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# Benchmarking Persistent Contaminants in Several Egyptian Wastewater Treatment Plants

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**Abstract** - Anthropogenic activities, population increase, and urbanization pose more dangers to public health and the environment than ever before. The existence of both new and persistent chemicals is a big issue that threatens both human and environmental health. Untreated effluent streams from wastewater treatment plants, in general, constitute a threat to aquatic ecosystems and, by extension, human health when released into the environment. To the best of the authors' knowledge, no benchmarking of pesticide and pharmaceutical chemical presence in Egyptian wastewater streams has occurred. The goal of this study is to identify any pesticides or pharmaceutical chemicals that may be present in Egypt's municipal wastewater and to assess the efficacy of the country's various wastewater treatment plants in removing these contaminants. Samples were obtained from five separate WWTPs in the Greater Cairo region, from both the influent and effluent of each plant in Egypt. Six pharmaceutical compounds and four pesticides were found during the screening process for pharmaceutical compounds and pesticides in the collected samples from the selected WWTPs. Pharmaceutical chemicals and pesticides were found in both the influent and effluent of the specified wastewater treatment facilities. This finding is consistent with previous research and may imply that typical treatment technologies, such as activated sludge or trickling filters, are incapable of removing organic pollutants that stay in the water.

Keywords: Aquatic Systems, Benchmarking, Emerging contaminants, Ecotoxicity, Pollution, Wastewater

#### 1. Introduction

One major issue that poses a risk to both human and environmental health is the presence of both emerging and persistent chemicals generated from industrial activities [1]. Scientists face a challenge in finding solutions to properly remove or remediate these substances since they are not easily biodegradable, are resistant to microbes found in urban wastewater treatment plants, and have a high degree of stability [2], [3]. In this context, elicitation and estimations of pharmaceutical consumption and pollutant exposure to establish lifestyle benchmarks have become easier than before due to wastewater-based epidemiology, since wastewater is a mixture of effluent from some industrial operations, domestic waste, and human excretions [4]. Pharmaceuticals and pesticides are two examples of developing chemicals that, due to their extensive use, pose a serious threat to public health [5]. Wastewater treatment plants (WWTPs) fail to adequately remove persistent pollutants like pesticides and pharmaceuticals, despite the fact that this issue has received a lot of attention [6].

A wide variety of pharmaceutical compounds, including hormones, antibiotics, antidepressants, pain relievers, and others, can be found in aquatic habitats [7]. Urine and feces are the primary excretions of humans that reveal the presence of pharmaceutical compounds. Eventually, most of these pharmaceutical components are entirely or partially passed through conventional wastewater treatment processes, and they finally pass through treated wastewater to the natural water bodies [8]. As a result, these compounds get up in all sorts of water—surface water, groundwater, irrigation water, drinking water—because they were not effectively removed. Thus, the major concern is the ecotoxicity and the possible risks to public health posed by these substances. Furthermore, pharmaceutical compounds typically undergo biodegradation or photodegradation, interact with other substances in the effluent, or both. As a result, they produce new compounds with unexpected properties that differ from their original formula and pose health and environmental hazards that were not anticipated [9]. For example, antibiotic-resistance genes can be passed down from bacteria due to environmental antibiotic overuse. Hormonal and antidepressant chemicals, on the other hand, bioaccumulate and have detrimental effects on aquatic life, which can have repercussions for human health [10].

Pesticides, like pharmaceuticals, are hazardous, persistent toxins that pose a threat to the environment. In most cases, pesticides are either chemically manufactured or derived from natural sources. There is a diversity of pesticides with different domains of applications, for instance, herbicides, insecticides, fungicides, etc [11]. Their usage in preventing and controlling pests boosts output, which in turn increases food quality and yields substantial economic benefits [12]. The long half-life of pesticides makes them very mobile; they can travel long distances from their point of origin, contaminating land, air, and water, and endangering wildlife and humans simultaneously [13]. Besides, the dramatic increase in population concentration pushes the agriculture sector to heavily use pesticides to fulfil people's needs. Subsequently, with the heavy consumption of pesticides, their recalcitrance behaviour, and their sporadic use, they pose a huge threat to the ecosystem [14], [15]. Urban wastewater contaminated with pesticides usually comes from greywater from washing pesticides-contaminated tools and machines used in agriculture, and also washing of contaminated fruit and vegetables, as well as, improper disposal of leftover pesticides [16]. Additionally, human waste, including sewage, can include pesticide traces because of eating improperly washed vegetables and fruits. Industrial wastewater, like domestic wastewater, contributes to this type of contamination. Many industries produce pesticides or use them for industrial vegetation management.

