



# Monitoring and Risk Assessment of Organophosphorus Pesticide Residues in Surface and Drinking Water in Some Egyptian Governorates

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#### Abstract

The aim of this study was to track the presence of 12 organophosphorus pesticides (OPPs) in 144 surface and drinking water samples collected bimonthly in a one-year sampling campaign from the inlet and outlet of 6 drinking water treatment plants (DWTPs) in three Egyptian governorates (El-Kalyoubia, Kafr El-Sheikh, and Alexandria). The lifetime intake of polluted water was also evaluated for any potential non-carcinogenic health consequences. Results revealed that 41.6% and 8.3% of the surface and drinking water samples were polluted with OPPs, respectively. Out of the 12 OPPs analyzed, four were detected in both water samples at various concentrations. The most frequently found OPPs in both water samples were diazinon, followed by prothiofos and chlorpyrifos, which were detected in 13.9%, 5.6%, and 4.2% of samples, respectively. On the other hand, OPP residues did not exceed the maximum residue levels (MRLs). Based on our spatiotemporal monitoring, the detected OPP residues in both water samples collected from the three governorates exhibited fluctuations due to residential, industrial, and agricultural activities along the sampling points. The target hazard quotient (THQ) values for non-carcinogenic pesticide hazards observed in surface and drinking water were less than one. This indicates that drinking water exposure in the study areas poses no risk to humans.

Keywords: Pesticide residues; surface water; drinking water; THQ; Egypt

# 1. Introduction

Among the 17 sustainable development goals (SDGs) that were adopted by the United Nations in 2015, addressing water pollution has emerged as a significant issue in today's world. To achieve SDG on water and sanitation, it is important to handle water resources, wastewater, and ecosystems sustainably. Pesticide residues discharged into the environment from agricultural practices, urban use, and the pesticide industry constitute one of the sources of water pollution [1].

Pesticides occupy a unique position among the various compounds encountered in water due to their widespread use for agricultural and public health purposes [2]. Because of their persistence, mobility, and long-term adverse impacts on organisms, pesticides are among the most dangerous

environmental pollutants [3]. In 2020, 7.2 million metric tonnes (Mt) of formulated products and 2.7 million Mt of active ingredients were used as pesticides on farmland globally, costing 41.1 billion USD [4]. Pesticides have been applied annually to cropland at a rate of 1.58 kg per hectare over the previous three decades [4].

Their presence in drinking water sources poses a particular threat. Pesticide residues reach water bodies through a variety of mechanisms, including direct runoff, leaching, irresponsible container disposal, equipment cleaning, and others [1]. The pollution of surface waters by OPPs has been extensively investigated at global levels around the world as a major concern [5, 6]. OPPs are the most frequent, versatile, and flexible type of pesticide currently in use [7].

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It has been proven that OPPs are the most extensively used pesticides in the world, responsible for roughly 38% of all pesticides applied [8]. The use of OPPs in agricultural and urban areas has led to the contamination of natural water supplies, such as surface water [9], because they are comparatively short-lived in ecosystems and have a high solubility in water [10]. OPPs may nevertheless accumulate and spread via food chains and biological enrichment. Numerous studies have shown that OPPs have endocrine-disrupting effects [11], mutagenicity [12], cytotoxicity [13], and immunosuppressive effects [14]. The European Union established the maximum OPP residual limits for water to minimize the risk to humans. In addition, the US Environmental Protection Agency's THO is extensively used to evaluate the possible non-carcinogenic risks to human health associated with prolonged consumption of polluted water [15]. The THQ-based risk assessment approach provides a valuable indication of the level of risk associated with pollutants exposure [16].

Water resources in Egypt are burdened by severe pollution issues caused by inappropriate solid and liquid domestic and industrial waste disposal practices, agrochemical contamination, and a lack of effective wastewater management [7]. Polluted surface water is eventually used as a direct source for DWTPs, since the drinking water supply mainly comes from the Nile River and its tributaries, which are contaminated by pesticide residues in multiple studies [17-19].

Monitoring pollutants in the Nile River is essential for gathering quantitative information about the most plentiful pollutants, identifying their sources and environmental fate, adhering to rules and human health implications, and improving the targeting of modern treatment methods [17]. Unfortunately, limited information on drinking water contamination is available [20]. In addition, as part of the mitigation effort to reduce the toxicity impact of these compounds on riverine ecosystems and public health, it is also crucial to determine OPP residues in drinking water and conduct risk assessment studies.

