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DETECTION OF ENDOCRINE DISRUPTING CHEMICALS IN VARIOUS WATER SOURCES IN ASSIUT GOVERNORATE

WALAA OTIFY [1]; HOSNIA ABDEL-MOHSEIN [1]; MANAL MAHMOUD [1]; NAGWA ABO EL-MAALI [2] AND REEM DOSOKY [1]

[1] Department of Animal, Poultry Hygiene and Environmental Sanitation, Faculty of Veterinary Medicine, Assiut University, Assiut, 71526 Egypt
[2] Department of Analytical Chemistry, Faculty of Science, Assiut University, Assiut, 71526 Egypt

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ABSTRACT

The occurrence of endocrine disrupting chemicals in various water sources is a growing problem worldwide. Endocrine disrupting chemicals are considered persistent contaminants in the aquatic environment, affecting various species including humans, due to their massive usage in daily life. The objective of the current study was to detect their presence in waste and irrigation water sources in Assiut Governorate using Liquid-liquid Extraction (LLE) procedure, followed by separation with Gas Chromatography with Mass Spectrometry (GC-MS). The analysis revealed the presence of several endocrine disrupting chemicals, including fluoxetine, caffeine, and phthalate esters, such as diethyl phthalate, di-n-propyl phthalate, di-butyl phthalate and butyl benzyl phthalate, along with phenolic compounds such as 4-nonyl phenol, 4-octyl phenol and 4-tert butyl phenol. Notably, fluoxetine showed the highest detection rates, with ٨٣.٣% and 50% in waste and irrigation water samples, respectively. The results of the current study will contribute significantly to the research about endocrine disrupting chemicals in water sources and further control of its presence to preserve the environment.

***Keywords*:** Emerging Contaminants, Fluoxetine, Phthalates esters, Gas Chromatography-Mass Spectrometry

INTRODUCTION

Endocrine disrupting chemicals (EDCs) have been recently considered emerging pollutants due to their widespread use and increased contamination of different environmental sections (Ismail *et al.*, 2017). EDCs refer to a range of chemical agents that interfere with human body systems' processes, including the synthesis, secretion, transport, metabolism and binding action of natural blood-borne hormones (Darbre, 2019). These substances originate either from natural or synthetic sources, functioning as agents that interfere with the regulatory mechanisms and release of chemical hormones (La Merrill *et al.*, 2020).

Natural sources of EDCs found in living organisms are categorized into estrogens, androgens, progestogens and phytoestrogens (Gmurek *et al.*, 2017). On

Corresponding author: WALAA OTIFY
E-mail address: Walaa.Otify@aun.edu.eg
Present address: Department of Animal, Poultry Hygiene and Environmental Sanitation, Faculty of Veterinary Medicine, Assiut University, 71526 Egypt.

the other hand, synthetic EDCs are divided into six groups: phthalates, pesticides, phenolic compounds, polyhalogenated compounds, drugs, and pharmaceutical and personal care products (Wee & Aris, 2017). Among the most frequently studied EDCs are estrone, 17β-estradiol, ethinyl estradiol, estriol, bisphenol A, 4-nonyl phenol, nonyl phenol ethoxylates, octyl phenol and triclosan are among the most common (Aris *et al.,* 2020; Maciuszek *et al.,* 2020; Barrera *et al.,* 2021; Pollock *et al.,* 2021).

EDCs permeated the aquatic ecosystems through multiple channels, including wastewater treatment plants (WWTP) that process pharmaceutical and medical waste, leaching chemicals from household and industrial products, such as detergents and personal care items, and the runoff of pesticide residues from agricultural activities (Pironti *et al.,* 2021).

EDCs have been detected in surface and wastewater all over the world, with phthalates, nonylphenol and bisphenol A being among the most frequently identified compounds (Pironti *et al.,* 2021). In Portugal, estrone, 17β-estradiol, estriol, alkyl phenols and ethoxylates of alkyl phenols were detected in different rivers using enzyme-linked immunosorbent assay (ELISA) (Rocha *et al.,* 2019). Bisphenol A, triclosan, 4-nonylphenol, 4-tert octyl phenol, methyl paraben, propyl paraben, butyl paraben, benzyl butyl phthalate, di (2-ethylhexyl) phthalate and di-n-butyl phthalate have been investigated in river, groundwater samples and agricultural soil samples in India using liquid chromatography with tandem mass spectrometry (LC–MS/MS) (Saha *et al.,* 2022).

