

Occurrence and Assessment of Pharmaceuticals and other Toxic Industrial Chemical Pollutants in the Lower Tennessee River Basin

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Article History:

Received: 12 May 2013

Accepted: 7 June 2013

ABSTRACT

The aim of this study was to determine the occurrence and distribution of organic pollutants in the Lower Tennessee River Basin's soil/sediment matrix and develop the hazard quotient for the Flint Creek and Flint River watersheds. Pharmaceutical and industrial pollutants represent the newest pollutants discovered at these watersheds. Gas Chromatography — Electron Capture Detection/Photo-ionization was used to detect all compounds. A modest to substantial amount of the compounds were detected in samples collected from both watersheds during the winter season of 2011. Results showed that there was an increasing trend of polycyclic aromatic hydrocarbons (PAH) in Flint River. Pharmaceuticals, gasoline products, SVOCs, and other organic chemicals, were all present in Flint River in large doses as well. Distribution of the industrial pollutants in the Flint Creek showed that it contained more pharmaceuticals and gasoline components than the Flint River. The results of the Ecological Risk Assessment or Hazard Quotient (HQ) for the pollutants for all sites indicated a potential for adverse ecological effects, and that a more thorough study is necessary. Testing in the Flint Creek and Flint River watersheds mirrors national studies that show it's a real problem almost everywhere, with unknown consequences. The findings from this study will fill an existing gap in knowledge, and allow environmental agencies to improve management decisions and develop meaningful guidelines for protecting Alabama's water resources.

Keywords: Soil/sediment matrix, Hazard Quotient, Industrial Pollutants, SVOCs, PAH, Pharmaceutical and Gasoline products.

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INTRODUCTION

Recent studies by environmental researchers, chemical industries, water utility companies, and local environmental agencies have discovered high concentrations of pharmaceuticals and gasoline products in soils/sediments and ground water in many states in the U.S. [1-5]. The elevated concentration has been linked to anthropogenic activities and underground gasoline-storage-tanks, oil seeps, and petroleum spills. Frequent occurrence of low to intermediate concentrations of these products has been discovered in some reservoirs used for public water supply (PWS) [6], and in surface waters. Here in Northern Alabama, the problem is very severe, but has largely gone unnoticed.

This study of two major watersheds (Flint Creek and Flint River) determined the occurrence and distribution of pharmaceutical and industrial pollutants in the Lower Tennessee River Basin's soil/sediment matrix. Before now, little was known about the concentrations of industrial organic compounds in Flint Creek (FC) and Flint River (FR) and its tributary streams. During 1999 and 2000, the USGS collected the first data documenting the presence of pesticides and herbicides in FR [7], but not the pharmaceuticals and gasoline components, such as, benzene, toluene, and xylenes in FR or FC [7]. Organic compounds investigated during this study include: volatile organic compounds of gasoline components (such as, Toluene, Heptane, and 3, 4, 5-Trimethyl-1-hexane), soluble pesticides, polycyclic aromatic hydrocarbon (such as, Fluoranthene, and Pyrene), and pharmaceutical products (such as, 7-Oxabicyclo [4.1.0] heptane, Squalene, and Ceanothine C.). Gasoline components and pharmaceutical chemical compounds were found in all of the samples collected from FC and FR watersheds during the winter season of 2011. Every sample taken from the rivers during the winter/spring months had detectable concentrations of VOCs and SVOCs, such as, PAHs. USEPA has determined that benzo[k]fluoranthene and pyrene, which were detected in most of the samples from all FR sites (WR-FR, BF-FR, and HR-FR) are probable human carcinogens. PAHs enter surface water/sediment through discharges from industrial plants, waste water treatment plants, exhaust from automobiles and trucks, and they can also be released to soils at hazardous waste sites if they escape from storage containers, but most stick to solid particles and settle to the bottoms of rivers or lakes. According to ATSDR-CDC [8], the primary sources of exposure to PAHs for most of the U.S. population are inhalation of the compounds in

tobacco smoke, wood smoke, coal tar production plants, bitumen, and asphalt production plants, coal-gasification sites, coal tarring facilities, degradation of tires, and municipal refuse incinerators.

PAHs can break down into longer-lasting products by reacting with sunlight and other chemicals in the air, generally over a period of days to weeks. Studies have shown that PAHs have been found in some drinking water supplies in the U.S. [9].

Toluene is a by-product of gasoline, and it is one of the most toxic components of gasoline. Gasoline sometimes leaks from storage tanks (particularly older ones), including, underground ones found at many gas stations. Leaking gasoline, and with it toluene, often finds its way into the sediments in depositional areas. Some of it can seep into underground water supplies. In addition, wells that tap into such aquifers can become contaminated with toluene, making them unfit for human use.

For years, the clarity of Flint Creek's water has been decreasing. The cause of this loss of clarity by visual inspection may be due to increased algae populations within the river at the VB-FC site (FC tributary), and from the results of this study, may be industrial pollutants that have made their way into it. Scientists and regulators require more information that would allow them to make appropriate decisions on remedial actions needed to reverse this trend. A large amount of sewage effluent is also exported into FC. Increased urbanization and its associated activities may also be an important contributor to the reduction of FC's clarity. Pesticide and fertilizer use, leaking underground fuel storage tanks, and atmospheric deposition can all be important sources of toxic industrial organic compounds that could upset the natural ecological systems within the river. The objectives of this study are: (1) to determine the occurrence and distribution of industrial pollutants in the watersheds, and (2) develop the VOC's and SVOC's Ecological Risk Assessment or Hazard Quotient (HQ) for the FC and FR. The results of this study will provide useful benchmarks from which future comparisons can be made.

