

Occurrence, human health and ecotoxicological risk assessment of pesticides in surface waters of the River Nile's Rosetta Branch, Egypt

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Abstract

In Egypt, the shortage of freshwater resources and their pollution constitutes a growing concern. Therefore, the objectives of this study were to (i) monitor the occurrence and spatiotemporal variations of 100 pesticides in surface water samples collected monthly (from July 2018 to June 2019) from El-Rahawy, Sabal, and Tala sampling sites along the Rosetta branch of the River Nile in Egypt, (ii) identify potential non-carcinogenic health risks for the local people through the lifetime consumption of contaminated drinking water, and (iii) perform an ecological risk assessment of aquatic organisms upon exposure to pesticides detected in surface waters based on the risk quotients (RQs) method. Of the 100 pesticides analyzed, 22 belonging to 11 chemical families were detected, and 75.5% of surface water samples were contaminated with one or more pesticide residues. The most frequently detected pesticide was malathion (57%), followed by chlorpyrifos (54%), atrazine (23%), and carbendazim (20%). Spatial distribution showed that the El-Rahawy site had the highest pesticide load (38.47 µg/L), and Sabal had the lowest (16.29 µg/L). Temporal variations revealed that the highest total pesticide concentrations were detected in summer (27.98 µg/L) compared to spring (23.16 µg/L), winter (19.18 µg/L), and autumn (11.85 µg/L). For non-carcinogenic risks of pesticides detected in surface water, the target hazard quotient (THQ) values were less than one. This implies that there is no potential human risk from exposure to drinking water at the sites under study. However, 13 pesticides presented high-risk quotients ($RQ > 1$), posing potential ecological risks to aquatic organisms.

Introduction

The River Nile flows through 11 African countries, including Egypt, before discharging into the Mediterranean Sea. In Cairo, the river is divided into two branches, the Rosetta and Damietta, which form the Nile Delta. Due to population growth, rapid urbanization and industrialization, and extensive agriculture, the demand for irrigation, domestic water supply, and industrial water supply from the Rosetta Nile Branch continues to grow (NBI, 2005). The Rosetta branch receives enormous amounts of contaminated water daily from numerous sources, including industrial, agricultural, and municipal wastewater, and feed waste from fish cages. All such sources cause severe negative impacts on the aquatic environment (Abbassy, 2018). The use of pesticides in agriculture and residential areas involves their unintentional releases to adjacent non-target ecosystems such as rivers (Schulz, 2004). Surface waters are more vulnerable to pesticides in intensive agricultural areas, constituting a major concern for human water consumption. Residues of pesticides in river systems are not only a threat to human health by means of water and fish consumption but also a threat to aquatic species (Zheng et al., 2016).

Monitoring pollutants in the River Nile is essential to provide quantitative data on dominant pollutants, identify their origins and environmental fate, comply with regulations, contend with human and environmental health issues, and enable advanced treatment technologies for accurate targeting (Eissa et al., 2020). Despite the importance of regular pesticide monitoring programs, most studies to date (Dahshan et al., 2016; Shalaby et al., 2018; El-Alfy et al., 2019) have focused on the analysis of limited numbers and few classes of pesticides with infrequent sampling. Also, these studies have not considered human health or ecotoxicological risk assessment of pesticides in surface water.

Chronic ingestion of pollutants into humans above a safe threshold can have adverse effects and pose non-carcinogenic risks such as neurological disorders and hepatorenal alterations (Farmer et al., 2011). The target hazard quotient (THQ), established by the US EPA, is widely used to assess the potential non-carcinogenic human health risks associated with long-term exposure to contaminated water through the oral route (US EPA, 1989). A useful indicator of risk levels linked with exposure to contaminants can be found in the THQ-based risk assessment method (Wang et al., 2012).

The ecological risk assessment of pesticides is described in terms of environmental exposure and ecotoxicological impacts. The potential aquatic ecotoxicological risk assessment of detected pesticide residues was calculated using the risk quotient (RQ) method, which is the ratio of the measured environmental concentration (MEC) of a single pesticide to the predicted no-effect concentration (PNEC) (Palma et al., 2014).

