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Short Communication

Pesticide Accumulation in Turkey's Meriç River Basinwater and Sediment

Cem Tokatlı[1]*, Esengül Köse[2], Arzu Çiçek[3], Özgür Emiroğlu[4]

[1]Trakya University, İpsala Vocational School, Department of Laboratory Technology, İpsala/Edirne, Turkey
[2]Eskişehir Osmangazi University, Department of Environmental Protection and Control, Eskişehir, Turkey
[3]Anadolu University, Applied Environmental Research Centre, Eskişehir, Turkey
[4]Eskişehir Osmangazi University, Department of Biology, Eskişehir, Turkey

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Abstract

The Meriç River is located in the Thrace Region of Turkey, which has great importance in terms of agricultural potential and is known as "Rice Land". The Meriç is also the longest river in the Balkans and is known to be exposed to intensive pollution by means of special agricultural pressure on the system. The aim of this study was to determine pesticide accumulation in water and sediment of the Meriç River Basin. For this purpose, water and sediment samples were collected in spring (rainy) of 2017 from 24 stations selected on the basin and pesticide contents. A total of 174 different pesticide varieties were investigated in water and sediment samples using liquid chromatograph mass spectrometry LC/MS. According to detected data, the concentration of pesticide residues ranged from 30.4 ng/L (thiabendazole in Meriç River) to 291,310 ng/L (carbendazim in Ergene River) for water samples, and from 12.4 ng/L (spiroxamine in Gala Leke) to 15,947 (carbendazim in Ergene River) for sediment samples. There was a clear dominance of the carbendazim in all the investigated aquatic habitats. It was also determined that pesticide concentrations detected in the Meriç River Basin, especially in the Ergene River, were found to be at quite high levels and the system has Class III–IV water quality in terms of total pesticide accumulation.

Keywords: Meriç River Basin, Balkans, water, sediment, pesticides

Introduction

Aquatic ecosystem quality around the globe is decreasing daily because of the rapid growth of the world's population and the development of industry. Pesticides are a widespread group of chemical substances used to improve agricultural production and they have become an integral part of society and are being used for diverse activities ranging from crop protection from insect pests, weeds, rodents, and fungal diseases to animal husbandry and public health applications. However, they are hazardous for living organisms, human and environmental health, even at low concentrations, and can reach fish, birds and humans by means of the food chain. Their toxicity and long persistence in the environment has raised global concern [1-3].

*e-mail: tokatlicem@gmail.com

Table 1. Coordinate information of selected stations.

Stations		North	East	Stations		North	East
Gala Lake	GL1	40.78189	26.21059	Meriç River	M1	41.66233	26.55130
	GL2	40.78089	26.19306		M2	41.63857	26.57971
	GL3	70.77093	26.18911		M3	41.40480	26.63160
	GL4	40.76386	26.16486		M4	41.13640	26.48129
	GL5	40.75516	26.17714		M5	40.94286	26.33319
Sığırcı Lake	SL1	40.84322	26.32872		M6	40.86219	26.23841
	SL2	40.84114	26.34372		M7	40.73987	26.11582
	SL3	40.82173	26.32836	Sazlıdere Stream	SD1	41.61810	26.67925
	SL4	40.82173	26.30954		SD2	41.45525	26.61781
	SL5	40.81802	26.32438	Ergene River	E1	41.28431	26.69829
Tunca River	T1	41.83295	26.58769		E2	41.13641	26.48129
	T2	41.66759	26.55344		E3	41.06200	26.36463

The Meriç River, which is the longest river in the Balkans, is known as the lifeblood of the Thrace Region of Turkey. The Tunca and Ergene rivers are the main branches of the Meriç. Gala and Sığırcı lakes are the most important lentic parts of the system. They are located on the Meriç Delta, where is formed on about 45,000 ha area at the mouth of the Meriç and is listed as Class A of International Wetlands. The Meric Delta is very rich in terms of biological resources and can be classified as an internationally important wetland because of its location along a bird migration route. This significant basin is being exposed to intensive organic and inorganic pollution by means of agricultural applications. Over the last few decades, the aquatic ecosystems located in the Meriç River Basin have been significantly contaminated by persistent pollutant of agricultural origin; because of monoculture practices, mainly rice cultivation is conducted around the region. It is reported that about 25% of total rice production of Turkey is being supplied from this basin. Industrial activities conducted around the Ergene River, once known as one of the most polluted lotic habitats of Turkey, are also one of the main contamination sources of the system [4-6].

