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PHYTOREMEDIATION OF POLLUTED SOILS: RECENT PROGRESS AND DEVELOPMENTS

Spatio-temporal distribution of pyrethroids in soil in Mediterranean paddy fields

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Abstract

Purpose The demand of rice by the increase in population in many countries has intensified the application of pesticides and the use of poor quality water to irrigate fields. The terrestrial environment is one compartment affected by these situations, where soil is working as a reservoir, retaining organic pollutants. Therefore, it is necessary to develop methods to determine insecticides in soil and monitor susceptible areas to be contaminated, applying adequate techniques to remediate them.

Materials and methods This study investigates the occurrence of ten pyrethroid insecticides (PYs) and its spatio-temporal variance in soil at two different depths collected in two periods (before plow and during rice production), in a paddy field area located in the Mediterranean coast. Pyrethroids were quantified using gas chromatography–mass spectrometry (GC–MS) after ultrasound-assisted extraction with ethyl acetate. The results obtained were assessed statistically using non-parametric methods, and significant statistical differences ($p < 0.05$) in pyrethroids content with soil depth and proximity to wastewater treatment plants were evaluated. Moreover, a geographic information system (GIS) was used to monitor the occurrence of PYs in paddy fields and detect risk areas.

Results and discussion Pyrethroids were detected at concentrations ≤ 57.0 ng g^{-1} before plow and ≤ 62.3 ng g^{-1} during rice production, being resmethrin and cyfluthrin the compounds found at higher concentrations in soil. Pyrethroids were detected mainly at the top soil, and a GIS program was used to depict the obtained results, showing that effluents from wastewater treatment plants (WWTPs) were the main sources of soil contamination. No toxic effects were expected to soil organisms, but it is of concern that PYs may affect aquatic organisms, which represents the worst case scenario.

Conclusions A methodology to determine pyrethroids in soil was developed to monitor a paddy field area. The use of water from WWTPs to irrigate rice fields is one of the main pollution sources of pyrethroids. It is a matter of concern that PYs may present toxic effects on aquatic organisms, as they can be desorbed from soil. Phytoremediation may play an important role in this area, reducing the possible risk associated to PYs levels in soil.

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1 Introduction

Rice (*Oryza sativa L.*) is the cereal grain most widely consumed, and it represents the third highest worldwide production (http://faostat.fao.org/site/339/default.aspx; accessed 8 June 2015). Its cultivation under hydric conditions is a very complex system due to water-soil interactions and anthropic

interventions (Nawaz et al. 2013). Moreover, the high demand of water to keep the fields continuously flooded and the low rainfall in the Mediterranean areas make necessary the use of poor quality water such as regained water from wastewater treatment plants (WWTPs). Unfortunately, as some authors have pointed out, the treatment of this water will not satisfactorily remove all contaminants (Feo et al. 2010; Alonso et al. 2012; Campo et al. 2013; Weston et al. 2013). Hence, the spreading of contaminants, such as insecticides and biocides, through agricultural soils may take place (Arias-Estevez et al. 2008), where they can be considered pseudo-persistent due to their daily release into the environment.

Pyrethroid insecticides (PYs) were derived from chrysanthemic acid to obtain more stable compounds in the environment. They have been intensively used in agricultural, industrial, and urban areas (Amweg et al. 2005; Aznar et al. 2014; Song et al. 2015), since they are a replacement of other banned pesticides, such as organochlorine and organophosphate pesticides. The occurrence of PYs is of concern because although they are retained in soil due to their hydrophobicity and low water solubility (see Table 1), PYs can be toxic to the aquatic life (Amweg et al. 2005; Weston et al. 2005; Song et al. 2015).

However, in contrast to the data of PYs levels documented in aquatic ecosystems, information on the levels of these insecticides in soil ecosystems is scarce. Given the universal dependence on hydric soils for rice production and their high ecological value, their maintenance in good environmental conditions is crucial. Hence, it is necessary to monitor the presence of PYs regularly and evaluate their potential risk to the environment (Huang et al. 2015).

The aim of this work was to monitor and assess the occurrence and distribution of PYs in soil samples collected from paddy fields in a Mediterranean region at different depths (0–40 and 40–60 cm) and during two campaigns (plow and rice production periods). To determine PYs in soil, a method based on ultrasound-assisted extraction and gas chromatography–mass spectrometry (GC–MS) was developed. In addition, a geographical information system (GIS) was used to assess the main sources of pollution as well as to identify and indicate areas where PYs may be toxic and phytoremediation may be a good management practice to mitigate contamination (Moore et al. 2009; Mahabali and Spagnoghe 2014). To the best of our knowledge, this is the first time that these insecticides are studied and monitored in soil at different depths in paddy fields.

