

# Influence of irrigation on the occurrence of organic and inorganic pollutants in soil, water and sediments of a Spanish agrarian basin (Lerma)

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## Abstract

In order to understand the several possible environmental impacts caused by irrigation, the existence of a study area under transition from unirrigated to irrigated land is a great advantage. This work investigates the presence of 44 pesticides and metabolites, 11 organochlorinated compounds, 17 polycyclic aromatic hydrocarbons (PAHs), 13 polychlorinated biphenyls (PCBs), and several metals and metalloids such as Cd, Cr, Cu, Ni, Pb, Zn, As, Se and Hg, in the soil, water and sediments of an agrarian basin in Northeast Spain. The study area was unirrigated until 2006, when irrigation began. The objective of this work was to verify if the first irrigation years influenced the concentrations of the substances and elements analyzed. The main contaminants detected were organochlorinated compounds, PAHs and metals in the soil; atrazine, desethylatrazine, terbuthylazine, dicofol and pp'-DDT in the water; and PAHs, 1,2,4 trichlorobenzene and metals in the sediments. Until the conclusion of this study, no serious contamination issues existed related to the analyzed substances, and for the moment, irrigation has not significantly influenced the concentrations of such substances in the basin. Nevertheless, slightly elevated punctual values were observed for endrin in the soil, pp'-DDT in the water, and Ni and Zn in the sediments.

**Additional key words:** contamination; environmental impacts; metal; organochlorinated compounds; pesticide.

## Resumen

### Influencia del riego en la presencia de contaminantes orgánicos e inorgánicos en suelos, aguas y sedimentos de una cuenca agrícola española (Lerma)

Para comprender los diversos posibles impactos ambientales producidos por el riego, el estudio de una cuenca en transformación de zona en seco a condiciones de regadío supone una gran ventaja. Este trabajo investiga la presencia de 44 plaguicidas y metabolitos, 11 compuestos organoclorados, 17 PAHs, 13 PCBs, y varios metales como Cd, Cr, Cu, Ni, Pb, Zn, As, Se y Hg, en los suelos, aguas y sedimentos de una cuenca agrícola del nordeste de España. La zona de estudio se encontraba en condiciones de seco hasta el año 2006, cuando comenzó a regarse. Los muestreos del presente trabajo se realizaron en 2008, y el principal objetivo ha sido comprobar si estos primeros años bajo riego tienen influencia en las concentraciones de las sustancias y elementos analizados. Los principales contaminantes detectados fueron compuestos organoclorados, PAHs y metales en los suelos; atrazina, desetilatrizona, terbutilazina, dicofol y pp'-DDT en las aguas; y PAHs, 1,2,4 triclorobenceno y metales en los sedimentos. Se ha de-

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Received: 07-06-10; Accepted: 17-01-11.

Abbreviations used: DOC (dissolved organic carbon), EC (electric conductivity (water)), ECe (electric conductivity of the saturated extract (soil)), GC/MS (gas chromatography/mass spectrometry), GPC (gel permeation chromatography), ICP-MS (inductively coupled plasma mass spectrometry), ICP-OES (inductively coupled plasma, with an optical emission spectrometer), OM (organic matter), P<sub>A</sub>, P<sub>B</sub>, P<sub>C</sub>, P<sub>D</sub> and P<sub>E</sub> (sampling locations A, B, C, D and E), P<sub>basin</sub> (sampling location of water drained from the entire Lerma basin), P<sub>unirrigated</sub> (sampling location with no influence of irrigation), PAH (polycyclic aromatic hydrocarbon), PCB (polychlorinated biphenyl), PEC (probable effect concentration), TC (total carbonates), TEC (threshold effect concentration), 0A and 0B (plots that never received irrigation), 1A and 1B (plots that had been under irrigation for one year), 2A and 2B (plots that had been under irrigation for two years), 3A and 3B (plots that had been under irrigation for three years).

mostrado que, hasta la finalización del estudio, no existen graves problemas de contaminación relacionados con las sustancias analizadas, y que por el momento, el riego no ha influido prácticamente en las concentraciones de dichas sustancias en la cuenca. Sin embargo, se han descubierto puntualmente valores ligeramente elevados de endrín en el suelo, pp'-DDT en el agua y Ni y Zn en los sedimentos.

**Palabras clave adicionales:** contaminación; compuestos organoclorados; impactos ambientales; metal; plaguicida.

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## Introduction

Agrarian activities can cause the accumulation of several substances in the environment, especially pesticides, mainly due to the agricultural supplies utilized to achieve greater production. Such contamination does not represent a danger exclusively to the agrarian area, as it can be transported to other zones, especially during heavy rain events (Carter, 2000; Schulz *et al.*, 2001). In general, the surface waters of the Ebro basin present a low level of pesticide contamination in accordance to the vulnerability limits imposed by European Union legislation. Even so, it is estimated that annually the waters of the Ebro river discharge approximately 1,300 kg of polar pesticides (mainly atrazine) in the Mediterranean sea (Gómez-Gutiérrez *et al.*, 2006).

