Sigma J Eng Nat Sci, Vol. 40, No. 4, pp. 762–771, December, 2022

Sigma Journal of Engineering and Natural Sciences
Web page info: https://sigma.yildiz.edu.tr
DOI: 10.14744/sigma.2022.00092

Research Article

Environmental monitoring of pesticide residues in surface waters of Buyuk Menderes River

Meltem KAÇIKOÇ[1*], Mehmet CENSUR[1]

[1]*Faculty of Engineering, Department of Environmental Engineering, Suleyman Demirel University, Isparta, 32200, Türkiye*

ARTICLE INFO

Article history
Received: 01 March 2021
Revised: 29 April 2021
Accepted: 08 September 2021

Keywords:
Büyük Menderes River; Pesticides; Water Framework Directive; Surface Water Quality Regulation

ABSTRACT

The use of pesticides adversely affects the chemical and ecological condition of water resources. The Water Framework Directive (WFD), developed for the conservation and improvement of water resources, is the most current and valid environmental legislation in Europe. WFD aims to achieve a good chemical and ecological status in all water resources. Parameters mainly used to assess chemical and ecological status are respectively priority substances and specific pollutants. Most of the substances classified as priority substances and specific pollutants are pesticides, making them key contaminants according to WFD requirements. The aim of this study is to monitor pesticide residues in the Büyük Menderes River, Turkiye. Monthly samples were collected for the duration of three years, from January 2016 to December 2018, on six different monitoring points. The most frequently detected pesticides in the river water samples were: imidacloprid, acetamiprid, parathion-methyl, dimethoate, metolachlor, clopyralid, carbendazim, and piperonyl butoxide. Since the limit values have been exceeded due to the current pressures in the basin, it is of high importance to take the necessary precautions to prevent the pesticides reaching the body of water.

Cite this article as: Kaçıçkoç M, Censur M. Environmental monitoring of pesticide residues in surface waters of Buyuk Menderes River. Sigma J Eng Nat Sci 2022;40(4):755–764.

INTRODUCTION

Rapid developments in industrialization, the emergence of new technologies, increase in population, and consequently the heavy use of chemicals such as pesticides have significantly increased in order to meet the demand on food [1]. While pesticides can increase food production, they can also contaminate soil, water, turf, and other vegetation thus threatening the aquatic ecosystem and being detrimental to human health [2]. Pesticide residues move into surface waters via both point (wastewater discharges and farm field activities such as tank filling, spillages, faulty equipment, etc.) [3] and diffuse (drift, surface runoff, erosion, drainage, wet deposition, leaching to groundwater, etc.) sources [4]. More and more pesticides are widely and acutely used in intensive agriculture, which leaves waters

***Corresponding author.**
*E-mail address: meltemkacikoc@sdu.edu.tr

This paper was recommended for publication in revised form by Regional Editor Eyup Debik

Published by Yıldız Technical University Press, İstanbul, Turkey

located in those fields more vulnerable to pesticide contamination [5, 6]. The degree of contamination of the surface water sources by pesticide residue is dependent on surface water characteristics (surface area, depth, flow, etc.), distance to the cultivated areas, and climatic conditions (temperature, humidity, wind, precipitation, etc.) [7]. After pesticides reach the surface waters, they are subjected to complex dynamic physical, chemical and biological site-specific processes that are often difficult to predict [8, 9]. Monitoring of pesticide residues is essential to control pesticide contamination [10].

The adverse effects of pesticides are not limited to pests that are targeted, but they can be toxic to innumerous other organisms including birds, fish, beneficial insects, as well as non-target plants and organisms including humans [11, 12]. Occurrence levels of pesticides in environmental samples are measured generally in the microgram and nanogram levels [1, 6]; However, pesticide residues are also mobile and bioaccumulative [13]. Therefore, even in small quantities, releases into the environment in the long term result in the accumulation and biomagnification of these emerging pollutants, potentially complicating their negative effects [1]. It has been reported that pesticides impact the health of humans in different ways that include but are not limited to endocrine disruptions, neurological disturbances, immune system influences, and reproductive harms [11, 14]. Consequently, the toxic effect of pesticides on non-target organisms has created a major concern worldwide [14].

In the European countries, intensive industrialization over the last decades and the use of chemicals in abundance affected water resources and resulted in pollution. The Water Framework Directive (WFD) entered into force in 2000 with the idea that water is not a commercial product but a natural resource to be protected [15]. WFD was developed for the protection and improvement of water resources and is the most current and valid environmental legislation in Europe to achieve favorable chemical and ecological water status. According to the Directive, priority substances and specific pollutants must meet environmental quality standards (EQS) in order to achieve these goals. Quality elements used to assess chemical and ecological status are respectively priority substances and specific pollutants. Most of the priority substances and specific pollutants in question are pesticide-group chemicals.

During the WFD harmonization process, studies have been initiated to harmonize Turkish water resources legislation with the EU water management policy. Accordingly, some of the Turkish regulations were completely repealed and replaced by new ones, and some of them were revised. Among these regulations, the "Surface Water Quality Regulation (SWQR)" was first put into effect in the Official Gazette numbered 28483 and published on November 30, 2012 and [16]. SWQR is a regulation developed for the classification of water bodies in accordance with WFD. "Specific Pollutants and Environmental Quality Standards for Surface Water Resources" and "Priority Substances and Environmental Quality Standards for Surface Water Resources" are included respectively in Annex V Table 4 and Table 5 of the Regulation [16]. The Büyük Menderes River is located in the Büyük Menderes River Basin, which is among the priority basins. While 1% of the basin area is covered by surface water bodies, pesticides are used in agricultural areas covering approximately 40% of the basin. In this study, pesticides stated in the priority substance list and specific pollutant list were investigated. The aim of this study is to reveal the pesticide pollution by evaluating the monitoring results of the Büyük Menderes River for the pesticide residues included in the priority substance and certain pollutant lists according to SWQR.

