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Mitigation of organophosphate pesticide pollution in agricultural watersheds

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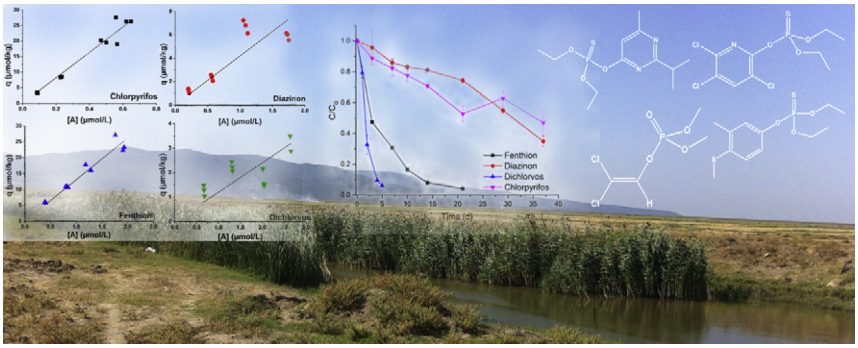
HIGHLIGHTS

- Higher k_{oc} values were observed in sediments with higher humic aromaticity.
- Higher pesticide biodegradation observed in sediments with higher humic content.
- Wetland hydroperiod likely affects pesticide mitigation.
- Optimum wetland design for mitigation differs among the studied pesticides.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption and biodegradation processes for four organophosphate pesticides (chlorpyrifos, diazinon, fenthion, dichlorvos) in wetlands and agricultural drains in Meric-Ergene Basin, Turkey have been investigated. K_{oc} (organic carbon normalized partition coefficient) values for all pesticides except diazinon were higher in more aromatic Pamuklu Drain sediments, indicating the possible influence of aromaticity on the extent of adsorption. The average half-lives of pesticides in Gala Lake sediments and Pamuklu agricultural drain sediments ranged from 2.25 to 69.31 days with chlorpyrifos exhibiting the slowest biotransformation rate and dichlorvos having the fastest biotransformation rate. The presence of humic substances and hydroperiod of wetlands have been identified as possible factors that affected the behavior of organophosphate pesticides in this study. The results from this study provide insight into the constructed wetland design offered for the mitigation of organophosphate pesticides in the basin.

1. Introduction

The widespread use of agricultural pesticides poses a big threat to the environment because of their toxic effects and bioaccumulation tendencies in non-target organisms (Schulz, 2004). Organophosphate

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pesticides are among the most widely used pesticides in the world (Singh and Walker, 2006). In Turkey, 33 million kg of pesticides are applied each year and 29% of it consists of insecticides (Tiryaki et al., 2010).

The Meric-Ergene basin is a sub-basin of the Meric transboundary river system located at the north-western part of Turkey. Water quality in the basin suffers from agricultural activities. Overall, 37.9% of the total area in the basin is agricultural land dominated by paddy fields providing 54% of the rice production in Turkey (Republic of Turkey Ministry of Agriculture and Forestry, 2008). Through surface runoff from treated fields, nonpoint source pollutants such as nutrients and pesticides reach downstream water bodies including Meric River, negatively impacting water quality as well as the overall biodiversity and productivity of the transboundary Meric Delta. In a previous study conducted in Gala Lake wetland, organophosphate pesticides such as azinphos-methyl, diazinon, dichlorvos, terbufos and malathion were detected at μg/L levels in the wetland water (Oterler, 2009). Given the hydrophobic nature of some of these insecticides, much higher levels of them can be expected to be present in wetland sediment. In 2013, The Turkish Ministry of Forestry and Water Affairs established a research group to study the impact of pesticides and herbicides on water quality and to set environmental standards on the usage of these compounds. Within the scope of these studies, a priority list of compounds has been prepared based on the past and current usage in Turkey. The organophosphate pesticides in this study (chlorpyrifos, diazinon, fenthion, dichlorvos) have been selected based on this list and their usage in the basin.

