

Evaluation of Volatile Organic Compounds and Polyaromatic Hydrocarbons in Barker Reservoir in Houston, Texas after the 2017 Hurricane Harvey

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Abstract

Analysis of volatile organic compounds (VOCs) and polyaromatic hydrocarbons (PAHs) in the Barker Reservoir in Houston, Texas, United States is reported. Samples were collected within one week after the August 2017 Hurricane Harvey. Using a gas chromatograph equipped with a mass spectrometer, 4 VOCs and 13 PAHs were found in the Barker Reservoir. Concentrations of acetone, benzene, chloroform, and toluene were 1500, 380, 830, and 290 parts per million (ppm), respectively. Benzene and chloroform are classified as probable human carcinogens by the U.S. Environmental Protection Agency (EPA). Six PAHs including benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, and dibenz[a,h]anthracene are probable human carcinogens. The most concentrated PAH was acenaphthylene at 0.068 ppm, while the least one was fluoranthene at 0.00046 ppm. Results revealed water contaminants in Houston and its vicinities during the flooding season and served as references for water monitoring purposes in the future.

Keywords

Hurricane Harvey, Barker Reservoir, VOCs, PAHs, Human Carcinogen, Gas Chromatography, Environmental Monitoring, Environmental Health

1. Introduction

The Barker Reservoir located just south of Interstate 10 in Houston, Texas, USA, was built by the U.S. Army Corps of Engineers in the 1940s [1]. The Barker Reservoir watershed covers portions of the cities of Houston (the fourth largest city

in the USA) and Katy with about 126 square miles and includes two primary streams: Upper Buffalo Bayou and Mason Creek [1]. The reservoir remains essential to the area's flood control system and acts to connect Houston and its vicinities' watersheds to the Galveston Bay and the Gulf of Mexico. Water that flows into the Barker Reservoir does not just stay inside the reservoir as some of the water continues to flow down to the downtown of Houston and other lower areas. Thus, the chain of contamination spreads to the other areas of the city should there be contaminants from the water sources. It should be noted that the Barker reservoir also serves entertainment and recreation areas for Houston residents. The geographical location of the Barker Reservoir is shown in **Figure 1**. Houston and its surrounding areas with a combined population of about 6.7 million people have many chemical plants, oil refinery facilities, thousands of new commercial complexes, and residential communities under development. The Houston metropolitan area has more than 22 watersheds that each goes into 22 major waterways (see **Figure 2**). This study thus presents the environmental impact on the water system during the flooding season, serving as a relevant example for other cities around the world with similar environments and conditions.

According to the National Weather Service, Harvey began as a tropical wave that emerged off the west coast of Africa on August 13, 2017. Four to five days later, it became a tropical storm over the Caribbean and weakened to a tropical wave by the time it moved into the Yucatan Peninsula by August 22, 2017. Due to the warm waters in the Bay of Campeche and the Western Gulf of Mexico, Harvey became a tropical depression on August 23, 2017, and headed towards the Texas Coast. On August 25, 2017, Harvey, a hurricane category 4, made landfall over South Texas. For the next few days, Harvey stalled over South and Southeast Texas, which the areas in Southeast Texas received historical rain. Some areas received more than 40 inches of rain amounts in less than 48 hours. Many areas in Houston received at least 30 inches of precipitation. The Cedar



Figure 1. The geographical location of Barker Reservoir, Houston, Texas, USA (adapted from <https://www.google.com/maps/@29.7651643,-95.6624972,10.93z>).