MATERIALS AND METHOD

Study Area

Büyük Menderes River Basin is located between 37°06'N-38°55'N latitude and 27°E-30°36'E longitude in south-west Turkiye. Büyük Menderes River, which gives its name to the basin as well, is 584 km long, making it the longest river in the Aegean Region [17]. The upstream of the river is located in the caves of karstic origin in the north-east of Dinar District. While the Büyük Menderes River flows from upstream to the downstream, it joins with its tributaries such as Banaz, Çürüksu, Dandalaz, Akçay and Çine, and flows into the Aegean Sea from the west of Bafa Lake by forming a delta [18]. Büyük Menderes River drainage area is approximately 25000 km^2 and 44% of this drainage area is covered by agricultural lands [17]. In addition to intensive agricultural activities in the basin, there are many point and diffuse sources of pollution such as domestic and industrial wastewaters, solid waste storage areas, olive mill wastewaters, geothermal waters, and mining activities [19].

Monitoring Points and Sampling Procedure

Within the scope of this study, water samples collected at 6 different monitoring points on the Büyük Menderes River (Figure 1) were evaluated in terms of pesticide levels. The aforementioned monitoring points are surveillance monitoring points located on the main branch of the river which DSI routinely uses for the same purpose. Located at upstream of the river, BM1 is influenced by wastewater treatment facilities and agricultural activities. Located within the provincial border of Denizli, BM2 is exposed to contamination by agricultural activities and BM3 by domestic and industrial wastewaters. BM4, BM5 and BM6 are located in the city of Aydın. For BM4, the primary source of contamination is, again, agricultural activities while for BM5 and BM6, apart from these activities geothermal power plants are also sources of contamination. Water samples were collected by the personnel of Directorate General for State Hydraulic Works (DSI) 21st Regional Directorate in accordance with the "Water

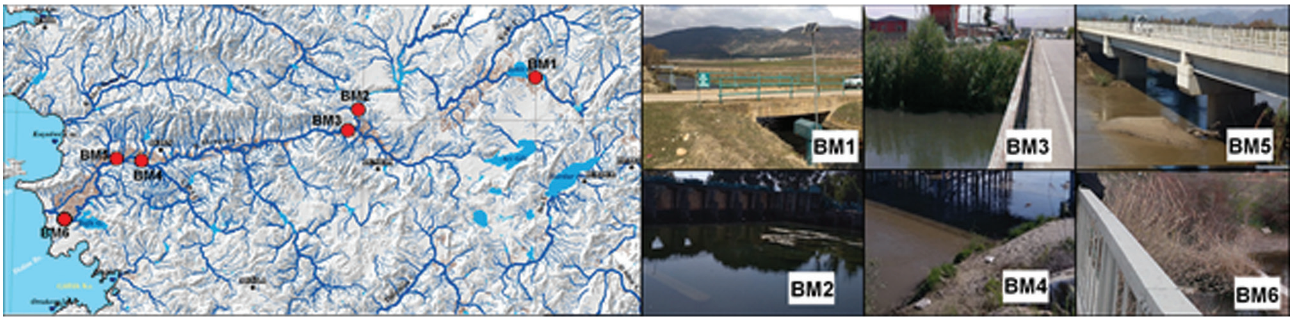

Figure 1. Location of the monitoring points on Büyük Menderes River.

Pollution Control Regulation Sampling and Analysis Methods Notification" published in the Official Gazette numbered 27372 and published on October 10, 2009. Water samples which were collected in dark colored glass bottles were delivered to the analysis laboratory as soon as possible under appropriate protection conditions. The sampling was carried out on a monthly basis between January 2016 and December 2018.

Analyses of Pesticides

The analyses were carried out in the laboratory of DSI Technical Research and Quality Control (TAKK) Department accredited by the Turkish Accreditation Agency. Pesticides such as organophosphate, carbamate, and triazole were analyzed by Liquid Chromatography-Mass/Mass Spectrometry (LC-MS/MS) system. The analysis of organochlorine pesticides was carried out with the Gas Chromatography-Mass/Mass Spectroscopy (GC-MS/MS) system. The analysis was based on the US EPA Method 540 (for LC-MS/MS) and US EPA Method 525.3 (for GC-MS/MS). Water samples were extracted using solid-phase extraction (SPE).

Instrumental conditions (GC–MS/MS): GC-MS/MS analyses were performed on the Agilent 7890A GC System coupled to the Agilent 7000 GC-MS Triple Quad (Agilent Technologies, Santa Clara, CA, USA). The initial column temperature of 70 °C for 1 min, 50 °C min^{-1} ramp to 150 °C, then 6 °C min^{-1} ramp to 200 °C, followed by 16 °C min^{-1} to 280 °C, held for 5 min [20]. The injector port temperature was fixed at 250 °C and a 1 μL volume was injected in splitless mode. Ultra-high purity helium (≥99.999 %) was used as a carrier gas, and the flow rate (constant) was 2.4 mL/min.

