BASELINE DETERMINATION OF GASOLINE ADDITIVE METHYL TERTIARY BUTYL ETHER (MTBE) AND PETROLEUM DERIVATIVES (BTEX) IN WATER RESOURCES

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Abstract

This research aims to investigate the possible occurrence, distribution, and sources of the newly added gasoline oxygenate, methyl tertiary butyl ether (MTBE) and gasoline components of benzene, toluene, ethyl benzene and xylenes (BTEX) group in Jordan's water resources through a preliminary assessment study. The study has focused on monitoring the levels of (MTBE) and (BTEX) in Amman-Zarqa Basin and Northern Governorate. Comprehensive sampling campaigns were conducted covering groundwater wells on different locations from the gas stations. Purge and trap gas chromatography-mass spectrometry was used for the determination of (MTBE) and (BTEX) in groundwater, which is capable to detect µg/l levels. The levels of MTBE and BTEX detected for the first phase of the study were below the Lowest Reportable Value (LRV), which is 1 µg/l and comply with international and national standards. The second phase of the research will concentrate on the analysis of soil samples besides ground water samples to investigate the release of petroleum derivatives from underground fuel tanks in any case of detecting significant amount of MTBE and BTEX in water resources.

Introduction

The intense search for an effective and economical octane boosting alternative to lead as a gasoline additive has continued since the past decades. Oxygenates have emerged as alternatives for improving the octane number and the oxygen content in gasoline. The most important of these oxygenates has been methyl tertiary butyl ether (MTBE) added to gasoline to help reduce air pollution (Hamdan and Al-Subaih, 2002). In USA, MTBE has been added to gasoline since the late 1970s to increase octane and reduce vehicle emissions (USGS and NHDES 2004). Its use significantly increased with the production of reformulated gasoline (RFG) after amendments to the Clean Air Act in 1990 required the use of cleaner burning fuels. This additive material, which is believed to cause cancer, has relatively high solubility in water, low soil adsorption, and is slowly biodegraded. Thus, once it has been released to the environment through spills, leaking storage tanks, or other pathways, it has the potential for pervasive and persistent contamination of ground water (USGS and NHDES 2004). Although no Federal drinking-water standard has been established for MTBE in the USA until 2004, the U.S. Environmental Protection Agency (USEPA) (1997) has tentatively classified the compound as a possible carcinogen and has set a drinking-water

advisory at 20 to 40 micrograms per liter (µg/L). The State of New Hampshire (2000) for example has adopted a maximum contaminant level of 13 µg/L for MTBE in drinking water.
For years, MTBE has been considered one of the best agents for reducing automobile emissions that create ozone (smog), but states and the USEPA have moved to ban MTBE because of its propensity to contaminate ground and drinking water supplies. In March 1999, California became the first state to officially ban MTBE when Governor Gray Davis issued an executive order for a three-year phase out of the gasoline additive. MTBE has shown up in hundreds more underground fuel links and water quality experts have raised their estimate of the number of MTBE spills from 4,500 to nearly 6,600, a nearly 32 percent increase over the past year of the time of banning.

In March 2000, EPA and US Department of Agriculture joined in calling for Congress to amend the Clean Air Act to remove the oxygenate requirement from the RFG program. The Clinton administration hoped to replace the requirement with a mandate for renewable energy content. This would open the door for ethanol to replace MTBE as the dominant additive in unleaded benzene. In addition to the call for Congressional action, EPA planned to phase out MTBE use through rulemaking authority provided under the Toxic Substances Control Act. The law allowed EPA to ban chemicals that pose an unreasonable risk to public health.

In Hashemite Kingdom of Jordan, Jordan Petroleum Refinery is the only provider in the Kingdom to supply oil products to citizens of the country by refining crude oil and its derivatives. During the concession agreement with the refinery, three types of gasoline have been used in the Kingdom, according to standard specifications identified in Jordan as follows: regular gasoline containing lead with Octane number of 87; super gasoline contains lead with octane number of 95, and unleaded gasoline with octane number of 92 (Mahasneh, 2008). Production of unleaded gasoline in Jordan began in 1995 in limited quantities and high price because of the limited quantities produced by refinery (Mahasneh, 2008).

