEC**		**> PEC**	
		TEC		**MEC**		**PEC**		
Aℓ - Max		NG*		NG*		NG*		
Ave		NG*		NG*		NG*		
Fe - Max		20,000		30,000		40,000		Ontario (1993)[1]
Ave		20,000		30,000		40,000		
Mn-Max		460		780		1,100		Ontario (1993)[1]
Ave		460		780		1,100		
As - Max		9.8		21.4		33		CBSQG (2000a)[2]
Ave		9.8		21.4		33		
Pb - Max		36		83		130		CBSQG (2000a)[2]
Ave		36		83		130		

* NG = No Guidelines

1. Persuad, et al., 1993.1.
2. McDonald, et al., 2000a.

3. RESULTS AND DISCUSSION

The results show that the variation between mean concentrations of the metals is significant ($p > 0.05$). Statistical analysis was performed to explore the possible associations existing between different variables. (See Table 6a and 6b.) All metals were statistically significant (at $P \leq 0.05$) by watershed.

Table 6a: SAS Proc Means was used to Show the Simple Statistics and t-Test for the Heavy Metals from the Depositional Sediments of the Watersheds.

Simple Statistics of Heavy Metals For all the Sites					**t-Test**
Metals	**Mean**	**Std. Dev**	**Min**	**Max**	**Pr > [t]**
Aℓ	12562.08	5785.04	5840.00	25800.00	<0.0001
Fe	19867.92	11334.30	7100.00	51700.00	<0.0001
Mn	1005.38	458.92	127.00	1820.00	<0.0001
As	6.31	3.25	2.16	13.20	<0.0001
Pb	13.78	4.13	8.46	22.70	<0.0001

Table 6b: SAS Proc Means was used to Show the Simple Statistics and t-Test for the Heavy Metals from the Upland (Reference Area) Soil Samples of the Watersheds.

Simple Statistics of Heavy Metals For all the Sites					**t-Test**
Metals	**Mean**	**Std. Dev**	**Min**	**Max**	**Pr > [t]**
Aℓ	10981.00	4762.00	3300.00	23300.00	<0.0001
Fe	12785.00	5499.00	3300.00	22700.00	<0.0001
Mn	826.71	512.84	56.00	2010.00	0.0165
As	6.07	3.69	1.21	15.20	0.0399
Pb	24.46	14.09	4.83	57.90	<0.0116

Table 7a shows a correlation matrix for the metals. Most metals are well correlated (p<0.001). The most noticeable positive correlations were As vs. Aℓ (**0.987**), As vs. Fe (**0.958**) (these are near perfect relationships), Fe vs. Aℓ (**0.893**), Pb vs. Aℓ (**0.784**), Mn vs. Fe (**0.766**), As vs. Mn (**0.691**), and Pb vs. Mn (**0.672**). There was weak relationship between Pb vs. Fe, and Pb vs. As.

Table 7a: Pearson Correlation Matrix (SAS Proc Corr) for Depositional Areas.

Metals	**Aℓ**	**Fe**	**Mn**	**As**	**Pb**
Aℓ	1.000				
Fe	0.893	1.000			
Mn	0.578	0.766	1.000		
As	0.987	0.958	0.691	1.000	
Pb	0.784	0.304	0.672	0.287	1.000

Red = Correlated to near perfect correlation among the metals of concern.

Black = No significant correlation between the metals.

Table 7b shows a correlation matrix for the metals in the upland (reference area). Most metals are well correlated (p<0.001). The most noticeable positive correlations were Aℓ vs. Fe **(0.839)**, Aℓ vs. Mn **(0.0.712)**, Aℓ vs. As **(0.643)**, Aℓ vs. Pb **(0.896)**, Mn vs. As **(0.703)**, Mn vs. Pb **(0.831)**, and the rest were weak relationships. The highly significant correlation between Al and the other elements (Fe, Mn, As, and Pb) confirms that these elements are associated with aluminosilicate minerals at both watersheds. Furthermore, according to Okweye and others, the highly significant correlations between metals indicated that these metals probably had similar sources.

Table 7b: Pearson Correlation Matrix (SAS Proc Corr) for Upland Soil Samples.

Metals	Aℓ	Fe	Mn	As	Pb
Aℓ	1.000				
Fe	0.839	1.000			
Mn	0.712	0.478	1.000		
As	0.643	0.309	0.703	1.000	
Pb	0.896	0.426	0.831	0.492	1.000

Red = Correlated to near perfect correlation among the metals of concern.
Black = No significant correlation between the metals.

The groupings by location showed that all the heavy metals were present at all the sites. Fe was present at a concentration higher than the other contaminants in the depositional area and at all sites, and Aℓ has the highest concentration in the upland area at all locations. (See Tables 8a and 8b.)

Table 8a: Heavy Metal Grouping by Location in Upland (Reference) Soil Samples.

	WR-FR	BF-FR	HR-FR	RB-FC	MB-FC	VB-FC
Aℓ	4.14^{a}	4.11^{a}	4.23^{a}	3.91^{b}	3.96^{b}	3.64^{c}
Fe	4.23^{a}	4.24^{a}	4.25^{a}	$3.87^{c,b}$	3.99^{b}	3.79^{c}
Mn	2.99^{a}	3.03^{a}	3.00^{a}	2.89^{a}	2.82^{a}	1.87^{b}
As	$0.75^{b,a}$	0.95^{a}	$0.73^{b,a}$	0.47^{b}	0.57^{b}	$0.81^{b,a}$
Pb	$1.22^{b,c}$	1.62^{a}	$1.19^{b,c}$	1.12^{c}	$1.45^{b,a}$	$1.30^{b,a,c}$

Note: SAS Proc Anova with t-Tests (LSD) (a, b, c, d = Log T average means (LSD Grouping) with the same or common letter are not significantly different). groupings by location

Table 8b: Heavy metal grouping by location in depositional sediments.

