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PYRETHROIDS LEVELS IN PADDY FIELD WATER UNDER MEDITERRANEAN CONDITIONS:MEASUREMENTS AND DISTRIBUTION MODELLING

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Abstract

The cultivation of rice (Oriza sativa L.) under Mediterranean conditions regularly requires the use of treated wastewater due to shortage of freshwater. As a consequence, the intensification of rice production to supply the uprising demand of grain could break the stability between agriculture and environment. In this work, we studied the occurrence and distribution of pyrethroids in surface water and groundwater collected during two periods (flooding and dry soil conditions) in paddy fields located in the Spanish Mediterranean coast. Pyrethroids were detected at concentrations ranging from 14 to 1450 ng L-1 in surface water and from 6 to 833 ng L-1 in groundwater. The results obtained were evaluated statistically using principal component analysis, and differences between both sampling campaigns were found, with lower concentrations of the target compounds during the flooding sampling event. Moreover, a geographic information system program was used to represent a model distribution of the obtained results, showing wastewater treatment plants as the main sources of contamination and the decrease of pyrethroids during flooding condition when water flows over the paddy fields. The impact of these compounds on water quality was discussed.

Keywords Groundwater, Surface water, GIS, Paddy fields, Pyrethroids, WWTPs

Introduction

Water is the main limiting factor to produce rice in Mediterranean countries because they are located in arid or semiarid regions. Thus, due to the shortage of freshwater, wastewater has been used in the last decades to fulfill water needs of rice cultivation (Rodríguez-Liébana et al. 2014). The most prevalent risks associated with the use of these poor quality waters are: pH, salinity, pathogens, heavy metals and organic chemicals (Albalawneh et al. 2015).

The presence of pesticides in irrigation water is one of stressors that aquatic organisms face (Smiley et al. 2014), pointing out the interest of the relationship between biodiversity and agriculture (Swift et al. 2015). In particular, the use of pyrethroids (PYs) has increased in the last years as a replacement for organophosphates, which had already substituted organochlorine compounds, due to their relatively lower mammalian toxicity and lower environmental persistence. Although the application of PYs in rice fields is scarce and needs individual authorization, they are extensively used in urban and industrial areas and livestock farms to control pests such as mosquitoes and lice. Several studies report that these compounds are not completely eliminated in conventional wastewater treatment plants (WWTPs) (Campo et al. 2013; Weston et al. 2013), and thus they can be introduced into the environment through WWTPs effluents.

Pyrethroids have raised concern because they may have a negative impact on the environment, primarily on water bodies, due to their proven toxicity to arthropods and fish (Solomon et al. 2001; Weston et al. 2005) and to their bioaccumulation potential in fish (Corcellas et al. 2015).Therefore, vulnerable areas such as rivers, lakes, wetlands, aquifers and other sources of freshwater are assessed in the environmental exposure to these insecticides and are the focus of their aquatic risk assessment (Hendley et al. 2001).

Although there are available data on the presence of PYs in surface water (Feo et al. 2010a; Kuivila et al. 2012; Moschet et al. 2014; Pistocchi et al. 2009), there is no information on the occurrence and fate of these compounds in paddy fields under flooding conditions in a Mediterranean area irrigated with WWTPs effluents. Moreover, groundwater has received little attention so far (McManus et al. 2014) and this could be explained due to the more difficult sampling of groundwater and because these compounds are very hydrophobic, with log Kow 5–6, and therefore, lower concentrations than in surface water could be expected. However, groundwater resources are an important supply of drinking and irrigation water in many countries and their contamination by a large range of pesticides has been reported (Hildebrandt et al. 2007; McManus et al. 2014), making necessary the determination of these compounds to assess its quality. To the best of our knowledge, this is the first time that PYs are monitored in groundwater and surface water from an intensified rice production area.

The aim of this study was to assess the levels of pyrethroids in surface water and groundwater collected during two sampling periods (flooding and dry soil conditions) in a paddy field area irrigated in part with WWTPs effluents. Moreover, this paper assesses their spatial variations in the studied area by statistical interpretation of principal component analyses (PCA) and their distribution using a geographic information system (GIS) program, as well as their impact on groundwater quality.

Material and methods

Standards and reagents

Ethyl acetate, hexane and acetonitrile were purchased from Scharlab (Barcelona, Spain). Sodium azide (≥99.5 %) to preserve water samples was purchased from Sigma (Steinheim, Germany).