Therefore, the objectives of this study were to (i) monitor the occurrence and spatiotemporal variations of 100 pesticide belonging to different chemical classes in surface water samples collected monthly (from July 2018 to June 2019) for the first time from El-Rahawy, Sabal, and Tala sampling sites situated along the Rosetta Branch of the River Nile in Egypt, (ii) identify potential non-carcinogenic health risks for the local people through the lifetime consumption of contaminated drinking water, and (iii) perform an ecological risk assessment of aquatic organisms upon exposure to pesticides detected in surface waters based on the risk quotients (RQs) method.

Materials And Methods

Study area and sampling campaign

The sampling strategy was adopted based on the presence of three drains (El-Rahawy, Sabal, and Tala) that receive untreated, partially treated, and/or treated wastewater from wastewater treatment plants (WWTPs) that eventually discharge their effluents directly into the Rosetta Branch of the River Nile. Monitoring surveys were conducted at three sampling points along the Rosetta Branch over 12 sampling periods from July 2018 to June 2019. In the three sampling sites, 144 surface water samples were collected in duplicate as follows: 1 km before (upstream) and 1 km after (downstream) the outlet of (1) the El-Rahawy drain (Giza Governorate; coordinates of 30° 12' 26.21" N and 31° 1' 58.90" E), (2) the Sabal drain (Minoufiya Governorate; coordinates of 30° 32' 13.47" N and 30° 51' 07.09" E) and (3) the Tala drain (Kafr El-Zayat, Gharbiya Governorate; coordinates of 30° 49' 01.74" N and 30° 48' 47.77" E), as described in our previous study (Eissa et al., 2020) and shown in Fig. 1. A complete list of pesticides as target pollutants, their recovery rates, and coefficient of variation at various standard levels and limits of quantification (LOQ) are provided in the Supplementary Material (Table S1).

Surface water samples (sampled at a depth of about 50 cm from the middle section of the Rosetta Branch) were collected in 2.5 L amber glass bottles. The bottles were filled to the seal, left no space for air bubbles, labeled, and transferred in an icebox to the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food in Giza. Upon arrival, water samples were immediately vacuum filtered using a glass fiber filter (GC-50, diameter: 47 mm; pore size: 0.5 µm, Advantec) to remove suspended particles. Each filter was

then washed with 5 mL of methanol, which was added to the filtrate. All samples were refrigerated at $\pm 4\text{ }^{\circ}\text{C}$ until extraction.

Extraction of pesticide residues

Pesticides were extracted from surface water samples according to Rocha et al. (2012) with some modifications. Oasis HLB cartridges were sequentially washed with 5 mL of ethyl acetate followed by 5 mL of methanol and 10 mL of deionized water at a 2 mL/min flow rate. Surface water samples (500 mL) were loaded into solid-phase extraction (SPE) cartridges at a constant flow rate of 5 mL/min. After passing the sample, cartridges were dried under vacuum for 30 minutes. The adsorbed pesticides were then eluted with 10 mL of ethyl acetate into 10 mL tubes at a speed of 1 mL/min. Four mL of the eluate was transferred and evaporated under a stream of nitrogen and taken up in 2 mL of acetonitrile before injecting into the LC-MS/MS system. Another 4 mL of the eluate was transferred and evaporated under a stream of nitrogen and taken up in 2 mL of ethyl acetate before injecting into GC-MS/MS.