	WR-FR	BF-FR	HR-FR	RB-FC	MB-FC	VB-FC
Aℓ	3.86^{d}	4.03^{c}	4.38^{a}	4.16^{b}	4.03^{c}	3.92^{d}
Fe	$2.98^{b,a}$	2.81^{b}	3.21^{a}	2.78^{b}	$2.98^{b,a}$	$2.87^{b,a}$
Mn	4.60^{a}	$4.29^{c,b}$	4.37^{b}	4.20^{c}	4.04^{d}	3.94^{d}
As	1.07^{a}	0.84^{b}	0.88^{b}	0.65^{c}	$0.59^{d,c}$	0.44^{d}
Pb	$1.09^{c,b}$	1.13^{b}	1.31^{a}	1.128^{b}	$1.08^{c,b}$	0.99^{c}

Note: SAS Proc Anova with t-Tests (LSD) (a, b, c, d = Log T average means (LSD Grouping) with the same or common letter are not significantly different). groupings by location

3.1 Grain Size and Total recoverable elements in sediment

Most of the sediment samples constitute clay, sand, and silt. Overall, the mean size of the sand in sediments is 23.45%, silt 11.81%, and clay 64.74%. The samples contain minimum of 9.52% and maximum of 44.13% sand, 0.63 - 31.85% silt, and 46 - 74.1% clay. It shows that the samples comprise mostly of clay sediments. It is no surprise that the heavy metals in sediments are almost a thousand-fold greater than those in surface water (Table 10 a and 10b). The other variables and parameters are as shown in Table 9.

3.2 Total recoverable metals in sediment

All of the total elements (Aℓ, Fe, Mn, As, and Pb) determined, were detected in all sediment samples from six sites. (See Tables 6a and 6b above.)

1. Aℓ was present in all sediment samples, and concentrations ranged from 5,310 to 25,800 mg/kg dry weight. These levels are well above the average background level of 12,516 mg/kg for reference soils, below 89,000 mg/kg for regional soils in North American Shale Composite (NASC), and 80,000 mg/kg international soils using Turekian and Wedepohl (T&W) data. There are no established background levels for Aℓ in Alabama soils for determining thresholds.
2. Fe was present in all sediment samples, and concentrations ranged from 3,300 to 33,800 mg/kg dry weight. These levels are well above the average background level of 20,306 mg/kg for reference soils, below 40,000 mg/kg for regional soils in NASC, and 47,200 mg/kg international soils using T&W data. There are no established background levels for Fe in Alabama soils for determining thresholds.
3. Mn concentrations ranged from 56.4 to 2,010 mg/kg dry weight. There are no established background levels for Mn element, but these sample levels are well above the average background level of 970 mg/kg for reference soils.
4. As concentrations ranged from 1.21 to 15.2 mg/kg dry weight. These levels bracketed the average (6.39 mg/kg) of reference soils. Concentrations greater than 7.0 and 11.0 µg/g dry weight have been considered elevated and heavily polluted in other areas according to Ingersoll; Beyer; and Crayton. Six of twelve sediment samples from HRFR-U sites on FR contained concentrations above 7.0 µg/g.
5. Pb was detected in sediment at concentrations that ranged from 4.83 to 57.9 mg/kg dry weight. Bayer, 1990, suggested that sediment with Pb concentrations > 40 mg/kg dry weight were classified as polluted.

Table 9: Simple Statistics (SAS Proc t-Test) of the Physicochemical Parameters, Grain Sizes and the Total Heavy Metals in Surficial Soil/Sediment.

Physicochemical Parameters and Heavy Metals Simple Statistics						
Variable	N	Mean	Std Dev	Sum	Min	Max
pH	72	7.14	0.45	85.63	6.11	7.81
OM	72	0.29	0.25	3.54	0.02	0.81
EC	72	339.42	175.03	4073.00	119.00	644.00
Sal	72	0.18	0.076	2.10	0.10	0.30
TDS	72	162.33	84.45	948.00	57.00	309.00
Sand	72	23.45	10.50	281.37	9.52	44.13
Silt	72	11.81	10.45	141.75	0.63	31.85
Clay	72	64.74	9.13	776.83	46.37	74.10
Aℓ	72	12516.00	5958.00	150190.00	5840.00	25800.00
Fe	72	20306.00	12302.00	243670.00	7570.00	51700.00
Mn	72	970.08	550.02	11641.00	127.00	1820.00
As	72	6.40	3.37	76.76	2.16	13.20
Pb	72	13.03	3.83	156.31	8.46	21.20

The spatial variations in sediment characteristics and organic matter content in 72 samples and from 6 sites in the upper and lower reaches of FC and FR watersheds, which is polluted from different sources were studied. Variations in color and texture of sediments were brought about by changes in the grain size and state of oxidation of organic matter. The color of the sediment varied from brownish at Sites 1 and 2, grayish black at Site 3, red/brown/black/and grayish at Site 4, grayish at Sites 5 and 6.

3.3 Distribution of total heavy metals at the watersheds

The concentrations and spatial distribution of heavy metals can be related to clay or organic matter content. Therefore, the Pearson correlation coefficient was calculated for these parameters using SAS code PROC CORR software. The concentration levels of Aℓ, Fe, Mn, As, and Pb at the six sites in Northern, Alabama, which runs through industrial belt, is reported. All metals showed some degree of variation over the area studied. As shown, the lowest variation of Fe, Aℓ, Mn and Pb values were found to vary with sites. (See Figures 8a and 8b above and Tables 10a/10b below.)

