Impacts of the Petrochemical Industries on Groundwater Quality

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ABSTRACT

Global interest in groundwater resource management is significant, with petrochemical industrialization identified as a potential source of groundwater pollution. Petrochemical industrial processes cause significant impacts on groundwater quality through the discharging of highly contaminated waste with oil and chemicals. This study aims to determine the impact of the heavy petrochemical industrial city of Jubail Saudi Arabia on groundwater quality and identify special sources of pollution using a statistical approach. Samples from 47 groundwater wells were collected and analyzed for 23 indicators, mainly chlorinated hydrocarbons, 1,1-olefin hydrocarbons, vinyl chlorides, 1,1,2-trichloroethylene and chloroform, 1,2-dichloroethylene, chlorobenzene, and benzene. The results were compared with permissible standard limits to identify the level of exceedance. The results showed an exceedance in the concentrations of chlorinated hydrocarbons, total petroleum hydrocarbons, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-trichloroethane, and vinyl chloride more than ten times above the permissible limits of these concentrations. The study revealed the high impact of the petrochemical industries on groundwater quality. Since the current monitoring program depends only on annual sampling of groundwater, there has been a recommendation to install an online groundwater monitoring system to conserve water quality and achieve sustainable management.

Keywords: petrochemical, industrial pollution, water monitoring, groundwater quality, degradation.

INTRODUCTION

Groundwater is considered a major water resource for drinking, agricultural, and industrial uses. This role is becoming more important for arid and semi-arid regions [1, 2]. However, groundwater may impose several pollution sources that lead to quality deterioration, which may become worse for regions with limited groundwater resources [3]. Today, assessing groundwater quality is a key issue in preventing and controlling sources of pollution. Despite the superior quality of groundwater compared to surface water, direct and indirect interactions with surface water and pollutant sources can expose it to contamination. The degree of groundwater contamination is a factor of vulnerability, hazardousness, and groundwater development and utilization [4]. The prevention strategy is a key plan to protect soil and groundwater from seepage and contaminated discharge, especially in areas of high water table [5]. The pollutant plume could transport and affect water quality for several kilometers from the source [6]. Many variables impact the quality of groundwater sources in all locations, including the lithology of the area, air intake, climatic...
conditions, and human activities [7]. Municipal and industrial wastewater discharge continuously contributes to pollution, while climate conditions greatly influence surface drainage, a seasonal phenomenon. Wastewater ponds used in the treatment of contaminated water can lead to groundwater pollution if the waterproof layer is not operated properly [8]. Also, heavy metals from the petrochemical industry are a significant source of water contamination [9].

Groundwater contamination and its long-term management need deep attention since they have a significant influence on human health. Natural processes such as changes in rainfall inputs, soil erosion, and corrosion of crusted rock degrade groundwater, limiting its utility for drinking, industrial, agricultural, and recreational [10]. Previous works have demonstrated that small pollution sources can significantly affect large aquifers, posing serious hazards to groundwater [11]. The impacted groundwater is considered an urgent case for assessment and remediation [12]. The deterioration of groundwater quality may become worse if the assessment and identification tools for pollution sources do not exist or considered [13]. Research-based approaches can guide and assist decision-makers in determining the best strategy to mitigate the impact by treating the discharge or utilizing other management techniques [14]. For high-risk anthropogenic activities to groundwater quality, like the petrochemical industrial sector, there have been several tools available to draw attention and use proper responses and evaluations [15].

