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Occurrence and ecotoxicological risk assessment of pesticides in sediments of the Rosetta branch, Nile River, Egypt

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ABSTRACT

This study aimed to (1) monitor the occurrence and spatiotemporal variations of 100 pesticides in sediments collected monthly from July 2018 to June 2019 from sampling sites in El-Rahawy, Sabal, and Tala, along the Rosetta branch of the Nile River, Egypt, and (2) perform an ecological risk assessment for aquatic organisms upon exposure to the detected sediment pesticides based on the risk quotient (RQ) method. Out of the 100 pesticides monitored, 16 pesticides belonging to seven chemical families were detected, and 55% of the sediment samples were contaminated with one or more pesticide residues. The mean concentration (mg/kg dry weight (dw)) and detection frequency (%) of the four most frequently detected pesticides in the sediment samples were as follows: chlorpyrifos (0.18 mg/kg dw and 34%), *p,p'*-DDE (0.018 mg/kg dw and 30%), cypermethrin (0.03 mg/kg dw and 14%), and deltamethrin (0.026 mg/kg dw and 13%). The spatial distribution exhibited that El-Rahawy had the highest pesticide load (2.86 mg/kg dw) among the studied sites, whereas the temporal variations revealed that the highest total pesticide concentrations were detected in winter season (1.73 mg/kg dw). Meanwhile, 12 pesticides showed high RQs (>1), posing a potential ecological risk to aquatic species that live and feed on such sediments.

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Introduction

The Nile River flows through 11 African countries, including Egypt, before discharging into the Mediterranean Sea. In Cairo, the river splits into two branches, namely, Rosetta and Damietta, which form the delta of the Nile River. Given the population growth, rapid urbanization, industrialization, and extensive agriculture, the demands for water supply of the

Rosetta branch of Nile River for irrigation, domestic water supply, and industrial uses are continuously increasing (Nile Basin Initiative, 2005). However, the Rosetta branch receives enormous amounts of contaminated waters daily from numerous sources, including industrial, agricultural, and municipal wastewater, in addition to feeding waste from fish cage feeds. All such conditions 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). The pesticide residues in river systems are not only a threat to human health by means of water

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and fish consumption but also to aquatic species (Zheng et al., 2016). Sediments can provide valuable information about water quality, and they are known as compartments for accumulated pollutants carried by the water column (Bonai et al., 2009).

Monitoring of pollutants in the Nile River is essential to provide quantitative data about the most abundant pollutants, to identify their origins and environmental fate, comply with regulations, and human and environmental health implications, and to improve the targeting of advanced treatment technologies (Eissa et al., 2020). Despite the importance of regular pesticide monitoring programs, previous studies on sediments in the Nile River in Egypt (Yamashita et al., 2000; Khallaf et al., 2018; Shalaby et al., 2018) have been limited to the analysis of a small number and a few classes of pesticides; these studies also had low sampling frequencies and excluded the ecotoxicological risk assessment of pesticides.

Pesticides may end up in freshwater sediments by adsorption onto the suspended particulate matter present on the surface water and may eventually deposit on the bottom of water bodies, forming sediment layers (Barbieri et al., 2019). Sediments therefore play a key role in the transport and fate of various hydrophobic organic contaminants. Sediments often reflect long-term pollution of the water as a pollution sink and can be utilized to assess the effect of human activities with slow alterations on their pollution pattern (Pinto et al., 2016). The presence of pesticides in sediments can permanently lead to adverse effects on the quality of the aquatic environment as a result of their water-sediment phase partition balance (Kreuger et al., 1999; Ma et al., 2001). The ecological risk assessment of pesticides is described in terms of the environmental exposure and ecotoxicological impacts. The potential aquatic ecotoxicological risk assessment for the detected pesticide residues is evaluated based on the risk quotient (RQ) method, which is the ratio of the measured environmental concentration (MEC) of a single pesticide in the sediment (converted into its corresponding concentration in pore water due to the lack of sediment toxicity data) to the predicted no-effect concentration (PNEC) ($RQ = MEC/PNEC$) (Palma et al., 2014; Sumon et al., 2018; Tyohemba et al., 2020; Merga et al., 2021; Pérez et al., 2021; Wei et al., 2021).

Therefore, this study aimed to (1) monitor the occurrence and spatiotemporal variations of 100 pesticides belonging to different chemical classes for the first time in sediments that were collected monthly from July 2018 to June 2019 from sampling sites in El-Rahawy, Sabal, and Tala, along the Rosetta branch of the Nile River, Egypt, and (2) perform an ecological risk assessment for aquatic organisms upon exposure to the pesticides detected in sediments based on the RQ method.