Besides pesticides and their metabolites, other compounds and toxic elements can increase in concentration due to agrarian activities. The main sources of such contamination are: manures (Schipper *et al.*, 2008; Sheppard *et al.*, 2009); sewage sludge and other residues disposed of into the soil (Senesi *et al.*, 1999); irrigation water (Nicholson *et al.*, 2003; He *et al.*, 2005; Fatta *et al.*, 2007); and commercial fertilizers and pesticides, as these products contain not only the active principle but several other substances in their composition (Senesi *et al.*, 1999; He *et al.*, 2005).

Several authors consider that the sources of Cd, Cu, Se and Zn in agrarian regions are mainly associated with the agrarian activities carried out there, while Cr, Ni, Pb, As and Hg are related to other human activities (*e.g.* Pb would originate principally from the gases emitted by vehicles) or natural causes (Facchinelli *et al.*, 2001; Nicholson *et al.*, 2003; Micó *et al.*, 2006; Rodríguez *et al.*, 2008; Sheppard *et al.*, 2009).

Thus, it is important to monitor the agrarian zones for the presence of these substances, with the objective of verifying and comparing the values found with the current legislation and studying the temporal evolution of concentrations in the environment.

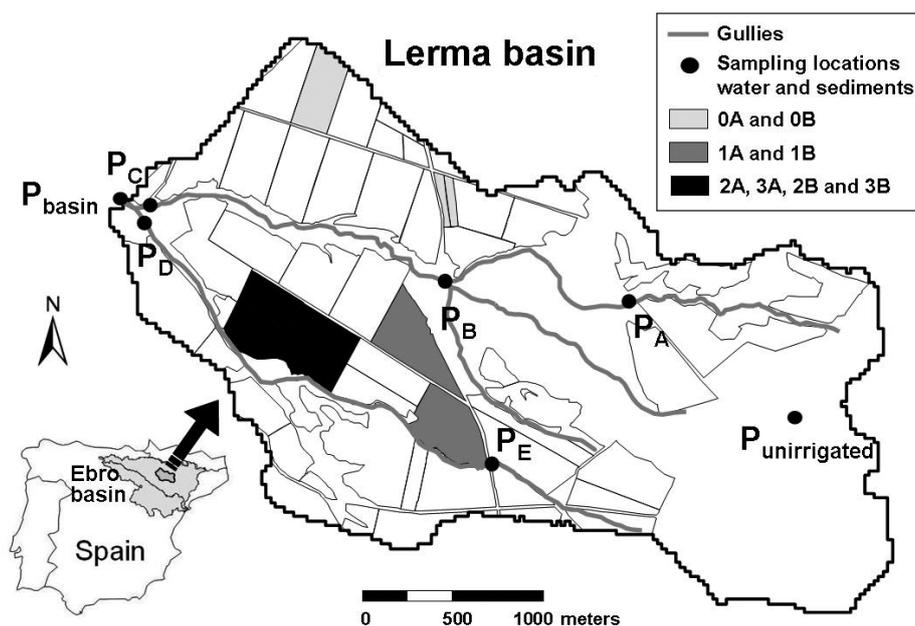
This work contributes to the knowledge regarding the presence of pesticides, organic compounds and metals in the soil, water and sediments of a basin under transformation from nonirrigated to irrigated land. The study verifies whether irrigation influenced the concentrations of such contaminants during the first years of transformation of the area. The results obtained also serve to characterize the basin for future comparative and evaluation studies on the impacts of irrigation.

## Material and methods

### Description of study area

The study zone corresponds to the surface hydrological basin of the Lerma gully (752 ha), located on the left margin of the Ebro river medium valley, in Northeast Spain (Fig. 1). This basin was unirrigated until 2006, when irrigation began for 31% of the planned irrigation area (405 ha), progressively continuing the transformation in 2007 (68%) and 2008 (85%), when the samples were collected for this study. The climate of the area is dry, with hot summers and cold winters. Precipitation in the basin in 2008 was 361 mm (SIAR, 2008).

Sprinkler (86%) and drip irrigation (14%) were the irrigation systems implemented. Corn was the most widespread crop during the three first irrigation years, occupying 40% of the irrigated area in 2008. Other important crops were winter cereal and tomato (23 and 15% respectively, in 2008). The predominant active principles of the pesticides utilized in the basin were: metolachlor, atrazine, terbutylazine and chlorpyrifos. The principal fertilizers utilized were: NPK compounds (mainly 8-15-15 and 15-15-15), urea (46% N) and liquid fertilizers (32% N). During the irrigation period (2006-2008), organic fertilizers and sewage sludge were not applied to the soils of the basin. However it could have been possible that manures were applied prior to irrigation (before 2004).



**Figure 1.** Sampling locations of water and sediments ( $P_{\text{basin}}$ ,  $P_A$ ,  $P_B$ ,  $P_C$ ,  $P_D$ ,  $P_E$  and  $P_{\text{unirrigated}}$ ) and plots of soil sampling (0A, 0B, 1A, 1B, 2A, 2B, 3A, 3B) in the Lerma basin.