Instrumental conditions (LC–MS/MS): LC-MS/MS analyses were performed with the Agilent 6400 series Triple QQQ LC-MS instrument equipped with an electrospray ionization source (ESI). The chromatographic separation was achieved using a high efficiency Agilent Poroshell 120 SB-C18 column. Column temperature was maintained at 35 ^{0}C. The injection volume and flow rate were 100 μL and 0.6 mL/min, respectively. Separation was performed by gradient elution using methanol (mobile phase, solvent A) and 5 mM ammonium formate/0.1% formic acid in water (mobile phase, solvent B). The MS instrumental conditions are summarized as follows: drying gas temperature 350 ^{0}C, gas flow 5 L/min, nebulizing pressure 45 psi, capillary voltage 3500 V, sheath gas temperature 250 ^{0}C, and sheath gas flow 11 L/min [21].

The limits of detection (LOD) and quantification (LOQ) have been presented in Table 2. Calibration curves were linear in the concentration range of 5 ng/L to 5 μg/L. For all pesticide species the R^2 values for the linearized calibration curves were between 0.995 and 0.999. To ensure data quality, the quality assurance/quality control (QA/QC) programs, including calibration and LOD and LOQ, were followed as described in the Standard Methods [22].

RESULTS

Within the scope of this study, 22 types of pesticide stated in the priority substance list and 89 types of pesticide stated in the specific pollutant list were analyzed in the water column at DSI TAKK Department's laboratory and results are reported. The results of the pesticide analysis that were higher than the limit of quantification (LOQ) were examined and pesticide residues frequently found in the Büyük Menderes River were evaluated. Table 1 shows the properties of pesticides frequently detected in the Büyük Menderes River during the monitoring period. The most common pesticides found in river waters were imidacloprid, acetamiprid, parathion-methyl, dimethoate, metolachlor, clopyralid, carbendazim, and piperonyl butoxide. Table 2 presents descriptive statistics of these pesticides for the period 2016-2018 and all monitoring points, and for each pesticide the LOQ, LOD, and legislation limits. For the calculation of statistics, values below the LOD were assumed to be equal to half of the detection limits [23, 24].

Figure 2 shows the boxplot graphs of imidacloprid, acetamiprid, parathion-methyl, and dimethoate and Figure 3 shows the boxplot graphs of metolachlor, clopyralid, carbendazim, and piperonyl butoxide.

Table 1. Properties of pesticides frequently detected in Büyük Menderes River

Pesticide CAS number	Chemical formula	Solubility in water[a] (at 20 °C) (mg/L)	Octanol-water partition coefficient[a] K_{ow} (at pH 7, 20 °C)	Pollutant group	Banned[b] Yes/No	Chemical class[a]
Imidacloprid 138261-41-3	$C_9H_{10}ClN_5O_2$	610	0.57	Specific pollutants	yes (19.12.2018)	neonicotinoid insecticide,
Acetamiprid 135410-20-7	$C_{10}H_{11}ClN_4$	2950	0.8	Specific pollutants	no	neonicotinoid insecticide
Parathion-methyl 298-00-0	$C_8H_{10}NO_5PS$	55	3	Specific pollutants	yes (31.08.2011)	organophosphate insecticide
Dimethoate 60-51-5	$C_5H_{12}NO_3PS_2$	25900	0.75	Specific pollutants	yes (30.09.2020)	organophosphate insecticide
Metolachlor 51218-45-2	$C_{15}H_{22}ClNO_2$	530	3.4	Specific pollutants	yes (31.08.2011)	chloroacetamide herbicide
Clopyralid 1702-17-6	$C_6H_3Cl_2NO_2$	7850	-2.63	Specific pollutants	no	pyridine compound herbicide
Carbendazim 10605-21-7	$C_9H_9N_3O_2$	8.0	1.48	Specific pollutants	yes (01.01.2018)	benzimidazole fungicide
Piperonyl butoxide 51-03-6	$C_{19}H_{30}O_5$	14.3	4.75	Specific pollutants	no	cyclic aromatic synergist

a: [25], b: [26].

Table 2. Descriptive statistics of the frequently detected pesticides in the Büyük Menderes River

Pesticides	Concentrations							
	LOQ (µg/L)	LOD (µg/L)	Min (µg/L)	Max (µg/L)	Mean (µg/L)	SD (µg/L)	AA-EQS (µg/L)	MAC-EQS (µg/L)
Imidacloprid	0.010	0.003	<LOD	0.759	0.012	0.060	0.14	1.4
Acetamiprid	0.010	0.003	<LOD	0.130	0.007	0.018	44	44
Parathion-methyl	0.005	0.0015	<LOD	0.628	0.009	0.051	1.4	2.5
Dimethoate	0.010	0.003	<LOD	0.251	0.006	0.021	15	15
Metolachlor	0.025	0.0075	<LOD	0.297	0.008	0.030	3.3	88
Clopyralid	0.010	0.003	<LOD	1.521	0.049	0.170	200	200
Carbendazim	0.010	0.003	<LOD	1.538	0.041	0.149	2.7	77
Piperonyl butoxide	0.010	0.003	<LOD	0.211	0.004	0.016	3.3	350