1. Materials and methods

1.1. 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 industrial, agricultural, and municipal wastewater that eventually discharge their effluents directly into the Rosetta Branch of the Nile

River. Monitoring surveys were conducted at three sampling points along the Rosetta branch and over 12 sampling periods from July 2018 to June 2019. For the three sampling sites, 144 sediment samples were obtained in duplicate as follows: 1 km before (upstream) and 1 km after (downstream) the outlet of (1) the El-Rahawy drain (Giza governorate; coordinates: 30°12'26.21"N and 31°1'58.90"E), (2) the Sabal drain (Minoufiya governorate; coordinates: 30°32'13.47"N and 30°51'07.09"E), and (3) the Tala drain (Kafr El-Zayat, Gharbiya governorate; coordinates: 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 different standard levels as well as limits of quantification (LOQ) are given in the Supplementary Material (Appendix A Table S1).

The upper sediment (5–10 cm) from the middle of the Rosetta branch riverbed was sampled with an Ekman dredge sampler, labeled, and transferred in an icebox to the Central Laboratory of Residue Analysis of Pesticides and Heavy Metals in Food in Giza. The sediment samples were stored in 500 mL plastic bottles at -20°C in the dark until analysis. Afterwards, the composite sediment samples were defrosted at laboratory room temperature, air-dried, grinded, and sieved through a 2 mm sieve. The mean percentage of water content of sediment samples was ($48.39 \pm 4.52\%$) as the fraction of mass loss of known weight relative to the initial wet sediment weight after drying until constant weight. Total organic carbon (TOC) concentrations in the sediment samples were measured as the difference of total carbon (TC) and total inorganic carbon (IC) measurements using TOC-SSM-5000A a solid sample module, TOC-VCSN (Shimadzu-total organic carbon analyzer, Japan) at 980 and 200°C for TC and IC, respectively.

1.2. Pesticide residue extraction

About 10 g of each sediment sample was weighed into a 50 mL centrifuge tube; 10 mL MilliQ water and 10 mL acetic acid 1% were added, and the mixture was shaken for 2 min followed by ultra sonication for 1 min. Then, 10 mL acetonitrile was added to the tube, and the mixture was shaken vigorously for 2 min. Extraction kits based on the QuEChERS methodology were added, and the tube was closed immediately, shaken vigorously for 2 min, and then centrifuged for 5 min at $2683 \times g$. Next, 2 mL acetonitrile phase was filtered and transferred into a glass vial for liquid chromatography–tandem mass spectrometry (LC/MS-MS analysis). An aliquot of 6 mL acetonitrile phase was transferred to a 10 mL centrifuge tube containing 200 mg PSA and 1 g magnesium sulfate, and the mixture was shaken vigorously for 30 sec and centrifuged for 2 min at $1509 \times g$. The supernatant was evaporated to dryness and then reconstituted using 2 mL *n*-hexane:acetone (9:1, V/V) containing 0.1 mg/L aldrin as the internal standard, followed by 30 sec of ultrasonication. The sample was filtered into a glass vial for gas chromatography–tandem mass spectrometry (GC/MS-MS) analysis (ILNAS-EN 15662, 2018).

1.3. GC/MS-MS analysis

As described in our previous study (Eissa et al., 2020), an Agilent 7890A GC system fitted with a 7000B triple quadrupole

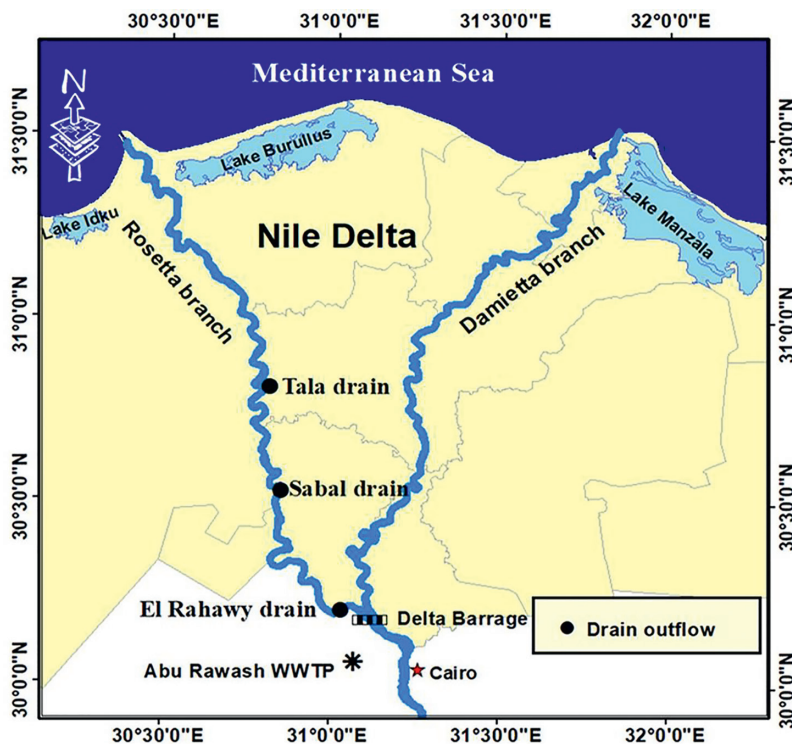


Fig. 1 – The sampling sites map of sediments from the Rosetta branch, Nile River, Egypt.