Natural treatment systems such as vegetated ditches and wetlands have been proposed as a mitigation option for organophosphate removal (Liu et al., 2019). Adsorption is the most important process in the short-term fate of hydrophobic organophosphate pesticides (Rogers and Stringfellow, 2009). After sorption equilibrium is reached, degradation processes become important in determining the ultimate fate of these compounds (Karpuzcu et al., 2013). It has been shown that microbial degradation is a major factor determining the fate of organophosphate pesticides in the environment (Liu et al., 2019; Yang et al., 2005). Organophosphate pesticides contain phosphoester linkages which are prone to hydrolysis. The biodegradation mechanism of these pesticides have been shown to be similar where the first step involves the hydrolysis of P-O-alkyl and P-O-aryl bonds. After this step, usually more soluble by-products with increased mobility are formed (Singh and Walker, 2006). The main by-product of chlorpyrifos (3,5,6-trichloro-2-pyridinol), the main by-product of diazinon (2-isopropyl-4-methyl-6-hydroxypyrimidine), the main by-product of fenthion (3-methyl-4-(methylthio)phenol) and the main by-product of dichlorvos (trimethyl orthophosphate) are much more soluble than their parent compounds (Druzina and Stegu, 2007). A variety of bacteria capable of degrading organophosphate pesticides have been isolated and listed. Examples of these include *Pseudomonas* spp., *Flavobacterium* spp., *Agrobacterium* spp., *Arthrobacter* spp., *Enterobacter* spp. and *Bacillus* spp. (Singh and Walker, 2006; Ning et al., 2010; Liu et al., 2019). There is a clear need for a better understanding of the fate and transformation mechanisms of these pesticides in wetland systems of the Meric-Ergene basin to mitigate their environmental impacts and protect downstream water bodies.

The main objective of this study was to investigate two important fate processes- adsorption and biodegradation- of organophosphate pesticides in wetlands receiving agricultural drainage and to determine the effectiveness of constructed wetlands as Best Management Practices (BMPs) for pesticide mitigation in the basin. With this information, optimized constructed wetland design and management strategies for organophosphate pesticide removal can be developed and potential risks to humans and aquatic organisms posed by these contaminants can be minimized.

2. Materials and methods

2.1. Study area and sampling locations

The Meric basin, one of the major river systems of the eastern Balkans, is shared by Bulgaria, Greece and Turkey. The Meric transboundary river system rises in Bulgaria and flows along the Turkish-Greek border into the Aegean Sea. The Meric Delta area is a significant ecological site, listed in Class A of International Wetlands and protected under the RAMSAR Convention (Kramer and Schellig, 2011; Kubas et al., 2010). In 1991, Gala Lake wetland and its 2360 ha surrounding area has been declared as a Nature Conservation Area. Later in 2005, the wetland gained National Park status (Kubas et al., 2010). Gala Lake and other wetlands in the basin have been severely degraded by agricultural practices, which makes them suitable locations to study fate of pesticides. Gala Lake and one typical agricultural drain site (Pamuklu Drain) have been selected as sampling locations for this study (Fig. 1). Land use in the vicinity of the sampling locations and the former wetland areas are also shown in Fig. 1. Gala Lake wetland has a surface area of 560 ha with an average water depth of 1 m. During wet seasons (late Fall and Winter), the depth can increase up to 2 m, while it can drop to 0.5 m during dry seasons (late Spring and Summer). The pH values in the wetland water have been reported to vary seasonally between 7.95 and 8.65 (Oterler, 2018). The wetland has outlets to the Meric River (118.7 m^3/s) and through Dalyan Lake to the Aegean Sea (45 m^3/s). Based on these flowrates, the average hydraulic retention time in the wetland is 0.4 days (Oterler, 2009). Dominant aquatic plants in the wetland are *Typha latifolia* and *Phragmites australis* (Oterler, 2018). Pamuklu Drain does not have a dense vegetation cover inside the drain, only small patches of *Phragmites australis* has been observed during sampling. During dry seasons, the flowrate in the drain depends on the amount of agricultural runoff.

2.2. Sample collection

Sediment and water samples from Gala Lake and Pamuklu Drain were collected two times during irrigation season. Approximately 500 g of sediment samples and 500 mL of water samples were collected from each site. A stainless steel shovel and wide mouth glass jars were used in sample collection. The shovel was washed with detergent (Alconox Inc.) and rinsed thoroughly with deionized water and subsequently with wetland water before each use. Samples were transported to the laboratory in a cooler on ice on the same day and kept at 4 °C in the dark until analysis. Experimental analyses were initiated within 3 days after sampling.

2.3. Sample characterization

Organic carbon content (f_{oc}) of the sediment samples was analyzed by a Shimadzu TOC - V series SSM-5000 A type TOC analyzer. Calibration was carried out using D-glucose. TOC (Total Organic Carbon) measurements in water samples were also carried out by the same TOC analyzer. Water samples were passed through 0.45 μm filters before analysis. pH measurements were made with a benchtop pH-meter (Hanna Instruments Inc., USA). Results of these analyses are given in Table S1 (Supplementary information).

UV–visible absorption spectra of the water samples were measured with a HACH-Lange DR 5000 type spectrophotometer and can be seen in Figs. S1 and S2 (Supplementary information).