Gas chromatography-tandem mass spectrometry (GC/MS-MS) analysis

As described in our previous study (Eissa et al., 2020), we used an Agilent 7890A gas chromatography system tailored with a 7000B triple quadrupole Agilent mass spectrometer. The column was a DB-35MS Ultra Inert Capillary Column (35% Phenyl-65% dimethylpolysiloxane, 30 m length \times 0.18 mm internal diameter \times 0.25 μm film thickness, Agilent Technologies). The GC oven temperature program started at 70 $^{\circ}\text{C}$ for 1.3 min and rose to 150 $^{\circ}\text{C}$ at 70 $^{\circ}\text{C}/\text{min}$. It was then raised to 270 $^{\circ}\text{C}$ at 12 $^{\circ}\text{C}/\text{min}$ and finally to 310 $^{\circ}\text{C}$ at 18 $^{\circ}\text{C}/\text{min}$ and held for 6.3 min for a total run time of 21 min per sample. The inlet temperature was 250 $^{\circ}\text{C}$, the injection volume was 1 μL , and the injection was performed in splitless mode. Helium was used as the carrier gas at a constant flow rate of 0.7 mL/min, and nitrogen was used as the collision gas. Electron impact mode was used, and the ionization energy was 70 electron-volts (eV). The ion source temperature was 320 $^{\circ}\text{C}$, the GC-MS/MS interface temperature was 320 $^{\circ}\text{C}$, and the quadrupole temperature was 180 $^{\circ}\text{C}$. MassHunter software was used for instrument control and data acquisition/processing.

Liquid chromatography-tandem mass spectrometry (LC/MS-MS) analysis

As described in our previous study (Eissa et al., 2020), we used the LC-MS/MS system consisting of an Agilent 1200 Series HPLC connected to an API 4000 Qtrap MS/MS from Applied Biosystems (Foster City, CA, USA). The separation was performed on an Agilent C18 ZORBAX Eclipse XDB column with a length of 150 mm, an inner diameter of 4.6 mm, and a particle size of 5.0 μm . The temperature of the column was 40 $^{\circ}\text{C}$, and the volume of injection was 5 μL . The separation was performed by gradient elution between two components; A: 10 mM of ammonium formate solution in methanol: water (1:9 v/v) and B: methanol. The initial flow rate was 0.5 mL/min, starting with 100% of component A, gradually changing to 5% A (95% B) over 6 min, and held constant for 17 min at a flow rate of 0.3 mL/min. After this 23 min run time, a 2 min post time was followed using the initial 100% of A at a flow rate of 0.5 mL/min. The MS/MS analysis was performed using electrospray ionization (ESI) in the positive ion mode in multiple reaction monitoring mode (MRM). The following source and gas parameters were used: 450 $^{\circ}\text{C}$ temperature; 25 psi curtain gas;

medium collision gas; 5000 V ion spray voltage; 1, 40 psi ion source gas; and 2, 40 psi ion source gas. Analyst Software version 1.6. was used for instrument control and data acquisition/processing.

Quality assurance

All analytical methods and instruments were entirely validated as part of a laboratory quality control and assurance system (ISO/IEC 17025:2005). They were audited and accredited by the Centre for Metrology and Accreditation, Finnish Accreditation Service (FINAS), Helsinki, Finland. In order to estimate extraction efficiency, the blank and spiked samples were analyzed according to the methods mentioned above. The mean recovery of the selected pesticides in surface water samples ranged from 70 to 120%. The coefficient of variation at various standard levels was < 20%, while the limit of quantification (LOQ) was 0.05 µg/L for pesticide residues. These data are provided in Table S1 (Supplementary Material).

Human risk assessment

The potential non-carcinogenic health risks associated with the consumption of contaminated water with pesticide residues were assessed based on the target hazard quotient (THQ), which was estimated using the following equation (USEPA, 1989):

$$\text{THQ} = (\text{EF} \times \text{ED} \times \text{FIR} \times \text{C}) / (\text{RfD} \times \text{BW} \times \text{AT})$$

where EF is the exposure frequency (365 days/year), ED is the exposure duration (70 years; equivalent to the average human lifetime), FIR is the water ingestion rate (2000 mL/person/day), C is the pesticide concentration in water (mg/L), RfD is the oral reference dose (USEPA, 2019) (Table 3), BW is the body weight (70 kg/person), and AT is the average time for non-carcinogens (365 days/year × ED). If the THQ value is ≥ 1, exposed individuals may experience health risks by consuming contaminated water. Therefore, interventions and protective measures need to be taken.

Ecotoxicological risk assessment

The potential aquatic ecotoxicological risk was assessed based on the risk quotient (RQ) method (ECC, 2003) for detected pesticide residues in surface water. This is the ratio between the measured environmental concentration (MEC) of a single pesticide and the predicted no-effect concentration (PNEC) ($\text{RQ} = \text{MEC}/\text{PNEC}$) (Palma et al., 2014). For calculating PNEC, the lowest no observed effect concentration (NOEC) values were used. In the absence of NOEC, the median effective concentration (EC_{50}) or the median lethal concentration (LC_{50}) values, taken from the pesticide properties database (Lewis et al., 2016), were used.