Agilent mass spectrometer was used. 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°C for 1.3 min and rose to 150°C at 70°C/min. It was then raised to 270°C at 12°C/min and finally to 310°C at 18°C/min and held for 6.3 min for a total run time of 21 min per sample. The inlet temperature was 250°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°C, the GC–MS/MS interface temperature was 320°C, and the quadrupole temperature was 180°C. MassHunter software was used for instrument control and data acquisition/processing.

1.4. LC/MS-MS analysis

As described in our previous study (Eissa et al., 2020), 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) was used. 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°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°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.

1.5. Quality assurance

All analytical methods and instruments were entirely validated as parts 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, Helsinki, Finland. In order to estimate extraction efficiency, the blank and spiked samples were analyzed according to the methods mentioned above. The mean recoveries of the selected pesticides in the sediment samples ranged from 70% to 114%. The coefficient of variation at different standard levels was < 20%, whereas the limits of quantification (LOQ) ranged from 0.01 to 0.05 mg/kg for pesticide residues. These data are provided in Appendix A Table S1.

1.6. Ecotoxicological risk assessment

The potential aquatic ecotoxicological risk was assessed based on the risk quotient (RQ) method (ECC European Com-

munity Commission, 2003) for detected pesticide residues in the sediments. This is the ratio between the measured environmental concentration (MEC) of a single pesticide and the predicted no-effect concentration (PNEC) ($RQ = MEC/PNEC$) (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 (Table 3). The PNEC values were estimated by dividing the long-term NOEC or the short-term 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, (1) an AF of 1000 is used when at least one short-term assay is available at one trophic level; (2) an AF of 100 is used when data are available from a single long-term assay of either fish or zooplankton; (3) AFs of 50 and 10 are used when two and three long-term assays are available, respectively. The concentrations of pesticides detected in the sediments were converted into their corresponding concentrations in pore water due to the lack of sediment toxicity data in accordance with previous works (Di Toro et al., 1991; Sumon et al., 2018; Tyohemba et al., 2020; Merga et al., 2021; Pérez et al., 2021; Wei et al., 2021), as indicated in the Eq. (1):

$$C_{pw} = C_s / (K_{oc} \times f_{oc}) \quad (1)$$

where, C_{pw} (mg/L) is the pesticide concentration in pore water, C_s (mg/kg) is the pesticide detected concentrations in the sediment, K_{oc} is the organic carbon–water partitioning coefficient for the pesticide detected, and f_{oc} is the fraction of total organic carbon measured in the sediment samples. We determined the ecological risk of each pesticide for the aquatic ecosystem at each sampling site using the mean detected concentrations of the pesticides.

2. Results and discussion

2.1. Spatiotemporal distribution of pesticide residues in sediments along the Rosetta branch of the Nile River

As shown in Tables 1 and 2, out of the 100 pesticides monitored, 16 pesticides belonging to seven chemical families were detected. Overall, 55% of all the sediment samples (38% of the upstream and 74% of the downstream samples) were contaminated with one or more pesticide residues.

With respect to the number of pesticides detected per category in all the sediment samples, the insecticides were the most commonly detected pesticides (41%; all organophosphorus and pyrethroids pesticides besides pyriproxyfen), followed by fungicides (9%; fludioxonil and folpet) and acaricides (5%; dicofol).

With regard to the pesticides per chemical family, organophosphorus pesticides (OPPs; chlorpyrifos, profenofos and prothiofos) were the most frequently detected group being found in 34% of the total sediment samples, followed by organochlorine (30%; dicofol, *o,p'*-DDD, *p,p'*-DDD and *p,p'*-DDE) and pyrethroids (14%; cyfluthrin, cypermethrin, deltamethrin,

