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**Construction Waste in Benzene Removal by Column Study in
Ground Water – A Pragmatic Approach**
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M. Senthil Kumar, GVT. Gopalakrishna and V. Sivasankar
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Abstract

Benzene (colorless liquid) is an additive for petrol to increase the octane number. Due to its combustion as fuel in vehicles, the ambient air quality gets deteriorated, and as a consequence the groundwater contamination is resulted. The present research work explored the concentration of benzene in 90 groundwater samples at the proximity of petrol bunks and residential places at Madurai District for a stretch of about 20 kms. The variation in the benzene concentration was observed for the groundwater samples taken during January 2011, February 2011 and March 2011 and they sample were determined for benzene in 2016 April. The attribution of these benzene level fluctuations may be accounted with respect to varying vehicular emissions and evaporation of hydrocarbons from petrol stations, leaking petrol tanks and automobile industries in the City. Most of these samples found to exceed the prescribed level for benzene recommended by WHO, EPA, CCME and USNDS. The concentration levels are interpreted using Arc GIS and box – whisker plots. An immediate monitoring and attention may be the need of the hour in order to curtail the concentration of benzene in the groundwater.

Key Words: Benzene, groundwater, Madurai, GIS

1. Introduction

1.1. Water Source

In the world, 50 percent of people using groundwater for drinking purpose, live in rural areas. The major use of groundwater is to irrigate crops. Groundwater supplies are replenished or revitalized by precipitation and snow liquefies. In some areas of the world, people face serious

water shortages because groundwater is used faster than it recharge. In other areas groundwater is polluted by human activities. In areas where substance above the aquifer is porous, pollutants can readily sink into groundwater supplies. Landfills, septic tanks, underground leakage of gas tanks and from overeat of fertilizers and pesticides is the major source of groundwater pollution, If groundwater becomes impure, it will no longer be secure to drink.

Guarantee of drinking-water security is a basis for the preclusion and control of waterborne diseases. World Health Organization (WHO) constructs global norms on water quality in the form of guidelines that are used as the basis for regulation and standard locale worldwide (WHO Report, 2013)

1.2 Sources of Benzene

The molecular formula C_6H_6 of Benzene is an organic chemical compound. It is shortened as Ph-H. Benzene is a colourless and enormously flammable liquid with a syrupy smell and a comparatively high melting point. Because it is predictable as a carcinogen, its use as an preservative in gasoline, but it is a most important industrial solvent and precursor in the drugs production, plastics, synthetic rubber, and dyes. Benzene is a natural ingredient of crude oil, and may be synthesized from other composite in petroleum. Benzene is an aromatic hydrocarbon), a repetitive hydrocarbon with a unbroken pi bond. It is also related to the functional group arene which is a generalized structure of benzene.

In groundwater, the concentration of benzene based on the geological, physico - chemical inimitability of an aquifer, the porous and sharpness of the soil and rocks, the temperature, the accomplishment of other chemicals, and the depth of wells.

1.3 Exposure of Benzene

Outdoor environmental levels of benzene series from 0.2 $\mu\text{g}/\text{m}^3$ (0.06 ppb) in remote rural areas to 349 $\mu\text{g}/\text{m}^3$ (107ppb) in industrial centres with a high bulk of motor vehicle traffic. The percentage of benzene in unleaded petrol is roughly 1–2%. Driving a motor vehicle one hour per day is estimated to add 40 μg of benzene to a person's every day intake. Levels up to 10,000

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$\mu\text{g}/\text{m}^3$ (3,000 ppb) have been measured in air at petrol stations. Paying a slight under 2 min/week to refill a car at the petrol station is the reason to an extra predictable daily intake of 10 μg . Benzene has been detected at levels as high as 500 $\mu\text{g}/\text{m}^3$ (154 ppb) in indoor residential air.