2 Materials and methods

2.1 Site description

The study was carried out in Albufera of Valencia, a natural park located in the Spanish eastern coast (Fig. 1). This area is a wetland composed of three distinct environments as follows: the lake, the marsh area where rice is cultivated, and the sand barrier. The area was formed due to sedimentary contributions of the Turia and Júcar rivers closing a gulf in the Mediterranean Sea. In the eighteenth century, the lake had an area of 300 km^2, but nowadays, the lake's area is 23 km^2, being currently the largest freshwater lake in Spain. The lake's area reduction was caused by two main processes as follows:

Table 1 Properties of the target compounds and abbreviations

Chemical	Abbreviation	Log Kow	Log Koc	Solubility (mg L^{-1})	Soil aerobic half-life (days)	Soil anaerobic half-life (days)
Resmethrin	RESM	5.4[a]	5[e]	<1[c]	–	–
Bifenthrin	BIFE	6.0[a]	5.4[b]	0.1[a]	96.3[b]	425[b]
Fenpropathrin	FENP	6.0[a]	5[e]	0.014[a]	22[d]	276[d]
λ-Cyhalothrin	CYHA	6.9[a]	5.5[b]	0.003[a]	42.6[b]	–
Permethrin	PERM	6.5[a]	5.4[b]	–	39.5[b]	197[b]
Cyfluthrin	CYFL	5.9[a]	5.1[b]	0.002[a]	11.5[b]	33.6[b]
α-Cypermethrin	CYPE	6.6[a]	5.5[b]	0.004[a]	27.6[b]	55[b]
τ-Fluvalinate	FLUV	4.3[a]	–	0.002[a]	–	–
Esfenvalerate	ESFE	4.0[a]	5.4[b]	0.0002[a]	38.6[b]	90.4[b]
Deltamethrin	DELT	6.1[a]	–	<0.002[a]	24[d]	29[d]

Kow octanol-water partition coefficient, *Koc* organic carbon-soil partition coefficient
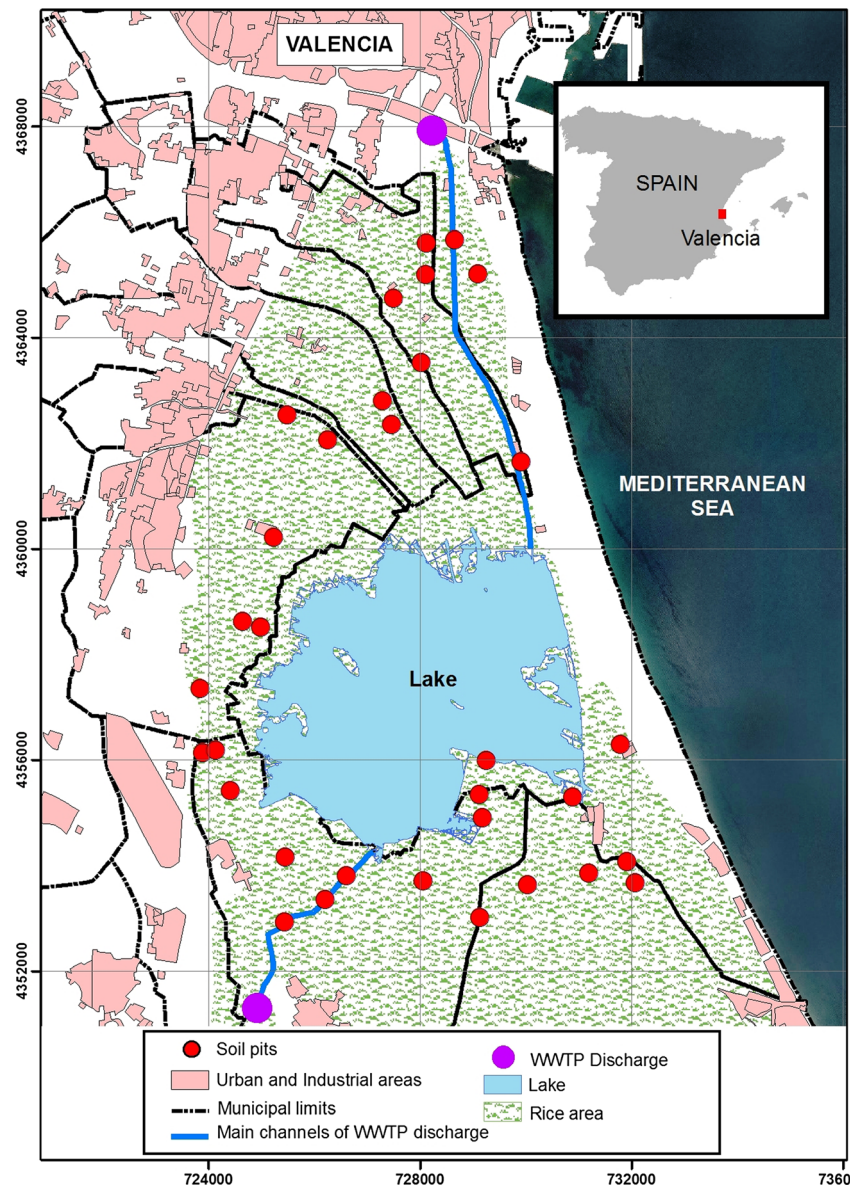
[a] Oros and Werner (2005)