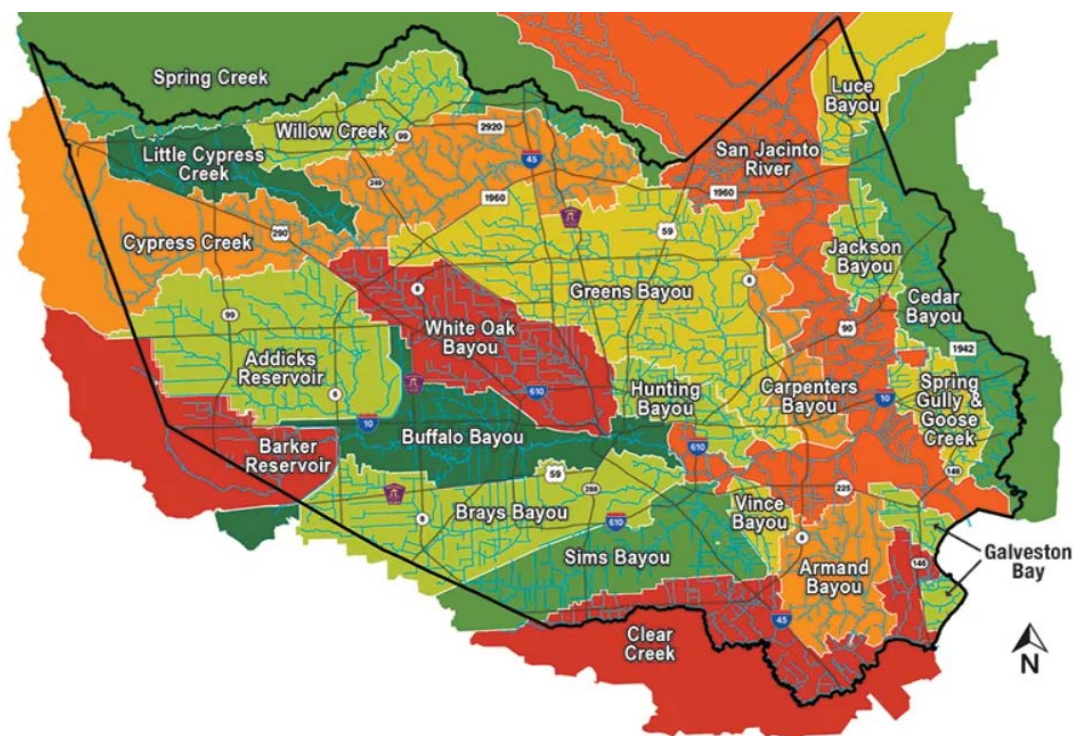


Figure 2. The geographical location of the Houston metropolitan's watersheds (adapted from <https://www.hcfcd.org/Additional-Resources/Drainage-Network/Harris-Countys-Watersheds>).

Bayou in Houston received a record total of 51.88 inches of rainfall during the ordeal [2]. One-third of Houston was underwater. Heavy flooding forced about 32,000 people out of their residences, damaged over 300,000 structures, and 500,000 vehicles. Overall, Hurricane Harvey caused about \$125 billion in damage [3].

Volatile organic compounds (VOCs) are organic chemicals with boiling points of $\leq 100^{\circ}\text{C}$ and/or vapor pressures > 1 mmHg at 25°C that easily evaporates under room temperature and participate in photochemical reactions in ambient air [4]. Many household products contain VOCs, for example, adhesives, cleaning products, refrigerants, etc. The burning of fuel also releases abundant VOCs [5] [6] [7]. Polycyclic aromatic hydrocarbons (PAHs) are a subgroup of VOCs with boiling points ranging from $240^{\circ}\text{C} - 260^{\circ}\text{C}$ to $380^{\circ}\text{C} - 400^{\circ}\text{C}$ [8] [9]. Some VOCs and PAHs that are classified by the US Environmental Protection Agency (US EPA) as probable carcinogens are benzene, chloroform, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, and dibenz[a,h]anthracene [10]-[26]. **Figure 3** shows structures of some probable carcinogens in this study.

According to our knowledge, there is no literature report on VOCs and PAHs in the Barker Reservoir right before or immediately after the 2017 Hurricane Harvey. A recently available report was testing *E. coli* levels in floodwater samples from the Houston area after Hurricane Harvey. This study reported that *E. coli* levels were 125 times higher than is considered safe for swimming [27].

