The Environmental Impact of a Complex Hydrogeological System on Hydrocarbon-Pollutants’ Natural Attenuation: The Case of the Coastal Aquifers in Eleusis, West Attica, Greece

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Abstract: The study area is the Thriassion Plain, an important area, in antiquity, surrounding the famous ancient town of Eleusis, 20 km west of Athens. The modern town and port and the entire area were heavily industrialized (1965–1995) coupled with unregulated urban and agricultural development. The presence of two crude oil refineries and other oil-related industries have strongly impacted the entire environment, including soils, waters and sediments of the broader area. The purpose of this work is to better understand how a multi-layered groundwater system affects the potential underground spread of certain fuel volatile compounds, namely the BTEX (benzene, toluene, ethylbenzene and total xylenes) as well as their attenuation after their direct or indirect release into the aquifer system. The spatial distribution of BTEX in groundwaters show that they were concentrated mainly in four rather restricted locations. Three of them were spotted, as expected, in the close vicinity of known pollution sources (a military airfield and two crude oil refineries). The other one corresponds to an abandoned site with no outstanding pollution sources where wells exist, eventually used for illegal dumping of oily wastes. It is important that the concentrations decrease significantly from autumn to spring. This decline could be characterized as natural attenuation, related to natural dilution phenomena and a flushing out of pollutants discharging through underwater springs to the sea during the rainy period (October to April). This, in turn, could be associated to the specific geological conditions affecting the hydrology, such as the unconsolidated non-permeable deposits and the multi layered formations of the area’s aquifers.

Keywords: BTEX natural attenuation; hydro-stratigraphy; multi-layered aquifer; Thriassion Plain; confined and unconfined aquifer; coastal aquifer; Gulf of Eleusis
1. Introduction

Our study area is the Thriassion Plain, in the Attica Prefecture, located 25 km west of Athens. It covers a surface of 480 km$^2$, characterized by a relatively smooth relief with altitudes up to 100 m and comprises the town of Aspropyrgos, Eleusis (pronounced Elefsis) and Magoula (Figure 1). The broader area is a historical and cultural landmark of Greece since prehistory. In the period 1965–1995, the area experienced a rapid unprogrammed, industrialization, which, in combination with the lack of environmental infrastructures, resulted in generation and accumulation of urban and industrial wastes, natural resources degradation and environmental hazards [1–3], turning the area into one of the most polluted Mediterranean regions. The drainage receptor of the study area is the Gulf of Eleusis, a semi enclosed embayment within the Saronikos Gulf, one of the most important areas in terms of the ecological status- and climate change-related coastal hazards [4,5] and biomonitoring [6] in the Eastern Mediterranean Sea. The Gulf of Eleusis and the Saronikos Gulf represent the seaward boundary of the metropolitan area of Athens and Piraeus whereas within the Thriassion Plain some of the biggest industrial installations of the country exist, such as oil refineries, steel mills and cement factories, and shipyards. The industrialization and land use changes have affected the sea bottom sediments [7–9], the soil [10,11], and the water column dynamics of the Gulf of Eleusis [12,13] which is the final receptor of human activities in the plain [14–17]. Among the industries involved with oil refining, processing and transport, the Refinery of Aspropyrgos (known as ELPE), the Refinery of Eleusis, and the relics of a petroleum recycling unit (CYCLON), along with the Military Airfield may potentially be responsible for hydrocarbon leakages to the groundwater, which is used in industries and for irrigation of agricultural lands. The first evidence of groundwater contamination from hydrocarbons was reported by Kounis et al. [18]. Ever since, the presence of aliphatic and PAHs pollution in coastal marine waters and tissues was documented [19] while some groundwater oil-remediation was merely reported for the area of the Refinery of Aspropyrgos [20].

The present study investigates the potential groundwater pollution from BTEX (benzene, toluene, ethylbenzene and xylenes) within the complex aquifer system of the Thriassion Plain. It was carried out by the National and Kapodistrian University of Athens and supported by the General Secretariat of Research and Technology. The research was considered of critical importance by the Local Authorities because it provided feedback to the environmental management of the area as well as a starting point for further investigations necessary to address the complex pollution issues of the region.
2. BTEX Characteristics and Fate into the Aquifers

The BTEX forms about the 16% of a typical gasoline blend and is associated with adverse impact on human-health. Although the individual BTEX compounds are widely used as solvents and in manufacturing, gasoline leaks from underground storage tanks and distribution pipelines are the primary contributor of BTEX contamination in ground water [21].