The petrochemical industry has a significant impact on groundwater as it is discharging total petroleum hydrocarbons (TPH) [16, 17]. Organic contamination of groundwater, particularly by nitrobenzene (NB), benzene, styrene, and chlorobenzene, is a major concern [18–20]. Several statistical approaches have been used for estimating and assessing the quality of water exposed to pollution sources [21]. These sources are part of natural processes or anthropogenic invasion of the salt intrusion, hydrologic cycle, eutrophication, urbanization, and industrialization [21]. The three most common statistical techniques have shown their effectiveness in identifying the magnitude and probable sources of pollution in the context of land-use changes [15]. These three pairwise variable statistical comparison techniques were widely used for identifying interactions between chemical parameters in groundwater quality assessment: Pearson’s correlation, principal component analysis, and cluster analysis [12]. These techniques were used for the most significant contributors to total pollution, possible source identification, and pollution source categories, i.e., septic tanks, agricultural interferences, and chlorine pollution [21]. Statistical approaches have shown success in identifying the spatial distribution of pollutants for shallow and deep groundwater and for different pollutant categories and magnitudes. These approaches included multivariate statistical techniques, hydro-geochemical indicators, pollution indexes, and water evaluation indices by considering physicochemical parameters [21]. The water quality indicators are a function of concentration and relative toxicity. However, the quality index has been evaluated for water quality based on heavy metal limitations, for instance, the maximum desirable and permissible limits of each heavy metal [22]. However, due to the nonrelaxation category consideration of several heavy metals, the indexes were based on only the highest desirable concentration [23]. Similar indices have also been identified in the literature including the heavy metal evaluation index, the Nemerow index, and the ecological risks of heavy metals in groundwater [21].

Several studies globally addressed the impact of petrochemical activities on groundwater quality. Leaks from fuel storage facilities have shown its contribution to rise TPH into groundwater and changes in pH and EC values [11]. TPH, methylene chloride, chlorobenzene, and benzene concentrations in groundwater have been shown to be impacted from fuel leak in Saudi Arabia as well as levels of pH, total dissolved solids, nitrate, and chloride [24]. None of these studies addressing the impact of petrochemical industries on groundwater quality in Saudi Arabia. Most of the petrochemical industries in Saudi Arabia are located in arid areas with limited water resources and a harsh climate. More than 7% of the world’s petrochemicals are produced in Jubail industrial city, which contributes about 12% of the national GDP (RC, 2024). Since surface water is rare in Saudi Arabia, groundwater is considered the main source of water for drinking, irrigation, and industry. Globally, many researchers have reported the high impact of petrochemical industries on groundwater and the significant deterioration of water quality. To the best of the author’s knowledge, this is the first published research regarding groundwater quality in areas occupied by heavy
petrochemical industries in the study area. There is no comprehensive study covers all chemical indicators related to petrochemical industry found in groundwater and addressing the relationship between these indicators and water quality. For this reason, this study will investigate the relationship between petrochemical discharge and groundwater pollution.

This study aims at assessing the impact of petrochemical industrial processes on groundwater quality. The assessment focuses on the spatial impact of these activities on groundwater quality using statistical approaches. Concentrations of chlorinated hydrocarbons, 1,1-olefinhydrocarbons (TPHs), vinyl chlorides, 1,1,2-trichloroethylene and chloroform, 1,2-dichloroethylene, chlorobenzene, and benzene were measured from 47 groundwater monitoring wells during the winter season. Simultaneous physical parameters, pH, EC, DO, VOC, and DOC were measured at the monitoring wells for interrelation and quality monitoring purposes. The spatial concentration distributions of the pollutants were presented, and control measures were suggested accordingly. The results can be used for quantitative and qualitative groundwater resource management and help decision-makers identify the suitability of groundwater for various uses.

METHODOLOGY

Study area

The Groundwater investigation was conducted in the Jubail Industrial City. Jubail Industrial City is considered the largest industrial project in the world. It is located in the Eastern province of the Saudi Arabia with a total area of 1016 km2 hosting heavy industries such as petrochemicals, refining, steel and iron, energy, food, concrete, metals, pipes, phosphate, plastic..etc, Jubail industrial city produces about 7% of the total world’s petrochemicals and contributes more than 11% of the Saudi GDP [25]. Physical parameters have been measured in situ for 47 groundwater monitoring wells in Jubail industrial city in the eastern arid region of the Kingdom of Saudi Arabia, located between 27.0000° N and 49.6667° E [26] (Fig. 1). The air temperature in the study area ranges in the summer between 37 and 45 °C during the day hours and from 27 to 28 °C during the night. The air temperature in winter ranges between 8 and 20 °C and the average annual rainfall rate varies between 6 and 100 mm.

