Spatial and temporal distribution of surface water contaminants in the Houston Ship Channel after the Intercontinental Terminal Company Fire

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Abstract

Background: The fire at the Intercontinental Terminals Company (ITC, Deer Park, La Porte, TX, USA) from March 17-20, 2019 resulted in substantial releases of chemical contaminants to the environment, including the surface waters of the Houston Ship Channel.

Objective: To characterize spatial and temporal trends, as well as potential human health risks, from these releases.

Methods: Out of 433 substances with available data, seven were selected for analysis: benzene, toluene, ethylbenzene, xylenes, oil & grease, suspended solids, and total petroleum hydrocarbons. Spatial and temporal concentration trends were characterized, and hazard quotients and cancer risks were calculated to estimate the potential for human health impacts from these contaminants.

Results: Temporal analysis showed presence of these chemical contaminants in water immediately after the event; their concentrations dissipated substantially within 4 weeks. The spatial distribution of contaminants indicated the highest concentrations in the waterways within about 1km of the ITC. The greatest potential human health risks stemmed from presence of benzene.

Significance: A short-term but substantial spike in the concentrations of a number of hazardous contaminants occurred near the incident, with concentrations returning to apparent baseline levels within one month likely due to a combination of volatization, dilution and degradation.

Keywords

BTEX; water pollutants; disaster response; volatile organic compounds (VOCs)
1. Introduction

As a side effect of industrial growth, the number of industrial accidents, such as chemical leakage, collapse, explosion, and fire remains constantly high since the mid-1990s. Many government agencies, industries, and researchers invest their budget and effort to investigate the cause and effect of these accidents and to devise strategies for control and prevention. Still, a large number of emergency events associated with industrial facilities occur annually and are almost always associated with the release of the hazardous chemicals into the environment with the potential for adverse effects on human health and the environment. One such example of a large-scale accidental industrial fire occurred in March 2019 at the Intercontinental Terminals Company (ITC) Deer Park facility in Houston, Texas. After investigations of the cause of the fire, the final report from the Harris County Fire Marshal’s Office and the Bureau of Alcohol, Tobacco, Firearms, and Explosives concluded that the fire was likely caused by a failure within the manifold power frame of a tank resulting in the release of naphtha. The blaze rapidly spread out to 15 other tanks containing petroleum hydrocarbons and was extinguished only after three days. Two days after the fires were put out, a dike wall preventing further spread of contaminants from the damaged storage containers and fire-fighting materials partially collapsed; therefore, unknown types and an estimated 20 million gallons of chemical waste were released into Tucker Bayou which flows into Buffalo Bayou, part of Houston Ship Channel.

Several recent studies assessed the releases of pollutants during the ITC Fire accident. An Han et al. investigated air quality and health concerns of affected residents over a 6 week period following the accident. While this study found no elevations in the air concentrations of benzene, total volatile organic compounds, or particular matter (2.5 μm diameter), a small-size (13 individuals) health effects survey identified mild respiratory and post-traumatic stress disorder symptoms during the fire and two weeks afterwards. Additionally, Aly et al. collected surface water samples in the Houston Ship Channel over a 6-month period after the incident and examined spatial and temporal trends of per- and polyfluoroalkyl substances (PFAS), because an estimated 5 million liters of firefighting foams were used to extinguish the ITC fires.

Extensive water quality monitoring was also conducted by the Texas Commission on Environmental Quality (TCEQ), the Environmental Protection Agency (EPA), the Coast Guard, and ITC contractors to determine which chemicals were released and their amounts. TCEQ and EPA contractors sampled water from 43 points from Tucker Bayou to the Houston Ship Channel and Galveston Bay for about two months after the incident. Surface water samples were analyzed at certified water laboratories and using a number of analysis methods for a large number of hazardous substances and other water quality parameters: volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), chemical oxygen demand (COD), oil and grease (O&G), nitrogen, and metals. All data from TCEQ and EPA water quality analyses after this incident were publicly released on the TCEQ ITC Response story map – Water Sampling. The data are organized by location and the associated data matrix for each sampling site provides the numerical and descriptive information on analyzed contaminants. Although these data are publicly available, no spatial or temporal analysis or risk characterization has been conducted.
Therefore, this study aimed to fill this gap by characterizing the extent, duration, and potential health risks of surface water contamination released during the ITC fire, utilizing the publicly available TCEQ and EPA water quality dataset.