In the study period, the highest concentration of imidacloprid was found at the BM6 monitoring point as 0.759 µg/L in March 2018. The "annual average concentration environmental quality standards" (AA-EQS) for imidacloprid is 0.14 µg/L and the "maximum allowable concentration environmental quality standards" (MAC-EQS) is 1.4 µg/L. Imidacloprid level measurements show that the concentration is below the MAC-EQS value, but the level sometimes exceeds AA-EQS values at some monitoring points (BM3, BM4, and BM6). During the monitoring period, imidacloprid levels did not show a significant temporal trend. When the data for the monitoring period are evaluated, the highest acetamiprid level was observed at the BM6 monitoring point in August 2016 and 2018 as 0.13 µg/L. According to SWQR, MAC-EQS and AA-EQS values for acetamiprid were determined to be 42 µg/L, and the acetamiprid concentrations in the river are well below these limit values.

The analysis of the temporal variation of acetamiprid values show that it was detected more frequently in the Büyük Menderes River in 2016, and the frequency decreased significantly in the following years. During the

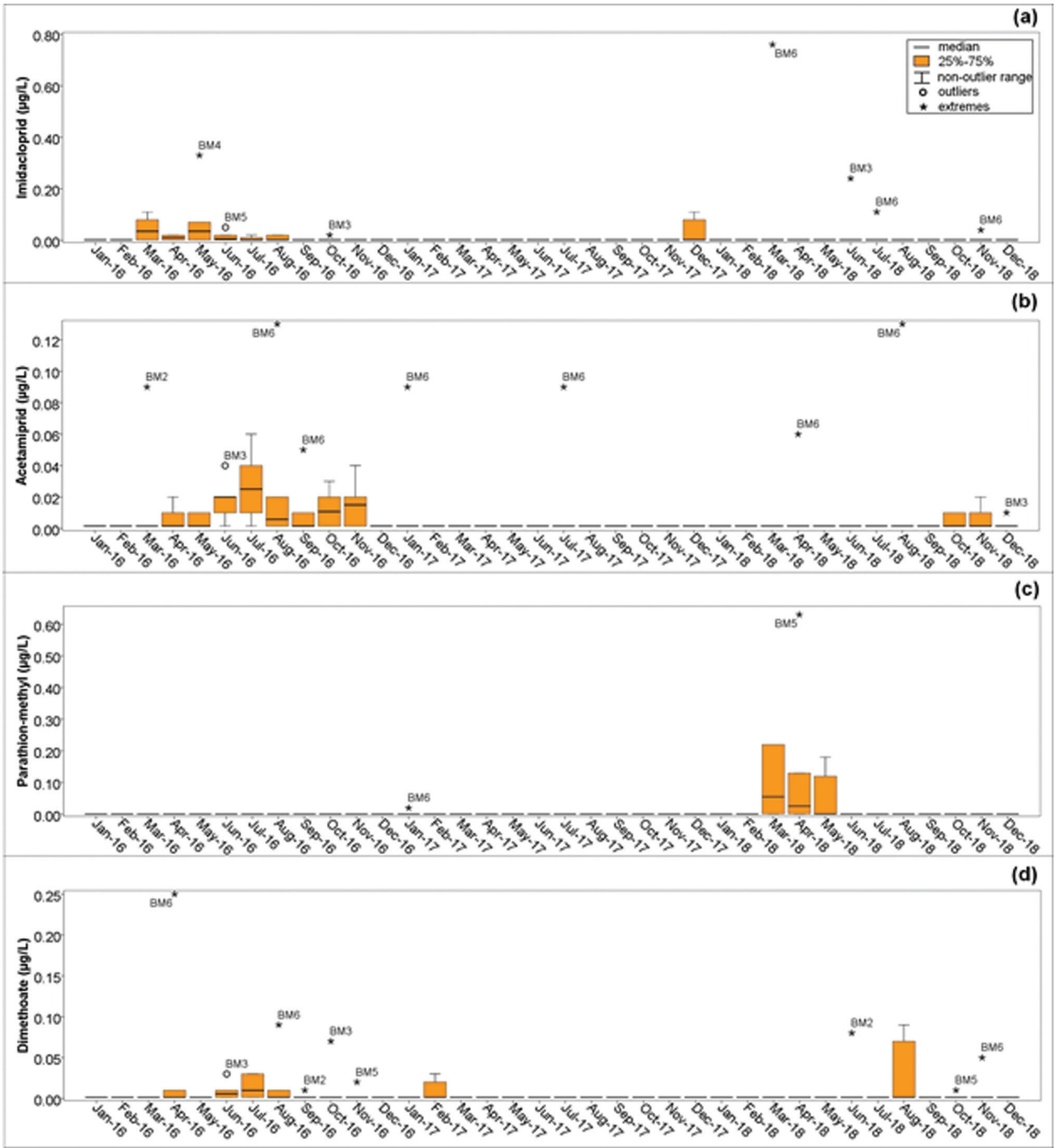

Figure 2. Boxplot diagrams showing of the (a) imidacloprid, (b) acetamiprid, (c) parathion-methyl, and (d) dimethoate in Büyük Menderes River.

monitoring period, the highest level of parathion-methyl was found at the BM5 monitoring point as 0.628 μg/L in April 2018. The parathion-methyl values were observed to be within the AA-EQS and MAC-EQS levels in the river, not exceeding the standard. In the spring of 2018, parathion-methyl was traced at all monitoring points except BM1. The highest concentration of dimethoate was 0.251 μg/L at BM6 monitoring point in April 2018. Dimethoate values measured in the river are below AA-EQS and MAC-EQS. Dimethoate, which was found relatively frequently at the BM6 monitoring point, did not show a significant temporal trend.

