Human health risk assessment for exposure to BTEXN in an urban aquifer using deterministic and probabilistic methods: A case study of Chennai city, India

Bokam Rajasekhar a, Indumathi M. Nambi a,*, Suresh Kumar Govindarajan b

a Environmental and Water Resources Engineering, Department of Civil Engineering, Indian Institute of Technology Madras, 600036, India
b Reservoir Simulation Laboratory, Petroleum Engineering Programme, Department of Ocean Engineering, Indian Institute of Technology Madras, 600036, India

ABSTRACT

The aquifer in Tondiarpet, Chennai, had been severely contaminated with petroleum fuels due to an underground pipeline leakage. Groundwater samples were analyzed quarterly for priority pollutants such as benzene, toluene, ethylbenzene, xylenes, and naphthalene (BTEXN) using purge and trap gas chromatography and mass spectrometer from 2016 to 2018. The maximum concentrations of BTEXN in groundwater at the site were found to be greater than the permissible limits significantly. Among the five sampling locations (MW1, MW2, MW3, MW4, and MW5), mean BTEXN levels were found to be higher near MW2, confirming the source location of petroleum leakage. Human health risk assessment was carried out using deterministic and probabilistic methods for exposure to BTEXN by oral and dermal exposure pathways. Risk analysis indicated that mean cancer and non-cancer risks were many times higher than the allowable limits of 1E-06 and 1 respectively in all age groups (children, teens, and adults), implying the adverse health effects. Oral exposure is predominately contributing (60–80%) to the total health risk in comparison to the dermal exposure route. Variability and uncertainty were addressed using the Monte Carlo simulations and the resultant minimum, maximum, 5th, 95th, and mean percentile risks were predicted. Under the random exposure conditions to BTEXN, it was estimated that the risk would become unacceptable for >98.7% of the exposed population. Based on the sensitivity analysis, exposure duration, and ingestion rate are the crucial variables contributing significantly to the health risk. As part of the risk management, preliminary remediation goals for the study site were estimated, which require >99% removal of the BTEXN contamination for risk-free exposures. It is suggested that the residents of Tondiarpet shouldn’t utilize the contaminated groundwater mainly for oral ingestion to lower the cancer incidence related to exposure to BTEXN.

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1. Introduction

Petroleum fuel (e.g., Diesel, Kerosene) contains hundreds of hydrocarbons that can be majorly classified as aromatics and alkanes. For example, in diesel fuel, aromatics constitute 25%–35%, and alkanes constitute 65%–75% (Cookson et al., 1985; Wang et al., 2003). The minor fraction of aromatics would pose severe health risks compared to the alkane counterparts upon exposure to them. Of these aromatic compounds, BTEXN are of significance in terms of their relatively high solubility in water and hazardous health effects. The health effects due to BTEXN have been reported to be carcinogenic and non-carcinogenic, which include leukemia, kidney problems, disorders in human blood, and damages to reproductive organs, immune system and central nervous system (ATSDR, 2007, 2005, 2004). Both benzene and naphthalene have been classified as Group-A and Group-C carcinogens, respectively by the United States Environmental Protection Agency (US EPA) (ATSDR, 2018; RAIS, 2019). Exposure to these petroleum hydrocarbons by various exposure routes such as oral ingestion and dermal contact, can increase the risk of detrimental health effects in local residents near contaminated sites. Therefore the evaluation of health risk is immediately required in the impacted sites.

* This paper has been recommended for acceptance by Da Chen.
* Corresponding author.
E-mail address: indunambi@iitm.ac.in (I.M. Nambi).
Health risk assessment can be addressed by the two methods such as deterministic and probabilistic methods. The deterministic method represents the output health risk as a single point value that gives partial information about the health risk. On the other hand, Probabilistic method using Monte Carlo simulations yields the output risk as a range of values (in the form of probability distributions) by accounting the inherent randomness and uncertainty associated with exposure variables such as body weight, exposure duration and ingestion rate (Durmusoglu et al., 2010; Fallahzadeh et al., 2018, 2017; Omidi et al., 2019; Rajasekhar et al., 2018; Sarria-Villa et al., 2016; US EPA, 2001).

An up-to-date literate review on the risk assessment of BTEX in drinking or groundwater was presented in Table S1. Of the available research works, majority of the studies centered on the deterministic approach (Clay and Harris, 2002; Fan et al., 2009; Flores-Serrano et al., 2012; Iturbe et al., 2005; Lee and Park, 2002; Maurice et al., 2019; Santos et al., 2013; Senthil kumar et al., 2017; Tieyu et al., 2014; Zhang et al., 2016). The studies of the probabilistic risk assessment (PRA) were found to be very scant, especially for BTEX contaminants in petroleum contaminated aquifers (Kavcar et al., 2006; López et al., 2008). Moreover, the probabilistic risk evaluation by Kavcar et al. (2006) and Lopez et al. (2008) addressed just a few elements, such as percentile estimates and sensitivity analysis.

Kavcar et al. (2006) measured concentrations of benzene (0.01–0.1 µg/L), toluene (0.007–160 µg/L), p-xylene (0.001–0.05 µg/L) and naphthalene (0.004–0.90 µg/L) in household drinking water samples of Izmir district, Turkey. Probabilistic risk assessment was carried out for only single age group of adults with oral exposure route. The mean (4.73E-08) and 95th percentile (1.34E-07) values of cancer risk found to be less than the safety risk of 1-in-1 million, indicating the cancer risk was negligible at the detected concentrations (Table S1). López et al. (2008) investigated BTEX contamination of aquifers due to an oil storage tank rupture at a residential cum industrial site in Spain. Mean concentrations of BTEX were measured to be 7.58E-04, 1.3E-04, 1.07E-04 and 8.08E-05 µg/L respectively. The Monte Carlo simulations were applied and the results showed that the mean and 90th percentiles of carcinogenic and non-carcinogenic risks were acceptable for both children and adults. It was observed that the exposure variable ‘ingestion rate’ significantly contributed to the health risk based on the sensitivity analysis (Table S1). Zhang et al. (2016) performed a health risk assessment of exposure to BTEX compounds in groundwater near the oil production industries at the detected concentrations of 1.53, 1.76, 2.11 and 0.30 (µg/L), respectively. Even at these lowest concentration levels of BTEXs, the cancer risk in the adults was found to be higher than one-in-one million, which was unacceptable. Senthil kumar et al. (2017) reported benzene concentrations that were nearly 28 times higher than the US EPA maximum contaminant level (5 µg/L) of benzene in the residential bore wells of Madurai city, India. The ground water samples were obtained in the vicinity of petrol filling stations. Health risk analysis showed that 23 out of 10,000 adult receptors were potentially under cancer risk. Maurice et al. (2019) analyzed concentrations of BTEX (160 ng/L to 1769 ng/L) in groundwater of Amazon region. The risk of cancer was found to be greater than the allowable limit of 1-in-1 million, with children being sensitive receptors than adults. It has been reported that the risk of exposure to BTEX was significantly contributed by oral route than the dermal route (Fan et al., 2009; Flores-Serrano et al., 2012; López et al., 2008; Maurice et al., 2019; Santos et al., 2013). Risk assessment studies by Clay and Harris (2002) and Lee and Park (2002) have shown that the benzene is a critical compound in the BTEXN (Table S1).