2. Materials and Methods

2.1. Data Extraction

From March 19th to May 21st in 2019, TCEQ, and U.S. EPA conducted surface water sampling in the waterways near the ITC fire incident site. The analytical methods for data reported by TCEQ and U.S. EPA are listed in Supplemental Table 1. The raw data were downloaded from the TCEQ “story map” website using a Python code. Specifically, by adding internet links for each location on the maps into the code, HTML codes of the webpage were converted into text, and then each cell’s data in the tables could be extracted and appended to a new data frame. As a result, after this web-scrapping, the tables with chemical compound information in water samples from each point were aggregated into a tabular form for further analyses. Collectively, water samples from a total of 43 locations in Tucker Bayou, Buffalo Bayou, San Jacinto River, and Galveston Bay were examined at various time points after the incident. The complete raw dataset consisted of 79,820 records, including 433 different substances (Supplemental Table 2). The exact sampling locations, sampling dates, distances from the ITC site, sampling agencies, and numbers of chemicals at each site are detailed in Supplemental Table 3. Of the 43 locations included in the database, 38 had numerical data.

2.2. Data processing

First, 1,979 duplicate data rows were removed from the raw data matrix. Because this study focused on surface water contamination, 440 rows which were analyses of a “solid” sample type were excluded from further analyses. Next, 160 rows that contained PFAS data collected by the US EPA on March 21, 2019 were excluded because these data were available only for one time point. Detailed temporal and spatial analysis of PFAS contamination of local waterways after ITC Fire incident has been previously reported. Finally, the data on metals (1,078 rows) that were reported as % (450 rows) or total ion chromatogram (TIC, 610 rows) were also removed because they were deemed not interpretable for the purpose of the analysis in this study. Next, differences in reporting across the different analyses were harmonized. Specifically, identical chemicals with slight variations or typos in their name were merged, and all concentration units were standardized to mg/L. Results were then categorized as “non-detect” based on laboratory result qualifiers “U”, “U *”, “U F1”, “U F2”, “U R” and “UJ” (Supplemental Table 4), with the remaining data categorized as valid for the analyses reported herein.

2.3. Data selected for further analysis

After data cleanup, 1773 of the 75,103 records had “valid,” non-zero concentrations. Of these, only 17 locations had more than 10 valid, nonzero records. We further selected only surface water locations near the ITC site, but excluding the data from locations in the public access-restricted areas immediately adjacent to the ITC, where general population exposures are unlikely (Containment, OF3-01, Upstream Tucker Bayou, and TB-02). This
resulted in 15 geographic locations (BB-01 through BB-12, Dow Bridge at Tucker Bayou, Mouth of Tucker at Buffalo Bayou, at Tucker Bayou and Buffalo Bayou). Based on these locations, the vast majority of analytes had few valid, non-zero data; 49 chemicals had at least one non-zero but most of them were monitored for a limited time period or remained below the human health criteria. We selected seven representative analytes of concern for mapping and spatio-temporal analysis: benzene, toluene, ethylbenzene, xylenes (BTEX), oil and grease, total suspended solids (TSS), and total petroleum hydrocarbons (TPH). BTEX substances were included because they are substances of common concern from drinking water exposures. Oil and grease, TSS, and TPH were included because they are useful indicators of the general distribution of the potentially hazardous components in petroleum hydrocarbon spills. The final dataset used for the analyses in this study is available as Supplemental Table 5. Of the remaining analytes, 42 had non-zero and 9 of them had health criteria on the U.S.EPA Comptox Chemical Dashboard. Three observations (1,2-dibromo-3-chloropropane, bis(2-ethylhexyl) phthalate, and styrene) were above these criteria.