In general, untreated effluent streams pose a threat to aquatic ecosystems and, by extension, human health when released into the environment [17]. To determine the suitable remediation technology, benchmarking the presence of the emerging contaminant in wastewater streams is needed. Benchmarking allows for pinpointing and determining the most critical contaminants in wastewater and hence allows for the development of an effective prioritized plan for intervention. It also plays a vital role in safeguarding the ecosystem and human health with the effective implementation of wastewater management methods. In order to ascertain the associated possible risks to ecosystems and human health, it permits the easy calculation and detection of such contaminants in various waste streams. There has not been any benchmarking of pesticide and pharmaceutical chemical presence in Egyptian wastewater streams to the best of the authors' knowledge. Thus, the purpose of this research is to identify any pesticides or pharmaceutical chemicals that may be present in Egypt's municipal wastewater and to evaluate the efficacy of the various WWTPs in this country in removing these pollutants. The specific objectives of this study are as follows: (1) to identify pharmaceutical compounds in the influent to different WWTPs; (2) to identify pesticides in the influent to different WWTPs; (3) to compare the effectiveness of WWTPs with suspended growth processes (activated sludge processes) and attached growth processes (trickling filters) in removing these contaminants; and (4) to compare the reported results with existing literature to gain a better understanding of the characteristics of wastewater in Egypt. Findings from this study can shed light on the state of wastewater in nations where pesticide and pharmaceutical use is way out of control. In addition, the results can serve as a foundation for proposing suitable mitigation strategies, either at the source of generation or by upgrading the existing treatment WWTPs.

#### 2. Material and Methods

# 2.1. Selected WWTPs for samples collection

Samples were collected from five different WWTPS in the Greater Cairo region from both the influent and the effluent of each plant in Egypt. The selected WWTPs were Zenin WWTP, Al Gabal El Asfar WWTP, Badrashen WWTP, Hawamdya WWTP, and Orasqualia WWTP. Figure 1 shows a Google Earth image of the five WWTPs.

Zenin WWTP is located in the Giza governorate and is considered the second largest in the governorate. Al Gabal El Asfar WWTP is located in Cairo governorate and is considered the largest in Egypt. Badrashen and Hawamdya WWTPs are both serving rural areas and villages in the Giza governorate, and the treatment process is trickling filters for both of them. Orasqualia WWTP is located in Cairo governorate, where it was built recently, and serves many regions in the east of Cairo governorate. A comparison among the capacities, treatment technologies, and influent and effluent characteristics of the selected WWTPs is included in Table 1.

#### 2.2. Samples collection

2h-composite samples (a mixture of 5 samples over 2 hours, taken every 30 minutes,) were collected during the morning period, which is the most used approach to wastewater sampling. All the sampled materials were gathered in one container throughout the sampling period. This data, collected over time, will be representative of a wastewater

treatment plant's typical performance during that time. Collected were kept in a dark cold fridge at 4 °C before further analyses were performed.