Statement of the Problem

Research sampling conducted in winter/spring 2011 revealed that all the sites at the FC and FR watersheds were contaminated with VOCs at levels exceeding Alabama Department of Environmental Management (ADEM) and USEPA Water Standards. VOCs and SVOCs in surface sediments of the FC and FR might be of ecological concern because PAHs are potent carcinogens, and the USEPA regulates their concentrations in drinking water from PWSs. According to a study conducted by Avril et al., [10], exposure to PAHs causes varied and wide-ranging toxic effects in a variety of organisms, such as, invertebrates, fish, birds, and mammals, including humans. VOCs and SVOCs could possibly be present in the sediments of the watersheds from underground storage tanks, abandoned old gas stations, degradation of tires found in both watersheds, vehicle traffics, leaching from landfills, and from oil seep and petroleum spills. USEPA's sediment quality criteria for VOCs and SVOCs [11] indicates that these pollutants can even cause toxic effects in aquatic plants, aquatic invertebrates, and young fish at relatively low water/sediment concentrations. Thus, the seep or dumping might threaten the ability of the rivers to support macro-invertebrate and fish communities and the wildlife that feed on them. The area of concern has been identified as all sites on the watersheds and the associated leachate seeps. According to USEPA studies, pharmaceuticals and personal care products (PPCPs) may have an impact on human health and they have a much greater impact on fish and other aquatic wildlife [12]. These organisms are more susceptible to problems from PPCPs because they have continual exposures, multi-generational exposures, and exposure to higher concentrations of PPCPs in untreated water. PPCPs get into our water from many different sources. These include pharmaceutical industries, hospitals, medical facilities, households, veterinary drug use (especially antibiotics and steroids) and agricultural areas [13]

The findings from this study are consistent with a recent report from the city of Decatur in Morgan County. According to an article that appeared in the Decatur Daily, 2008, city council is urging the Decatur Utility Company to apply stricter regulations on industrial wastewater [9]. In the report, their treatment plant that was built to treat domestic wastewater, accounted for 35% of industrial wastewater of the treatment plant's intake in 1983. Over the years, the standards set by ADEM and the USEPA have become stringent while Decatur Utilities ordinance has remained static. Now, the treatment plant is unable to handle the increasing industrial wastewater entering the plant; because over 65% of the wastewater entering the plant comes from industries and they are "laced with difficult-to-treat chemicals" [14]. The report also confirmed that the plant that is built along the FC was not prepared for the chemical overload [14, 15]. Furthermore, Huntsville Times in Madison, Alabama reported recently that ADEM has sued the Hanceville Water and Sewer Board citing unpermitted discharges of over 2 million gallons of raw or untreated sewage into the creek [16]. Notably the releases of large quantities of a variety of toxic synthetic chemicals, such as organics, hydrocarbons, pharmaceuticals, and petrochemicals into watersheds and the environment from point sources (PSs) that are permitted to dump chemicals into the rivers in Alabama are becoming a major concern.

MATERIALS AND METHODS

Study Area and Sampling Location

The areas chosen for this study are the two major watersheds in Lower Tennessee River (TR) basin in Northern Alabama and South-Central Tennessee. The Flint River and Flint Creek are tributaries to the TR. The two watersheds are located within the Wheeler Lake (WL) basin. Sampling locations were geo-referenced utilizing Leica GS-50 GPS unit. The FC watershed encompasses Cullman, Lawrence, and Morgan Counties at 34°30' North Latitude, 86°57' West Longitude. The FR watershed encompasses Southern Tennessee, and Madison County, Alabama at 34°30' North Latitude and 86°28' West Longitude [17]. Three sampling sites per watershed were chosen to collect water samples (Fig.-1a, 1b and Table-1).

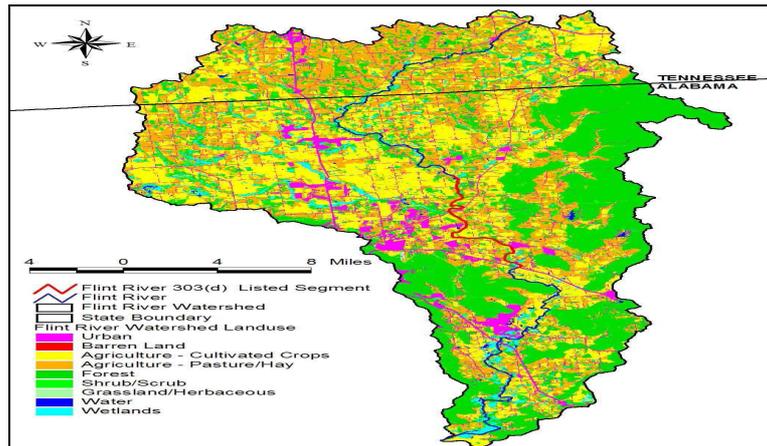


Fig.-1a: Sampling sites: Geographic coordinate points of sampling locations at the Flint River watershed [18].

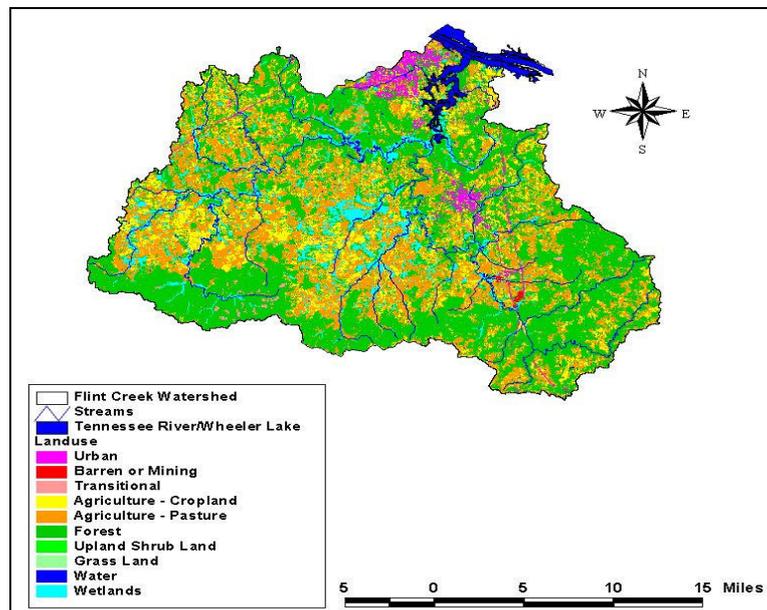


Fig.-2: Sampling sites: Geographic coordinate points of sampling locations at the Flint Creek watershed [18].

Sediment Sampling

Six sampling sites were chosen along the Flint Creek and Flint River and their tributaries at the inlet opening to the Tennessee River. Three of these sites were within FC and three sites were along the FR (Table-1).