Sampling and field works

The measurements included surface water depth, well depth, stagnant water volume in the well, water temperature, pH, and electrical conductivity (EC). A peristaltic pump with a low flow rate of 500 ml/min has been used to collect water samples. Triplicate samples have been gathered for each sampling point and stored in the recommended containers upon analysis. Samples were carried out at the sampling point in compliance with the American Society for Testing Materials standards (ASTM) using different calibrated standard instruments [27]. The sampling protocol included information on the sampling sites, sampling and analysis procedures for groundwater, equipment used, decontamination procedures, the chain of custody, sample handling, labeling, storage, and transportation, the field and laboratory QA/QC plans, and health and safety plans.

The depth of the groundwater well was measured using the HT water level meter Triangle frame with a length of 150 m. The probe is made of stainless-steel nickel-plated brass with a length of 20 cm and a diameter of 15 mm. Air-water contact was avoided during sampling procedures for chemical compounds and ammonia analysis by capping, tilting, and gently tapping the vials to avoid bubbles existing in the samples. Sample containers were promptly shut to limit aeration for TOC testing. All vials were washed before collection to decrease the likelihood of cross-contamination, and preservatives were applied for VOC analysis according to RC and EPA criteria for sampling preservation. Water samples were collected in 40-ml glass vials made by Teflon® septa for VOC analysis and preserved using concentrated HCL. The chemical testing approach was developed to detect contaminants that were suspected to be present in the samples collected. The chemical testing strategy was followed exactly as specified in the sample protocol. The pH and temperature were measured using a pH meter (HANNA-HI 8424), which was calibrated before each measurement campaign with three standard solutions (pH 4.01, 7.01, and 10.01; ± 0.2 mV). The EC was measured by using a conductivity meter (HM Digital, 0-9990 µS, ±2%, 0–80 °C). Field duplicate samples were obtained at intervals of about 10% of samples, with 3 samples of groundwater field duplicate samples collected. In each batch of shipping, laboratory QC samples for laboratory control sample (LCS), method blank (MB), laboratory duplicate/replicate (DUP), and matrix spike (MS) were conducted.
RESULTS AND DISCUSSION

Physical analysis and contamination assessment

Water temperature ranged between 13.8 °C and 33.4 °C during the cold season and this variation may be referred to the isolation effect of the overburden, which causes the groundwater temperature to be influenced by the average yearly surface temperature rather than the daily temperature at the ground surface [28]. The lower the temperature, the greater the overall depth and water level below the earth of the matching well. This reflects the fact that, due to the isolation effect of the overburden, the water temperature in the comparatively deeper wells does not correlate to the surface temperature at the time of sampling but to the approximate yearly temperature. pH values have significantly varied among sampling sites and ranged between 6.06 and 8.13 (average = 6.96 ± 0.64) as illustrated in Table 1. The electrical conductivity values ranged between 250 µS/cm and 30900 µS/cm (average = 4379 µS/cm ± 5325). These values reflected the total dissolved solid contents in the samples. The high salinity at some of the wells may be attributed to the seawater intrusion, where the site is close to the coastal area. The wide range of these values for each parameter (max-min) could be attributed to the impact of pollution on some wells, water depth, and the distance between the well and the pollution source. DO mean values of 7.12 mg/L ± 2.78 (ranging between 2.8 and 10.8 mg/L).

Chemical parameters

Oil and grease values exceeded the SLS of 614 (2013) of 0.2 mg/L at seven wells and ranged between 6 and 1580 mg/L, with mean values of 326 mg/L ± 701. Grease and oil are common pollutants discharged by the petrochemical industry, explaining the high concentration of oil and grease in the groundwater samples [29]. COD values varied among sampling sites, with mean values of 438.6 mg/L ± 730 (ranging between 9 and 2220 mg/L), respectively. Table 2 and Figure 2 show that, samples have higher COD values (ranging between 9 mg/L and 2220 mg/L) than the COD threshold value of 40 mg/L required for class V in the environmental quality standards for surface water (GB3838-2002) that applies for agricultural uses and in the general landscape [30, 31]. A significant correlation between DO and COD
Table 1. Basic hydrochemical parameters, minimum, maximum, mean, standard deviation, and variable coefficient (the ratio of the standard deviation to the mean), for the groundwater including water temperature (T), pH, electrical conductivity (EC), and dissolved oxygen (DO).