In this context, this study aimed to track the presence of OPPs in surface and drinking water samples collected bimonthly in a one-year sampling campaign from the inlet and outlet of 6 DWTPs in three Egyptian governorates (i.e., El-Kalyoubia, Kafr

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El-Sheikh, and Alexandria) to (a) evaluate the efficiency of purifying treatments and (b) reveal possible non-carcinogenic health concerns for nearby citizens from pesticide-contaminated water consumed on a regular basis.

# 2. Materials and methods

# 2.1. Chemicals and reagents

Twelve OPPs (i.e., "ethoprophos, phorate, diazinon, dimethoate, pirimiphos-methyl, chlorpyrifos, fenitrothion, quinelphos, prothiofos, fenamiphos, ethion, and triazophos") have been the research chosen for based on their physicochemical properties, analytical detectability, and recent studies. The OPP reference standards with purities >98.5% were purchased from Dr. Ehrenstorfer, Augsburg, Germany. All other organic chemicals and solvents were of analytical grade, and they were purchased from reputable commercial vendors.

# 2.2. Sampling sites

Surface and drinking water samples were collected every two months from May to March in a one-year sampling campaign from six DWTPs (inlet and outlet of each plant) in three Egyptian governorates, namely, Alexandria (Elseyouf 31°13'12"N 29°59'27"E and Elkilo 40 30°57'57"N 29°50'52"E), Kafr El-Sheikh (Kafr El-Sheikh city 31°06'42"N 30°57'26"E and Metoubes 31°16'54"N 30°31'18"E), and Kalyoubia (Mostorod 30°08'11"N 31°17'32"E and ShoubraElKheima 30°08'01"N 31°14'11"E). The monitoring points were located in El-Sharkawia canal (ShoubraElKheima), El-Ismailia canal (Moustrod), Meet Yazid canal (Kafr El-Sheikh), Rosetta Branch (Metoubes), El-Mahmoudia canal (Elseyouf), and El-Noubarya canal (Elkilo 40). El-Noubarya and El-Mahmoudia are the main canals in the Western Nile Delta. They are fed mainly from El-BeheriRayah, diverted from the main stream of the Nile River. The El-Noubarya and the El-Mahmoudia canals are also supplied from other water sources, the NaseriRayah and the Nile's Rosetta Branch, respectively. The El-Ismailia and the El-Sharkawia canals emerge from the Nile in Cairo. The Nile River's Rosetta branch

supplies a large drinking water treatment plant at Metoubes, while the Nile River's Damietta branch supplies the Meet Yazid canal, which provides clean water to a water treatment plant in Kafr El-Sheikh city. The water flows from the Zefta Barrage of the Damietta Branch of the Nile into the El Abasy Branch, where the subsequent outlet discharges into the Bahr Shebin canals. A portion of this flow is discharging into the Meet Yazid Canal. All of the sampling points listed above are close to potential agricultural, urban, or industrial sources of pollution. The sampling site map for DWTPs from three Egyptian governorates is shown in Fig. 1.



Fig. 1: Sampling sites map for DWTPs from three Egyptian governorates.

#### 2.3. Sample collection:

One hundred and forty-four samples (3 L each) were collected bimonthly in a one-year sampling campaign in brown glass bottles of surface water (50 cm below the surface water layer from the middle part of the water body) and drinking water inlets and outlets of the six DWTPs at different seasonal periods. The bottles were covered with screw caps, labelled, and transferred immediately by ice box to the Central Agricultural Pesticides Laboratory for analysis. Before analysis, suspended particles are removed from the surface and drinking water samples under vacuum, employing a glass fiber filter (Advantec GC-50, diameter 47 mm, pore size 0.5  $\mu$ m).

#### 2.4. Analytical procedure:

#### 2.4.1. Extraction:

Surface and drinking water samples (1 L each) were partitioned thrice with 50 mL of dichloromethane in a 2-L separatory funnel after the addition of a 10 mL saturated solution of NaCl. Samples were shaken vigorously, the organic layer was obtained, and the combined extracts were dried over anhydrous  $Na_2SO_4$  and then evaporated to dryness using a rotary evaporator at 35 °C. The residue was then dissolved in 2 mL of ethyl acetate and transferred into vials for gas chromatography-flame photometric detector (GC-FPD) determination.