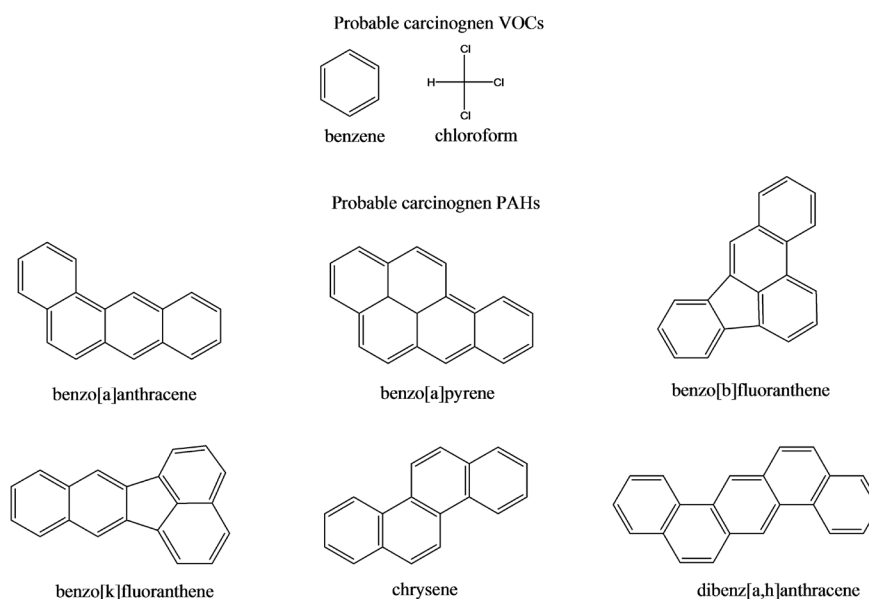


Figure 3. Structures of some probable carcinogen contaminants.

Thus, the objective of this study is to examine the concentration of volatile organic compounds and polyaromatic hydrocarbons in the Barker Reservoir. Results are referred to as potential health effects indicated by the US EPA. Chromatographic applications are used to evaluate contaminants in this study.

2. Experimental

2.1. Sample Collection and Processing

Water samples were collected at the Barker Reservoir in Houston, Texas, USA in one week after August 2017 Hurricane Harvey (**Figure 1** and **Figure 2**). Sample collection and processing were followed procedures reported in the literature [27]. Samples for VOCs analysis were collected in a pre-treated vial with no head-space. The vials were immediately sealed and placed in a cooler filled with ice at a temperature measured at 4°C. Samples for PAHs evaluation were collected in a pre-treated 1L bottle and immediately placed in a cooler of ice with a temperature of about 4°C. Due to the heavy flooding condition and safety issue, a combination of four different samples collected in four different segments of each sampling site were mixed into one for representative analysis of the area. Water samples were then filtered using a 1-mm membrane filter to remove the suspended solids within 24 h. The samples were acidified with hydrochloric acid to pH < 2 to eliminate the presence of microorganisms.

Extractions of VOCs and PAHs from water samples for analysis were followed reported procedures [28] [29]. The liquid-liquid extraction (LLC) technique was used to extract the water samples with HPLC grade CH₂Cl₂. About 50 ml of CH₂Cl₂ was added to 50 ml of water sample and then vigorously agitated for 1.5 h, and the organic layer was removed, concentrated down, and stored in cleaned vials at 4°C for analysis.

2.2. Quality Control

All standards in this work were obtained from Sigma Aldrich, USA, and stored as required until the time of equipment calibration and analysis. The calibration mix was used in accordance with the US EPA method 625. Acetone, dichloromethane, and toluene were purchased from Fisher Scientific. All reagents were obtained with HPLC graded level. Parameters were set for GC-MS analysis to meet the accepted quantification limits and to measure the detection limits of the system (see supporting information). Before each analysis, a blank sample was done and it was determined to contain no traces of targeted analyte or the surrogate compound to be added to the samples. There were surrogate and calibration standards (1,2-dichloroethane-d₄, 4-bromofluorobenzene, dibromofluoromethane, toluene-d₈ for VOCs and 2,4,6-tribromophenol, 2-fluorophenyl, 2-fluorophenol, 4-terphenyl-d₁₄, nitrobenzene-d₆, and phenol-d₆ for semi-VOCs) used in this study and for the calibration of the instrument. They were strictly used as identifiers and for quantification purposes.