17β-estradiol, bisphenol A, 4-nonyl phenol and 4-tert octyl phenol were identified in the wastewater of the Metropolitan area of Monterrey, Mexico utilizing gas chromatography coupled with mass spectrometry (GC-MS) (López-Velázquez *et al.,* 2021). Additionally, EDCs from personal care and pharmaceutical category were detected in the wastewater of Volos, Greece using LC–MS/MS (Papageorgiou *et al.,* 2016).

EDCs are known to bioaccumulate within organisms, and their concentrations tend to rise in the food chain reaching their maximum concentrations in the top predator (Pironti *et al.,* 2021). Furthermore, the cumulative effects of EDCs have been reported, which might have serious consequences (i.e., the cocktail effect) (Barouki, 2017). The World Health Organization emphasized that decision-makers must take action, since exposure to these chemicals poses a risk to both human and wildlife, imposing the protection of water supply from sewage, effluents, and chemical pollutants (Bergman *et al.,* 2013; Wafy, 2019).

The effect of EDCs varies across species, producing different effects. In fish, feminism has been observed, along with lower reproductive fitness, lower sperm quantity and alteration in reproductive characteristics (Carnevali *et al.,* 2018). Reproductive dysfunctions and abnormalities were reported in reptiles (Matthiessen, 2013). In avian species, issues such as eggshell thinning, functional alterations that reduce fitness and populations, as well as reproductive and growth factors have been reported (Bodziach *et al.,* 2021).

Human health effects involves impacts on the nervous system, such as brain injury, non-reproductive neural effects and neurogenesis effects (Engler-Chiurazzi *et al.,* 2017). Reproductive health issues comprise ovulation disorders, breast cancer, endometriosis, uterine fibroids, pregnancy and fertility problems (Sifakis *et al.,* 2017). Additionally, EDCs act as metabolic and cellular disruptors, contributing to cardio-vascular diseases, obesity, alterations in sex and growth hormones, abnormal cell proliferation, and prostate cancer cells

(Giulivo *et al.*, 2016; Wang *et al.*, 2016). The effect of EDCs on the growth and development comprise growth and mental retardation, and early puberty (Botton *et al.*, 2017). The serious and significant implications of EDCs on both wildlife and human necessitate urgent need for their detection and management in aquatic environments.

MATERIALS AND METHOD

1. Study sites

For detection of EDCs, waste and irrigation water samples were collected from eight sites in Assiut Governorate, Egypt, as presented in Figures 1 and 2 during the period from June to September 2022. Six sites representing wastewater samples and two sites representing irrigation water samples were analyzed. From each site, four samples were taken from distinct four places, each spaced 10-15 meters apart, and then pooled to represent that site. Influent samples from the WWTP were taken directly from the tank.

Table (1) provides information about the sampling sites, including their longitude and latitude, as determined using the GPS Coordinates website**.** EL Malah canal (EMC) is approximately 5 KM Northwestern Assiut city and is subjected to domestic sewage disposal. Arab Al madabegh (AA) location was presented by a wastewater sample from urban Arab Al madabegh WWTP, which is highly contaminated with domestic waste of Assiut city and some surrounding villages. EL Zenar drain (EZD) is a drain canal that has become polluted due to the accumulation of refuse from sweeping vehicles and household waste.

Markaz El Fath site 1 (MF1) samples were collected from the major canal that runs parallel to the main road, which is exposed to animal, public, and agricultural waste, as well as effluent from the paper factory located there. Samples from Markaz El Fath site 2 (MF2) were taken from a branched canal, mainly polluted by nearby residents' public activities. The New Assiut (NA) site was represented by a wastewater sample taken from New Assiut city WWTP, which receives effluents from various industries including mills, cosmetics, and food processing factories beside domestic wastes from the local population.

Irrigation water samples were represented by two pooled samples from distinct two sites. Arab Motir (AM) samples were collected from El Manaa canal, which is mainly contaminated with agricultural and domestic effluents. El Masaraa (EM) samples were taken from Salibt El Masaraa canal, which is contaminated with both domestic and agricultural wastes.