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# 2.4.2. Quantitative Determination:

The extract was injected into a GC (Aglient 6890) equipped with FPD and a 7683A autosampler. GC analysis was carried out on a PAS-1701 (Agilent, Folsom, CA) capillary column of 30 m length, 0.32 mm id., 0.25  $\mu$ m film thickness. Oven temperatures were set between the initial temperature of 160 °C (held for 2 min) and 210 °C at a rate of 5 °C min<sup>-1</sup> (held for 3 min) and then increased to 240 °C at a rate of 5 °C min<sup>-1</sup> (held for 1 min), and finally to 270 °C at a rate of 20 °C min<sup>-1</sup> (held for 10 min). The injector and detector temperatures were preserved at 240 and 260 °C, respectively. Nitrogen was employed as a carrier gas at a flow rate of 3 mL min<sup>-1</sup>. The flow rates of hydrogen and air were 75 and 100 mL min<sup>-1</sup>, respectively.

# 2.5. Quality Assurance (QA):

QA procedures included the analysis of matrix spikes, laboratory blanks, and validation. As for blanks, solvents, and anhydrous Na<sub>2</sub>SO<sub>4</sub> used in the extraction of OPPs from surface and drinking water samples were subjected to the same procedures as the tested samples to detect any probable traces of the targeted pesticides, and their values were subtracted from the results. By comparing sample retention times with those corresponding to pure OPP standards, the peaks were identified (Fig. 2), and samples were analyzed with full GC-MS scanning to confirm GC-FPD results. The average recovery percentages of the monitored OPPs in water samples ranged from 86.5% to 98.7%, while the repeatability expressed a relative standard deviation (RSD) was less than 20% for fortified samples, as shown in Table 1.



Fig. 2: GC-FPD chromatogram of the standards mixture of 12 OPPs

#### Table 1

Retention time, recovery percentage, relative standard deviation (RSD) and limits of detection (LOD) of OPPs

	Organophosphorus	Retention time	Recovery	RSD	LOD
		(min.)	percentage	%	mg $L^{-1}$
1	Ethoprophos	11.38	90.2	6	0.001
2	Phorate	12.63	93.2	8	0.001
3	Diazinon	15.39	97.5	4	0.002
4	Dimethoate	16.65	90.0	9	0.004
5	Pirimiphos-methyl	19.86	96.4	7	0.002
6	Chlorpyrifos	20.54	97.4	6	0.001
7	Fenitrothion	21.09	88.5	3	0.002
8	Quinelphos	23.74	98.7	8	0.005
9	Prothiofos	25.24	86.5	5	0.004
10	Fenamiphos	27.08	87.0	7	0.004
11	Ethion	28.71	88.0	4	0.002
12	Triazophos	31.08	94.9	10	0.002

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# 2.6. Human health risk assessment:

Health risk assessment refers to the process of predicting the potential effects of pollutants on human health over a lifetime [21]. There are some guidelines provided by different international organizations to evaluate the risk of drinking water for human health.

In the present study, the guidelines were used to assess the risk of OPPs in water. The risk assessment could be conducted by comparing the determined levels of OPPs in the present samples with the levels set by laws and guidelines. In general, the WHO's acceptable daily intake (ADI) was used to assess the risk, which can protect the global population, but other aspects, such as various drinking habits, were not taken into account [22].

The risk to human health linked to drinking contaminated water containing pesticide residues was assessed according to US Environmental Protection Agency (USEPA) guidelines [23]. The potential noncarcinogenic health risks were assessed using the target hazard quotient (THQ), which was calculated as previously mentioned by USEPA [15] using the following equation:

# $THQ = (EF \times ED \times WIR \times C) / (RfD \times BW \times AT)$

where EF is the exposure frequency (365 days/year), ED is the exposure duration (70 years; equivalent to the average human lifetime),WIR is the

water ingestion rate (2000 mL/person/day), C is the pesticides concentration in water (mg/L), RfD is the oral reference dose, BW is the body weight (70kg/person), and AT is the average time for non-carcinogens (365 days/year × ED). If the THQ value is  $\geq$ 1, exposed individuals may experience health risks from consuming contaminated water. Therefore, interventions and protective measures need to be taken.

