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Research Article

PESTICIDE RESIDUES IN WATER AND SEDIMENT OF ERGENE RIVER AND TRIBUTARIES IN TURKEY

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ABSTRACT

Ergene River is located in the north-west part of Turkey and it is the most significant river ecosystem of Thrace Region. It is also the most important tributaries of Meriç River that is the longest river in Balkans. Despite such great importance of Ergene River, it is being exposed to an intensive pollution by means of especially agricultural, industrial and domestic activities conducted around its watershed.

The aim of this study was to determine the pesticide residues in water-sediment of Meriç and Ergene Rivers and its 10 significant tributaries. Water-sediment samples were collected in spring season (rainy) of 2018 from 21 stations and pesticide concentrations (total of 174 different pesticide varieties) were investigated in water and sediment samples by using LC/MS.

According to detected data, the concentration of pesticide residues ranged from 0.0034ppb (propamocarb-hydrochloride in Safaalan Creek) to 12.0250ppb (carbendazim in Çorlu Stream) for water samples and from 0.0244ppb (acetamiprid in Çorlu Stream) to 1173.5320ppb (prochlorazin in Ahmetbey Creek) for sediment samples. It was also determined that pesticide accumulations detected in the Ergene River Basin, especially in Çorlu Stream and Ergene River, were found to be in quite high levels and the system has II–III. Class water quality in terms of total pesticide accumulations, in general.

There were clear dominances of carbendazim (in water) and prochloraz (in sediment) of the entire investigated basin. Çorlu Stream (in terms of water) and Ahmetbey Creek (in terms of sediment) were recorded as the most contaminated aquatic components of the system.

Keywords: Ergene River Basin, water – sediment quality, pesticide residues.

1. INTRODUCTION

Pesticides, which are being widely used to improve agricultural production, are a widespread group of chemical substances. However, these substances could be persistent in water and accumulative in sediment and also bioaccumulative in biota depending on their solubility. They are very hazardous even at low levels for living organisms, human and environment. The use of pesticides is a significant global concern today due to their toxicity and long persistence in the environment (Erkmen and Kolankaya, 2006; Chopra et al., 2010; Ccanccapa et al., 2016).

Meriç River is a transboundary river and has a great importance for the Balkans. Ergene River, where is known as one of the most polluted aquatic habitats of Turkey, is the main branches of Meriç River. Ergene River is being threatened by industrial and domestic wastes

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originating from regional factories and settlement areas and agricultural contaminants originating from intensive cultivation activates (Tokatlı, 2014; 2015; 2017; Tokatlı and Baştatlı, 2016). But maybe the most important factor on the pollution of this system is very weak environmental awareness in the local people (Tokatlı and Gürbüz, 2014). These organic and inorganic pollutions significantly threaten the water resources and soil of the basin and also human health, who lives in the Thrace Region.

The main objective of this study was to determine the residues of 174 kinds of pesticides in the surface waters and sediments of Ergene River Basin and to evaluate the toxicological significance of the investigated contamination in the aquatic components of the basin including Meriç and Ergene Rivers and total of 10 significant tributaries of the basin.

2. MATERIAL AND METHOD

2.1. 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 2018, when the precipitation and surface runoff have increased significantly in the region. After a preliminary field study, 21 stations were selected on the Ergene River Basin considering the main basin components and pollution sources. 9 of the stations were located on the Ergene River, 2 of the stations were located on the Meriç River, 10 of the stations were located on the significant tributaries of Ergene River. Location information is given in Table 1 and map of study area is given in Figure 1.

Water samples were collected 0.5 m below the water surface in 1 L pre-cleaned glass bottles and kept at 4 ^{0}C until the chemical analysis. Sediment samples were collected form the upper 10 cm of sediments with an ekman grab sampler in 1 L sterile glass bottles and kept at 4 ^{0}C until the chemical analysis. Water and sediment samples were collected.