2.4. Experimental design

2.4.1. Adsorption experiments

Four organophosphate pesticides (chlorpyrifos, diazinon, fenthion, dichlorvos) commonly used in the basin were selected for analysis in this study. Prior to the experiments, sediments samples were extracted

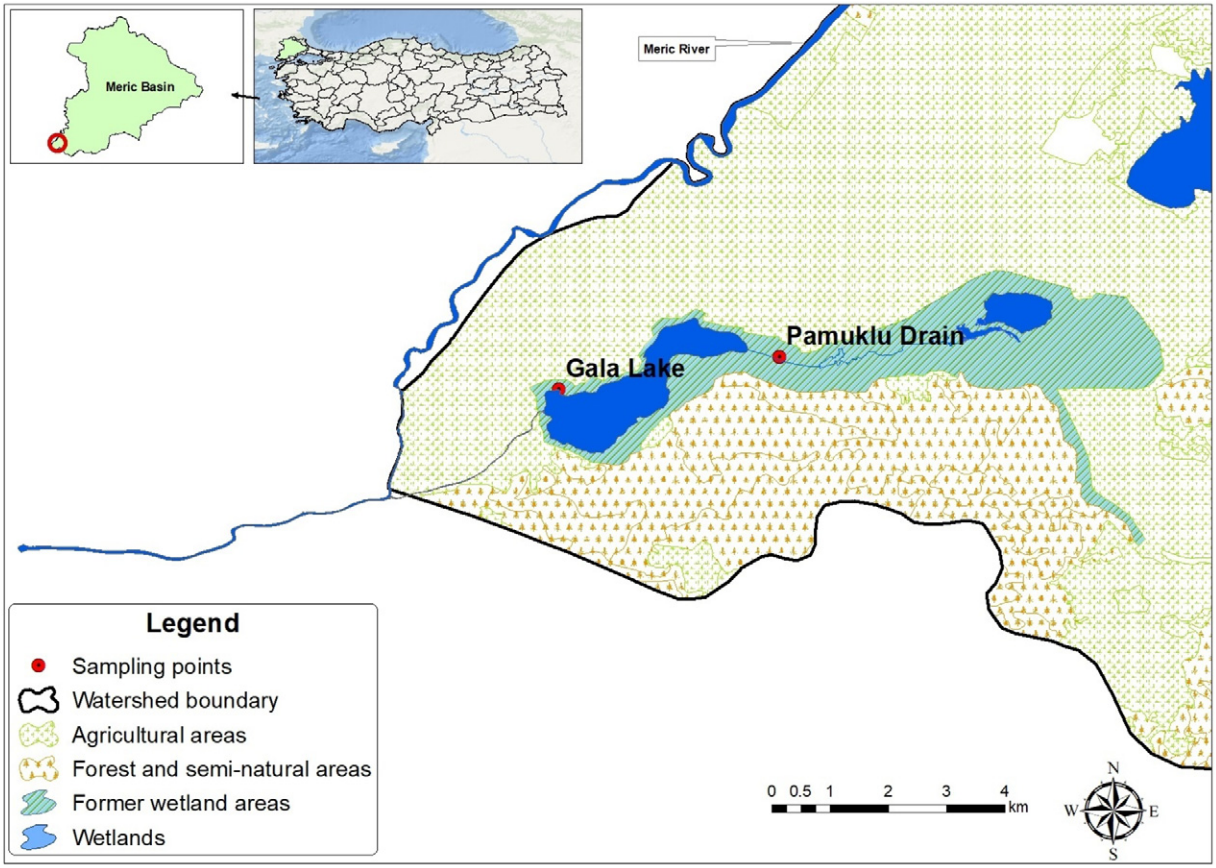

Fig. 1. Map of the study site showing sampling points and land use.

and analyzed to make sure they did not contain background OP pesticide concentrations. The adsorption of pesticides to sediments was measured using a batch equilibrium method (Wu and Laird, 2004). One gram sediment samples were placed in 50 mL glass centrifuge tubes with Teflon-lined screw caps. Aqueous pesticide solutions of different concentrations (0.25, 0.5, 0.75 and 1.0 mg/L) in 25 mL aliquots were prepared for each pesticide and added to the centrifuge tubes. Apart from these tubes, control tubes containing only the same concentration of pesticides without sediment were prepared. The tubes prepared in triplicate were vortexed to wet the adsorbent, then placed in a shaking incubator where they were kept at 25 °C for 16 h in the dark. At the end of 16 h, tubes were centrifuged at 4500 rpm for 15 min. To measure the concentration of pesticides remaining dissolved in the liquid phase in the tubes, 10 mL of the supernatant were transferred to 16 mm × 125 mm glass extraction tubes for extraction. Pesticides were preconcentrated by liquid-liquid extraction. Considering the relatively polar structure of dichlorvos, it was extracted using ethyl acetate. 10 mL of supernatant was extracted with 2 mL of ethyl acetate for 2 h on a rotating tube shaker (Thermo Scientific Inc., USA). For the rest of the pesticides, 10 mL sample aliquots were amended with 2 mL of hexane and extracted on the rotating shaker for 2 h. At the end of the extraction period, approximately 1 mL of solvent extract was transferred to a clean vial, evaporated in dry air, resuspended in distilled water and transferred to vials for HPLC analysis. Average extraction recovery efficiency was 72 ± 3% for diazinon, 80 ± 10% for chlorpyrifos, 97 ± 1% for fenthion and 82 ± 6% for dichlorvos. Pesticide concentrations were measured by a Shimadzu SPD-M20A HPLC equipped with a multiwavelength UV absorbance detector. An Inertsil ODS-3 V column (25 cm × 4.6 mm; 5 μm) was used for chromatographic separation. More technical details of the HPLC analysis are described in Supplementary information. In order to obtain the adsorbed pesticide concentrations on the sediments, the measured pesticide concentration remaining in the supernatant was subtracted from the average pesticide concentration remaining in the control tubes. The mass of pesticide adsorbed per mass of sediment, q (μmol kg^{-1}) was subsequently calculated. Adsorption isotherms were created by plotting the aqueous pesticide concentrations at equilibrium (μmol L^{-1}) on the x-axis and q (μmol kg^{-1}) on the y-axis. Adsorption coefficients K_d (L/kg) were determined by linear regression analysis.