Based on the analysis of the literature review, none of the previous studies addressed the following important research gaps linked to the BTEXN contamination of urban aquifers: (1) lack of systematic characterization and long-term monitoring of BTEX compounds; (2) lack of health risk studies for multiple agegroups (0–5, 6 to 10, 11 to 18 and 19–70 years) to identify sensitive receptors; (2) lack of essential information to be obtained from the probabilistic evaluation such as percentage of population at risk higher than the deterministic values, the proportion of population that would face unacceptable risks after random exposure; identification of reasonable maximum exposure estimates (RME); risk management decisions to evaluate the need for remediation, prediction of conservative risk based preliminary remediation goals and selection of appropriate remediation technologies that will mitigate the high end risks.

To the best of our knowledge, the present study is the first report on the long term monitoring of BTEXN concentrations in the contaminated groundwater of north Chennai. Moreover, the current site was not investigated either by deterministic or probabilistic approaches for health risk assessment. In order to resolve the research gaps listed above, the following objectives were addressed in this study: 1) characterization and monitoring of BTEXN levels in the ground water of north Chennai site; 1) conduct human health risk assessment using the deterministic and probabilistic techniques for exposure to BTEX in groundwater; 2) identifying sensitive receptors within various age groups as well as identifying critical contaminants of health risk; 3) determine the sensitive input parameters of health risk by performing sensitivity analysis; 4) estimate the preliminary remediation goals (PRGs) for the study site that can act as a site-specific guidance criteria for the local environmental regulators; and 5) finally, detail the succesful in-situ and ex-situ remediation techniques that are suitable for the decontamination of the study site.

2. Materials and methods

2.1. Study site

The current site of investigation, Tondiarpet, is located in north Chennai, India. Chennai is one of the largest metropolitan cities in India, with a population of 8,653,521 (Census, 2020). The study area is occupied with close structures of residential buildings, commercial buildings such as shops and hotels, theatres, hospitals, and schools (Fig. S1). In a recent study, Nambi et al. (2017) reported an adverse contamination of groundwater with the petroleum hydrocarbons (BTEX and diesel range alkanes), which occurred due to an underground pipeline leakage in Tondiarpet. In addition to the recent spill, two more studies by Clement (1993) and Brindha and Elango (2014) revealed that the north Chennai aquifer has been enduring the oil pollution for more than five decades due to the functioning of oil storage terminals. In the year 2013, residents of Tondiarpet had first reported the presence of oil in their household borewells. Subsequent field scale investigations in our earlier study (Nambi et al., 2017) had revealed that (a) approximately 25 mm—840 mm free phase oil thickness was accumulated above the groundwater table; (b) a large amount of oil was also trapped in soil pores in both unsaturated and saturated regions of the aquifer; (c) groundwater was contaminated with dissolved phase hydrocarbons such as BTEXN; (d) GC-MS analysis showed that the nature of the oil was resembling the diesel range hydrocarbons. The key cause for the occurrence of oil in the subsurface was the rupture of an underground pipeline belonging to an oil storage facility located in the vicinity of the study location (Nambi et al., 2017). Groundwater at this site naturally flows into the Bay of Bengal (part of the Indian Ocean) in the east direction. The most possible exposure routes of contaminated groundwater by local residents were oral...
ingestion and dermal contact (by bathing and washing). The geological profile for the study site was reported by Nambi et al. (2017) in their preliminary site characterization studies. Briefly, geologically, the site has sandy layers of varying gradations up to ~12 m below ground level (bgl). At least ~6 m thick clayey stratum followed sandy layers at all locations of monitoring wells. Beyond 18–24 m, it was hard rock. The construction of monitoring wells (for sampling) was facilitated by the use of hollow-stem auger (HSA) drilling equipment. The HSA ensures the prevention of cross-contamination across geological layers and also does not require any drilling fluids for bore-well construction in order to avoid the dilution of groundwater contamination levels.

2.2. Sampling

Sampling was undertaken on a quarterly basis from June 2016 to June 2018 in five separate monitoring wells located close to the oil leakage region as well as at distant down gradient points (Fig. S1). The choice of monitoring wells was based on the groundwater flow. A hand bailer was employed to draw the water samples from all monitoring wells (MW). Fresh groundwater samples were collected manually from all monitoring wells (MW1, MW2, MW3, MW4, and MW5) after bailing the stagnant water. Samples were filled in 40 ml amber glass vials with no headspace and sealed tightly with Teflon caps to avoid volatilization and photodegradation. All the sampled glass vials were placed in the ice chiller before being shipped to the laboratory for Gas Chromatography and mass spectrometry (GC-MS) analysis.

2.3. BTEXN analysis and quality control

Groundwater samples were analyzed for priority pollutants (BTEXN) using GC-MS (Hewlett 6890 GC - 5973 MSD) externally connected to the purge and trap (P&T) module (Agilent Tekmaker Dohrmann) according to the US EPA method 5030C (EPA, 2003). The sample preparation and analytical conditions for P&T and GC-MS can be found in Text S1 and Table S2 in supplementary information.

