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Quantification of benzene in groundwater sources and risk analysis in a popular South Indian Pilgrimage City – A GIS based approach

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Abstract The present research work quantified the concentration of benzene in a total of hundred groundwater samples at the proximity of petrol bunks and residential places in Madurai District. The average values recorded in Jan 2011, Feb 2011 and Mar 2011 were 0.100 mg L^{-1} (10 times of PL), 0.138 mg L^{-1} (14 times of PL) and 0.060 mg L^{-1} (6 times of PL) respectively. A significant variation in the benzene level during February–March 2011 was validated through Student's *t*-test analysis. Hierarchical cluster analysis using dendograms revealed the un-symmetric distribution of benzene during the study period. The cancer risk analysis at corporate locations among children was seven folds higher as compared to the risk of adults. The benzene concentration levels are interpreted using Arc Geographical Information System (Arc GIS) through thematic maps.

1. Introduction

BTEX (benzene, toluene, ethylbenzene and xylenes), the defined priority pollutants by USEPA (Frazer et al., 1995; Phelps and Young, 1999) are widespread contaminants of groundwater and soils. They have been widely used as industrial solvents and are constituents of fossil fuels. Dispersion of these volatile and water soluble chemicals may be frequent and possible due to accidents, transportation and storage tank leakages (Deeb et al., 2000; Baehr et al., 1999; Squillace et al., 1996; Pawlowski, 1998). They represent a threat to human health and ecosystems because of their toxicity (ATSDR, 2004). Primary local sources of BTEX are on-road and non-road gasoline vehicles and engines, with emissions from petroleum transport/storage and solvent usage also making substantial contributions (USEPA, 2005). Association of BTEX concentrations consistent with high traffic density was reported by earlier researchers (Wheeler et al., 2008; Bruno et al., 2006; Kwon et al., 2006; Kerner et al., 2010). Among the hydrocarbons, benzene is a liquid hydrocarbon with the formula C_6H_6. At ambient temperatures it evaporates

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rapidly and is highly flammable. It has a characteristic aromatic odor and is slightly soluble in water (1.5 g/L at 20 °C). Although benzene is found in crude petroleum (~4 g/L), the main source of benzene in groundwater is due to human activities. Benzene is naturally broken down by chemical reactions in the atmosphere. The residence time of benzene vapor in air varies between a few hours and a few days depending on certain other factors such as climate and the concentration of other chemicals in air, such as nitrogen and sulfur dioxides. Benzene can be removed from air by rain, leading to the contamination of surface water and groundwater. However, due to its volatility, benzene does not remain in water for more than a few hours. Mobility of benzene in soil leads ultimately into groundwater where its degradation rate is very slow by anaerobic bacteria between weeks and months. Benzene, a well known environmental and occupational carcinogen finds its origin from habitual active smokers. However, its exposure for non-smokers is derived from auto exhausts inhaled from the outdoor. The present concentration limit established by the United States Environmental Protection Agency and the German guideline value is 1 μg L^{-1} for benzene in drinking water (USEPA, 2005). Risk assessment is one of the fastest evolving tools to evaluate the impact of the hazards on human health and to determine the level of treatment required to solve a specific environmental problem (Asante-Duah, 1993; LaGrega et al., 1994). Pollutants are usually classified as carcinogens and non-carcinogens for estimating their human health risks. To better evaluate the health risks, long-term measurement of pollutants is needed. Research studies prompted that the on- and off-site contamination of groundwater, soil and surface soil due to benzene can cause cancer mortality and birth defects (Logue and Fox, 1986). The groundwater contamination due to petroleum industries was already reported from Love Canal (Paigen et al., 1987), Superfund site, Pennsylvania (Budnick et al., 1984) and New Jersey (Najem et al., 1994). Evidently, Delhi Pollution Control Committee (DPCC) point toward benzene hotspots in heavy traffic locations and around refueling stations in Delhi. Petrol pump workers, dealers and vehicle users are at serious risk of exposure due to the volatile nature of benzene. Along with big cities like Delhi (Roychoudhury, 2012), Kolkata (Basu, 2010) and Mumbai (Chattopadhyay, 2007) cities like Bengaluru, Kanpur and Pune have reported detrimental levels of benzene in the atmosphere. Residents of Kudikkadu in Cuddalore District, Tamil Nadu complained headache, dizziness, rashes and chest pains due to the highly polluting industries which use organic solvents including benzene for the manufacture of pesticides, paints, dyes and pharmaceuticals (Anonymous, 2007). Benzene level more than 50 times of USEPA was quantified at Kodungaiyur of Chennai District in Tamil Nadu (The Hindu, 2012).

In the recent days, GIS has been widely used in risk mapping (Singh and Lawrence 2007; Singh et al. 2007; Khalifa and Arnous, 2012; Arnous et al., 2011; Ghodeif et al., 2011) and has become an integral and indispensable component of many comprehensive environmental modeling systems. Groundwater pollution vulnerability, risk and quality maps may be used to assist planners, managers, and local officials to evaluate the potential of contamination from various sources of pollution.

The present research work explored the possible contamination of benzene in the groundwater sources of Madurai District in Tamil Nadu, India at certain commercial and residential locations. Though this work was aimed at estimating BTEX in the groundwater sources, the chromatogram results with respect to benzene alone were detectable. Hence the authors realized the presence of benzene in groundwater and accordingly made interpretations using Arc GIS and Hierarchical cluster analyses.

2. Materials and methods

2.1. Details of the study area

Madurai, a world famous classic South Indian Pilgrimage City of more than 2500 years old is located at 9°58′N latitude and 78°10′E longitude and occupies an area of about 140 km^2 .This metropolitan city, situated on the banks of the River Vaigai, is the 24th largest town in India (population wise) and third largest in the state of Tamil Nadu after Chennai and Coimbatore. As per the 2001 census, the estimated population of the city of Madurai is 1,194,665.