Table 1. Location information of selected stations

Meriç and Ergene Rivers		**Tributaries**		
Station	**Location**	**Station**	**Name of Potamic**	**Location**
E1	Kavacık	**T1**	Safaalan Creek	Karlı
E2	Muratlı	**T2**	Çorlu Stream	Muratlı
E3	Karamusul	**T3**	Ahmetbey Creek	Ahmetbey
E4	Eskibedir	**T4**	Köprüaltı Creek	Lüleburgaz
E5	Oklalı	**T5**	Ana Creek	Sinanlı
E6	Pehlivanköy	**T6**	Hayrabolu Stream	Karakavak
E7	Uzunköprü	**T7**	Büyükdere Creek	Babeski
E8	Yenicegörece	**T8**	Kuleli Stream	Kumköy
E9	Adasarhanlı	**T9**	Ana Stream	Bakışlar
M1	Küplü	**T10**	Irrication Canal	Küçükaltıağaç
M2	Sarıcaali			

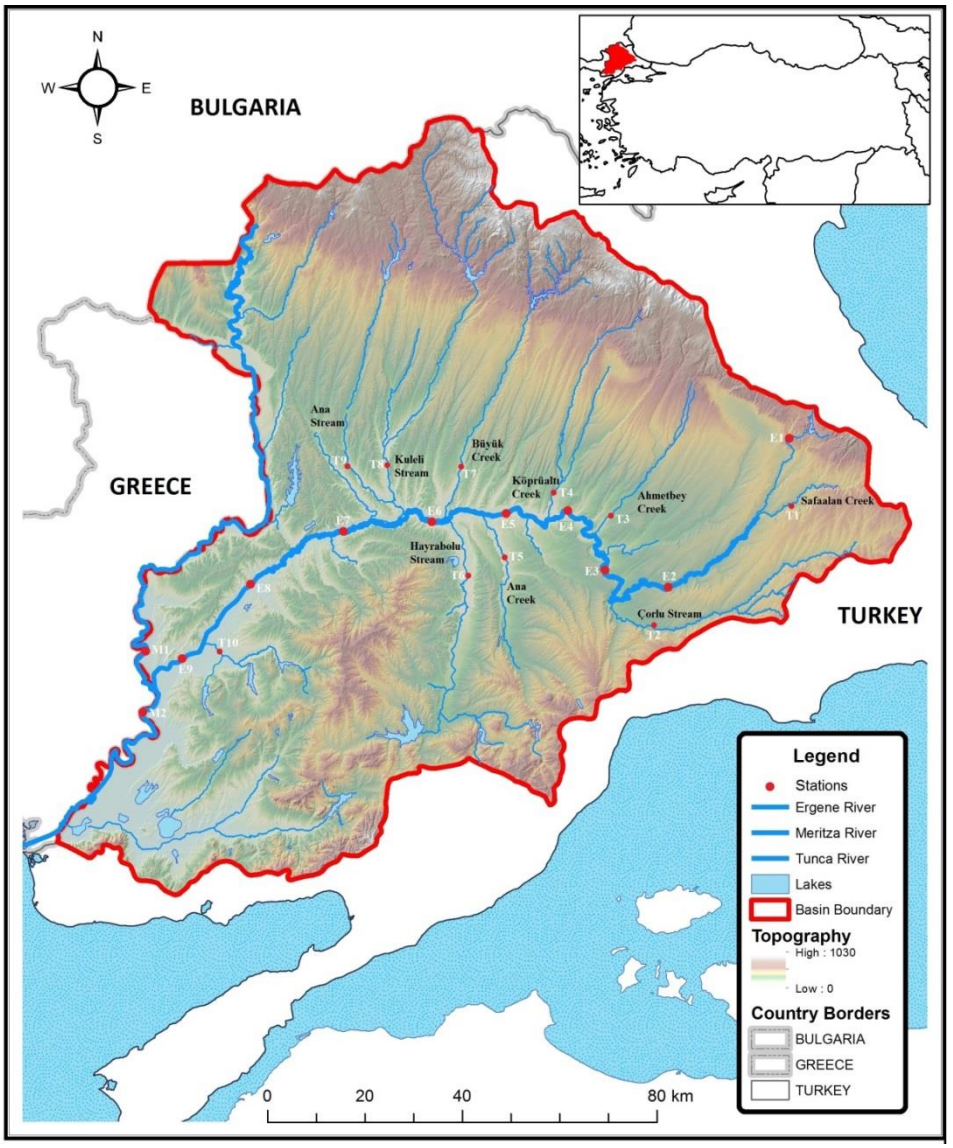

Figure 1. Topographic map of Erg ene River Basin and selected stations

2.2. Pesticide analysis

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 by 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) (Schenck and Hobbs, 2004). 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, matrix spikes were evaluated. The reliability of the calibration method and sample preparation was evaluated on the spiked samples. The calibrated midpoints (10,000 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%.