Pesticides resmethrin (RESM), bifenthrin (BIFE), fenpropathrin (FENP), λ- cyhalothrin (CYHA), permethrin (PERM), cyfluthrin (CYFL), α-cypermethrin (CYPE), τ-fluvalinate (FLUV), esfenvalerate (ESFE) and deltamethrin (DELT) (purity > 99 %) were supplied by Riedel-de Haën (Seelze, Germany), and trans-permethrin-D6 (PERM-D6) (purity > 99 %), used as surrogate standard, was supplied by Symta (Madrid, Spain).

A mixed stock solution of 1000 ng mL^{-1} containing all analytes was prepared by dilution with acetonitrile of the individual stock solutions. A working mixture solution at 100 ng mL^{-1} was prepared weekly by dilution with acetonitrile of the mixed stock solution. A solution containing the surrogate standard was prepared in acetonitrile at the same concentration as the working mixture solution. All solutions were stored in the darkness at 4 ºC up to 8 weeks.

Area of study

This study was carried out in the Natural Park of Albufera of Valencia, Spain (Fig. 1) that covers 211 km^2 of which 23 km^2 are lake. The lake is surrounded by paddy fields 70 % of the park, which is also surrounded by small and medium enterprises (SME) and urban areas, including Valencia, the third largest city in Spain (1.5 million of inhabitants).

The area of study was formed due to sediment depositions of the Turia and Jucar Rivers, and because of the need to increase the production area of rice, farmers started to regain land to the lake, decreasing its size during the last century. Nowadays, the hydrological cycle of the park is adapted to produce rice but due to the insufficient contribution of freshwater from both rivers regained water from WWTPs is being used. Nowadays, the main sources to irrigate paddy fields are the Turia and Jucar Rivers and the two WWTPs and water enters to the fields situated at the highest levels. The fields are set up with a gently slope in direction to the lake and from the highest levels water flows through the fields by gravity until it reaches the lake (Fig. 1).

The hydrological cycle (Fig. ESM. 1) starts when the lake reaches its maximum level, flooding the paddy fields (November - January). In January, the gates, which connect the lake with the Mediterranean Sea, are opened and the fields are drained allowing the lake to reach its normal water level. From the end of February till May, paddy fields are dried and they can be plowed and prepared prior to sowing. From May to September (rice growing season), the paddy fields are completely flooded. In September, paddy fields are drained again to allow the heavy machinery to harvest the grain, and then the rice cultivation cycle will restart.

Following the Soil Taxonomy classification (Soil Survey Staff 2014), soils are defined as Entisols and Aridisols (Moreno-Ramón et al. 2015) and they show a hydromorphic character as they are flooded most of the time (Fig. ESM 1). These soils are carbonated, saline and show a moderate surface organic carbon content due to the rice management (incorporation of post-harvest residues) (Aznar et al. 2016a). The aquifer is formed by two permeable levels of detrital Quaternary materials and Miocene sands (Duran et al. 2005), having two aquifers (one superficial, object of this study, and other lower). The upper section is formed by an alternation of sands and Quaternary gravels interbedded in a silty-clay formation that reaches a maximum thickness of 200 meters. The lower section acts as impermeable substrate with a thickness of 600 meters. This section shows a lower transmissivity and is made up of detritus with sandstone, calcarenite and bioclastic limestone, mixed with a marl-clay formation. Aquifer recharge system is due mainly to the surrounding area by direct precipitation and transmission between adjacent aquifers (Duran et al. 2005). In addition, the aquifer is in direct contact with the Mediterranean Sea (Gimenez-Forcada, 2014).

Water sampling

Surface water (SW) (0.1 L) was sampled in mid-channel at 0.5 m of depth of the most important channels and influents of the Natural Park. Groundwater (GW) (0.1 L) was collected from a network of sealed piezometers laid in the study area installed in 2010 (Fig. 1). Piezometers were 2 meters long tubes of Ppolyvinyl chloride (PVC) in contact with soil and the aquifer by means of eight perforations of 5 mm made in the bottom of the tube. The piezometer installation process was carried out according to the USDA guidelines (Sprecher, 2008).