2.2. Sampling and analysis

One hundred and twenty groundwater samples from bore well sources were collected in pre-cleaned bottles in the months of Jan 11, Feb 11 and Mar 11 from corporate and residential locations of Madurai District. The six corporate locations were Arasaradi (A), TPK road (TPK), Periyar Bus Stand (PBS), Theppakulum road (TR), North Veli Street (NVS) and KK Nagar (KKN) and the ten residential locations were Iyyar Banglow, Anna Nagar, Tirunagar, North Car Street, Kannadasan Street, SS Colony, Pudhur, Kochadai, Krishnapuram and Simmakkal. The collected samples were stored in the refrigerator (8–10 °C) before the estimation of BTEX. At the time of estimation, the chilled water samples were equilibrated to room temperature followed by vacuum filtration using a 0.4 μm filter paper. All the reagents were of HPLC grade purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany). The sampling spots of commercial and residential locations are shown in Fig. 1.

Benzene was estimated using High Pressure Liquid Chromatography (HPLC), Shimadzu Model SPD-M20A (Liquid Chromatography module 20AT) with class VP software. Standard solutions of benzene, toluene, ethyl benzene and xylene of 2000 mg L^{-1} were prepared and diluted to 500 mg L^{-1} (primary dilution standard) in acetonitrile (as per the certified standard mixture 1:4) and stored in amber colored bottle at 4 °C. Fresh aqueous working standard solutions were prepared daily by diluting the primary dilution standard solution in water of HPLC grade. After the zero correction was done, 20 μl of the standard was injected using a micro syringe (pre cleaned with isopropyl alcohol) with initially set run time of 20 min. From the knowledge of retention time (RT), the samples in triplicates were injected and the corresponding chromatograms were saved in the data path. A representative standard chromatogram for benzene, toluene, xylene and benzene–toluene–ethyl benzene mixture is given (Figs. S1 and S2). The BTEX concentration was estimated using the formula as follows.

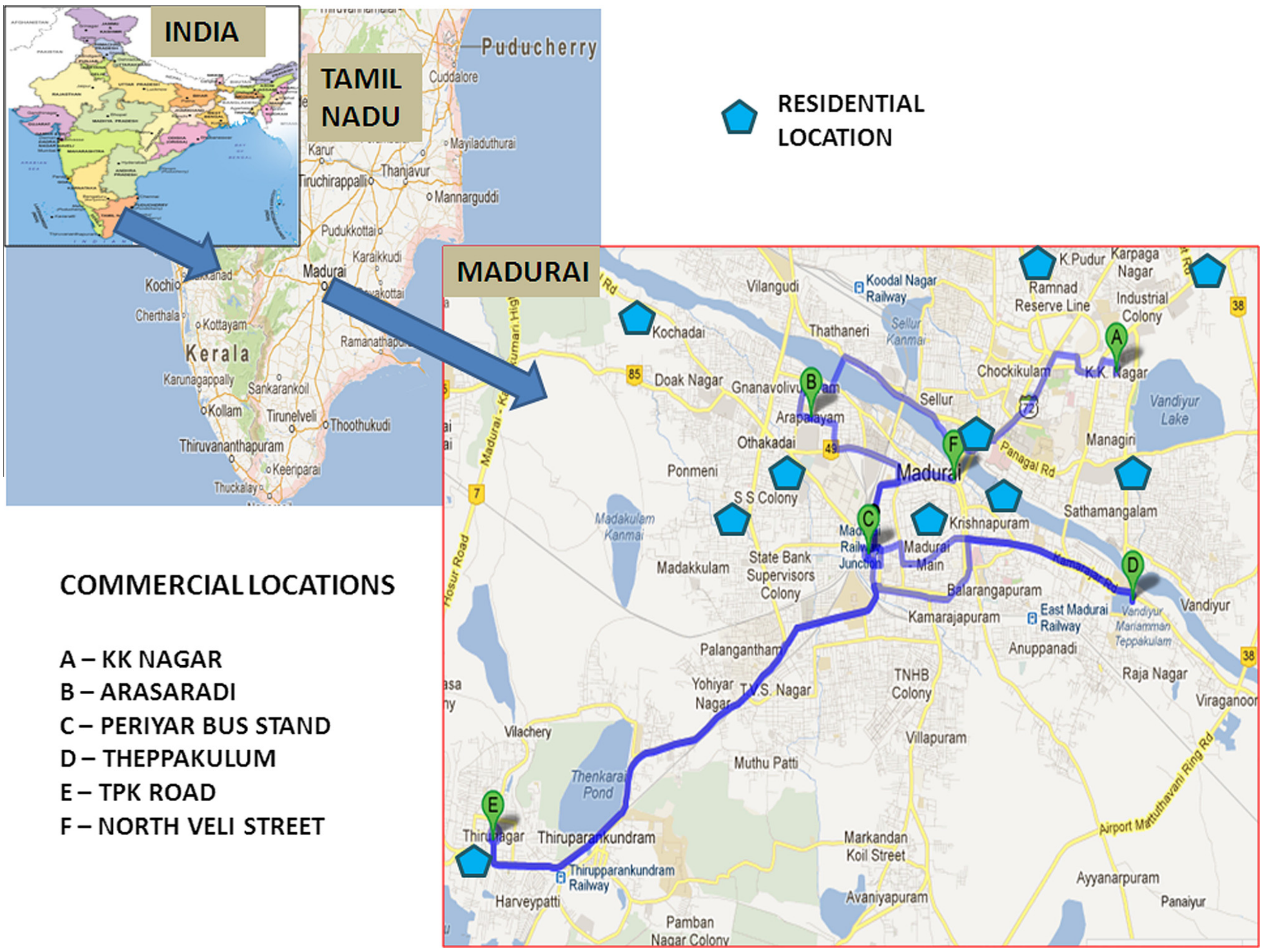

Figure 1 Details of groundwater sampling locations in Madurai District, South India.

$$\text{BTEX concentration} = \frac{\text{Area of the peak in the sample} \times \text{Concentration of the standard solution}}{\text{Area of the peak in standard solution}} \quad (1)$$

The total alkalinity of all the groundwater samples was estimated by the volumetric method using hydrochloric acid of 0.02 N and methyl orange as indicator.