Cigarette smoke contribute considerable quantities of benzene to the levels accounted in indoor air, with smokers inhaling approximately 1,800 μg benzene/d compared to 50 $\mu\text{g}/\text{d}$ by non-smokers. Benzene can also occur in foods and drinks as a product of reaction between benzoate and ascorbic acid, and has been found in soft drinks. Most important sources of benzene in water are stated in the environment, spills of petrol and other petroleum products, and chemical plant seepages. Ranges of up to 179 $\mu\text{g}/\text{litre}$ have been accounted in chemical plant effluents (2). In seawater, levels were accounted to be in the level of 5–20 ng/litre (coastal area) and 5 ng/litre (central part) (4). Levels between 0.2 and 0.8 $\mu\text{g}/\text{litre}$ were reported in the Rhine in 1976) (7). Levels of 0.03–0.3 mg/litre were found in groundwater contaminated by max out emissions (8). Benzene was detected in 50–60% of potable water samples taken at 30 treatment amenities across Canada; significant concentrations varies from 1 to 3 $\mu\text{g}/\text{litre}$ (highest range 48 $\mu\text{g}/\text{litre}$) (9). Federal drinking-water investigations in the USA calculate approximately that 1.3% of all groundwater structures contained benzene at concentrations superior than 0.5 $\mu\text{g}/\text{litre}$ (highest level reported 80 $\mu\text{g}/\text{litre}$) (5).

1.4 Adverse of Benzene

Benzene is a health hazard compound, the undersized health effects of experience above the maximum contaminant level is anemia, impermanent nervous system disorders and immune system dejection. The long term effect of exposure above the maximum contaminant level of Benzene is cancer and chromosome aberrations. Consuming water with high levels of benzene in excess of a long time is a source of health effects such as Central nervous system dysfunction, wide-ranging hemorrhaging, Pancytopenia, augment risk of cancer.

2. Objective and Scope

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It is necessary to estimate the extent of petroleum product contamination in groundwater because of the above serious health effects. HPLC-Methodology and Gas Chromatography are used successfully in many recent studies for this estimation. The quantitative results help to arrive with the proper remediation methodology and awareness scenario.

The overall objective of the works is to quantitatively estimate the benzene concentration and thereby determining the quality of the water. The study objective is to estimate Benzene in groundwater samples collected in commercial, residential and surface water bodies in and around Madurai. The identification of vulnerable areas with maximum risk of consuming low quality groundwater is also our objective. The remediation process is executed by the column technique in batch process technique and providing recommendations for preventing future contaminations.

2.1 Details of the Study Area

Madurai city, which is more than 2500 years old is situated at 9°58' N latitude and 78°10' E longitude and engage an area of about 140 km². The metropolitan city, located on the banks of the River Vaigai, it is the 24th major city in India (population wise) and Madurai is the third largest in the state of Tamil Nadu. The population stress on the city is always rising. The population of Madurai is 11, 94,665 it based upon 2001 survey.

3. Methodology

Sampling and Analysis

One hundred and twenty groundwater samples from bore well resources were collected in pre – cleaned bottles in the months of Jan – 11, Feb – 11 and Mar – 11 and thirty six samples collected in April – 16 to identify the ranges from corporate and residential locations of six corporate, thirteen residential location and three surface water bodies of Madurai District. The collected samples were stored in the refrigerator (8 - 10°C) before the estimation of Benzene. At the time of estimation, the chilled water samples were equilibrated to room temperature followed

by vacuum filtration using 0.4 μm filter paper. The estimation of benzene is done by High Pressure Liquid Chromatography (HPLC) and Gas Chromatography (GC-FID).

High Pressure Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (**HPLC**) is a form of column chromatography that pumps a sample mixture or analyte in a solvent (known as the mobile phase) at high pressure through a column with chromatographic packing material (stationary phase). The stationary phase is nonpolar (hydrophobic) in nature, while the mobile phase is a polar liquid, such as mixtures of water and methanol or acetonitrile. It works on the **principle** of hydrophobic interactions hence the more nonpolar the material is, the longer it will be retained.