Among the four BTEX compounds, benzene is classified as a carcinogen by the European Union Council Directive 98/83/EC, the U.S. Environmental Protection Agency and the International Agency for Research on Cancer. As a result of this concern, threshold levels in freshwater have been established, namely the Maximum Contamination Limits (MCL) [22,23]. Nevertheless, respective thresholds or permissible levels in groundwaters have not been set, so far. Table 1 presents the BTEX MCLs, expressed in parts per million (ppm, or mg/L) in the EU and several other countries with high recorded oil pollution.

Table 1. The MCLs of BTEX.

|          | EU (mg/L) | US EPA (mg/L) | China (mg/L) | Canada (mg/L) | New Zealand (mg/L) | Japan (mg/L) |
|----------|-----------|---------------|--------------|---------------|--------------------|--------------|
| Benzene  | 0.001     | 0.005         | 0.01         | 0.005         | 0.01               | 0.01         |
| Toluene  | Not legislated | 1           | 0.7          | 0.024         | 0.8                | 0.2          |
| Xylenes  | Not legislated | 0.7        | 0.3          | 0.0024        | 0.4                | Not legislated |
| Ethylbenzene | Not legislated | 0.7      | 0.3          | 0.0024        | 0.4                | Not legislated |

It is well known that many organic contaminants exist in a liquid phase and are not soluble in water. These are the Non-Aqueous Phase Liquids (NAPLs) which include fuels (gasoline, aviation fuel), chlorinated solvents, and polychlorinated biphenyls. In a typical petroleum hydrocarbon contamination incident, such as an underground leaking of a storage tank or pipeline, the escaping organic substance (e.g., gasoline) usually moves downwards through the unsaturated or vadose zone until it reaches the aquifer. There, the mobility of the organic substance (e.g., hydrocarbon) decreases as water saturation increases respectively and accumulation takes place particularly at the interface, above the water-table.

Some important parameters determining the environmental fate of the organic substance are the compound’s volatility (gaseous phase), solubility in water (aqueous phase), specific weight determining floating or sinking in the aqueous zone, and affinity to minerals and other organic compounds and surfaces, determining sorption (absorption/adsorption and dissolution) [24]. Furthermore, the degradation rate of the compound depends on the presence of bacteria and fungi species, the environmental conditions (temperature, aquifer minerals, organic matter content), and the availability and concentration of carbon sources available to the microbial consortia. The rate of biodegradation tends to slow down when DO concentrations are less than about 1–2 ppm. Anaerobic biodegradation of benzene appears to be more aquifer specific than that for the other monoaromatic hydrocarbons [25–27].

3. Geology and Hydrogeological Characteristics of the Study Area

The Palaeozoic formations, 300 to 400 m thick, are the geological basement of the broader area. The Palaeozoic is represented by (a) clastic materials, shales and sandstones, which alternate with greywackes and conglomerates; (b) basic igneous volcanic rocks; and (c) lenticular intercalations of thin bedded carbonate units. Weak metamorphosis, successive folds and schistosity are also observed. This background is overlain by Mesozoic sediments such as: (a) phyllites and sandstone, (b) meta-pyroclastic and meta-volcanic rocks hornstones and tuffs; (c) Triassic limestones, dolomitic limestones and dolomites; and (d) Cretaceous limestones. The Cenozoic is represented by: (a) Paleocene flysch; (b) Neogene deposits of marls with lignite intercalations in places, sandstone, marly limestone; and (c) Pleistocene (clay, sands, gravels, torrential fans of loosely and cohesive conglomerates) and Late Quaternary alluvial deposits (clay, loams, sands and gravels) at the top [28–30]. The geological settings are illustrated in Figure 2.
The hydrogeology of the broader area has been extremely influenced by hydro-stratigraphic and tectonic factors as well as sea level changes [29–34]. The paleogeographic evolution, the aquifer geometry and thickness, the salinity controls, and the groundwater input are important features for the water source management. In past studies two main aquifer systems were described: (1) the Plio–Pleistocene sediments and (2) the Triassic limestone/dolomite and the Cretaceous limestone [18,28,35,36].