3. RESULTS AND DISCUSSION

The mean values of the pesticide residues recorded in water and sediment of the Ergene River Basin components are given in Table 2 and 3. The proportional values of pesticides detected in water and sediment and the mean values of the total pesticide loads detected in Meriç and Ergene Rivers and tributaries of the basin are given in Figure 2 and 3.

Table 2. Mean pesticide accumulations in waters of basin components (ppb)

Potamic	Pesticide	Residue	Potamic	Pesticide	Residue
Safaalan Creek	Propamocarb-hydrochloride	0.0034	**Çorlu Stream**	Propamocarb-hydrochloride	0.2066
	Carbendazim	0.1705		Carbendazim	12.0250
	Imazalil	0.0470		Acetamiprid	0.0731
	Forchlorfenuron-706	0.1228		Forchlorfenuron-706	0.4817
Ahmetbey Creek	Carbendazim	0.1015	**Ana Stream**	Carbendazim	1.5696
	Acetamiprid	0.0241		Thiamethoxam	0.0968
	Forchlorfenuron-706	0.2880		Forchlorfenuron-706	0.5146
Köprüaltı Creek	Carbendazim	0.6862	**Irrication Canal**	Carbendazim	0.1251
	Thiamethoxam	0.1029		Acetamiprid	0.0239
	Acetamiprid	0.6429		Forchlorfenuron-706	0.2730
	Forchlorfenuron-706	0.6089	**Büyük Creek**	Carbendazim	0.1039
	Azoxystrobin	5.4597		Forchlorfenuron-706	0.0506
Hayrabolu Stream	Pymetrozine	0.0504	**Ana Creek**	Pymetrozine	0.0367
	Carbendazim	0.3951		Carbendazim	2.0559
	Thiamethoxam	0.4453		Thiamethoxam	0.3284
	Acetamiprid	0.0657		Acetamiprid	0.1114
	Forchlorfenuron-706	0.3060		Forchlorfenuron-706	0.1125
	Azoxystrobin	0.1580		Azoxystrobin	0.1934
Kuleli Stream	Carbendazim	0.1505	**Meriç River**	Carbendazim	1.0734
	Forchlorfenuron-706	0.3252		Forchlorfenuron-706	0.2646
Ergene River	Acetamiprid	0.153798	**Ergene River** (continue)	Secbumeton	0.0461
	Carbendazim	8.13466		Spiroxamine	0.3816
	Dimethoate	0.0346		Terbumeton	0.0596
	Forchlorfenuron-706	0.418172		Thiabendazole	0.04334
	Methamidophos	0.031162		Thiacloprid	0.074
	Mexacarbate	0.0559		Thiamethoxam	0.0717
	Prometon	0.0356		Thiophonate Methyl	0.17135
	Propamocarb-hydrochloride	0.055007		Tricyclazole-753	0.0191

Table 3. Mean pesticide accumulations in the sediments of basin components (ppt)