## Sample collection

The samples of water drained from the entire Lerma basin were collected between March and May in 2008, in three uniformly-spaced dates throughout the period. The location of the sample collections correspond to  $P_{\text{basin}}$  in Figure 1. For the spatial characterization of the waters of the basin, five other locations ( $P_A$ ,  $P_B$ ,  $P_C$ ,  $P_D$  and  $P_E$ ) were selected for collection of samples on March 25, 2008. Locations  $P_A$ ,  $P_B$  and  $P_E$  receive drainage from zones with little influence of irrigation, while the drainage of more transformed zones flows through  $P_C$ ,  $P_D$  and  $P_{\text{basin}}$  (Fig. 1).

Sediments were also collected in the six sampling locations for water, as well as in a location with no influence of irrigation ( $P_{\text{unirrigated}}$ ). The time spent under irrigation was taken into consideration when the soil samples were collected in the cultivable zone of the basin. In this way, two plots were selected for each of the following typologies: plots that never received irrigation (0A and 0B), and plots that had been under irrigation for one year (1A and 1B), two years (2A and 2B) and three years (3A and 3B). The crop cultivated in these irrigated plots was corn. The representative soil samples for each plot were obtained through a mixture of soils, drilled to a depth of 25 cm, in 10 locations uniformly distributed in the plot, resulting in a compound sample for each plot. All samples (water and

solids) were stored in amber glass containers and kept in a refrigerator at a temperature of 4°C (USEPA, 1995a, 1999).

## Analysis of water samples

Duplicate analyses were accomplished for 44 pesticides and metabolites in water (Alachlor, aldrin, ametryn, atrazine, chlorfenvinphos, chlorpyrifos, pp'-DDD, op'-DDE, op'-DDT, pp'-DDT, desethylatrazine, 3,4-dichloroaniline, 4,4'-dichlorobenzophenone, dicofol, dieldrin, dimethoate, diuron,  $\alpha$ -endosulfan, endosulfan-sulfate, endrin,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, heptachlor, heptachlor epoxide A, heptachlor epoxide B, hexachlorobenzene, isodrin, 4-isopropylaniline, isoproturon, metolachlor, methoxychlor, molinate, ethyl parathion, methyl parathion, prometon, prometryn, propazine, simazine, terbutylazine, terbutryn, tetradifon and trifluralin), as well as for electric conductivity (EC) and dissolved organic carbon (DOC).

The determination of the pesticides was carried out through solid-liquid extraction and posterior analysis through GC/MS (gas chromatography/mass spectrometry). The methodology described by USEPA (1995b) was applied. Method 5310B of the «Standard Methods» was followed for the determination of DOC, filtering the samples (0.45  $\mu\text{m}$  pore diameter filter) before

analysis (APHA, 2005). EC was obtained utilizing a conductivimeter.

### Analysis of solid samples: sediments and soil

Duplicate analyses were accomplished for the aforementioned 44 pesticides and metabolites in the sediment and soil samples, as well as for 11 organochlorinated compounds (1,3,5-trichlorobenzene; 1,2,4-trichlorobenzene; 1,2,3-trichlorobenzene; hexachlorobutadiene; 1,2,3,5-tetrachlorobenzene; 1,2,4,5-tetrachlorobenzene; 1,2,3,4-tetrachlorobenzene; pentachlorobenzene; pentachlorophenol; *op'*-DDE and *op'*-DDD), 17 polycyclic aromatic hydrocarbons (PAHs) (naphthalene; acenaphthylene; acenaphthene; fluorene; phenanthrene; anthracene; carbazole; fluoranthene; pyrene; benzo(a)anthracene; chrysene; benzo(b)fluoranthene; benzo(k)fluoranthene; benzo(a)pyrene; dibenzo(ah)anthracene; indeno(123-cd)pyrene; benzo(ghi)perylene), and 13 polychlorinated biphenyls (PCBs) (PCB-087; 095; 101; 105; 138; 141; 149; 153; 170; 174; 180; 187 and 194). For these analyses, the samples were submitted to a solid-liquid extraction process at elevated pressure and temperature. Then, the purification of the extract was accomplished by gel permeation chromatography (GPC) for the later GC/MS analysis. All procedures

followed the methodology described in USEPA (1995c) and USEPA (1996).

Moisture, organic matter and metals such as Cd, Cr, Cu, Ni, Pb, Zn, As, Se and Hg were determined for the soil samples, as well as pH, electric conductivity of the saturated extract at 25°C (ECe), total carbonates (TC) and texture. For the determination of metals in the soil and sediments, the samples were dried and sieved. Next, an acid digestion was accomplished with HNO<sub>3</sub> in a microwave oven. The concentrations of Cd, Cr, Cu, Ni, Pb and Zn were determined by the inductively coupled plasma method, with an optical emission spectrometer (ICP-OES) (USEPA, 1994). For Se and As the inductively coupled plasma mass spectrometry (ICP-MS) method was utilized. Hg was determined through thermal decomposition, amalgamation, and atomic absorption spectrometry, according to the methodology described in USEPA (2007).