2.4.2. Aerobic biodegradation experiments

Biodegradation rates of pesticides in sediments were measured by a standardized aerobic biodegradation assay (Karpuzcu et al., 2013). Sediment samples were homogenized, placed in 500-mL Erlenmeyer flasks and spiked with pesticides such that the initial concentration would be 100 μg/g for each pesticide. Control flasks without sediments were prepared to obtain abiotic hydrolysis rates under experimental conditions. Formalin amended sediment controls were prepared to distinguish between biotic and abiotic degradation and to account for any losses from mechanisms other than biodegradation. All flasks were sealed and placed in a shaking incubator where they are kept at 25 °C in the dark. At days 0, 1, 7, 14, 21, 28 and 37, triplicate 10 mL aliquots of slurry from the flasks were taken and transferred to 16 mm × 125 mm glass culture tubes for solvent extraction with the same method described previously. After the extraction of the slurry, sodium chloride has been added to the tubes to facilitate phase separation. Average extraction recovery efficiency in Gala Lake sediments was 71 ± 2% for diazinon, 98 ± 4% for chlorpyrifos, 99 ± 4% for fenthion and 75 ± 8% for dichlorvos. In Pamuklu Drain sediments, average extraction recovery efficiency was 90 ± 18% for diazinon, 93 ± 3% for chlorpyrifos, 96 ± 4% for fenthion and 85 ± 12% for dichlorvos. Pesticide concentrations were measured by HPLC as described previously. The experiments were stopped after 37 days, when biodegradation slowed down and the degradation curves reached a plateau for relatively slow degrading chlorpyrifos and diazinon. A first order decay model was used to estimate the biodegradation rate constants k_{deg} (d^{-1}) of the pesticides according to the Eq. (1), where C_t is the pesticide concentration (μg/g) at a given time, t (d) and C_0 is the initial pesticide concentration.

$$C_t = C_0 e^{-k_{\deg} t} \tag{1}$$

Half-lives ($t_{1/2}$) were calculated using Eq. (2).

$$t_{1/2} = \frac{\ln(2)}{k_{\deg}} \tag{2}$$

Finally, degradation rates obtained from control flasks were subtracted from degradation rates observed in biodegradation flasks to correct for abiotic degradation rates. More details about the experimental setup is presented in the Supplementary information (SI).

3. Results and discussion

3.1. Adsorption experiments

For each pesticide, adsorption isotherms were created for both field sites by plotting values of q (μmol kg^{-1}) versus the concentration at equilibrium (μmol L^{-1}) (Fig. 2a, b). Linear adsorption coefficients K_d (L/kg) determined by regression are listed in Table 1. K_d values derived for chlorpyrifos were 40.77 L/kg and 76.61 L/kg for Gala Lake and Pamuklu Drain sediments, respectively. These values were within the range reported in literature which ranged from 13.4 to 1820 L/kg (Gebremariam et al., 2012; Howard, 1991; Rogers and Stringfellow, 2009; Wu and Laird, 2004). Diazinon had a higher K_d value in Gala Lake sediments (4.19 L/kg) compared to the Pamuklu Drain sediments (2.64 L/kg). K_d values for diazinon ranging from 0.84 to 19.72 L/kg have been reported in different studies (Arienzo et al., 1994; Bondarenko and Gan, 2004; Hernández-Soriano et al., 2007) which are in agreement with the results obtained in this study. Fenthion had a K_d range of 10.75 to 13.07 L/kg, well within the range of values reported in literature (1.4 to 348.1 L/kg) (Motoki et al., 2016; Weber et al., 2004). As the most hydrophilic among the studied pesticides (log k_{ow} = 1.16, Table S1, Supplementary information), dichlorvos had the lowest K_d values among the pesticides analyzed, with a K_d value of 1.20 L/kg for Gala Lake and 2.59 L/kg for Pamuklu Drain sediments. Values ranging from 0.88 to 3.10 L/kg have been reported for dichlorvos in previous studies (Sánchez-Camazano and Sánchez-Martín, 1994). The ranking of pesticides according to their K_d values were consistent with their hydrophobicity based on their log k_{ow} values (Table S1, Supplementary information).