A stainless steel soil probe was used for collecting soils from the river banks, upland (reference areas), and an 8-ft. pole sediment sampler–Pakar (Pakar by Paul/Garner–patent pending) was used for collecting sediments from the depositional areas in the middle of the rivers. At each site, sediment was collected during an almost 30-day period

in winter/spring, 2011. Seventy-two composite sediment samples were collected from the two watersheds. Samples were collected from the uppermost layer of the sediment (1 to 10 cm) taking care to minimize contamination. In the laboratory, samples were refrigerated until processing and analysis. Surface sediment was collected for analysis because it provides information on the most recently deposited sediment materials and helps in understanding the horizontal variation in sediment properties and the distribution of contaminants [18, 19]. (Fig.-2)

Table-1: Description of sampling locations and their codes

Flint River (FR) Watershed (Huntsville, Alabama)				
Sites	Stream	Codes	Coordinate Points	Elevation
1	Winchester Road	WR-FR	N 34° 30' 12.5" W 86° 28' 00.4"	721.5 +/-19"
2	Briar Fork Rd	BF-FR	N 34° 47' 23.15" W 86° 29' 05.4"	751.5 +/-36"
3	Hobbs Island Road	HR-FR	N 34° 32' 19.5" W 86° 55' 52.6"	660.5 +/-30"
Flint Creek (FC) Watershed (Decatur, Hartselle, Alabama)				
Sites	Stream	Codes	Coordinate Points	Elevation
4	Red Bank Rd	RB-FC	N 34° 30' 22.5" W 86° 57' 20.8"	788.5 +/-50"
5	Means Bridge	MB-FC	N 34° 29' 37.8" W 87° 01' 34.9"	602.5 +/-42"
6	Vaughn Bridge Rd	VBFC	N 34° 27' 48.15" W 86° 57' 52.4"	521.5 +/-56"

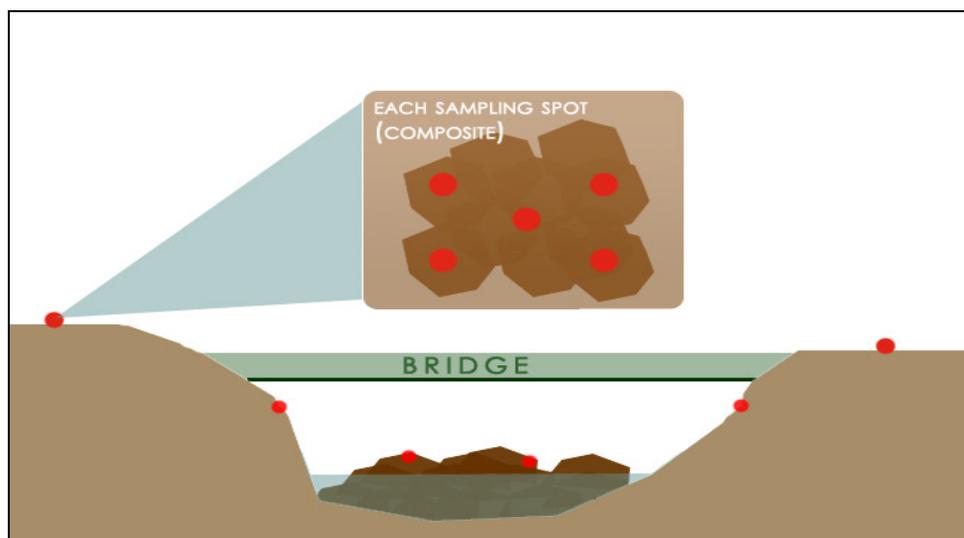


Fig.-2: Soil/sediment sampling site, side view of bridge [18].

Quality Control and Data Validation

Sediment samples from all the sites, including the two tributary streams were sent to a contract laboratory for determination of organochlorines (PAHs) and volatile compounds (~20 gasoline product compounds) using methods described by the USEPA [20].

A multi-residue technique was used for the extraction. The analytes collected were thermally desorbed in gas chromatographic inlet and detected by mass spectrometry. The instrumental parameters were optimized before the analysis of samples. Line purge and trap technique followed by Gas Chromatography—Electron Capture Detection/Photo-ionization Detection was used for the VOCs and SVOCs. The instrumental detection limits were in the range of $\mu\text{g}/\text{kg}$ level. The sediment samples were analyzed for industrial organic compounds including: gasoline products, pharmaceutical products, solvents, and PAHs.

The analyses were performed in accordance with Standard Methods, The Solid Waste Manual SW-846, USEPA Methods for Chemical Analysis of Water and Wastes [21]. The testing laboratory asserts that the analytical data was validated using standard quality control measures performed as required by the analytical method. Moreover, that the quality assurance, instrumentation maintenance and calibration were performed in accordance with guidelines established by the USEPA, National Environmental Laboratory Accreditation Program (NELAP), and the United States Army Corps of Engineers (USACE). The instruments were calibrated to eliminate or minimize bias in the overall measurement system.

Analysis for Chemical Parameters

Soil/Sediment Background Levels

Background levels of some representative PAHs in the air are reported to be 0.02-1.2 ng/m³ in rural areas such as FC and 0.15-19.3 ng/m³ in urban, areas such as FR. Background levels of PAHs in drinking water range from 4 to 24 ng/L [22]. The safe drinking water act of 1974 required EPA to determine safe levels of chemicals in drinking water which may cause health problems. In 2009, the USEPA set the non-enforceable levels, based solely on possible health risks and exposure to most VOCs called Maximum Contaminant Level (MCL) goals at zero (0), and enforceable standard called MCL at between (0.005 to 0.2 ppb (µg/L) [Maximum Contaminant Level (MCL) goals at zero (0), and enforceable standard called MCL at between (0.005 to 0.2 ppb (µg/L) [23].

Analysis for Soil/Sediment pH

Collected sediment samples for organic compound analysis were air dried in the greenhouse, and analyzed for pH as follows: The pH of sediment samples were measured on sediment to water (1:1) suspension using Fisher Accumet model 15 pH meter as described in Methods of Soil Analysis [24].

Analysis for Soil/Sediment for Pharmaceuticals, VOCs and SVOCs

Sediment samples (~1 g) were precisely weighed and extracted by pressurized solvent extraction (ASE 200; Dionex) with dichloromethane (DCM)/acetone (3:1, v/v) [25]. The PAH and other VOCs were identified by gas chromatography-electron capture detector (HP 5890 series II Plus – [CALIF-USA]).