Fig. 1. Topographic map of Meriç River Basin and selected stations.

The main objective of this study were to identify and quantify pesticide residues in water and sediment samples and to evaluate the toxicological significance of the investigated contamination in the aquatic components of the Meriç River Basin (Gala and Sığırcı lakes and Tunca, Ergene and Meriç rivers).

Material and Methods

Study Area and Collection of Samples

Samples were collected from the middle of the rivers (over the bridges on the rivers) in spring (rainy) season of 2017, when the precipitation and surface runoff have increased significantly in the region. After a preliminary field study, 24 stations were selected on the Meriç River Basin considering the main basin components and pollution sources. Two of the stations were located on the Tunca River, 3 of the stations were located on the Ergene River, 7 of the stations were located on the Meriç River, 2 of the stations were located on Sazlıdere

Stream, 5 of the stations were located on Gala Lake and 5 of the stations were located on Sığırcı Lake. Coordinate information is given in Table 1 and a map of study area is given in Fig. 1.

Water samples were collected 0.5 m below the water surface in 1 L pre-cleaned glass bottles and kept at 4ºC until chemical analysis. Sediment samples were collected from the upper 10 cm of sediments with an Ekman grab sampler in 1 L sterile glass bottles and kept at 4ºC until chemical analysis. Water and sediment samples were collected.

Pesticide Analysis

The QUECHERS (quick, easy, cheap, effective, rugged, safe) method has been applied for the extraction of pesticides in the sample and the determination of pesticides has been done using a ZİVAK TANDEM GOLD LC-MS/MS device (the detection limit was 10 ppt) in Trakya University Technology Research and Development Application and Research Center (TÜTAGEM) [7]. The center has an international accreditation certificate within the scope of TS EN/ ISO IEC 17025 issued by TÜRKAK (representative of the World Accreditation Authority in Turkey). The element analyses were recorded as means triplicate measurements.

Regarding the quality control procedures, parameters such as laboratory and field blanks and matrix spikes were evaluated. The reliability of the calibration method and sample preparation was evaluated on the spiked samples. The calibrated midpoints (10000 ppt) were spiked with pesticide-free water, and QUECHERS stages were applied. As a result of the analysis, the recoveries were determined between 80-120%.

Results and Discussion

The averages of the pesticides detected in water and sediment samples of the lotic and lentic components of the Meriç River Basin are given in Tables 2 and 3. The proportional values of pesticides detected in water and sediment samples and the proportion values of the total pesticide loads recorded in the basin components are given in Fig. 3.

According to the results of this study, pesticide concentrations detected in the Meriç River Basin, especially in the Ergene River, were found to be at quite high levels. From the investigated 174 pesticide varieties in the Meriç River Basin, a total of 13 pesticide varieties were found in water samples and a total of 26 pesticide varieties were found in sediment samples. It has also been found that the most widely used pesticide variety in the region is carbendazim, and the most polluted ecosystem among the investigated aquatic habitatsis the Ergene River. According to the Water Pollution Control Regulation in Turkey, Gala Lake, Sığırcı Lake, Meriç River, Tunca River and Sazlıdere Stream are Class III

Table 2. Mean pesticide values in the waters of basin component stations (ppt).

Pesticide	Mean±SD
Gala Lake (5 stations)	
Carbendazim	3458±1788
Thiabendazole	1479±21.38
Forchlorfenuron-706	5956±30.59
Sığırcı Lake (5 stations)	
Carbendazim	4271±1502
Thiabendazole	59.80±9.085
Thiophonate Methyl	2021±490.0
Forchlorfenuron-706	3494±26.05
Meriç River (7 stations)	
Propamocarb-hydrochloride	3726±3121
Carbendazim	11747±7827
Thiabendazole	30.40±6.885
Thiamethoxam	175.0±168.9
Thiacloprid	45.90±49.76
Forchlorfenuron-706	1515±1250
Metalaxyl	104.5±30.38
Cyproconazole	124.7±120.1
Azoxystrobin	576.6±560.6
Dimoxystrobin-688	300.7±281.8
Tunca River (2 stations)	
Carbendazim	4042±774.3
Thiabendazole	1518±56.75
Forchlorfenuron-706	4468±332.6
Sazlıdere Stream (2 stations)	
Carbendazim	2944±1657
Thiabendazole	1535±53.10
Thiamethoxam	125.4±56.13
Forchlorfenuron-706	7009±44.46
Ergene River (3 stations)	
Carbendazim	291310±285049
Thiabendazole	1627±6.072
Acetamiprid	862.7±359.5
Forchlorfenuron-706	6748±3167
Metalaxyl	833.6±246.8
Spiroxamine	5689±5057

Table 3. Mean pesticide values in the sediments of basin component stations (ppt).