2.4. Spatial and temporal trends in chemical contaminants

Four-weeks of available data of selected contaminants, each of which had at least one “valid” point during the whole sampling period, were extracted and grouped by week starting from March 19th, 2019. Kriging was performed for the data from locations for which there was at least one valid value for BTEX, oil and grease, total suspended solids, and TPH using ArcGIS software (version 10.7.1) and its spatial analyst and geostatistical analysis extensions as detailed elsewhere. Kriging is a widely used geostatistical interpolation method for spatial analysis and computer experiments in geographic information system (GIS) mapping. This geostatistical technique is capable of producing a prediction surface and providing the certainty of the prediction. The Average Nearest Neighbor Tool, which measures the distance between each feature and its nearest neighbor's location, was used to determine the lag size of 0.003 used in Kriging. Kriging was performed with the Spatial Analyst Tool with the default Spherical semivariogram model. The concentrations of each substance in each week for individual locations were combined as arithmetic averages. The resulting values for each location for each week were log_{10} transformed for Kriging due to the wide range of values at each time point. A Houston Ship Channel shape file, obtained from the Houston-Galveston Area Council GIS data set and modified to demonstrate the shape of the creek upstream of Tucker Bayou, was used to mask the Kriging results to show concentration along waterways. Cross-validation using ArcGIS geostatistical analyst was performed for each substance and time point in order to assess interpolation errors.

2.5. Risk characterization

Water quality criteria for human health were used for comparison to the measured concentrations. The maximum contaminant level (MCL), which is the highest level of a contaminant that is allowed in drinking water, were obtained from the EPA National Primary Drinking Water Regulations that are legally enforceable primary standards and treatment techniques that apply to public water systems. The human health ambient water quality criteria which are specific levels of chemicals or conditions in a water body that are not expected to cause adverse effects to human health were obtained from the EPA National 16.
Recommended Water Quality Criteria - Human Health Criteria Table 17. The water quality criteria for organism were established to protect the consumption of fish and shellfish. Although short-term criteria have not been established for ambient water quality, they are available for drinking water health advisories for children, so those values are also included for comparison. 18 The exact values of MCLs, human health ambient water quality criteria, and short-term drinking water advisories used in this study are listed in Supplemental Table 6.

The estimation of risk that is expected to result from the ingestion of contaminants in water was performed. Hazard quotient (HQ) and cancer risk unit are widely used parameters to estimate the risk of adverse effects of noncarcinogenic and carcinogenic compounds, respectively. Concentrations of benzene, toluene, and ethylbenzene were divided by human health ambient water quality criteria for water and organism; likewise, total xylenes’ concentrations were divided by the maximum contaminant limit. These ratios for the other three noncarcinogenic substances signify their hazard quotients. Because benzene is a known human carcinogen, and the water quality criterion is based on this endpoint, the values that represent the concentrations divided by the water quality criterion are interpreted as cancer risk units per million people for a lifetime exposure. The criterion for benzene is presented as a range, so the more conservative end of the range was used. Comparisons to short-term health advisory levels were based on the HQ.

2.6. Software

RStudio with R version 4.0.3. and the ggplot2 R Package, and ArcGIS software (version 10.7.1) and its spatial analyst and geostatistical analysis extensions were used for analysis.

3. Results

A summary of the data for the 7 substances selected for further analysis is shown in Table 1, with temporal and spatiotemporal trends summarized in Figures 1, 2, 3, 4, 5, and 6.

3.1. Temporal trends

Temporal patterns in the concentrations in the substances analyzed in this study are shown in Figure 1A and Figure 2. Decreasing trends over the four weeks of sampling data are evident for all substances examined. Data on oil & grease, TSS, and TPH (Figure 1A) are indicative of the spillage of petroleum hydrocarbon-containing materials, this grouping was supported by their high correlation of at least 0.8 (see Supplemental Figure 1). Although there were fluctuations in their concentrations over 4 weeks, overall, their peak concentrations were detected in week 1 after the incident. The analysis of oil & grease across different samples was conducted using two different methods - Wet Chem and 1664A_Calc HEM, and SGT-HEM by Extraction and Gravimetry (1664A), based on the contract laboratory where the samples were processed: these differences are indicated by different shapes in Figure 1A. The outliers were predominantly from the Wet Chem analysis method, and the fluctuation of medians and quartiles may be attributable to differences between analysis methods. Nonetheless, a gradual and consistent decline in the concentration of the outlier locations is also evident. Despite a limited number of samples with valid measurements, both TSS and
TPH also followed overall decreasing trends. Similarly, all BTEX substances demonstrated consistently decreasing trends in concentrations over time (Figure 2). Notably, median levels of benzene in the first week after the incident exceeded both the MCL and water criteria, but gradually declined to levels below the criteria in subsequent weeks. Similarly, the median of ethylbenzene concentration was above MCL in the first week, but declined below all criteria at later time points. For both toluene and total xylenes, the proportion of samples exceeding each criterion decreased over time, while their median concentrations did not exceed any of the criteria in all 4 weeks. The percentage of benzene and toluene observations exceeding the short-term health advisory levels dwindled after Week 1, and reached zero eventually. Ethylbenzene and total xylenes had no samples above these short-term advisory levels for all 4 weeks.