Recent detailed hydrogeological research studies [37,38] have recalculated the aquifer characteristics, providing a revised hydrogeological model of three distinct groundwater hydrostratigraphic units (including their subunits): (a) the Neogene-Quaternary sediments comprising (a.1) the Holocene -Upper Pleistocene aquifer system, generally unconfined and semi-confined consisted of clays, sands and gravels. It is recharged by rainfall and upward leakage from lower aquifers. The Holocene clays form local barriers to groundwater flow, causing the formation of marshes and swamps and/or upward leakage. The coastal clay strata prevent the lower standing aquifers from direct seawater intrusion where groundwater of good quality was found 90 m below sea level (m.b.s.l.) [37,38]; (a.2) the Pleistocene system, made up of marls with lignite layers in places, sands and marly limestones which is a multi-layered confined aquifer. There is Pleistocene sediments recharge and preferential lateral flow from the carbonate basement. The direction of the groundwater flow within the confined layers is SE, where a partly upward leakage onto the coastal zone occurs while, the main water volume is moving very slowly towards the Saronikos Gulf with hydraulic gradient 1–2‰. (b) The Cretaceous aquifer, flow to the southwest and discharge partly through coastal springs near the city of Eleusis and the entire North-Western coastline of the Eleusis Gulf and partly into Neogene–Quaternary deposits [39,40]. From this field work, the seasonal water level fluctuations in the unconfined aquifer were measured 0.4–0.5 m and within the confined aquifers 1.2–1.5 m. A conceptual model of the deposits in Figure 3 illustrates the multi-level aquifer conditions within the Pleistocene strata, where lenticular intercalation consists of a water-yielding formation [31].
4. Materials and Methods

The sampled area included all major potential polluting sources, from crude oil refineries and other related industries and the Military Airfield, as well as the city of Eleusis itself. Thirty-four (34) to forty-five (45) groundwater samples were collected, twice a year, in November and May, when the water level was at the lowest and the highest level, respectively. The whole investigation lasted three years, from 2003 to 2005. The results of the in-situ survey, including water level measurements, and lithology identification of each sampling location, are reported in Table 2. Sampling, storage, shipping and laboratory characterization of the target analytes were carried out according to USEPA Analytical Method 524.2 [41] in the Laboratory of Environmental Chemistry, Department of Chemistry, National and Kapodistrian University of Athens (NKUA). The samples were collected from the first five centimeters of the water surface of the wells or by pumping from the boreholes. The Solid Phase Microextraction (SPME) was applied to pre-concentrate the BTEX [42–44]. Gas Chromatography (GC) was applied to separate the compounds from the water samples, and Mass Spectrometry (MS) to detect them. The chromatography results were validated through the protocol procedures (linearity, precision, recover, standards). The Limits of Detection (LOD) achieved with the method applied were 0.095 ppb for benzene, 0.077 ppb for toluene, 0.099 ppb for ethylbenzene and 0.089 ppb for total xylenes [44]. The quantified results were illustrated on a GIS database to assess the distribution of the pollutants within the aquifers. The estimation of the groundwater spatial dispersion (spatial analysis) was accomplished using an ArcGIS software. The data layers were digitized and stored in the database, including sampling-well locations with the analytical data, main industries and drainage network, road network and towns/settlements. The concentrations were presented on concentration-contour maps. Using the Geostatistical analyst extension of ArcGIS, the initial values of each parameter (i.e., concentration BTEX compound) for a sampling season were interpolated in grid layers with a cell size of 20 × 20 m. The inverse squared distance (ISD) method was used to interpolate the data obtained. The contour maps provided, refer to the concentrations of benzene for all sampling seasons. The classification of the concentration values in the contour maps is different among the four target analytes, therefore when a target analyte has a wide range of concentrations (e.g., xylenes) there are more classes in the GIS map.