Table 10a: Distribution of Total Heavy Metals in FR Surface Water and Soil/Sediment. Means are Only Given where All Samples are Above Detection Limits.

Heavy Metals in Surface Water (n = 96), mg/kg						**Heavy Metals in Soil/Sediment** (n = 72), mg/kg					
Sites	**Aℓ**	**Fe**	**Mn**	**As**	**Pb**	**Sites**	**Aℓ**	**Fe**	**Mn**	**As**	**Pb**
WR-FR						**WR-FR**					
Ave	48.55	59.89	6.501	1.75	5.14	Ave	10342	29625.0	1004.75	9.01	14.45

Max	93.6	91.0	10.1	5.0	20.3	Max	14300	33800.0	1140.0	13.2	17.5
Min	8.0	20.0	4.0	ND	ND	Min	5840	14000.0	908.0	5.41	10.5
BF-FR						**BF-FR**					
Ave	164.91	130.33	9.3	1.74	11.95	Ave	11240	17425.0	735.25	8.27	27.93
Max	409.0	276.8	15.0	5.0	32.6	Max	10900	18800.0	1190.0	15.2	57.9
Min	28.0	32.0	7.0	ND	ND	Min	9320	16000.0	420.0	5.73	11.8
HR-FR						**HR-FR**					
Ave	131.31	167.1	20.84	3.3	29.91	Ave	21000	19900.1	1463.75	6.67	20.75
Max	200.7	330.5	29.0	8.0	123.0	Max	25800	25600.0	1820.0	8.21	28.7
Min	80.0	45.0	13.0	ND	ND	Min	13600	12000.0	962.0	3.89	15.4

ND=Not Detected; below Detection Limit

Table 10b: Distribution of total heavy metals in FC Surface Water and Soil/Sediment. Means are only given where all samples are above detection limits.

Heavy Metals in Surface Water (n = 96), mg/kg						**Heavy Metals in Soil/Sediment** (n = 72), mg/kg					
Sites	**Aℓ**	**Fe**	**Mn**	**As**	**Pb**	**Sites**	**Aℓ**	**Fe**	**Mn**	**As**	**Pb**
RB-FC						**RB-FC**					
Ave	142.85	193.16	27.045	1.85	7.79	Ave	11452	12442.5	862.9	3.93	13.29
Max	221.3	340.2	47.6	4.5	34.1	Max	16500	21400.0	2010.0	6.76	17.6
Min	41.0	51	10.3	ND	ND	Min	6290	5720.0	127.0	2.75	8.85
MB-FC						**MB-FC**					
Ave	122.65	185.94	46.96	0.85	9.26	Ave	10148	10725.0	9055.0	3.96	21.78
Max	171.8	230.9	84.6	2.4	37.9	Max	12000	12200.0	1400.0	4.38	49.4
Min	63.0	169.01	13.6	ND	ND	Min	8920	10100.0	626.0	3.63	11.8
VB-FC						**VB-FC**					
Ave	150.81	155.09	45.83	0.8	4.08	Ave	6622	7745.0	504.08	5.55	17.07
Max	329.8	310.1	90.0	2.2	17.3	Max	9990	10900.0	1630.0	15.1	42.9
Min	86.0	9.0	19.6	ND	ND	Min	5310	3300.0	56.4	1.21	4.83

Pearson Correlation Coefficients (SAS Proc Corr), N = 72, Prob > [r] under H0: Rho = 0

ND=Not Detected; below Detection Limit

Table 13: EF Results Applied to Metal Normalized by Al for FC and FR Watersheds.

	Aℓ	**Fe**	**Mn**	**As**	**Pb**
WR-FR	5.78 Sig.E	2.48 Mod.E	0.00078 Dep.ME	2.35 Mod.E	0.81 Dep.ME
BF-FR	6.67 Sig.E	2.36 Mod.E	0.00095 Dep.ME	1.24 Dep.ME	0.32 Dep.ME
HR-FR	4.45 Mod.E	0.405 Dep.ME	0.00068 Dep.ME	2.32 Mod.E	0.63 Dep.ME
RB-FC	10.32 Sig.E	5.95 Sig.E	0.00077 Dep.ME	4.78 Mod.E	1.05 Dep.ME
MB-FC	8.85 Sig.E	4.02 Mod.E	0.00118 Deap.ME	3.32 Mod.E	0.44 Dep.ME
VB-FC	1.91 Dep.ME	0.66 Dep.ME	0.0109 Dep.ME	1.59 Dep.ME	0.58 Dep.ME

Sig.E = Significantly Enriched

Mod.E = Moderately Enriched;

Dep.E = Depletion to Minimal Enrichment

Surface sediments in the FC and FR are enriched in Aℓ, Fe, Mn, As, and Pb relative to local background and consensus-based reference levels. Aℓ, Fe, and As (moderate to significant) are the most elevated, with maximum enrichment occurring in upper FR (WR-FR) and upper FC (RB-FC). On average, enrichment decreases downstream, apparently reflecting both increased distance from the inferred source (Wheeler Lake reservoir), as well as, increased dilution by locally derived, but unenriched, materials. Aℓ, Fe, and As display marked enrichment throughout the watersheds. Mn and Pb were minimally enriched in all watersheds. Aℓ, Fe, and As seem to be associated mainly with defined Fe oxide phase, whereas the majority of the Mn and Pb seem to be matrix-held. Overall, FC watershed is more enriched in heavy metal than FR that may be due to sewage dump and heavy run offs. The temporal difference in enrichment between the FR and the FC may reflect the latter's greater distance from the presumed source of the enrichment (WL basin). However, the difference is more likely the result of the effect of old mining and related activities, sewage on the sediment-trace element geochemistry of FC and its surroundings.