2. Sample collection and transportation

The samples were collected in opaque glass bottles. These bottles were sterilized with methanol, followed by distilled water before sampling. At the sampling sites, the bottles were thoroughly cleaned with water and filled with 1-2 liters of water samples. The bottles were tightly closed and immediately placed in an ice box, for transport to the laboratory, where the analysis was conducted within 2-3 hours (Kotb & Ahmed, 2019).

3. Sample Extraction

Detection of EDCs was conducted according to Manickum *et al.* (2016). For each water sample, 800 ml was extracted with 30 ml dichloromethane (DCM) (Fisher Chemical, UK) in a 1 L separating funnel. The combined DCM extracts were dried over anhydrous sodium sulphate (Dop Organik kimya, Turkey) and then evaporated to a volume of 2 mL. After being transferred into a calibrated GC auto sampler vial, the 2 mL extract was concentrated to a final volume of 1 mL by using nitrogen gas. The resulting 1 mL DCM extract was subsequently analyzed using gas chromatography-mass spectrometry (Agilent Technologies Model:

7890-5975, Carrier gas is Helium, USA), utilizing an HP-5m Column (30m*0.25mm *0.25µm).

Data acquisition was performed in scan mode, with Wiely 08 Nist 08 Library. The oven equilibration time was set to 0.5 min and a max temperature of 280 °C. The Oven Program was ٤٠° C for 2 min, then 10 °C/min to 150 °C for 6 min, then 10 °C/min to 220 °C for 6 min, followed by 15 °C/min to 280 °C for 15 min. The total run time was 51 min plus 2 min post run. The Flow Program was set at 0.5 mL/min for 10.9 min, then 1 mL/min for the subsequent 30 min.

Table 1: Sampling locations with their codes and type of water

Sampling sites	Code	Type of water	Latitude (N)	Longitude (E)
EL Malah canal	EMC	Wastewater	31.1126	27.1022
Arab Al madabagh	AA	WWPT influent	31.1479325	27.1640354
New Assiut	NA	WWPT influent	31.2820882	27.2619838
El Zenar drain	EZD	Wastewater	31.1557567	27.1679136
Markaz El Fath site 1	MF1	Wastewater	31.1917299	27.2131857
Markaz El Fath site 2	MF2	Wastewater	31.1957667	27.2062464
Arab Motir	AM	Irrigation water	31.2968109	27.2664862
El Masaraa	EM	Irrigation water	31.1407	27.1133

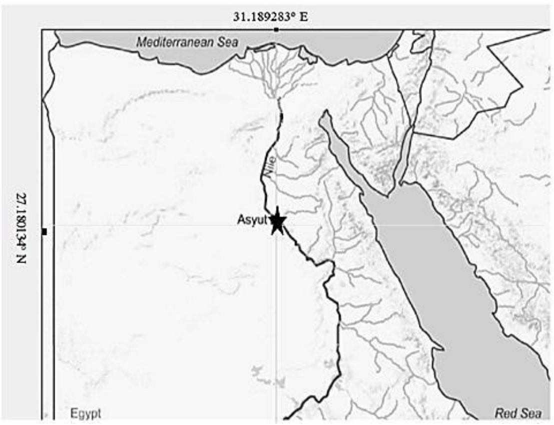

Figure 1: Map of Egypt representing Assiut Governorate location with its longitude and latitude

RESULTS

Various EDCs were identified in wastewater samples. As displayed in Table (2), 4-nonyl phenol, 4-octyl phenol, 4-tert butyl phenol and di-n-propyl phthalate were detected in El Malah canal. Additionally, di (2-ethylhexyl) phthalate, diethyl Phthalate, caffeine, epichlorohydrin and fluoxetine were found in WWTP influent at Arab Al madabegh (Table 3). Table (4) reveals the presence of decamethylcyclopenta-siloxane (D5) and fluoxetine in the influent of WWTP in New Assiut city. As presented in Table (5), fluoxetine and di-n-propyl phthalate were detected in El Zenar drain. Finally, fluoxetine was identified in both sites in Markaz El Fath (Tables 6 and 7).

