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Organic Compounds Residues Investigation in Groundwater at Assiut Governorate, Egypt

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Abstract

However the adverse impact of organic pollutants and their occurrence in the food chain in Egypt, scarce studies have dealt with these pollutants in water resources. The aim of this work is the non-targeted organic compounds investigation in Assiut Governorate groundwater, Egypt. Thirty-four samples were collected and analyzed for their chemical oxygen demand (COD), and three of them were selected for the non-targeted survey of organic compounds by GC-MS instrument. The COD values ranged from 0 to 216 mg O_2/l, indicating the pollution of some samples with organic compounds. The GC-MS results indicated the occurrence of plastic, petroleum, pesticides and pharmaceutical residues in the analyzed samples. The source of these compounds may be household effluents, improper disposal of wastewater through absorption septic tanks, improper application of panned pesticides and leakage from fuel tanks. Finally, the groundwater needs targeted investigation of organic pollutants in the study area.

Keywords: Groundwater; Quaternary aquifer; Nile Valley; Organic residuals; Plastics; Gasoline; Pesticides

1. Introduction

Groundwater is the second source of freshwater, after Nile River, in the Nile valley for drinking and irrigation purposes [1, 2]. The geogenic processes and anthropogenic activities in the Nile Valley impact groundwater quality [3, 4]. Seleem et al. [5] pointed out the impact of water pollution with heavy metals at Assiut Governorate on human health. The Quaternary Aquifer in the Nile Valley is highly vulnerable to pollution owing to its hydrogeological and land use/land cover characteristics [6, 7].

The pollution of water bodies with organic compounds has become of great importance owing to their adverse impact on water quality and biota. General, organic pollution degree of water body can be assessed by measuring Chemical Oxygen Demand (COD) [8, 9]. The high COD values are found mainly in water, which may be due to the mixing of domestic and industrial waste [10, 11]. Non-targeted GC-MS surveying of organic chemicals becomes a powerful tool in environmental quality evaluation, especially in exploring studies of complex mixtures of pollutants. Typical complex environments, such as groundwater, wastewaters, soil, sediments, and air particles, may contain hundreds of organic chemicals [12]. Besides occurring natural organics, many anthropogenic substances are produced and used daily, including, agrochemicals pharmaceuticals, cosmetics and plastic additives. These chemicals can be harmful and could degrade or transformed into harmful products [13].

The used pesticides application in agricultural practice not only polluted the surface water resource but also percolate into groundwater aquifer in Nile Valley. The advantage of groundwater over surface water is its low content of pesticides [14], this may be related to the role of silty clay layer, which prevents part of these pollutants from the groundwater [15]. Masoud et al. [15] detected many types of pesticides in the groundwater collected from Al-Gharbiya Governorate. Many toxic phthalate esters (DiBP, DnBP, DnOp and DEHP) and PAHs (phenanthrene, fluoranthene and pyrene) were observed in the agricultural soil of Sohag Governorate, Egypt [16].

Unfortunately, 6 organochlorine pesticides residues (dielderin, DDT, endrin, heptachlor, lindane and heptachlor epoxide) were recorded in cow milk collected from different villages of Sohag Governorate [17]. Also, some pesticides were recorded in human breast milk [18, 19] indicating

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their transport through the food chain. However, the studies on the groundwater in Egypt focused on inorganic [4, 5, 7] and microbial [9, 20] pollution. So, the current study focuses on the organic pollution of groundwater wells in the Northwestern part of Assiut Governorate, Egypt.

2. Materials and methods

Thirty-four groundwater samples were taken from wells in the Northwestern part of Assiut Governorate, Egypt (Fig. 1). Pre-rinsed brown glass bottles were filled with the samples, sealed tightly. The Chemical Oxygen Demand (COD) was determined by $K_2Cr_2O_7$ reflux method by using HANNA Spectrophotometer (HI 83399). For organic compound determination, the sample (1 L) was acidified with sulfuric acid to pH 2 and extracted twice with redistilled CH_2Cl_2 [21]. The combined extracts were evaporated, dried with anhydrous Na2SO4 and then concentrated to 1 ml using stream of pure nitrogen. The extracts were diluted with dichloromethane and analyzed by gas chromatography.