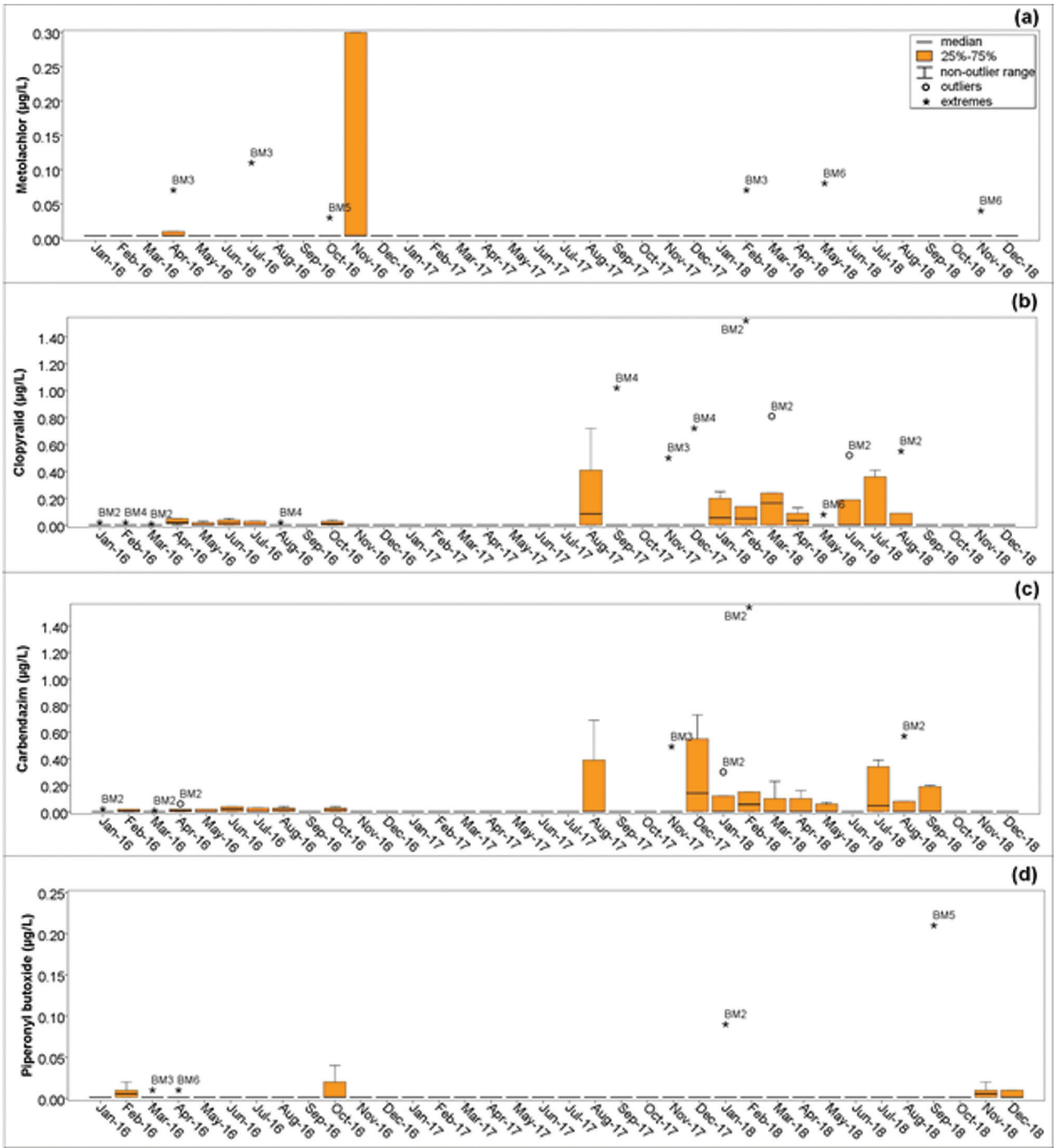

Figure 3. Box plot diagrams showing of the (a) metolachlor, (b) clopyralid, (c) carbendazim, and (d) piperonyl butoxide in Büyük Menderes River.

The highest value for metolachlor was measured at the BM6 monitoring point as 0.297 µg/L in November 2016. The metolachlor level, which did not show a significant temporal and spatial trend, did not exceed the AA-EQS and MAC-EQS values. During the monitoring period, the highest concentration of clopyralid was determined as 1.521 µg/L in February 2018 at the BM2 monitoring point. Clopyralid level measured in the river is well below the AA-EQS and MAC-EQS of 200 µg/L set by the SWQR. Clopyralid detection frequency has increased since mid-2017 during the 3-year monitoring period. Clopyralid was found relatively more frequently at BM2 monitoring point than at other monitoring points.

Highest concentration of carbendazim was measured as 1.538 μg/L at BM2 monitoring point in February 2018. The carbendazim level is lower than both the AA-EQS and MAC-EQS values, but close to the AA-EQS value of 2.7 μg/L. The frequency of carbendazim detection increased in the last period of this study, particularly at the BM2 monitoring point. The highest value for piperonyl butoxide was measured as 0.211 μg/L at BM5 monitoring point in September 2018. Piperonyl butoxide did not show a significant temporal and spatial trend during the monitoring period and did not exceed the AA-EQS and MAC-EQS values.