[b] Laskowski (2002)

[c] http://www.inchem.org/documents/pds/pds/pest83_e.htm#1.3.2

[d] http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/environmental_fate.pdf

[e] http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34303

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

the natural process of silting (sediments from both rivers over the years) and anthropogenic processes to gain land to produce rice over the last century (Pascual-Aguilar et al. 2015). This area is usually flooded due to rice production management and the presence of the water table near the soil surface. Following the soil taxonomy classification (Soil Survey Staff 2014b), soils are defined as entisols and aridisols (Moreno-Ramón et al. 2015). These soils are carbonated saline and show a moderate surface organic carbon content due to the rice management (incorporation of post-harvest residues).

The area studied is ruled by the rice production cycle (Fig. 2). It starts with a period of fallow when the lake reaches its maximum level, flooding part of the rice fields (November–January). In January, the gates connecting with the Mediterranean Sea are opened, and the fields are drained reaching the lake its normal water level. From the end of

February until May, paddy fields are dried, so they can be plowed and prepared prior to sowing. In May, the rice-growing season starts, water flows around the whole park, and the paddy fields are flooded again. In September, the period of harvest starts, paddy fields are drained to allow harvest by the heavy machinery, and the rice cultivation cycle will start again. Water inputs come from the Júcar and Turia rivers that run south and north in the area of study, respectively. Due to the shortage of fresh water during summer, water from two WWTPs located 6–8 km from the lake (Fig. 1) is used to irrigate rice fields.

2.2 Standards and reagents

Ethyl acetate (EtAc) and Florisil (magnesium silicate adsorbent, 150–250 μm, 60–100 mesh for chromatography) were

Fig. 2 Hydrological cycle of rice production and the two sampling periods
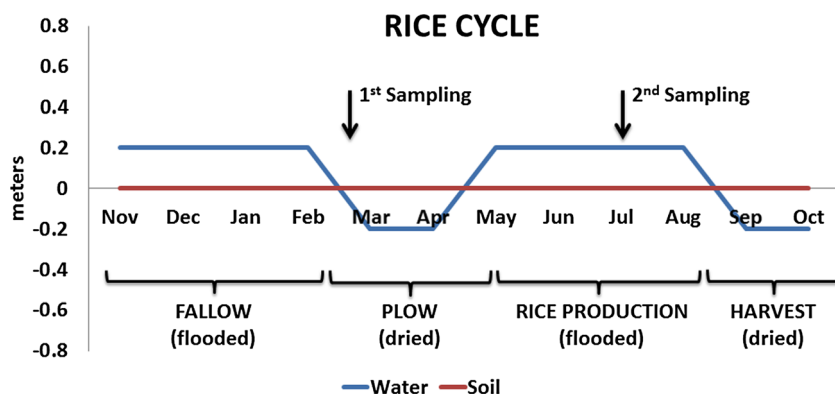
purchased from Scharlab (Barcelona, Spain). Sodium sulfate (purity ≥ 99 %) was obtained from Aldrich (Steinheim, Germany).

Insecticides 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), whereas the surrogate standard trans-permethrin-D6 (purity >99 %) was supplied by Symta (Madrid, Spain). The list of investigated compounds is shown in Table 1 along with their physicochemical properties.

Individual stock solutions of each compound at 500 μg mL^{-1} were prepared in EtAc and stored in the darkness at 4 °C up to 8 weeks. A mixed stock solution of 1000 ng mL^{-1} containing all analytes was prepared by dilution with EtAc of the individual stock solutions. A working mixture solution at 200 ng mL^{-1} was prepared weekly by dilution with EtAc of the mixed stock solution. A solution containing the surrogate standard was prepared in EtAc at the same concentration as the working mixture solution.

2.3 Apparatus

2.3.1 Extraction equipment

Glass columns (20 mL) of 10 cm × 20 mm i.d., Afora, Spain, and Whatman No.1 filter paper circles of 2-cm diameter (Whatman, Maidstone, UK) were used.

An ultrasonic water bath (Raypa, Barcelona, Spain) was used in the extraction step. A vacuum manifold (Supelco, Visiprep, Madrid) was employed to collect the extracts.

2.3.2 Detection equipment

Gas chromatography–mass spectrometry (GC–MS) analysis was performed with an Agilent 6890 (Waldbronn, Germany) gas chromatograph equipped with a mass spectrometric detector, model HP 5977A. The operating conditions are summarized in Table S1 (Electronic supplementary material).

The target and qualifier abundances were determined by injection of standards under the same chromatographic conditions using full-scan with the mass/charge ratio ranging from 50 to 400 m/z. The compounds were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier to target ratios. Retention times must be within ±0.1 min of the expected time and qualifier to target ratios within a 20 % range for positive confirmation. The quantification was accomplished by calibration with the surrogate standard at 10 ng g^{-1}. To reduce possible memory effects of the column, prior to the analysis of samples, the inlet was flushed by heating at 300 °C for 30 min, and procedural blanks were analyzed after every four samples.