To facilitate comparison among soils with different organic carbon contents, the organic carbon normalized partition coefficient K_{oc} (K_d divided by the organic carbon content, f_{oc} of the soil) has been proposed (Ahmad et al., 2001; Schwarzenbach et al., 2003). However, the variation of K_d among soils with the same organic carbon content and the variation of K_{oc} among different soils in various reports indicated that the quality and source of the organic carbon was also an important factor affecting adsorption (Ahmad et al., 2001; Schwarzenbach et al., 2003). Ahmad et al. (2001) reported that K_{oc} values for nonionic pesticides strongly correlated with the aromaticity of soil organic matter. In the present study, obtained K_{oc} values were also different for the adsorption of pesticides to Gala Lake and Pamuklu Drain sediments. Specific UV absorbance or SUVA254 (UV absorption at 254 nm divided by dissolved organic carbon (DOC) concentration), has been used as a measure of dissolved organic matter (DOM) aromaticity for a large number of humic substance isolates (Weishaar et al., 2003). SUVA254 values measured for Gala Lake and Pamuklu Drain were 1.56 and 2.05 L cm^{-1} mg^{-1}, respectively. The higher SUVA254 value of Pamuklu Drain indicates a higher aromatic content of DOM in its water and likely a higher aromaticity of its sediments. Previous studies have shown that aquatic humus can be released from lake sediments into the water column, while allochthonous DOM in the water column can also be transferred to the lake sediments through sedimentation (McKnight and Aiken, 1998; von Wachenfeldt and Tranvik, 2008). All of the pesticides except Diazinon exhibited a higher K_{oc} value in Pamuklu Drain sediments, indicating that aromaticity may possibly influence the extent of adsorption of organophosphate pesticides to sediments (Table 1). For chlorpyrifos, K_{oc} values ranged from 1836 to 4788 L/kg, similar to values reported in literature (Mackay et al., 2006), while diazinon had a K_{oc} range between 165 and 189 L/kg. Values of K_{oc} ranging from 26.6 to 1589 L/kg have been reported in different studies for diazinon (Alfonso et al., 2017; Hernández-Soriano et al., 2007; Mackay et al., 2006). K_{oc} values derived for fenthion and dichlorvos ranged from 589 to 672 L/kg and 54 to 162 L/kg, respectively. In previous studies, K_{oc} values between 499 and 1500 L/kg have been reported for fenthion (Mackay et al., 2006; Zambonin et al., 2002), while values ranging from 27.5 to 151 L/kg have been reported for dichlorvos (Mackay et al., 2006; Worrall et al., 2000). Both results were consistent with previously reported data.

3.2. Aerobic biodegradation experiments

The average half-lives of pesticides measured at the Gala Lake sediments and Pamuklu agricultural drain site sediments under aerobic conditions ranged from 2.25 to 69.31 days with chlorpyrifos exhibiting the slowest biotransformation rate and dichlorvos having the fastest biotransformation rate (Table 2, Fig. 3). For chlorpyrifos, half-lives in Gala Lake and Pamuklu Drain sediments were 69.31 and 63.01 days, respectively. In previous studies, chlorpyrifos half-lives ranged 58 to 144 days in constructed wetland sediments (Budd et al., 2011) and reported to be 27 to 77 days in nursery recycling pond sediments (Lu et al., 2006). The rate of abiotic chlorpyrifos hydrolysis was 0.013 d^{-1}, which corresponds to a half-life of 53.32 days, and is in agreement with previously reported data (Liu et al., 2001; Liu et al., 2019; Mackay et al., 2006).

Diazinon exhibited a faster biodegradation rate at Pamuklu Drain sediment with a half-life of 43.32 days compared to a half-life of 53.32 days in Gala Lake sediment. In previous studies, half-lives ranging from 20 to 100 days have been reported for diazinon dissipation (Aggarwal et al., 2013; Mackay et al., 2006). It should be noted, however, most of these studies did not distinguish between abiotic hydrolysis and biodegradation. Under the experimental conditions of the current study, abiotic hydrolysis half-life of diazinon was 115 days, comparable to the values reported in literature (Mackay et al., 2006).