Moisture and organic matter (OM) as volatile solids were obtained following method 2540G of «Standard Methods» (APHA, 2005); pH of the soil samples was determined in a soil-water suspension (1:2.5); ECe was obtained through a conductivimeter after dilution (1:5). The Bernard calcimeter method (Harvey, 1906) was applied to obtain total carbonates and the method of Bouyoucos (Soil Survey Laboratory, 1995) was applied to obtain the texture of soil samples.

Quantification limits of all analyses realized in this study are shown in Table 1.

**Table 1.** Quantification limits of the analyses of water and solid samples for pesticides, organochlorinated compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and metals

	Water samples	Solid samples
<i>Pesticides</i>		
Atrazine	0.100 µg L <sup>-1</sup>	5.0 ng g <sup>-1</sup>
Ametryn, <i>pp'</i> -DDD, <i>op'</i> -DDT, <i>pp'</i> -DDT, desethylatrazine, 3,4-dichloroaniline, dicofol, dimethoate, diuron, heptachlor, hexachlorobenzene, 4-isopropylaniline, isoproturon, ethyl parathion, methyl parathion, prometon, prometryn, simazine, terbutryn	0.030 µg L <sup>-1</sup>	5.0 ng g <sup>-1</sup>
Remaining pesticides	0.015 µg L <sup>-1</sup>	5.0 ng g <sup>-1</sup>
<i>Organochlorinated compounds</i>		
<i>PAHs</i>	—	5.0 ng g <sup>-1</sup>
<i>PCBs</i>	—	5.0 ng g <sup>-1</sup>
<i>Metals</i>		
Cd, Cr	—	0.8 mg kg <sup>-1</sup>
Cu, Ni, Pb	—	4.0 mg kg <sup>-1</sup>
As	—	0.04 mg kg <sup>-1</sup>
Se	—	0.40 mg kg <sup>-1</sup>
Hg	—	0.005 mg kg <sup>-1</sup>
Zn	—	60 mg kg <sup>-1</sup>

## Statistical procedures

The Mann-Whitney (1947) nonparametric test was followed to verify the influence of irrigation on the concentration of metals in the soil, comparing all possible typology pairs as well as the nonirrigated and irrigated for one year plots (0A, 0B, 1A and 1B) with the plots under irrigation for two and three years (2A, 2B, 3A and 3B). The same statistical test was utilized to compare the results of metals in sediments. In this case all possible locations were compared, and  $P_{\text{unirrigated}}$  was compared with the six locations influenced in some manner by irrigation. The compared groups were considered significantly different with an error probability of less than 5% ( $p < 0.05$ ).

## Results and discussion

### Soil

#### *Analysis of pesticides, PAHs, PCBs and organochlorinated compounds*

Small concentrations of the compounds were detected in the analyzed soil samples (Table 2). With only one exception, the reference levels fixed by the Spanish legislation (BOE, 2005) were not exceeded. The exception being the value of endrin in a sample corresponding to the plot under irrigation for one year (1A), where the concentration found ( $10.7 \text{ ng g}^{-1}$ ) barely exceeded the reference level set by legislation ( $10 \text{ ng g}^{-1}$ ). Currently the European Union has no fixed concentration limits for these substances in the soil.

The compound pp'-DDT was detected in two samples (1A and 2A), and pp'-DDD + op'-DDT in another sample (3A), all below the quantification limit ( $5 \text{ ng g}^{-1}$ ). The concentration levels were quite below those fixed by Spanish legislation ( $200 \text{ ng g}^{-1}$  for pp'-DDT and  $700 \text{ ng g}^{-1}$  only for pp'-DDD).

Since 1977, Spain has prohibited the use of DDT as well as other organochlorinated compounds (Mañosa *et al.*, 2001). However, some authors have considered the possibility of these compounds having been utilized after the prohibition in Spain (Fernández *et al.*, 2000) and in the Ebro basin (Gómez-Gutiérrez *et al.*, 2006). However, due to the great persistence of such compounds in the environment, the contamination of soils could have occurred in years prior to the beginning of this study, when the plots were cultivated in nonirrigated

**Table 2.** Concentrations ( $\text{ng g}^{-1}$  dry weight) of polycyclic aromatic hydrocarbons (PAHs), organochlorinated compounds, remaining pesticides and polychlorinated biphenyls (PCBs) in the soil of the Lerma basin