Figures 1B and Figures 3A-6A show the temporal trends at specific locations in close proximity to, upstream from, and downstream from the ITC site. Specifically, the Mouth of Tucker Bayou at Buffalo Bayou (MoT@BB) location was selected because it was in close proximity to the site of the ITC incident and was the most data-rich location. BB-01 is a point upstream of the ITC, and BB-03 was the closest downstream point. Because ethylbenzene lacked valid sampling results of locations BB-01 and BB-03, locations BB-02 and BB-04 are shown as substitutes in Figure 5A. BB-02 was a suitable surrogate because it is further away from the ITC site than MoT@BB and samples were collected at this location as frequently as at BB-01. BB-04 was likewise an appropriate substitute for BB-03 because it was the closest downstream location point with data for ethylbenzene. At MoT@BB, peak concentrations for oil & grease and BTEX were observed on the first day of sampling and declined afterward. Similarly, there were downward trends of concentrations of other contaminants in both upstream and downstream samples. The elevated concentrations of BTEX in week 1 and/or week 2 declined below detection limits and remained undetectable in all samples collected after week 2. The relatively lower concentrations of the substances of interest upstream and downstream from MoT@BB could be explained by a dilution caused by dispersing water movement from tides and wind forces in this area as reported elsewhere. One exceptionally high value of ethylbenzene of BB-02 in week 1, a location that is close to MoT@BB, is evidence of the reliability in the sampling results because two locations are in close proximity.

3.2. Spatiotemporal distribution

Figures 1C and 3B-6B show the spatial distribution of the contaminants in weeks 1, 2, and 4 as interpolated from Kriging analyses. Under cross-validation, root mean square errors were around one log_{10} unit during Weeks 1-2, when values varied by orders of magnitude across locations, to at most ½ log_{10} unit in week 4, when values were less variable.

Clear patterns of substantial time- and location-dependent decline in concentrations of all substances were observed. Similar to the decreasing temporal trends shown above, the concentrations of all substances were the highest in week 1, considerably lower in week 2, and were the lowest in week 4. In addition, overall, the area immediately near the incident site showed higher concentrations of contaminants as compared to distal locations in weeks 1 and 2. Week 4 has little or no spatial variation, in comparison to previous weeks, as
contaminants appeared to have been sufficiently diluted. The same analysis was conducted for TSS and TPH (Supplemental Figure 2), but both substances had limited numbers of sampling locations, so not all time points could be Kriged. Note that the flow direction of the water body in the Houston Ship Channel is both upstream and downstream because of both tidal and wind. Additionally, for ethylbenzene, no data were available at BB-01, so the kriging was performed on a smaller spatial extent, and the decline with distance in the westerly direction could not be characterized.

3.3. Risk characterization

To evaluate human health risks from potential water ingestion exposures to chemical contaminants released during the ITC incident, cancer risks and non-cancer hazard quotients were calculated by relating the EPA water criteria to the concentrations of each substance using a risk characterization approach. Results of these analyses are presented in Table 2, with detailed calculations shown in Supplemental Table 7, and summarized in a heat map for visualization in Figure 7. EPA drinking water regulation criteria are available only for BTEX, hence oil & grease, TSS, and TPH were excluded from the risk characterization. For benzene, a known human carcinogen, the resulting risk was quantified as the cancer risk per million people assuming lifetime exposure. For toluene, ethylbenzene, and total xylenes, the risk was characterized by a hazard quotient because these substances are not classified as known human carcinogens. All four chemicals, for each location, showed immediate spikes and temporal declines in both cancer risks and hazard quotients (Figure 7, Table 2). For benzene at MoT@BB location, the cancer risk in week 1 reached 0.048 lifetime risk, well above the typical screening level of $10^{-6}$, but declined to 0.0013 lifetime risk in week 2, and eventually dropped to $2.4 \times 10^{-5}$ lifetime risk in week 4. For toluene, a few locations had HQ>1 in weeks 1-3, indicating excess non-cancer hazard; however, overall the values were below 1. For ethylbenzene and xylenes, only in week 1 were there any samples with an HQ>1. As expected, there was a negative correlation between the relative distance from the site and cancer risks or hazard quotients: locations close to the site tended to have higher cancer risks and hazard quotients than distal points (Figure 7).