Potamic	Pesticide	Residue	Potamic	Pesticide	Residue
Ahmetbey Creek	Carbendazim	1.2990	**Köprüaltı Creek**	Carbendazim	2.3964
	Acetamiprid	2.0028		Thiamethoxam	0.1228
	Thidiazuron-747	0.7223		Acetamiprid	0.0277
	Imazalil	1.5116		Imazalil	2.2038
	Azoxystrobin	7.9727		Azoxystrobin	127.0282
	Epoxiconazole	20.1094		Epoxiconazole	6.1998
	Tebuconazole	73.2832		Tebuconazole	19.0737
	Prochloraz	1173.5320		Prochloraz	212.4226
	Propiconazole	15.4181		Propiconazole	4.0181
Ana Creek	Pymetrozine	3.5472	**Kuleli Stream**	Carbendazim	3.6511
	Carbendazim	4.9622		Clothianidin	0.8572
	Thiamethoxam	0.1538		Acetamiprid	0.2820
	Acetamiprid	5.2478		Imazalil	0.9941
	Imazalil	1.6263		Cyproconazole	0.9890
	Cyproconazole	1.8751		Azoxystrobin	16.1187
	Azoxystrobin	26.5398		Epoxiconazole	8.3246
	Epoxiconazole	38.9446		Prochloraz	36.2022
	Prochloraz	585.2052		Tebuconazole	13.2834
	Tebuconazole	165.1282		Propiconazole	8.7658
	Propiconazole	74.2774		Difenoconazol	5.4184
Hayrabolu Stream	Pymetrozine	3.8740	**Büyük Creek**	Carbendazim	1.1758
	Carbendazim	2.1633		Acetamiprid	0.3274
	Thiamethoxam	0.4436		Imazalil	1.8707
	Acetamiprid	3.4751		Cyproconazole	0.3613
	Imazalil	0.7772		Azoxystrobin	16.4166
	Azoxystrobin	2.7806		Epoxiconazole	6.8362
	Epoxiconazole	7.2947		Prochloraz	32.0535
	Prochloraz	149.7365		Tebuconazole	8.3549
	Tebuconazole	36.8510		Propiconazole	6.2555
	Propiconazole	6.9100		Difenoconazol	13.6894
Ana Stream	Carbendazim	2.5415	**Irrication Canal**	Carbendazim	0.8968
	Thiamethoxam	0.3885		Acetamiprid	0.6616
	Acetamiprid	0.1119		Imazalil	4.9117
	Imazalil	2.0258		Chlorotoluron	0.9103
	Chlorotoluron	0.2702		Cyproconazole	1.0787
	Cyproconazole	1.4835		Azoxystrobin	26.6647
	Azoxystrobin	25.1946		Epoxiconazole	9.7438
	Epoxiconazole	17.3496		Prochloraz	90.3261
	Prochloraz	45.2769		Tebuconazole	18.8510
	Tebuconazole	17.8928		Metconazole -718	2.5984
	Propiconazole	10.2578		Propiconazole	14.9129
	Difenoconazol	11.0282		Difenoconazol	4.5181
Ergene River	Acetamiprid	0.372795	**Safaalan Creek**	Carbendazim	0.4466
	Azoxystrobin	7.684818		Imazalil	0.9124
	Carbendazim	4.630187		Azoxystrobin	0.7944
	Diuron	0.690328		Prochloraz	90.8343
	Epoxiconazole	5.198424		Tebuconazole	4.2461

	Fluometuron	0.670262		Propiconazole	2.4586
	Flutolanil-703	7.4983		Propamocarb-hydrochloride	0.0557
	Imazalil	7.166455		Carbendazim	13.8809
	Methamidophos	0.149791		Thiabendazole	0.0328
	Prochloraz	38.08541		Acetamiprid	0.0244
	Propamocarb-hydrochloride	0.062294	**Çorlu Stream**	Thidiazuron-747	0.5141
	Propiconazole	3.905677		Imazalil	0.0850
	Pymetrozine	0.427766		Azoxystrobin	3.2722
	Spiroxamine	0.230354		Epoxiconazole	1.7240
	Tebuconazole	14.13984		Prochloraz	58.6444
	Tetraconazole	4.207396		Tebuconazole	12.0135
	Thiabendazole	0.042496		Propiconazole	2.7281
	Thidiazuron-747	0.665355		Diuron	2.237478
	Tricyclazole-753	0.009668		Epoxiconazole	6.672109
Meriç River	Acetamiprid	0.393643	**Meriç River** (continue)	Fluometuron	2.022203
	Azoxystrobin	18.47035		Imazalil	2.323652
	Carbendazim	2.566561		Prochloraz	5.379746
	Chlorotoluron	0.336573		Propiconazole	3.735819
	Cyproconazole	0.826351		Tebuconazole	8.241894
	Dimoxystrobin-688	1.419074		Thiamethoxam	0.220711

As a result of this study, from investigated 174 kinds of pesticides in Ergene River Basin, a total of 19 pesticide varieties were found in water and a total of 26 pesticide varieties were found in sediment and the most widely used pesticide varieties in the region are carbendazim and prochloraz (Figure 2). It has been also recorded that pesticide accumulations detected in the Ergene River Basin, especially in the Ahmetbey Creek, Çorlu Stream and Ergene River, were found to be in quite high levels (Figure 3).