3.4 Enrichment contributions from Anthropogenic and Lithogenic sources

From results on Table 14a through 14f and Figures 4a through 4f, the anthropogenic contribution of heavy metals into aquatic environment far exceeds natural inputs. The increased anthropogenic influence 90% in the FC and FR has probably resulted in a reduction in benthic biodiversity, where pollutant-tolerant species may probably be found to take over the vacated niche.

Table 14a: WR-FR enrichment contributions from Anthropogenic and Lithogenic sources.

Anthropogenic versus lithogenic heavy metal enrichment contributions (WRFR)		
$[M]_{total\ (mg/kg)}$	$[M]_{Anthropogenic\ (mg/kg)}$	$[M]_{Lithogenic\ (mg/kg)}$
6485.0	5959.31	525.69
42750.0	39284.55	3465.45
924.5	849.56	74.94
12.5	11.49	1.01
11.6	10.66	0.94
TOTAL %	91.90%	8.10%

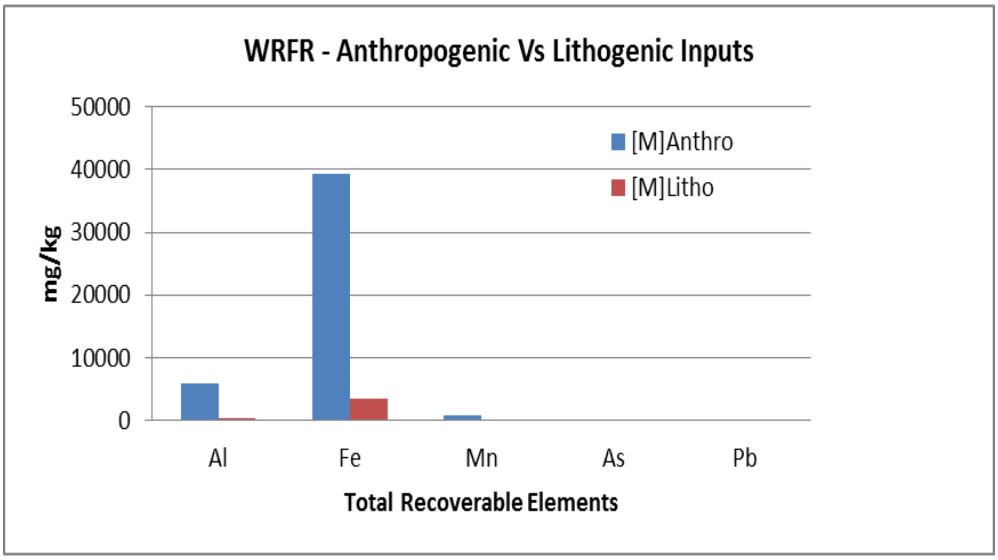

Figure 4a: WRFR data showing the Relationship and Patterns for enrichment contributions between Anthropogenic and Lithogenic sources.

Table 14b: BF-FR enrichment contributions from Anthropogenic and Lithogenic sources.

Anthropogenic Versus Lithogenic Heavy Metal Enrichment Contributions (BFFR)		
[M]$_{total}$ (mg/kg)	**[M]$_{Anthropogenic}$ (mg/kg)**	**[M]$_{Lithogenic}$ (mg/kg)**
10120.0	8839.82	1280.18
17450.0	15242.57	2207.43
579.5	506.19	73.31
6.075	5.305	0.77
11.8	10.31	1.49
TOTAL %	87.4%	12.6%

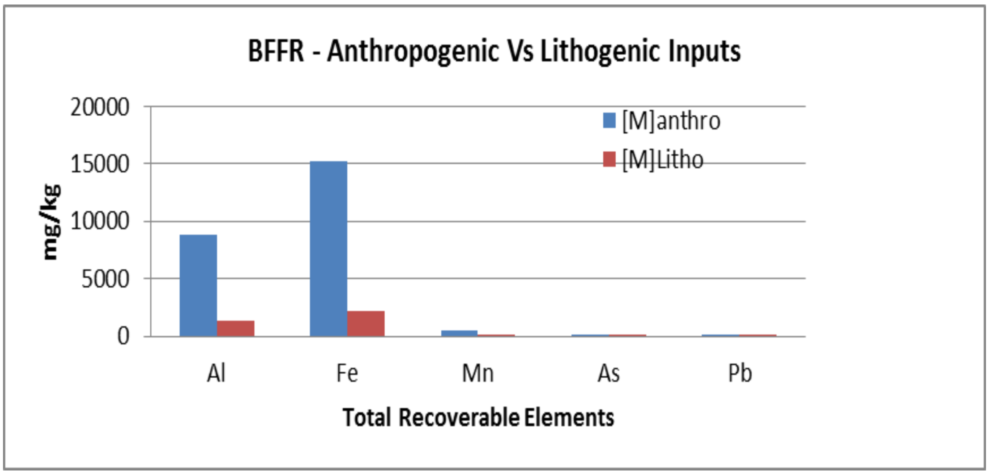

Figure 4b: BF-FR Data Showing the Relationship and Patterns for Enrichment Contributions between Anthropogenic and Lithogenic Sources.

Table 14c: HR-FR Enrichment Contributions from Anthropogenic and Lithogenic Sources.