As part of the quality control, sampling equipment (e.g., bailer) was washed with a detergent solution (Alconox) followed by sequential rinsing with clean water and well water prior to sampling in each well. Fresh glass vials were used to fill contaminated groundwater samples during all sampling events. Samples were collected in duplicates for the purpose of substitutes (in case of loss in original samples) as well as for replicate analysis. Deionized water (Millipore) was used to rinse the laboratory apparatus and to prepare calibration standards. Analysis of trip blanks and procedural blanks had not shown detectable levels of target pollutants. The limit of detection (LOD) values were determined to be < 5 µg/L for benzene, toluene, ethylbenzene, and xylenes, whereas < 0.1 µg/L for naphthalene. Signal to noise ratio was greater than 5 for all the pollutants of interest. An intermediate standard of known concentration was frequently analyzed (during every batch) to assess the change in GC-MS response. The variation in GC-MS response was found to be ±15% of the original response for all the target analytes in this study. Percentage recoveries were measured in the groundwater matrix for all target analytes with known concentrations within the range of calibration standards. The mean percentage recoveries were found to be ~98% (benzene), 96% (toluene), 98% (ethylbenzene), 97%–99% (xylenes) and 98% (naphthalene).

2.4. Risk assessment

The compounds such as benzene, toluene, ethylbenzene, xylenes, and naphthalene with their geometric mean concentrations were considered for health risk assessment.

2.4.1. Exposure assessment

Residential buildings mainly cover the current study area, and hence the exposure assessment was carried out for the residential scenario. As the potential use of groundwater by residents of this area was mainly for drinking and bathing, the exposure routes for the assessment were considered to be dermal and oral. To determine the sensitive receptors of health risk, the population was divided into the following age groups: 0–5 years, 6–10 years, 11–18 years, and 19–70 years (Arthur et al., 2018; Hayes et al., 2019; US EPA, 2005). Chronic daily intake for direct water ingestion was estimated by (US EPA, 2001)

\[
CDI = \frac{C_W \times CF \times IR \times EF \times ED}{BW \times AT} \tag{1}
\]

Exposure dose for the dermal intake was quantified by (US EPA, 2004)

\[
DAD = \frac{DA_{event} \times EV \times ED \times EF \times SA}{BW \times AT} \tag{2}
\]

Where

\[
DA_{event} = 2FA \times K_P \times C_W \times \left[ \frac{t_{event}}{1 + B} \right] + 2 \times \left[ \frac{t_{event}}{(1 + B)^2} \right] \tag{4}
\]

Where CDI is Chronic daily intake (mg/kg-day); DAD is Dermal adsorbed dose (mg/kg-day), CW is the concentration of a pollutant in groundwater (mg/cm³), CF is unit conversion factor (cm³/L), t event is the time to reach steady-state (hr). The details of the exposure parameters such as IR, EF, ED, BW, EV, and AT with their values for the risk models had been summarized in Table S3 (Burmaster and Crouch, 1997; Ganyaglo et al., 2019; NNMB, 2002; US EPA, 2011; Wu et al. 2011). The chemical-specific parameters are Kp; skin permeable coefficient (cm/hr); B: The ratio of the permeability coefficients of stratum corneum and viable epidermis of skin(-); t event: lag time per event (hr/event). The values of Kp, t event, and B for the BTEXN were given in Table S4. For the deterministic exposure assessment, the mean values of all the variables were considered as input to the risk models (Table S3).

2.4.2. Risk characterization

The incremental cancer risk (ICR) was estimated by

\[
ICR_D = \frac{CDI \times CSF_{FO}}{R_{fdO}} \quad \text{for oral cancer risk} \tag{5}
\]

\[
ICR_D = \frac{DAD \times CSF_{ABS}}{R_{fdABS}} \quad \text{for dermal cancer risk} \tag{6}
\]

The non-cancer risk was estimated by

\[
HQ_D = \frac{CDI}{R_{fdO}} \quad \text{for oral non – cancer risk} \tag{7}
\]

\[
HQ_D = \frac{DAD}{R_{fdABS}} \quad \text{for dermal non – cancer risk} \tag{8}
\]

Where HQ is a hazard quotient, generally used to represent the non-cancer risk, and ICR denotes incremental lifetime cancer risk. RfdO and RfdABS represent oral and dermal reference doses.
respectively. Similarly, CSF\textsubscript{O} and CSF\textsubscript{ABS} indicate oral and dermal cancer slope factors respectively. The hazard quotient of 1 and the cancer risks of 1E-04 and 1E-06 (one-in-one million) were set as allowable risks for screening criteria (US EPA, 2015, 2004, 2001). The total risk in this study was considered to be the sum of risks due to oral and dermal exposures as a result of the five contaminants of concern. HQ > 1 and cancer risk higher than 1E-04 and 1E-06 signify unacceptable health risks. In BTEXN compounds, benzene, ethylbenzene and naphthalene were considered to be carcinogenic and thus the risk of cancer was determined for only these three compounds. On the other hand, the non-cancer risk was estimated for all BTEXN compounds (ATSDR, 2004; Dehghani et al., 2018; IRIS, 2019; RAIS, 2019).

2.4.3. Probabilistic health risk assessment

The deterministic method of risk assessment considers only the point values for input variables such as BW, ED, SA, IR, and EF, and hence the output risk is a single point value. Variability was not accounted for input variables by the deterministic approach. The US EPA risk models (Eq. (1) to Eq. (8)) had been developed with many underlying assumptions, such as that the skin comprises only two layers of stratum corneum and viable epidermis, diffusion of contaminants into the skin follows Fick’s second law of diffusion, the diffusion of contaminants is a long term process and there are no metabolite effects (US EPA, 2004). The use of constant values of input parameters, as well as assumptions, could lead to an unrealistic estimation of health risks by the deterministic method. In contrast, the probabilistic approach by Monte Carlo simulation addresses the variability and uncertainty associated with the risk input variables (Dong et al., 2015; Kaur et al., 2020; US EPA, 2001). In the process of Monte Carlo simulations, the risk was estimated several times, each time considering a random value for each input variable. The values of the input variables for the Monte Carlo simulations have been summarized with the appropriate probability distributions (Table S3). The simulations were performed in the commercial software @Risk 7.5 version. A total of 10,000 iterations were given input for simulations for all age groups after ensuring the numerical stability of the results.