Comparison with short-term drinking water health advisories showed similar patterns, but at lower levels of risk (Supplemental Figures 3-4, Supplemental Table 8). Specifically, 10-day advisory levels were only exceeded in Week 1 for benzene and toluene, and in Weeks 2-3 for benzene. With respect to 1-day advisory levels, the only exceedances were for benzene in weeks 1-3. Additionally, in all cases, HQ values > 1 were only found at the locations closest to the ITC.

4. Discussion

The ITC fire resulted in a sustained release of a variety of contaminants to both ambient air and surface water. While most direct exposure to the public from such an incident is likely from inhalation, exposure due to surface water is also possible as the Houston Ship Channel is used for recreation. For instance, several public parks provide access to this massive body of water, and anglers are commonly seen in the area despite the presence of fish advisories. Although extensive sampling was conducted by TCEQ and U.S. EPA after...
this incident, prior to this study, the spatial and temporal trends in these data have not been characterized.

We found that even though the chemical characterization of the water samples extended over 2 months and included hundreds of analytes, only a few substances exhibited high concentrations in the locations near the ITC site during the first week before decreasing rapidly to levels generally below EPA water quality criteria. Specifically, temporal analysis showed that rapid decrease in chemical concentrations occurred, with most analytes declining to steady-state or below detectable levels after 1-2 weeks. Spatial analysis demonstrated that chemicals reached the highest concentration immediately near the ITC site and then were diluted substantially at distances of 1 km or more from the inlet to the HSC. Risk characterization indicated that levels of benzene initially exceeded water quality criteria by up to 50,000-times at locations near the ITC site; still, while most locations quickly returned to acceptable levels, a few concentrations remained elevated even after 4 weeks. It should be noted that the Houston Ship Channel is not used for drinking water, so there are conservative estimates. However, benzene remains elevated even using the less stringent TCEQ health criteria for fish of 0.581 (other TCEQ criteria were the same as those from EPA)\textsuperscript{23}, as well as in comparison to short-term health advisory levels. These results contrast with the spatial-temporal extent of PFAS released due to the use of firefighting foams at the same incident, as studied by Aly et al. (2020). Specifically, PFAS levels remained elevated for a much longer period (months) and high concentrations extended over a much larger geographic area (several kilometers up and down stream). The reason for the differences is likely due to PFAS being much more resistant to both volatilization and degradation as compared to the volatile and semi-volatile organic substances analyzed by TCEQ and EPA.

Overall, typical post-spill field studies include only limited spatial and temporal characterization of the chemical contaminants in water. The detailed characterization of long-term BTEX plumes migration and degradation rates normally involves controlled releases of complex test substances that are monitored to discern the role exerted by water flow dynamics\textsuperscript{24}. Most of the data and modeling of BTEX dissolution and biodegradation are available from studies of oil spills. For example, in a stationary body of water (i.e., in a lake), the anaerobic biodegradation prevails over dissolution for toluene and o-xylene; however, for benzene, ethylbenzene, and m,p-xylene the dissolution is the primary path for reducing the concentrations over time\textsuperscript{25}. Longitudinal studies of hydrocarbon substance-contaminated water in oil-producing regions are conducted using either remote sensing\textsuperscript{26}, or physical sampling with extensive chemical analyses\textsuperscript{27}. Albeit few previous studies conducted as granular and extensive chemical analysis as one that was performed after the ITC fires, the findings in our study of a rapid gradual decline in concentrations of spill-derived contaminants is commensurate with the observations in surface water samples from other large-scale oil spills\textsuperscript{27-29}.