Figure 3. Conceptual hydro-stratigraphic column of the Plio-Pleistocene.
Table 2. Hydrogeological characteristics of the wells; (U), (C) and (L) stands for unconfined, confined and semi-confined aquifer respectively; hydraulic head.

| Well (W)/Borehole (B) Id | Age, Lithology, Aquifer Type | Hydraulic Head (M.A.S.L.) |
|-------------------------|----------------------------|--------------------------|
|                         |                           | 03 November | 04 May | 04 November | 05 May | 05 November |
| 1B                      | Triassic carbonate (U)     | 140.00 to 160.00 |
| 3B                      | Triassic carbonate (L)     | 78.00 to 80.00 |
| 8W                      | Pleistocene sediments (C)  | 4.35        | 4.68   | 4.37        | 4.77   | 4.63       |
| 12W                     | Pleistocene sediments (L)  | 5.00        | 5.53   | 5.47        | 5.55   | 5.65       |
| 15W                     | Pleistocene sediments (L)  | no data     |        |             |        |            |
| 16W                     | Pleistocene sediments (L)  | 4.90        | 5.51   | 4.22        | 6.57   | 5.24       |
| 20W                     | Pleistocene sediments (L)  | 4.85        | 5.35   | 4.99        | 5.47   | 4.88       |
| 22W                     | Pleistocene sediments (U)  | 5.53        | 5.88   | no data     |        |            |
| 23/24W                  | Holocene clay (U)          | 5.98        | 4.15   | 4.16        | 4.01   | 3.13       |
| 27W                     | Holocene clay (U)          | 2.91        | 3.56   | 2.82        | 3.43   | 2.91       |
| 29W                     | Pleistocene sediments (C)  | 3.10        | 4.52   | 4.93        | 4.73   | 4.68       |
| 32W                     | Pleistocene sediments (L)  | no data     |        |             |        |            |
| 37W                     | Holocene clay (U)          | 2.20        | 2.95   | 3.38        | 3.35   | 3.40       |
| 38W                     | Holocene clay(U)           | 1.85        | 2.22   | 2.80        | 2.32   | 1.75       |
| 44W                     | Holocene clay (L)          | 1.96        | 2.23   | 1.93        | 2.17   | 1.78       |
| 45W                     | Holocene clay (U)          | 1.65        | 1.90   | 2.36        | 1.96   | 1.48       |
| 46W                     | Holocene clay (U)          | 2.38        | 2.70   | 2.40        | 2.10   | 1.69       |
| 47W                     | Holocene clay (U)          | 1.13        | 1.40   | 1.45        | 1.45   | 1.20       |
| 54W                     | Pleistocene sediments (L)  | 4.03        | 4.56   | 4.42        | 4.69   | 4.05       |
| 55W                     | Pleistocene sediments (L)  | 6.10        | 4.93   | 3.09        | 5.08   | 4.21       |
| 58W                     | Pleistocene sand with clay intercalations (C) | 3.60 | 4.10 | 4.90 | 5.13 | 3.88 |
| 61W                     | Pleistocene pebbles (L)    | 4.96        | 5.01   | 4.74        | 4.82   | 4.52       |
| 62W                     | Pleistocene pebbles (L)    | 5.37        | 7.19   | 5.35        | 7.10   | 6.38       |
| 63W                     | Pleistocene pebbles with clay intercalations (L) | 3.60 | 4.39 | 3.89 | 4.67 | 3.92 |
| 66W                     | Pleistocene sediments with clay intercalations (L) | 1.00 | 1.40 | 1.20 | 1.50 | 0.77 |
| 67W                     | Pleistocene with clay intercalations (L) | 2.40 | 2.73 | 2.45 | 2.10 | 1.69 |
| 72W                     | Pleistocene gravels (U)    | 4.90        | 5.70   | 5.38        | 6.04   | 5.43       |
| 86/88W                  | Clay (L)                   | 3.30        | 3.90   | 4.86        | 4.96   | 5.25       |
| 95W                     | Pleistocene sediments (U)  | 1.12        | 1.82   | 0.62        | 1.92   | 1.22       |
| 98W                     | Pleistocene sediments (U)  | 4.98        | 5.26   | 5.03        | 5.10   | 4.61       |
| 100W                    | Pleistocene sediments (U)  | 4.20        | 4.40   | 4.15        | 4.25   | 3.90       |
| 102W                    | Pleistocene pebbles (U)    | 2.65        | 2.95   | 2.90        | 2.88   | 2.35       |
| 104B                    | Pleistocene pebbles (U)    | 2.60 to 27.00 |
| 106W                    | Holocene sediments and pebbles (U) | 0.70 | 1.20 | 0.55 | 1.28 | 1.60 |
| 134W                    | Pleistocene sediments (C)  | 4.80        | 6.00   | 5.30        | 7.40   | 6.99       |
| 136W                    | Pleistocene sediments (C)  | 5.20        | 6.05   | 4.95        | 5.90   | 7.01       |
| 142W                    | Pleistocene sediments (C)  | 6.10        | 6.14   | 5.92        | 6.24   | 7.11       |
| 152W                    | Pleistocene sediments (C)  | 95.00 to 102.00 |
| 169B                    | Triassic carbonate (L)     | 85.00 to 88.00 |
| 187W                    | Pleistocene (U)            | 3.26        | 3.76   | 3.40        | 3.74   | 3.19       |
| 1000W                   | Pleistocene sediments (U)  | 3.66        | 4.02   | 3.95        | 4.12   | 3.89       |
| 2000W                   | Triassic carbonates (U)    |              |        |             |        |            |
| 3000W                   | Pleistocene aggregates (U) | 1.50 | 1.65 | 1.84 | 1.50 | 1.76 |
| 5000W                   | Pleistocene conglomerates (U) | 3.29 | 4.40 | 3.70 | 4.65 | 4.60 |
| 4000W                   | Pleistocene conglomerates (U) | 6.29 | 6.63 | 6.42 | 6.48 | 6.15 |
| (Petrola) 1              | Holocene clay (U)          | no data     | 6.92   | 7.00        | no data |
| (Petrola) 10300W         | Holocene clay (U)          | no data     | 1.66   | 2.00        | no data |
| (Pyrkal) 10500W          | Holocene clay (U)          | no data     | 0.25   | 0.25        | no data |
| (Pyrkal) 10600W          | Triassic carbonate (L)     | no data     | 2.50   | 2.43        | no data |