The PNEC values were estimated by dividing the NOEC or the EC_{50} or LC_{50} values of the most sensitive species by an appropriate assessment factor (AF) for the three trophic levels (algae, *Daphnia* sp., and fish) used. According to the European Commission's Technical Guidance Document on Risk Assessment: (i) an AF of 1000 is used when at least one short-term assay is available at one trophic level; (ii) an AF of 100 is used when data are available from a single long-term assay of either fish or zooplankton; and (iii) AFs of 50 and 10 are used when two and three long-term assays are available, respectively. Thus, we determined each

pesticide ecological risk for the aquatic ecosystem at each sampling site, using the mean detected concentrations of the pesticides.

Results And Discussion

Spatiotemporal distribution of pesticide residues in surface water along the Rosetta Nile branch

Of the 100 pesticides analyzed, 22 pesticides (12 insecticides, six fungicides, two herbicides, one acaricide, and one breakdown product) belonging to 11 chemical families were detected. Overall, 75.5% of all surface water samples (69% of the upstream and 82% of the downstream samples) were contaminated with one or more pesticide residues, as shown in Tables 1 and 2.

Regarding the number of pesticides detected per category in all surface water samples, insecticides were the most frequently detected pesticides (72%), followed by herbicides (27%), fungicides (24%), and acaricides (5%).

With regards to the pesticide families, the organophosphorus pesticides (OPPs) were the most frequently detected group found in 68% of the total surface water samples. This was followed by triazines (23%) and benzimidazoles (20%), while carbamates and neonicotinoids were similar (7%). Organochlorine and pyrethroid pesticides displayed the same detection frequency (5%), followed by benzoylureas (2%), and finally, anilinopyrimidines, carboxamides, and phthalimides, which all exhibited the same detection frequency (1%). The overall frequency of OPPs detection may be due to the widespread use of these compounds in Egyptian agriculture due to their efficiency and low cost.

The detection frequency (%) and mean concentrations ($\mu\text{g/L}$) of the most frequently detected pesticide compounds in all surface water samples were malathion (57% and $0.42 \mu\text{g/L}$), followed by chlorpyrifos (54% and $0.183 \mu\text{g/L}$), atrazine (23% and $0.084 \mu\text{g/L}$), carbendazim (20% and $0.082 \mu\text{g/L}$), phenthoate (15% and $1.63 \mu\text{g/L}$), diazinon (14% and $0.257 \mu\text{g/L}$), chlorpropham (7% and $0.131 \mu\text{g/L}$), and imidacloprid (7% and $0.312 \mu\text{g/L}$). In addition, permethrin, heptenophos, and dicofol exhibited the same detection frequency (5%), with mean concentrations of 0.666, 0.103, and $0.083 \mu\text{g/L}$, respectively. In this study, the highest pesticide concentrations were $6.04 \mu\text{g/L}$ for phenthoate measured downstream of Sabal in the spring and $5.1 \mu\text{g/L}$ for malathion measured at El-Rahawy in the summer. The detection of banned pesticides in surface water samples indicates their persistence or illegal use in agricultural activities.

Of the 144 analyzed surface water samples, 18, 24, 12, 10, 4, 2, and 4% were contaminated with 1, 2, 3, 4, 5, 6, and 7 pesticide compounds, respectively. Of the 144 surface water samples, 24% contained residues $\leq 0.1 \mu\text{g/L}$ (ranging from below LOQ to $0.08 \mu\text{g/L}$), 32% contained residues $\geq 0.1 \mu\text{g/L}$ (ranging from 0.1 to $0.47 \mu\text{g/L}$), 6 % contained residues $\geq 0.5 \mu\text{g/L}$ (ranging from 0.5 to $0.94 \mu\text{g/L}$), and 15 % contained residues $> 1 \mu\text{g/L}$ (ranging from 1.02 to $9.6 \mu\text{g/L}$). The pesticide load found at the Rosetta Branch occurs through various transportation routes, including surface water runoff, leaching, erosion, spray drift, drain outflow, and agricultural, residential, and industrial effluent discharge (Eissa et al., 2020).