2.4 Samples

2.4.1 Sample collection

Soils from thirty-three sites were sampled in rice fields at two different depths (0–40 and 40–60 cm). Sampling points were located with a virtual reference station (Leica GPS 1200) that supplied the universal transverse mercator (UTM) coordinates for the geostatistical treatment (Tables S2–S3, Electronic supplementary material).

The first layer (0–40 cm) of soil is the plow surface in which rice crop residues are incorporated. On the other hand, the deeper layer of soil (40–60 cm) remains unchanged and is usually saturated by the presence of a saline water table. A stainless steel Eijkelkamp auger was used for soil sampling according to a stratified sampling design. After soils were sampled, they were transported to the laboratory, where they were air dried at room temperature (21 °C) in darkness to avoid PYs photodegradation (Katagi 2004), sieved through a 2-mm mesh, thoroughly mixed, and kept frozen (−18 °C) in glass containers until analysis.

Two sampling campaigns were carried out. The first campaign was at the end of February, before plow period, when fields are dried to prepare them to produce rice, and the second sampling was in July when the fields are flooded (Fig. 2).

2.4.2 Physical-chemical properties of soil samples

Soil properties may affect insecticides behavior (transport, persistence, leaching, etc.), and, therefore, they were determined. Granulometric fractions of soil (sand, silt, clay) were determined for each sample following the Bouyoucos method. Soil pH was measured in a 1:2.5 (soil/distilled water) extract shaken for 15 min and measured after 2 h. Soil organic carbon was analyzed by the ignition method and carbonate content by Bernard calcimeter method. Finally, soil salinity was measured by the electrical conductivity (EC) 1:5 (soil/distilled water) (Tables S2–S3, Electronic supplementary material). All the methodologies described in this paper have been carried out according to Soil Survey Staff (2014a).

2.4.3 Insecticides analyses in soil

Extraction of PYs from soil was carried out by ultrasound-assisted extraction as one of the most favorable techniques to extract the target compounds (Albaseer et al. 2010). Briefly, 1 g of sieved soil was placed in a glass column containing 1 g sodium sulfate and 1.5 g of Florisil over a paper filter and a frit.

Soil samples were extracted twice for 15 min in an ultrasonic water bath with 5 mL EtAc, and an additional 1 mL was used to wash the glass material. The combined extracts were collected in 10-mL graduated tubes using a multiport vacuum manifold, concentrated to 0.1 mL using a gentle stream of air, and analyzed by GC–MS. To counteract matrix effects, a surrogate standard was used.

2.5 Method validation and quality control

In order to evaluate the method developed for the detection of insecticides in soil, different quality parameters were studied: recoveries, reproducibility, linearity, and sensitivity.

For the recovery studies, samples were previously fortified with a mixture of the different analytes to reach final concentrations of 10 and 2 ng g^{-1} and the labeled surrogate standard at 10 ng g^{-1}. They were kept at room temperature overnight to allow solvent evaporation. The recoveries obtained for all the studied compounds were satisfactory, ranging from 75 to 107 % (Table 2). The precision of the analytical procedure, expressed as relative standard deviations (RSD, %) of the analysis of four replicates, ranged between 1 and 11 % (Table 2).

Limits of detection (LODs) and quantification (LOQs) of the developed method were determined using ten replicates of soil extracts, spiked at 1 ng g^{-1}. The equation to calculate the LOD was the following: LOD = t_{99} × S, where t_{99} is the Students' value for a 99 % confidence level and n-1 degrees of freedom and S is the standard deviation of the replicate analyses. The LOQ was calculated as ten times the standard

Table 2 Mean recoveries (%) with their relative standard deviation (RSD, %), limit of detection (LOD, ng g^{-1}), and limit of quantification (LOQ, ng g^{-1}) of the studied insecticides

| Compounds | Fortification levels (ng g^{-1})[a] | | | | LOD[b] | LOQ[b] |
| | 10 | | 2 | | | |
	Mean	RSD	Mean	RSD		
RESM	104	3	75	1	0.4	1.2
BIFE	103	2	100	8	0.1	0.3
FENP	107	3	107	3	0.2	0.7
CYHA	95	9	96	9	0.1	0.4
PERM	94	5	98	11	0.1	0.5
CYFL	97	4	102	4	0.3	1.1
CYPE	96	7	97	10	0.2	0.8
FLUV	92	8	107	4	0.3	1.0
ESFE	101	8	106	7	0.3	1.0
DELT	99	7	75	2	0.3	0.9

[a] $n = 8$
[b] $n = 10$

deviation of the results of the replicate analysis used to determine LOD. Low limits were obtained due to the high selectivity and sensitivity of GC–MS. As shown in Table 2, LODs ranged from 0.1 to 0.4 ng g^{-1} and LOQs from 0.3 to 1.2 ng g^{-1} allowing the detection of insecticides at trace levels in soil samples.