lambda-cyhalothrin and permethrin), whereas dinitroaniline (pendimethalin), juvenile hormone mimic (pyriproxyfen), phenylpyrrole (fludioxonil), and phthalimide (folpet) all exhibited the same frequency (2%). The high overall detection rate for the OPPs was possibly due to the wide use of the detected compounds in Egypt for agriculture owing to their efficiency and low costs. These findings indicate the continuous and intensive use of profenofos which is among the top 10 most widely used pesticides by farmers in Egypt according to the statistics of the Egyptian agricultural pesticide committee. The $\log K_{ow}$ for profenofos is 4.44 (Tomlin, 2002), indicating that it would be expected to bind strongly to sediment (Kumar and Chapman, 2001). According to the concentrations and detection frequencies, profenofos was the most dominant pesticide recorded in sediment samples collected from different locations in the River Ravi at Balloki Headworks, Pakistan (Mahboob et al., 2015). Although the usage of organochlorine pesticides (OCPs) was banned in Egypt in the 1980s, their continuous detection in sediment samples is due to their environmentally persistent nature, illegal usage in agriculture and disease vector control, and release from contaminated soils and obsolete stocks (Ndunda et al., 2018). In addition, the water from the Nile River that arrives in Egypt is contaminated with various pesticides, including the persistent OCPs (El-Sebae et al., 1993). Long-range transport potential of pesticides should also take into consideration. Nineteen out of 45 current-use pesticides were found to transport over longer distances in water than in air (Matthies et al., 2009). According to Pesticide Properties DataBase the solubility of folpet in water at 20°C is 0.8 mg/L and the Octanol–water partition coefficient at pH 7, 20°C is 3.02, this may explain its tendency to bind with the sediment rather than water. The European regulation changed in 2016 following the reasoned opinion of the European Food Safety Agency (EFSA), to include phthalimide in the residue definition of folpet (sum of folpet and phthalimide expressed as folpet) (Huertas-Pérez et al., 2019).

The detection frequency (%) and mean concentrations (mg/kg dry weight) of the most frequently detected pesticides in all sediment samples were chlorpyrifos (34% and 0.18 mg/kg dw) followed by *p,p'*-DDE (30% and 0.018 mg/kg dw), cypermethrin (14% and 0.03 mg/kg), deltamethrin (13% and 0.026 mg/kg dw), lambda-cyhalothrin (11% and 0.027 mg/kg dw), and *p,p'*-DDD (11% and <LOQ mg/kg dw), respectively. The high detection frequency (%) of chlorpyrifos maybe attributed to its top rank position among the top ten widely used pesticides in Egypt. Chlorpyrifos is classified as a pseudo-persistent organic pollutant owing to its wide use and frequent release into the environment (Li et al., 2014). The occurrence of pesticides in sediments is closely related to their octanol–water partition coefficient ($\log K_{ow}$) values, which are frequently used as indicators for their bioaccumulative and lipophilic potential (Xu et al., 2016). All the pesticides detected in the sediments had $\log K_{ow}$ values higher than 3.

Of the 144 analyzed sediment samples, 30%, 4%, 7%, 4%, 2%, 2%, 2%, 4%, and 2% were contaminated with 1, 2, 3, 4, 5, 6, 7, 8, and 9 pesticide residues, respectively. A total of 13% of the 144 sediment samples contained residues > 0.1 mg/kg dw (range: 0.19–0.88 mg/kg dw), 29% contained residues ≤ 0.1 mg/kg dw (range: 0.01–0.09 mg/kg dw), and 14% contained residues <

Table 1 – Spatiotemporal distribution of detected pesticide residues (Conc.: mg/kg dry weight) in upstream sediment samples collected from the Rosetta branch, Nile River, Egypt.

Detected pesticide	Summer 2018			Autumn 2018			Winter 2019			Spring 2019			
	El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala	
Chlorpyrifos	Conc.	BQL	BDL	BDL	BDL	BDL	0.01	BDL	0.04	BDL	BDL	0.01	BDL
	range												
	Mean	-	-	-	-	-	0.01	-	0.04	-	-	0.01	-
Cypermethrin	Freq.	33%					50%		33%	-		100%	
	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BQL	BDL	BDL	BDL	BDL
	range												
Deltamethrin	Mean	-	-	-	-	-	-	-	-	-	-	-	-
	Freq.	-	-	-	-	-	-	-	33%	-	-	-	-
	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL
Fludioxonil	range												
	Mean	-	-	-	-	-	-	-	0.01	-	-	-	-
	Freq.	-	-	-	-	-	-	-	33%	-	-	-	-
Dicofol	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BQL	BDL	0.03
	range												
	Mean	-	-	-	-	-	-	-	-	-	-	-	0.03
o,p'-DDD	Freq.	-	-	-	-	-	-	-	-	-	50	-	50%
	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BQL
	range												
p,p'-DDD	Mean	-	-	-	-	-	-	-	-	-	-	-	-
	Freq.	-	-	-	-	-	-	-	-	-	-	-	50%
	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BQL	BDL	BQL
p,p'-DDE	range												
	Mean	-	-	-	-	-	-	-	-	-	-	-	-
	Freq.	-	-	-	-	-	-	-	-	-	50%	-	50%
Permethrin	Conc.	BDL	BDL	BDL	BDL	BDL	BQL	BDL	BQL	BQL	0.02	BDL	0.02
	range												
	Mean	-	-	-	-	-	-	-	-	-	0.02	-	0.02
Permethrin	Freq.	-	-	-	-	-	100%	-	33%	25%	50%	-	50%
	Conc.	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.04	BDL	BDL	BDL	BDL
	range												
Permethrin	Mean	-	-	-	-	-	-	-	0.04	-	-	-	-
	Freq.	-	-	-	-	-	-	-	33%	-	-	-	-

The mean concentration of each season or sampling site represents the mean value of three months. BDL: Below detection limit. BQL: Below quantification limit. A dash (-) indicates that the value is nil or negligible.