Water samples were collected using a stainless barrel and placed in amber glass bottles. Sodium azide was added at 0.5 g L^{-1} immediately after sampling to inhibit potential biological activity (with no interference during the analyses). Samples were maintained in darkness at 4 ºC and transported to the laboratory. Once in the laboratory, samples were filtered through 0.7 µm glass fiber filters (Whatman, Maidstone, UK) and stored at -8 ºC until analysis within two weeks of collection. Water samples were collected at two different events, in March (dry soil conditions) before the rice cycle started and in July (flooded soil conditions), during the rice growing season. A total number of 34 groundwater and 23 surface water samples were collected at each sampling event (Table ESM 2-5). These samples were georeferenced with a virtual reference station (Leica GPS 1200) that supplied the universal transverse mercator (UTM) coordinates (Table ESM 2-5)

Water analysis

The extraction of the target pesticides from water samples was carried out by ultrasonic assisted liquid-liquid extraction. A 20 mL aliquot of filtered water was shaken intensively by hand for 1 min and sonicated twice at room temperature for 15 min with 5 mL of ethyl acetate-hexane (90:10, v/v). Prior to the extraction, the surrogate standard at 100 ng L^{-1} was added to all samples. The combined extracts were collected in 10 mL graduated tubes, evaporated until dryness and reconstituted to 0.1 mL with acetonitrile before the GC-MS analysis.

A concentration factor of 200 was obtained with the developed method, allowing the use of a low sample volume and obtaining limits of detection in the range of ng L^{-1}. In order to evaluate the method developed for the detection of insecticides in water, different quality parameters were studied: recoveries, reproducibility, limits of detection and quantification, linearity and sensitivity following SANCO guidance (2013). The analytes were added in tap water at three levels (500, 100 and 20 ng L^{-1}) to four sample replicates, and the recoveries obtained ranged between 73 and 108 % with relative standard deviations < 8 % (Table 1). Limits of detection (LODs) and quantification (LOQs) of the developed method were determined using ten replicates of tap water, spiked at 5 ng L^{-1}. Low LODs, ranging from 0.2 to 5.4 ng L^{-1} were obtained due to the high selectivity and sensitivity of GC-MS that allowed the detection of pesticides at trace levels in water samples (Table 1). A multipoint calibration curve with five standard solutions at different concentration levels (from 5 to 2000 ng L^{-1}) and surrogate standards at 100 ng L^{-1} for all levels was used. A good linearity of the calibration curves was obtained in the studied range with $R > 0.999$ for all compounds.

Statistical and geostatistical analysis

A standard statistical analysis was carried out to study the levels of pesticides in surface water and groundwater using STATGRAPHIC CENTURION. To study the distribution of the pesticides, PCA was used, as one of the best tool to study diffuse contamination and patterns from data obtained in large-scale monitoring (Figs. 2, 3) (Hildebrandt et al. 2008). PCA is a technique that recognizes pattern and attempts to explain the variance of a large set of correlated variables by transforming them into a smaller set of independent variables (Monica and Choi, 2016). The PCA was performed with those pesticides that presented a high detection rate (CYFL, CYPE and ESFE) in surface water (S) and groundwater (G). To create the matrix, a pretreatment of the data was necessary. Pesticide residues at levels < LOQ were converted into numerical values by adding a value of half their LOQ (Farnham et al. 2002).

In order to study the distribution of contaminants a geostatistical analysis model was carried out. ARCGIS 9.3 software and the BMEGUI module were used and the cartography was performed by the Bayesian Maximum Entrophy (BME) methodology, which allowed a complete stochastic description of those non-sampling areas (Money et al. 2009). BME maps showed gentle transitions between the different mapping units which reflected the normal behavior of continuous variables like water contaminants (Fig. 4).

Results and discussion

Ten pyrethroids were determined in surface water and groundwater samples collected in two sampling periods, flooded and dry soil conditions, from paddy fields of the Natural Park of Albufera. Table 2 summarizes the overall results obtained, showing the range of concentrations found and the detection frequencies for each compound. The complete set of concentration values together with water physical–

chemical properties (electrical conductivity (EC) and pH) and the coordinates of points sampled are shown in Online Resource 2.

Surface Water

During dry soil conditions (March), nine out of the ten pesticides studied were detected (Table 2). CYFL, CYPE and ESFE were the compounds detected more often, up to 80 % of the analyzed samples, with levels of 1325 ng L^{-1} (Table ESM 2) in the case of ESFE in the effluent of the North WWTP (Figs. 3, 4). The presence of these pyrethroids could be explained by their non-efficient removal during WWTPs processes (Campo et al. 2013; Weston et al. 2013). DELT was the only pyrethroid not detected in any of the studied samples and PERM was quantified in one sample. However, during the flooded soil conditions (July), the levels of pesticides in surface water decreased in general, and only four of the ten pesticides were detected, although CYPE showed a level of 1450 ng L^{-1} (Table ESM 4) in the area close to the South WWTP (Figs. 3, 4).