1 Refinery of Eleusis.
5. Results and Discussion

The nonspatial analysis which involves the results of the target pollutants laboratory determination, is provided with the concentration values presented in Supplementary Material (Table S1 for benzene, Table S2 for toluene, Table S3 for ethylbenzene and in Table S4 for the xylenes). All values are expressed in parts per billion (ppb). The sample id “22” was considered unsuitable for chromatographic determination, because its oily texture and odor appeared likely to provoke damage to the instrumentation. The produced results of the first year indicated the need to broaden/expand the sampling area.

The BTEX are not commonly found in nature, as for instance the metals, and since they are hazardous for human health, it could be considered that every concentration over a non-detectable level may be regarded as “pollution” or “contamination”. Regarding benzene values, we remark that seventeen (17) out of forty-five (45) samples exceeded the EU MCL in all autumn monitoring seasons, and another five (5) once or twice again in autumn. Overall, benzene pollution might be alleged as not-at-a-high-risk, though significant. More specifically, in November 2003, the concentrations of benzene range from the detection limit up to 29 ppb, in May 2004 the water level had an average rise of 0.45 m and the maximum concentration was 14 ppb, whereas the concentrations of all other samples were significantly lower than the ones in November 2003. In November 2004, new samples were collected from the Refinery of Eleusis (id Petrola “10300”, Petrola “10400”) and the industrial area of Pyrcal (id “10500”, “10600”, at the western boundary of the study area). Exactly at the same area, the maximum concentration (57 ppb) was found. Between May and November 2004, the average fall of the water level was 0.24 m. In May 2005 concentrations ranged from the detection limit up to 16 ppb, and the average rise of the water level was 0.39 m. Finally, in November 2005, the concentrations ranged from the detection limit up to 20 ppb and it seems that they were slightly lower than in the previous autumn sampling periods. Moreover, the sample id “22” was a mix of water and oil, which raised the question of its origin (a “backdoor” discharge?). This sample was not chromatographically characterized at all, to avert damage to the analytical instrumentation but has served as a “guide” for new sampling in the surrounding area.