In terms of EDCs found in irrigation water samples, fluoxetine was detected in Arab Motir site (Table 8). Furthermore, the presence of 4-nonyl phenol, di-n-propyl phthalate, benzyl butyl phthalate and dibutyl phthalate at El Masaraa site (Table 9). The other compounds found in waste and irrigation water samples having a high percentage of total samples were not identified as EDC.

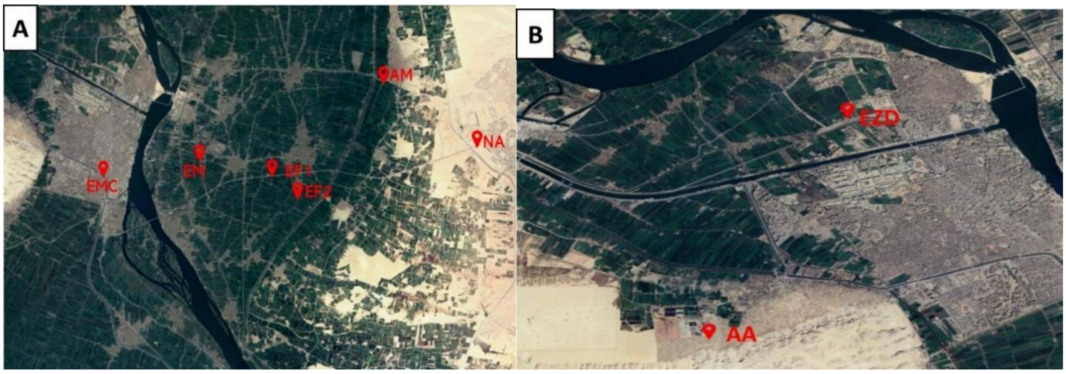

Figure 2 (A&B): Map of different sampling sites with codes (EMC: El Malah canal, MF1: Markaz El Fath1, MF2: Markaz El Fath2, NA: New Assiut, EM: El Masaraa, AM: Arab Motir, AA: Arab Al madabegh , EMC: El Zenar drain).

The detection frequency of EDCs is presented in Table (10). In wastewater, each phenolic compound- 4 Nonyl phenol, 4-octyl phenol, 4-tert butyl phenol- represents a detection frequency of 16.7%. The frequency rates for phthalates esters, including di-n-propyl phthalate, di (2-ethylhexyl) phthalate, and diethyl phthalate were recorded at 33.3%, 16.7%, 16.7%, respectively. The frequency rates for decamethylcyclopentasiloxane, caffeine, epichlorohydrin, and fluoxetine were 16.7%, 16.7%, 16.7% and ٨٣.٣%, respectively, in the wastewater samples. In the irrigation water samples, fluoxetine, 4-nonyl phenol, di-n-propyl phthalate, benzyl butyl phthalate and dibutyl phthalate the frequency rate of each compound was 50%.

Table 2: Investigation of the presence of endocrine disrupting chemicals in El Malah

	Chemical name	Mol Weight (amu)	% of Total
1	4 Nonyl phenol*	220	4.99%
2	Di-N-propyl phthalate*	250	3.98%
3	4 Octyl phenol*	206	2.97%
4	4 Tert butyl phenol*	150	2.96%
5	Phthalic acid, 3-methylphenyl propyl ester	298	1.05%
6	2-Amino-3-methylbutane	87	٠,١٧%
7	N-Dodecyl methylamine	199	0.42%
8	2-Octanamine	129	0.16%
9	Chloroacetamide	93	0.08%
10	Cystine	240	0.03%

* Endocrine disrupting chemical

Table 3: Investigation of the presence of endocrine disrupting chemicals in Arab Al madabagh

	Chemical name	Mol Weight (amu)	% of Total
1	Palmitinic acid	256.24	44.84%
2	Oleic Acid	282.256	24.01%
3	Stearic acid	284.272	6.20%
4	trans-2-Tetradecene	196.219	0.26%
5	**Fluoxetine***	309.134	٠,٢٢%
6	Diethyl Phthalate*	222.089	0.20%
7	Di (2-ethylhexyl) phthalate*	390.277	1.51%
8	Squalene	410.391	١,١٠%
9	Caffeine*	194.08	0.10%
10	Epichlorohydrin*	92.003	0.03%

* Endocrine disrupting chemical

Table 4: Investigation of the presence of endocrine disrupting chemicals in New Assiut