The data presented in this study have a number of important limitations. First, significant data gaps existed not only between locations but also between sampling dates (see Supplemental Table 9). For instance, eleven locations had less than 5 samples, and 34 locations even had no data after April 20\textsuperscript{30}, 2019. Additionally, after the collection of water
samples, different laboratories that were contracted with different government agencies used similar but different analytic methods. For example, oil and grease had two different methods – 1664A and Wet Chem – and two methods have quite different value ranges: the values of Wet Chem had a greater range than those of 1664A. Furthermore, a large number of reported values were below detection and/or quantification limits (LOQ). Thus, even though the data cover many other chemicals, for most chemical contaminants, detection was inconsistent, hampering the ability to analyze any trends.

Overall, these limitations suggest that sampling plans can be better optimized in terms of timing, spatial locations, and analytes so as to produce the most information most efficiently. One challenge is that it is not always known a priori what chemicals might have been released after a disaster. For water monitoring, most of the studies of post-disaster monitoring have been in the context of wildfires. Wildfire usually induces increases in phosphorus, nitrogen, total suspended solids, and metals in surface water; therefore, most post-fire water quality responses are likely to prioritize the analysis of those chemical substances \(^{30-32}\). Industrial fires, however, account for a small portion of the entire number of large-scale fire incidents, and their byproducts are not only different from those of wildfire but also vary in the types of the industry caught in fires. Volatile organic compounds and the substances related to oil spillage were studied in this study and these chemicals were obviously associated with the fact that the tanks containing naphtha, toluene, and xylene were impacted by the fire. In cases where the likely releases are unclear, two-step process whereby untargeted analysis is first used to prioritize samples and analytes, followed by targeted chemical analysis to quantify analytes likely to be detected, could help to better allocate resources devoted to chemical analysis after these types of disasters.

In summary, this study demonstrates the temporal and spatial patterns of chemical contaminants released from ITC fire into water and their possible hazards. Out of 433 substances analyzed by TCEQ and EPA, seven of them that were of potential concerns for human health and had sufficient data were selected for analysis: BTEX, Oil & Grease, Suspended Solids, and Total Petroleum Hydrocarbons. Temporal analysis showed that the chemical concentrations in water had been diluted over one month and that they eventually reached a steady-state or below the lower limit of quantitation after 1-2 weeks. Additionally, the spatial distribution of contaminants clearly indicated the highest concentrations near the ITC site and the substantial dilution outside of 1km from the inlet to the Houston Ship Channel. Hazard quotients and cancer risk calculated by the concentrations were used to estimate the potential risk on human health from exposure to the substances, with the greatest potential risks stemming from benzene. Overall, the surface water concentrations of contaminants released from the ITC fire surged in week 1 and recovered to apparent baseline levels within 4 weeks.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.
Acknowledgments:

We thank the Texas Commission on Environmental Quality and the U.S. Environmental Protection Agency for making their sampling and analysis data available to the public.

Funding:

This work was funded, in part, by the National Institutes of Health (P42 ES027704 and T32 ES026568) and the National Academies Gulf Research Program (#2000008942). The views expressed in this manuscript do not reflect those of the funding agency. The use of specific commercial products in this work does not constitute endorsement by the authors or the funding agencies.