	0A	1A	2A	3A
<i>PAHs</i>				
Phenanthrene	<5.0	<5.0	<5.0	<5.0
Fluoranthene	<5.0	ND	<5.0	<5.0
Pyrene	<5.0	ND	<5.0	<5.0
Chrysene	<5.0	ND	<5.0	<5.0
Benzo(k)fluoranthene	<5.0	ND	<5.0	<5.0
Benzo(b)fluoranthene	<5.0	ND	<5.0	<5.0
Dibenzo(ah)anthracene	<5.0	ND	<5.0	<5.0
Benzo(ghi)perylene	<5.0	ND	<5.0	<5.0
<i>Organochlorinated</i>				
1,2,4-Trichlorobenzene	ND	<5.0	ND	ND
$\alpha$ -HCH	ND	<5.0	ND	ND
$\beta$ -HCH	ND	<5.0	ND	ND
$\gamma$ -HCH	ND	<5.0	ND	ND
$\delta$ -HCH	ND	<5.0	ND	ND
Aldrin	ND	<5.0	ND	ND
4,4'-Dichlorobenzophenone	ND	<5.0	ND	ND
Endrin	ND	10.7	ND	ND
pp'-DDD + op'-DDT	ND	ND	ND	<5.0
pp'-DDT	ND	9.6	5.0	ND
Dicofol	ND	11.4	ND	ND
Tetradifon	ND	<5.0	ND	ND
<i>Remaining pesticides</i>				
	ND	ND	ND	ND
<i>PCBs</i>				
	ND	ND	ND	ND

ND: not detected.

conditions. Hildebrandt *et al.* (2009) also found small concentrations of DDT isomers in soil samples from other agrarian zones of the Ebro basin.

Due to the elevated number of substances studied, Table 2 shows only the substances detected. Although atrazine, metolachlor, terbuthylazine and chlorpyrifos are present in the principal pesticides applied in the basin, they were not detected in the soil. It is possible that the absence of such substances in the samples was due to leaching to deeper layers of soil or runoffs, circumstances normally caused by precipitation events or irrigation after the application of pesticides (Carter, 2000; Schulz *et al.*, 2001). The analyzed PCBs were not detected in the samples either, as they normally originate from industrial areas (Mañosa *et al.*, 2001).

The non-detection of the majority of the tested compounds and the low concentrations of the compounds detected manifest the adequate environmental condi-

tion of the soils of the basin regarding these contaminants. The temporal comparison between the soils of plots irrigated for two and three years (2A and 3A) and soils irrigated for less time or unirrigated (1A and 0A, respectively) showed that, until the conclusion of this study (2008), irrigation had not contributed to the increase in such concentrations.

### Analysis of metals

Samples 0A, 0B, 1A, 1B, 2A, 2B, 3A and 3B were analyzed for the study of metals. Among the investigated metals, Zn and Cr were found in greater concentrations in the soils of the basin. The mean values of the detected metals were classified as follows: Zn > Cr > Ni > Pb > Cu > As > Se > Hg (Table 3).

The soils of the Lerma basin are very homogeneous regarding characteristics such as pH (mean of 8.4), organic matter content (2.6%), ECe (0.2 dS m<sup>-1</sup>), total carbonates (32%) and texture.

Currently there is no legislation for the European Union that establishes limit concentrations for metals in the soil. Therefore, the concentrations of the metals detected were compared with other works carried out in the Ebro basin (Navas and Machín, 2002; Rodríguez *et al.*, 2006) and in other parts of the world (Senesi *et al.*, 1999; He *et al.*, 2005). It was verified that for all samples the concentrations were below the tolerance levels.

**Table 3.** Properties and metal concentrations (mg kg<sup>-1</sup> dry weight) in the soils of the Lerma basin

Variable	Mean	SD	Min.	Max
pH (extract 1:2.5)	8.4	0.1	8.3	8.6
Electric conductivity, dS m <sup>-1</sup>	0.2	0.04	0.1	0.26
Organic matter, %	2.6	0.2	2.1	2.73
Total carbonates, %	32	3	29	37
Sand, %	54	5	44	61
Lime, %	24	4	17	29
Clay, %	2	2	19	27
Mercury, mg kg <sup>-1</sup>	0.03	0.003	0.02	0.03
Cadmium, mg kg <sup>-1</sup>	—	—	<0.8	<0.8
Arsenic, mg kg <sup>-1</sup>	2.1	0.3	1.3	2.27
Chromium, mg kg <sup>-1</sup>	30.3	4.6	22.2	38.2
Copper, mg kg <sup>-1</sup>	8.4	0.6	7.4	9.43
Nickel, mg kg <sup>-1</sup>	20.4	1.9	17.4	22.6
Lead, mg kg <sup>-1</sup>	17.3	3.1	12.3	22.6
Selenium, mg kg <sup>-1</sup>	0.8	0.1	0.7	0.9
Zinc, mg kg <sup>-1</sup>	—	—	<60	149

SD: standard deviation.

The comparison between the values was purely orientative but demonstrated that the soils of the study area did not present contamination regarding the investigated elements. In the case of Cd, none of the samples exceeded the quantification limit of the analytical method (0.8 mg kg<sup>-1</sup>).

According to several authors, a more precise establishment of reference values for the quality of soils should be carried out at a regional level, as in many cases these elements are naturally present in the soil (Holmgren *et al.*, 1993; De Miguel *et al.*, 2002; Micó *et al.*, 2007).