Sediment	
Pesticide	Mean±SD
Gala Lake (5 stations)	
Carbendazim	323.7±92.58
Forchlorfenuron-706	169.7±311.4
Spiroxamine	12.40±3.412
Cyproconazole	57.50±48.44
Azoxystrobin	329.9±38.17
Prochloraz	335.3±17.80
Propiconazole	358.4±72.99
Pyriproxyfen	555.6±1.591
Sığırcı Lake (5 stations)	
Carbendazim	719.3±455.6
Thiabendazole	130.1±0.936
Forchlorfenuron-706	210.2±166.7
Spiroxamine	13.50±1.109
Propiconazole	272.5±46.51
Pyridaben	737.5±6.553
Meriç River (7 stations)	
Propamocarb-hydrochloride	147.5±6.739
Carbendazim	1056±621.4
Thiabendazole	104.2±10.16
Thiamethoxam	143.6±183.6
Acetamiprid	13.70±8.351
Tricyclazole-753	11.20±10.58
Thiacloprid	10.60±10.33
Flutriafol	137.3±145.6
Forchlorfenuron-706	122.5±68.76
Metalaxyl	51.20±14.51
Fenproprimorph	1085±105.2
Spiroxamine	63.60±65.96
Azoxystrobin	413.2±103.1
Prochloraz	788.3±788.6
Dimoxystrobin-688	197.2±11.65
Difenoconazol	414.3±95.50
Pyraclostrobin	580.1±3.961
Pyriproxyfen	572.9±44.42
Etoxazole	996.6±5.220
Tunca River (2 stations)	
Carbendazim	196.0±199.6
Forchlorfenuron-706	523.5±216.1
Azoxystrobin	573.9±100.6
Epoxiconazole	274.2±52.45
Prochloraz	616.0±123.1
Rotenone-739	6749±62.47
Propiconazole	329.7±141.8
Pyridaben	1727±2.362
Sazlıdere Stream (2 stations)	
Carbendazim	554.2±632.4
Forchlorfenuron-706	201.8±130.6
Azoxystrobin	629.3±166.6
Epoxiconazole	373.2±236.1
Prochloraz	889.4±357.5
Rotenone-739	218.8±154.6
Propiconazole	440.0±256.6
Pyridaben	1722±0.616
Ergene River (3 stations)	
Methamidophos	677.4±744.6
Carbendazim	15947±10328
Thiabendazole	140.4±8.076
Acetamiprid	151.5±129.2
Thiacloprid	26.80±26.99
Forchlorfenuron-706	160.9±72.94
Spiroxamine	30.20±31.47
Azoxystrobin	554.2±41.32
Prochloraz	934.1±2100
Propiconazole	393.3±191.6
Difenoconazol	651.3±51.98
Pyriproxyfen	768.0±7.452
Etoxazole	528.6±10.83
Pyridaben	734.5±29.25

water quality, and the Ergene River is Class IV in terms of total pesticide contents [8]. In a study performed in the Meriç Delta, residues of organochlorine pesticides in surface water, sediment, and fish samples were analyzed. In contrast to the results of the present study, it was revealed that the Meriç Delta was declared as low contaminated of organochlorine pesticides and their residues [9].