According to Mahasneh (2008), the Jordan Standard Specifications specified the use of fourth ethyl lead as an oxygenate (150 mg/liter) for Regular and Super gasoline as a maximum, and (5 mg / liter) for Unleaded gasoline. As a result of the desire of the Jordan Ministry of Energy and natural resources to observe aspects of environmental health and safety activities in the downstream petroleum sector, and the repeated and multiple claims by the Ministry of Environment, the Ministry of Health, Jordan Institute for Standards and Metrology, and the United Nations Environmental Program to phase out the different kinds of lead in gasoline and to shift towards the use of unleaded gasoline. A study in this regard has been carried out by both the Ministry of Energy and Mineral Resources and Jordan Petroleum Refinery Company, and concluded that the absence of units to improve the quality of oil products within the structure impeded the refinery to produce oil products (gasoline, diesel and fuel oil) that is compatible with the standard specifications and requirements.

The alternative available to phase out lead in the gasoline is to use (MTBE) as it is being used in Europe and many Arab countries and others. The study which was prepared by the Ministry of Energy and Mineral Resources and Jordan Petroleum Refinery Company was submitted to the Cabinet Council, and got approval on 6 / 6 / 2006. Also a committee comprising the respective representatives assessed the status of oil products tanks at gasoline stations and developed mechanisms to replace the faulty tanks, and to develop recommendations on the funding mechanism.

BTEX is an acronym that stands for benzene, toluene, ethylbenzene and xylenes. These compounds are volatile organic compounds (VOCs) found in petroleum derivatives such as gasoline. BTEX compounds are found in groundwater if contamination of petroleum derivatives occurred. As of 2008, we believe to the best of our knowledge we think no other studies so far have addressed the issue of MTBE and BTEX contamination in Jordan's water. We also believe there are no standards for MTBE in public water supplies in Jordan. The potential risk of exposure to MTBE through drinking water in Jordan may be greatest in areas of intense urbanization such as Amman-Zarqa basin, which has the largest population in the country and the largest population served by groundwater. In Jordan, heavy reliance on ground water for domestic and public supply adds urgency to the government and health organization

Because of our concerns over concentrations of MTBE and BTEX in ground water, it was very important to initiate a comprehensive study to assess the distribution and concentrations of these substances in water resources, to compare the concentrations of MTBE to drinking-water standards or advisories, and to determine whether there are factors associated with high rates of occurrence of MTBE and BTEX in groundwater. The proposed study's findings may have implications for future water-resources management in Jordan and other areas with similar hydrogeologic settings. We are mainly interested in determining if there are certain areas or aquifers that are more susceptible to MTBE and/or BTEX or that have greater concentrations of theses toxic materials.

Literature Review

There have been no investigations of the occurrence and distribution of MTBE and BTEX in groundwater in Jordan. Hamdan and Al-Subaih (2002) conducted a study that aimed at investigating the effect of MTBE addition to gasoline on its octane number and, hence, the performance of an engine. Also, its effect on the emitted gases was investigated. Locally produced gasoline was blended with five different percentages of MTBE, namely 0%, 5%, 10%, 15% and 20%. Then, these fuels were burned in an engine, which is coupled to a gas analyzer. It was found that the octane number of the gasoline increases continuously and linearly with MTBE percentage in the gasoline. The best performance of the engine occurs at around 10% MTBE addition, and this percentage also gives the best reduction in exhaust gases emissions. However, Hamdan and Al-Subaih's study did not deal with pollution aspects of MTBE in the environment.

METHODOLOGY

The Study Area

The Amman-Zarqa Basin is one of Jordan's biggest groundwater basins. The study area is about 850 km^2. Almost half of the population of Jordan lives in the big cities of Amman, Zarqa and the other nearby smaller towns. The average annual rainfall varies from less than 200 mm Northeast to more than 500 and 600 mm Northwest close to Bal'ama station and West close of Salt station over the basin, respectively.The domestic water supply is based entirely on groundwater abstracted from the upper aquifer B2/A7 and the lower aquifer A4 aquifers and which together have a predicted safe yield of 87.5 million cubic meters per year. The area is highly developed and there is a continuous and *increasing demand for water to meet the* industrial, irrigation and domestic requirements.

Sites Selection Justification

The wells and spring in Amman Zarqa groundwater basin were selected for the following reasons:

- Locations of wells and springs nearby gas stations within less than 1 km approximately.
- Most of gas stations in selected area are old design and there is absence of monitoring on storage tanks.
- Presence of car services stations around inside protection zone 2 for water resources.
- Geological characteristics for wells and springs location, which are mainly described as recharge area and have direct connecting to aquifer especially in Zarqa river watershed.
- Importance of selected wells for domestic use and drinking water usage.
- Facilitation to reach the selected wells and springs.
- Groundwater flow direction.