The analyses for the organic compound prepared samples were carried out using USEPA standard approved methods [20]. Each analytical batch contained (1) a method blank, (2) a matrix spike, and (3) duplicate samples. A reagent blank was used to assess artifacts and precision was verified by duplicate analyses. Sample spikes were used as an additional check on accuracy. For gas chromatography-electron capture detector/mass spectrometry (GC-ECD/MS) analysis, calibration standards were injected after each group of 5 samples. Analyte recoveries as well as Method Standard Deviations (MSDs) and Method Detection Limits (MDLs) were determined by analyzing sediments spiked with volatile components and PAH standards. The recovery coefficient was taken into account for calculating the final concentrations of analytes. The recoveries were 82–97% and 90–110% for volatile and PAH compounds, respectively. The MDL, which was calculated as a triple standard deviation, was less than 0.19 µg/g dry weights.

Soil samples collected for laboratory determination of VOCs require special handling to prevent loss of VOCs that can lead to low-biased results. Interestingly the concentrations from the results for the VOCs were quite high for this study. It could have been much higher, but due to the nature of the compounds, some must have been lost from soil and sediment samples due to volatilization and biodegradation during collection, storage, and analysis. This usually leads to low-biased results. Sample collection procedures and associated handling both in the field and in the laboratory may have led to underestimation of VOC concentrations. Some researchers in this area agree that some commonly used techniques in sampling for VOCs are prone to relatively large losses and results are potentially biased quite low. The techniques that were used in this study involved collection and preservation of disturbed (composite) soil/sediment samples and storage in soil jars with air-tight seals to minimize such losses. The detection limits (LOD) for most classes of the contaminants present in the soil/sediments that were analyzed for this study are listed on Table-2.

Particle Size

Sediment particle sizes generally range from sand, sandy-silt, to clays, although shells and detritus (other organic compounds) may also be a significant proportion of many types of sediment. The surface areas of these materials vary over orders of magnitude, and they also differ on binding sites for metals and organic contaminants. The particle size ranges seen at the depositional areas for this study were: sand (9.52 to 44.13%), silt (0.63 to 31.85%), and clay (46.37 to 74.1%). It is important to only compare sediments that have similar grain size distribution, such as, FC and FR; because particle size greatly affects the distribution of contaminants.

Table-2: Summary of Limits of Determination (LOD) for analysis for common contaminants in soil/sediments [27].

Sediment Chemicals	LOD	Units
Silver (Ag), As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Vanadium (V), Zn	0.2-1	mg/kg
Mercury	0.001	mg/kg
Methylmercury	0.01	mg/kg
Tributyltin (TBT)	0.05	µg/kg
PAHs	0.01-0.2	mg/kg
Total Petroleum Hydrocarbons (TPHs)	25-100	mg/kg
Benzene, Toluene, Ethylbenzene, Xylene (BTEX)	0.5-1	mg/kg
Total Polychlorinated Biphenyls (PCBs)	0.01-0.1	mg/kg
Phenols	0.1-2	mg/kg
Organochlorine Pesticides	0.01-0.001	mg/kg
Organophosphate Pesticides	0.01	mg/kg
Synthetic Pyrethroids	0.05	mg/kg
Carbamates	0.05	mg/kg
Phenoxy-Acid Herbicides	0.1	mg/kg
Phthalates	1-2	mg/kg
Carbamates	0.05	mg/kg
Bromoxynil, Propyzamide, Glyphosate	0.1-1	µg/kg

Data Analysis

Using Screening-Level for Ecological Risk Calculations

A quantitative screening-level risk can be estimated using the exposure estimates and the screening ecotoxicity values developed according to USEPA [11]. For the screening-level risk calculation, the Hazard Quotient (HQ) approach, which compares point estimates of screening ecotoxicity values and exposure values, is adequate to estimate risk [27-29]. As described in USEPA [18], a screening ecotoxicity value should be equivalent to a documented and/or best conservatively estimated chronic Screening Benchmark or no-adverse effects level (NOAEL) concentration. Thus, for each contaminant and environmental medium, the HQ can be expressed as the ratio of a potential exposure level to the Screening Benchmark. Surface sediment data was used for analysis because it provides information on the most recently deposited sediment materials and helps in understanding the horizontal variation in sediment properties and the distribution of contaminants.

Ecological Risk Assessment for industrial pollutants was estimated numerically using the ratio HQ approach. The HQ was used to estimate if risk to harmful effects is likely or not due to the contaminant in question. The HQ was calculated using Equation (1).

$$HQ = EEC/\text{Screening Benchmark} \quad (1)$$

Where, EEC is estimated (maximum) contaminant in the soil, sediment, or water (e.g: mg contaminant/kg soil); and Screening Benchmark is generally a no-adverse effects level concentration. If the contamination concentration is below this level, the contaminant is not likely to cause adverse effects to aquatic habitats [30, 31] (Figure 3).

If an HQ is calculated to be ≥ 1 for a particular contaminant, that contaminant is then referred to as a Contaminant of Potential Ecological Concern [32]. Furthermore, it is important to note that how large the HQ is (i.e., by how much it exceeds one) is not relevant to a Screening Ecological Risk Assessment. This is because USEPA has not recognized any official means of evaluating the size of the results of these calculations, only whether or not the HQ exceeds one. (Table-3)

Ecological risk assessment is a risk or impact evaluation. There are two functions of the ecological risk assessment, to:

1. Document whether actual or potential ecological risks exist at a site; and
2. Identify which contaminants present at a site pose an ecological risk to sediment dwelling organisms.

It is very important to note that, currently, there are no nationally accepted screening criteria or comparative values for evaluating human health hazards that may be associated with exposure to contaminated sediments. According to the Agency for Toxic Substances and Disease Registry [33], standardized evaluation of chemical hazards from contaminated sediments is difficult because exposure potential varies greatly from site to site.