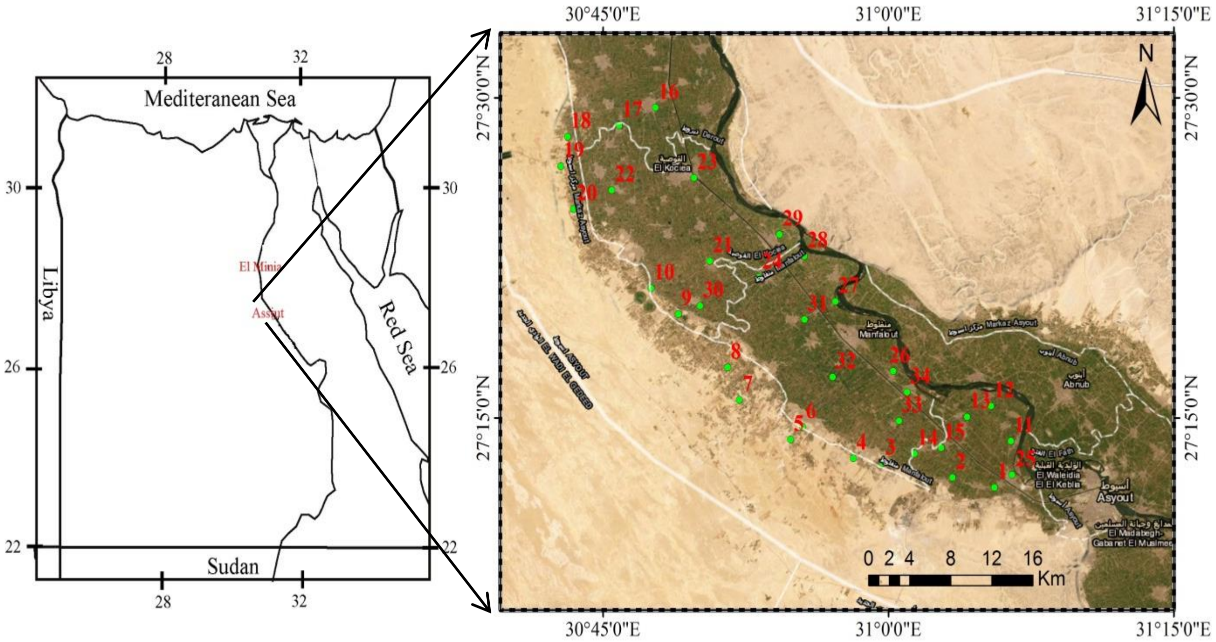


Fig. 1. Location map of the studied samples

Maps were constructed by using ArcGIS (10.4.2) software [22]. Inverse distance weighting (IDW) was used to create spatial distribution map of COD within the study area.

Assiut Governorate, represents an important part of central Nile Valley, contains many big industries (cement, petrochemical, fertilizers, detergents and food), urbanization and agricultural activities [23]. The northern part of Assiut Governorate, between latitudes 27° 10' and 27° 31' N and longitudes 30° 41' and 31° 8' E (Fig. 1), was the target of this study.

The GC-MS system (Agilent Technologies) was equipped with gas chromatograph (7890B) and mass spectrometer detector (5977A) at Central Laboratories Network, National Research Centre, Egypt. The GC was equipped with HP-5MS column (30 m x 0.25 mm internal diameter and 0.25 µm film thickness). Analyses were carried out using hydrogen as the carrier gas at a flow rate of 1.5 ml/min at a splitless, injection volume of 2 µl and the following temperature program: 45 °C for 2 min; rising at 10 °C /min to 310 °C and held for 10 min. The injector and detector were held at 280 °C and 300 °C, respectively. Mass spectra were obtained by electron ionization (EI) at 70 eV; using a spectral range of m/z 25-700. Identification of different constituents was determined by comparing the spectrum fragmentation pattern with those stored in Wiley and NIST Mass Spectral Library data.