PCA analyses were used to evaluate the pesticide occurrence, and using only two principal components (PC), the 85.2 % of the variance was explained. Fig. 2 shows the variable loadings for each compound studied statistically. The first PC (PC1) clearly explained CYFL and ESFE (Fig. 2) and the second PC (PC2) was mainly explained by CYPE (Fig. 2). Fig. 3 illustrates the score plots for PC1 vs. PC2 and both sampling events could be clearly distinguished as dry soil sampling event presented a wider range of contamination levels compared to the flooded soil sampling event. The highest levels of CYFL and ESFE in surface water correspond to sampling points located near North WWTP (203 and 1325 ng L^{-1}, respectively) and South WWTP (100 and 910 ng L^{-1}, respectively), (Tables ESM 1 and 3). These levels can be explained by the use of CYFL and ESFE in urban and SME areas. On the other hand, PC2 presents a positive loading for CYPE with the highest value (1450 ng L^{-1}) corresponding to surface water collected in summer near South WWTP.

Fig. 4a represents the interpolation of the results for surface water samples collected during dry soil conditions. Fig. 4a1 shows how the concentration of CYFL is distributed in the area object of study. As it is used in SME and urban areas, CYFL appears to enter the water cycle of the Natural Park through WWTP effluents, where the concentrations are higher (darkest color). This pattern of distribution is also observed for ESFE as it is depicted in Fig. 4a2; in this case, another area with significant concentrations was observed in the western border of the park that could be explained by direct discharges from small nearby villages.

Comparing with previous studies, in the Ebro River Delta (Spain), CYPE presented the same detection rates than in our work but at lower concentrations (Feo et al. 2010b). In California, BIFE was found in water samples from urban creeks in around 100 % of the samples but in our work it was detected only in 50 % of them (Weston et al. 2009). Permethrin presented a detection rate > 75 %, however in our work it was almost null. On the other hand, ESFE was the compound more frequently detected in our monitoring but it was not detected in California (Hladik and Kuivila, 2009; Weston et al. 2009). The mean levels reported by other authors (Feo et al. 2010b; Hladik and Kuivila, 2009; Weston et al. 2009) are lower than those reported in this work, which may be due to the impact of population living nearby the studied area and the effect of effluents from WWTPs (Fig. 1).

Finally, the highest levels detected nearby the WWTPs discharges may present toxicity to invertebrates. The half maximal effective concentration (EC_{50},48 h) for ESFE for example is 900 ng L^{-1} for *Daphnia magna* (European Commission, 2005), which is lower than the concentrations found nearby North WWTP (1325 ng L^{-1}) and South WWTP (910 ng L^{-1}). However, as can be appreciated in Fig. 4, ESFE levels of pollutants decrease through the park before reaching the lake. This fact could be explained the adsorption of PYs in soil, where these compounds have been detected at maximum level of 57.1 ng g^{-1} also in the same area (Aznar et al. 2016a). Moreover, PYs may be absorbed and accumulated into aquatic plants (typically used in phytoremediation, *Phragmites australis, Typha angustifolia*) and rice plants, where also have been detected (*Typha a.* 6 ng g^{-1} of CYFU and in rice plants 235 ng g^{-1} of ESFE) (Aznar et al 2016b). Thus, paddy fields ecosystem may be working as a buffer area of contamination, contributing to improve the water quality and reducing the toxicity that of organic pollutants such as pyrethroids may present to some invertebrates before reaching the lake.

Groundwater

The analysis of groundwater showed that in the dry sampling event nine out of the ten pesticides studied were detected and ESFE was the pesticide with the highest levels ranging from 138 to 833 ng L^{-1} (Table 2). During the flooded sampling event, the number of pesticides detected was reduced to five and ESFE was again the pesticide that presented the highest detection rate with concentrations up to 114 ng L^{-1}

Fig. 3 illustrates that in the dry sampling event, the variance and PY levels are higher than during flooded soil conditions. Groundwater in the dry sampling event was mainly polluted by CYFL and ESFE at sites G19 (278 and 726 ng L^{-1}, respectively) and G30 (206 and 779 ng L^{-1}, respectively), which are near to WWTPs discharge areas

Fig. 4b represents the interpolation of the results obtained for groundwater collected during the dry sampling event. Although several factors affect groundwater recharge, it could be noted that the areas with higher insecticides levels match those found in surface water (near WWTPs discharge areas). The similar distribution of contamination levels in surface water and groundwater may be explained because sampling was done in a shallow aquifer in a hydromorphic area. However, similar high levels of CYPE were not observed in surface water and groundwater.

On the other hand, samples collected during flooded soil conditions presented lower contamination levels, which may be explained by the dilution and degradation of the contaminants in this event, showing that the ecosystem of rice production plays an important role decreasing the contamination on the area.