Anthropogenic Versus Lithogenic Heavy Metal Enrichment Contributions (HRFR)		
$[M]_{total\ (mg/kg)}$	$[M]_{Anthropogenic\ (mg/kg)}$	$[M]_{Lithogenic\ (mg/kg)}$
23550.0	16617.47	6932.53
23200.0	16370.50	6829.50
1675.0	1181.92	493.08
7.725	5.46	2.27
19.45	13.72	5.73
TOTAL %	70.54%	29.46%

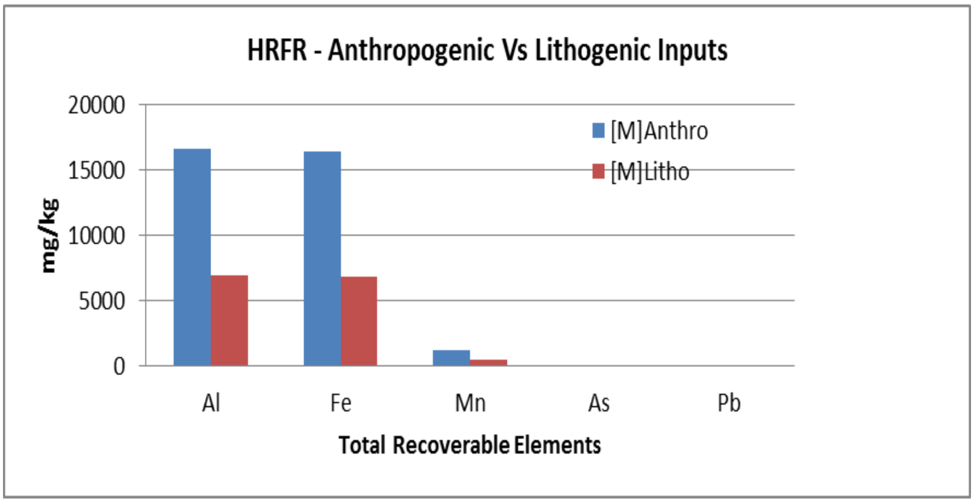

Figure 4c: HR-FR Data Showing the Relationship and Patterns for enrichment contributions between Anthropogenic and Lithogenic Sources.

Table 14d: RB-FC Enrichment contributions from Anthropogenic and Lithogenic sources.

Anthropogenic Versus Lithogenic Heavy Metal Enrichment Contributions (RBFC)		
$[M]_{total\ (mg/kg)}$	$[M]_{Anthropogenic\ (mg/kg)}$	$[M]_{Lithogenic\ (mg/kg)}$
14950.0	11969.30	2980.70
18000.0	14636.20	3363.80
618.5	502.9	115.60
5.14	4.18	0.96
13.23	10.76	2.47
TOTAL %	81.33%	18.67%

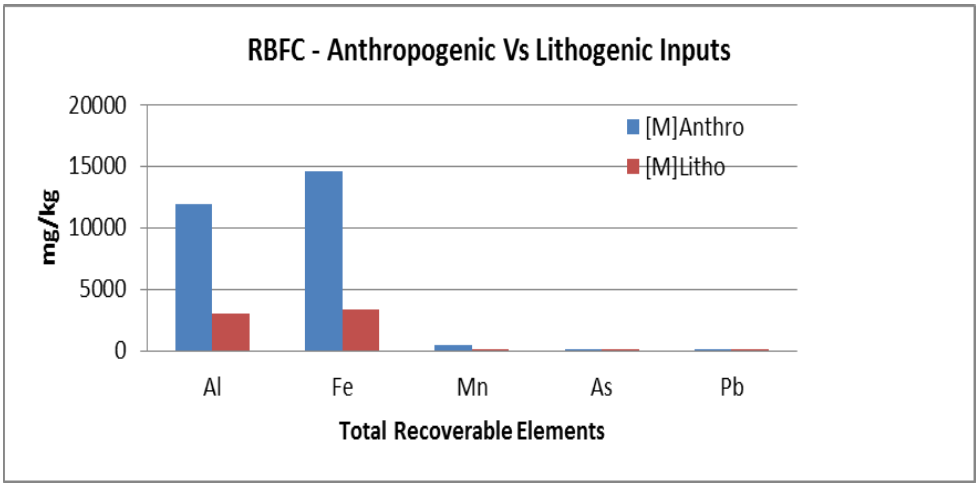

Figure 4d: RB-FC Data Showing the Relationship and Patterns for Enrichment Contributions between Anthropogenic and Lithogenic Sources.

Table 14e: MB-FC Enrichment Contributions from Anthropogenic and Lithogenic Sources.

Anthropogenic Versus Lithogenic Heavy Metal Enrichment Contributions (MBFC)		
$[M]_{total\ (mg/kg)}$	**$[M]_{Anthropogenic\ (mg/kg)}$**	**$[M]_{Lithogenic\ (mg/kg)}$**
11050.0	9523.72	1526.28
11200.0	9653.00	1547.00
1093.0	942.03	150.97
4.005	3.45	5.53
11.8	10.17	1.63
TOTAL %	86.19%	13.81%