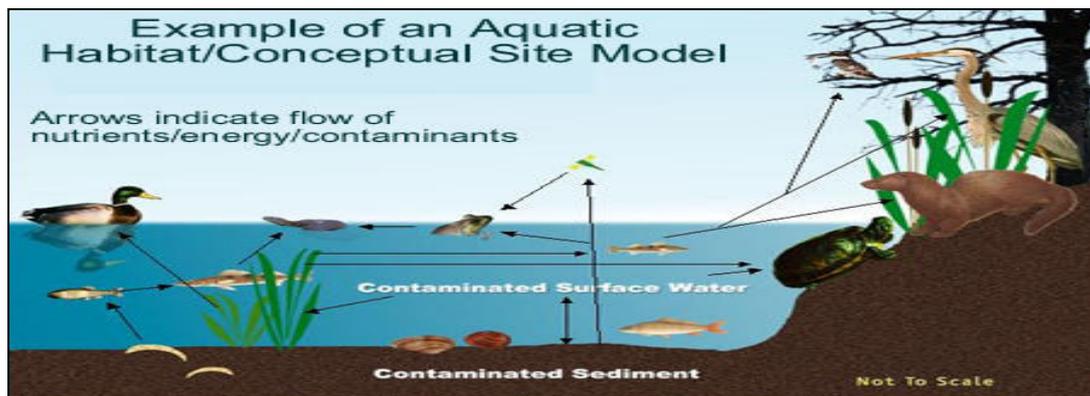


Fig.-3: Example of Aquatic Conceptual Site Model [23]

Table-3: USEPA - Region 4 Waste Management Division Soil Screening values for Hazardous Waste Sites and Region 5 Superfund [33]

If...	Then...
HQ > 1.0	Harmful effects are LIKELY due to the contaminant in question
HQ = 1.0	Contaminant ALONE is not likely to cause ecological risk
HQ < 1.0	Harmful effects are NOT likely

RESULTS AND DISCUSSION

Distribution of Industrial Pollutants in the Flint River

The results showed that there was an increasing trend of PAH in FR. Interestingly, PAH, such as fluoranthene and pyrene were only present in samples from the upland (reference) areas of the three sites and none were found in the depositional or bank area of the FR, suggesting anthropogenic sources. PAH sources include: automobile exhaust, degradation of tires, oil and fuel spills, and industrial solvents. The proportion of PAH compounds could have been from combustion sources, such as vehicle exhaust and this may have been a result of increased urban sprawl over the last ten years. Pharmaceuticals such as gamma-sitosterol = 1549 µg/kg; gasoline products, such as hexatriacontane = 644.9 µg/kg; volatile compounds, such as 2,5-dimethylpentane = 341.5 µg/kg; organic solvents, such as, 2,5-dimethylheptane = 310.4 µg/kg; fatty-acids, such as hexadecanoic acid = 127 µg/kg; SVOCs, such as (e)-9-eicosene = 194.6 µg/kg; and organic chemicals, such as 1,2,3,5,7,8,8-naphthalene = 2382.1 µg/kg were all present in this river in large dose. It should be noted that inhalation or exposure to large amounts of pollutants, such as, 2-hexanone that are no longer produced in the U.S., but detected in the FR can harm the nervous-system. EPA studies also showed that inhaling pollutants such as 1,2,3,5,6,8a-he-naphthalene in large doses destroys red blood cells [33-36]. Table 4a shows the percentages for each group of organic contaminants. Interestingly, FR which is located in Madison County that showed the greatest percentage of urban land use also showed the largest percentage in pollutant concentrations. This suggests that urbanization around FR is affecting the water quality of the watershed, since most volatile organic contaminants enter the water supply through atmospheric deposition.

Distribution of Industrial Pollutants in the Flint Creek

The results showed that there are more pharmaceutical and gasoline components in FC than in FR. The concentration of PAH and volatile components were less in FC. Pharmaceutical compounds found at the bank of Site 2 were also found at the bank of Site 4 in FC. Piperidine (28.3 µg/kg) at Site 1 was used illicitly in the 1970's to produce recreational drugs called angel dust and PCP. Combinations of human growth hormones, such as testosterone (233.4 µg/kg) and squalene (531.3 µg/kg) were only present in samples from the depositional areas of the FC, suggesting anthropogenic sources. Pharmaceuticals, such as, beta-sitosterol = 1408.1 µg/kg,

methacrylamide = 49.3 µg/kg, and 7-oxabicyclo[4.1.0]heptane = 222.1 µg/kg); gasoline products, such as, 2-methyloctane = 94.6 µg/kg; volatile compounds such as 2,6-dimethylpentane = 176.7 µg/kg; organic solvents, such as, 1,1,2-trichloroethane = 31.8 µg/kg; fatty-acids, such as, 2-methyl,2-propanoic acid = 124.1 µg/kg; SVOCs, such as, tricycle[4.3.0.07.9]nonane = 1136.1 µg/kg were all present in large doses at all sites in FR. It should be noted, that health effects related to inhalation or exposure to large amounts of pollutants, such as the hexacosane detected in FC can lead to defects in development and childbirth [37](Table-4b).

Overall, soluble herbicides rarely were detected in sediment samples from the WL basin (FC and FR watersheds). Herbicide concentrations found in these samples were low, in the 0.01 to 0.03 µg/L range, which was below detection limits. No organochlorine or organonitrogen herbicides were detected in the samples collected from all the sites.

Table-4a: Percentages of Various Classes of Organic Pollutants in Flint River watersheds

	Pharmaceuticals # of detections / %	Hydrocarbons # of detections / %	Petrochemicals # of detections / %	Unknown # of detections / %	Total
WR-FR					
Deposit	11 (44%)	10 (40%)	6 (24%)	0	25
Bank	10 (45%)	12 (55%)	4 (18%)	0	22
Upland	9 (36%)	9 (36%)	10 (40%)	0	25
BF-FR					
Deposit	5 (29%)	8 (47%)	3 (18%)	2 (12%)	17
Bank	7 (30%)	8 (35%)	7 (30%)	3 (13%)	23
Upland	11 (42%)	9 (35%)	7 (27%)	1 (4%)	26
HR-FR					
Deposit	8 (32%)	9 (36%)	6 (24%)	4 (16%)	25
Bank	8 (35%)	7 (30%)	6 (26%)	5 (22%)	23
Upland	11 (46%)	10 (42%)	10 (42%)	0	24

Table-4b: Percentages of various classes of organic pollutants in Flint Creek watershed.