The spatial distribution of the detected pesticides in surface water samples along the Rosetta Branch of the River Nile revealed that El-Rahawy had the highest sum of all pesticide concentrations with 38.47 µg/L (4.15 µg/L in the upstream and 34.32 µg/L in the downstream samples), followed by Tala with 27.41 µg/L (11.23 µg/L in the upstream and 16.18 µg/L in the downstream samples), and Sabal with 16.29 µg/L (3.5 µg/L in the upstream and 12.79 µg/L in the downstream samples). Furthermore, 50% of El-Rahawy samples were contaminated with the highest number of pesticides (18 compounds). For comparison, 88% of the Sabal and Tala samples were contaminated with 13 and 10 pesticides, respectively. Moreover, downstream surface water samples contained more pesticides in terms of number and concentration than those collected from upstream sampling sites. In particular, surface water downstream of the El-Rahawy sampling site showed relatively higher levels of pesticide residues than Tala and Sabal due to receiving primary treated wastewater from the Abu-Rawash wastewater treatment plant (WWTP) through the El-Rahawy drain. This is considered the main cause of water quality deterioration at the River Nile's Rosetta Branch. Köck-Schulmeyer et al. (2013) found high levels of pesticides in WWTP effluents, even in WWTPs with tertiary treatment, despite the common belief that this treatment produces water with adequate quality for use in various fields. Furthermore, conventional urban WWTPs have not been originally designed to remove pesticides. Therefore, the efficient removal of pesticides depends on many factors, such as the specificity of the pesticides and the employed treatment methods (Deblonde et al., 2011).

Based on temporal variations, the highest total pesticide concentration detected for 14 pesticides in the summer was 27.98 µg/L (0.43 µg/L in the upstream and 27.55 µg/L in the downstream samples) compared to 8 pesticides in the spring that was 23.16 µg/L (6.68 µg/L in the upstream and 16.48 µg/L in the downstream samples), 15 pesticides in the winter that was equal to 19.18 µg/L (8 µg/L in the upstream and 11.18 µg/L in the downstream samples), and 12 pesticides in the autumn that amounted to 11.85 µg/L (3.77 µg/L in the upstream and 8.08 µg/L in the downstream samples). Meanwhile, during summer, the El-Rahawy samples recorded the highest total pesticide concentration equal to 23.61 µg/L (0.2 µg/L in the upstream and 23.41 µg/L in the downstream samples). Likewise, samples collected from the El-Rahawy area during autumn were the most contaminated with a total pesticide concentration of 7.91 µg/L (2.55 µg/L in the upstream and 5.36 µg/L in the downstream samples). Conversely, during winter and spring, the Tala samples contained the highest total pesticide concentration equal to 10.71 µg/L (5.84 µg/L in the upstream and 4.87 µg/L in the downstream samples) and 12.69 µg/L (4.83 µg/L in the upstream and 7.86 µg/L in the downstream samples), respectively. Seasonal differences in pesticide residues can be attributed to the additional impact of urban and industrial activities on neighboring activities that coexist with agricultural activities. Elevated pesticide levels in the summer may also be due to partitioning from their reservoirs accumulated in sediments.

These findings are partially consistent with previous studies in other rivers around the world. For example, Gao et al. (2009) found malathion in 43.5% of surface water samples collected in 2003 and 2004 from seven major river basins and three major internal river drainage areas in China. Fadaei et al. (2012) showed that surface water samples of the Babolrood River in Iran were contaminated by malathion and diazinon at mean concentrations of 55.7 to 75.9 µg/L and from 77.6 to 101.6 µg/L, respectively. Their results also showed that the amount of detectable OPPs in the water samples diminished in cold weather. Sangchan et al. (2014) revealed that chlorpyrifos was frequently present in water samples (75 %) collected from the Mae

Sa river in Thailand. Montuori et al. (2015) showed the presence of nine organophosphate pesticides at concentrations between 5.58 and 39.25 ng/L in water samples from the Sarno River in Italy. Ccanccapa et al. (2016) indicated that chlorpyrifos, diazinon, and carbendazim were the most frequent pesticides in the water samples of the Ebro River in Spain (found in 95, 95, and 70% of the samples, respectively). Dahshan et al. (2016) detected chlorpyrifos in water samples along the River Nile at a mean concentration of 0.578 µg/L. Aisha et al. (2017) found that chlorpyrifos and diazinon were the most abundant pesticides in the surface water of rivers in Lebanon.