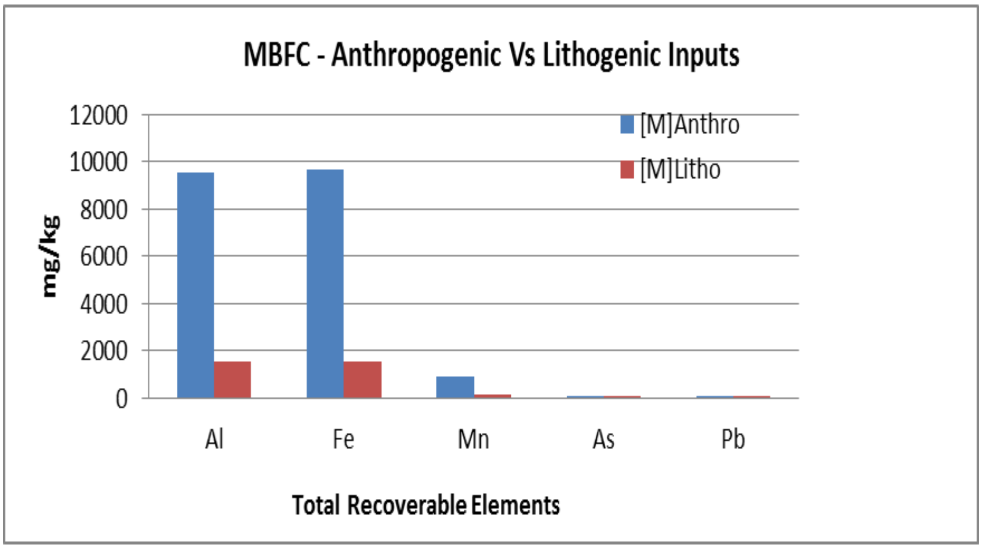

Figure 4e: MB-FC Data Showing the Relationship and Patterns for Enrichment Contributions between Anthropogenic and Lithogenic Sources.

Table 14f: VB-FC Enrichment Contributions from Anthropogenic and Lithogenic Sources.

Anthropogenic Versus Lithogenic Heavy Metal Enrichment Contributions (VBFC)		
[M]$_{total (mg/kg)}$	**[M]$_{Anthropogenic (mg/kg)}$**	**[M]$_{Lithogenic (mg/kg)}$**
8940.0	7940.95	999.05
9235.0	8202.99	1032.01
930.5	826.52	103.98
2.935	2.605	0.33
10.28	9.13	1.15
TOTAL %	88.81%	11.19%

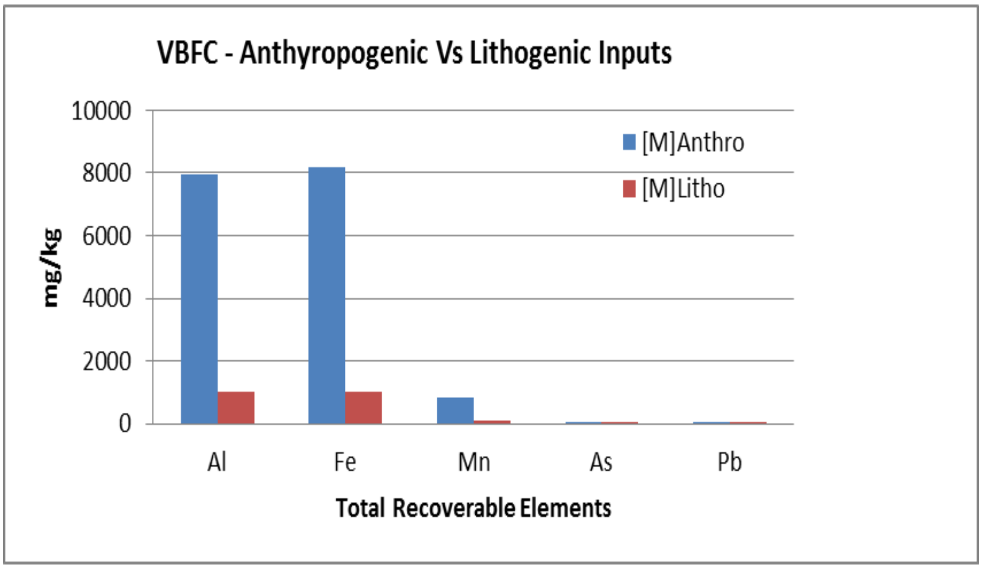

Figure 4f: VB-FC Data Showing the Relationship and Patterns for Enrichment Contributions between Anthropogenic and Lithogenic Sources.

These results prove that anthropogenic inputs, from industries in and around Decatur and Huntsville, have given rise to a gradient in concentration of metals in FC and FR sediments. Metal accumulation, probably initiated by precipitation of Fe complexes, is probably responsible for the enrichment of Aℓ, Fe, Mn, As and Pb in the watersheds, whereas the reference sediments (upland area) did not accumulate them to the same degree. Also, the impact of heavy metal pollution to watersheds' ecologies could be substantial because of the variety of inputs to these areas. Potential land-based sources of heavy metals include river inputs, local runoff and atmospheric deposition.

3.5 Evaluation using the PLI

Results of the CF shows that Aℓ, Fe, Mn, As and Pb was generally found at all sites, but Mn and Pb has the highest CF at all sites. The highest CFs for Mn were at the two tributaries HR-FR and VB-FC and HR-FR and RB-FC for As. The PLI for the watersheds were highest to lowest in HR-FR>WR-FR>RB-FC>BF-FR>MB-FC>VB-FC. Discharge of industrial effluents has led to the present level of metal contamination in the watersheds; in this condition, the hazard associated with the metals released during mineralization could be available to biota. The overall, Pollution Load Index for FR seem to be higher than FC watershed. Accumulation (loading) of metals in this watershed system may be aggravated by weak flushing. These pressures are deemed inevitable with urban growth initiated in Madison County and associated with ongoing big city (Huntsville) development, the PLI represents the number of times by which the heavy-metal concentrations in the sediment exceeds the background level concentration and gives a summative indication of the overall level of heavy-metal toxicity in a particular sample. The PLI is proposed as a standardized system for detecting pollution that permits a comparison of pollution levels between different sites. (See Table 15 and Figure 4.)

$\mathrm{CF} = \mathrm{C}_{\mathrm{metal}} / \mathrm{C}_{\mathrm{Background\ value}}$

CF = Contamination Factor

$\mathrm{PLI} = 5\sqrt{(\mathrm{CF}_{1*}\ \mathrm{CF}_{2*}\ \mathrm{CF}_{3*} * \mathrm{CF}_{n})}$,

n = (root) number of metals.

Table 15: CFs and PLIs for FC and FR Watersheds.