As for the concentrations of toluene, ethylbenzene and xylenes, their values were much lower than their MCLs (Supplementary Material). More specifically, the pollution of toluene can be assumed as negligible to low, since its concentration values are much lower than the MCL. The maximum concentration of 45 ppb (still, lower than the MCL) was reported in the installations of the “Pyrcal” industry (id “10500” and “10600”). For ethylbenzene, almost all values are close to the detection limit. For the xylenes, the pollution should also be considered as negligible to low, compared to its MCL. Moreover, it is remarkable that, after the winter rainfall, the BTEX concentration values in May are significantly reduced, reaching very low to non-detectable levels. This may be attributed to the significant dilution of the target compounds by the recharge of the aquifer, which at the end, discharges to the sea through submarine water springs at the western boundary of the study area, mainly.

Concerning the spatial distribution depicted on the GIS contour maps, four separate locations of benzene pollution are developed: (a) northeast of the Hellenic Refinery of Aspropyrgos (ELPE), (b) at the western and the eastern boundaries of the Military Airfield of Eleusis, (c) south-east of the town of Aspropyrgos and (d) next to the Refinery of Aspropyrgos (ELPE). Figures 4–8 illustrate the estimated groundwater distribution. The spatial distribution of toluene, ethylbenzene and xylenes is the same as benzene; therefore, the results are not presented and commented for each compound individually.

The standard deviation is very high only for benzene for all monitoring seasons. As for the other compounds, the variability is potentially attributed to, either the existence of a non-permanent pollution input or, an eventually differentiated natural attenuation. The examination of the \((B + T)/(E + X)\) ratio could provide some useful information on the original time of gasoline release [44,45]. Due to the difference in their mobility, concentration ratios of the individual BTEX compounds (e.g., \(B/E, T/X, \text{etc.}\)) in fuel-contaminated groundwater tend to change uniformly with time. The relative content of BTEX compounds in manufactured gasoline has varied with time; initial ratio values are often unavailable, which limits wide application of these ratios as time indicators. Although, in the study area we cannot
identify numerous oil industries or fuel stations that have undertaken historically serious changes, we could still use the BTEX ratio: $R_B = (B + T)/(E + X)$ in an attempt to better comprehend some environmental changes in dissolved plumes, if any.

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Figure 4. The estimated groundwater distribution of benzene in November 2003.

Figure 5. The estimated groundwater distribution of benzene in May 2004.

Figure 6. The estimated groundwater distribution of benzene in November 2004.

The standard deviation is very high only for benzene for all monitoring seasons. As for the other compounds, the variability is potentially attributed to, either the existence of a non-permanent

Figure 7. The estimated groundwater distribution of benzene in May 2005.

Figure 8. The estimated groundwater distribution of benzene in November 2005.
The standard deviation is very high only for benzene for all monitoring seasons. As for the other compounds, the variability is potentially attributed to, either the existence of a non-permanent

Kaplan’s multiple investigations [45,46], mostly empirical, have shown that near the source and immediately after a gasoline spill, $R_b$ reaches values between 1.5 and 6, which indicates a recent release (typically $<5$ years). In the absence of NAPL, $R_b$ in a dissolved gasoline plume is close to that of the original gasoline ($0.8 < R_b < 1.1$). The ratio then decreases as a function of time, and values less than 0.5 usually reflecting gasoline residence time longer than 10 years. $R_b = 6.6$ confirms the presence of a thick gasoline rich layer. In general, a two-fold decrease of $R_b$ occurs in 2.3 years.