3. Results and Discussion

In this study, for assessing the organic pollution levels in groundwater, the chemical oxygen demand (COD) was measured (Table 1 and Fig. 2). Based on the results, it should be observed that the highest COD level (216 mg O2/l) was observed in sample 30. On the other hand many locations groundwater were free from COD. The very low levels of COD in most of the studied samples may be attributed to the un-contamination or diesel contamination. Diesel contains some straight-chain aliphatic, aromatic, and nitrogenous compounds that are not readily oxidizable [24] leading to COD's low value. The permissible limit of COD in irrigation water is 75 mg O2/l [25]. Chapman and Kimstach [26] mentioned that COD value >20 mg O2/l could be due to effluents. Only 3 samples (Nos. 30, 31 and 32) have COD value more than 20 mg O2 /l indicating the occurrence of effluent in these sites. This may be resulted from the leakage of petroleum tanks (Fig. 3) and wastewater disposal the adsorption septic tanks. Most countries did not have water quality standards for COD, but available standards in Japan is 5 mg O2/l limit and Taiwan is 25 mg O2/l [27]. Accordingly, the values at the study area are quite alarming at only three sites. Also, 2 samples were considered unacceptable for irrigation based on COD values >75 mg O2/l. It was observed that the central part of the study area has the highest COD values (Fig. 2).

Table 1: Groundwater samples content of COD (mg O_2/l).

SN	COD	SN	COD
1	4	18	2
2	0	19	0
3	1	20	7
4	1	21	4
5	0	22	0
6	12	23	5
7	3	24	0
8	6	25	13
9	2	26	10
10	3	27	7
11	0	28	0
12	1	29	0
13	5	30	216
14	1	31	32
15	2	32	81
16	0	33	16
17	5	34	0

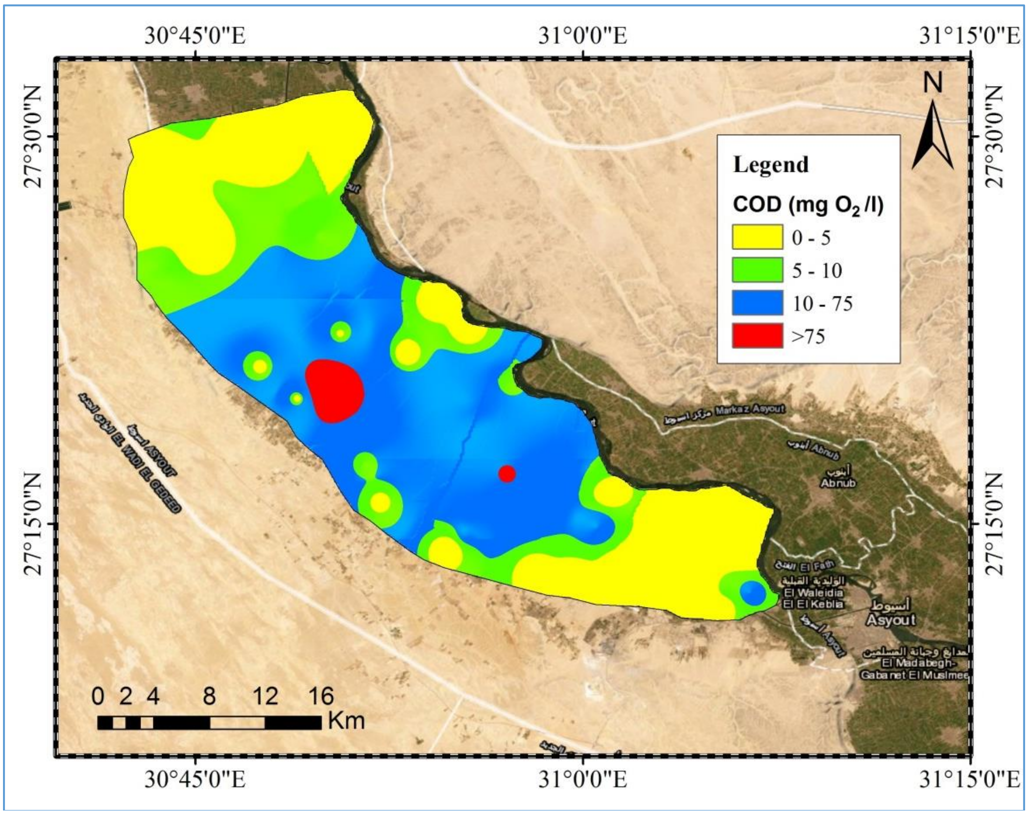


Fig. 2.Spatial distribution map of COD in the study area.

Fig. 3. Photo showing the leakage of petroleum derivatives.