	Chemical name	Mol Weight (amu)	% of Total
1	Sulfur Dioxide	64	1.16%
2	Decamethylcyclopentasiloxane*	370	1.49%
3	**Fluoxetine***	309	0.55%
4	4,6-Diamino-5-pyrimidinyl hydrogen sulfate	206	0.45%
5	2-Iodohiistidine	281	0.18%
6	Calconcarboxylic acid	438	0.17%
7	Penta fluoro propionamide	163	0.14%
8	2-Hexanamine	101	0.11%
9	3-Sulfinoalanine	153	0.10%
10	dl-2-Aminopropanoic acid	89	0.09%

* Endocrine disrupting chemical

Table 5: Investigation of the presence of endocrine disrupting chemicals in El zenar

	Chemical name	Mol Weight (amu)	% of Total
1	Palmitinic acid	256.24	56.42%
2	Oleic Acid	282.256	6.35%
3	Stearic acid	284.272	6.00%
4	Myristic acid	228.209	1.35%
5	Tricosane	352.407	1.17%
6	Hexatriacontane	352.407	1.12%
7	**Fluoxetine***	309.134	0.89%
8	Octadecane	254.297	0.85%
9	Squalene	410.391	0.77%
10	Di-N-propyl phthalate*	149.084	0.46%

*Endocrine disrupting chemical

Table 6: Investigation of the presence of endocrine disrupting chemicals in El Fath site 1

	Chemical name	Mol Weight (amu)	% of Total
1	Cyclotetrasiloxane, octamethyl-	296	4.57%
2	9,9,10,10-Tetramethyl-9,10-Disila-9,10-Dihydroanthracene	268	3.37%
3	Oxime-, methoxy-phenyl-	151	3.15%
	Sulfur Dioxide	64	2.47%
4	Sarcosine, N-(3-cyclopentylpropionyl)-, tetradecyl ester	409	1.57%
5	١-Methyl-2-(P-nitrophenyl)-benzimidazole	253	1.51%
6	**Fluoxetine***	309	0.67%
7	Ethyl oxamate	117	0.33%
8	Aminomethanesulfonic acid	111	0.32%
9	L-Cysteine sulfinic acid	153	0.15%
10	N-Methyltaurine	139	0.12%

* Endocrine disrupting chemical

Table 7: Investigation of the presence of endocrine disrupting chemicals in El Fath site 2

	Chemical name	Mol Weight (amu)	% of Total
1	Docosane	310	3.81%
2	dl-Alanylglycylglycine	203	3.39%
3	Hexadecane	226	1.39%
4	l-Guanidinosuccinimide	141	0.95%
5	N-Dodecylmethylamine	199	0.69%
6	2-Formylhistamine	139	0.61%
7	2-Aminononadecane	283	0.49%
8	**Fluoxetine***	309	0.40%
9	Cystine	240	0.33%
10	Trichlorethanol	148	0.16%

* Endocrine disrupting chemical

Table 8: Investigation of the presence of endocrine disrupting chemicals in Arab Motir

	Chemical name	Mol Weight (amu)	% of Total
1	1,3-Dihydroxy-6-methoxy-1,2,3,4, -tertahydroquinolin-2-one	209	9.89%
2	Octamethyltetrasiloxane	296	4.59%
3	Cystine	240	1.61%
4	Ethyl Chloride	64	1.47%
5	Ethylene oxide	44	0.74%
6	**Fluoxetine***	309	0.58%
7	Calconcarboxylic acid	438	0.39%
8	N-Methyl-N-(2-phenylethyl) amine	135	0.29%
9	2-Chloro-2-deuteropropane	79	0.21%
10	2-Amino-3-methylbutane	87	0.20%

* Endocrine disrupting chemical

Table 9: Investigation of the presence of endocrine disrupting chemicals in El Masaraa

	Chemical name	Mol Weight (amu)	% of Total
1	p-tert-Amylphenol	164	7.95%
2	Di-N-propyl phthalate*	250	3.53%
3	4-Nonyl phenol*	220	2.69%
4	2-Amino nonadecane	283	0.85%
5	Benzyl butyl phthalate*	312	0.81%
6	L-alanine	89	0.56%
7	Dibutyl phthalate*	278	0.54%
8	Cyanacetamide	84	0.26%
9	Acetonitrile-D3	44	0.23%
10	2-Hexanamine	101	0.20%