2.4.4. Preliminary remediation goals

Preliminary remediation goals (also known as cleanup concentrations) for all contaminants in this study were estimated by following the basic methodology suggested in the US EPA (1991). Since the methodology presented in the US EPA (1991) can only be applied to a single pollutant system, equation (11) was derived (based on combined oral and dermal exposure routes of this study) for a multi-pollutant system as follows:

\[
\text{Target risk (TR)} = \frac{\text{K}_O}{\text{Rfd}_O} + \frac{\text{K}_{\text{ABS}}}{\text{Rfd}_{\text{ABS}}} \quad \text{for the case of non-cancer risk}
\]

\[
\text{K}_O = \frac{1}{\text{Rfd}_O} \quad \text{and} \quad \text{K}_{\text{ABS}} = \frac{1}{\text{Rfd}_{\text{ABS}}} \quad \text{for the case of cancer risk}
\]

\[
\text{C}_{\text{PRG}} = \left[ \frac{\text{TR}}{\text{EF} \times \text{ED} \times \text{BW} \times \text{ATx}_i} \right] \left( \frac{\text{EF} \times \text{IR} \times \text{K}_O + \text{FA} \times \text{K}_P \times \text{K}_1 \times \text{EV} \times \text{SA} \times \text{K}_{\text{ABS}}}{\text{CF} \times \text{IR} \times \text{K}_O + \text{FA} \times \text{K}_P \times \text{K}_1 \times \text{EV} \times \text{SA} \times \text{K}_{\text{ABS}}} \right)
\]

\[
\text{TR} = \text{CDI} \times \text{K}_O + \text{DAD} \times \text{K}_{\text{ABS}}
\]

Substituting Eqs. (1) and (2) in Eqn. (10) produces Eqn. (11)

\[
\text{C}_{\text{PRG}_i} = \left[ \frac{\text{TR} \times \text{BW} \times \text{ATx}_i}{\text{EF} \times \text{ED} \times \left( \text{CF} \times \text{IR} \times \text{K}_O + \text{FA} \times \text{K}_P \times \text{K}_1 \times \text{EV} \times \text{SA} \times \text{K}_{\text{ABS}} \right)} \right]
\]

Where

\[
\text{K}_O = \text{CSF}_O \quad \text{and} \quad \text{K}_{\text{ABS}} = \text{CSF}_{\text{ABS}}
\]

3. Results and discussions

3.1. Site characterization

Table S5 shows the detailed concentrations of toxic aromatic compounds detected in five different monitoring wells (MW) from June 2016 to June 2018. The major sources of benzene, toluene, ethylbenzene, xylenes, and naphthalene (BTEXN) could be gasoline and diesel fuel, as initially reported by Nambi et al. (2017). In cases of high volume spills, these petroleum fuels are infiltrated through the vadose zone, comfortably overcoming the capillary forces, and are migrated vertically down to the groundwater table, as observed at the present investigated site. This resulted in the introduction of high levels of toxic pollutants such as benzene, toluene, ethylbenzene, xylene, and naphthalene, directly to groundwater and, eventually polluting the groundwater significantly. Unlike the Indian scenario, the US EPA listed four of these pollutants (B, T, E, and N) separately in the priority pollutants list owing to their significant toxicity. BTEXN concentrations of polluted groundwater varied between (min and max): 8.9 and 3566 µg/L for benzene, 13.9 and 3020 µg/L for toluene, 10.6 and 2225 µg/L for ethylbenzene, 10.6 and 11285 µg/L for xylenes, and 10.0 and 514 µg/L for naphthalene (Table 1). The US EPA, allowable limits for the BTEXN in drinking water, were 5, 1000, 700, 10000, and 100 (µg/L) for benzene, toluene, ethylbenzene, xylene, and naphthalene respectively (Table S6). It can be seen that the maximum concentrations of BTEXN in groundwater (associated with the current site) were found to exceed the permissible limits substantially (Table 1). This clearly shows that the current site was critically contaminated, and groundwater is not suitable for safe use. The concentration of xylenes, shown in Table 1, was represented for mixed xylenes (m-xylene, o-xylene, and p-xylene together). Benzene recorded the second highest concentration (3566 µg/L) which could be due to its high water solubility compared to all other compounds (Table S6). The maximum contaminant level (MCL) or the permissible limit of benzene was observed to be very low (5 µg/L), suggesting that it is a highly toxic one among BTEXN (Table S6). Even the minimum concentration of benzene (8.9 µg/L) detected in groundwater was found to exceed its MCL. Toxic health effects related to exposure to benzene at various doses have been reviewed and summarized in Table S7. These results were based on subchronic and chronic oral exposure studies on test animals. The exposure dose of benzene on test animals was ranged between 8 and 358 mg/kg-day. Compared to BTEX compounds, the lowest concentration range was found for naphthalene (10–514 µg/L) in groundwater. This is because, unlike the BTEX compounds, naphthalene is a polycyclic aromatic compound having a higher molecular weight (MW) and fused aromatic rings. Such high MW compounds are relatively less water soluble compared to low MW compounds such as BTEX (Table S6). US EPA (2018) had not given MCL for naphthalene, but the lifetime
(cumulative) standard was documented. Closer to the source (MW2 and MW3), even one-time field concentrations found for naphthalene is at par with the standard lifetime value (100 µg/L). Hence care should be taken before using this groundwater for various purposes. The toxic effects of naphthalene at different exposure doses were summarized in Table S8. If we look at the mean concentration values of naphthalene (Table 1) at the site, they are much below the minimum dose levels of naphthalene used in toxicity studies.

In the present study, to consider heterogeneities associated with in-situ groundwater aquifer, arithmetic mean (AM), geometric mean (GM) and harmonic mean (HM) values were estimated for various concentrations (Fig. S2). GM and HM values were found to be significantly different from standard arithmetic mean (AM) values. Mathematically, AM represents the condition of the isotropic and homogenous aquifer, which seldom occurs in the real field. In reality, there hardly exists such an aquifer with the so-called homogenous and isotropic properties. On the other hand, GM and HM represent different kinds of heterogeneity in the aquifer (Berg and Illman, 2011; Lachassagne et al., 1989). The relatively higher AM values compared to GM and HM were attributed to the effect of the outlier concentration points that occurred in September 2016 and March 2017 (in source wells MW2 and MW3) where concentrations were found highest (Table S5). It was also observed that the concentration of each compound varied by orders of magnitude (2–4 orders). In such a condition of high variability in the distribution of data, the most appropriate central tendency estimate was the geometric mean rather than the arithmetic and harmonic means (Berg and Illman, 2011). The choice of an appropriate mean value also has its implications for the management decisions on remediation process, design, and cost estimation. The consideration of GM will have a relatively low and fair cost estimation for the remediation process compared to the arithmetic mean that has higher concentration values. Out of the GM and HM, the consideration of HM will underestimate both health risk and remediation costs due to the lowest concentration values. Hence for the management of any contaminated aquifer, it is advisable to apply GM rather than HM values.