A multipoint calibration curve with five standard solutions at different concentration levels (from 1 to 100 ng g^{-1}), appropriate to the levels found in soil samples, was used. The surrogate standard was added at the concentration of 10 ng g^{-1} for all levels.

2.6 Risk assessment

In order to carry out the risk assessment, the concentrations of PYs in soil as well as in water were considered, because PYs can be desorbed into fresh water due to the hydric conditions of the area. Therefore, the maximum equilibrium concentration expected in water (ECEW$_{max}$) of PYs was calculated. The maximum concentration of each PY found in the soils studied and the adsorption coefficient (Kd) of each compound were used as shown in the following equation:

$$ECEW_{max} = \text{concentration in soil}_{max} \ / \ Kd$$

The Kd of each PY was calculated using the organic carbon-soil partition coefficient (Koc) values from Table 1 and the corresponding value of the organic carbon (OC) from the top layer of soil (Table 3).

$$Kd = Koc \times OC$$

Table 3 Soil characteristics

	0–40 cm			40–60 cm		
	Min.	Max.	Mean ± RSD	Min.	Max.	Mean ± RSD
EC (dS m^{-1})	0.4	2.0	0.6 ± 0.4	0.4	2.8	0.7 ± 0.5
pH	7.2	8.1	7.6 ± 0.2	0.5	8.4	7.6 ± 1.3
Carbonate (g kg^{-1})	278	502	358 ± 38	260	530	357 ± 55
OC (g kg^{-1})	18.6	104.9	31.2 ± 18.5	4.3	60.1	23.4 ± 11.3
SOC (g kg^{-1})	0.0	1.1	0.4 ± 0.3	0.0	1.2	0.4 ± 0.3

EC electrical conductivity, *OC* organic carbon, *SOC* soluble organic carbon

Moreover, with the aim of evaluating the possible toxic effects of PYs in the studied area, the potential toxicity of PYs was assessed for soil and aquatic organisms. It was accomplished by comparing the ecotoxicological index of lethal dose (LC_{50}) of terrestrial organisms, reported in previous publications (European Commission 2002, 2004, 2005), with the levels of PYs found in soil in the present study. In the case of aquatic organisms, the calculated $ECEW_{max}$ was compared with the median effective concentration (EC_{50}) or the no observed effect concentration (NOEC) values for three aquatic species obtained from previously published studies (Hill 1985; Fojut et al. 2012; Maund et al. 2012).

2.7 Software

Standard statistical analyses were carried out with SPSS statistical program (Mann-Whitney and Spearman correlation test) to determine the levels of insecticides in soil. The use of non-parametric methods was confirmed by the outcome of Shapiro-Wilk test, which did not show a normal distribution. The compounds included in the statistical analysis were those with detection rates higher than 70 %. To create the matrix, a pretreatment of the data was necessary. Values below quantification limit were converted in numerical results, by adding a value of half their limit of quantification.

Cartography was performed by the Bayesian maximum entropy method (BME) (Fig. 3) which allowed a complete stochastic description of those non-sampling areas (Money et al. 2009). The maps showed gentle transitions between the different mapping units which reflected the normal behavior of continuous variables like water contaminants. The software used was ARCGIS 9.3 with a BMEGUI module.

3 Results and discussion

3.1 Spatial and temporal distribution of PYs in soil

In general, soils sampled had an electrical conductivity of 0.72–0.95 dS m^{-1}, and many of them were calcareous. The maximum values registered in the $EC_{1/5}$ (2.89 dS m^{-1})

revealed that there was soil salinization in the area (Table 3). Regarding particle size, 39 % of the samples were classified as silty clay, followed by 30 % of the samples classified as clay loam according to USDA textural classes.

The developed method was applied to the analysis of PYs in soils from paddy fields collected in two periods, before plow and during rice production. The overall results obtained are summarized in Table 4, showing the range of concentrations found and the detection frequencies for each compound. The complete set of concentration values are shown in Tables S4–S7 (Electronic supplementary material).

Before plow period (March), when there is no water flowing through the rice fields, six out of the ten PYs studied were detected (Table 4). The compounds most often detected were RESM, CYFL, CYPE, and ESFE up to 70 % of the analyzed samples, with levels up to 57 ng g^{-1} in the case of ESFE near to an area of discharge of the North WWTP (Fig. 3). Four PYs studied were not detected in any of the samples (BIFE, PERM, FLUV, and DELT), and CYHA was quantified only in one sample. However, during rice production (July), when freshwater flows through the fields, the soil sampled presented a higher detection rate (almost 100 %) of RESM, BIFE, FENP, CYFL, CYPE, and ESFE, being seven PYs detected, up to 62.3 ng g^{-1} for RESM nearby the area close to the north WWTP (see Table S6, Electronic supplementary material).