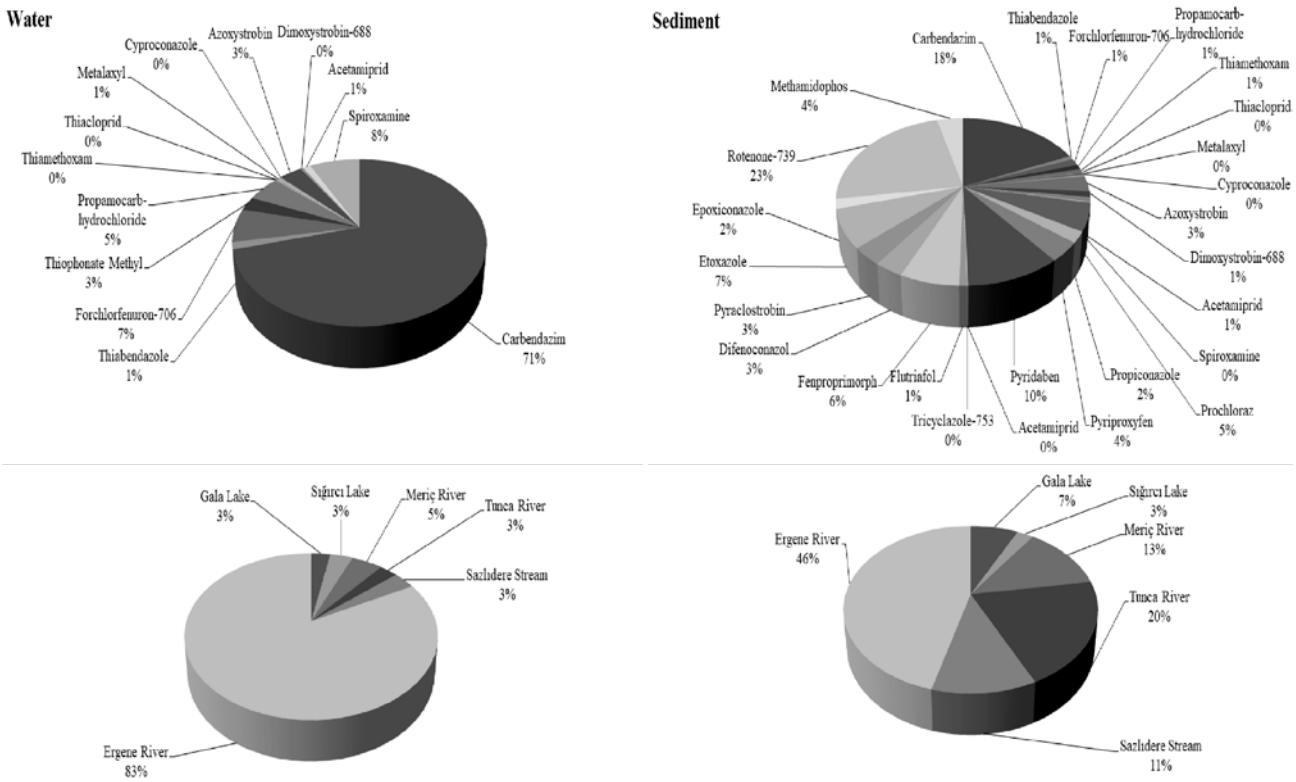

Fig. 2. Pesticide rates (upside) detected in the basin and rates of total pesticide loads (downside) in the basin components.

It was clearly reported that minute concentrations of pesticides are toxic to biological organisms and they threaten ecosystem integrity due to their stable structure and lipophilic character. They also tend to bioconcentrate, bioaccumulate and biomagnify, and are transferred to higher trophic levels through several food chains and may lead to toxicity in non-target organisms like vertebrates and non-vertebrates and even in humans [10-13].

The Meriç River Basin receives many point pollutant inputs like discharge of effluent from factories and industrial wastes by means of especially the Ergene River Basin and non-point inputs like intensive agricultural applications conducted almost all around the basin. In addition to these pollution factors, possible transfer of toxicants from the neighboring countries by means of Meriç and Tunca Rivers could elevate the pesticide contamination in the basin. However, the data of the present study clearly reveals that agricultural runoff is a major pollution source for all the aquatic components of the system and the use of unconscious pesticides in agricultural activities may cause significant health problems on both ecosystem and local people in the near future.

Conclusions

In the present study, pesticide accumulations in waters and sediments of lotic (Meriç, Ergene and Tunca Rivers) and lentic (Gala and Sığırcı Lakes) components of the Meriç River Basin were investigated. As a result of this research, the contamination potential of agricultural runoff on the abiotic components of the basin was clearly revealed. The Ergene was found to be the most polluted ecosystem among the aquatic system components, and carbendazim was found to be the most widely used pesticide variety in the Meriç River Basin.

In order to protect the sustainability of this significant aquatic ecosystem, monoculture practices in agricultural activities should be changed and local people should be encouraged to adopt polyculture practices. Also, the use of unconscious chemical fertilizers and pesticides should be avoided by giving the necessary training and environmental awareness for local people.

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Conflict of Interest

The authors declare no conflict of interest.

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