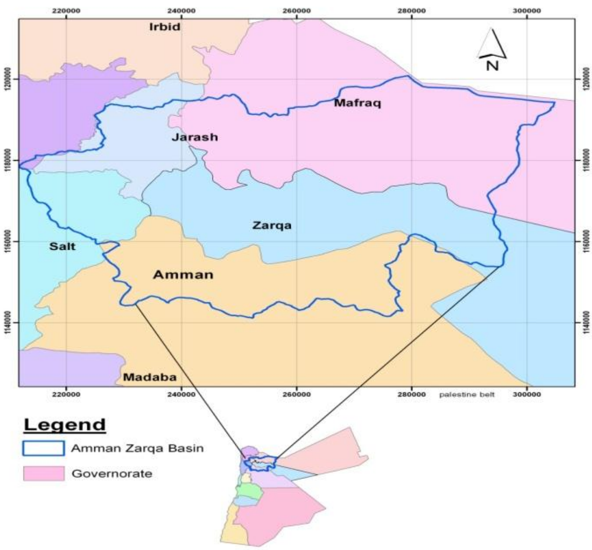

Fig-1- Locations Map of the Study area

Field Trips

Sample locations were specified using Geographic Information System (GIS) maps as shown in Figure 2 and Geographic Positioning System (GPS) tools. 76 Samples were collected in winter and summer 2011 as shown in Table (3) to observe the seasonal variation effect on the levels of MTBE and BTEX. The GIS map shows the gas stations and wells in Amman-Zarqa Basin.

Private Wells and public system owners were contacted to obtain permission to sample and to schedule sampling activities. All sampling sites were field-located using (GPS) system to accuracy of approximately 5 m and measured in the field for temperature, pH, specific conductance, dissolved oxygen concentration and redox potential. Samples were collected directly into 40-mL glass clean vials as mentioned in

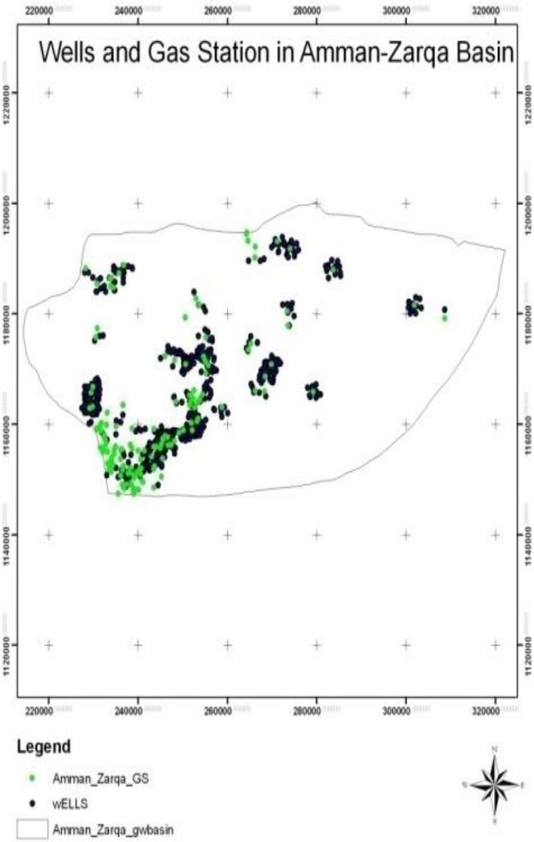

Fig -2- Gas Stations and Wells in Amman-Zarqa Basin Amman-Zarqa

section of handling, transporting and storing of samples.

Handling, transporting, storing of samples

Dried glass bottle sample (40ml) is filled just to the overflowing without passing air bubbles through sample or trapping air bubbles in sealed bottle. A reducing agent such as sodium thiosulfate (3mg/40 ml) is added if the source is chlorinated. The sample was maintained at 4 °C during transporting to the laboratory and was analyzed immediately. Delays between sampling and analysis necessitate preservation by using reducing agent such as HCl (4 drops 6N HCl / 40ml). Samples were analyzed within the maximum holding time of 14 days.

Analytical Method

Purge and Trap Concentrator-Gas Chromatograph-Mass Spectrometer Technique (P&T –GC-MS) was used to analyze MTBE and BTEX compounds.
The principal of the method is that highly volatile organic compounds are extracted from the sample by bubbling an inert gas through a 5 ml fritted Sparger at room temperature. Purged sample components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is trapped in a tube containing a sorbent material (trap). When purging is complete, the trap is heated and back flushed with helium to desorb the volatiles onto a gas chromatographic capillary column .The gas chromatography is temperature programmed to separate the volatiles which are then detected with a mass spectrometer and their concentrations are calculated by a data system. Potential interferences refers to the presence of volatile materials in the laboratory, therefore analysis of reagent water blank gives information about the presence of these contaminants. In case of their presence it is necessary to change the purge gas and its filter.