<table>
<thead>
<tr>
<th>Item</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean value</th>
<th>Standard deviation</th>
<th>Variable coefficient (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (ºC)</td>
<td>13.8</td>
<td>33.4</td>
<td>26.7</td>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>pH</td>
<td>6.32</td>
<td>9.9</td>
<td>7.6</td>
<td>0.6</td>
<td>0.08</td>
</tr>
<tr>
<td>EC (µS/cm)</td>
<td>255</td>
<td>29750</td>
<td>4380</td>
<td>5325</td>
<td>1.2</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>2.8</td>
<td>7.6</td>
<td>7.12</td>
<td>2.8</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2. Hydrochemical statistical characteristics, including minimum, maximum, mean, standard deviation, and variable coefficient (the ratio of the standard deviation to the mean), for sampling points.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean value</th>
<th>Standard deviation</th>
<th>Variable coefficient (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>9</td>
<td>2220</td>
<td>438.6</td>
<td>730</td>
<td>1.7</td>
</tr>
<tr>
<td>Ammonia (mg/L)</td>
<td>0.51</td>
<td>276</td>
<td>27.75</td>
<td>74.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Oil and grease (mg/L)</td>
<td>&lt;5</td>
<td>1580</td>
<td>326</td>
<td>131</td>
<td>2.91</td>
</tr>
<tr>
<td>Phenols (mg/L)</td>
<td>0</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Phosphorus (mg/L)</td>
<td>0</td>
<td>55</td>
<td>6</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Sulfide (mg/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total organic carbon (mg/L)</td>
<td>1</td>
<td>25600</td>
<td>616</td>
<td>3768</td>
<td>6</td>
</tr>
<tr>
<td>Chlorinated hydrocarbon (mg/L)</td>
<td>89</td>
<td>101000</td>
<td>32194</td>
<td>37499</td>
<td>1</td>
</tr>
<tr>
<td>1,1 Dichloroethane (mg/L)</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Total petroleum hydrocarbon (mg/L)</td>
<td>0</td>
<td>179</td>
<td>14</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>1,2 Dichloroethane (mg/L)</td>
<td>0</td>
<td>92</td>
<td>16</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>1,1,2 Trichloroethane (mg/L)</td>
<td>0</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Trichloromethane (mg/L)</td>
<td>0</td>
<td>64</td>
<td>11</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>0</td>
<td>64</td>
<td>11</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Chlorobenzene (mg/L)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Chloroethene (mg/L)</td>
<td>0</td>
<td>11</td>
<td>4</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Benzene (mg/L)</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 2. Boxplots of total ammonia (TN), Oil and grease, dissolved oxygen (DO), pH, phenols, and TOC concentrations log scale (mg/l) for 43 groundwater wells. The square boxes show the 25 and 75 percentile range. Median and mean values are indicated by horizontal lines and open squares, respectively.
has been observed ($r = -0.74, p < 0.05$) for all sampling sites. COD has shown to be significant correlated with pH values ($r = -0.64, p < 0.05$). Low DO concentration could be explained by the presence of biological activity that consumed DO from water. High COD values (Fig. 3) may come from the settleable high-strength non-biodegradable matter in petrochemical wastewater that ends up in the groundwater [32]. Two sampling sites (W37 S1 and W37 S2) have extremely high COD values of 2220 and 1850 mg/L, respectively, and extremely low DO values of 2.8 and 3.5 mg/L, respectively. See appendix. However, COD values were exceeded the results presented for groundwater in other petrochemical industrial contaminated areas of 228 mg/L [33].