2.3. Risk analysis

Risk assessment process is defined by a model which may use different mathematical and empirical models in arriving at the estimate of risk. A conceptual exposure model is derived by tracing the chemical from its source to the receptor. The life time risk for adults and children can be calculated using the formula given below. Chronic Daily Intake (CDI) was calculated for 70 years life time (mg kg^{-1} day^{-1}).

$$\text{CDI (for adults)} = [\text{Total Dose (mg)}/\text{Body Weight (70 kg)} \times \text{life time (days)}] \quad (2)$$

$$\text{CDI (for children)} = [\text{Total Dose (mg)}/\text{Body Weight (10 kg)} \times \text{life time (days)}] \quad (3)$$

2.4. Interpretation through statistical and GIS tools

In this study, hierarchical cluster analysis was used to group bore wells into separate clusters based on a similar benzene concentration. Although there are a number of hierarchical clustering techniques, all of which are not regularly applied the most widely used measure of ordering is Ward's criterion, which uses an analysis of variance approach that minimizes the sum of squares within the clusters and maximizes the variance between separate clusters (Ward, 1963). The results are represented via a dendrogram, or tree plot and are separated into different clusters. The sample locations are grouped on the vertical axis, and the linkage distances, representing the relative differences between clusters, are shown on the horizontal axis.

Geographic Information Systems (GIS) provide platforms for managing data, computing spatial relationships such as distance, connectivity and directional relationships between spatial units, and visualizing both the raw data and spatial analytic results within a cartographic context.

The GIS based analysis of the spatiotemporal behavior of benzene level in groundwater in the study area was done using the spatial analyst module of Arc GIS 9.3 powerful spatial analysis is feasible once the database is established. The interpolation technique used in the analysis is the inverse distance weighted (IDW) method. IDW is an algorithm for spatially interpolating or estimating values between measurements. Each value estimated in an IDW interpolation is a weighted average of the surrounding sample points. Weights are computed by taking the inverse of the distance from an observation location to the location of the point being estimated (Burrough and Mcdonnell, 1998). The inverse distance can be raised to a power (e.g. linear, squared, and cubed) to model different (e.g. line, area, volume) geometries (Guan et al., 1999). In a comparison of several different deterministic interpolation procedures, a squared distance term yielded results most consistent with original input data using IDW. This method is suitable for datasets where the maximum and minimum values in the interpolated surface commonly occur at sample points (ESRI, 2002). Toposheets were used to prepare the base map and to understand the general nature of the study area. GPS is used to map the location of each sampling well and finally the results were taken to GIS for further analysis.

2.5. Student's test for difference of means

A student's (t) test was carried out for testing the significant difference between the means of factors for Jan–Feb 2011, Feb–Mar 2011 and Jan–Mar 2011 periods against the left sided alternative hypothesis. The test statistic, which follows t distribution with $(n - 1)$ degrees of freedom, is given by

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{S_2(1/n_1 + 1/n_2)}} \quad (4)$$

where x_1 is the mean of variable of one month (January or February or March), x_2 is the mean of variable of another month (January or February or March), s_2 is the variance of combined sample, n_1 is the number of observations on variable of one month and n_2 is the number of observations on variable of another month. If the computed value is greater than the critical value, the difference is significant.

3. Results and discussion

3.1. Benzene contamination level at corporate locations

The benzene concentration levels estimated in the groundwater samples at different corporate locations in the months of Jan 2011, Feb 2011 and Mar 2011 are shown in Table. 1. The average values of groundwater samples at corporate locations were in the range of 0.016–0.041 mg L^{-1}, 0.060–0.099 mg L^{-1}, 0.026–0.138 mg L^{-1}, 0.044–0.100 mg L^{-1}, 0.030–0.099 mg L^{-1} and 0.028–0.057 mg L^{-1} for Arasaradi (A01–A05), Thirupparankundram road (TPK01–TPK05), Periyar Busstand (PBS01–PBS05), Theppakulam road (TR01–TR05), North Veli Street (NVS01–NVS05) and KK Nagar (KKN01–KKN05), respectively. A representative chromatogram for a groundwater sample is shown in Fig. S3. The recommended permissible level (PL) of benzene in groundwater by World Health Organization is 0.01 mg L^{-1}. The average values recorded in the months of Jan 2011, Feb 2011 and Mar 2011 were 0.100 mg L^{-1} (10 times of PL), 0.138 mg L^{-1} (14 times of PL) and 0.060 mg L^{-1} (6 times of PL), respectively. The groundwater samples PBS03 and A01 were estimated to be within the safe limit of World Health Organization (WHO) in Jan 2011 and Feb 2011, respectively. Fig. 2 depicts the recorded benzene concentrations (average values) at various sampling spots of Madurai District. From the estimated benzene levels, it was observed that 7% of samples in Jan 2011 decrease to 3% in Feb 2011 (Fig. 2) with respect to the samples recommended under the safe limit of WHO. But, in March 2011, no sample was recorded under the safe limit of WHO. Based on the permissible limit for drinking, prescribed by Environmental Protection Agency (EPA) and Canadian Council of Ministers of Environment (Canadian Council of Ministers of the Environment, 1999a,b), all the groundwater samples at corporate locations registered above the permissible limit of 0.005 mg L^{-1}. The fluctuating percentage levels in the three months with respect to CCME (fresh, marine and estuary aquatic lives) are shown in Fig. 5.