According to the Water Pollution Control Regulation in Turkey, Safaalan Creek, Ahmetbey Creek, Büyük Creek, Kuleli Stream and Irrigation Canal have I. Class water quality; Köprüaltı Creek, Ana Creek, Hayrabolu Stream and Meriç River have II. Class water quality; and Çorlu Stream and Ergene River have III. Class water quality in terms of total pesticide contents, in general (Turkish Regulations, 2015). In a study, which was performed in Meriç Delta, organochlorine pesticide accumulations in surface water, sediment and fish tissues were investigated. In contrast to the results of the present study, it was indicated that, Meriç Delta was declared as low contaminated of organochlorine pesticide residues (Erkmen and Kolankaya, 2006).

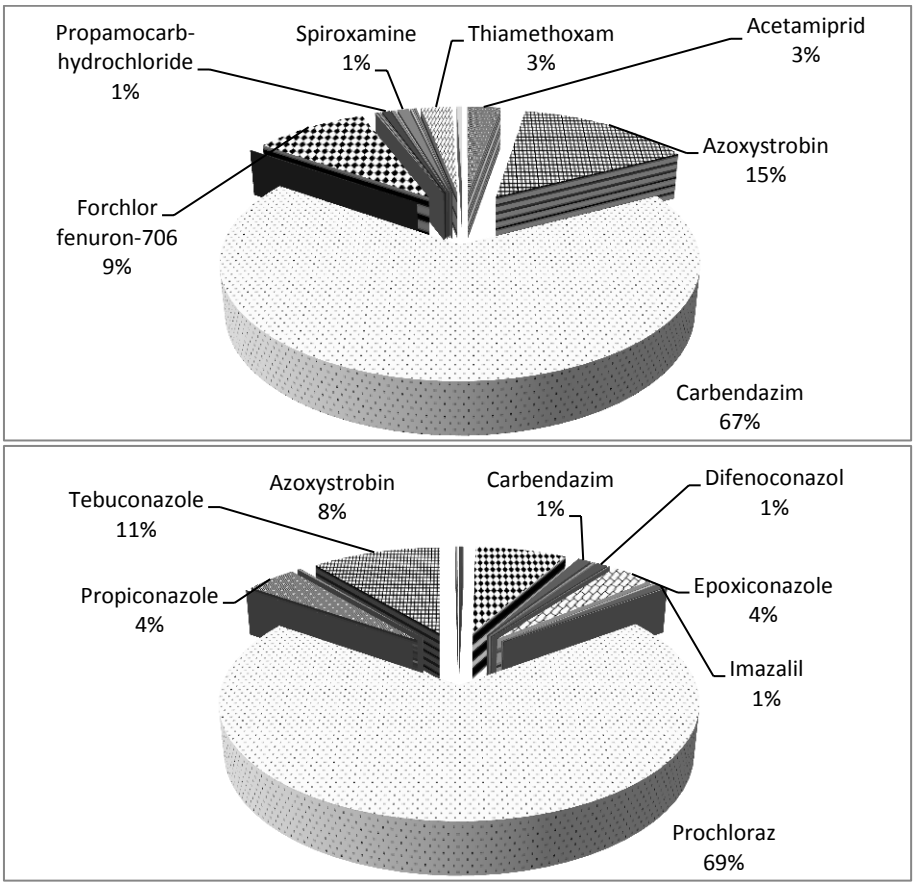

Figure 2. Total pesticide rates detected in water (up) and sediment (down)

According to the results of many researches, it was clearly revealed that even trace doses of pesticides, which are threaten ecosystem integrity due to their stable structure and lipophilic character, are significant toxicants for biological organisms. Pesticides also tend to bioaccumulate and biomagnify and transferred to higher trophic levels through several food chains. As a result of this biomagnification they may lead to toxicity in non-target organism and even in human (Ogunfowokan et al., 2012; Masia et al., 2013; Wang et al., 2013).

Ergene River Basin receives many point contaminant inputs like discharge of effluent from factories and industrial wastes by means of especially Çorlu and Çerkezköy settlement areas located on the east part of the basin and non-point inputs like intensive agricultural activities conducted almost all around the basin (Sungur et al., 2014; Sari et al., 2016; Tokatli, 2018). Agricultural activities carried out in the region have been generally performed in the form of monoculture applications for many years. This situation causes the agricultural pests to have significant resistance gains over time and to increase the amount and quantity of pesticides used by the local producers every year.