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Figure 1.
Temporal and spatial patterns of oil and grease (O&G), suspended solids, and total petroleum hydrocarbons (TPH) from March 19th to April 15th. (A) The boxplots showing concentrations of analytes across the period. O&G was analyzed by two different methods —Wet Chem (black triangles) and 1664A_Calc HEM and SGT-HEM by Extraction and Gravimetry (black circles). (B) Temporal plots for O&G from locations near the site (Mouth of Tucker at Buffalo Bayou: Mot@BB), upstream (BB-01), and downstream (BB-03). Valid values are marked with black dots and non-detected values are marked with empty upside-down triangle. Exact locations are shown in Week 1 of Figure 1C by blue circles. Lines are smoothed values using Loess. Temporal plots for suspended solids and TPH are in Supplemental Figure 2 because only their week 1 data were eligible for analysis. (C) Spatial interpolation of O&G concentration for week 1, week 2, and week 4. ITC site is indicated by red fire symbol. Blue and black dots demonstrate locations with one or more valid values. The concentrations are visualized as a continuous red-blue color scale. The chemical traveled both upstream and downstream due to tidal flow and wind. The small blue arrow shows the direction of Galveston Bay and the Gulf of Mexico.
Figure 2.
Boxplots showing concentrations of benzene, toluene, ethylbenzene, and total xylenes (BTEX) from March 19th to April 15th. Maximum contaminant level (MCL), which is the highest level of a contaminant that is allowed in drinking water, of each chemical is indicated by red lines. Human health ambient water quality criterion, that are not expected to cause adverse effects to human health, of each chemical for both water and organism is indicated by blue lines (or band), and that for organism only is indicated by green lines (or band). Ten-day and one-day health advisories for drinking water from the EPA are indicated by light-blue dotted lines and dark blue dash-dotted lines, respectively. Total xylenes do not have exact criteria of human health ambient water quality.
Figure 3.
Temporal and spatial patterns of benzene from March 19th to April 15th. (A) Temporal plots for benzene from locations near the site (Mouth of Tucker at Buffalo Bayou: Mot@BB), upstream (BB-01), and downstream (BB-03). Valid values are marked with black dots and non-detected values are marked with empty upside-down triangle. Exact locations are shown in Week 1 of Figure 3B by blue circles. Lines are smoothed values using Loess. (B) Spatial interpolation of benzene concentration for week 1, week 2, and week 4. ITC site is indicated by red fire symbol. Blue and black dots demonstrate locations with one or more valid values. The concentrations are visualized as a continuous red-blue color scale. The chemical traveled both upstream and downstream due to tidal flow and wind.
Figure 4.
Temporal and spatial patterns of toluene from March 19th to April 15th. (A) Temporal plots for toluene from locations near the site (Mouth of Tucker at Buffalo Bayou: Mot@BB), upstream (BB-01), and downstream (BB-03). Valid values are marked with black dots and non-detected values are marked with empty upside-down triangle. Exact locations are shown in Week 1 of Figure 4B by blue circles. Lines are smoothed values using Loess. (B) Spatial interpolation of toluene concentration for week 1, week 2, and week 4. ITC site is indicated by red fire symbol. Blue and black dots demonstrate locations with one or more valid values. The concentrations are visualized as a continuous red-blue color scale. The chemical traveled both upstream and downstream due to tidal flow and wind.
Figure 5.
Temporal and spatial patterns of ethylbenzene from March 19th to April 15th. (A) Temporal plots for ethylbenzene from locations near the site (Mouth of Tucker at Buffalo Bayou: Mot@BB and BB-02), and downstream (BB-04). Valid values are marked with black dots and non-detected values are marked with empty upside-down triangle. Exact locations are shown in Week 1 of Figure 5B by blue circles. Lines are smoothed values using Loess. (B) Spatial interpolation of ethylbenzene concentration for week 1, week 2, and week 4. ITC site is indicated by red fire symbol. Blue and black dots demonstrate locations with one or more valid values. The concentrations are visualized as a continuous red-blue color scale. The chemical traveled both upstream and downstream due to tidal flow and wind, as shown in previous modeling. A different pattern from other analytes was observed because there is no data point on BB-01.
Figure 6.
Temporal and spatial patterns of total xylenes from March 19th to April 15th. (A) Temporal plots for total xylenes from locations near the site (Mouth of Tucker at Buffalo Bayou: Mot@BB), upstream (BB-01), and downstream (BB-03). Valid values are marked with black dots and non-detected values are marked with empty upside-down triangle. Exact locations are shown in Week 1 of Figure 6B by blue circles. Lines are smoothed values using Loess. (B) Spatial interpolation of total xylenes concentration for week 1, week 2, and week 4. ITC site is indicated by red fire symbol. Blue and black dots demonstrate locations with one or more valid values. The concentrations are visualized as a continuous red-blue color scale.
Figure 7.
Heatmaps of cancer risk per million people and hazard quotient of BTEX. Values are indicated with a continuous red-white color scale. For benzene cancer risk per million, average benzene concentrations of each week from each location point were divided by the maximum contaminant level (MCL) of 0.00058 mg/L. Average toluene, ethylbenzene, and total xylenes concentrations of each week from each location point were divided by their individual MCL to obtain their hazard quotient. Exact values and calculations are in detailed in Table 2 and Supplemental Table 6, respectively. Heatmaps of hazard quotient of BTEX calculated using ten-day and one-day exposure criteria are in Supplemental Figures 3 and 4. Location points are ordered by the relative distance from the ITC fire site.
Table 1.
Summary of the data on selected analytes.