The presence of PYs could be explained by their application to local crops as well as their non-efficient removal during WWTP processes (Campo et al. 2013). During rice production period, when there is not enough freshwater to keep fields flooded to produce rice properly, the use of regained water from WWTPs is required. However, effluents from WWTPs are an important source of PYs release, as reported by other authors (Weston et al. 2013), and as a result, these compounds are introduced into the environment increasing the contamination of soil, which is an important reservoir. The outcome of non-parametric statistical analyses (Table 5) showed that water source had a clear influence over PYs levels in the area, particularly for CYFL and ESFE. The distribution in the area of these compounds shows that the main sources were the WWTPs (Fig. 3). In the case of BIFE, the increase of

Fig. 3 Spatial representation of CYFL and ESFE. **a** First sampling of top soil (0–40-cm depth), **b** First sampling of deep soil (40–60-cm depth)
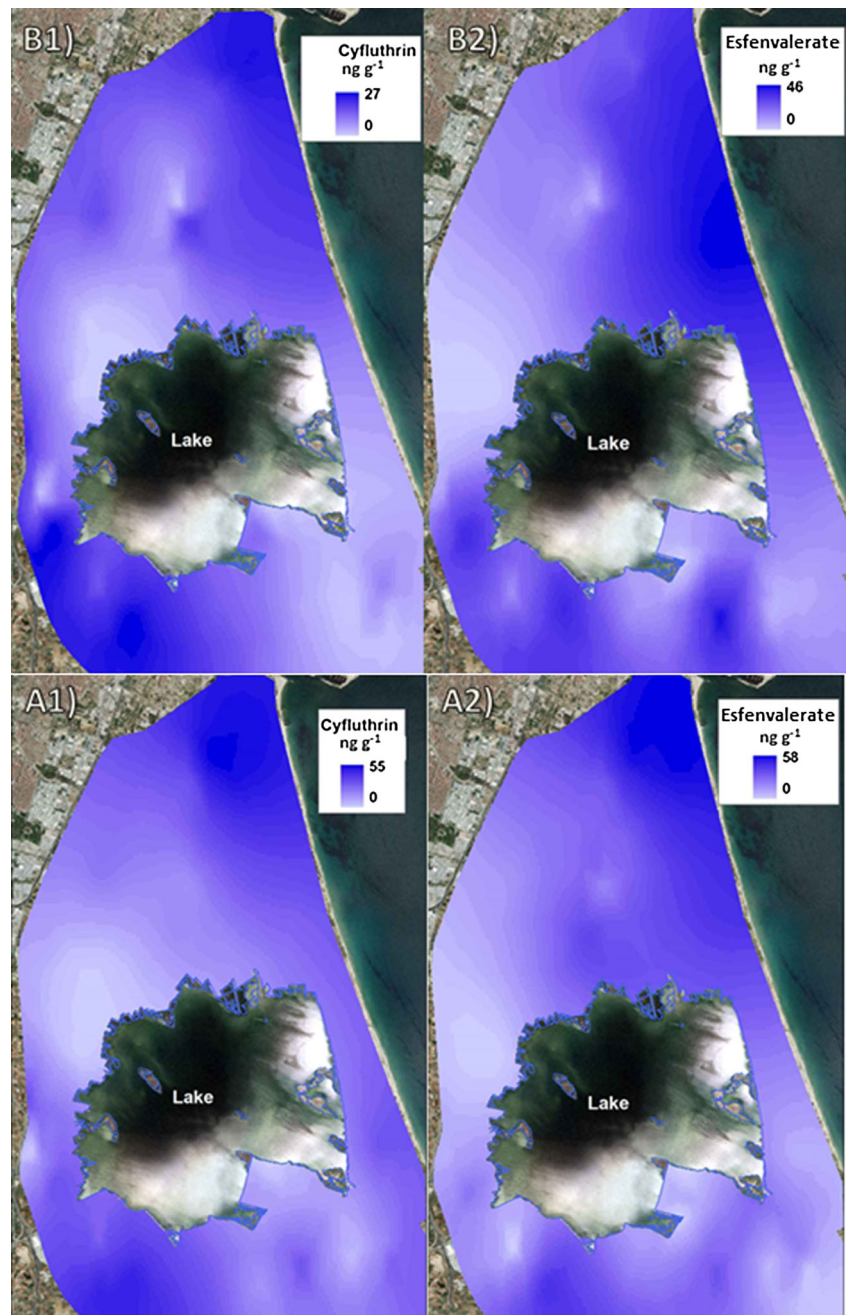
contamination along the area studied (Fig. 4) could be explained by its enrichment during transport by runoff (Gan et al. 2005), resulting in progressively higher pesticide levels in the soil downstream from the source. However, the contamination of CYFL and ESFE decreased along the park indicating that the marsh area may act as a buffer, retaining the contamination before reaching the lake. Therefore, phytoremediation may be a good management practice to mitigate contamination as it has been proven to work in wetlands (Moore et al. 2009; Mahabali and Spagnoghe 2014). Nevertheless, further work needs to be done to assess the main paths of pollutant dissipation in the marsh area. *Arundo donax*

L. and *Typha angustifolia L.*, among the typical plants used in phytoremediation and rice, may play an important role reducing the concentration of contaminants and improving the environmental conditions of the area studied.