Ammonia values ranged between 0.51 mg/L and 276 mg/L, with a mean value of 27.75 mg/L (Table 2). One sampling site (W36 S1) has been noted to have an ammonia value of 276 mg/L, while the next peak was measured to be 24.2 mg/L for the W26 S1 sampling site. According to WHO guidelines, three out of thirteen samples had ammonia concentrations that exceeded the upper limits for groundwater quality appropriate for agricultural use [34]. However, groundwater has shown its sensitivity to industrial wastewater resulting from petrochemical activities, where ammonia concentrations have significantly increased [35]. Wastewater discharge from petroleum industries has been reported to contain between 20 and 80 mg/L of ammonia-nitrogen, which explains the industry’s significant impact on groundwater quality [36].

Seven out of 25 samples have phenol content above the maximum permissible limits by WHO of 0.1 mg/L, and values ranged from 0.06 mg/L to 3.13 mg/L with a mean value of 0.6 mg/L ± 1.1 (Fig. 2). One out of the samples exceeded the intervention value of the Dutch Standards for groundwater of 0.200 mg/L. According to PME guidelines, all the remaining samples are above the limit of 0.005 mg/L. The petrochemical industry discharges high-quality phenol and may reach more than 1500 ppm in wastewater from oil refinery plants [37]. Phosphorus ranged from 0.04 mg/L to 55.4 mg/L, and one sample had a concentration below 0.01. See the Appendix for more information. Sulfide contents were below the allowable limit of 0.1 mg/L for all samples.

TOC values ranged between 1 and 696 mg/l (mean = 60.5±148.7 mg/L), and it has shown a significant correlation with COD ($r = 0.7, p < 0.05$) at 12 sampling sites (W11 S1 to MW-44 S1 except for W36 S1 well where the TOC value of 25600 mg/L exceeded the 3 times of the standard deviation. A significant correlation between COD and TOC may be attributed to the presence of high-strength organic matter in groundwater samples, which was reported as both TOC and COD. TOC have been shown to be an indicator and can be used effectively to delineate petroleum-related groundwater contamination thus help identify groundwater contamination points [38]. One sample (W11S1) has the maximum values for 1.1 trichloromethane (chloroform) (64 mg/L), dichloroethane (1.1 mg/L), trichloroethene (0.676 mg/L), and benzene (0.76 mg/L). High trichloromethane (chloroform) values have been observed for two sampling sites W37S1 and W37S2 of 18.3 and 20.4 mg/L, respectively. These sampling points had also extremely high COD values, and data were shown that there

![Figure 3. Relationship between measured COD (mg/l) and DO (mg/l) for 13 measured sampling sites.](image-url)
has been a significant correlation between COD and trichloromethane (chloroform) ($r = 0.49$, $p < 0.05$) (Fig. 4). However, several reports show that trichloromethane, tetrachloromethane, ethylbenzene, benzene, and trichloroethylene compounds showed potential lifetime cancer risk [39].

**TPH compounds**

About 55% of the samples have been considered to be contaminated with TPH, according to PME guidelines, TPH should not exceed the 0.2 mg/L limit. TPH values have ranged from 0.070 mg/L to 179.200 mg/L (mean = 14.2 mg/L ± 32.8). TPH mean value exceeded numbers presented for groundwater pollution from fuel storage facilities (9.7 mg/L) [11], oil fields sites [33, 40] and oil spill and petrochemical industry (28.7 mg/L ± 1.3) [41]. There has been a significant correlation between TPH and TOC values ($r = 0.77$, $p < 0.05$) (Fig. 5). TPH concentration has been shown to significantly influence TOC accumulation in surface sediment samples [42]. Significant correlations between TOC and TPH have also been noted and used as an indicator of contamination in petrochemical industries [38].