Applying the $R_b$ values onto our reported concentrations, we may conclude that for the Refinery of Eleusis (id “10300”, “10400”, “10500” and “10600”), located at the western boundaries of the contour maps, where the highest concentration values were reported, the calculated $R_b < 0.5$ indicates a long permanent BTEX occurrence. For the second most polluted area surrounding the Military Airfield, (sample id “98”, “5000” at west, “3000”, “44” at south, “54”, “55” at east), the calculated $1.5 < R_b < 6$ reveals a recent release of BTEX, consistent to the nature of the pollution source, including heavy local atmospheric pollution from the fuel used in planes and the washing out of the atmosphere by rain. The fact that the groundwater from the southern boundaries of the Airfield (id “102”, “104”, “106”) seems not to be affected by BTEX release due to the confined nature of the groundwater system, might be partly attributed to geomorphological and hydrological specifications not yet fully understood.

As for the concentrations near the Refinery of Aspropyrgos (id “8”), the $R_b < 0.5$ indicates a long permanent BTEX source. Apparently, the city of Eleusis itself seems not to be polluted from BTEX, though it is located at the furthest downgradient part of the aquifer flow lines. Theoretically, the
pollution should “track” the groundwater flow into the Gulf of Eleusis and, thus pollution should have visibly affected the southern areas, near the coastline. It is likely that the benzene has not reached the gulf because of biodegradation along the flow paths. Biodegradation is an important process attenuating benzene and other BTEX constituents in groundwater in many areas.

Finally, it is worthwhile to examine the occurrence of 0.6 ppb and 2.4 ppb at the boreholes with id “1”, “3”, located within the Triassic carbonates (limestone/dolomites). There, the groundwater is pumped within the Mesozoic limestones from a depth of 78 up to 160 m, with no evident pollution source nearby. If we exclude an ad hoc illegal pollution, benzene contamination may be explained by some hydraulic communication between the Pleistocene sediments and the carbonate ones.

Overall, the local character of the BTEX occurrence may be documented by the confined, multi-layered hydro-stratigraphic system as well as, the existence of impermeable aquifer barriers. Additionally, the very low concentrations of the spring sampling periods reveal both a good aeration and a dynamic seasonal enrichment/dilution of the groundwater system.

6. Conclusions and Suggestions

The laboratory determination and the spatial analysis and study of BTEX, in the Thriassion Plain lead to some useful general conclusions: Some high concentrations from BTEX were identified in autumn when the water table is at the furthest downgradient level. Benzene concentration values are much more elevated than those of the other BTEX compounds. The spring concentrations of all compounds are very low. The considerably reduced rainfall of the summer months coupled with enhanced abstraction through groundwater pumping could explain the difference between the autumn and spring benzene concentrations. The high values of benzene as well as the empirical Kaplan’s values, indicate that the pollution originates mainly from permanent sources namely oil refinery and handling sources, located relatively close to the sampling points. The spatial distribution of BTEX in groundwaters show that they were concentrated mainly in four, rather restricted locations. Three of them were in the close vicinity of evident pollution sources (a military airfield and two crude oil refineries), whereas, the other one corresponds to an abandoned site with no outstanding pollution sources where wells exist, eventually used occasionally for illegal dumping of oily wastes. The town of Eleusis seems not to be polluted from BTEX, despite the fact that it is located at the lowest part of the aquifer flow lines. This could be attributed to impermeable strata working as water and pollution barriers. The hydro-stratigraphic particularities, along with general hydrogeochemical conditions play an important role to the BTEX fate and attenuation rate.

Recent developments in the expansion of the works of the refineries, including changes in the operations of the Military airport, make it necessary, in our point of view, to proceed to a new and deeper BTEX pollution investigation, to revisit our approached attenuation after 15 years of operation. In case that further studies and monitoring demonstrate that the pollution persists, the National and Local Authorities should take urgently active and effective measures to prevent further deterioration and environmental damage. The designation of the city of Eleusis as cultural capital of Europe 2021, though somehow disturbed by COVID-19, may offer an opportunity for also refocusing on environmental pollution and the groundwater as a valuable natural resource that requires further attention including by keeping it free from hydrocarbon pollution.

Supplementary Materials: The following are available online at http://www.mdpi.com/2077-1312/8/12/1018/s1, Table S1. Concentrations of benzene, Table S2. Concentrations of toluene, Table S3. Concentrations of ethylbenzene; and Table S4. Concentrations of xylenes.

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