3.2 Distribution of pyrethroids with soil depth

Soil organic carbon showed a decrease in depth due to the rice management in the area, because straw is incorporated in soil after the harvest at first 40 cm increasing its content in the top soil. The average content was around 31 g kg^{-1} of soil. On the contrary, the soluble organic carbon showed an increase in

Table 4 Levels (ng g^{-1}) and detection rate (% det.) of PYs during plow and rice production period from 33 soil sampling points at different depths

Plow period									
	0–40 cm					40–60 cm			
	Min.	Max.	Mean	% det.		Min.	Max.	Mean	% det.
RESM	0.0	52.0	19.5	97.0	RESM	1.6	53.4	23.9	100.0
BIFE	nd	nd	nd	nd	BIFE	nd	nd	nd	nd
FENP	nd	44.9	6.2	24.2	FENP	13.7	29.8	8.1	42.4
CYHA	nd	nd	nd	nd	CYHA	nd	1.5	0.0	3.0
PERM	nd	nd	nd	nd	PERM	nd	nd	nd	nd
CYFL	nd	54.2	20.3	90.9	CYFL	nd	27.3	11.0	81.8
CYPE	nd	17.9	5.0	69.7	CYPE	nd	11.1	1.7	42.4
FLUV	nd	nd	nd	nd	FLUV	nd	nd	nd	nd
ESFE	nd	57.0	19.4	84.8	ESFE	nd	46.3	19.7	90.9
DELT	nd	nd	nd	nd	DELT	nd	nd	nd	nd
Rice production period									
	0–40 cm					40–60 cm			
	Min.	Max.	Mean	% det.		Min.	Max.	Mean	% det.
RESM	2.0	62.3	23.2	100.0	RESM	4.5	57.9	28.2	100.0
BIFE	nq	32.2	4.2	100.0	BIFE	nq	13.5	3.0	100.0
FENP	nd	47.5	13.9	97.0	FENP	nq	40.2	13.3	100.0
CYHA	nd	20.7	3.0	93.9	CYHA	nd	41.1	7.7	97.0
PERM	nd	nd	nd	nd	PERM	nd	nd	nd	nd
CYFL	nq	39.0	15.7	100.0	CYFL	nq	54.9	22.0	100.0
CYPE	nd	26.2	3.9	84.8	CYPE	nd	31.9	4.1	97.0
FLUV	nd	nd	nd	nd	FLUV	nd	nd	nd	nd
ESFE	nd	57.1	23.4	87.9	ESFE	nd	48.8	20.3	97.0
DELT	nd	nd	nd	nd	DELT	nd	nd	nd	nd

nd not detected, *nq* not quantified

depth, and this trend can be explained due to the hydric characteristics of soils. Soluble compounds were accumulated in depth because at 40–60 cm, there was a permanent water table. In the upper parts, the water table can be intermittent depending on the crop management period.

In general, the target compounds tend to be found in the first 40 cm of soil, where higher content of organic matter is present. However, PY concentrations against depth showed that CYFL, BIFE, FENP, CYHA, and ESFE (Table 5) did not present that trend whereas RESM and CYPE show

Table 5 Statistical analysis of PYs levels in relation with soil depth and origin of irrigation water (Mann-Whitney and Spearman tests)

Factor	Subfactor	Average rank (Mann-Whitney)						
		RESM	CYFL	CYPE	ESFE	BIFE	FENP	CYHA
Water origin	WWTPs	70.3a	79.6a	76.9a	85.2a	31.9a	29.2a	39.2a
	Rivers	64.6a	59.9b	61.3b	57.1b	34.3a	35.7a	30.6a
Soil depth	0–40	58.5a	69.4a	77.0a	67.2a	33.7a	33.2a	30.9a
	40–60	74.5b	63.6a	56.0a	65.8a	33.3a	33.8a	36.1a
		Spearman coefficients						
Distance to WWTP		RESM	CYFL	CYPE	ESFE	BIFE	FENP	CYHA
		0.216*	0.418**	0.254**	0.288**	0.046	0.006	0.3*

Different letter means $p < 0.005$ (inside the same factor)

*$p < 0.05$

**$p < 0.001$

Fig. 4 Spatial representation of BIFE showing the areas marked in *red*, where BIFE levels (>10.1 ng g^{-1}) may present a negative effect to aquatic invertebrates

significant statistical differences (*p* value <0.001). The compound RESM, which presents the highest water solubility of the studied family of insecticides (Table 1), may be translocated deeply under hydric conditions and accumulated

at the second layer studied (40–60 cm). On the other hand, the low solubility in water of CYPE, and their application during rice production to eradicate common armyworm, may explain the accumulation of this insecticide in the top layer.