Atrazine is a triazine herbicide that is a common surface water contaminant owing to its high application rates and chemical properties (Callicott and Hooper-Bùi, 2019). Although atrazine has been banned since 2003 in the European Union, it is still regularly detected in surface waters in that region (Barchanska et al., 2017). Carbendazim is a benzimidazole fungicide that is widely used in crop protection. It is also frequently applied as a preservative for fiber, leather, rubber, and polymerized materials as well as a preservative for construction materials such as building facades (Coutu et al., 2012). The presence of carbendazim in surface water and wastewater samples has been documented in Denmark (Bollmann et al., 2014), Germany (Launay et al., 2016), and China (Xu et al., 2020). Carbendazim concentrations in the range of 600–6000 ng/L have been recorded in particular areas of Spain, where this substance was widely used in agriculture (Masiá et al., 2015). In addition, from 2007 to 2012, carbendazim was the most frequently detected pesticide in the surface waters of Costa Rican river basins (Carazo-Rojas et al., 2018). Merel et al. (2018) suggested that carbendazim in surface water originates primarily from treated municipal wastewater discharge. Moreover, paper and textile industries have been found as new potential sources of carbendazim due to the discharge of their effluents. Chlorpropham is widely applied as a sprout inhibitor in stored potatoes, contaminating the storeroom fabric, atmosphere, soil, and waterways (Douglas et al., 2018). The high residual level of dicofol found in the surface water is associated with its use in agriculture as it is a cheaper pesticide. It has also been identified as an additional source of *o,p'*-DDT (Wei et al., 2008). Another study conducted by the U. S. Geological Survey demonstrated that at least one neonicotinoid was found in 53% of surface water samples collected from rivers across the United States. Here, imidacloprid was the most frequently detected neonicotinoid occurring in 37% of samples (Hladik and Kolpin, 2016).

Risk assessment of water for human consumption

The potential health risks of individual pesticides detected in the Rosetta Branch of the River Nile's upstream surface water were assessed using the target hazard quotient, THQ (USEPA, 1989). According to WHO recommendations, each adult should drink 2 Liters of water every day. Assuming that the drinking water treatment plants do not remove pesticides using the conventional treatment techniques (Zheng et al., 2016), calculations were undertaken. Regarding non-carcinogenic risks of the detected pesticides in surface water samples, as shown in Table (3), the THQ values were lower than 1. This implies no potential risk to the human body due to the drinking water exposure in the study areas. Surface water samples from the El-Rahawy area showed the highest THQ values, i.e., 0.04 and 0.016 for diazinon and chlorpyrifos, respectively. Likewise, diazinon THQ values were the highest at Tala (0.018) and Sabal (0.017). These results agree with those obtained by Gao et al. (2012) who demonstrated that the non-carcinogenic risk hazard quotient values of the detected OPPs in the Haihe River water were less than one, indicating the health risk caused by these

compounds was at an acceptable level. Papadakis et al. (2015) showed that pesticides in the northern Greece Rivers pose low potential risks to humans due to exposure to drinking water. Zheng et al. (2016) revealed that the health risk associated with the Jiulong River water consumption in South China was low, despite the river water contained pesticide residues at detectable levels.

Ecotoxicological risk assessment

The risk quotients (RQs) correlated with exposure to individual pesticides detected in surface water samples were calculated for three representative trophic levels, viz., algae, *Daphnia* sp., and fish. The average detected concentrations at each site were used to determine the RQ and identify the high-risk sites. These were compared to the levels of concern recorded in the literature (i.e., $RQ \geq 1$: high-risk; $0.1 \leq RQ < 1$: medium risk; $RQ < 0.1$: low risk) (Sánchez-Bayo et al., 2002).