DISCUSSION

In this study, in order to evaluate pesticide pollution in Büyük Menderes River in accordance with SWQR, pesticide levels in the water were determined through collection of data between January 2016 and December 2018 on a monthly basis. Pesticides reaching the Büyük Menderes river were subjected to biogeochemical processes such as biotransformation, photolysis, and adsorption and were not in high concentration in the water column. Also, monitoring points are located on the main branch of the river with tributaries feeding it, creating a high water flow. This may have caused the dilution of pesticides in a big body of water, masking their existence and leaving the measurements below the EQS values. It was found that four types of insecticides (imidacloprid, acetamiprid, parathion-methyl, dimethoate), two types of herbicides (metolachlor and clopyralid), one type of fungicide (carbendazim) and one type of synergist (piperonyl butoxide) were frequently detected in water samples taken from the Büyük Menderes River.

Concentration of imidacloprid was high in river water even though it was recently banned in Turkiye, suggesting that it was heavily used up until it became illegal. It persists at pH 7 for more than 30 days in the environment [27]. However, repeated use causes imidacloprid to remain in soil, water, and plant material for several months or even years [28]. Apart from its heavy use in the region, its high water soluble characteristic like other neonicotinoid group insecticides may be the reason for high concentration of imidacloprid in the river water, explaining its dangerously high level in terms of limit values. Like imidacloprid, acetamiprid is also a member of the neonicotinoid insecticide group and is effective in controlling aphids, insects, pests on leaflets, plants and leafy vegetables, as well as fleas for pets [29]. Acetamiprid levels in the river water may be due to the fact that it is used as a substitute for banned imidacloprid. In addition, acetamiprid has the potential to leak from soil to water and is the most efficient and most purchased pesticide group in the world [30]. In the study area where agricultural activities create a significant problem, acetamiprid with high water solubility is expected to be found in river water samples. Acetamiprid, which was detected much more frequently in Büyük Menderes River in 2016, was observed to have a significant decrease in the frequency in the following years. In this case, it can be concluded that the use of insecticides whose active ingredient is acetamiprid has decreased in the region. It was detected at BM6 monitoring point during the monitoring period. This may be due to the fact that BM6 is located downstream, making it more susceptible to the cumulative effect of pollution.

Parathion-methyl and dimethoate found in Büyük Menderes river is an organophosphate insecticide widely used to control pests for plants, fruits, and vegetables. Although parathion-methyl was banned approximately 10 years ago, it was present in the river waters. This may be because of its heavy use in the region before this change in regulation and its persistence in the environment. Parathion-methyl, which has relatively low solubility in water, is moderately adsorbed by the soil [31]. As parathion-methyl has a lower bioaccumulation compared to other organophosphate pesticides and is banned in our country, we do not expect to detect it in the river water. However, parathion-methyl was detected at almost all monitoring points only in the spring of 2018. In this case, it can be stated that it may have reached the river with a natural event (heavy rainfall, erosion etc.) that happened in those months. Unlike parathion-methyl, dimethoate was not banned and was in use during the monitoring period in Turkiye. However, due to its endocrine-disrupting effect [32], its use was banned on 30 September 2020 in Turkiye. The fact that it is frequently detected in water samples of the Büyük Menderes River, especially at the BM6 monitoring point located downstream is due to its high solubility in water. Also, dimethoate which disintegrates rapidly in the environment was found in the river waters potentially because in the Büyük Menderes river basin where 20% of olive production of Turkiye is done, dimethoate is heavily used against pests on olive plants.

Although metolachlor is an herbicide whose use was banned in Turkiye in 2011, it was frequently detected during the monitoring period in the river water. When the product pattern of the Büyük Menderes river basin as cotton, corn, and sunflower is taken into consideration, we can deduce that it was used heavily in the region until its ban. Also, its characteristics such as the fact that it does not adsorb well with soil particles, it is high water soluble, and it has a medium persistence in the environment [33, 34] support the fact that it was frequently found during monitoring. Clopyralid, which is an herbicide with a wide spectrum that is used in vegetable production [35], was also detected in Büyük Menderes river. Clopyralid was detected more frequently in BM2 monitoring point located in Denizli where intensive agriculture is done. Clopyralid is especially stable against hydrolysis and photolysis. Its chemical stability combined with the ability to move help this herbicide permeate the soil and contaminate the subsurface waters as well as surface waters in the long term [36]. Due to these characteristics, it is expected to be found in river water samples.

Within the scope of this study, carbendazim was often found in the river waters. "Determination of Water Pollution as a Result of the Usage of Plant Protection Products and Determination of Environmental Quality Standards based on Substances or a Group of Substances" (BIKOP) which was carried out in 2016 shows that the most frequent pesticide in Büyük Menderes River is carbendazim, and close monitoring for the future is recommended [37]. Carbendazim, a fungicide of the carbamate group, protects the products, but also has an endocrine disrupting effect for non-target organisms [38]. It is also a very persistent pesticide due to its slow degradation rate [39]. Although carbendazim has been banned in Turkiye due to its severe toxicity, frequent detection of this pesticide in water samples of the Büyük Menderes River can be explained by its persistent nature and its low water solubility. Piperonyl butoxide which was frequently found in Büyük Menderes river waters during the monitoring period does not act as a pesticide alone, but is also a synergist that increases the effect of other pesticides such as carbamate, pyrethrin, pyrethroid, and rotenone [40]. It was expected to come across Piperonyl butoxide in Büyük Menderes river waters since it is used to increase the effects of other pesticides to protect produce in the river basin product pattern, mainly the grain products such as barley and wheat.