3.2. Benzene contamination level at residential locations

The groundwater samples from bore well sources were also identified with benzene contamination at 10 residential locations in Madurai District. Fig. 3 illustrates the average value of estimated benzene levels in bore wells at residential locations in the months of Jan 11, Feb 11 and Mar 11. In accordance with WHO guidelines, 20% of the residential samples were found to be fit for drinking. But, taking into account, the guidelines of EPA and CCME, the benzene concentration (0.005 mg L^{-1}) of groundwater samples in all the residential locations exceeded the recommended limit. The recommended quality criteria by CCME (for fresh aquatic, marine and estuary lives) reveal that 90% of the residential groundwater samples were found to be under the permissible limit (Fig. 4). The percentage of groundwater samples within the prescribed limit of WHO and CCME was greater in the residential locations than that in the corporate locations. In both the locations, no sample was registered within the prescribed drinking limit (USEPA) of 0.005 mg L^{-1}. The fluctuations in the benzene concentration levels with respect to months may be attributed to the natural attenuation (Lee and Lee, 2003). Research studies prompted that on- and off-site contamination of groundwater due to benzene can cause cancer mortality and birth defects (Logue and Fox, 1986). In the study area, a total of 21 petrol bunks were located within a stretch of 30 km between 17 and 28 years old in Madurai District. On counting the age of petrol bunks, leakage of hydrocarbons in the subsurface region is possible where benzene is recalcitrant under anaerobic condition but degrades moderately in the presence of oxygen (Johnson et al., 2003). Thus the subsurface leakage of benzene causing deterioration of groundwater quality may also be accounted in addition to the other anthropogenic factors (Guo et al., 2012). Evidently, to support the subsurface leakage, it was reported that the leaching of benzene (ATSDR, 2007; IPCS, 1993) was possible from the soil based on its aqueous solubility and octanol–water partition coefficient (K_{ow}). Also the sorption behavior of benzene onto Suspended Organic Matter (SOM) varies with other soil properties and environmental conditions (Environment Agency, 2003).

The possible mechanism for the deterioration of groundwater by benzene with reference to Zhang et al. (2010) is as follows. In the first stage, the movement of benzene occurs by gravitational forces (Freeze and Cherry, 1979). At this seepage stage, lateral migration of benzene takes place by capillary

Table 1 Details of the sampling locations with benzene concentration levels in the months of Jan 2011, Feb 2011 and Mar 2011.

	Sampling spot	GPS measurement	Jan 11	Feb 11	Mar 11
Arasaradi					
A01	Indian Oil Corporation (within bunk limit)	479 ft; 09°55.689′N; 078°06.512′E	0.020	0.010	0.017
A02	Jail road (within 50 m)	480 ft; 09°55.650′N; 078°06.006′E	0.024	0.028	0.021
A03	Bharat petrol bunk (within bunk limit)	482 ft; 09°55.648′N; 078°05.962′E	0.032	0.017	0.013
A04	Karimedu (within 20 m from Bharat petrol bunk)	524 ft; 09°55.689′N; 078°05.897′E	0.038	0.012	0.032
A05	Bharat petrol bunk, Mothilal Street	490 ft; 09°55.710′N; 078°05.998′E	0.090	0.013	0.021
TPK Road					
TPK01	Indian Oil, Moolakkarai	569 ft; 09°53.263′N; 078°04.532′E	0.193	0.110	0.040
TPK02	Reliance petrol bunk, Pasumalai	485 ft; 09°53.652′N; 078°04.873′E	0.033	0.035	0.093
TPK03	Bharat petrol bunk, Alagappa Nagar	492 ft; 09°54.129′N; 078°05.713′E	0.032	0.194	0.103
TPK04	Indian Oil, Palanganatham	478 ft; 09°54.204′N; 078°05.812′E	0.039	0.137	0.035
TPK05	Hindustan Petroleum, Vasanth Nagar	482 ft; 09°54.380′N; 078°05.966′E	0.031	0.021	0.030
Periyar Bus Stand					
PBS01	Railway junction (inside)	492 ft; 09°55.134′N; 078°06.672′E	0.164	0.144	0.038
PBS02	Karpagam Hotel (adjacent to railway junction)	515 ft; 09°55.299′N; 078°06.712′E	0.042	0.034	0.015
PBS03	Hindustan Petroleum (within bunk limit)	498 ft; 09°55.323′N; 078°06.721′E	0.007	0.060	0.023
PBS04	Indian Oil Corporation (within bunk limit)	509 ft; 09°55.384′N; 078°06.743′E	0.033	0.311	0.034
PBS05	Bharat Petroleum (within bunk limit)	488 ft; 09°55.363′N; 078°06.753′E	0.039	0.140	0.020
Theppakulam Road					
TR01	Thiagarajar College (inside campus)	569 ft; 09°53.263′N; 078°04.532′E	0.124	0.050	0.044
TR02	Reliance petrol bunk (within bunk limit)	486 ft; 09°53.997 N; 078°06.662′E	0.133	0.035	0.097
TR03	Indian Oil corporation (within bunk limit)	485 ft; 09°53.363′N; 078°06.753′E	0.150	0.048	0.038
TR04	Bharat petroleum (within bunk limit), Kamarajar road	492 ft; 09°54.129′N; 078°05.713′E	0.022	0.064	0.023
TR05	Hindustan Petroleum (within bunk limit)	478 ft; 09°54.204′N; 078°05.812′E	0.071	0.025	0.074
North Veli Street					
NVS01	Tamil Sangam Road	469 ft; 09°55.542′N; 078°06.972′E	0.013	0.064	0.079
NVS02	Work shop Road	449 ft; 09°55.527′N; 078°06.034′E	0.022	0.113	0.038
NVS03	Bharat petrol bunk (within bunk limit)	475 ft; 09°55.524′N; 078°06.086′E	0.010	0.118	0.041
NVS04	Bell Hotel (within 50 m from Bharat petrol bunk)	453 ft; 09°55.547′N; 078°06.097′E	0.045	0.137	0.040
NVS05	Indian Oil Corporation (within bunk limit)	492 ft; 09°55.097′N; 078°06.139′E	0.062	0.064	0.083
KK Nagar					
KKN01	Bharat petrol bunk (within bunk limit)	521 ft; 09°56.195′N; 078°08.558′E	0.041	0.020	0.028
KKN02	Courier office (within 20 m from Bharat petrol bunk)	492 ft; 09°56.185′N; 078°08.586′E	0.013	0.050	0.086
KKN03	AR Hospital	470 ft; 09°56.195′N; 078°08.614′E	0.019	0.034	0.032
KKN04	Indian Oil Corporation (within bunk limit)	491 ft; 09°56.308′N; 078°08.714′E	0.030	0.112	0.107
KKN05	Hindustan Petroleum (within bunk limit)	555 ft; 09°56.648′N; 078°09.242′E	0.035	0.055	0.034