* Endocrine disrupting chemical

Table 10: Detection frequency % of endocrine disrupting chemicals in waste and irrigation water in Assiut Governorate

	Compound	Detection frequency % in wastewater	Detection frequency % in irrigation water
١	4 Nonyl phenol	16.7%	50%
٢	4 Octyl phenol	16.7%	0%
٣	4 Tert butyl phenol	16.7%	0%
٤	Di-N-propyl phthalate	33.3%	50%
٥	Di (2-ethylhexyl) phthalate	16.7%	0%
٦	Diethyl Phthalate	16.7%	0%
٧	Benzyl butyl phthalate	0%	50%
٨	Dibutyl phthalate	0%	50%
٩	Decamethylcyclopentasiloxane	16.7%	0%
١٠	Caffeine	16.7%	0%
١١	Epichlorohydrin	16.7%	0%
١٢	Fluoxetine	83.3%	50%

DISCUSSION

Three of the seventeen Sustainable Development Goals (SDGs) are addressed in our research: protecting and sustainably using water resources for sustainable development; ensuring availability and sustainable management of water and sanitation; and promotion of well-being for individuals of all ages. These goals are integral to the 2030 Agenda for Sustainable Development, which has been approved by all member states of the United Nations and is regarded as an urgent call to action for both developed and developing nations (UN, 2015).

The obtained results indicated the occurrence of different types of EDCs at locations express public, agricultural and industrial contamination, all of which are considered sources of EDCs. As illustrated in Table (2), phenolic compounds as 4-nonyl phenol, 4-tert-butyl phenol and 4-octyl phenol were detected, each accounting for a frequency rate of 16.7% of the wastewater samples (Table 10). It is important to remember that industrial and urban activities serve as the main sources of these compounds (Cavalheiro *et al.,* 2014). So, it is anticipated to find these compounds in wastewater samples, such as those from El Malah canal, which receives discharges from the major areas in Assiut Governorate.

The reported frequency in the current study was lower than that reported by Bina *et al.* (2018) who detected 4-nonyl phenol and 4-tert-octyl phenol in 100% of the wastewater samples collected from urban, rural areas and hospitals in Iran using GC–MS. Furthermore, researchers have suggested that the presence of these alkyl phenols can be attributed to the use of detergents and surfactants containing these chemicals in both hospital and urban areas. An investigation done by López-Velázquez *et al.* (2021) on the presence of EDCs in WWTPs in Mexico using GC–MS, revealed that 4-nonyl phenol and 4-octyl phenol were detected in relatively higher frequencies of 41.7-50% and 58.3-100%, respectively.

Di-(2-ethylhexyl) phthalate and di-ethyl phthalate were detected in Arab Al madabegh WWTP influent (Table 3) with frequency rate at 16.7% of the wastewater samples (Table 10). Di-n-propyl phthalate was found in both El Malah canal (Table 2) and El Zenar drain (Table 5) with a frequency rate of 33.3% (Table 10). Phthalate esters are often found in everyday handled products, as well as plasticizers which explains its presence (Zareh *et al.*, 2020). Our finding indicates a lower frequency of phthalates than that reported by Kotowska *et al.* (2020), who discovered di-(2-ethylhexyl) phthalate and di-ethyl phthalate in WWTPs in Poland using GC-MS. In their study, Di-(2-ethylhexyl) phthalate was the most abundant (97% of the samples), while di-ethyl phthalate was found in 58% of the samples. Their use in medications, cosmetics and personal hygiene items may be connected with their presence. Another study done by Le *et al.* (2021) detected di-(2-ethylhexyl) phthalate, di-ethyl phthalate and di-propyl phthalate in 100% of the wastewater influent samples collected from Hanoi, Vietnam using GC-MS. Their presence indicated that the main source of phthalates in urban Hanoi was the domestic discharge.