The GC-MS detected organic compounds in the analyzed groundwater samples are illustrated in Table (2) and Figure (4). About 33 organic compounds were recorded in the studied samples. The highest number of organic compounds, 19 compounds, was discovered in groundwater sample 6; 14 organic compounds were found in groundwater sample 30; 16 organic compounds were isolated in groundwater sample 32. These compounds are follow up plastics, petroleum, pesticides, pharmaceuticals and other organic residues

Plastics are now the most widespread substances used and replace many other materials [16]. The degradation of plastics in the environment can produce many toxic substances as “Tris(2,4-di-tert-butylphenyl) phosphate (DtBPP)” (Eq 1). DtBPP is considered very toxic material with III Cramer toxicity class. The DtBPP proposed maximum daily intakes for the adults is 58.4 ng/kg/day [13]. DtBPP is the major degradation product of Irgafos 168 (tris(2,4-di-tertbutylphenyl)phosphite) (Eq. 1) by thermal and sunlight exposure [28]. Many other plastics degradation products; 17-Pentatriacontene [29], 7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione [30] and 2,4,6-Trimethyl-1-nonene [31] were detected in the studied groundwater (Table 2).

Oil products applied daily in all sectors are numerous and often complex; are commonly named total petroleum hydrocarbons (TPHs). TPHs such as gasoline, diesel, and heavy oil are the most widespread TPHs and are stored in tanks at gas stations, which are common contamination sites worldwide [32]. Diesel is widely used in transport vehicles and the groundwater abstraction pumps (diesel pump) (Fig. 3). The occurrence of aliphatic hydrocarbons such as heneicosane, hexadecane, docosane, heptacosane, nonadecane, tetradecane, 2-methyltetracosane, and pentatriacontane could be explained by diesel pollution [33]. 2-Bromononane is a petroleum hydrocarbon [34]. Also, 2,2,4-Trimethyl-3-pentanone is a gasoline pollution tracer. Oxalic acid, allyl hexadecyl ester is one of the polar metabolites of petroleum biodegradation [35]. The 14.-.beta.-H-Pregna is a short chain sterane isomer, often found in petroleum [36]. The “14-beta-H-pregna” is naturally found in plants [37]. Melegy et al. [16] pointed out the pollution of agricultural soil in the Nile Valley with petroleum hydrocarbons.

Pesticides are a common groundwater contaminant [38]. The incorrect application of pesticides and fertilizers in agricultural practice is the major source of pesticides. It is widely used in preventing and controlling the diseases and pests of crops and can leach through the soil profile into the groundwater [39]. In the current study hexadecanoic acid was recorded in the studied samples. Hexadecanoic acid is a soap concentrate insecticide and acaricide applied to combat soft-bodied pests. Also used as an additive in formulations and as an adjuvant in many pesticides manufacturing [40]. It is also used as nematicide as well as antioxidant, hypocholesterolemic, lubricant, antiandrogenic and hemolytic [41]. Also, Tris(2,4-di-tert-butylphenyl) phosphate is widely used in pesticides [13]. The presence of pesticides in groundwater can be due to diffuse or point pollution [38]. One of the most important recorded compounds is 3,5-DTBP (3,5-bis(1,1-dimethylethyl)-Phenol). DTBP family is toxic lipophilic phenols naturally produced by many organisms. It is exhibited significant toxicity in all testing organisms even the producing species. Insecticidal Activities warehouse beetles, mites Antifungal Activities. It has cytotoxicity in human cells and animals, phytotoxicities, insecticidal (e.g. warehouse beetles and mites), antimicrobial and nematicidal activities [42]. The 3,5-bis(1,1-dimethylethyl)-Phenol act as herbicides and are involved in plastics and cosmetics [43]. The point source can be attributed to the input of chemicals in the irrigation system and reverse injection into the aquifer.

Thousands of pharmaceuticals are being produced for saving human life; however they emerged as a new class of environmental pollutants. These compounds have been documented in all environmental compartments; groundwater, surface waters, sea water, wastewater treatment plants

Table 2: GC-MS identified organic compounds in groundwater.