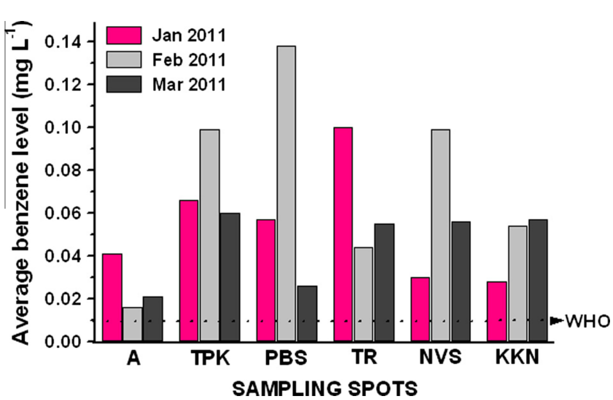

Figure 2 Average benzene levels in the groundwater samples of Madurai District, Tamil Nadu.

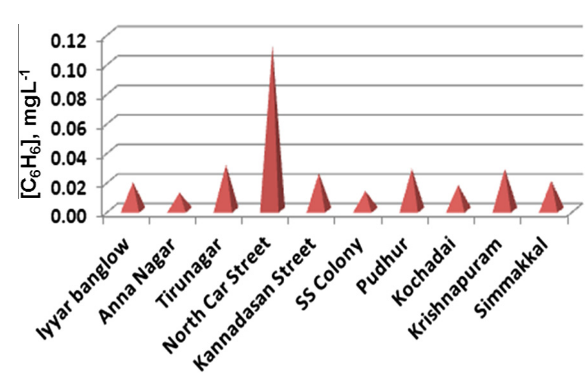

Figure 3 Average benzene concentration levels (Jan–Feb–Mar 2011) in some residential locations of Madurai District.

forces which causes a zone called 'oil-wetting zone' around the core of infiltration body. In the oil-wetting zone, the capillary forces are dominant with lessening outward saturation of oil. In the second stage, the seepage of benzene ceases when it reaches the water table and ultimately floats on the groundwater. The third stage involves the contemporary mass with sep-

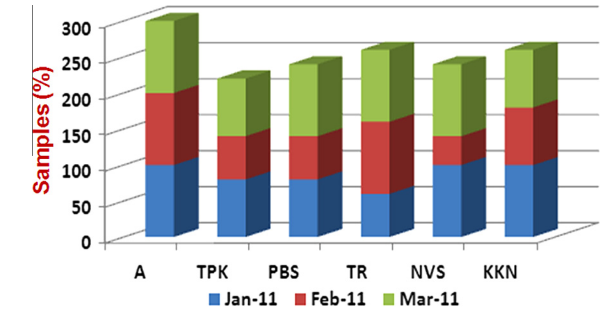

Figure 4 Percentage of groundwater samples within the recommended level of CCME for marine and estuary aquatic life.

arate phase migration, vaporization and dissolution of some of the benzene into groundwater. The dissolution further leads to the transport of benzene along with groundwater flow. The major reported sources of benzene in water are atmospheric deposition, spills of petrol and other petroleum products, and chemical plant effluents (WHO, 1996). The role of petroleum industries in groundwater contamination by benzene was reported at Love Canal (Paigen et al., 1987), Superfund site, Pennsylvania (Budnick et al., 1984) and New Jersey (Najem et al., 1994).

Fifteen traffic signals in this 30 km stretch may also be another valid reason which attributes to the benzene contamination in groundwater samples. The accumulation of benzene due to cigarette smoke, vehicular emissions, combustion of solid biomass (Sinha et al., 2006), petrol evaporation from automobiles and petrol stations may be the associated risk causing factors in the study area and, as benzene is soluble in water (Bennett et al., 1993; Eganhouse et al., 1993), its transport into soil may also be due to rainfall in the study area. Evidently, influence of rainfall (as a vehicle) could facilitate the movement of benzene into the subsurface of the soil (Wadge and Salisbury, 1997). Various possible sources leading to benzene concentration in air are represented in Table 2 such that the fate of groundwater sources is registered with respect to deterioration by benzene concentration (Ritchie et al., 2003). The consistency in the association of benzene due to high traffic density (Wheeler et al., 2008; Bruno et al., 2006; Kwon et al., 2006) and tobacco smoke (Maestri et al., 2004) was already reported. The presence of hydrocarbons was reflected by the alkaline nature (Fig. 5) of groundwater samples in the study area. The correlation value between benzene and total alkalinity was 0.287. The present observation was supported by earlier reports (Cozzarelli et al., 2001; Lee et al., 2001; Borden et al., 1995; Basberg et al., 1998).

To examine the month-wise effect of benzene in groundwater, *t*-tests were carried out for the combined data of Jan–Feb 2011, Feb–Mar 2011 and Jan–Mar 2011. The results of the *t*-test for the combined data are 1.439, 2.322 and 0.745 for Jan–Feb 2011, Feb–Mar 2011 and Jan–Mar 2011, respectively. As the computed value of *t-test* was greater than the critical value of 1.699 (df = 29), the difference of means was significant at 5% level for Feb–Mar 2011. The difference of means for Jan–Feb 2011 and Jan–Mar 2011 was insignificant with respect to the values obtained from *t*-test. Hence, the results