As recorded in the current study, caffeine was detected in WWTP influent of Arab Al madabegh (Table 3) which is considered one of the major WWTP as it receives domestic and industrial waste from Assiut Governorate, with a detection frequency of 16.7% of the wastewater samples (Table 10). Caffeine is a prominent constituent in various food and beverages products, and is recognized as the most broadly used drug in the world (Kleywegt *et al.*, 2019). The presence of caffeine in the wastewater in Egypt was previously detected in municipal Tezmant WWPT located in Beni-Suef Governorate using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). In that study, caffeine was found in 100% of the influent samples, which was higher than our finding. The authors explained that the Egyptian community's high rate of coffee and tea consumption might be the cause of its occurrence (Younes *et al.*, 2018).

Nevertheless, previous studies have found caffeine in many nations with higher frequency rates than those found in this study. Caffeine was detected in WWTP influent in Italy using UHPLC–MS/MS with a frequency rate of 93% from the samples (Di Marcantonio *et al.*, 2021). A study conducted by Gumbi *et al.* (2022) detected caffeine in 2WWTPs in South Africa using GC-MS, and the presence was due to excessive soft drink, coffee and tea consumption, along with inappropriate disposal of these beverages.

Epichlorohydrin was detected in Arab Al madabegh WWTP influent (Table 3) with a detection rate of 16.7% (Table 10). Epichlorohydrin is considered an endocrine disrupter, and is utilized as an inert component in the manufacturing of synthetic paper, textiles, inks, paints and pharmaceuticals as well as flocculants for wastewater treatment and construction of drinking water pipes (Yalçın *et al.*, 2019; Tasmia *et al.*, 2020). Gaca and Wejnerowska, (2006) detected epichloro-hydrin in sewage samples collected from a treatment facility that processed a mix of waste from chemical plants and cities in Poland. Epichlorohydrin was detected in the influent of three WWTPs in Spain using GC-MS (Lasa *et al.*, 2006). However, there is a lack of research regarding the detection of epichlorohydrin in water sources.

Decamethylcyclopentasiloxane (D5) was detected in the influent sample taken from WWTP at New Assiut city (Table 4) which receives both industrial and domestic sewage, with a detection rate at 16.7% of the wastewater samples (Table 10). The fact that D5, a methyl siloxane commonly used in production of home goods and personal care products, may rationalize its presence in influent of WWTP that receives residential sewage from homes and services (Capela *et al.*, 2017). Silva *et al.* (2021) detected D5 in approximately 70% of the sludge samples from urban WWTPs near Oporo, Portugal using GC-MS. Additionally, a study conducted by Nu Nguyen *et al.* (2021) investigated D5 in wastewater influents collected from Hanoi, Vietnam using GC-MS. Moreover, D5 was detected in about 45% of influent tank samples from WWTP in Guangzhou, China using GC-MS (Zhang *et al.*, 2024).

Fluoxetine was the most commonly detected compound in 5 locations: Arab Al madabegh , New Assiut city, El Zenar drain, Markaz El Fath1 and Markaz El Fath 2, with a detection frequency of 83.3% in the wastewater samples (Table 10). All these sites receive domestic sewage, and this is consistent with the fact that fluoxetine is currently among the most detected pharmaceuticals in aquatic environments close to populated regions (Mole & Brooks, 2019). Our results are similar to those of Afsa *et al.* (2020), who detected fluoxetine in hospital wastewater and WWTP influent with detection frequencies of 38.9% and 83.3%, respectively. Moreover, the authors added that in Mahdia, Tunisia using UPLC-MS/MS with triple quadrupole, the high frequency of fluoxetine might be due to the ease of access to the drug without a prescription, mainly in developing countries.

Our result was higher than that reported by Kosma *et al.* (2019), who detected fluoxetine in 67% and 60% of the samples collected from hospital and municipal WWTP influents, respectively, in Ioannina city, Greece using UHPLC-MS. Fluoxetine was detected in one sample of irrigation water (50%) from Arab Motir (Tables 8 and 10) which receives domestic and agricultural wastes, suggesting that fluoxetine may pollute the environment through the runoff from landfills and agricultural areas (McDonald, 2017). Our detection rate was similar to that of Ma *et al.* (2016), who revealed 55% detection rate in West Dongting samples, although it was lower than the rate in East Dongting samples (100%) from Dongting Lake, China using UPLC-MS/MS. Moreover, our detection rate was lower than that reported by Wu *et al.* (2017), who detected fluoxetine in 100% of the samples from the Huangpu River in Shanghai, China in November 2015 using LC-MS/MS of samples, and the high frequency is indicative of its widespread use.