LOQ. The pesticide loadings found in the Rosetta branch occurs via different transport routes, including surface water runoff, leaching, erosion, spray drift, drains outflow, agricultural, residential, and industrial effluent discharge (Eissa et al., 2020).

The spatial distribution of the pesticides detected in the sediment samples indicated that El-Rahawy contained the highest sum of all pesticide concentrations at 2.86 mg/kg dw (0.02 mg/kg dw in the upstream and 2.84 mg/kg dw in the downstream samples), followed by Sabal at 0.56 mg/kg dw (0.11 mg/kg dw in the upstream and 0.45 mg/kg dw in the downstream samples), and Tala at 0.24 mg/kg dw (0.08 mg/kg dw in the upstream and 0.16 mg/kg dw in the downstream samples). The data also showed that 40% of El-Rahawy samples (20% of the upstream and 60% of the downstream samples), 60% of Sabal samples (40% upstream and 80% downstream), and 69% of Tala samples (56% upstream and 86%

downstream) were contaminated with pesticide residues. Furthermore, the El-Rahawy sediment samples were contaminated with a comparatively higher number of pesticides (13) than Sabal (9) and Tala (7). Consequently, the downstream sediment samples contained more pesticides, in terms of the number and concentration, than those collected from the upstream sampling sites. The El-Rahawy sampling site receives treated wastewater primarily from the Abu-Rawash WWTP through the El-Rahawy drain, which is considered to be the main cause of water quality deterioration at the Rosetta branch of the Nile River. Köck-Schulmeyer et al. (2013) reported high levels of pesticide residues in wastewater treatment plants (WWTPs) effluents in WWTPs with tertiary treatment despite the common belief that this treatment generates sufficient amount of quality water for reuse in various fields. Furthermore, conventional urban WWTPs are not originally designed to remove pesticides, and their removal

Table 2 – Spatiotemporal distribution of detected pesticide residues (Conc.: mg/kg dry weight) in downstream sediment samples collected from the Rosetta branch, Nile River, Egypt.

Detected pesticide		Summer 2018			Autumn 2018			Winter 2019			Spring 2019		
		El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala	El-Rahawy	Sabal	Tala
Chlorpyrifos	Conc. range	0.04 – 0.36	BDL	BQL	0.65	BQL-0.02	BDL	0.32 – 0.46	BQL-0.24	0.02	BDL	BDL	0.01
	Mean	0.24	-	-	0.65	0.02	-	0.39	0.24	0.02	-	-	0.01
	Freq.	100%	-	50%	50%	100%	-	67%	100%	33%	-	-	50%
Cyfluthrin	Conc. range	BDL	BDL	BDL	0.03	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL
	Mean	-	-	-	0.03	-	-	0.01	-	-	-	-	-
	Freq.	-	-	-	50%	-	-	33%	-	-	-	-	-
Cypermethrin	Conc. range	0.01 – 0.03	BDL	BDL	0.08	BDL	0.01	0.03 – 0.04	0.01	BDL	BDL	BDL	BDL
	Mean	0.02	-	-	0.08	-	0.01	0.035	0.01	-	-	-	-
	Freq.	67%	-	-	50%	-	50%	67%	33%	-	-	-	-
Deltamethrin	Conc. range	0.01	BDL	BDL	0.05	BDL	BDL	0.03 – 0.05	0.02	BDL	BDL	BDL	BDL
	Mean	0.01	-	-	0.05	-	-	0.04	0.02	-	-	-	-
	Freq.	67%	-	-	50%	-	-	67%	33%	-	-	-	-
Folpet	Conc. range	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.04	BDL	BDL	BDL
	Mean	-	-	-	-	-	-	-	-	0.04	-	-	-
	Freq.	-	-	-	-	-	-	-	-	33%	-	-	-
Lambda-cyhalothrin	Conc. range	0.01 – 0.02	BDL	BDL	0.06	BDL	BDL	0.02 – 0.03	0.02	BDL	BDL	BDL	BDL
	Mean	0.015	-	-	0.06	-	-	0.025	0.02	-	-	-	-
	Freq.	67%	-	-	50%	-	-	67%	33%	-	-	-	-
o,p'-DDD	Conc. range	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Mean	-	-	0.01	-	-	-	-	-	-	-	-	-
	Freq.	-	-	50%	-	-	-	-	-	-	-	-	-
p,p'-DDD	Conc. range	BDL	BDL	BQL	BDL	BDL	BDL	BQL	BDL	BQL	BDL	BDL	BQL
	Mean	-	-	-	-	-	-	-	-	-	-	-	-
	Freq.	-	-	50%	-	-	-	33%	-	33%	-	-	50%
p,p'-DDE	Conc. range	BQL	0.01	0.04	BDL	BDL	BDL	BQL	0.02	0.01 – 0.03	BDL	0.01	BQL-0.01
	Mean	-	0.01	0.04	-	-	-	-	0.02	0.02	-	0.01	0.01
	Freq.	33%	33%	50%	-	-	-	33%	33%	67%	-	100%	100%
Pendimethalin	Conc. range	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL
	Mean	-	-	-	-	-	-	-	0.01	-	-	-	-
	Freq.	-	-	-	-	-	-	-	33%	-	-	-	-
Permethrin	Conc. range	BDL	BDL	BDL	BDL	BDL	BDL	0.06 – 0.08	0.07	BDL	BDL	BDL	BDL
	Mean	-	-	-	-	-	-	0.07	0.07	-	-	-	-
	Freq.	-	-	-	-	-	-	67%	33%	-	-	-	-
Profenofos	Conc. range	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	Mean	-	-	-	0.01	-	-	-	-	-	-	-	-
	Freq.	-	-	-	50%	-	-	-	-	-	-	-	-
Prothiofos	Conc. range	BQL	BDL	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL
	Mean	-	-	-	-	-	-	0.01	-	-	-	-	-
	Freq.	33%	-	-	-	-	-	33%	-	-	-	-	-
Pyriproxyfen	Conc. range	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL
	Mean	-	-	-	-	-	-	-	0.01	-	-	-	-
	Freq.	-	-	-	-	-	-	-	33%	-	-	-	-