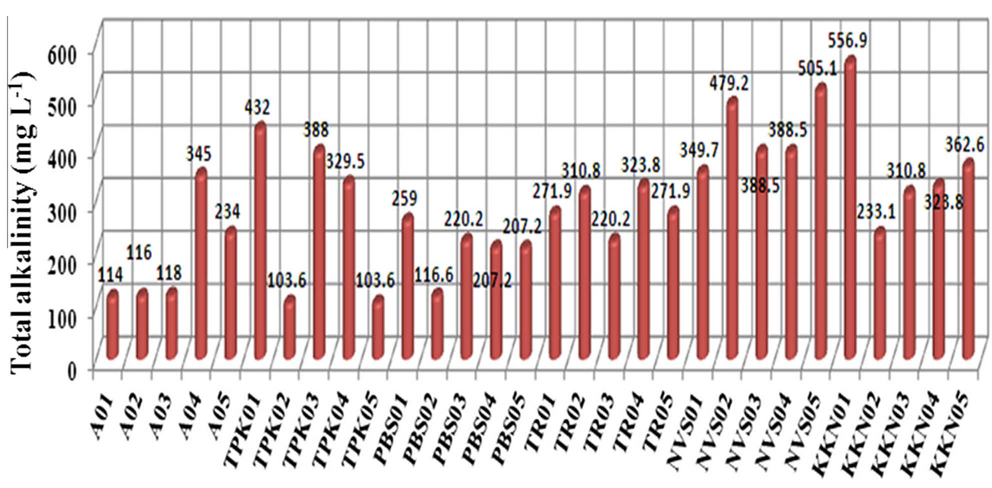

Figure 5 The distribution (average) of total alkalinity in the groundwater samples of Madurai District, South India.

Table 2 Possible sources of benzene in the study area.

Sampling station	No. of signals/petrol bunks located	Age of petrol bunks	Possible sources for benzene contamination
A	3/4	17	Smoking
TPK	1/6	28	Smoking, Car service station
PBS	4/3	21	Smoking, Automobiles
TR	3/3	20	Smoking, Automobiles
NVS	2/2	23	Smoking, Automobiles
KKN	2/3	17	Smoking

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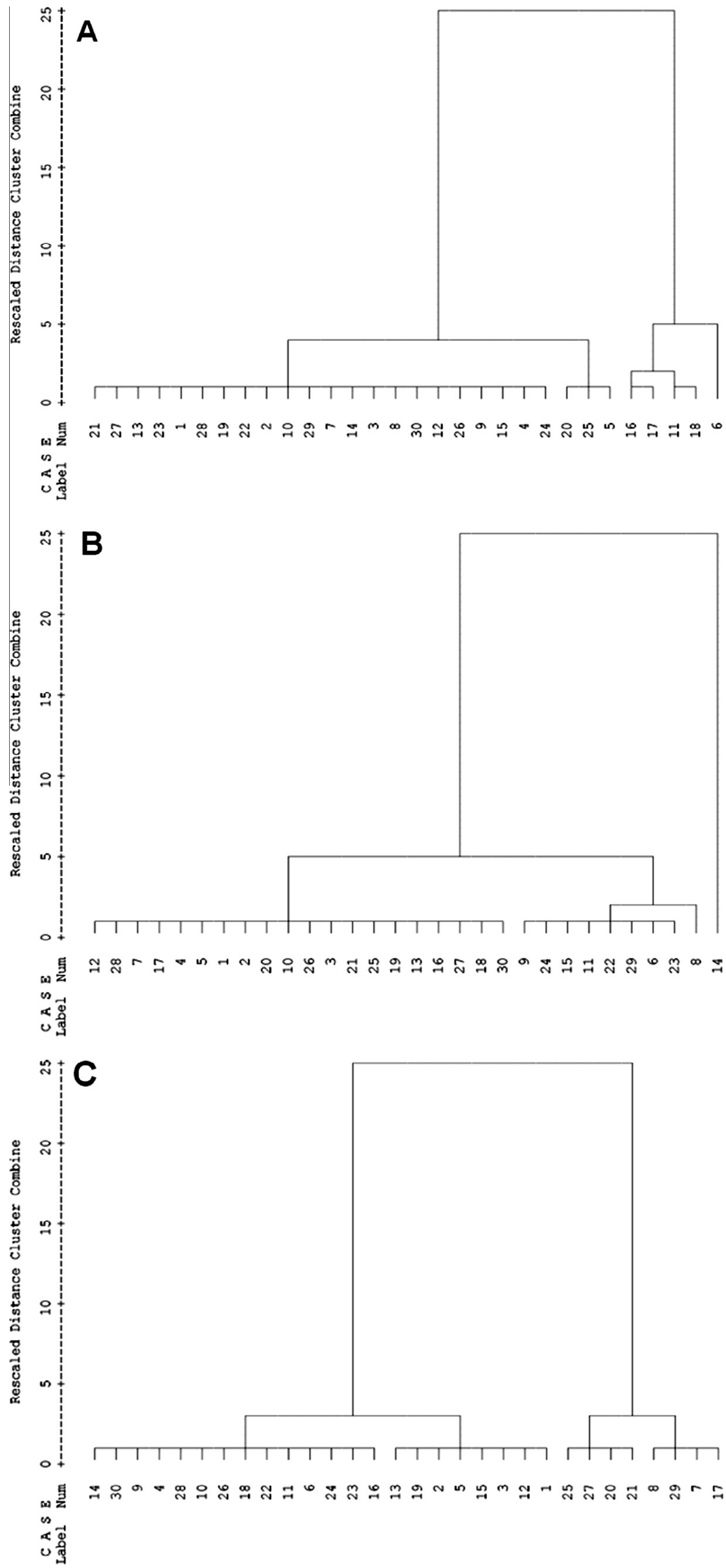

Figure 6 Dendograms using Hierarchical cluster analysis for the distribution of benzene in groundwater in Jan 2011, Feb 2011 and Mar 2011.

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Table 3 Summary statistics of benzene concentrations for the groups resulting from cluster analysis for Jan 11, Feb 11 and Mar 11.