Fenthion degradation was fast, with a half-live of 2.47 days in Pamuklu Drain sediment and 5.55 days in Gala Lake sediment (Table 2, Fig. 3). These were within the wide range of values reported in literature (1.8 to 93 days) (Cripe et al., 1989; Mackay et al., 2006). Compared to its biodegradation rate, abiotic hydrolysis of fenthion was much slower with a half-life of 138 days, suggesting that it has a negligible effect on the overall dissipation of fenthion.

Dichlorvos degraded rapidly in both sediments, with half-lives 1.97 days and 1.74 days for Gala Lake and Pamuklu Drain sediments, respectively. Half-lives ranging from 0.5 to 16 days have been reported previously (Gan et al., 2006; Howard, 1991; Mackay et al., 2006; Worrall et al., 2000). Dichlorvos had an abiotic hydrolysis half-life of 2.88 days, indicating that hydrolysis plays an important role in dichlorvos degradation. At pH 7.0 and 22 °C, similar to the conditions in the present study, abiotic hydrolysis of dichlorvos was previously reported as 2.9 days (Tomlin et al., 1994).

All of the pesticides included in this study had faster biodegradation rates in Pamuklu Drain sediments compared to Gala Lake sediments. As mentioned previously, Pamuklu Drain sediments had a lower organic carbon content but had a more aromatic character. The presence of humic substances might have increased the observed biodegradation rates by acting as a carrier medium facilitating access of microorganisms

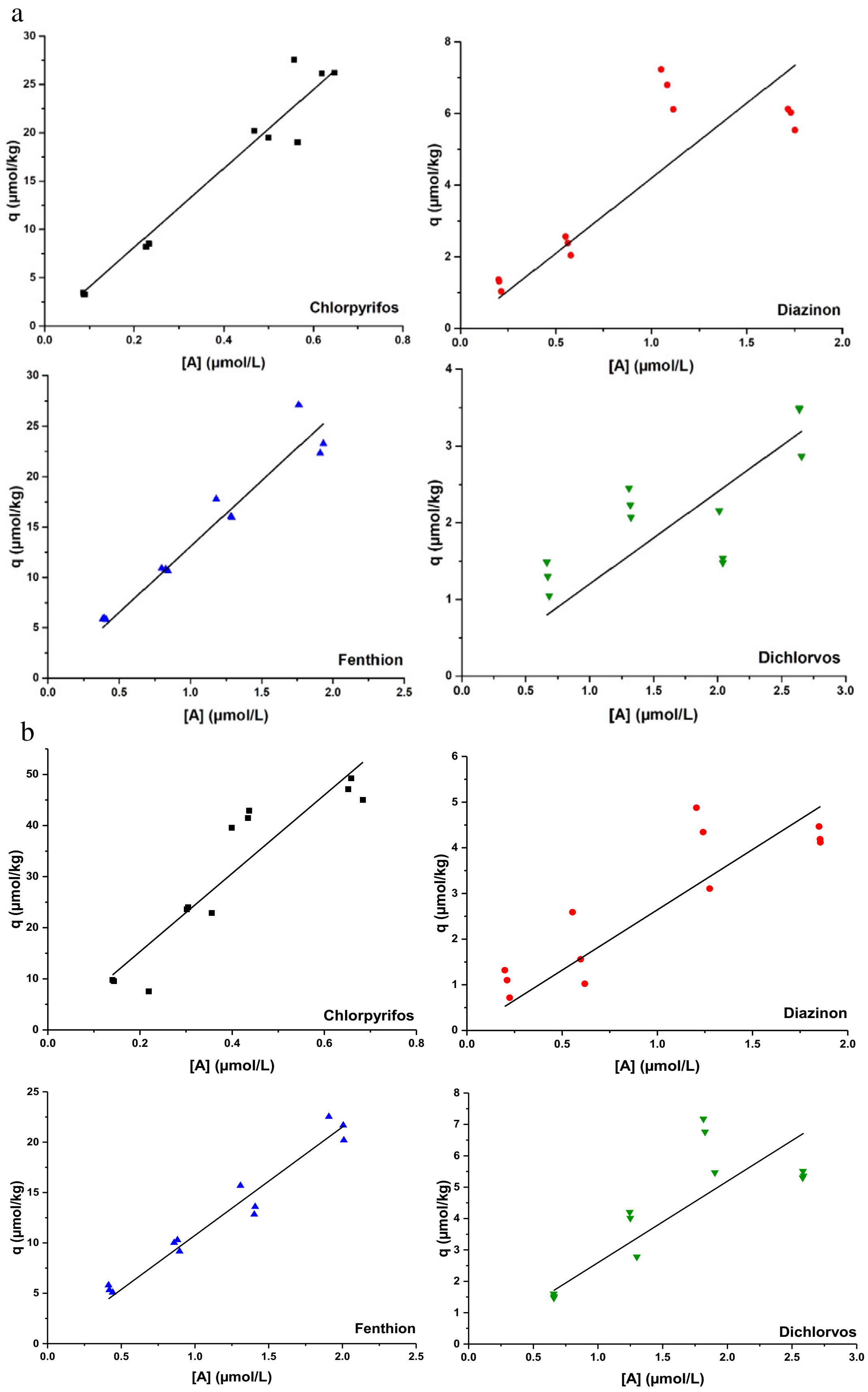

Fig. 2. a. Linear Adsorption Isotherms of the organophosphate pesticides in Gala Lake sediments. b. Linear Adsorption Isotherms of the organophosphate pesticides in Pamuklu Drain sediments.