Fig. 1 shows the concentration of the total aromatics (sum of B, T, E, X, and N concentrations) from June 2016 to June 2018 in the five monitoring wells (MW). MW2 and MW3 are the closest downstream wells to the source location where the oil pipeline is believed to have broken, while MW4 and MW5 are farthest downstream wells, as indicated in Fig. S1. The concentration of total aromatics was dominant (greater than 12000 µg/L) in MW2 and MW3 during September 2016. Beyond March 2017, concentrations were observed to be decreased and ranged from 21 to 1350 µg/L in MW2 and 748–3434 µg/L in MW3 (Fig. 1). This reduction in concentration may be attributed to the dilution effect following heavy rainfall in Chennai due to cyclone Vardah during December 2016 (Pattanaik, 2016). In the distant downstream wells of MW4 and MW5, the concentration of the total aromatics ranged from 39 to 1389 µg/L and 83–2076 µg/L respectively between June 2016 and June 2018. The time-averaged concentrations (calculated as geometric mean of all nine sampling events) of total aromatics over the two years were estimated to be ~773, 1217, 1244, 311 and 544 (µg/L) in MW1, MW2, MW3, MW4, and MW5 respectively. As expected, MW2 and MW3 contain relatively high concentration of total aromatics among all wells, as they may be located in close proximity to the source. MW4 and MW5 were located away from the source. As a result, low average concentrations were found in these wells. In Sep 2016, the concentrations of total aromatics in MW4 and MW5 were found to be ~40 µg/L and ~138 µg/L, respectively, the lowest values of all the monitoring wells. After Sep 2016, the concentration in MW4 and MW5 began to rise (Fig. 1). This increase in concentration indicates that the pollutants could have been slowly transported (along with the groundwater flow) by the advection mechanism from the source point to the regions of MW4 and MW5. This rise in concentrations also suggested the possibility of continuous release of fuels. Apart from the convection mechanism, local pumping gradients (due to groundwater abstraction), LNAPL properties, and subsurface characteristics (such as subsurface heterogeneity, relative permeability, wettability, and saturation) would strongly influence the transport of these pollutants in the aquifer.

Past studies that reported concentrations of benzene (B), toluene (T), ethylbenzene (E), xylenes (X) and naphthalene (N) in different aquifers in the world were B: 7.58E-04 µg/L; E: 1.07E-04 µg/L; L: 1.53E-04 µg/L and X: 89.0 µg/L (Maurice et al., 2019); T: 0.09 µg/L; X: 0.01 µg/L and N: 0.06 µg/L (Kavcar et al., 2006); B: 1.53 µg/L; T: 1.76 µg/L; E: 2.11 µg/L and X: 0.30 µg/L (Zhang et al., 2016); B: 138 µg/L (Senthil kumar et al., 2017); T: 0.33 µg/L; L: 1.182 µg/L; E: 0.109 µg/L and X: 0.143 µg/L (Maurice et al., 2019); T: 1.01 µg/L; E: 8.04 µg/L and X: 89.0 µg/L (Tieyu et al., 2014) (Table S1). Compared to the previous studies, higher concentrations of BTEXN in aquifers are also influenced by local geology and land use pattern. The geology of the Tondiarpet consists of sandy layers up to ~12 m with a water table normally

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Mean, minimum and maximum concentration of BTEXN in ground water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name of the compound</td>
<td>Geometric mean (µg/L)</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Benzene</td>
<td>221.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>63.6</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>148.9</td>
</tr>
<tr>
<td>Xylenes</td>
<td>285.3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>49.0</td>
</tr>
</tbody>
</table>

Fig. 1. Total concentration of aromatics in each monitoring well from June 2016 to June 2018.
encountered at smaller depths (~8–9 m). Sandy soils were known to be more porous and would allow for greater penetration of petroleum products unlike that of clay soils which are low permeable and protective. As a result of sandy soils immediately above the water table, the groundwater in Tondiarpet was highly susceptible to petroleum contamination resulting in a high concentrations of BTEXN. When the water table sinks during the summer season, the oil containing BTEXN compounds will migrate to the deeper soil layers of the aquifer. There is a 6–12 m thick clay layer beneath the sandy layer in the study area (Nambi et al., 2017). BTEXN compounds tend to bind to the clay layer through adsorption and slowly undergo dissolution into the groundwater (Zytnier, 1994). Therefore, BTEXN pollution in the sample region is expected to persist for a number of years. Waterbodies contaminated with petroleum hydrocarbons (PHCs) such as BTEXN are typically resistant to self-cleaning process due to the persistent nature of the PHCs. Consequently they continue to accumulate in to soil, water and can enter the human body through various exposure pathways leading to potential health risks.