Cluster	Jan 2011				Feb 2011				Mar 2011			
	Minimum	Maximum	Average	SD	Minimum	Maximum	Average	SD	Minimum	Maximum	Average	SD
C-1	0.124	0.193	0.153	0.027	0.031*				0.093	0.107	0.100	0.006
C-2	0.007	0.045	0.028	0.011	0.110	0.194	0.137	0.026	0.074	0.086	0.080	0.005
C-3	0.062	0.090	0.074	0.014	0.010	0.064	0.036	0.018	0.013	0.023	0.019	0.004
C-4	***	***	***	***	***	***	***	***	0.028	0.044	0.036	0.005

C – Cluster; SD – Standard Deviation.

reflected a significant variation in the benzene level between February and March 2011.

The dendrograms resulting from the hierarchical cluster analysis shown in Fig. 6(A–C) display the presence of four clusters in March 2011 and three clusters in Jan and Feb 2011. The bore well samples are grouped according to the benzene concentrations. Table 3 represents the minimum, maximum, average and SD of benzene concentration for each cluster.

The average values of each cluster revealed the heterogeneous distribution of benzene between the average values of 0.028 and 0.193 mg L^{-1}in the bore wells in Jan 2011. Three clusters for the month of Feb 2011 were obtained with two clusters showing the average benzene level almost equal but the other in four-folds. The prevalence of unsymmetric distribution of benzene level was studied in a close range. Four different contamination ranges were corroborated in the month of Mar 2011 which were approved from the clusters. The minimum and maximum differences in the benzene level were 0.017 mg L^{-1} and 0.081 mg L^{-1}, respectively. The division of clusters in the month of Mar 2011 was greater than Jan 2011 and Feb 2011 which reflects that benzene distribution was more heterogeneous in Mar 2011.

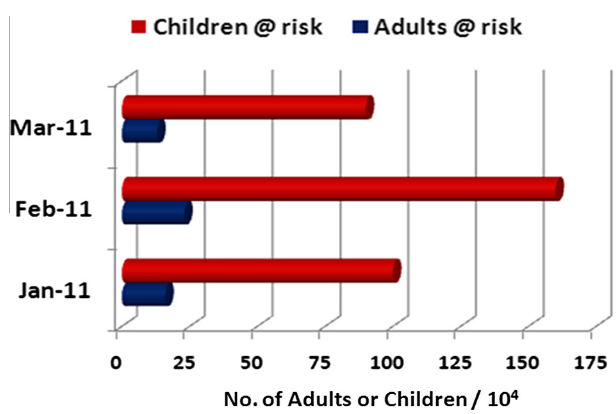

Figure 7 Estimated cancer risk analysis among adults and children around commercial locations of Madurai District, South India.

3.3. Cancer risk analysis among adults and children

The estimated cancer risk among adults and children due to benzene contamination in groundwater in the corporate locations was calculated and shown in Fig. 7. In every 10^4 adults, an average of 16, 23 and 13 persons were found to be under cancer risk in the months of Jan 11, Feb 11 and Mar 11, respectively. The risk analysis among children was in seven folds as compared to the risk of adults. The children who were at risk were in the average range of 90–160 per 10,000 in the study area between Jan 11 and Mar 11. The risk analysis revealed that a high magnitude of adults and children were at cancer risk in the corporate locations namely Thirupparankundram, Periyar Bus stand and KK Nagar in the months of Jan 11, Feb 11 and Mar 11, respectively. The cancer risk analyzed in the residential samples corroborated the possibility of a greater risk among adults than children (Fig. 8A and B). The cancer risk in every 10^4 adults was evaluated in the following order: North Car Street > Tirunagar > Krishnapuram > Iyyar banglow > Kochadai > SS Colony > Anna Nagar > Kannadasan Street.

3.4. Geographic information system (GIS) analysis

The thematic maps for the benzene contaminated bore wells in six corporate locations in the months of Jan 11, Feb 11 and

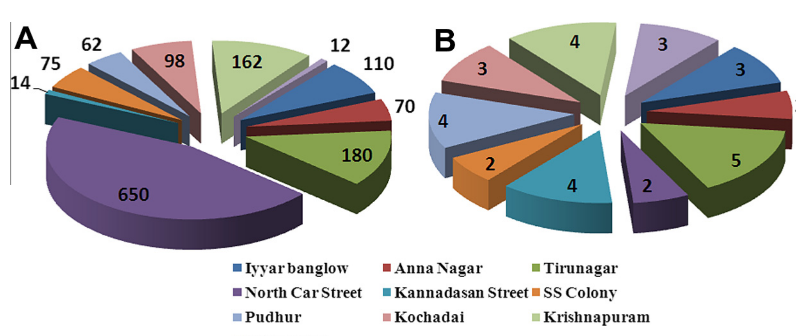

Figure 8 Number of adults at cancer risk per 10^4 (A) and children at cancer risk per 10^7 (B) due to the benzene contaminant level in the residential locations of Madurai District, South India.