Comparing the maps generated by GIS depicted in Fig. 3, it can be observed that CYFL and ESFE contamination on top soil matched the highest points of pollution at deep soil, which are nearby WWTPs discharge (Fig. 1). On the other hand, the adsorption of PYs is higher in organic matter and mineral particles with a large surface area (Zhou et al. 1995). Moreover, wetland soils due to natural conditions and paddy soils due to the rice management tend to accumulate organic matter in the surface layers. Thus, the presence of PYs in the area studied may be explained by the content of organic matter in soils, where PYs can be bounded making more unlikely their degradation.

The correlation between distance to the WWTP and insecticides levels showed a significant statistical relationship. It should be noted that RESM, CYFL, CYPE, and ESFE showed higher concentration in the locations near north WWTP discharge. The Spearman coefficient between CYFL and distance showed a high-moderate correlation ($r = 0.42$; $p < 0.001$), whereas the rest of the data set showed a low-moderate correlation grade (Table 5).

3.3 Ecotoxicological assessment

The purpose of this study was to identify the areas that may be of special concern with respect to the present status of contamination. The toxicity of PYs to soil organisms, earthworms, and other non-target soil organisms is very low, with $LC_{50} > 1{,}000{,}000$ ng g^{-1} for *Eisenia fetida* (European Commission 2002, 2004, 2005). Thus, the concentrations found in this field-based study indicate negligible toxic effects for terrestrial organisms. However, invertebrates have been found to be the species most sensitive to PYs, presenting low LC_{50} (Amweg et al. 2005). These invertebrates are

Table 6 Ecotoxicological assessment in the studied area on aquatic organisms

Compound	Kd (L kg^{-1})	ECEW$_{max}$ (ng L^{-1}) in the studied area	EC$_{50}$ (ng L^{-1}) Algae	NOEC (ng L^{-1}) Invertebrates *Daphnia magna*	Fish *Pimephales promelas*
BIFE	7787	4	–	1.3[a]	40[a]
CYHA	9803	2	>1000000[c]	3.8[a]	31[a]
CYFL	7787	7	>991000[c]	20[a]	140[a]
CYPE	9803	3	>1300000[c]	20[b]	77[a]

Kd adsorption coefficient, *ECEW$_{max}$* maximum equilibrium concentration in water, *EC$_{50}$* median effective concentration, *NOEC* no observed effect concentration

[a] Fojut et al. (2012)

[b] Hill (1985)

[c] Maund et al. (2012)

present in aquatic and semiaquatic habitats and are an important food supply for fish and insectivorous birds, and the alteration of invertebrates' population could break the ecological equilibrium of the area. Thus, due to the hydromorphic conditions of the soils studied (Fig. 2), PYs in soil can be desorbed, and aquatic organisms should be also taken into account in this study.

The maximum equilibrium concentration expected in water, calculated as indicated in "Materials and methods" section, and the toxic effects of PYs in three aquatic trophic levels are summarized in Table 6. In algae, the EC_{50} is high for all PYs (*Scenedesmus subspicatus* EC_{50} (72 h) $>1 \times 10^7$ ng L^{-1} for CYFL) (Maund et al. 2002), and no toxic effect is expected. Moreover, as shown in Table 6, the NOEC data of PYs for fish is higher than the calculated equilibrium concentration in water in the studied area (no toxic effects expected). On the other hand, the NOEC data for invertebrates is closer to those equilibrium concentrations in water as aquatic invertebrates are the most sensitive organisms to PYs (Fojut et al. 2012, Hill 1985). Particularly, the calculated equilibrium values of BIFE in water are higher than the NOEC, which means that some toxic effects may be produced to the invertebrate community in the area studied.

The areas in which the concentration of BIFE in soil may present harmful effects for aquatic invertebrates are those with levels higher than 10.1 ng g^{-1}, which corresponds to an equilibrium concentration in water of the NOEC value (Table 6). The GIS program reported above was used to identify these areas where mitigation measures should be applied (Fig. 4).

4 Conclusions

Pyrethroid insecticides were monitored at two depths in soils collected during the two seasons in a paddy field area within the Natural Park of Albufera to assess their occurrence in the environment. During the period before plow, RESM, CYFL, CYPE, and ESFE were the compounds detected more often, up to 70 % of detection rate, but at lower concentrations than during the second sampling period (rice production), when soils sampled presented a higher rate of detection (almost 100 %) of RESM, BIFE, FENP, CYFL, CYPE, and ESFE. The results provided in this field-based study combined with GIS showed that water from WWTPs and field application are the main sources of soil contamination by these insecticides. It was a matter of concern that the levels of BIFE may cause harmful effects on the aquatic invertebrates within the area monitored, and an area where BIFE levels may present a risk was highlighted. Phytoremediation can be applied to reduce this risk but further work needs to be done to assess how phytoremediation should be performed to be effective in situ.

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