	Sample 6			Sample 30			Sample 32		
Peak	RT	Name	Area %	RT	Name	Area %	RT	Name	Area %
1	12.161	Hexadecane	0.92	21.169	Heneicosane	1.28	15.508	2,4,6,8-Tetramethyl-1-undecene	0.1
2	12.556	Phenol, 3,5-bis(1,1-dimethylethyl)-	0.77	21.959	Pentatriacontane	1.34	16.897	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	0.11
3	12.708	2,4,6-Trimethyl-1-nonene	0.62	21.997	Pentatriacontane	1.55	17.231	Tridecane, 3-methyl-	0.11
4	13.315	1,1-Difluoro-2-ethylhexane	0.82	22.793	Docosane	5.07	17.512	Hexadecanoic acid	0.34
5	14.62	2-Bromononane	1.34	23.552	Heptacosane	9.77	19.302	Oxalic acid, allyl hexadecyl ester	0.17
6	15.083	2(3H)-Furanone, dihydro-3-hydroxy-4,4-dimethyl-, (R)-	0.71	24.273	Tetrapentacontane, 1,54-dibromo-	12.48	20.889	8-Methyl-6-nonenamide	0.15
7	15.508	2,4,6,8-Tetramethyl-1-undecene	1.21	24.971	14-.BETA.-H-PREGNA	13	21.071	Heneicosane	0.23
8	16.866	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	0.91	25.647	7,8-Epoxylanostan-11-ol, 3-acetoxy-	17.51	21.875	Tetradecane	0.41
9	17.231	Tridecane, 3-methyl-	1.03	26.292	17-(1,5-Dimethyl-hexyl)-4,4,9,13,14-pentamethylhexadecahydrocyclopenta[a]phenanthren-3-one	15.42	22.642	Hexadecane	1.04
10	17.428	Hexadecanoic acid	3.71	26.891	17-Pentatriacontene	9.15	23.378	Nonadecane	0.94
11	19.325	Oxalic acid, allyl hexadecyl ester	1.17	27.468	14-.BETA.-H-PREGNA	5.32	24.099	Carbonic acid, eicosyl prop-1-en-2-yl ester	2.66
12	20.843	8-Methyl-6-nonenamide	1.94	28.227	3-(6,6-Dimethyl-5-oxohept-2-enyl)-cycloheptanone	2.28	24.288	Tetrapentacontane, 1,54-dibromo-	0.18
13	21.048	Heneicosane	0.69	28.561	Pentalene, octahydro-1-(2-octyldecyl)-	0.28	24.766	2-methyltetracosane	0.24
14	22.596	2,2,4-Trimethyl-3-pentanone	0.8	29.32	Tris(2,4-di-tert-butylphenyl) phosphate	5.55	25.427	1-Octanol, 2-butyl-	0.15
15	23.977	2,4,4-Trimethyl-2-penten-1-ol	3.37				28.128	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)	9.07
16	24.266	Tetrapentacontane, 1,54-dibromo-	1.19				29.244	Tris(2,4-di-tert-butylphenyl) phosphate	84.11
17	28.098	Phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1)	10.84						
18	29.206	Tris(2,4-di-tert-butylphenyl) phosphate	58.31						
19	35.618	4-(4-Chlorophenyl)-2-(2-phenylethyl)-6-[4-[bis(4-fluorophenyl) methyl]piperazinyl	9.64						