	Pharmaceuticals # of detections / %	Hydrocarbons # of detections / %	Petrochemicals # of detections / %	Unknown # of detections / %	Total
RBFC					
Deposit	8 (35%)	9 (39%)	5 (22%)	5 (22%)	23
Bank	5 (36%)	3 (21%)	7 (50%)	1 (7%)	14
Upland	9 (36%)	6 (24%)	10 (40%)	6 (24%)	25
MBFC					
Deposit	15 (60%)	5 (20%)	6 (24%)	0	25
Bank	7 (28%)	7 (28%)	7 (28%)	4 (16%)	25
Upland	7 (28%)	7 (28%)	7 (28%)	5 (20%)	25
VBFC					
Deposit	15 (60%)	6 (24%)	4 (16%)	1 (4%)	25

Bank	9 (39%)	8 (35%)	4 (17%)	2 (9%)	23
Upland	12 (48%)	5 (20%)	6 (24%)	3 (12%)	25

Modest to substantial amount of gasoline components (VOCs), pharmaceutical products, and SVOCs (including PAHs) were detected in all samples collected from the FC and FR watersheds during the winter season of 2011. There were more than 420 individual organic compounds detected in the surface soil/sediment. The number of PAH compounds and their combined concentrations were generally higher in samples from FR, than those from FC and its sub-watersheds. Areas of high-motorized boating activity at the RB-FC on FC had the largest number and highest concentrations of VOCs. The most commonly detected PAH's in streams during winter/spring runoff were fluoranthene, pyrene, and benzo(k)fluoranthene. FC, which has recreational forest area in its drainage basin, had the largest number and highest combined concentration of pharmaceutical and other industrial pollutants of all stream samples. Other pharmaceutical products detected in samples included: dyes (6-ethyl-1,4-naphthoquinone), anti-cholesterol (gamma-sitosterol), chemicals for manufacture of plastics (2-methyl,2-propanoic acid), car wash detergents (hexadecylmethylsulfoxide), deodorants (1,1-dimethyl-2-cyclohexane), anti-ulcer (olean-12-ene), epoxides (7-oxabicyclo[4.1.0]heptane, and anti-aging agents (oxacycloheptadecan-2-one).

Most samples from tributary streams and rivers with little or no motorized boating had high detectable concentrations of gasoline components. PSs, such as motorized boating at RB-FC, VB-FC, HR-FR sites, underground storage tanks from old and abandoned gas stations along the FC and pipelines appear to be directly linked to the occurrence of these gasoline components. Other sources of gasoline components to FR and FC watersheds, such as the atmosphere, surface runoff, and subsurface flow, appear to be minor compared to the input by leaks from underground storage tanks. Results show that upland reference areas hold more of these pollutants than the depositional or riverbanks suggesting anthropogenic influences.

Particle Size

Particle size often defines whether sediment is a suitable habitat for biota and they can also influence benthic community structure [38]. Sediment grain sizes for these two watersheds are generally fine grained (31.85% silt and 74.1% clay). Past studies have shown that fine sediments are typically those that are most heavily contaminated because of greater surface area and more binding sites for metals and organic compounds, such as those detected at the watersheds.

Ecological Risk Assessment

The results of the Ecological Risk Assessment in Tables-5a through 5f indicate that:

1. HQ = MSL, the HQ is not adequate to make a decision at this point, and the ecological risk assessment process should proceed.
2. HQ > or >> MSL, the HQ indicates a potential for adverse ecological effects, and a more thorough study is necessary.
3. HQ < MSL, there is enough information to conclude that ecological risks are very low and therefore, there is no need to clean up the site on the basis of ecological risk assessment alone [32].

CONCLUSIONS

PAHs originate mainly from petrogenic and pyrolytic (break down of organic compounds) sources. The high concentrations of PAHs suggest that petroleum and or combustion products have been the major sources of PAHs to the watersheds. PAHs, gasoline components, pharmaceutical agents are known to be derived mainly from direct discharges, urban runoff, combustion of fossil fuels, and forest fires [39]. They are not directly produced from biological sources at significant levels [40, 41]. Therefore, their sources might be anthropogenic in origin.

Concentrations of PAHs in sediment ranged from 47.3 to 1136 µg/g, wet weight. These concentrations are considerable. Consumption of contaminated fish from these rivers may lead to human exposure. Higher molecular weight PAHs are the predominant compounds and these were found in sediments. This suggests greater bioaccumulation potential of higher molecular weight PAH compounds. In particular, pyrene was prevalent in most of the samples from all sites.

The subsurface maximum PAH concentrations of 1,1,2,2-tetrachloroethane demonstrated ineffective regulation of the use of some banned PAHs, such as, 1,1,2,2-tetrachloroethane in the U.S. since 1977. However, since 1,1,2,2-tetrachloroethane was still detected in surface sediment layers that suggests some leakage from storage places or re-suspension and remobilization of PAHs accumulated in sediments in the reaches of both rivers [42]. The WR-FR (Flint River) had the highest number of compounds projecting negative effect at – four, and VB_FC (Flint Creek)

was observed to be the most polluted of the two watersheds; its highest number of compounds projecting negative effect at – eleven.

Studies have shown that the environmental behavior of these compounds reveals that PAH solubilities are very low and the hydrophobic sorptive capacity (K_{ow}) is correspondingly high [38]. This coupled with low volatilities (Henry’s Law constant) and general chemical stability means that PAHs are environmentally persistent compounds that are strongly held to both suspended particles and bottom sediments. In all, the direct evidence indicates that the surface sediments at all sites are impaired and not supporting a healthy, balanced community of benthic organisms. These may have secondary impacts to higher level organisms, such as birds and wildlife that use the habitat as a foraging base.

The existence of VOC and SVOC contaminated sediments cannot be ignored; mainly because the results from this study have shown that a large pool of these pollutants exists in the depositional, bank, and upper sediments, and this pool is easily re-mobilized into the base of the food web by fish and benthic organisms.

The results of the Ecological Risk Assessment (HQ) for industrial pollutants in Tables-5a through 5f shows that the HQ ($HQ > \text{or } \gg \text{ MSL}$) for each site indicates a potential for adverse ecological effects, and that a more thorough study is necessary. Furthermore, there may be a need to remediate the sites pending additional ecological risk assessment.

Table-5a: Ecological Risk Assessment for WR site in Flint River

WR-FR	Organic Compounds	HQ	
	(MSL = 330 µg/kg for VOCs and SVOCs)		
Deposit	2,5-dimethylheptane	=	1
	Heneicosane	>	1
	Hexatriacontane	>>	1
	Gamma-Sitosterol	>>	1
	Alpha-1-naphthalenopropanol	>	1
	1,2,3,5,6,7,8,8-naphthalene	>>	1
	1,1-dimethyl-2-cyclohexane	>	1
Bank	2,5-dimethylheptane	>	1
	4-hydroxy-4-met-2-pentanone	>	1
	Gamma-Sitosterol	>>	1
	22-dien-3-ol-ace-ergosta-14	>	1
Upland	2,5-dimethylheptane	>	1
	Caryophyllene	>	1
	Deca-1h-cycloprop(e)azulene	>	1

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; “**BOLD**” Compounds projecting negative effect

Table-5b: Ecological Risk Assessment for BF site in Flint River.