2.3. Gas Chromatography

An Agilent 7890/5975C XL gas chromatography-mass spectrometry XL System equipped with a flame ionization detector and a DB-5 column (25 m × 0.25 mm) was used for quantitative analysis of water samples. The concentrations of VOCs and PAHs were calculated according to the literature [30] [31]. It should be noted that internal standards were selected to have peaks close but clearly separate from peaks derived from samples. GC conditions were 2 µL split/splitless injection (injector temperature of 250°C) at 40°C, a splitless time of 60 s, a 5 hold, programed of 5°C/min to 250°C, and a helium carrier gas velocity of 25 cm/s. Minimum detection limits (MDL) for VOCs and PAHs were less than 100 and 130 parts per trillion (ppt), respectively. To establish linearity, five calibration points were used for quantitative analysis of VOCs and PAHs. To establish a baseline before the completion of each analysis, a blank was run.

3. Results

All volatile and organic compounds (VOCs) and polyaromatic hydrocarbons (PAHs) found in Barker Reservoir by gas chromatography-mass spectrometry (GC-MS) are listed in **Table 1**. Chromatograms for VOCs and PAHs are provided in the supporting information. The obtained data were being referenced to the mass spectral databases of NIST/EPA/NIH mass spectral library-NIST98.

It should be noted that about six months up to two weeks before Hurricane Harvey occurred, our laboratory has collected water samples on monthly basis and tested for targeted VOCs and PAHs; however, none of the eight targeted VOCs (acetone, benzene, chloroform, ethylbenzene, m,p-xylene, n-butyl alcohol, o-xylene, and toluene) and none of the fifteen targeted SVOCs (acenaphthalene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenz[a,h]

anthracene, fluoranthene, fluorine, phenanthrene, phenol, and pyrene) were found to be in the water body of Barker Reservoir (see **Table 1**). Samples were collected and prepared for examination in a very similar method to the post-Hurricane Harvey analysis of VOCs and PAHs (see **Table 1**).

Table 1. Concentrations (ppm) reported for targeted VOCs and PAHs found in Barker Reservoir.

Group	Compounds	Concentration, ppm*	
		Before Hurricane Harvey	After Hurricane Harvey
VOCs	Acetone	0	1500
	Benzene	0	380
	Chloroform	0	830
	Ethylbenzene	0	0
	m,p-Xylene	0	0
	n-Butyl alcohol	0	0
	o-Xylene	0	0
	Toluene	0	290
PAHs	Acenaphthalene	0	0
	Acenaphthylene	0	0.068
	Anthracene	0	0.032
	Benzo[a]anthracene	0	0.030
	Benzo[a]pyrene	0	0.028
	Benzo[b]fluoranthene	0	0.031
	Benzo[g,h,i]perylene	0	0.028
	Benzo[k]fluoranthene	0	0.029
	Chrysene	0	0.031
	Dibenz[a,h]anthracene	0	0.033
	Fluoranthene	0	0.0046
	Fluorene	0	0.043
	Phenanthrene	0	0.039
	Phenol	0	0
	Pyrene	0	0.034

*Each value is the average of three runs. LOD: limit of detection.

As shown in **Table 1**, four out of eight targeted VOCs identified were acetone, benzene, chloroform, and toluene. Interestingly, no trace of ethylbenzene, m,p-xylene, n-butyl alcohol, or o-xylene was detected under the experimental condition. The concentration of acetone was found remarkably at a high level of 1500 ppm. The concentrations of benzene, chloroform, and toluene were found at 380, 830, and 290 ppm, respectively. **Figure 4(a)** shows the VOCs component in the Barker Reservoir after the August 2017 Hurricane Harvey.