![Figure 4](image1.png)  
**Figure 4.** Relationship between measured chemical oxygen demand (COD (mg/L)) and trichloromethane (mg/L)) for 13 sampling sites

![Figure 5](image2.png)  
**Figure 5.** Relationship between measured total organic carbon (TOC (mg/L)) and total petroleum hydrocarbon (TPH (mg/L)) for 13 sampling sites
Chlorinated hydrocarbons

Chlorinated hydrocarbons concentrations varied from 89 mg/L (GMW6 S1) to 101,000 mg/L (W26 S1). According to PME guidelines, chlorinated hydrocarbons in groundwater are prohibited, and an excessive percentage of chlorinated hydrocarbons causes kidney damage in adults [43]. Despite the existence of high chlorinated hydrocarbon concentrations at 13 wells, chlorine measurements were below the detectable limit of 0.2 mg/L. 1,1-dichloroethane contents ranged from 0.010 mg/L to 1.0 mg/L, where 15% of the total sampling sites exceeded the intervention value according to the Dutch standards for groundwater for such substances, which is 0.9 mg/L. Dichloroethane is not carcinogenic for humans, but exposure to high levels of volatile chlorinated hydrocarbons is associated with potential health risks, where the organs and immune systems are the main targets [44, 45]. The noncarcinogenic health effects extended to liver damage, kidney injury, and nervous system diseases [46]. The relationship between chlorinated hydrocarbon concentration, chlorine concentration, and hydro-ion concentration has been discussed for karst aquifers to be varied [47]. It has been shown that for karst aquifers, the dynamic characteristics of trichloromethane and 1, 1, 2-trichloroethane can indicate those of chlorinated hydrocarbons, where the rate of natural attenuation was observed to decrease with decreasing concentrations of hydrocarbon compounds. 1, 2-dichloroethane (EDC) ranged from 0.013 mg/L to 92.300 mg/L. The intervention value of Dutch standards is 0.400 mg/L for such substances. According to these standards, all the samples can be contaminated with this substance except 4 sampling sites (GMW-6 S1, W12 S1, W23 S1, and MW-44 S1). Regarding 1,1,2 trichloroethane, 4 samples were below the maximum contaminant level/EPA of 0.005 mg/L, and the contents of the remaining samples ranged from 0.194 mg/L to 7.400 mg/L, which are above the maximum contaminant level/EPA. The intervention value according to the Dutch standards for groundwater for such substance is 0.130 mg/L. This means that all remaining groundwater samples are contaminated with this substance, which imposes severe health impacts for long-term exposure that increases the risk of cancer [48]. Regarding trichloromethane (chloroform), the contents of the groundwater samples ranged from 0.036 mg/L to 64.000 mg/L. The intervention value according to the Dutch standards for groundwater for such substances is 0.400 mg/L. This means that all the groundwater samples except for (GMW-6 S1), (W35 S1), and (W12S1) are contaminated with this substance. According to PME guidelines, it should not exceed 0.001 mg/L. Regarding Trichloroethylene, about half of the samples were at LOR (0.020 mg/L), and the contents of the remaining samples ranged from 0.020 mg/L to 0.676 mg/L. The intervention value according to the Dutch standards for groundwater for such substances is 0.500 mg/L. Trichloromethane has ranged between 0.036 and 64 mg/L with a mean value of 10.8 ± 17.3 mg/L. This means that only one groundwater sample (W11 S1) can be considered contaminated with this substance. Regarding chlorobenzene, 4 out of 13 samples were above the maximum contaminant level/EPA permissible limit of 0.1, and the values varied from 0.025 mg/L to 0.444 mg/L. Intervention values according to the Dutch standards for groundwater for chlorobenzene components, that were not analyzed individually here, mono, di, tri, tetra, penta, and hexachlorobenzene, are 0.180, 0.050, 0.010, 0.0025, 0.0010, and 0.0005 mg/L, respectively. This means (if we consider the less stringent component (monochlorobenzene)) that samples (W11 S1), (W36 S1), and (W39 S1) can be considered contaminated with such substances. Contaminated water samples with chlorobenzene above the permissible limit can increase the risk of liver or kidney problems. Concerning chloroethene (vinyl chloride), all the groundwater samples were below the 0.200 mg/L value except for W28 S1, W39 S1, and MW-44 S1, with 2.030, 10.900, and 0.210 mg/L, respectively. The intervention value according to the Dutch standards for groundwater for such substances is 0.005 mg/L. This implies that we can consider the aforementioned groundwater samples contaminated with the substance. Moreover, all the other samples could be potentially contaminated with this substance, but this cannot be proven unless a more sensitive analysis method below the 0.005 mg/L range is employed. According to PME guidelines, the contents of this substance should not exceed 0.001 mg/L. Benzene contents were below 0.001 for 28 samples, while the remaining samples...
ranged from 0.002 mg/L to 3.110 mg/L. The intervention value according to the Dutch standards for groundwater for such substances is 0.030 mg/L. This implies that we can consider all the remaining samples contaminated with this substance. According to PME and maximum permissible limits, benzene contents in water should not exceed 0.005 mg/L, and exceedance levels may cause anemia, a decrease in blood platelets, and increased risk of cancer. Styrene contents were below 0.05 mg/L for all samples (Figure 6), and these values are below the Dutch and maximum permissible limits for groundwater for such substances, which are 0.300 mg/L. Therefore, it is not possible to consider any of these samples as contaminated with this substance. Styrene is used as an intermediate in many industries including petrochemical ones. It was classified by EPA’s as a carcinogen [49].