3.2. Risk assessment

3.2.1. Deterministic risk assessment

As discussed in the previous section, the geometric mean concentration reported for each pollutant from the wells was used for the deterministic risk assessment. The pollutant concentrations used in risk models were 221.8, 63.6, 148.9, 285.3, and 49.0 (μg/L), respectively, for benzene, toluene, ethylbenzene, xylenes, and napthalene. Cancer and non-cancer risk assessments were performed for four different age groups in the population with different exposure variables (Table 2). The average incremental risk of developing cancer was found to be 5.98E-05 (~60 in 1 million), 4.52E-05, 5.14E-05 and 2.96E-04 for age groups 0–5 years, 6–10 years, 11–18 years and 19–70 years respectively for oral and dermal exposure combinations. US EPA generally considers 1E-04 and 1E-06 to be the upper and lower limits of acceptable cancer risks, but the choice depends on a case-by-case basis and on a nation-by-nation basis (ITRC, 2005; Kelly, 1991; Paweiczzyk et al., 2018; US EPA, 2015). For example, in order to protect most population from cancer effects, the US EPA explicitly recommends 1E-04 and 1E-06 to be the upper and lower limits of acceptable cancer risks, but the choice depends on a case-by-case basis and on a nation-by-nation basis (ITRC, 2005; Kelly, 1991; Paweiczzyk et al., 2018; US EPA, 2015). For example, in order to protect most population from cancer effects, the US EPA explicitly recommends 1E-04 and 1E-06 to be the upper and lower limits of acceptable cancer risks, but the choice depends on a case-by-case basis and on a nation-by-nation basis (ITRC, 2005; Kelly, 1991; Paweiczzyk et al., 2018; US EPA, 2015). For example, in order to protect most population from cancer effects, the US EPA explicitly recommends 1E-04 and 1E-06 to be the upper and lower limits of acceptable cancer risks, but the choice depends on a case-by-case basis and on a nation-by-nation basis (ITRC, 2005; Kelly, 1991; Paweiczzyk et al., 2018; US EPA, 2015).

The estimated cancer risks for receptors in 0–18 years agegroup was found to be less than 1 in 10,000, which indicates an acceptable risk (Table 2). However, the estimated risks are still not sufficiently protective since the values are one to two orders of magnitude greater than 1E-06, the safest acceptable limit. At the otherhand, the cancer risk in adults was found to be higher than 1E-04, which is completely unacceptable in nature. Hence the associated health consequences cannot be taken to be neglected. The mean total hazard quotients (Oral + dermal) for all age groups were found to be varied from 2.14 to 4.61. The hazard quotient (HQ) values exceeded the US EPA safety hazard quotient of one (Table 2), implying a risk of occurring non-cancer adverse health effects due to BTEXN in groundwater. In the case of cancer risk, oral ingestion accounted for 60%–71% of the total risk, while the dermal route accounted for 29–40% for all age groups (Fig. 53). Although the contribution of dermal exposure to cancer risk was relatively low, the dermal cancer risk was found to be much higher than the allowable risk of 1-in-10,000 in adults (Table 2). This implies that both exposure routes have the potential to cause cancer health effects, with the oral route being the highest. In the case of non-cancer risk, the percentage contributions of oral and dermal exposure routes were 71–80% and 20–29%, respectively (Fig. 53). In all age groups, the HQ values for dermal exposure were less than the safety limit of one, while for oral exposure, HQ exceeded one (Table 2). This represents that the non-cancer health consequences could be totally developed by drinking water ingestion rather than skin contact with contaminated groundwater.

It was estimated that benzene cancer risk accounted for 48%–52% of total cancer risk, whereas ethylbenzene and napthalene accounted for 11% and 37%–40% of the total cancer risk respectively (Table 59). Similarly, in the non-cancer risk category, benzene had the highest hazard quotient in each age group and thus accounted for 84%–86% of the total non-cancer risk (Fig. 54). Remaining four compounds (TEXN) together contributed to just 14%–16%. Since the benzene and napthalene were predominantly contributing to the health risk (both cancer and non-cancer), these can be regarded as critical compounds of all five aromatic compounds. It may be noted that the xylenes concentration in groundwater was comparatively high, but the contribution to the health risk was much smaller (~4%). This was due to xylenes having the least toxicity as indicated by the highest reference dose which outweighed the concentration effect on the health risk (Table 54).

In Table 2, the results were represented for the condition of average exposure duration in each population group (For e.g., ED: 2.5 years in 0–5 year age group; 26 years in 19–70 year age group). This treatment cannot provide the actual sensitive receptors of health risk because of the unequal exposure duration. In order to find true sensitive receptors, risk calculations were repeated in all age groups for an equal exposure duration of 3 years as a real-time exposure assessment. It can be noted that cancer risk value was found to exceed the US EPA safety value of 1E-06 even with a shorter period of exposure of 3 years, especially for teenagers and adults (Table S10). Children under the age of five were found to be the most susceptible age group. The cancer risk and non-cancer risks of the 0–5 year age group are 2.1 times higher than the adults’ risks (19–70 years). This implies that children at the spill site in Tondiarpet are two times more sensitive than adults on exposure to the same concentration levels of BTEXN compounds and for the same period of exposure. Both the total cancer risk and the total hazard quotient have a decreasing trend with an increase in population age (Table S10). It is conclusive that the probability of a person getting adverse health impacts is inversely proportional to the age when they get exposed to this spill for the same exposure

<table>
<thead>
<tr>
<th>Table 2</th>
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<tr>
<td>Point value estimates of cancer risks and total hazard quotients for exposure to BTEXN.</td>
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<td>Age group (years)</td>
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<td>19 to 70</td>
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duration. Results from this study are in accordance with previous risk assessment studies. In the studies by Zhang et al. (2016), risk exceeded the allowable limits despite the concentrations of BTEX were lower than MCLs. Senthi kumar et al. (2017) found that children were sensitive receptors than adults for exposure to the same concentration levels of benzene.

3.2.2. Probabilistic risk assessment

The conventional use of constant values for input parameters in the deterministic method and conservative assumptions in the risk models would either overestimate or underestimate the true risk. The exposure variables such as body weight, exposure frequency, exposure duration, ingestion rate, and skin surface area of the individuals vary randomly across the exposed population. The use of Monte Carlo simulations takes into account the inherent randomness associated with all input variables by using the most appropriate probability distributions, and hence they can provide more meaningful results of risk. Log-normal distributions were assigned to input variables of body weight, event, skin surface area, and drinking water ingestion rate. Exposure frequency and Exposure duration were assigned with triangular and uniform distributions respectively (Table S3). These defined probability distributions were observed to be the most frequently employed in the literature for such variables (Burmaster and Crouch, 1997; Ganyaglo et al., 2019; Qu et al., 2015; Sarria-Villa et al., 2016; US EPA, 2001). Numerical stability was achieved much before 500 iterations during the process of simulations.