# 2.3. Analysis of Wastewater Samples

Extracted samples were run on a Shimadzu single quadrupole gas chromatograph-mass spectrometer (GC/MS) model GCMS-QP2020 (Shimadzu, Koyoto, Japan) equipped with a Shimadzu AOC-20i autosampler utilizing the following optimized method. Onto a wool packed splitless liner (Shimadzu Part#:221-48876-03), 2  $\mu$ L of sample is injected onto the instrument installed with an Agilent J&W HP-5MS (30 m × 0.25mm, 0.25  $\mu$ m) column (Agilent Technologies, Santa Clara, California, USA). Utilizing helium as the carrier gas, the instrument operated in constant flow mode at a 1.0 mL/min rate. The GC oven was programmed as follows: held at the initial temperature of 70°C for 2 min then ramped at 15°C/min to 300°C and held for 10 min for a total run time of 27.33 min. The injection port, transfer line, and source were set at 250°C, 280°C, and 200°C respectively. The MS operated in full scan mode, scanning ions from 35-550 m/z at an event time of 0.20 seconds (sec) from 3.50-27.33 minutes. Shimadzu GC/MS solutions laboratory software operated the instrument control and data processing.



Fig. 1: A Google Earth image of: (1) Zenin WWTP, (2) Gabal El Asfar WWTP, (3) Badrashen WWTP, (4) Hawamdya WWTP, and (5) Orasqualia WWTP

Table 1: Capacities and Average Wastewater Analysis for the selected WWTPs.

WWTP	Treatment technology	Capacity (m <sup>3</sup> /d)	Influent			Effluent			
			COD, mg/l	BOD, mg/l	TSS, mg/l	COD, mg/l	BOD, mg/l	TSS, mg/l	
Zenin	activated sludge process	450,000	300	140	135	35	10	11 11	
Gabal El	activated sludge process	2,500,000	275	150	200	27	11	8	
Asfar	8 1	,,,,,,,,,							
Badrashen	Trickling filters	20,000	750	500	500	80	50	50	
Hawamdya	Trickling filters	20,000	600	500	500	80	50	50	
Orasqualia	activated sludge process	250,000	464	275	290	26	16	29	

#### 3. Results and Discussion

#### 3.1. Detection of pharmaceutical compounds in the chosen WWTPs

Analysis of collected samples showed the abundance of six pharmaceutical compounds which are: cycloheximide, duloxetine, fenretinide, loperamide, Hexadecamethyl Octasiloxane, and trihydroxyphenylalanine. Cycloheximide is an antibiotic that prevents the growth of fungi and bacteria by inhibiting protein synthesis. The sources of cycloheximide in wastewater include the discharge from pharmaceutical manufacturing plants, hospitals, and research laboratories. It can also be present in wastewater from farms where it is used to prevent fungal infections in crops [18], [19]. Duloxetine is a medication that belongs to the class of drugs called selective serotonin and norepinephrine reuptake inhibitors. It is used to treat major depressive disorder, generalized anxiety disorder, fibromyalgia, and neuropathic pain. Sources of Duloxetine in wastewater include human excretion through urine and feces, incomplete metabolism during wastewater treatment, and improper disposal of unused medication [8], [20]. Fenretinide is a synthetic retinoid compound that has shown potential as an anticancer drug. It is currently being tested in clinical trials for the treatment of various types of cancer, including breast cancer and neuroblastoma. Fenretinide is not commonly found in wastewater as it is primarily used in clinical studies and is not widely used in commercial products [21]. Loperamide is an opioid medication used to treat diarrhea. It works by slowing down the movement of the gut. Loperamide can enter wastewater through excretion by humans who are taking the medication, either through urine or feces. It can also be released into the environment through the disposal of unused medication [22]. Hexadecamethyl Octasiloxane has potential applications in drug delivery due to their ability to act as a carriers for drugs or other therapeutic agents. The large organic group in this compound could potentially be used to attach drugs or other therapeutic agents and transport them to specific tissues or cells. One potential advantage of using organosilicon compounds as drug carriers is their biocompatibility. Organosilicon compounds are generally well-tolerated by living organisms and do not produce harmful side effects. Additionally, the properties of organosilicon compounds can be tailored to optimize drug delivery, such as by modifying the size, shape, or surface properties of the carrier molecule [23]. Trihydroxyphenylalanine, is a chemical compound used in the treatment of parkinson's disease and other neurological disorders. Sources of trihydroxyphenylalanine in wastewater can include pharmaceutical manufacturing and research, as well as hospital and household sewage [24], [25]. These compounds' chemical and structural formulas are shown in Table 2. Other compounds were found in trace levels.