	Site Code	PLI	CF/Aℓ	CF/Fe	CF/Mn	CF/As	CF/Pb
1A	WR-FR	0.459	0.081	0.906	**1.088**	0.440	0.580
2A	BF-FR	0.333	0.127	0.369	0.683	0.214	0.590
3A	HR-FR	0.596	0.294	0.492	**1.971**	0.272	0.973
1B	RB-FC	0.362	0.187	0.381	0.728	0.181	0.662
2B	MB-FC	0.323	0.138	0.237	**1.286**	0.141	0.590
3B	VB-FC	0.264	0.112	0.196	**1.095**	0.103	0.514

Overall, mean PEC quotients for all samples and each sampling site varied from 863 to 1820, the lowest mean was RB-FC and highest mean (>PEC) was HR-FR at the FR tributary, suggesting that there is a probable risk effect of manganese on benthic organisms at WR-FR, HR-FR, RB-FC, and MB-FC sites. According to the CBSQGs, adverse biological effects on the sediment living organisms are to be expected frequently. The lowest and highest range of mean for ≤ or > MEC was 504 - 33800 for Fe and Mn at WR-FR-Fe, RB-FC, MB-FC, VB-FC-Mn, and the highest values were calculated for the bed sediments of WR-FR at FR 33,800 $\mathrm{mg.kg^{-1}}$. All the sites were less or equal to the threshold effect concentration. Based on this classification approach, and with the exception of the HR-FR tributary where toxic effects are very probable, the overall reaches of all the other sites would be ranked as an area with moderate to very high toxicological risks due to heavy metals. The percentage of heavy metals from average samples from each site that exceeded TEC were 2.25% - Fe, 69.97%-Mn, and 6.49% for As. (See Table 16.)

Table 16: Risk effects concentration.

Risk Effects Concentration	**Sediment Metal Concentrations (mg kg^{-1})**				
	Aℓ	**Fe**	**Mn**	**As**	**Pb**
TEC[a]	NG	20,000	460	9.8	36
MEC[b]	NG	30,000	780	21.4	83
PEC[c]	NG	40,000	1,100	33	130
Average values for metal of concern from the study areas	NG	20,450	1,531.67	10.48	35.67
% samples which exceeded TEC	NA	**2.25**	**69.97**	**6.49**	0
% samples which exceeded MEC	NA	0	**49.08**	0	0
% samples which exceeded PEC	NA	0	**28.18**	0	0

[a] Threshold Effect Concentration (TEC)

[b] Mid-Point Effect Concentration (MEC)

[c] Probable Effect Concentration (PEC) (McDonald, et al., 2000).

NG = No Guidelines

NA = Not Applicable

Red = Highly Significant Exceedances

4. DISCUSSION

This study addressed the assessment of the ecological relevance of heavy metal pollution in the Flint Creek and Flint River, which drains heavily industrialized and densely inhabited Madison County and sparsely inhabited, but industrialized, Morgan County in Northern, Alabama. There has been no previous comprehensive study to the author's knowledge that outlined hazardous inputs of total elements and organic contaminants from this polluted watershed.

The selected metals analyzed (Aℓ, Fe, Mn, As, and Pb) were based on previous research on surface water by the same author and the pollution influences found in the FC and FR watersheds. However, Aℓ, Fe, and Mn were the only detected heavy metals in the samples collected from the surface water of the rivers. As and Pb were not detected in most of the water samples. All the heavy metals of concern were detected in all sediment samples for this study. However, the concentration of metals in bed sediments (depositional) was, in general, lower in most samples than in reference (upland) sediments. This could be attributed to the prevention of sedimentation process by water currents.

The pH, TDS, EC, Salinity, sediment OM content and mean concentrations of sediment metals, including standard deviations, for each site were presented in Table 9. In general, the alkalinity of the watersheds is low at all sites due to the underlying bedrock. The highest pH values were recorded in the BF-FR in Huntsville; which may be due to heavy deposits of flint-stones; the high pH in RB-FC and MB-FC in Decatur sites may be due to localized limestone deposits. It should be noted that Decatur is near the Limestone County.

All the metals analyzed show significant variation in average concentration among the different sites (Figures 10a and 10b). In the upper stream section of the FR sub-watersheds, the rivers show low mean concentration compared to the middle stream, and highest mean concentrations of heavy metals overall at the tributary (HR-FR). The mean concentration of all metals in FC sub-watersheds shows a more uniform distribution throughout the whole watershed. This uniformity can probably be attributed to the underlying bedrock geology. An exception to this is the VB-FC site, where Arsenic concentrations are as high as 11% (Table 10). Pb concentrations are also elevated in the FC river sediments, along with minor increases in other metals.

The correlation coefficients observed among various metals in surficial sediments are significantly higher for those observed in suspended sediments with high clay content. The data showed significant positive correlations at 95% confidence level with the total metal content of the samples. Due to its large surface area most pollutants are generally concentrated in the fine grained (silt + clay) particle fraction of the sediments.[37] The distribution of metals in different fractions of the bed sediments indicated lower concentrations with decrease in the fine sediment fractions. It is clearly evident from the results (Figures 5a and 5b) that the concentration of different metals was dramatically different in various fractions of the sediments and generally increased with the decreasing particle size of the sediments.

The metal contents and their strong positive interrelationships (Aℓ, Fe, Mn and Pb) in the sediment indicate that the upper, middle sites of FC and FR are influenced by potential toxicity (PS) contaminants. The statistical analysis of the data revealed that the FR tributary, HR-FR, has the highest amount of heavy metals; due to PS of contaminants, especially metal-based industries situated in and around part of the study area in Huntsville, are responsible for the higher heavy-metal input in HR-FR sediments. It was observed that the highest content of Aℓ, Mn, and Pb were recorded in the sediments of the southern part of the FR. A strong positive correlation is seen in one cluster between Mn, As, and Pb, in another cluster between Aℓ, Mn, As, and Pb; however, their variation in their mean size, overall, in the sediments. The diagram of Table 8 of these metals and mean size also gave similar results.