All values were below 0.005 mg/L for 1, 2 dichloroethane (EDC) contents except for two samples (W17 S1 and MW-45 S1) values were 0.013 mg/L and 0.014 mg/L, respectively. These values are below the intervention value of the Dutch standards for groundwater of 0.400 mg/L. Total petroleum hydrocarbons (TPH) were at LOR (0.050 mg/L) for seven samples out of 33 samples, while they ranged for 26 samples from 0.07 mg/L to 45.500 mg/L.

All the data points except for phosphorus have a strong correlation, coefficient almost exactly equal to 1 or 100% within the 0.05 alpha precision value. This suggests that all sampling points have been influenced by the pollution source. It is clear from the 3-D shape distribution (Figure 7) and 2-D contour image distributions (Figure 8) that the pollution source is an identified location that is represented in graphs by the maximum of all chemical parameters assessed and minimized at the dissolved oxygen which is a good indication of the pollution from that point location.

CONCLUSIONS

Groundwater is the most vulnerable to contamination, especially from the petrochemical production process. Contamination in many of the groundwater samples has been noticed during the sampling period. There has been a substantial exceeding of the acceptance limits for phenol, chlorinated hydrocarbons, 1, 1 dichloroethane, dichloroethylene, chlorobenzene, and vinyl chloride concentrations at all sampling sites within the industrial zone as per Dutch standards and PME guidelines. Further studies are recommended to review all measures that are taken, particularly in the production area, to reduce discharges and leakages to the land surface and eventually to the groundwater. To make a comparison with the monitoring results of the previous years to interpret the cumulative tendency of the pollutants in the groundwater and the dynamic shifts in the hydrology and the water table in the facility area to find out the potential relation of some of the analyzed parameters with the

![Figure 6](image-url). Box-plot for VOC measurements for the groundwater. The square boxes show the 25 and 75-percentile range. The median and mean values are marked by horizontal lines and open squares, respectively
Figure 7. 3-Dimensional distribution of the chemical parameters tested
Figure 8. 2-Dimensional (contour map) distribution of the chemical parameters tested.
nature of the lithological layers of the monitoring wells that were not available to us. More interesting insights can be gleaned from the correlation table. Except for phosphorus, it is evident that all the data points have a strong correlation with one another. Chemical parameters showed a significant correlation among others, with a correlation coefficient almost equal to 1 or 100% within the 0.05 alpha precision. This may indicate that the same source of pollution affects all the wells in the research. Overall, the petrochemical industry poses a risk of groundwater contamination, and measures need to be taken to prevent and mitigate this pollution.

Acknowledgments

The authors would like to express their sincere gratitude to the European Union under the ENI CBC Mediterranean Sea Basin Programme, Project B_A.2.1_0088_MED-QUAD, for their support of the “Smart Water Use Applications (SWUAP)” living laboratory to provide the necessary equipment to conduct sample tests. Special thanks to Al-Balqa Applied University, and Ajloun National University for making this work possible.

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