BF-FR	Organic Compounds	HQ	
	(MSL = 330 µg/kg for VOCs and SVOCs)		
Deposit	2,5-dimethylheptane	>	1
	2,6-dimethylheptane	>	1

Bank	Hexacosane	>	1
	Unknown	>	1
	Alpha-1-naphthalenepropanol	>	1
	Tricyclo[4.3.0.07.9]nonane	>	1
Upland	3,8-dimethyldecane	>	1
	Pentadecane	>>	1
	1,2,3,5,6,7,8,8-naphthalene	>	1
	1,2,3,5,6,7,8,8a-oc-azulene	>>	1
	Dimer-cyclooctenone	>>	1

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; **“BOLD”** Compounds projecting negative effect

Table-5c: Ecological Risk Assessment for HR site in Flint River

HR-FR	Organic Compounds	HQ	
	(MSL = 330 µg/kg for VOCs and SVOCs)		
Deposit	2,5-dimethylheptane	>	1
	4-hydroxy-4-met-2-pentanone	>	1
	1,2,3-trimethylcyclohexane	>>	1
	(3e,5e,7e)-6-methyl-8-(2,6,6)	>>	1
Bank	1,2-benzenedicarboxylic acid	=	1
	Beta-sitosterol	=	1
	7-methanoazulen-5-ol-1h-3a	>	1
Upland	VOCs and SVOCs < MSL		0

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; **“BOLD”** Compounds projecting negative effect

Table-5d: Ecological Risk Assessment for RB site in Flint Creek.

RB-FC	Organic Compounds	HQ	
	(MSL = 330 µg/kg for VOCs and SVOCs)		
Deposit	VOCs and SVOCs < MSL		0
Bank	VOCs and SVOCs < MSL		0
Upland	Eicosane	>	1
	Octahyd-2(h)-naphthalene	>>	1
	Cyclopropa(d)naphthalene-2-4a	=	1
	5-butyl-6-hexyl-1h-indene	>>	1

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; **“BOLD”** Compounds projecting negative effect

Table-5e: Ecological Risk Assessment for MB site in Flint Creek.

MB-FC	Organic Compounds (MSL = 330 µg/kg for VOCs and SVOCs)	HQ	
Deposit	1-bromo-3-methyl-2-butene	>	1
	3,7-dimethyl-6-octen-1-ol	=	1
	9-hexadecenoic acid	>	1
	Hexadecanoic acid	>>	1
	Bis(2-ethylhexyl)phthalate	>>	1
	Eicosane	>	1
	Squalene	>>	1
	10-methyleicosane	>>	1
	7-hexyltridecane	>>	1
	2-(7-heptadecynyl)-2H-pyran	>	1
	22-diene-ergosta-4	>	1
	Beta-sitosterol	>>	1
	Benzo[b]naphtho[2,3-d]furan	>	1
	4-bicyclo[7.2.0]undec-4-ene	>	1
	1h-cyclopenta[a]pentalen-7-0	>>	1
Deca-1h-cycloprop[e]azulene	>>	1	
Bank	2,3-dimethyl-2-nitrobutane	>>	1
	2,6-dimethyl-1-hexene	>	1
	1,2-benzenedicarboxylic acid	>	1
	Alpha-1-naphthalenepropanol	>>	1
	2,3,3-trimethylcyclohexanone	>	1
Upland	2-cyclopropanoic acid	>	1
	23,24-epoxystigmastane	>>	1

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; **“BOLD”** Compounds projecting negative effect

Table-5f: Ecological Risk Assessment for MB site in Flint Creek

VB-FC	Organic Compounds (MSL = 330 µg/kg for VOCs and SVOCs)	HQ	
Deposit	3,3-dimethyl-1-pentene	>	1
	2-heptadecanone	>	1

	Octadecanoic acid	>	1
	2-Nonadecanone	>>	1
	Heneicosane	>	1
	Tetracontane	>	1
	Beta-sitosterol	>>	1
	2,7-dimethyl-1, 8-nonadiene	>	1
	4a,4b,3(4h)-phenanthrene	>>	1
Bank	4-ethyl-1-hexene	>	1
Upland	2,3-dimethyl-2-nitrobutane	>>	1
	3-penten-2-ol	>	1
	4-hydroxy-4-met-2-pentanone	=	1
	Gamma-sitosterol	>>	1
	Tricyclo [4.3.07.9] nonane	>	1

MSL = maximum screening level

"=" HQ is equal to MSL; ">" HQ is greater than MSL; ">>" HQ is significantly greater than MSL, and "0" HQ is less than MSL; **“BOLD”** Compounds projecting negative effect

Significant Findings

Below are the significant findings of this study-

1. Surprisingly, none of the herbicides analyzed for and commonly used in agricultural areas such as, Madison or Morgan Counties were detected in sediment or surface water of FC and FR watersheds.
2. Among the significant findings are that VOCs, SVOCs, pharmaceutical products, fatty acids, and some unknown organic compounds were detected in all sites in FC and FR. The fact is, inhalation of large doses of tetrachloroethylene (PERC) detected in RB, or fluoro-4-methylbenzene detected at MB in FC can be fatal [33-36].
3. A total of about 420 individual compounds were detected at the watersheds; 210 from FC and 210 compounds from FR.
4. All the samples (100%) had detections above an EPA threshold of 0.2 µg/kg (what pollutant exactly is this threshold for). The most frequently detected VOCs were squalene and PAHs.

ACKNOWLEDGMENTS

We thank Dr. B. Onuma Okezie for his technical support and Alabama A&M University Title III Strengthening Grants Program for their financial support.

REFERENCES

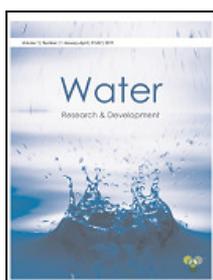
1. U. S. Environmental Protection Agency (2012). Pharmaceuticals and Personal Care Products. Accessed March 16, 2013.
2. Kümmerer, K. (2008). Pharmaceuticals in the Environment – A Brief Summary. In: Kümmerer, Klaus (Ed.). Pharmaceuticals in the Environment (ISBN 978-3-540-74663-8), 3rd Edition: Springer Berlin Heidelberg, pp. 3-21
3. Bohannon, J. "Hard Data on Hard Drugs, Grabbed From the Environment." Science Magazine, published April 6, 2007. Accessed March 20, 2013.
4. U. S. Environmental Protection Agency. "Origins and Fate of PPCPs in the Environment." Accessed April 20, 2013.
5. Tong, A.Y.; Peake, B., and Braund, R., Environment International, **37**(2011) 292.
6. Koch B., Dale M.S., Zogorski M.S., Delzer J. S., and Grady G. C. (2003), Occurrence of MTBE and VOCs in drinking water sources of the United States: Denver, Colorado, American Water Works Association Research Foundation, p.189.