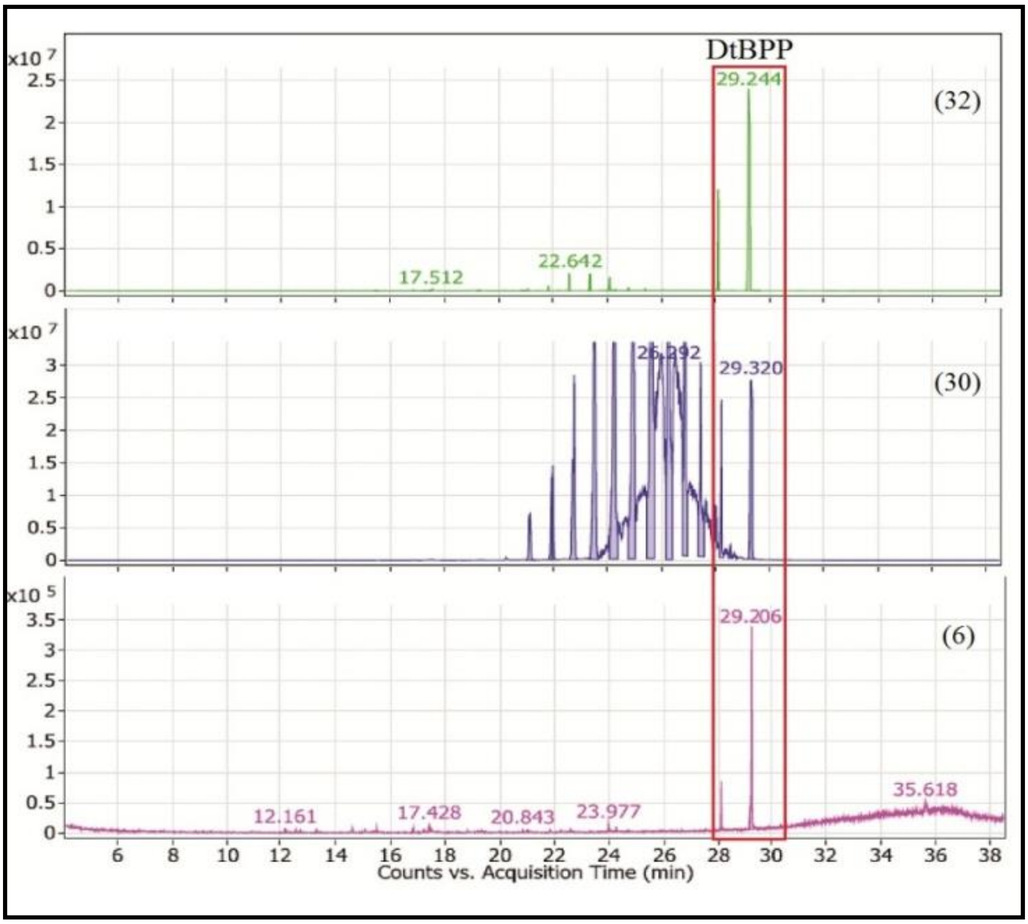
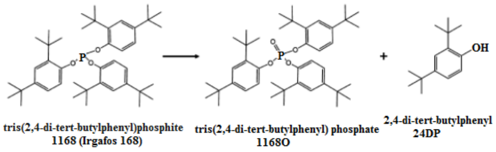


Fig. 4. Comparison between total ion chromatograms of samples extract



Eq. 1

(influents and effluents), soils, and sludge [44]. Pharmaceuticals residues in the environment can have chronic and acute harmful effects on natural flora, fauna and human health, and considered as “compounds of emerging concern” [45]. Many of these compounds are persistent, degradation resistance in aqueous systems [46]. The main source of pharmaceuticals in water systems is human excretion of metabolized and unmetabolized drugs, disposal of unused medicines, and applying pharmaceutical- containing matrices directly in agricultural fields [47, 48]. Bound and Voulvoulis [49] observed that only 22% of the Southeast England population return pharmaceuticals to sellers for proper disposal while 66% and 12% of the population put extra pharmaceuticals into household wastes and flush them down sinks and drains, respectively. Several compounds were identified in the studied groundwater samples, which were attributed to the group of pharmaceuticals. Dihydro-3-hydroxy-4,4-dimethyl-, (R)- 2(3H)-Furanone (R-Pantolactone), which is used as an intermediate in the production of cosmetics and pharma products is detected in sample 7. The 3-acetoxy-7,8-Epoxylanostan-11-ol was detected in sample 30, widely used as anti-inflammatory agents [50, 51] and an antidepressant activity for animals [52].

4. Conclusion

The groundwater of the study area contains considerable concentration of COD in some localities as a result of wastewater effluents, agricultural activities and fuel leakage. The main emerging organic pollutants were plastics and petroleum residues. The Tris(2,4-di-tert-butylphenyl)phosphate is the most plastics degradation product recorded in the studied samples. Many petroleum residues have been recorded; heneicosane, hexadecane, docosane, heptacosane, nonadecane, etc., indicating the subject of the aquifer into petroleum effluents. The water resources in Egypt need more surveys with respect to organic pollutants. Also toxic pesticides residues, DTBP, DtBPP and hexadecanoic acid, have been detected. The variation in the non-targeted GC-MS detected compounds pointed out the variation of pollution sources in the study area and the vulnerability of the aquifer. The present results are expected to be a supportive addition for the protection of groundwater resources in the Nile Valley to achieving safe drinking water and protecting human health.

Conflicts of interest

"There are no conflicts to declare".

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