CONCLUSIONS

During the three-year monitoring period, pesticides that are frequently found in the Büyük Menderes River are imidacloprid, acetamiprid, parathion-methyl, dimethoate, metolachlor, clopyralid, carbendazim, and piperonyl butoxide. The presence of banned pesticides in river water samples is evidence that water pollution from pesticide residues is an ecological disaster that will last for many years. All pesticides detected in Büyük Menderes River were found at concentrations below EQS; However, these findings do not guarantee that it will not exceed the EQS values in the future. In recent years, natural events caused by climate change such as heavy rainfall, floods, erosion, etc. have demonstrated the significance of chemical pollution of surface waters, especially through pesticide pollution. In order to prevent pollution, it is crucial to plan future strategies for the use of pesticides as well as regularly monitor pesticides not only in water but also in sediment and biota, as well as designing models of these pesticides for the future. Monitoring not only provides insights on existing pollution levels, but also allows for the evaluation of present methods and policies of reduction in terms of efficiency, encouraging further recovery. It is necessary to boost the public awareness and remedy the need of farmers who are the focus group of pesticide pollution, so that farmers are encouraged to use pesticides that are biodegradable and less toxic with correct timing and appropriate quantity.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

REFERENCES

[1] Tankiewicz M, Fenik J, Biziuk M. Determination of organophosphorus and organonitrogen pesticides in water samples. Trends Analyt Chem 2010;29:1050–1063. [CrossRef]

[2] Kumari B, Madan VK, Kathpal TS. Status of insecticide contamination of soil and water in Haryana, India. Environ Monit Assess 2008;136:239–244. [CrossRef]

[3] Carter A. How pesticides get into water - and proposed reduction measures. Pestic Outlook 2000;11:149–156. [CrossRef]

[4] Miyamoto M, Tanaka H, Katagi T. Ecotoxicological risk assessment of pesticides in aquatic ecosystems. Sumitomo Kagaku R&D Report 2008;1:1–18.

[5] Zhang B, Zhang QQ, Zhang SX, Xing C, Ying GG. Emission estimation and fate modelling of three typical pesticides in Dongjiang River basin, China. Environ Pollut 2020;258:113660. [CrossRef]

[6] Ccanccapa A, Masiá A, Andreu V, Picó Y. Spatio-temporal patterns of pesticide residues in the Turia and Júcar Rivers (Spain). Sci Total Environ 2016;540:200–210. [CrossRef]

[7] Vryzas Z, Vassiliou G, Alexoudis C, Papadopoulou-Mourkidou E. Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece. Water Res 2009;43:1–10. [CrossRef]

[8] Holvoet KMA, Seuntjens P, Vanrolleghem PA. Monitoring and modeling pesticide fate in surface waters at the catchment scale. Ecol Model 2007;209:53–64. [CrossRef]

[9] Kerle EA, Jenkins JJ, Vogue PA. Understanding pesticide persistence and mobility for groundwater and surface water protection. Oregon State University Extension Service, 2007.

[10] Hossain MS, Chowdhury MAZ, Pramanik MK, Rahman MA, Fakhruddin ANM, Khorshed Alam M. Determination of selected pesticides in water samples adjacent to agricultural fields and removal of organophosphorus insecticide chlorpyrifos using soil bacterial isolates. Appl Water Sci 2015;5:171–179. [CrossRef]

[11] Carvalho FP. Pesticides, environment, and food safety. Food Energy Secur 2017;6:48–60. [CrossRef]

[12] De Souza RM, Seibert D, Quesada HB, De Jesus Bassetti F, Fagundes-Klen MR, Bergamasco R. Occurrence, impacts and general aspects of pesticides in surface water: A review. Process Saf Environ Prot 2020;135:22–37. [CrossRef]

[13] Kouzayha A, Rabaa AR, Iskandarani MA, Beh D, Budzinski H, Jaber F. Multiresidue method for determination of 67 pesticides in water samples using solid-phase extraction with centrifugation and gas chromatography-mass spectrometry. Am J Analyt Chem 2012;3:257–265. [CrossRef]

[14] Lushchak VI, Matviishyn TM, Husak VV, Storey JM, Storey KB. Pesticide toxicity: A mechanistic approach. Excli J 2018;17:1101–1136.

[15] EC. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 Establishing a Framework for Community Action in the Field of Water Policy; 2000.

[16] Yerüstü Su Kalitesi Yönetmeliği (YSKY). 28483 sayılı 30 Kasım 2012 tarihli Resmi Gazete. Ankara; 2012.

[17] Çevre Yönetimi Genel Müdürlüğü (ÇYGM). Büyük Menderes Nehir Havzası Yönetim Planı Nihai Taslak, T.C. Çevre ve Orman Bakanlığı, Ankara; 2010.

[18] Güney Ege Kalkınma Ajansı (GEKA). Proje No: TR32/11/DFD-007-019 (Büyük Menderesi Kirletmek Geleceğini Kirletmektir), Proje Sonuç Raporu, Aydın; 2012.