The mean concentration of each season or sampling site represents the mean value of three months. A dash (-) indicates that the value is nil or negligible.

Table 3 – Toxicity endpoints for the detected pesticides residues in sediment samples collected from three sampling sites (El-Rahawy, Sabal, and Tala) along the Rosetta branch, Nile River, Egypt.

Pesticide	LC ₅₀ fish (mg/L)	NOEC fish (mg/L)	EC ₅₀ daphnia (mg/L)	NOEC daphnia (mg/L)	EC ₅₀ algae (mg/L)	NOEC algae (mg/L)	AF
Chlorpyrifos	0.025	0.00014	0.0001	0.0046	0.48	0.043	50
Cyfluthrin	0.00047	0.00001	0.00016	0.00002	> 10	-	50
Cypermethrin	0.00151	0.00003	0.00021	0.00004	> 0.0667	1.3	50
Deltamethrin	0.00015	< 0.000032	0.00056	0.0000041	> 0.00047	-	50
Dicofol	0.51	0.0044	0.14	125	0.075	0.05	50
Folpet	0.233	0.0081	0.68	0.002	> 10	-	50
Lambda-Cyhalothrin	0.00021	0.000031	0.00023	0.0000022	> 0.005	> 0.31	50
o,p'-DDD	> 0.07	-	0.009	-	-	-	1000
p,p'-DDE	0.032	-	0.001	-	-	-	1000
Pendimethalin	0.196	0.006	0.147	0.0145	0.004	0.003	10
Permethrin	0.0125	0.000093	0.0006	-	0.0125	0.0009	100
Profenofos	> 0.08	0.002	> 0.5	-	-	-	100
Prothiofos	> 0.5	-	0.014	-	2.3	-	1000
Pyriproxyfen	> 0.27	0.0043	0.4	0.000015	0.15	-	50

A dash (-) indicates that the value is not available.

LC₅₀: the median lethal concentration; NOEC: no observed effect concentration.

EC₅₀: the median effective concentration; AF: assessment factor.

Source: Pesticide Properties DataBase, <https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>

efficiency depends on various factors, such as the specificity of pesticides and the treatment methods that are employed (Deblonde et al., 2011).

The temporal variations revealed that the highest total pesticide concentrations were detected for 14 pesticides in winter season (1.73 mg/kg dw; 0.11 mg/kg dw in the upstream and 1.62 mg/kg dw in the downstream samples) compared with eight pesticides in autumn (0.92 mg/kg dw; 0.01 mg/kg dw in the upstream and 0.91 mg/kg dw in the downstream samples), 10 pesticides in summer (0.88 mg/kg dw; not detected in the upstream and 0.88 mg/kg dw in the downstream samples), and five pesticides in spring (0.13 mg/kg dw; 0.09 mg/kg dw in the upstream and 0.04 mg/kg dw in the downstream samples). Meanwhile, the El-Rahawy samples registered the highest total pesticide concentrations during summer, autumn, and winter, accounting for 0.82, 0.88, and 1.14 mg/kg dw, respectively, whereas the Tala samples were the most contaminated with a total pesticide concentration of 0.07 mg/kg dw during spring. The variability over seasons in a specific area is most likely related to the neighboring urban, industrial, and agricultural activities. Given the closure period, the water level and flow of the Rosetta branch of the Nile River is low in winter, and hence, the concentration of pesticides is likely to be high. This condition is possibly also due to the temperature of cold water, which has been identified as a factor restricting natural attenuation processes, including biodegradation and photodegradation (Dai et al., 2015).