# 2.7. Statistical analysis

A value of zero was assigned for results below the limit of detection. The entire experimental set of measurements was done in triplicate. The mean  $\pm$  SE was used to express the data. Statistical analysis was undertaken using SPSS 28.0 for Windows (SPSS, Chicago, USA).

# 3. Results and discussion

# Tested OPP residues in surface and drinking water

OPP levels in 144 surface and drinking water samples collected from the inlets and outlets of 6 DWTPs from three Egyptian governorates (i.e., Kalyoubia, Kafr El-Sheikh, and Alexandria) bimonthly are shown in Tables 2-4.

# Table 2

Concentration (mg/L) of OPP residues detected in surface and drinking water samples collected from El-Kalyoubia governorate, Egypt, with percentages of removal efficiency

		El-Kalyoubiagovernorate							
Month	Detected OPPs	Sh	oubraElKł	neima		Mostorod			
		Inlet	Outlet	Removal efficiency %	Inlet	Outlet	Removal efficiency %		
	Diazinon	0.221+0.05	BDL	100	BDL0 111+0.02	BDL			
May Chlorpyrifos		BDI 0 01±0 002					100		
	Prothiofos	BDL0.01±0.002		100	BDL				
July	Prothiofos	0.01±0.003	BDL	100	BDL	BDL			
Sent	Diazinon	0.221±0.06	BDL	100	BDL	BDL			
Sept.	Dimethoate	BDL			1.23±0.3		100		
Nov.		BDL	BDL		BDL	BDL			
Ian	Diazinon	BDL	BDL		0.341±0.09	BDL	100		
Jan.	Chlorpyrifos				0.315±0.08		100		
March	Dimethoate	BDL	BDL		8.091±2.4	2.41±0.6	70.2		

All the values are expressed as means of triplicates  $\pm$  standard error

BDL: Below detection limit

#### Table 3

Concentration (mg/L) of OPP residues detected in surface and drinking water samples collected from Kafr El-Sheikh governorate, Egypt, with percentages of removal efficiency

		Kafr El-Sheikh governorate							
Month	Detected OPPs		Kafr El-Shei	kh		Metoube	s		
		Inlet	Outlet	Removal efficiency %	Inlet	Outlet	Removal efficiency %		
May	Chlorpyrifos	BDL	BDL		0.123±0.04	BDL	100		
July	Prothiofos	BDL	BDL		0.95±0.2	BDL	100		
Sept.		BDL	BDL		BDL	BDL			
Nov.	Diazinon	BDL	BDL		0.541±0.1	BDL	100		
Jan.	Diazinon	6.71±2.08	0.12±0.03	98.2	BDL	BDL			
March		BDL	BDL		BDL	BDL			
								_	

All the values are expressed as means of triplicates  $\pm$  standard error.

BDL: Below detection limit.

#### Table 4

Concentration (mg/L) of OPP residues detected in surface and drinking water samples collected from Alexandria governorate, Egypt, with percentages of removal efficiency

		Alexandria governorate						
Month	Detected OPPs	Elseyouf		Elkilo 40				
	-	Inlet	Outlet	Removal efficiency %	Inlet	Outlet	Removal efficiency %	
May	Diazinon	0.516±0.1	0.05±0.01	90.3	BDL	BDL		
July	Prothiofos	BDL	BDL		0.031±0.009	BDL	100	
Sept.	Diazinon	BDL	BDL		0.115±0.03	BDL	100	
Nov.		BDL	BDL		ND	BDL		
Jan.	Diazinon	BDL	BDL		0.981±0.3	BDL	100	
March		BDL	BDL		ND	BDL		

All the values are expressed as means of triplicates ± standard error

BDL: Below detection limit

Out of the 12 OPPs analyzed, 4, 3, and 2 were obtained from water samples collected from El-Kalyoubia, Kafr El-Sheikh, and Alexandria governorates, respectively, at various concentrations. In addition, 58.3, 33.3, and 33.3% of surface water samples collected from El-Kalyoubia, Kafr El-Sheikh, and Alexandria governorates were polluted by OPPs, respectively. The highest concentration of OPPs belonged to dimethoate (8.09 mg/L) in the El-Ismailia canal in ShoubraElKheima, followed by 6.71 mg/L diazinon in the Meet Yazid canal in Kafr El-Sheikh, indicating pollution from neighbouring activities.