Comparing with previous studies, in our work CYPE was detected in groundwater, however, it was not detected in a study carried out in Ireland (McManus et al. 2014).

Regarding groundwater vulnerability, following the Directive 2006/118/ (2006) on the protection of groundwater against pollution and deterioration, the active pesticide ingredients, their metabolites and reaction products cannot exceed 100 ng L^{-1}. Samples during dry soil condition showed the highest concentration of ESFE and CYFL with levels above 100 ng L^{-1} in 88 and 100 % of samples, respectively (Table 2). On the other hand, during the flooded sampling event, levels of PYs decreased drastically improving the groundwater quality, and in only 13 % of the samples ESFE were detected at levels slightly above 100 ng L^{-1}. The difference between these two events may be explained because during the flooded season the aquifers may be recharged due to the management of the paddy fields.

Conclusions

Pyrethroids were determined in surface water and groundwater collected in two periods in a paddy field area within the Natural Park of Albufera to assess their occurrence and distribution in the environment. During dry soil conditions, CYFL, CYPE and ESFE were the compounds detected more often, in around 80 % of the samples, and with concentration levels higher than during flooding soil conditions. Although the levels of the compounds studied are relative low, similar to those found in other areas around the world, the toxicity of these substances makes necessary monitoring the lake and surrounding areas to avoid adverse effects on aquatic life. The results provided in this field-based study combined with PCA and GIS showed that the use of water from WWTPs is the main pollution source. Levels of pyrethroids decreased during flooding condition when water flows over the paddy fields, showing that the surface water management practice to produce rice may improve the quality of groundwater and the environment. Further work needs to be done to assess the main processes which are responsible for organic pollutants mitigation in paddy fields, such as hydrolysis, photolysis, adsorption, microbial degradation and plant uptake. However, taking into account the potential risk for aquatic organisms of reusing water discharged from wastewater treatment plants, there is a need to improve the treatment of water in WWTPs to reduce the amount of organic pollutants, because due to the scarcity of fresh water more reused water will be needed in the future to irrigate paddy fields.

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Figure Captions

Fig.1 Map of the sites sampled in the paddy fields at the Natural Park in Valencia, Spain

Fig.2 Loadings for the two principal components by PCA. Solid bars explain more than 50 % of the results, versus dots that explain less than 50 %

Fig.3 Scores plot for PC1 vs. PC2. S: surface water and G: groundwater

Fig.4 Concentration of contaminants in surface water collected during the dry event (ng L^{-1}): a1) CYFL a2) ESFE; and groundwater collected during the dry event (ng L^{-1}): b1) CYFL b2) ESFE

Table 1. Mean recoveries (%) with their relative standard deviation (RSD), limit of detection (LOD, ng L^{-1}) and limit of quantification (LOQ, ng L^{-1}) of the studied pesticides.

	Spiking levels (ng L^{-1})[a]							
	500		100		20			
Compounds	Mean	RSD	Mean	RSD	Mean	RSD	LOD[b]	LOQ[b]
RESM	83	8	107	3	85	4	0.2	0.7
BIFE	101	3	97	6	103	5	0.4	1.2
FENP	79	1	99	7	87	6	0.4	1.5
CYHA	93	5	94	4	80	5	1.2	3.9
PERM	102	8	96	7	93	5	1.5	4.8
CYFL	101	1	101	7	101	7	2.5	8.4
CYPE	98	2	98	4	78	8	5.4	18.3
FLUV	91	7	108	4	89	6	2.9	9.5
FENV	105	2	98	7	75	8	4.8	16
DELT	77	4	103	3	73	8	4.1	13.6

[a]: (n=8)
[b]: (n=10)