The probability distributions of carcinogenic and non-carcinogenic risks arising from exposure to BTEXN at the current study site were presented in Figs. 2 and 3 for all age groups, respectively. Unlike in point estimates, it can be noticed that the output risks were obtained as a range of values varying from minimum to maximum. The mean cancer risks and mean hazard quotients were identified at various percentile positions in the output risk distributions (Table 3). For instance, the mean cancer risk of 5.98E-05 in the 0–5 year age group was found at a position of 68.7th percentile in the output cancer risk distribution (Table 3). It implies that the cancer risk exceeds the estimated mean value of 5.98E-05 for only 31.3% (100–68.7) of the exposed child population (0–5 years). It also means that the cancer risk is below the estimated mean value for the remaining 68.7% of the child population. Similarly, the mean HQ of 4.61 for the 0–5 year age group was found to be 72.9th percentile in non-cancer risk distributions (Table 3). It indicates that the HQ value was below 4.61 for ~73% of the exposed child population. The conventional deterministic method cannot furnish this kind of information on the basis of point risk estimates. By applying the Monte Carlo simulations, it was possible to find the extent of applicability of the point value mean risks. In the remaining age groups, the mean hazard quotients were found at 74.3rd, 74.5th and 82.1st percentiles for 6–10 years, 11–18 years, and 19–70 years respectively.

Mean risks reflect the most probable risk under chronic exposure conditions, taking into account the average values of all input parameters. However, as shown in Figs. 2 and 3, the output risks were found to be varied from minimum to maximum. The minimum cancer risk values were predicted to be 1.65E-09, 3.23E-09, 2.86E-09 and 3.39E-08 and the maximum cancer risk values were 3.13E-04, 1.79E-04, 2.70E-04, 1.12E-03 for age groups 0 to 5, 6 to 10, 11 to 18 and 19–70 years respectively (Fig. 2). Minimum cancer risk values were less than the US EPA allowable risks of both one-in-one million and one-in-a-thousand, thereby indicating a slight possibility of acceptable health risks in a few receptors despite the exposure to contamination. However, maximum cancer risk values were observed to be greater than the high-end acceptable risk of 1E-04. For non-cancer risk, the HQ varied (min to max) from 0.62 to 14.78, 0.58 to 8.20, 0.46 to 6.78, and 0.37 to 5.17 for age groups of 0–5 years, 6–10 years, 11–18 years and 19–70 years, respectively (Fig. 3). Maximum HQ values were observed to be ~5 to ~15 times greater than the US EPA allowable HQ of 1. Maximum risk corresponds to the acute chronic exposure condition, which entails the maximum values of all input variables in the risk models used for exposure assessment. This condition of maximum exposure is least likely to occur in the field and thus the maximum risks can be potential overestimates. Hence, 95th percentile risk value was emphasized as a useful high-end parameter in risk assessment guidance for decision making related to the management of contaminated sites (US EPA, 2001).

In order to estimate the proportion of the population free from cancer risk of benzene, ethylbenzene, and naphthalene, the percentile values of the US-EPA acceptable risks (1E-06 and 1E-04) were predicted for all age groups (Table 3). The percentages were 90.6% (0–5 years), 97.2% (6–10 years), 94.6% (11–18 years) and 27.2% (19–70 years) for 1E-04 larger risk. For example, a value of 27.2% (for 19–70 years) indicates that if a group of adult receptors were randomly exposed to BTEXN contamination at the site, there would always be 72.8% (100–27.2) of the likelihood that the cancer risk would exceed the safety limit of 1E-04. The corresponding percentile values for 1E-06 safety risk are 1.2%, 1.5%, 1.5% and 0.3% for the four studied age groups, respectively (Table 3). Similarly, in the non-cancer risk category, the percentile positions of the US EPA allowable HQ of 1 were identified at 0.3rd (0–5 years), 1.1st (6–10 years), 8.7th (11–18 years) and 17.3rd (19–70 years) percentiles (Table 3). Children of age group 0–5 years consist of a high percentage of the population (99.7% (100–0.3)) with the possibility of non-cancer health hazard occurrence.

The 5th and 95th percentile values of cancer and non-cancer risks were presented in Figs. 2 and 3 (shown as triangular marker points). It was predicted that the 95th percentile values of cancer risk and HQ exceeded the US EPA safety risks of 1E-04 and 1 respectively for the four age groups (Figs. 2 and 3). For example, in the least sensitive age group of adults, the 95th percentile was determined to be 5.22E-04 for cancer risk (Fig. 2d) and 2.90 for non-cancer risk (Fig. 3d). The 95th percentile value is known as the reasonable maximum exposure (RME) based on which remediation decisions must be made. If the RME values of the cancer risk or the hazard quotient are found unacceptable, the contaminated site is to be remediated according to the regulatory guidelines (US EPA, 2001, 1991). Even the low-end exposure estimates (5th percentile values) of cancer risk were found to be greater than 1E-06 in four age groups indicating the severity of the contamination levels and the need to expedite the remedial measures to be taken without further delay.

The results of the deterministic and probabilistic approaches were compared in Table S11. As can be observed, the deterministic approach produced a single output while the probabilistic approach generated a wide range of risk values (minimum to maximum) by accounting the data variability and uncertainty. Although both approaches provided details of sensitive agegroups and critical compounds, the vital information such as percentage of vulnerable population, remediation decisions, reasonable maximum exposure estimates and sensitive input variables was derived using the probabilistic method. As a result of this extended output from the probabilistic approach, the health risk to residents can be better regulated than the output of the deterministic approach.

3.2.2.1. Sensitivity analysis

Sensitivity analysis was performed in order to quantify the degree of impact of each random variable on the total health risk. The results from the sensitivity analysis were presented for the total cancer risk (Fig. S5) and non-cancer risk.
using the spearman rank correlation coefficient as an indicator for the assessment. Of the various input variables, exposure duration (ED) was found to be the highest-ranking variable indicating the most influential parameter of health risk, while surface area (SA) was found to be the least influential parameter among all age groups in the cancer risk category. On the other hand, the non-cancer risk was highly influenced by the ingestion rate variable with a coefficient value ranging from 0.83 to 0.88 (Fig. S6) followed by the body weight (BW). ED was the least sensitive variable with a coefficient value of 0.01. In the studies of the health risk due to BTEX in petroleum-contaminated groundwater by López et al. (2008), the parameter ingestion rate was reported to be predominantly contributing to the health risk. However, the work by López et al. (2008) did not consider the impact of other important variables, such as BW, EF, and ED on health risk of which the current study had addressed. In the present study, the variable ED had shown a significant effect on the cancer risk and a negligible effect on the non-cancer risk. This contrasting nature of ED can be explained mathematically based on the parameter averaging time (AT) used in health risk models (Eq. (1) and (2)). The value of AT is a lifetime constant (25550 days) for cancer risk whereas for non-cancer risk, AT was defined as ED x 365 (US EPA, 2004, 2001). When applying Eqs. (1) and (2) specifically for non-cancer risk, the ED variable gets cancelled out in numerator and denominator, making its overall effect negligible. BW variable exhibited a negative correlation to health risk, unlike other variables. This means that receptors of heavier bodyweight would be experiencing higher health risks when compared to lighter bodyweight receptors.