Analytical Conditions

The following conditions were used during purge and trap concentrator:

Purge time = 11 minutes.
Trap temperature = 190ºC.
Desorbs time = 0.5 minutes.
Trap bake temperature = 240ºC.
Baking time = 10 minutes.
Auto drain = On.

The gas chromatography was operated as follows:
Initial temperature: 50ºC Hold for 2 minutes
Temperature Program: 50 ºC to 150 ºC at a rate of 10ºC /min.
Final temperature: 150ºC Hold for 0.0 minutes.
The Mass spectrometer was operated under the following conditions:
Mass Range from 50 to 210 amu, scan time= 0.5 seconds
Window 1: 25.5 minutes.
Filament 2: ON
Electron Multiplier: ON

The reconstructed ion chromatogram of 4- Bromofluorobenzene (BFB) was observed before proceeding with the analysis and met the criteria mentioned in Table 1 according to the reference standard requirements (Eaton, 2005).

Table 1. BFB Mass Intensity criteria

M/Z (Mass to charge)	Required Intensity
50	15 to 40%of M/Z 95
75	30to 60%of M/Z 95
95	Base peak 100% Relative Abundance
96	5to 9%of M/Z 95
173	< 2%of M/Z 174
174	>50%of M/Z 95
175	5to 9%of M/Z 174
176	101%>M/Z174>95%
177	5to 9%of M/Z 176

25 ml of Standard and/or sample is injected into Purge and Trap Concentrator, MTBE and BTEX compounds are identified according to their mass spectrums with their 100% ion intensity as specified in Table 2. The concentration of MTBE and BTEX are calculated against external calibration standard.

Table 2. Characteristics masses (M/Z) for Purgeable Organic Compound

Compound	Primary Characteristic Ion
MTBE	73
Benzene	78
Toluene	*91*
Ethyl Benzene	*91*
m-Xylene	*91*
p-Xylene	*91*

The Lowest reportable value (LRV) of MTBE was 4 µg/l, improvement has been made to enhance LRV and increase the sensitivity of the analytical system by using 25ml sparger instead of 5ml. Therefore larger volume of sample (25 ml) was injected into Purge and Trap Concentrator and LRV of 1 µg/l was achieved. Regarding LRV of BTEX compounds, all are about 1 µg/l.

Quality of Results and statistical analyses

A number of standard statistical analyses were used to evaluate the data and assess possible relations between MTBE occurrence and various factors, including aquifer type (bedrock or unconsolidated deposits); bedrock geology; public water-system size; water-supply establishment type; reported well yield; well depth; population; land use; soils; roads; well proximity to underground gasoline storage tanks (USTs); and water-sample temperature, pH, specific conductance, and dissolved oxygen. Also samples were collected and analyzed as required and Several types of quality-control samples, representing 5 percent of the total samples including blank, duplicate, check standard and matrix spike.

Results and Discussions

The analytical results of MTBE and BTEX for the first phase of the study have revealed that concentrations of all monitored wells in Amman-Zarqa basin and Northern Governorate were not detectable and below the LRV (<1 µg/l) and comply with the national and international standards. In theory these results should positively correlate with the rainfall rate and negatively with the sampling depth/well depth, which means deep wells should be less subjected to contamination than shallow wells.

Since the age of underground fuel tanks in Zarqa is less than 14 years the sampled wells might not be affected by BTEX and MTBE yet due to the distance between the tanks and the sampled wells. Thus, these and future results will be interpreted in the context of groundwater models to take into consideration the groundwater flow velocity and direction. the transfer of these compound takes longer even though the solubility of MTBE in water is high and it is quickly moving in groundwater for long distances in comparison with BTEX compounds

Conclusions

This study covered water resources vulnerability due to MTBE and BTEX pollution in Amman-Zarqa Basin and Northern Governorate. The investigation considered the variation levels on the long term and their correlation with the type of underground fuel tanks and possibility to release oxygenated gasoline additives into the wells, taking into consideration the depth of wells and type of aquifers. This study is a first step in establishing a monitoring program for these substances in Jordan. Therefore Continuous monitoring of MTBE and BTEX leak to water resources is important and necessary to ensure the safety of water resources as well as monitoring the levels of MTBE and BTEX in soil samples underneath the fuel tanks in certain critical sites, also recommendation for the development of specifications for gas stations to maintain the integrity of the sustainability of the quality of these sources and to prevent the arrival of any pollutants in the future.

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