As presented in Table 9, butyl benzyl phthalate, dibutyl phthalate and di-n-propyl phthalate were found in one irrigation water sample (El Masaraa), which receives both domestic and agricultural wastes. Plus, each of these phthalates represents 50% of the total irrigation samples (Table 10). Regarding butyl benzyl phthalate compound, our detection frequency was quite similar to that reported by Dueñas-Moreno *et al.* (2024), who detected butyl benzyl phthalate in 62.5% of the samples collected from polluted urban rivers, which used for irrigation of agricultural land in Central Mexico using GC-MS. Also, our results were more or less similar to those of Schmidt *et al.* (2020), who detected butyl benzyl phthalate in ≈ 55%, but dibutyl phthalate was found in 100% of the surface samples from the Rhône river, France using GC-MS. They revealed that its presence might be related to the WWTP effluents reaching surface water. Additionally, Le *et al.* (2021) detected butyl benzyl phthalate, di butyl phthalate and di-propyl phthalate in 6 water lakes in Hanoi, Vietnam using GC-MS, and the three phthalates were found in 100% of the samples.

4 -Nonyl phenol was detected in El Masaraa (Table 9) with a detection rate of 50% from the total irrigation samples (Table 10). Our detection frequency was lower than that of Janousek *et al.* (2020), who detected 4 -nonyl phenol in Hesse, Germany using UPLC-MS with electrospray ionization with a frequency of 84% and 65% of surface waters in 2017 and 2018, respectively. Thi Thu *et al.* (2024) also detected 4-nonyl phenol in 100% of the surface water samples collected from rivers north of Vietnam using LC-MS/MS.

CONCLUSION

This study is the first to report EDCs found in different water sources (irrigation and wastewater) in Assiut Governorate.

According to the findings, fluoxetine, phthalates esters and phenolic compounds were among the most commonly detected in irrigation and wastewater samples, with their presence connected to human activities in these areas. This study clarifies the importance of continuous monitoring and controlling the examined EDCs over an extended period in the water supply.

Conflict of interest:
There is no conflict of interest

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الكشف عن المواد الكيميائية المسببة لاختلال الغدد الصماء في مصادر المياه المتنوعة بمحافظة أسيوط

ولاء عطيفي ، حسنية عبد المحسن ، منال محمود ، نجوي أبو المعالي ، ريم دسوقى

E-mail: Walaa.Otify@aun.edu.eg Assiut University website: www.aun.edu.eg

يعد تواجد المواد الكيميائية المسببة لاختلال الغدد الصماء في مصادر المياه المختلفة مشكلة متنامية في جميع أنحاء العالم. حيث تعتبر المواد الكيميائية المسببة لاختلال الغدد الصماء من الملوثات المستمرة في البيئة المائية والتي تؤثر على مختلف الأنواع بما في ذلك الإنسان بسبب استخدامها المكثف في الحياة اليومية .كان الهدف من الدراسة الحالية هو الكشف عن وجودها في مصادر مياه الصرف الصحي والري في محافظة أسيوط بواسطة طريقة استخلاص السائل-السائل متبوعة بالفصل باستخدام كروماتوغرافيا الغاز مع قياس الطيف الكتلي. يعد الفلوكستين، الكافيين، واسترات الفثالات مثل ثنائي إيثيل فثالات، وثنائي-ن-بروبيل فثالات، وثنائي بوتيل فثالات، وبوتيل بنزيل فثالات والمركبات الفينولية مثل ٤-نونيل فينول و٤-أوكتيل فينول و٤-ثالثي بوتيل فينول من بين المواد الكيميائية المسببة لاختلال الغدد الصماء التي تم العثور عليها. أظهر الفلوكستين أعلى معدل كشف بنسبة ٣, ٨٣ ٪ و ٥٠ ٪ في عينات مياه الصرف الصحي ومياه الري على التوالي. ستكون النتائج التي توصلنا إليها مفيدة لإثراء البحث حول وجود هذه المواد الكيميائية في مصادر المياه المختلفة في مصر ومزيد من السيطرة على وجودها للحفاظ على البيئة وتحقيق الاهداف المستدامة لصالح مصر ٢٠٣٠.