[19] Türkiye Bilimsel ve Teknolojik Araştırma Kurumu-Marmara Araştırma Merkezi (TÜBİTAK-MAM). Havza koruma Eylem Planlarının Hazırlanması Projesi-Büyük Menderes Havzası Nihai Raporu Cilt I, 495 s., Gebze-Kocaeli; 2010.

[20] Golge O, Cinpolat S, Kabak B. Quantification of pesticide residues in gherkins by liquid and gas chromatography coupled to tandem mass spectrometry. J Food Compos Anal 2021;96:103755. [CrossRef]

[21] Kittlaus S, Schimanke J, Kempe G, Speer K. Development and validation of an efficient automated method for the analysis of 300 pesticides in foods using two-dimensional liquid chromatography-tandem mass spectrometry. J Chromatogr A 2013; 1283:98–109. [CrossRef]

[22] American Public Health Association, Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. 20th ed. Washington DC: American Public Health Assoc;1998.

[23] Farnham IM, Singh AK, Stetzenbach KJ, Johannesson KH. Treatment of nondetects in multivariate analysis of groundwater geochemistry data. Chemom Intell Lab Syst 2002;60:265–281. [CrossRef]

[24] Navarro A, Tauler R, Lacorte S, Barceló D. Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro River Basin. J Hydrol 2010;383:18–29. [CrossRef]

[25] International Union of Pure and Applied Chemistry (IUPAC). Pesticide Properties Database. https://sitem.herts.ac.uk/aeru/iupac/search.htm. 2020.

[26] T.C. Tarim Ve Orman Bakanliği. Yasaklanan bitki koruma ürünleri aktif madde listesi. Available https://www.tarimorman.gov.tr/Konu/934/Yasaklanan-Bitki-Koruma-Urunleri-Aktif-Madde-Listesi; Accessed on Oct 27,2022.

[27] Pietrzak D, Kania J, Malina G, Kmiecik E, Wątor K. Pesticides from the EU first and second watch lists in the water environment. Clean-Soil Air Water 2019;47:1800376. [CrossRef]

[28] Li Y, Yang L, Yan H, Zhang M, Ge J, Yu X. Uptake, translocation and accumulation of imidacloprid in six leafy vegetables at three growth stages. Ecotoxicol Environ Saf 2018;164:690–695. [CrossRef]

[29] Zhang JJ, Wang Y, Xiang HY, Li MX, Li WH, Ma KG, et al. Oxidative stress: Role in acetamiprid-induced impairment of the male mice reproductive system. Agric Sci China 2011;10:786–796. [CrossRef]

[30] Singh TB, Mukhopadhayay SK, Sar TK, Ganguly S. Acetamiprid induces toxicity in mice under experimental conditions with prominent effect on the hematobiochemical parameters. J Drug Metab Toxicol 2012;3:1–5. [CrossRef]

[31] Morales JBL, Torres JBV, Bastidas PDJB, Escalante MÁA, Sánchez JIS, Lobo ALB, et al. Monitoring of pesticides residues in northwestern Mexico rivers. Acta Univ 2017;27:45–54. [CrossRef]

[32] Carazo-Rojas E, Pérez-Rojas G, Pérez-Villanueva M, Chinchilla-Soto C, Chin-Pampillo JS, Aguilar-Mora P, et al. Pesticide monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a tropical agro-ecosystem. Environ Pollut 2018;241:800–809. [CrossRef]

[33] Jin Y, Chen R, Wang L, Liu J, Yang Y, Zhou C, et al. Effects of metolachlor on transcription of thyroid system-related genes in juvenile and adult Japanese medaka (Oryzias latipes). Gen Comp Endocrinol 2011;170:487–493. [CrossRef]

[34] Rose CE, Coupe RH, Capel PD, Webb RMT. Holistic assessment of occurrence and fate of metolachlor within environmental compartments of agricultural watersheds. Sci Total Environ 2018;612:708–719. [CrossRef]

[35] Schütz S, Vedder H, Düring RA, Weissbecker B, Hummel HE. Analysis of the herbicide clopyralid in cultivated soils. J Chromatogr A 1996;754:265–271. [CrossRef]

[36] Huang X, Pedersen T, Fischer M, White R, Young TM. Herbicide runoff along highways. 1. Field observations. Environ Sci Technol 2004;38:3263–3271. [CrossRef]

[37] Tarım ve Orman Bakanlığı (TOB). Bitki Koruma Ürünlerinin Kullanımı Neticesinde Meydana Gelen Su Kirliliğinin Tespiti ve Madde veya Madde Grubu Bazında Çevresel Kalite Standartlarının Belirlenmesi Projesi (BIKOP). Ankara; 2016.

[38] McKinlay R, Plant JA, Bell JNB, Voulvoulis N. Endocrine disrupting pesticides: implications for risk assessment. Environ Int 2008;34:168–183. [CrossRef]

[39] Antić N, Radišic M, Radović T, Vasiljević T, Grujić S, Petković A, et al. Pesticide residues in the Danube river basin in Serbia – a survey during 2009–2011. Clean-Soil Air Water 2015;43:197–204. [CrossRef]

[40] Maples D. Piperonyl Butoxide. In: Wexler P, editor. Encyclopedia of toxicology. 3rd ed. Cambridge, Massachusetts: Academic Press; 2014. p. 958–959. [CrossRef]