Table 2: Details of Pharmaceutical Compounds found in wastewater Samples

Compounds	Chemical formula	Structural formula
Cycloheximide	C <sub>15</sub> H <sub>23</sub> NO <sub>4</sub>	O H H NH
Duloxetine	C <sub>18</sub> H <sub>19</sub> NOS	H o
Fenretinide	C <sub>26</sub> H <sub>33</sub> NO <sub>2</sub>	OH NH OH
Loperamide	C <sub>29</sub> H <sub>33</sub> ClN <sub>2</sub> O <sub>2</sub>	OH CI
Hexadecamethyl Octasiloxane	C <sub>16</sub> H <sub>50</sub> O <sub>7</sub> Si <sub>8</sub>	Si O

Trihydroxyphenylalanine	C <sub>9</sub> H <sub>11</sub> NO <sub>5</sub>	0 0
		N. III
		H. O. H.
		B.

# 3.2. Presence of pesticides in the chosen WWTPs

Screening of the collected samples to detect pesticides resulted in the detection of four pesticides, and they were: alachlor, methoprene, muscalure, and promecarb. Alachlor is a herbicide used to control weeds in various crops such as corn, soybeans, and peanuts. It inhibits plant growth by interfering with protein synthesis. It is not naturally occurring and can be found in wastewater from sources such as agricultural or industrial runoff. The sources of alachlor in wastewater can include agricultural runoff, stormwater runoff, and industrial discharge from herbicide manufacturing facilities or chemical plants that use alachlor in their processes [26], [27]. Methoprene is an insect growth regulator used to control the growth of insects and pests like mosquitoes, fleas, and ants. It mimics the action of a hormone that regulates insect growth and prevents the development of larvae into adult insects. Methoprene can enter wastewater through runoff from agricultural areas, as it is commonly used in mosquito control programs that involve spraying pesticides in outdoor areas. It can also be released into the environment through improper disposal of unused pesticides [28]. Muscalure is a pheromone that is used as a lure for male houseflies. It attracts the male flies and traps them, preventing them from mating and reproducing. Muscalure can enter wastewater through various sources such as manure from animal agriculture, waste from food processing facilities, and sewage [29]. Promecarb is a pesticide, specifically a carbamate insecticide. The active ingredient in promecarb is propoxur. Sources of promecarb in wastewater can include industrial and agricultural activities that use it, as well as from household use of insect sprays and foggers [30]. These compounds' chemical and structural formulas are shown in Table 3.

Table 3: Details of pesticides found in wastewater Samples

Compounds	Chemical formula	Structural formula				
Alachlor	C <sub>14</sub> H <sub>20</sub> ClNO <sub>2</sub>	0 N + CI				
		ő				
Methoprene	$C_{19}H_{34}O_{3}$	OCH3 O				
Muscalure	C <sub>23</sub> H <sub>46</sub>					
Promecarb	C <sub>12</sub> H <sub>17</sub> NO <sub>2</sub>	O NH				

# 3.3. Treatability levels of the existing conventional treatment technologies in Egypt for persistent chemical contaminants

Table 4 shows the pesticides and pharmaceutical compounds in the influent and the effluent of various WWTPs. As shown in the table, most of the compounds are present in both the influent and the effluent samples. This can be an indication that conventional treatment processes (activated sludge or trickling filters) cannot remove the persistent organic contaminants, and this finding is consistent with the literature. In general, conventional treatment technologies such as activated sludge systems and trickling filters have limited effectiveness in treating persistent chemical contaminants such as pharmaceuticals and pesticides due to their resistance to biodegradation and persistence in the environment [31]. These compounds can accumulate in the sludge and effluent produced by these systems and can also be toxic to the microorganisms used in the treatment process. Therefore, additional treatment methods may be necessary to effectively remove persistent chemical contaminants from wastewater. Modern technologies may have the potential to outperform activated sludge systems and trickling filters in removing persistent chemical pollutants from wastewater for several reasons [5]. For instance,

modern anaerobic technologies can prevent the proliferation of aerobic microorganisms, which are inefficient in degrading persistent chemical pollutants. Technologies with greater retention time than that of a trickling filter or activated sludge system can perform well in dealing with these contaminants. This is because the microorganisms can have enough time to break down persistent chemical pollutants. Technologies that rely on the adsorption process can also eliminate chemical pollutants from wastewater by tethering them to the adsorbent's surface [32].