The most common OPPs in water samples were diazinon, followed by prothiofos, chlorpyrifos, and dimethoate, which were detected in 13.9%, 5.6%, 4.2%, and 4.2% of samples, respectively, reflecting diazinon's higher application rate compared to the

other OPPs. Concentrations of diazinon, prothiofos, chlorpyrifos and dimethoate in water samples ranged from 0.05 to 6.71, ND to 0.95, ND to 0.315, and ND to 8.09 mg L-1, respectively. Due to their effectiveness and affordability, diazinon, prothiofos, and chlorpyrifos were widely used in Egyptian farmland, which may have contributed to their high detection rates. According to data from the Egyptian agricultural pesticide committee, diazinon and chlorpyrifos are two of the top 10 pesticides used in Egypt. Therefore, the high pesticide level in the surface water may be a result of the vast agricultural activities that take place on the banks of these places, which produce agricultural run-off. Furthermore, because OPPs have a relatively short half-life, their detection in water supplies indicates how frequently they are applied. These results are comparatively in line with earlier studies. For instance, chlorpyrifos

was found in water samples along the Nile by Dahshan et al. [24] at a mean concentration of 0.578  $\mu$ g/L. The prevalent pesticides found in the rivers of Lebanon's surface water were chlorpyrifos and diazinon [25]. Qiu et al. [26] compared the surface water of the Maozhou River to the main rivers of Shenzhen, China, and discovered that diazinon concentrations were high. As a result, there are excessive levels of pesticides in surface water due to the agricultural flow caused by the heavy agricultural activity on the shores of these areas. In addition, because most OPPs have short half-life values, their detection in water indicates how often they are used.

Current data also showed that 41.6 and 8.3% of drinking water and surface water samples were polluted with OPPs, respectively. Diazinon and dimethoate were detected in 5.5% and 2.7% of drinking water samples, respectively, and their residues were below the maximum residue levels (MRLs). These pesticides are mostly applied in agricultural fields to control crop and soil pests, and agricultural runoff may lead to high pesticide concentrations [27]. Similarly, Essumang et al. [28] reported that pesticide residues had an overall average value of 2.6384, 0.4992, 0.3045, and 1.3629 mg/L in water samples from four lagoons (Chemu, Korle, Fosu, and Etsii), respectively. In contrast, according to Rocha et al. [29], between February 2009 and September 2010, no traces of pesticide residues were detected in surface water samples collected from Center-Pivot irrigation zones in Brazil. On the other hand, seasonal changes in OPP concentrations in surface and drinking water samples could be sorted as follows: May> Jan. > Sep. > July> March> Nov. The added impact of urban and industrial operations on nearby practices that coexist with agricultural activities can be used to explain seasonal fluctuations in pesticide residue levels. Increased application rates, especially during the summer, as well as pesticides partitioning from their reservoirs and accumulating in sediments, may potentially contribute to elevated pesticide levels [30, 18]. The data also show that pesticide residues vary in the different locations; e.g., OPP residue levels found in Mostorodhad the highest residual values, followed by those in Sh. ElKheima, Metoubes, Elkilo 40, Kafr El-Sheikh, and Elseyouf, respectively. Therefore, the significant difference observed between the locations could be due to the various input source strengths and decay rates. Surface water

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has been exposed to much industrial, agricultural, and sewage pollution in these locations. Moreover, one of the important reasons for the pesticide residue problem was the use of huge amounts of pesticides and the lack of awareness among farmers regarding the required pesticide dosage, application techniques, and time. The obtained findings also indicate the weakness of management and a lack of direct control over pesticide usage.

Pollution of the Nile River and its tributaries has risen recently as a result of population growth, industrial development, and other activities along the Nile. It is common knowledge that the majority of pesticides are transported via multiple routes. Therefore, they frequently enter the aquatic environment through soil percolation, erosion, or water flows, impacting a variety of non-target species in the ecosystem [31]. The pesticide residues found in this study are comparable to those found by many authors, but it should be noted that a quantitative comparison across reported data is difficult due to variations in sample time, sites, and analytical methods used. Analysis of freshwater along the Mahmoudia canal has shown that detected concentrations of organophosphorus residues were high during the summer, which may be due to the extensive agricultural activities at this time of year [32]. Chlorpyrifos-methyl and prothiphos were found in only one water sample collected in the El-Embaby drain, El Menofiya, Egypt [33]. The most frequently detected pesticides in surface water collected from the sampling sites at El-Rahawy, Sabal, and Tala across the Rosetta branch of the River Nile were malathion (57%), followed by chlorpyrifos [18].