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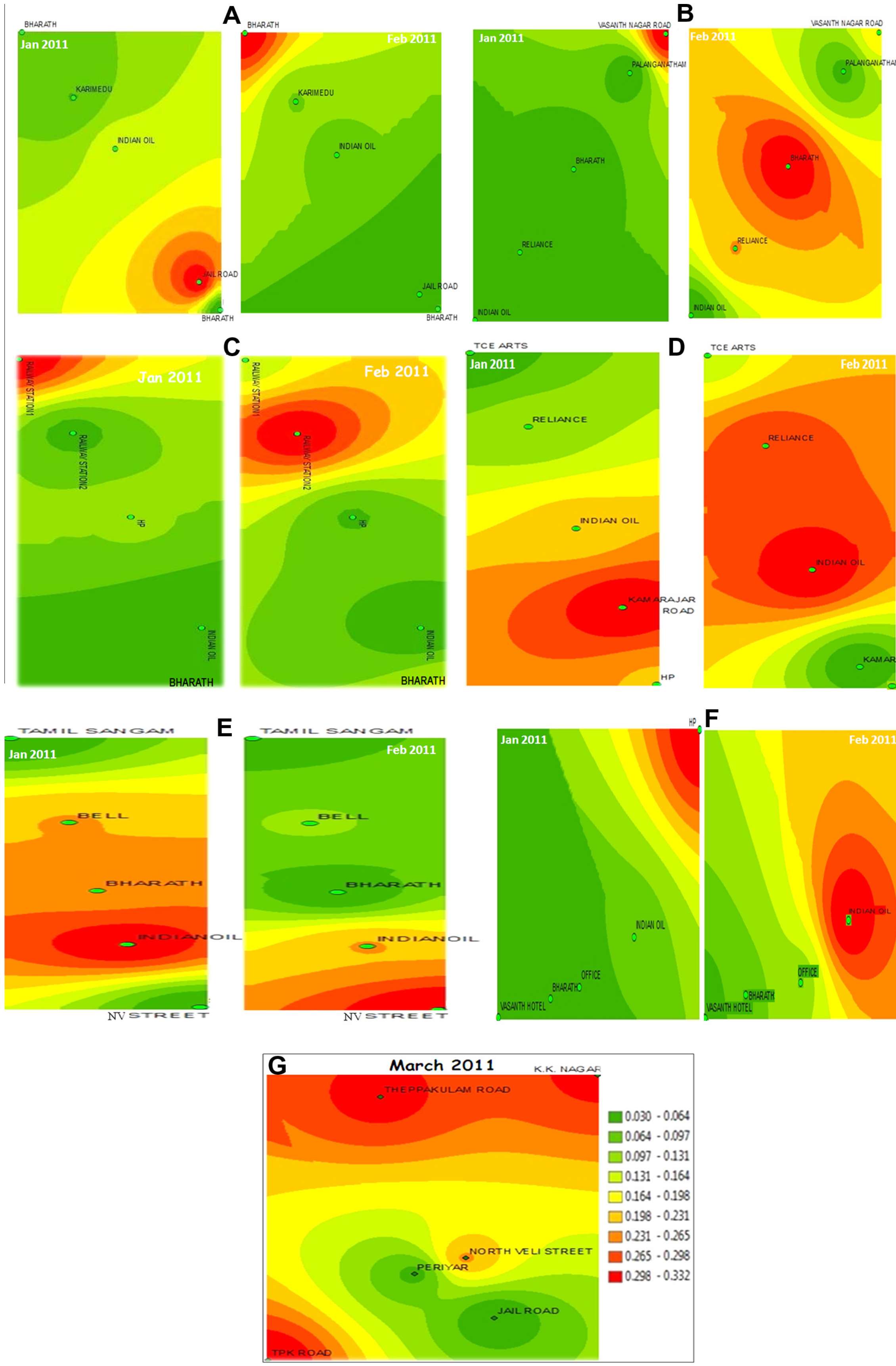

Figure 9 GIS based thematic maps depicting the benzene distribution in groundwater at Arasaradi (A), TPK Road (B), Periyar Bus Stand (C), Theppakulum (D), North Veli Street (E) and KK Nagar (F) in Jan–Feb 2011 and Mar 2011 (G).

Mar 11 was integrated using the addition function available in the Arc GIS software. We created a final benzene contaminated groundwater map by overlaying these thematic maps which are produced as a result of inverse distance weighted (IDW) interpolations. The spatial integration for benzene contaminated groundwater zone mapping was carried out using Arc GIS Spatial Analyst extension. The areas were delineated based on the benzene contamination level of bore well sources in accordance with nine benzene concentration levels as shown in Fig. 9(A–G).

The map shows mostly the distribution of benzene level in the range 0.030–0.164 mg L^{-1} in the TPK corporate locations during Jan 11. But in the month of Feb 11, a heterogeneous pattern of distribution in benzene was depicted from the contours with a high level of concentration at the center point (at Bharat Petroleum) of TPK area.

The Jan 11 contour pattern at Theppakulum shows the increased level of benzene from Thiagarajar College to Kamarajar Road between 0.030 and 0.332 mg L^{-1}. But the pattern of Feb 11 illustrates that the benzene level in this area was observed with variations in the contour pattern with a dominance level of 0.231–0.332 mg L^{-1}. At Northveli Street, the contours were observed with appreciable differences in the months of January and February 2011. In particular, the estimated benzene levels at NV Street, Bharat Petroleum and Bell hotel were with a striking change. Two sampling points, Bharat Petroleum (near Karimedu) and Jail Road at Arasaradi were spotted with a great reciprocation in Jan 11 and Feb 11 in the benzene levels. In March 2011, the concentration levels recorded at Theppakulum road, KK Nagar and TPK road were 0.231–0.332 mg L^{-1}. Periyar Bus Stand and Arasaradi (Jail road) registered between 0.030 and 0.198 mg L^{-1} and North Veli Street was observed with the benzene concentration range of 0.164–0.265 mg L^{-1}. TPK road–Theppakulum road–KK Nagar locations and Arasaradi–North Veli Street locations were observed with a homogeneous pattern of distribution in the benzene level in March 2011.

4. Conclusion

Contamination of benzene in the groundwater at six commercial and ten residential locations has been identified. The possible routes include leakage of hydrocarbon from petrol bunks and stations, tobacco smokes and vehicular emissions. Very less percentage of groundwater samples corroborated within the WHO limit. Based on the cancer risk analysis in the commercial locations, children were at a greater risk than adults. Conversely, at the residential locations, adults were at a greater risk than children. Student's *t*-test approved the significant variation of benzene between February and March 2011. Hierarchical Cluster and GIS based analyses were done interpreting the distribution of benzene in groundwater sources at corporate locations. The possible hydrocarbons in the other water sources in the study area for future investigation are also envisaged.

5. Suggestions

Petrol stations (and bunks) need to be monitored periodically to ensure zero leakage of hydrocarbons in the subsurface soil.

Petrol vapor recovery needs to be designed to prevent emissions of volatile organic compounds at the time of storage of petrol at terminals, dispensing fuels to vehicles and distribution to service stations.

Vehicular emissions need to be controlled to lessen the degree of air pollution.

Periodic cleaning of engines and suitable exhaust filters needs to be made mandatory.

Old engines particularly in buses, lorries and auto rickshaws should be replaced with new ones harnessing the latest technology.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2013.09.022.

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