Table 4: Pesticides and	pharmaceutical com	mounds in the	influent and th	ne effluent o	f various WWTPs
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Compound	Zenin		Gabal Asfar		Badrashen		Hawamdya		Orasqualia	
_	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Cycloheximide					✓		✓	✓	✓	✓
Duloxetine	✓	✓	✓	✓						
Fenretinide					✓	✓	✓	✓	✓	✓
Loperamide					✓	✓	✓	✓	✓	✓
Hexadecamethyl	✓	✓	✓	✓	✓	✓	✓	✓	<b>√</b>	<b>√</b>
Octasiloxane										
Trihydroxyphenylalanine					✓	✓	✓	✓	✓	<b>✓</b>
Alachlor					✓		✓	✓	✓	✓
Methoprene					✓		✓	✓	✓	✓
Muscalure					✓		✓	✓	<b>√</b>	<b>√</b>
Promecarb					✓		✓	✓	✓	<b>√</b>

# 3.4. Comparison of the Obtained Results with Available Literature

There are limited studies on wastewater surveillance for pharmaceutical compounds and pesticides. A study was carried out on the influent and effluent of three wastewater treatment plants in Spain to show the fate of some of pesticides. The study showed a poor overall removal of pesticides in all three plants [33]. Another study focused on the selection of samples obtained from four wastewater treatment plants in northern Italy. Carbamazepine metabolites were among the most frequently detected contaminants of emerging concern in wastewater [34]. In addition, a wastewater treatment plant located in China was studied with respect to pharmaceutical compounds. Among the detected compounds, 76 compounds were identified in all samples and 107 compounds (including 12 metabolites) were found in more than 50% of the samples [4]. Possible explanations for these poor removal rates are the deconjugation of metabolites and/or transformation products of contaminants, hydrolysis, and desorption of particulate matter during wastewater treatment. The composition of the influent and the variety of its physical structures are two of the many obstacles to the treatment of pesticides and pharmaceutical compounds from wastewater [11]. The results of these studies support the concept that conventional treatment processes are not sufficient for the removal of pesticides and pharmaceutical compounds.

#### 4. Conclusion

This study aimed to assess the effectiveness of Egypt's wastewater treatment facilities in eliminating pesticides and pharmaceutical compounds from municipal wastewater, as well as to identify any such substances that may be present. The benchmarking procedure involved investigating five WWTPs. Six pharmaceutical compounds—cycloheximide, duloxetine, fenretinide, loperamide, Hexadecamethyl Octasiloxane, and trihydroxyphenylalanine—were identified in the collected samples from the selected WWTPs. Four pesticides—alachlor, methoprene, muscalure, and promecarb—were identified during the screening process for pesticides in the collected samples from the selected WWTPs. Both the influent and the effluent of the chosen wastewater treatment facilities contained pharmaceutical and pesticide chemicals. This finding is in line with previous research and may suggest that traditional treatment methods, such as activated sludge or trickling filters, are unable to eliminate the organic pollutants that remain in the water. Because of their resistance to biodegradation and environmental persistence, persistent chemical pollutants, including pharmaceuticals and pesticides, are often difficult, to treat using traditional treatment methods like trickling filters and activated sludge systems. The results of this study can help researchers understand the problem of wastewater in countries where the use

of pesticides and pharmaceuticals is excessive. Furthermore, the findings can be used to develop appropriate mitigation methods, either by enhancing treatment WWTPs or at the site of generation.

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