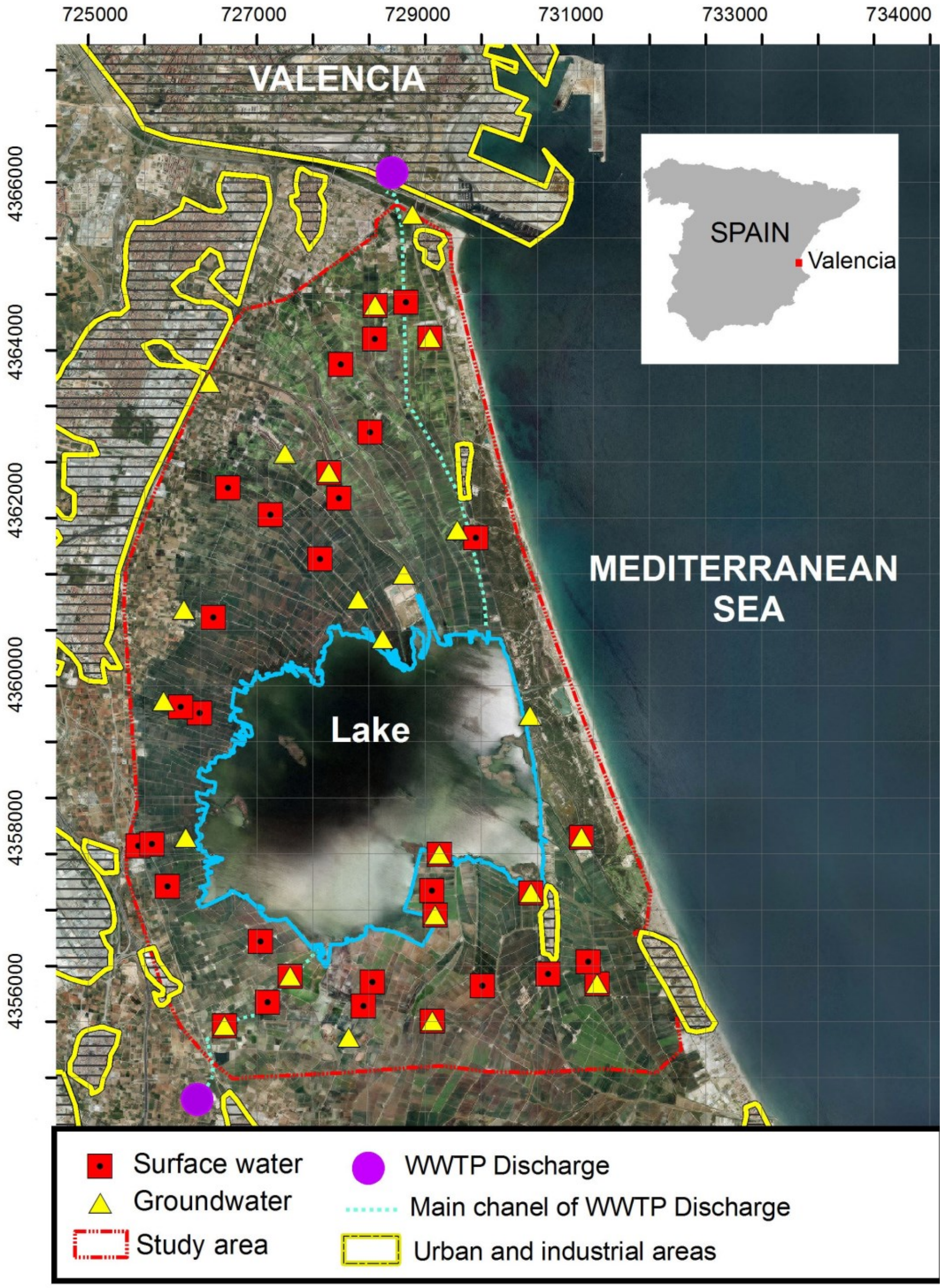
Table 2. Levels of pesticides in dry and flooded soil conditions

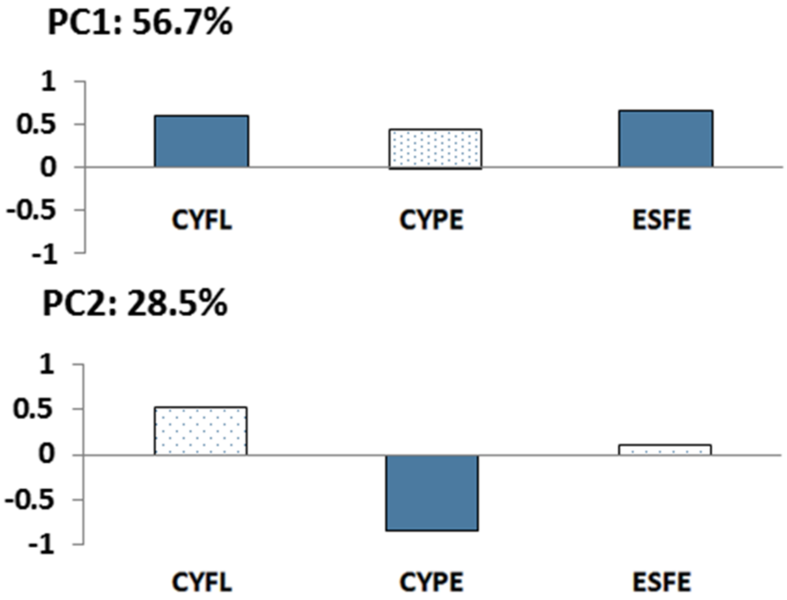
	Dry soil condition					
	Surface Water			Groundwater		
	Range (ng L^{-1})	Detection rate (%)	Samples (%, > 100 ng L^{-1})	Range (ng L^{-1})	Detection rate (%)	Samples (%, > 100 ng L^{-1})
RESM	nd-225	53	47	nd-333	9	9
BIFE	nd-14	24	0	nd-24	6	0
FENP	nd-320	59	24	nd-232	28	16
CYHA	nd-297	35	12	nd	0	0
PERM	nd-nq	3	0	nd-6	3	0
CYFL	nd-203	88	76	83-309	100	88
CYPE	24-132	100	29	29-387	100	19
FLUV	nd-58	18	0	nd-118	3	0
ESFE	nd-1325	88	82	138-833	100	100
DELT	nd	0	0	nd	0	0