Table 1
Adsorption coefficients for field sediments (R^2 represents coefficient of determination).

Pesticide	Gala Lake Sediment (f_{oc} = 2.22%)			Pamuklu Drain Sediment (f_{oc} = 1.6%)		
	K_d (L/kg)	K_{oc} (L/kg)	R^2	K_d (L/kg)	K_{oc} (L/kg)	R^2
Chlorpyrifos	40.77	1836	0.95	76.61	4788	0.85
Diazinon	4.19	189	0.67	2.64	165	0.71
Fenthion	13.07	589	0.94	10.75	672	0.95
Dichlorvos	1.20	54	0.41	2.32	145	0.60

to the pesticides. The effect of humic substances and aromaticity on biodegradation of hydrophobic organic chemicals such as polycyclic aromatic hydrocarbons (PAHs) have been investigated in several studies (Cai et al., 2017; Ortega-Calvo and Saiz-Jimenez, 1998; Smith et al., 2009; Tejeda-Agredano et al., 2014). These studies reported the ability of humic substances acting as surfactants, increasing the bioavailability of PAHs such as phenanthrene and thereby enhancing their biodegradation. It has also been shown that the biodegradation of the triazine pesticide atrazine was facilitated when it was sorbed onto clay-humic acid complexes (Besse-Hoggan et al., 2009). This phenomenon has only recently been studied for organophosphate pesticides. (Rong et al., 2019) showed that the interfacial reactions on clay surfaces increased biodegradation rates of methyl parathion and concluded that sorption of both bacteria and the pesticide on clay surfaces plays an important role in biodegradation. Thus, the effect of humic substances on the biodegradation of other organophosphate pesticides also warrants further study.

Another factor that might have partially affected biodegradation of organophosphate pesticides in the present study is the exposure history of the sediments to the pesticides. Pamuklu Drain sediments had a more direct exposure to the organophosphate pesticides compared to the downstream Gala Lake. There have been studies showing that sites with a higher pesticide exposure history had higher pesticide biodegradation rates through microbial acclimation and microbial community shifts (Guijarro et al., 2018; Singh et al., 2003).

Hydroperiod of wetlands have also been recognized as a factor affecting microbial community structure in wetland sediments (Ma et al., 2018). Natural systems, especially wetlands are often in a highly dynamic state with respect to redox conditions and contain mixed zones with different oxidation states. While wetlands operated under permanently flooded conditions can develop anoxic and anaerobic zones in their sediment layers, aerobic zones exist near the vicinity of the plant roots as a result of oxygen transfer through hollow stems of the aquatic emerging plants (Kadlec and Wallace, 2009). Imposing strictly anaerobic conditions on such sediments would result in much slower biodegradation rates than the rates obtained under aerobic conditions (Karpuzcu et al., 2013). In agricultural drain sediments that are occasionally exposed to the atmosphere, conditions more conducive to aerobic biodegradation can be expected. Further research is needed to determine the optimum hydroperiod that would accelerate organophosphate pesticide biodegradation.