Tables 4 to 6 show the ecotoxicological risks of detected pesticides based on their annual average concentrations and risk quotient approach. Of the sites monitored, the El-Rahaway site indicated the highest ecotoxicological risk, followed by Sabal and Tala. Risk quotient (RQ) values revealed high ecotoxicological risks (> 1) at all sites for chlorpyrifos, diazinon, malathion, and phenthoate. The highest RQ at the El-Rahaway site was for malathion, followed by permethrin, chlorpyrifos, and phenthoate with values of 1158.3, 1155.9, 230, and 211.8, respectively. Of all the pesticides detected at the Sabal and Tala sites, phenthoate displayed the highest RQ at 1047 and 982, respectively. At the Sabal site, high RQ values of 116.7, 41.9, and 35 were also found for malathion, diazinon, and chlorpyrifos, respectively. Regarding the Tala site, high RQ values of 129, 79.2, 29.5, and 9.8 were also found for permethrin, malathion, chlorpyrifos, and diazinon, respectively.

The high and unacceptable risks posed by these pesticides are mainly due to their relatively high toxicity to algae, *Daphnia* sp., and fish. This results in their relatively low PNEC values. Moreover, the increased risks observed also result from the combination of the relatively high MEC values and low PNEC values. This ecotoxicological risk assessment emphasizes that such pesticides ($RQ > 1$) must be prioritized for risk management, mainly because the River Nile is a habitat to numerous species. The high aquatic risk posed by pesticides leads to changes in fish and invertebrate populations in the long term, leading to a decrease in the most vulnerable species and an increase in the most resistant species, resulting in biodiversity loss (Palma et al., 2014; Kuzmanović et al., 2015).

Our findings agree with those of Ccanccapa et al. (2016) who found that detected OPPs posed high risks to algae, daphnia, and fish in the Ebro River in Spain. Wee and Aris (2017) indicated that the overall exposure to chlorpyrifos in the surface water of the Langat River in Malaysia posed a high risk ($RQ > 1$). Sumon et al. (2018) showed high RQs (> 1) for chlorpyrifos, diazinon, quinalphos, malathion, and fenitrothion in the surface water of different water bodies in northwestern Bangladesh. In some water samples from the Guangzhou waterways in China, permethrin was present at high-risk levels with RQ values greater than 1 (Li et al., 2019). Contrarily, RQ values for the pesticides detected in small streams in the European Union (Casado et al., 2019) were lower than the RQs calculated in this study for boscalid (0.01275) and carbendazim (1.279753) but higher for dimethoate (0.248765) and imidacloprid (5.235504).

Conclusions

This study presents the first monitoring campaign for 100 pesticides in the Rosetta Branch of the River Nile. This research was performed to assess the occurrence, spatiotemporal distribution, and risk assessment of pesticides. Twenty-two pesticides belonging to 11 chemical families were detected, and 75.5% of surface water samples were contaminated with one or more pesticide residues. Moreover, downstream surface water samples contained more pesticides in terms of number and concentration than those collected from upstream sampling sites. The THQ values of pesticides detected in surface water samples were lower than one, implying no potential risks to humans through exposure to drinking water in the study sites. However, 13 pesticides showed high-risk quotients ($RQ > 1$), posing a potential ecological risk to aquatic organisms. On the other hand, pesticides typically occur in aquatic ecosystems as a mixture of multiple pesticides rather than individually which require further research on their potential combined ecotoxicological impacts. There is also a need to increase assessments of urban, agricultural, and industrial wastewater released into surface waters and evaluate the treatment efficiency requirements of WWTPs. Hence, regular monitoring is recommended to assess the occurrence and potential sources of the River Nile pollution to define mitigation strategies.

Declarations

Ethical Approval

This research article does not contain any studies with human participants or animals performed by any of the authors.

Consent to Participate

The authors declare consent to participate.

Consent to Publish

All the authors approved the final manuscript and agreed to its submission to the Environmental Science and Pollution Research.

Authors Contributions

Fawzy Eissa: study design, data processing, results analysis, writing and editing.