The concentrations detected in this study are higher than those obtained by Kanzari et al. (2012), who demonstrated the occurrence of chlorpyrifos residues (0.01–0.02 µg/kg) and p,p'-DDE (0.34–0.68 µg/kg) on the surface sediments from the Arc River, France. Ccanccapa et al. (2016) and Tang et al. (2019) also revealed that chlorpyrifos was the most frequent pesticide in 82% and 43% of sediment samples in Ebro River, Spain and three rural rivers in Guangzhou, China, respectively.

Currently, pyrethroids are the world's third most extensively used class of insecticides; they are commonly used in agricultural and public health applications, accounting for 38% of the global market share of insecticides in 2015, due to their high efficiency and low mammalian toxicity (Tang et al., 2018). Pyrethroid residues have been frequently detected worldwide at various concentration ranges (8.27–71.90 ng/g in sediments from the Ebro River, Spain, 0.65–384 ng/g in sediments from the Pearl River, China; ND–19 ng/g in sediments from the Liaohe River, China, and 183–318 ng/g in sediments from the Indus River, Pakistan in the studies by Feo et al. (2010), Li et al. (2011), Fang et al. (2012), and Jabeen et al. (2015), respectively. Cypermethrin (up to 14.8 mg/kg) and lambda-cyhalothrin (649 mg/kg) have been detected in sediment samples in the peri-urban horticultural area of Gran La Plata, Argentina (Mac Loughlin et al., 2017). Sangchan et al. (2014) revealed that cypermethrin was found in all suspended sediment samples collected from Mae Sa river, Thailand. Sediments act as a significant sink for hydrophobic insecticides of this class (Li et al., 2014). Pyrethroids are persistent pesticides with low water solubility and high logK_{ow} (from 4.6 to 7.6), which explain their rapid water dissipation and strong affinity to organic matter in the sediment, respectively, after entering an aquatic system (Yang et al., 2006; Fojut and Young, 2011). Sediment-associated pyrethroids not only pose risk to non-target organisms that live in sediments (Ding et al., 2010; Siegler et al., 2015) but also act as a secondary source of pesticides that are released to the surface water and cause adverse effects to water column species (Li et al., 2014). In Guangzhou waterway sediments, cypermethrin was the pyrethroid most abundant, with mean concentrations of 149 and 278 ng/g during the dry and wet periods, respectively (Li et al., 2019).

DDT persists in the environment in its original form or maybe metabolized to DDE and DDD in the environment; its

Table 4 – Ecological risk assessment for detected pesticide residues in sediment samples collected from the three sampling sites (El-Rahawy, Sabal, and Tala) along the Rosetta branch, Nile River, Egypt.

Sampling site	Pesticide	MEC (mg/kg dw)	K_{oc}	F_{oc}	C_{pw}	PNEC	RQ
El-Rahawy	Chlorpyrifos	0.36	5509	0.0112	0.005835	0.000002	2917.3
	Cyfluthrin	0.02	123930	0.0112	1.44E-05	0.0000002	72.045
		0.038	307558	0.0112	1.10E-05	0.0000006	18.386
	Cypermethrin	0.03	10240000	0.0112	2.61E-07	0.00000008	3.1899
	Lambda-	0.028	283707	0.0112	8.81E-06	0.00000004	200.27
	<i>p,p'</i> -DDE	0.02	50000	0.0112	3.57E-05	0.000001	35.714
	Profenofos	0.01	2016	0.0112	0.000443	0.00002	22.144
	Chlorpyrifos	0.064	5509	0.0101	0.001150	0.000002	575.12
0.01							
Sabal	Cypermethrin	0.015	10240000	0.0101	1.45E-07	0.00000008	1.769
	Lambda-	0.02	283707	0.0101	6.98E-06	0.00000004	158.63
	<i>p,p'</i> -DDE	0.0125	50000	0.0101	2.48E-05	0.000001	24.752
	Pendimethalin	0.055	100000	0.0101	5.45E-05	0.0000009	58.554
	Pyriproxyfen	0.01	21175	0.0101	4.68E-05	0.0000003	155.86
	Chlorpyrifos	0.013	5509	0.0089	0.000265	0.000002	132.57
Tala	Cypermethrin	0.03	6064	0.0089	0.000556	0.000088	6.317
	Folpet	0.04	304	0.0089	0.014784	0.00004	369.60
	<i>p,p'</i> -DDE	0.01	131000	0.0089	8.58E-06	0.000009	0.953

MEC: measured environmental concentration of pesticide. K_{oc} : organic carbon partitioning coefficient. F_{oc} : fraction of total organic carbon; C_{pw} : pore water concentrations. PNEC: predicted no-effect concentration. RQ: risk quotient.

metabolites are more stable and persistent than the parent molecule (Bossi et al., 1992; Iwata et al., 1993). The residual level of dicofol in sediments is correlated with its application as a cheap pesticide in agriculture, and it can be specified as a further source of *o,p'*-DDT (Wei et al., 2008). Tao et al. (2020) concluded that anti-fouling paints containing dicofol and *p,p'*-DDT can be responsible for the current input of *p,p'*-DDT in sediments obtained from China's Taihu freshwater Lake.