### 3.2.3. Risk based preliminary remediation goals

Preliminary remediation goals (PRGs), also known as site-specific target levels, represent the cleanup concentrations to be achieved in any proposed remediation technique at contaminated sites, such that the overall health risk on the residents would eventually become insignificant. Since the RME values (95th percentiles) of the estimated risks for all age groups exceeded the US EPA allowable risks (Figs. 2 and 3), there is an immediate need to remediate the current site in order to reduce the BTEXN concentrations to lifetime safe exposure levels in groundwater. Hence the PRGs were estimated for each compound by considering three target risks such as HQ = 1 (non-cancer risk), 1E-04 and 1E-06 cancer risks using the exposure parameters of the sensitive receptor group (0–5 years). To obtain more conservative estimates of site cleanup concentrations, optimum values of exposure parameters (maximum values of ED, EF, SA, IR, and minimum value of BW) were given input to Eq. (11). Table S12 presents three different sets of PRGs, obtained based on the three different allowable risks. The PRGs for 1E-04 allowable cancer risk were predicted to be 10.4, 7.2
and 2.4 μg/L; whereas for 1E-06 allowable risk, the PRGs were 0.104, 0.072 and 0.024 μg/L for benzene, ethylbenzene and naphthalene respectively. The PRGs based on HQ = 1 were estimated to be 2.71, 0.78, 1.88, 3.60 and 0.623 μg/L for benzene, toluene, ethylbenzene, xylenes, and naphthalene respectively. For the most safe exposures, lowest PRGs must be chosen for any remediation process. Hence the final PRGs were considered to be 0.104, 0.078, 0.072, 3.60 and 0.024 μg/L for BTEXN compounds respectively. These values account for nearly 99.95%, 98.77%, 99.95%, 98.74% and 99.95% of the reduction in concentration of BTEXN from their respective mean initial concentrations. The PRGs for BTEXN obtained in this study appear to be highly conservative (1–3 order of magnitude lesser) than the respective drinking water standards prescribed by the US EPA (2018). This is because certain guideline values of US EPA (2018) were reported based on 1E-04 cancer risk, while in this study, the lowest PRGs were calculated based on 1E-06 (highly conservative) cancer risk based on combined exposure routes. This suggests that policies for setting the drinking water standards may have to be evolved further to more conservative limits, which can be on the basis of detailed risk assessment.

**Table 3** Percentile positions of mean CR, mean HQ and US EPA safety risks in output probability distributions.

<table>
<thead>
<tr>
<th>Age group (years)</th>
<th>Positions of mean CR</th>
<th>Positions of mean HQ</th>
<th>Positions of US EPA safety risks</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mean CR&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Percentile</td>
<td>Mean HQ&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>0 to 5</td>
<td>5.98E-05</td>
<td>68.7th</td>
<td>4.61</td>
</tr>
<tr>
<td>6 to 10</td>
<td>4.52E-05</td>
<td>67.4th</td>
<td>3.35</td>
</tr>
<tr>
<td>11 to 18</td>
<td>5.14E-05</td>
<td>69.0th</td>
<td>2.36</td>
</tr>
<tr>
<td>19 to 70</td>
<td>2.96E-04</td>
<td>73.6th</td>
<td>2.14</td>
</tr>
</tbody>
</table>

<sup>a</sup> CR: Cancer risk.

<sup>b</sup> HQ: Hazard quotient.

Fig. 3. Frequency distributions of total non-cancer risk (Dermal + oral) for exposure to BTEXN in ground water (a) 0–5 years (b) 6–10 years (c) 11–18 years (d) 19–70 years.
(Table 1) were found to be similar to the ranges reported for many of the contaminated sites listed in Table S13. Some of the effective in-situ remediation techniques were found to be air sparging, air sparging combined with soil vapor extraction and in-situ chemical oxidation with ozone. In addition, ex-situ treatment methods such as adsorption, advanced oxidation processes, including UV/H2O2, ozonation, electrochemical oxidation, and aeration, had also shown better removal efficiencies (Table S14).

4. Suggestions from this study

Based on the results from this study, the following risk mitigation measures may be suggested: a) completely avoiding oral exposure; b) minimizing exposure duration in the case of inexorable usage of water; c) prioritizing the removal of critical pollutants in the remediation. This study could be the basis for future epidemiological studies to determine the BTEXN levels in human blood and establishing the relationships between concentrations in blood and environmental samples in the study region. In addition, environmental regulators and risk assessors can focus on gathering health data from on-site residents on a regular basis in order to establish the associations between real concentrations and suspected toxic health effects. This will enable speeding up of remediation in groundwater impacted areas and developing policy and framework for implementation of regulatory norms.

4. Conclusions

In the present study, we have detected the impermissible levels of hazardous compounds such as BTEXN in an urban aquifer, contaminated due to a petroleum pipeline leakage. The aquifer, located in a dense residential area, is a major water source for the local population. A detailed health risk assessment of human receptors showed that mean cancer and non-cancer risks could be highly unacceptable due to BTEXN exposure. Among the four age groups of interest, kids (0–5 years) were found to be the most sensitive receptors of health risk. Even for a shorter exposure duration of 3 years, the health risk for BTEXN was estimated to be unsafe, signifying the immediate need for remedial action in the study area. Reasonable maximum exposure estimates have also confirmed the necessity of remediation. Benzene and naphthalene together accounted for ~89% of total risk indicating the critical pollutants. These results suggested that, under the circumstances of the limited resources for remediation (e.g., funds, time), targeting these critical compounds can eliminate the health risk to a greater extent.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2020.114814.

References