Table 2 shows human carcinogenicity for compounds found in the Barker Reservoir according to the US EPA. Acetone and toluene are not classifiable as to human carcinogenicity; whereas, benzene and chloroform are human carcinogens [10] [11] [12] [13]. The US EPA has classified acetone not a carcinogen; however, inhalation of acetone can cause abnormal feelings (e.g. confusion, dizziness, drowsiness, headache) and irritations (e.g. nose, throat), and direct physical contact can cause eye and skin irritations [10]. Prolonged, severe exposure to acetone can cause unconsciousness [10].

Table 2. Human carcinogenicity reported for targeted VOCs and PAHs found in Barker Reservoir according to U.S. EPA.

Compounds	Human Carcinogenicity*
VOCs	
Acetone	No
Benzene	Yes
Chloroform	Yes
Toluene	No
PAHs	
Acenaphthylene	No
Anthracene	No
Benzo[a]anthracene	Yes
Benzo[a]pyrene	Yes
Benzo[b]fluoranthene	Yes
Benzo[g,h,i]perylene	No
Benzo[k]fluoranthene	Yes
Chrysene	Yes
Dibenz[a,h]anthracene	Yes
Fluoranthene	No
Fluorene	No
Phenanthrene	No
Pyrene	No

*Yes: probable human carcinogen for human; No: not classifiable as to humancarcinogenicity.

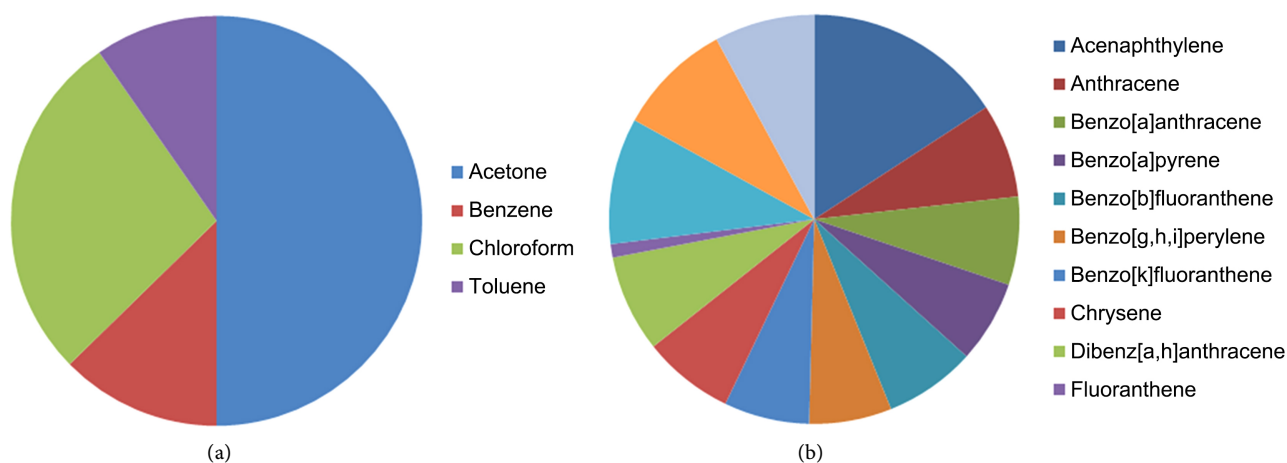


Figure 4. Comparison of (a) VOCs and (b) PAHs measured by ppm found in Barker Reservoir.

The US EPA classified chloroform as a likely carcinogen under high exposure [13]. Inhalation of chloroform for a long period of time causes depression, irritability, jaundice, and hepatitis [32]. Chloroform once was used anesthetic agent but not anymore due to its toxicity [33]. Morris *et al.*, McGeehin *et al.*, Vena *et al.*, King and Marrett, Doyle *et al.*, Freedman *et al.*, Cantor *et al.*, and Hildesheim *et al.* reported a relationship of drinking chlorinated water exposures to bladder, rectal, and colon cancers [34]-[41]. However, the US EPA found currently available data are inadequate to determine a connection between exposure to chlorinated drinking water and increased likelihood of getting cancer since chlorinated water can contain carcinogenic chemicals other than chloroform [13].