| Analyte                  | Total samples per analyte<sup>a</sup> | Samples with data (>LLOQ)<sup>b</sup> | First date<sup>c</sup> of sampling | Last date<sup>d</sup> of sampling | Data range (>LLOQ, mg/L)<sup>e</sup> |
|-------------------------|----------------------------------------|---------------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|
| Oil and Grease          | 310                                    | 286                                   | March 19                          | May 21                            | 1-47,000                             |
| Total Petroleum Hydrocarbons | 107                                   | 32                                    | March 19                          | May 15                            | 0.54-4,160                           |
| Suspended Solids        | 107                                    | 95                                    | March 19                          | May 21                            | 4-60,300                             |
| Benzene                 | 598                                    | 68                                    | March 19                          | May 13                            | 0-102                                |
| Toluene                 | 599                                    | 58                                    | March 19                          | May 15                            | 0-15.9                               |
| Ethylbenzene            | 599                                    | 32                                    | March 19                          | May 10                            | 0-1.37                               |
| Xylenes (Total)         | 312                                    | 51                                    | March 19                          | May 12                            | 0-17.7                               |

<sup>a</sup> A total number of samples collected for which the analyte was evaluated.

<sup>b</sup> A number of samples for which the analyte was evaluated and the data was reported as >LLOQ.

<sup>c</sup> The first date of sampling for which the analyte was evaluated, year 2019.

<sup>d</sup> The last date of sampling for which the analyte was evaluated, year 2019.

<sup>e</sup> The range in the data for samples for which the analyte was evaluated and the data was reported as >LLOQ.
Table 2.

Summary of the hazard quotients and cancer risk of BTEX. See Supplemental Table 6 for the calculation and data for each week and chemical

| Chemical                  | Criterion                      | Statistic | Week 1     | Week 2     | Week 3     | Week 4     |
|---------------------------|--------------------------------|-----------|------------|------------|------------|------------|
| Benzene (Cancer risk unit per million people) | 0.00058 mg/L                     | Median    | 45         | 0.97       | 0.97       | 0.97       |
|                           |                                 | IQR (Q1 - Q3) | 0.97 - 630 | 0.97 - 11  | 0.97 - 0.97 | 0.97 - 0.97 |
|                           |                                 | Range (Min - Max) | 0.97 - 48000 | 0 - 4000  | 0 - 590     | 0 - 34     |
| Toluene (HQ)              | 0.057 mg/L                      | Median    | 0.06       | 0.01       | 0.01       | 0.01       |
|                           |                                 | IQR (Q1 - Q3) | 0.01 - 0.84 | 0.01 - 0.03 | 0.01 - 0.01 | 0 - 0.01  |
|                           |                                 | Range (Min - Max) | 0.01 - 61 | 0.00 - 8.1 | 0 - 1.8     | 0 - 0.01   |
| Ethylbenzene (HQ)         | 0.068 mg/L                      | Median    | 0.02       | 0.02       | 0.02       | 0.02       |
|                           |                                 | IQR (Q1 - Q3) | 0.02 - 5.2 | 0.02 - 0.04 | 0 - 0.02    | 0 - 0.02   |
|                           |                                 | Range (Min - Max) | 0.02 - 20 | 0 - 0.59   | 0 - 0.02    | 0 - 0.02   |
| Xylenes, Total (HQ)       | 10 mg/L.a                       | Median    | 0.0016     | 0.0002     | 0.0002     | 0.0002     |
|                           |                                 | IQR (Q1 - Q3) | 0.00028 - 0.0039 | 0.00020 - 0.00028 | 0.00020 - 0.00020 | 0.00020 - 0.00020 |
|                           |                                 | Range (Min - Max) | 0.00020 - 1.8 | 0.00020 - 0.032 | 0 - 0.006 | 0 - 0.002 |

aMaximum contaminant limit (MCL) was used instead of human health ambient water quality criteria for both water and organism due to the absence of MCL for total xylenes in EPA document.