Mahmoud Al-Sisi: samples collecting, analysis, data processing and writing a first draft.

Khaled Ghanem: reviewing the manuscript.

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Competing interests

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

Availability of data and materials

The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Appendix A. Supplementary data

Supplementary data related to this manuscript can be found at...

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Tables

Due to technical limitations the Tables are available as a download in the Supplementary Files.

Figures

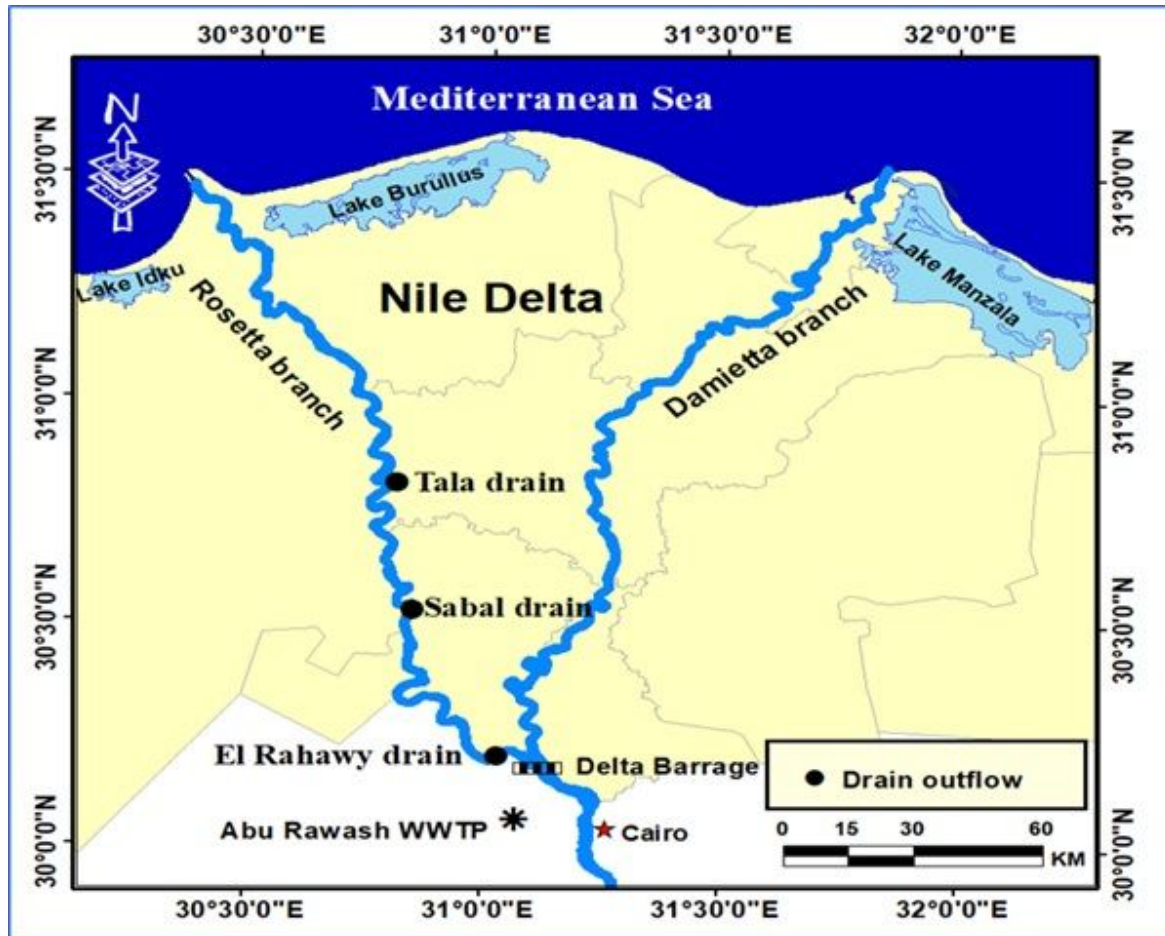


Figure 1

The sampling sites map of surface waters from the River Nile's Rosetta Branch, Egypt.

Supplementary Files

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