7. Hoos A., Robinson B., John A., Michael D. (2000), Sources, in stream transport, and trends of nitrogen, phosphorus, and sediment in the Lower Tennessee River Basin, 1980-96: U.S. Geological Survey Water-Resources Investigations Report 99-4139, p. 96.
8. Agency for Toxic Substances and Disease Registry (ATSDR) (1995), Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA., pp. 1-9.
9. U.S. Environmental Protection Agency (2007), Integrated Risk Information System (IRIS) on Polycyclic Organic Matter. National Center for Environmental Assessment, Office of Research and Development, Washington, DC.
10. Avril T., Attrill H., Zhang J., Raper A., Crocker P.R., *Biochemical Soc. Trans.*, **34**(2007)1024.
11. U.S. Environmental Protection Agency (1986), Quality criteria for water. Washington, DC: Office of Water, U.S. Environmental Protection Agency, EPA/440/5-86/001.
12. U.S. Environmental Protection Agency, 2012, Pharmaceuticals and Personal Care Products (PPCPs).<http://www.epa.gov/ppcp/>
13. Utah State University, 2013. Pharmaceuticals.<http://extension.usu.edu/waterquality/htm/whats-in-your-water/pharmaceuticals>
14. Decatur Daily News, April 8, (2008), Council studies DU plan for stricter industrial wastewater regulations, by Catherine Godbey Staff Writer, pp.1.
15. Decatur Utilities, (2008), Decatur Utilities Source of Water Supply. (Verbal communication with Decatur's, Gas, Water, Waste-water manager - Mr. Tom Cleveland), June 18.
16. Huntsville Times, (2008), ADEM files suit against Hanceville Water Board, June 15, pp. A20.
17. Okweye P.S., Tsegaye T. D. and Garner K. F., *Journal of Environmental Monitoring and Restoration*, (**33**) (2007) 91.
18. Okweye P.S., (2009), Ph.D Dissertation. Assessment of Water Quality for Selected Chemical Pollutants in Surface Water and Sediments of the Flint Creek and Flint River Watersheds of the Northern Alabama.
19. State of Ohio Environmental Protection Agency (2001), Sediment Sampling Guide and Methodologies (2nd Edition). Division of Surface Water, pp. 11-17.
20. U.S. EPA (1984), Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA Hazardous Waste Streams. EPA-600/2-80-018.
21. U. S. Environmental Protection Agency (2002). SW-846 Method 5035A, Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, USEPA Office of Solid Waste and Emergency Response.
22. U. S. Environmental Protection Agency (2008), Publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.
23. U. S. Environmental Protection Agency (2001), EPA Requirements for Quality Management Plans (QA/R-2), EPA/240/B-01/002, Office of Environmental Information.
24. U.S. Environmental Protection Agency, 2009. National Primary Drinking Water Regulations, EPA 816-F-09-004.
25. McLean M. R., Carter, E.G., Gregorich G.S. (1982), *Soil Sampling and Methods of Analysis*.
26. Ruchaya B., Gullaya W., A. Atsuko A., Yoshio I., Hedeshige T., *Marine pollution Bulletin*, **54** (2007)554.
27. Simpson S. L. and King C. K. (2005), *Handbook for Sediment Quality Assessment*.
28. U.S. Environmental Protection Agency (1992a), Framework for Ecological Risk Assessment, Washington, DC: Risk Assessment Forum, U.S. Environmental Protection Agency, EPA/630/R-92/001.
29. U.S. Environmental Protection Agency (1992b), Guidelines for Exposure Assessment: Notice. Federal Register, **57**,22888-22938.
30. U.S. Environmental Protection Agency (1992c), A Cross-Species Scaling Factor for Carcinogenic Risk Assessment Based on Equivalence of mg/kg^{3/4}/day, draft report, Federal Register, **57(109)**,24152-24173.
31. New York State Department of Environmental Conservation (1999), Technical Guidance for Screening Contaminated Sediments. Division of Fish, Wildlife and Marine Resources, pp. 1-17.
32. U.S. Environmental Protection Agency (1986), Guidelines for the health risk assessment of chemical mixtures. Federal Register 52:34014-34025.
33. U.S. Environmental Protection Agency (2011), Region 4 Waste Management Division Soil Screening Values for Hazardous Waste Sites and Region 5 Superfund. Ecological Risk Assessment Step 2.
34. Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs) (2010).

35. Katarina L., Polycyclic Aromatic Hydrocarbons (2011).
<http://toxipedia.org/display/toxipedia/Polycyclic+Aromatic+Hydrocarbons>.
36. Norbert E.K., Barbara L., Faubert K. and Michael P, Casarett and Doull's Toxicology (2008), Basic Science of Poisons, Seventh Edition, Mc-Graw-Hill, Inc. pp. 526.
37. Peter H.A., 2003, Petroleum and Individual Polycyclic Aromatic Hydrocarbons, In D. J. Hoffman, B. A. Rattner, G. A. Burton, J. Cairns (Eds.), Handbook of Ecotoxicology. Lewis Publishers, pp. 342-359.
38. USEPA, 1998. Study Of Hazardous Air Pollutant Emissions From Electric Utility Steam Generating Units Final Report To Congress, **2**.
39. Stuart S., Winters G.L., M. C. Fishbein M.C. (2005), Revision of the 1990 working formulation for the standardization of nomenclature in the diagnosis of heart rejection, Nov, **24 (11)**,1710-20. Pub. Med.
40. Neff J.M. (1979), Polycyclic Aromatic Hydrocarbons in the Aquatic Environment: Sources, Fates, and Biological Effects, Appl. Sci., London, UK, pp. 262.
41. Ird C.M., and Lynch J.M., Chem. Soc. Rev., **3**(1974) 309.
42. Kennish M.J. (1992), Ecology of Estuaries, Anthropogenic Effects. Boca Raton, CRC Press, p. 494.
[ijCEPr-263/2013]

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