Assessment of sediment contamination with heavy metals in the two watersheds using the I_{geo} classification, indicate that the two watershed areas has to be considered as "moderately" polluted in Mn, As, and Pb and "unpolluted to moderately" polluted in Aℓ and Fe. The upstream (WR-FR) would be ranked as "moderately to strongly" polluted in As and "moderately polluted" in Pb and Mn. Overall, the relative importance of pollution in the two watersheds showed the following order: As > Pb >Mn. The low metal concentration-to-Aℓ ratios for enrichment factor calculations suggest that the sediment metal concentrations in these watersheds are close to or at background levels and may be used as a baseline for subsequent comparative metal contamination studies.[38]

Higher heavy metal CF and PLI were recorded for FR, specifically the HR-FR. Apart from industrial effluents, it is observed that domestic sewage and rapid urbanization are becoming a major threat as indicated by increasing fine (% silt + % clay) size fraction in the sediments. The fine-grained sediments (silt 11.81% + clay 64.74%) have a greater surface area and provide a more efficient environment for the adsorption of metals (Wasserman, et al., 2008). It was observed that total metal content generally increases as the grain size decreases; this may be due to the higher ability of fine particles to collect both transition and heavy metals. The association of metals (Mn, Pb and Aℓ) with fine size sediments is shown by its good correlation with mean grain size in all the samples of the study area. Overall, the results of this study reveal that the toxic heavy metals of concern have been accumulating in the sediments of FC and FR watersheds and are being enriched. The enriched metal concentrations will possibly have a direct bearing on these watersheds and ecosystem and periodic study of effluent discharges is essential for effective management of the watersheds.

The results of the ecological risk assessment for the watersheds in relation to biological effects on benthic organisms in sediments sampled showed that the TEC for As (CBSQG = 9.79 mg/kg) was exceeded in some samples from WR-FR and BF-FR the upper stream of FR. The PEC for As (CBSQG = 33.0 mg/kg) was not exceeded in any samples, interestingly, according to the U.S. Fish and Wildlife Service,[39] the dietary effect level for As in fish is between 10 µg/g dry weight (no effect) and 30 µg/g (reduced weight gain,[40] The TEC for Pb (CBSQG =36.0 mg/kg) was exceeded in some samples from BF-FR, MB-FC, and VB-FC. The PEC for Pb (CBSQG =130.0 mg/kg) was not exceeded in any samples. Interestingly, Pb was detected in all samples from all sites. A study, that assessed relative toxicity of metals in sediment to benthic invertebrates by comparing levels found in their study with toxic thresholds reported in the literature (CBSQGs), ascertained that levels of Pb below 100.0 µg/g dry weight in the diet usually cause few significant reproductive effects in birds.[41] In another study, Beyer and Stafford[42] said that Pb in earthworms, at 150.0 µg/g dry weight or more, should be considered hazardous to sensitive species that eat earthworms. The maximum Pb level recorded in this study was 57.99 mg/kg dry weight in BF-FR and minimum was 4.83 mg/kg at VB-FC. Therefore, Pb concentrations from this study are far above acute or chronic levels for invertebrates and birds.

The TEC for Mn (CBSQG = 460.0 mg/g) was exceeded in all samples from all sites in both watersheds. The PEC for Mn (CBSQG =1,100.0 mg/kg) was exceeded in some samples from WR-FR, BF-FR, RB-FC, MB-FC, and VB-FC, and all samples from HR-FR.

The TEC for Fe (CBSQG =20,000.0 mg/kg) was exceeded in some samples from WR-FR. The PEC for Fe (CBSQG =40,000.0 mg/kg) was not exceeded in any samples. There are no guideline concentrations for Aℓ. This study identified a concern level for Fe in sediment of 20,000.0 mg/kg (dry weight). Most Fe concentration in samples from this study were much lower (except in some samples from WR-FR). The study also identified a concern level for Pb in sediment of 36.0 µg/g (dry weight). Pb concentrations in sediment samples from WR-FR, HR-FR, and RB-FC were much lower.

Comparing the heavy metal concentrations with the CBSQGs, TEC and PEC values developed by McDonald, et al., revealed that over 46% of the samples exceeded the TEC for all heavy metals (Aℓ, Fe, Mn, As, and Pb) considered, with most sample concentrations falling below the PEC (Table 13). Up to 90% of samples exceeded the PEC for Mn, while the Fe content exceeded the PEC in 12.5% of samples. According to the CBSQGs, adverse biological effects on the sediment dwelling organisms are to be expected frequently. Exceedances of SQGs values do firmly guarantee the occurrence of deleterious ecological effects, because they are also in agreement with the reference (Upland area), regional (NASC), and international (T&W) background data. However, the state's background levels for these trace elements in benthic organisms, fish, or birds and their propensity to bioaccumulate through the aquatic food chain to predators are not well known.

5. CONCLUSION

In summary, it appears, from results, that in comparison, FC sediments have higher levels of environmental contaminants than FR. The concentrations of most of the elements detected in samples from FR watersheds appeared to be below, and some are above, biologically significant threshold levels. However, concentrations of samples from FC are mostly above levels of regulatory concerns. Nevertheless, long-term bioaccumulation of these contaminants can result in impacts, it should be cause for concern, and further study focusing on the impact assessment of heavy metals in the Flint Creek, and Flint River watersheds are needed.

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CONFLICTS OF INTEREST

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