Gas Chromatography (GC-FID)

Chromatography is the separation of a mixture of compounds (solutes) into separate components. By separating the sample into individual components, it is easier to identify (qualitate) and measure the amount (quantitate) of the various sample components. It is estimated that 10-20% of the known compounds can be analyzed by GC. One or more high purity gases are supplied to the GC. One of the gases (called the carrier gas) flows into the injector, through the column and then into the detector. A sample is introduced into the injector usually with a syringe or an exterior sampling device. The injector is usually heated to 150-250°C which causes the volatile sample solutes to vaporize. The vaporized solutes are transported into the column by the carrier gas. The column is maintained in a temperature controlled oven.

Benzene Standard for HPLC & GC-FID Grade

Benzene was estimated using High Pressure Liquid Chromatography (HPLC) and Gas chromatography (GC-FID), Standard solutions of benzene of 2000 mg^{-1} was 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 and GC -FID grade. After the zero correction was done, 20 μl of the standard was injected using a micro

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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. The Benzene concentration was estimated using the formula as follows.

$$\text{Benzene Concentration} = \frac{\text{Area of the peak in sample} \times \text{Concentration of standard solution}}{\text{Area of the peak in standard solution}}$$

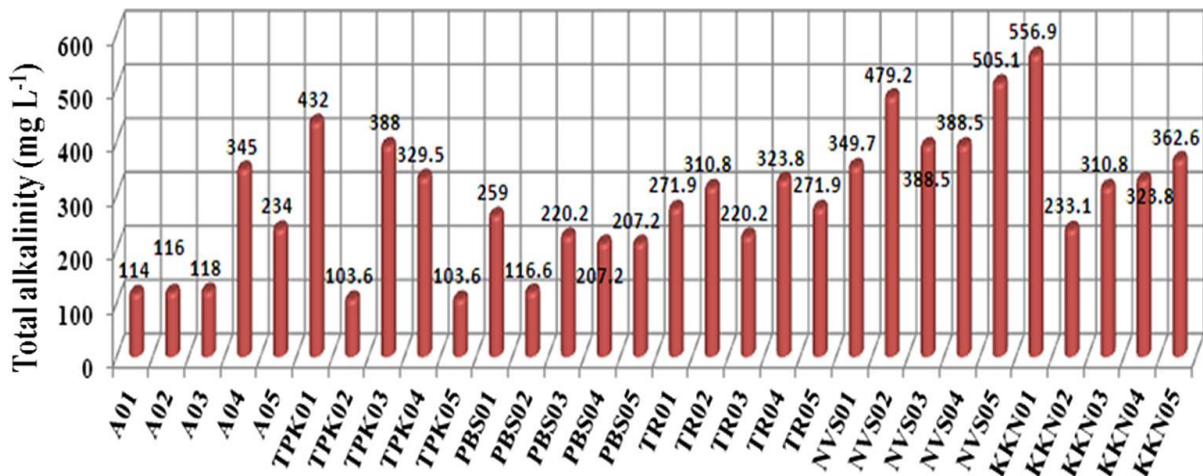


Fig1. Alkalinity range of groundwater sample

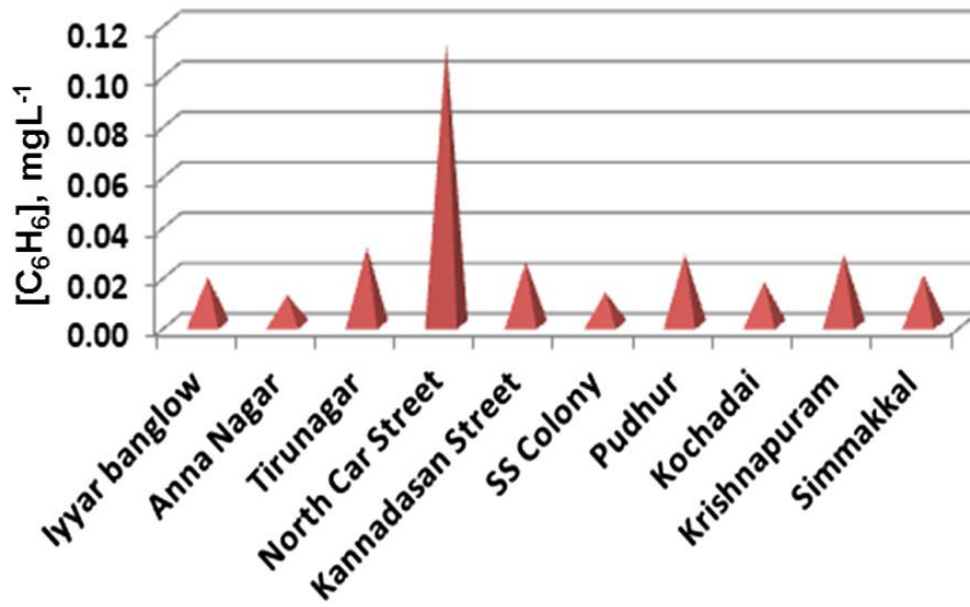


Fig 2. Benzene Concentration level in Madurai

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 ($\text{mg kg}^{-1} \text{day}^{-1}$).

$$\text{CDI (for adults)} = [\text{Total Dose (mg)} / \text{Body Weight (70 kg)} \times \text{life time (days)}] \dots\dots\dots(1)$$

$$\text{CDI (for children)} = [\text{Total Dose (mg)} / \text{Body Weight (10 kg)} \times \text{life time (days)}] \dots\dots\dots(2)$$

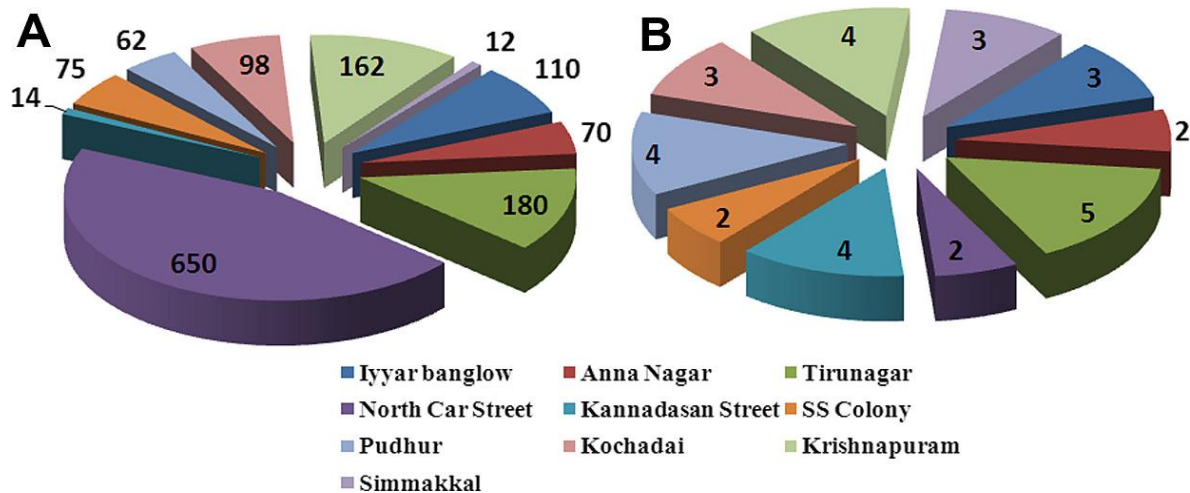


Fig 3. Risk changes level in all area of Madurai

Interpretation through GIS tools

Geographic Information Systems (GIS) provide platforms for managing the data, computing spatial relationships such as distance and connectivity. It is based on the analysis of spatiotemporal behaviour of the 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 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 observations location to the location of the point being estimated (Burrough and MC Donnell 1998).