In spatial characterization studies of the soils of the Ebro basin regarding the presence of Hg, Cd, Cu, Ni, Pb, Zn and Cr, Rodríguez *et al.* (2006 and 2008) found mean values similar to those obtained in this study. The authors indicate that the spatial variability in the concentration of such elements in the Ebro basin is mainly due to the composition of the bedrock and to the processes that affect the soil, being human activities of lesser influence. Nevertheless, the authors alert about the current increase in the concentrations of Cu, Zn and Pb in the agrarian soils of the basin due to the use of pesticides and fertilizers.

In the present work, the comparison between the concentrations of each metal in unirrigated soils and soils under irrigation for one, two, or three years did not reveal significant differences ( $p < 0.05$ , Mann-Whitney). The differences between the concentrations in the four typologies were minimal for all elements, and demonstrated that the recent transformation of the zone did not result in considerable changes until the conclusion of this study. Nevertheless, a gradual decrease was observed in the concentrations of Cu when the time under irrigation increased (from 9.4 mg kg<sup>-1</sup> in unirrigated soils to 7.8 mg kg<sup>-1</sup> in soils irrigated for three years). When comparing the concentrations of the unirrigated plots and plots under irrigation for one year with the plots under irrigation for longer times (two and three years), the Mann-Whitney test demonstrated significant differences ( $p < 0.05$ ) only for Cu and nonsignificant for the remaining elements. Furthermore, the only sample of soil that exceeded the quantification limit for Zn (60 mg kg<sup>-1</sup>) belonged to an unirrigated plot (149 mg kg<sup>-1</sup>).

A hypothesis to explain these results could be that during the study years (2004-2008) no manure was applied to the Lerma basin, but it is possible that in previous years it occurred. Cu and Zn are the principal elements related to contamination by manure (Senesi *et al.*, 1999; De Temmerman *et al.*, 2003; Nicholson *et*

*al.*, 2003; Berenguer *et al.*, 2008) and the small, but significant, decrease in their concentrations in the soil of the basin suggests that these elements are being gradually dragged. Until now, the greater volumes of pesticides and inorganic fertilizers applied during the years under irrigation have not caused significant increases for the other studied elements.

## Water

### *Analysis of pesticides*

In the surface waters of the basin, of the forty-four pesticides and metabolites analyzed, only atrazine, desethylatrazine, terbuthylazine, dicofol and pp'-DDT (Table 4) were detected.

Dicofol and atrazine were detected in 75% of the samples, although always below the quantification limits. Desethylatrazine and atrazine were detected in the three samples collected at the exit of the basin ( $P_{\text{basin}}$ ). The maximum admissible concentration of atrazine in European continental surface waters, published in Directive 2008/105/EC, related to environmental quality standards in the scope of water politics (OJEU, 2008), is  $2.00 \mu\text{g L}^{-1}$ . All values verified satisfied this limit.

Irrigation return flows of greater areas flow through locations  $P_C$ ,  $P_D$  and  $P_{\text{basin}}$ . In these locations the maximum values of EC were found, along with a greater proportion of samples with presence of atrazine and desethylatrazine as well as the only sample that presented pp'-DDT ( $P_D$ ). DOC presented maximum values in  $P_E$  ( $18.5 \text{ mg L}^{-1}$ ), in a location of reduced volume flow where the drainage of less irrigated zones passes by, and where the only detected pesticide was dicofol, below the quantification limit ( $<0.03 \mu\text{g L}^{-1}$ ).

Terbuthylazine was only detected in one sample of  $P_{\text{basin}}$  in May ( $0.06 \mu\text{g L}^{-1}$ ). The detection of atrazine and terbuthylazine in the water samples, in opposition to their absence in the soil samples suggests, as was explained previously, the leaching of these substances to deeper layers of the soil and the later release into the water courses of the basin. Dicofol is an acaricide generally used in vineyards and its presence in the basin could be due to atmospheric deposition (Guo *et al.*, 2009).

No temporal trends were verified for the studied period. Nevertheless, the detection of terbuthylazine only in May gives evidence of the use of this herbicide after April, mainly in the cultivation of corn, which is in accordance with the information given by the farmers on the pesticides utilized and dates of application.

Studies carried out by Claver *et al.* (2006) between 2002 and 2003 demonstrated that the most frequently found pesticides in high concentrations in the surface waters of the Ebro basin were: 3,4-dichloroaniline, atrazine, molinate, desethylatrazine, dimethoate, simazine, metolachlor and chlorpyrifos. The mean concentrations of atrazine and desethylatrazine in several rivers studied by those authors were in general more elevated than those of the present study. Navarro *et al.* (2010), when studying the presence of pesticides in the Ebro basin between 2004 and 2006, detected atrazine in more than 65% of the analyzed samples, obtaining mean values of  $0.06 \mu\text{g L}^{-1}$ , although some samples presented concentrations of up to  $0.82 \mu\text{g L}^{-1}$ . The values obtained for desethylatrazine (mean of  $0.11 \mu\text{g L}^{-1}$  with a maximum of  $0.38 \mu\text{g L}^{-1}$ ) were also more elevated than those of this study.