2.2. Ecotoxicological risk assessment

An assessment of the potential ecological risks associated with pesticides detected in sediments from the Nile River was undertaken, and the results are summarized in Table 4. Of all the monitored sites, El-Rahawy was under a high ecotoxicological risk, followed by Sabal and Tala. Twelve pesticides showed a high $RQ > 1$, posing a potential ecological risk for aquatic species that live and feed on those sediments. Three pesticides, including chlorpyrifos, cypermethrin, and *p,p'*-DDE, showed high potential risks for aquatic organisms, with $RQs > 1$ at all sampling sites. Among the evaluated pesticides, the highest RQs were calculated for chlorpyrifos in El-Rahawy (2917) and Sabal (575), followed by folpet (369)

in Tala and lambda-cyhalothrin (200) in El-Rahawy. However, pendimethalin in Sabal (0.1887) and *o,p'*-DDD in Tala showed a medium risk ($0.1 \leq RQ < 1$) for aquatic living organisms.

The high risk posed by the detected pesticides is mainly attributed to their high MEC values in certain cases and relatively high toxicity to algae, *Daphnia* sp., and fish, hence producing low PNEC values. The ecotoxicological risk assessment emphasizes that such pesticides ($RQ > 1$) should be given priority for risk management, particularly because the Nile River is also a habitat to numerous species. The high aquatic risk posed by pesticides will lead to changes in fish and invertebrate populations in the long-term, leading to declines in the most vulnerable species and increases in the most resistant ones, resulting in the loss in biodiversity (Palma et al., 2014; Kuzmanović et al., 2015).

The findings of this study are in accordance with previous research in the sense that they also calculated high RQs of different pesticides, e.g., Sumon et al. (2018) showed high RQs ($RQ > 1$) for chlorpyrifos, diazinon, quinalphos, malathion, and fenitrothion in the sediments of water bodies of north-west Bangladesh. Barbieri et al. (2019) also revealed that all pesticides detected in the sediments of Llobregar River, Spain, namely, terbutryn, dichlorvos, terbutylazine, diazinon, and irgarol, pose an environmental risk for aquatic

organisms. Onwona-Kwakye et al. (2020) reported that many pesticides may pose an acute risk to aquatic ecosystems adjacent to treated fields in the investigated regions in south Ghana, with lambda cyhalothrin, chlorpyrifos and cypermethrin, causing the highest chronic risks. Ecological assessment using RQs indicated that cumulative values for triazines and anilides/aniline herbicide classes detected in sediments from Lake St Lucia, South Africa presented low to medium risk for algae and aquatic invertebrate communities (Tyohemba et al., 2020). Wei et al. (2021) estimated risk quotients of 4 individual OPPs under either average (RQ_m) or extreme (RQ_{ex}) conditions from the corresponding average and maximum concentrations in the sediments for algae, *Daphnia magna*, and fish. Results revealed that chlorpyrifos posed high risks to the fish only at the maximum concentrations during the dry period in surface sediments of Guangzhou urban waterways, China. Moreover, Merga et al. (2021) demonstrated that the $\%RQ > 1$ were above 50% for chlorpyrifos, λ -cyhalothrin, α -cypermethrin and deltamethrin pesticides in sediment in Lake Ziway, Ethiopia, indicating that they can pose an acute and chronic risks at most of the sampling locations where they were detected.

3. Conclusions

This study provides the first monitoring campaign for 100 pesticides in the Rosetta branch of the Nile River. This research was performed to assess the occurrence, spatiotemporal distribution, and risk assessment of these pesticides. Sixteen pesticides were detected in the sediment samples. The downstream sediment samples contained more pesticides, in terms of the number and concentration, than those collected from the upstream sampling sites. Pesticide concentrations in sediments reflect the long-term usage of pesticides. The detection of banned pesticides in the sediment samples indicates their persistence or illegal usage. Owing to their repeated detection at high concentrations in sediments, pyrethroid residues pose an emerging threat to the aquatic ecosystem of the Rosetta branch. Furthermore, 12 pesticides showed high $RQ > 1$, posing a potential ecological risk for aquatic species that live and feed on these sediments. One of the key reasons for the high risks posed by these pesticides in aquatic ecosystems maybe their extensive usage. The removal of organic pollutants in Egyptian WWTPs is a challenge to be faced in the future considering the requirements related to increase their treatment efficiency. Hence, regular surveillance and monitoring are recommended to evaluate the occurrence and potential pollution sources in the Nile River to define mitigation strategies.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2021.08.047.

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