The inverse distance can be raised to a power (e.g. linear, squared, and cubed) to model different geometries (e.g. line, area, volume) (Guan et al., 1999). In a comparison of several different deterministic interpolation procedures, Burrough and Mc Donnell (1998) and Mathes et al., (2006) found that using IDW with a squared distance term yielded results most consistent with original input data. This method is suitable for datasets where the maximum and minimum values in the interpolated surface commonly occur at sample points (ESRI 2002).

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Topo sheets 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.

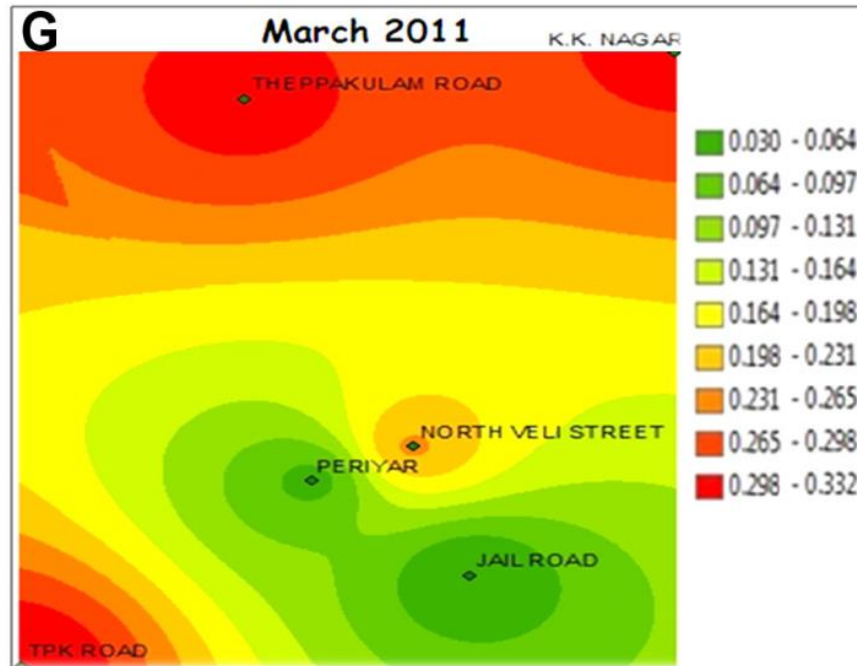


Fig 4. Pollution load interpretation on GIS

Benzene Removal Technique

Excess benzene in drinking water has to be removed before they are supplied to the community. There are various methods for benzene removal *viz.* using GAC, natural attenuation, anaerobic bio remediation, *in situ* bio remediation and intrinsic bio remediation. Due to factors like high operational costs these technologies are found to have limited access. Among the existing methods, adsorption is one of the most extensively used methods for the removal of benzene because of its ease of operation and cost effectiveness. In adsorption techniques, biomaterials are employed, activated and chemically modified forms.

The present study is concentrated on the removal of benzene in water by using adsorption technique by batch experiments. The zeolite materials were prepared from the brick. The sodium chloride solutions were used to remove microbial particles. Then the materials are washed by

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distilled water to produce plain adsorption material. It is sewed to produce uniform materials to produce consistent bed. All adsorbing materials were characterized before and after the benzene removal process. The benzene removal efficiency of all the adsorbing materials was explored by using the synthetic benzene removal solution. The benzene removal efficiency was studied as a function of contact time, pH, dose, initial benzene concentration and interfering anions. The reusability of adsorbing materials was decided by the benzene desorption from the exhausted adsorbing materials. The validity of different kinetic models (*viz*, pseudo-first order, pseudo-second order, intra particle diffusion and Elovich) and isotherm models (Freundlich and Langmuir) was corroborated. The practical applicability of all adsorbing materials was also ascertained from the results obtained after benzene removal experiments using ground water samples.



Fig 4. Column study for benzene removal

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

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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. The remediation of benzene is done by column technique in batch process mode. The removal efficiency is determined in different sized column. It conclude that the removal efficiency is high when the bed height in increased. At the same time the detention time also increased when the bed height in raised.

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