Terbuthylazine and dicofol were also found in the surface waters of the Ebro basin (Claver *et al.*, 2006), in concentrations closer to the values obtained in this study, while pp'-DDT was not detected or was below

**Table 4.** Results for dissolved organic carbon (DOC), electric conductivity (EC) and pesticides in the surface waters of six sampling locations in the Lerma basin ( $P_A$ ,  $P_B$ ,  $P_C$ ,  $P_D$ ,  $P_E$  and  $P_{\text{basin}}$ )

Variable	$P_A$	$P_C$	$P_C$	$P_D$	$P_E$	$P_{\text{basin}}^1$	$P_{\text{basin}}^2$	$P_{\text{basin}}^3$
DOC, $\text{mg L}^{-1}$	ND	ND	2.1	1.3	18.5	14.1	2.1	2.8
EC, $\text{dS m}^{-1}$	1.2	3.6	4.0	5.3	0.5	4.2	4.4	4.2
Atrazine, $\mu\text{g L}^{-1}$	ND	$<0.10$	$<0.10$	$<0.10$	ND	$<0.10$	$<0.10$	$<0.10$
Desethylatrazine, $\mu\text{g L}^{-1}$	ND	ND	ND	0.04	ND	0.04	0.09	0.04
Terbuthylazine, $\mu\text{g L}^{-1}$	ND	ND	ND	ND	ND	ND	ND	0.06
Dicofol, $\mu\text{g L}^{-1}$	$<0.03$	$<0.03$	$<0.03$	ND	$<0.03$	$<0.03$	ND	$<0.03$
pp'-DDT, $\mu\text{g L}^{-1}$	ND	ND	ND	0.09	ND	ND	ND	ND

ND: not detected. <sup>1</sup> March. <sup>2</sup> April. <sup>3</sup> May 2008.

the quantification limit for all samples (Claver *et al.*, 2006). The values of terbuthylazine found by Navarro *et al.* (2010) were also very similar to those obtained in this study.

## Sediments

### *Analysis of pesticides, PAHs, PCBs and organochlorinated compounds*

The location with no influence of irrigation ( $P_{\text{unirrigated}}$ ) was chosen for the analysis of pesticides, PAHs, PCBs and organochlorinated compounds in sediments. Phenanthrene, fluoranthene, pyrene, chrysene, dibenzo(ah)anthracene, benzo(ghi)perylene and 1,2,4-trichlorobenzene were found, although below the quantification limits ( $5 \text{ ng g}^{-1}$ ). The remaining compounds being analyzed were not detected.

### *Analysis of metals*

As in the soil, Zn and Cr were the metals found in greater concentrations in the sediments of the seven locations studied. The mean concentration values followed the trend found in the soil:  $\text{Zn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cu} > \text{As} > \text{Se} > \text{Hg}$ . The organic matter content in the sediments varied between 2.4 and 6.5%, with a mean of 5.1% (Table 5).

The maximum allowed levels for metal concentrations in sediments are not currently established in the European Union. Therefore, the values obtained for the sediments of the Lerma basin were compared with the limits proposed by MacDonald *et al.* (2000). From

**Table 5.** Concentrations of metals ( $\text{mg kg}^{-1}$  dry weight) and organic matter content in the sediments of the Lerma basin

Variable	Mean	SD	Min.	Max
Organic matter, %	5.1	1.2	2.4	6.5
Mercury, $\text{mg kg}^{-1}$	0.01	0.005	0.01	0.03
Cadmium, $\text{mg kg}^{-1}$	—	—	<0.8	<0.8
Arsenic, $\text{mg kg}^{-1}$	2.5	1.1	0.6	4.9
Cromium, $\text{mg kg}^{-1}$	21.5	7.9	9.7	37.7
Copper, $\text{mg kg}^{-1}$	8.7	3.4	5.6	17.6
Nickel, $\text{mg kg}^{-1}$	17.5	5.5	8.8	26.6
Lead, $\text{mg kg}^{-1}$	9.8	2.2	5.8	14.4
Selenium, $\text{mg kg}^{-1}$	0.8	0.1	0.6	1.1
Zinc, $\text{mg kg}^{-1}$	—	—	<60	1,018

SD: standard deviation.

a consensus between several values proposed previously, these authors fixed limit concentrations of two classes: TEC (threshold effect concentration) and PEC (probable effect concentration). It is considered that normally no harmful effect is observed if the values are below TEC, and represent probable harmful effects if the values exceed PEC.