Two of the targeted compounds, benzene at 380 and toluene at 290 ppm, respectively, found in the water are in the BTEX classification (benzene, toluene, ethylbenzene, and xylene). As very soluble organic compounds, BTEX can enter the ground and soil water systems and easily absorb through the skin of mammals. The US EPA has classified benzene as a known human carcinogen regardless of ways of exposure [12]. Exposure to benzene caused leukemia, lymphatic, and hematopoietic cancer [42]-[48]. The US EPA does not classify toluene, the most abundantly produced chemicals in the United States, as a carcinogenic substance to humans [11]. However, repeated exposure of toluene for a long period of time can cause eye and skin irritations, and serious neurological problems ranging from depression to brain damage [49] [50].

Thirteen out of fifteen targeted PAHs were identified by GC-MS in the water of Barker Reservoir with concentrations ranging from 0.00046 to 0.068 ppm as shown in Table 1. Figure 4(b) shows the comparison of PAHs component in the Barker Reservoir after the August 2017 Hurricane Harvey. Acenaphthalene, 1-octene, and phenol were not observed during the analysis. As shown in Table 2, six out of thirteen PAHs found in the reservoir are classified as human carcinogens including benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, and dibenz[a,h]anthracene [14]-[26]. The US EPA has not classified acenaphthylene and anthracene, found to be at 0.068 and

0.032 ppm respectively, as carcinogenic agents [14] [15]. Exposure to anthracene can cause skin allergy and respiratory irritation [15]. The five benzo-related structures including benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g,h,i]perylene, and benzo[k]fluoranthene, found with concentrations from 0.028 to 0.031 ppm, are classified as probable human carcinogens with the exception of benzo[g,h,i]perylene [16] [17] [18] [19] [20]. The US EPA classified chrysene and dibenz[a,h]anthracene as human carcinogens [21] [22]. The remaining targeted PAHs including fluoranthene, fluorene, phenanthrene, and pyrene are not classified as human carcinogens [23] [24] [25] [26].

The sudden increase in the level of acetone was detected due to the known fact that the emissions of acetone to the aquatic environment include wastewater discharges from industries and leaching from industrial and municipal landfills and many other products (paints, inks, surface coatings, paint removers, automotive care products, etc.). The increase of benzene was due to oil production and gasoline; chloroform due to industrial cooling water, municipal drinking water, and wastewater treatment, etc.; and toluene due to crude oil, paints, and many other household products. With widespread flooding and water all over Houston and its vicinities, a large volume of these chemicals from the surrounding oil and gas facilities, industrial complexes and residential communities drained into the reservoir together with the flooding water. Sources of some PAHs found in this study were from oil and gas.

4. Conclusion

Before the event of Hurricane Harvey, no volatile or semi-volatile organic contaminants were found in the Barker Reservoir. Results from analyses of water samples collected from the same reservoir about a week after the hurricane showed four VOCs and thirteen PAHs. These contaminants were thoroughly evaluated by GC-MS technique. The volatile organic contaminants (VOCs) were found at the high, alarming concentrations; whereas the semi-volatile ones (PAHs) were found at quite small levels. Results from this study clearly showed that the Barker Reservoir has been polluted by toxic chemicals, including two VOCs and 6 PAHs as human carcinogenic agents, due to the influx of flooding water from the surrounding areas. The nature of Houston and its vicinities with many chemical plants, oil refinery facilities, and new commercial and residential developments contributed sources of contaminants to the aquatic environment. Perhaps one of the possible ways to minimize is to use more environmental-friendly household products, reduce the use of crude oil, and spread out new commercial and residential development. This study can serve as an important reference for future watershed management and pollution control plans for Houston and its suburbs as well as for other cities around the world with similar conditions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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