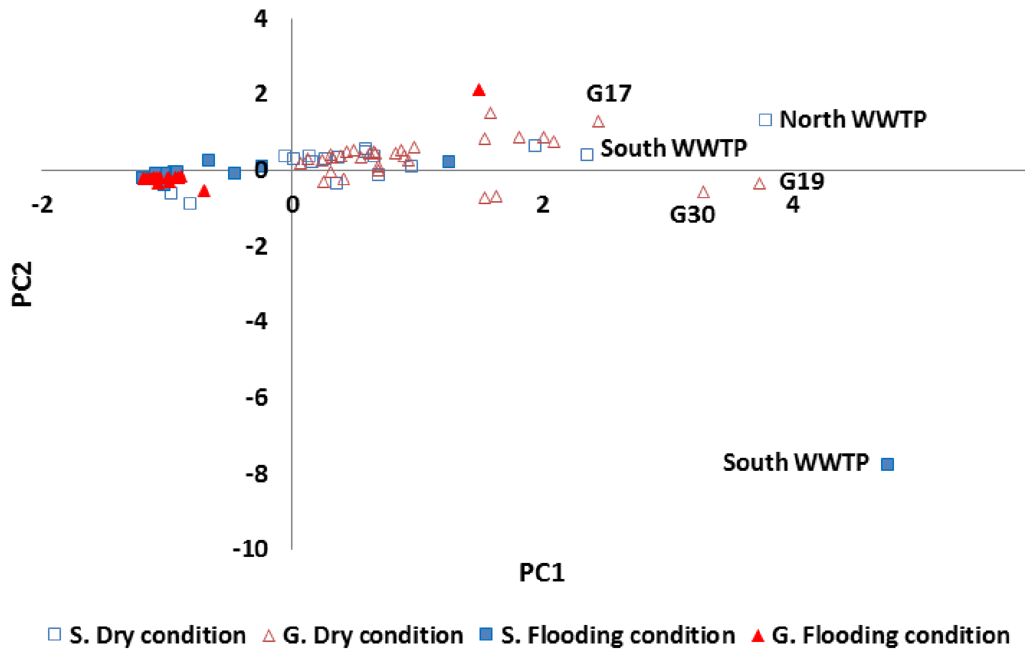
	Flooded soil condition					
	Surface Water			Groundwater		
	Range (ng L^{-1})	Detection rate (%)	Samples (%, > 100 ng L^{-1})	Range (ng L^{-1})	Detection rate (%)	Samples (%, > 100 ng L^{-1})
RESM	nd	0	0	nd	0	0
BIFE	nd-15	61	0	nd-49	47	0
FENP	nd	0	0	nd	0	0
CYHA	nd	0	0	nd	0	0
PERM	nd	0	0	nd	0	0
CYFL	nd-77	43	0	nd-383	6	6
CYPE	nd-1450	9	4	nd-64	13	0
FLUV	nd	0	0	nd	0	0
ESFE	nd-941	78	13	nd-114	84	13
DELT	nd	0	0	nd	0	0