The detected data of this study clearly reveals that agricultural runoff is a major contamination source for all the aquatic components of the Ergene River Basin and use of

unconscious pesticides may cause significant health problems not only for the ecosystem but also for the local people in the near future.

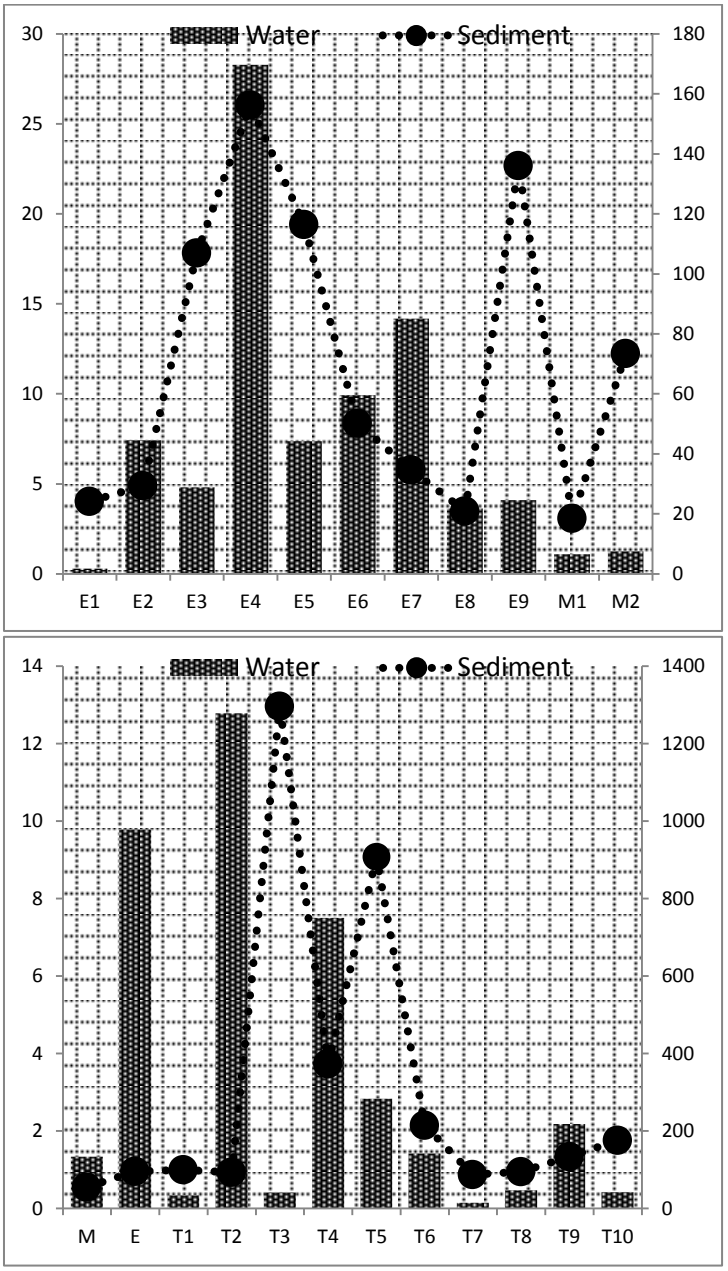

Figure 3. Total pesticide residues in Meriç – Ergene Rivers (left) and tributaries (right) (ppb)

4. CONCLUSIONS

In this study, pesticide residues in water and sediment of Ergene River Basin components including 10 significant tributaries were investigated. As a result of this investigation, agricultural pressure on the abiotic components of the Ergene River Basin was clearly revealed. Çorlu Stream and Ahmetbey Creek were found to be the most polluted ecosystems among the investigated basin components and fungicides mainly carbendazim and prochloraz were found to be the most widely used pesticide variety in the Ergene River Basin. It was also revealed that the basin has II. – III. Class water quality in terms of total pesticide concentrations, in general. For the protection and improve the quality of this significant river ecosystem, which is known as the lifeblood of the Thrace Region, monoculture practices in agricultural aplications should be changed and the farmers should be encouraged to polyculture practices. Also 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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