# Water risk assessment for consumption by humans

#### Human health risk assessment

In the current study, pesticides with varied values at the sampling points were selected and utilized for the non-carcinogenic health risk assessment model. The THQ values of the detected pesticides among the selected 12 OPPs in surface and drinking water are shown in Tables 5 and 6, respectively.

When the non-carcinogenic risk value is less than one, there is no obvious threat to human health [34]. Individual pesticides' non-carcinogenic risks were, by definition, lower than the overall non-carcinogenic risks. Therefore, each pesticide poses negligible to no potential health risks to humans at the concentrations detected in the evaluated drinking water. The THQ values for all pesticides found in surface and drinking water were less than one, which is in accordance with the results obtained by Eissa et al. [18]. This indicates that there is no potential human risk from exposure to both surface and drinking waters at the studied sampling sites. The findings also imply that the THQ values of diazinon were the highest, followed by prothiofos in surface water, compared to those of chlorpyrifos and dimethoate. Accordingly, diazinon was the main contaminant at the selected sites, and more concern should be paid to the remediation of this pesticide in the future. Remediation of pesticidecontaminated water could be undertaken by advanced oxidation processes, adsorption, biological treatments, and combined methods [35-37].

#### Table 5

Sampling site		Detected	Mean Conc.	ADI (mg/kg	RfD (mg/kg	THQ
		pesticides	(mg/L)	bw/d)	bw/d)	
El-	ShoubraElKheima	Diazinon	0.221	0.0002	0.025	0.030
Kalyoubiagovernorate	-	Prothiofos	0.01	0.0001	na	0.003
	Mostorod	Diazinon	0.341	0.0002	0.025	0.047
	-	Chlorpyrifos	0.213	0.001	0.005	0.006
	-	Dimethoate	4.66	0.001	0.01	0.013
Kafr El-Sheikh	Kafr El-Sheikh	Diazinon	6.71	0.0002	0.025	0.925
governorate		Diazinon	0.541	0.0002	0.025	0.075
	Metoubes	Chlorpyrifos	0.123	0.001	0.005	0.003
	-	Prothiofos	0.95	0.0001	na	0.262
Alexandria	Elseyouf	Diazinon	0.516	0.0002	0.025	0.071
governorate	Elkilo 40	Diazinon	0.548	0.0002	0.025	0.075
	-	Prothiofos	0.031	0.0001	na	0.008

Target hazard quotient (THQ) for detected OPP residues in surface waters in three Egyptian governorates

na, not available; ADI, acceptable daily intake; RfD, oral reference dose

#### Table 6

Target hazard quotient (THQ) for detected OPP residues in drinking water in three Egyptian governorates

Sampling site	Detected pesticides	Mean Conc. (mg/L)	ADI (mg/kg bw/d)	RfD (mg/kg bw/d)	THQ
El-Kalyoubia	Dimethoate	2.41	0.001	0.01	0.006
(Mostorod)					
Kafr El-Sheikh	Diazinon	0.12	0.0002	0.025	0.016
(Kafr El-Sheikh)					
Alexandria (Elseyouf)	Diazinon	0.05	0.0002	0.025	0.007

# 4. Conclusions

OPP residues in surface water samples mean that wastewater discharges into water bodies must be controlled and regularly monitored and should be undertaken at different seasons with a wide spectrum of pesticides to obtain clear baseline data. Furthermore, every effort should be made to achieve the highest quality of drinking water; otherwise, human health is subject to severe hazardous effects. There are no identified risks to people from drinking water exposure in the study areas, according to the THQ values of pesticides found in surface and drinking water samples that were less than one. More research is needed to understand whether various pesticide residues have synergistic, additive, or antagonistic impacts on human health. The results of this study can therefore assist with future monitoring, control, and management of OPPs as well as water resource management and regulatory issues.

# **5.** Conflict of interest

The authors have no conflicts of interest to declare that are relevant to the content of this research article.

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