In all 14 sediment samples the concentrations of Hg, Cd, Cu, Pb, Cr and As were inferior to those of TECs. The mean value for Ni was also inferior, although three samples exceeded TEC for this element ( $22.7 \text{ mg kg}^{-1}$ ). These samples belonged to location  $P_B$  in March ( $26.0 \text{ mg kg}^{-1}$ ) and  $P_E$  in March ( $26.6 \text{ mg kg}^{-1}$ ) and June ( $24.0 \text{ mg kg}^{-1}$ ). These concentrations did not exceed PEC ( $48.6 \text{ mg kg}^{-1}$ ). Ochieng *et al.* (2009) found similar values for Ni (between  $9.6$  and  $25.3 \text{ mg kg}^{-1}$ ) in sediments of the Rivers Sabaki, Ramisi and Vevesi, receivers of industrial effluents in Kenya and affluents of the Indian Ocean. N'Guessan *et al.* (2009) detected more elevated concentrations of Ni (between  $17.0$  and  $43.9 \text{ mg kg}^{-1}$ ) in sediments of three basins in the region of Gascogne, in France. This region is characterized by the predominance of agriculture (more than 75% of the area) and the authors attributed such values to natural factors and atmospheric deposition. In an agrarian basin in China, Zhang and Shan (2008) also found more elevated concentrations (between  $14.0$  and  $54.6 \text{ mg kg}^{-1}$ ) than those of this study. The authors indicated that in the last three decades the concentrations of Cu, Pb, Zn, Ni, Cd and Cr have increased in the sediments of agrarian zones of China due to the intensification in the use of fertilizers during this period.

In the present work, one of the samples presented an elevated concentration of Zn ( $P_{\text{basin}}$ ,  $1,018 \text{ mg kg}^{-1}$ ), being the only to exceed TEC ( $121 \text{ mg kg}^{-1}$ ), and even PEC ( $459 \text{ mg kg}^{-1}$ ) for this element. According to what was explained previously, Zn is present in considerable quantities in animal residues. A possible application of manure during the nonirrigated period might be the cause of this high value found in the sediments at the exit of the basin.

No TEC and PEC limits exist for Se (MacDonald *et al.*, 2000). The concentrations of this element in the sediments of the Lerma basin (between  $0.6$  and  $1.1 \text{ mg kg}^{-1}$ ) were similar to those found by Hu *et al.* (2009) in a zone of recent expansion of irrigation, in the Canadian prairies (between  $0.3$  and  $1.3 \text{ mg kg}^{-1}$ ). In San Joaquin Valley, an intensively irrigated area of the United States, serious biological effects were observed

on the local fauna due to high concentrations of Se (Presser and Ohlendorf, 1987). In the sediments of the bottom of a drainage canal in this area, concentrations between 3.1 and 210.0 mg kg<sup>-1</sup> were detected (Presser and Ohlendorf, 1987), exceptionally higher than those found in Lerma. In agrarian regions, the contamination by Se is generally due to natural causes (*e.g.*, sedimentary rocks with high concentrations of Se) that might be intensified with irrigation (Hu *et al.*, 2009).

P<sub>A</sub> presented the highest mean concentrations of Hg and Cu, P<sub>B</sub> presented the highest concentrations of Pb, while in P<sub>E</sub> the highest mean values of As, Cr and Ni were found. These three locations have as common characteristics a small drainage flow and a mainly nonirrigated influencing surface. The two locations closest to the exit of the basin (P<sub>C</sub> and P<sub>D</sub>) did not present the highest concentrations for any element. The highest mean values for Se and Zn were detected at the exit of the basin (P<sub>basin</sub>). The unirrigated zone location (P<sub>unirrigated</sub>) did not present highest concentrations for any element.

Although the results suggested that at the locations of lesser volume flow these elements tend to concentrate in the sediments and that irrigation might be diluting them, the differences found between the locations were not significant for any element (Mann-Whitney,  $p < 0.05$ ). Moreover, the comparisons between P<sub>unirrigated</sub> and the six locations influenced in some manner by irrigation did not provide evidence of significant differences ( $p < 0.05$ ), demonstrating that, as of the date of this study, the concentrations of the studied elements have not been affected by the irrigated surface.

## Conclusions

It has been demonstrated that in the Lerma basin, at the conclusion of this study (2008), there were no contamination issues related to the analyzed compounds: 44 pesticides and metabolites, 11 organochlorinated compounds, 17 PAHs, 13 PCBs, as well as Cd, Cr, Cu, Ni, Pb, Zn, As, Se and Hg. Nevertheless, slightly elevated values were punctually obtained for endrin in the soil, pp'-DDT in the water, and Ni and Zn in the sediments. During the first years of irrigation in the basin, irrigation has not significantly influenced the concentrations of the studied substances.

The results obtained were satisfactory for the characterization of the soils, water and sediments of the Lerma basin regarding the presence of the aforemen-

tioned substances and will serve as a comparative basis for future studies. These studies will verify whether irrigation influenced these concentrations after several years of irrigation in the zone.

## Acknowledgments

The authors wish to thank the staff of the Water Quality Laboratory at the Confederación Hidrográfica del Ebro, and projects CTM2008-01876/TECNO (MICINN/DGA-Caixa Agreement) and CGL2009-13410-C02-01 (MICINN). Raphael Abrahão is supported by the EU Program of High Level Scholarships for Latin America (Alβan Scholarship E07D400318BR).

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