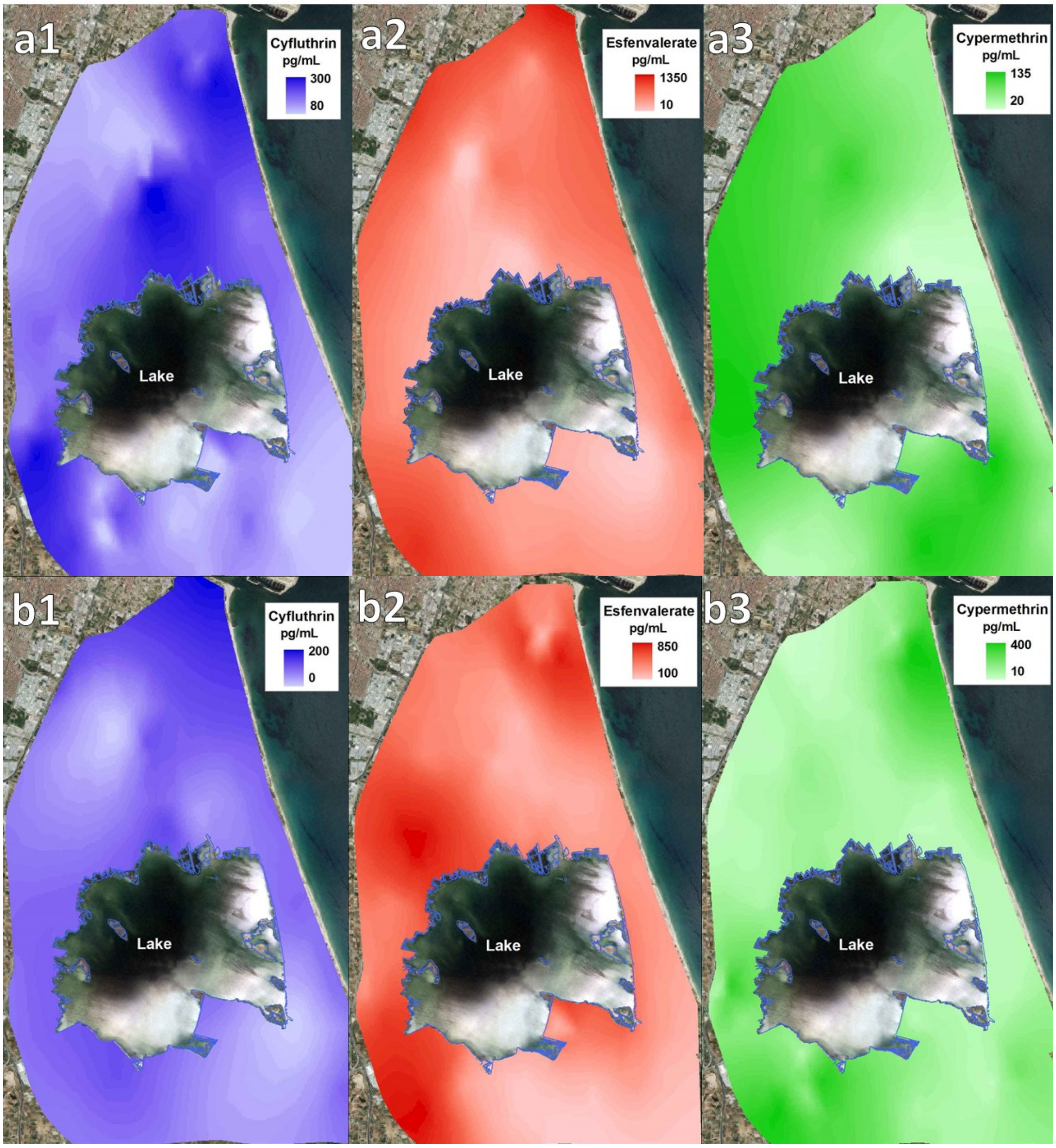
nd: not detected (value < than LOD)

nq: not quantified (value > than LOD but < than LOQ)


725000
727000
729000
731000
733000
734000
4366000
4364000
4362000
4360000
4358000
4356000
VALENCIA
SPAIN
Valencia
MEDITERRANEAN SEA
Lake
Surface water
Groundwater
Study area
WWTP Discharge
Main chanel of WWTP Discharge
Urban and industrial areas


PC1: 56.7%
1
0.5
0
-0.5
-1
CYFL
CYPE
ESFE
PC2: 28.5%
1
0.5
0
-0.5
-1
CYFL
CYPE
ESFE


PC2
PC1
4
2
0
-2
-4
-6
-8
-10
-2
0
2
4
6
G17
North WWTP
South WWTP
G19
G30
South WWTP
□ S. Dry condition
△ G. Dry condition
■ S. Flooding condition
▲ G. Flooding condition


a1
Cyfluthrin
pg/mL
300
80
Lake
a2
Esfenvalerate
pg/mL
1350
10
Lake
a3
Cypermethrin
pg/mL
135
20
Lake
b1
Cyfluthrin
pg/mL
200
0
Lake
b2
Esfenvalerate
pg/mL
850
100
Lake
b3
Cypermethrin
pg/mL
400
10
Lake