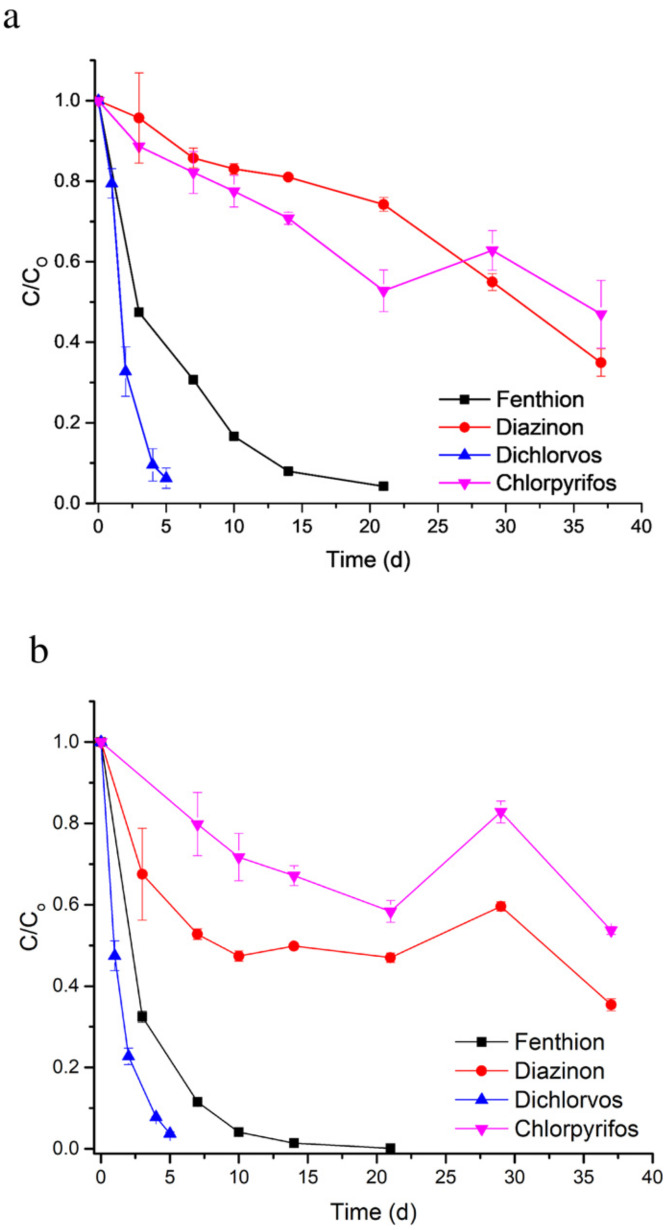

Fig. 3. a. Biodegradation curves of the organophosphate pesticides in Gala Lake sediments (error bars represent standard error of the mean). b. Biodegradation curves of the organophosphate pesticides in Pamuklu Drain sediments (error bars represent standard error of the mean).

Table 2
Biodegradation rates and half-lives of pesticides in Gala Lake and Pamuklu Drain sediments (R^2 represents coefficient of determination).

Pesticide	Gala Lake Sediment			Pamuklu Drain Sediment		
	K (d^{-1})	$t_{1/2}$ (d)	R^2	K (d^{-1})	$t_{1/2}$ (d)	R^2
Chlorpyrifos	0.010	69.31	0.84	0.011	63.01	0.96
Diazinon	0.013	53.32	0.87	0.016	43.32	0.71
Fenthion	0.125	5.55	0.97	0.281	2.47	0.99
Dichlorvos	0.352	1.97	0.98	0.398	1.74	0.99

Mitigation of organophosphate pesticide pollution using free water surface (FWS) constructed wetlands can be a viable option for the protection of the Meric-Ergene Basin. Gala Lake wetland currently serves as a buffer for the agricultural drainage waters that pass through the lake before reaching the Meric River. To protect the Gala Lake National Park and its wildlife, agricultural drainage water should be redirected to properly designed constructed wetlands before reaching surface waters. The hydrophobic pesticides chlorpyrifos and fenthion with high K_{oc} values will be expected to sorb on sediment and plant surfaces upon entering the constructed wetland system. The role of both sediment and plant surfaces in retention of these pesticides have been documented in previous studies (Moore et al., 2002; Sahin and Karpuzcu, 2019). Moderately hydrophobic diazinon will be present in both dissolved and sorbed phase. Previous studies have shown that in the presence of plants, diazinon will preferably be sorbed to the plant surfaces rather than sediments (Moore et al., 2007; Sahin and Karpuzcu, 2019). Hence, wetlands with high vegetation density and vegetated filter strips will probably be more effective on diazinon mitigation. Dichlorvos is the most hydrophilic and soluble pesticide in this study and will be present mostly in soluble form in water. Hence, hydraulic retention time (HRT) of the wetland will be an important factor for dichlorvos mitigation. The current HRT in Gala Lake (0.4 d) is not long enough for an effective dichlorvos removal. In a properly designed wetland with an HRT of at least a few days, dichlorvos will rapidly hydrolyze and its downstream impact will be minimized.

4. Conclusion

In this study, adsorption and biodegradation processes for organophosphate pesticides in wetlands have been investigated. K_{oc} values for all pesticides except Diazinon was higher in more aromatic Pamuklu Drain sediments, indicating the possible influence of aromaticity on the extent of adsorption. Biodegradation half-lives ranged from 2.25 to 69.31 days. The fact that all of the pesticides had faster biodegradation rates in Pamuklu Drain sediments with more aromatic character suggest the positive effect of humic substances on biodegradation of organophosphate pesticides included in this study. Further research is needed to determine if a similar effect is present for other organophosphate pesticides. The results from this study provide insight into the constructed wetland design offered for the mitigation of organophosphate pesticides in the basin. In addition to laboratory studies, establishment of models that are capable of simulating the fate and transport of organophosphate pesticides at basin scale is important to determine measures to be taken under different management scenarios.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.136261.

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