

# Pesticide contamination in groundwater bodies in the Júcar River European Union Pilot Basin (SE Spain)

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**Abstract** The change from a traditional agricultural model to a modern, more productive one, coupled with population growth, has entailed an increased consumption of water, fertilizers and pesticides. This transformation has led to a greater risk of groundwater contamination. This study has analysed for this purpose a total of 314 samples (period 2010–2013). In addition, 332 samples from the Mancha Oriental groundwater body (period 2001–2003) were also examined in order to gain a better perspective on the temporal evolution of pesticides in groundwater bodies. Using this database, this study aims to characterize pesticide pollution and to examine possible processes. Triazine herbicides are the most common pesticides found and also appear in the highest concentrations, with terbuthylazine having a noteworthy concentration of 900 ng/L. The irrigated agriculture and the physicochemical properties of pesticides are the most important factors influencing the concentration and type of pesticides that can reach groundwater. The spatial distribution of nitrate and pesticides do not correspond as they would if the two behaved similarly. Pesticides can completely biodegrade

before reaching the saturated zone, but it is also possible that their degradation products have not been analysed and, therefore, their concentrations are underestimated.

**Keywords** Groundwater · Pesticides · Agriculture · River basin management

## Introduction

Both population growth and current lifestyles involve a high consumption of natural resources and the discharge of a large number of contaminants into the environment. Furthermore, the emergence of new pollutants and a scarcity of accurate knowledge about their fate in the environment provide good reasons for their characterization and monitoring. In arid and semiarid areas, freshwater has always been a scarce resource, but this already demanding situation will become more challenging yet given the significant decrease in rainfall forecast by climate models for the Mediterranean region (Stocker et al. 2014). Therefore, the need to protect water resources from deterioration in areas with water scarcity has become increasingly evident.

During groundwater recharge processes, various organic and inorganic contaminants can enter the environment and contaminate water resources. The fate of pesticides is controlled by different physicochemical factors in the environment (texture, permeability and organic matter content of soil, pH, redox potential, adsorption capacity of the soil, etc.) and by the characteristics of the pesticide itself (solubility in water, persistence in the

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environment, etc.) (Gavrilescu 2005). However, natural attenuation processes may reduce the toxicity, concentration, and/or mobility of the contaminant without human intervention, through physical (dilution, sorption and precipitation) and biological processes (biodegradation) (Roling and van Verseveld, 2002).

One of the main causes of groundwater quality deterioration is a change in land use (Moratalla et al. 2009 and references therein). In agricultural regions, most pollution is diffuse source, and the main pollutants are derived from the application of fertilizers, pesticides and organic waste from livestock farms. The paradigm shift from traditional agriculture to more productive modern agriculture (promoted by the Green Revolution) has been coupled with population growth, leading to a substantially higher consumption of water, fertilizers and pesticides. The chemical pesticides industry achieved worldwide sales of approximately US\$61 billion in 2013, a 140% increase compared to 2000 (Pelaez and Mizukawa 2017). The expected continued population expansion in emerging countries (in which legislation for environmental protection is not as strict), along with increases in the extension and productivity of agriculture, may pose a significant risk to the environment in general and specifically to the quality of water resources and aquatic ecosystems. In fact, a European-level study integrating data from the institutions responsible for monitoring water quality and their ecosystems (Malaj et al. 2014) points out that chemical pollution in aquatic ecosystems is a large-scale environmental problem, with pesticides the biggest culprit.

In order to protect water resources in Europe, Directive 2000/60/EC (European Parliament and Council of the European Union 2000) was developed. Article 4 sets the environmental objective for European water bodies to achieve a “good ecological status” by the year 2015. The Water Framework Directive (WFD) stipulates that groundwater bodies must “register and invert any significant and sustained upward trend in the concentration of any contaminant”. Article 17 states that strategies for the prevention and control of groundwater pollution are to be developed subsequently in Directive 2006/118/EC (European Parliament and Council of the European Union 2006) on the protection of groundwater against pollution and deterioration. This directive establishes the threshold values for concentrations of nitrate (50 mg/L) and pesticides (100 ng/L for an individual pesticide and 500 ng/L for the sum total of all the pesticides) and the criteria for defining when a

groundwater body is considered to have a “good chemical status” and the need to reverse the trend of increasing contaminant concentrations.

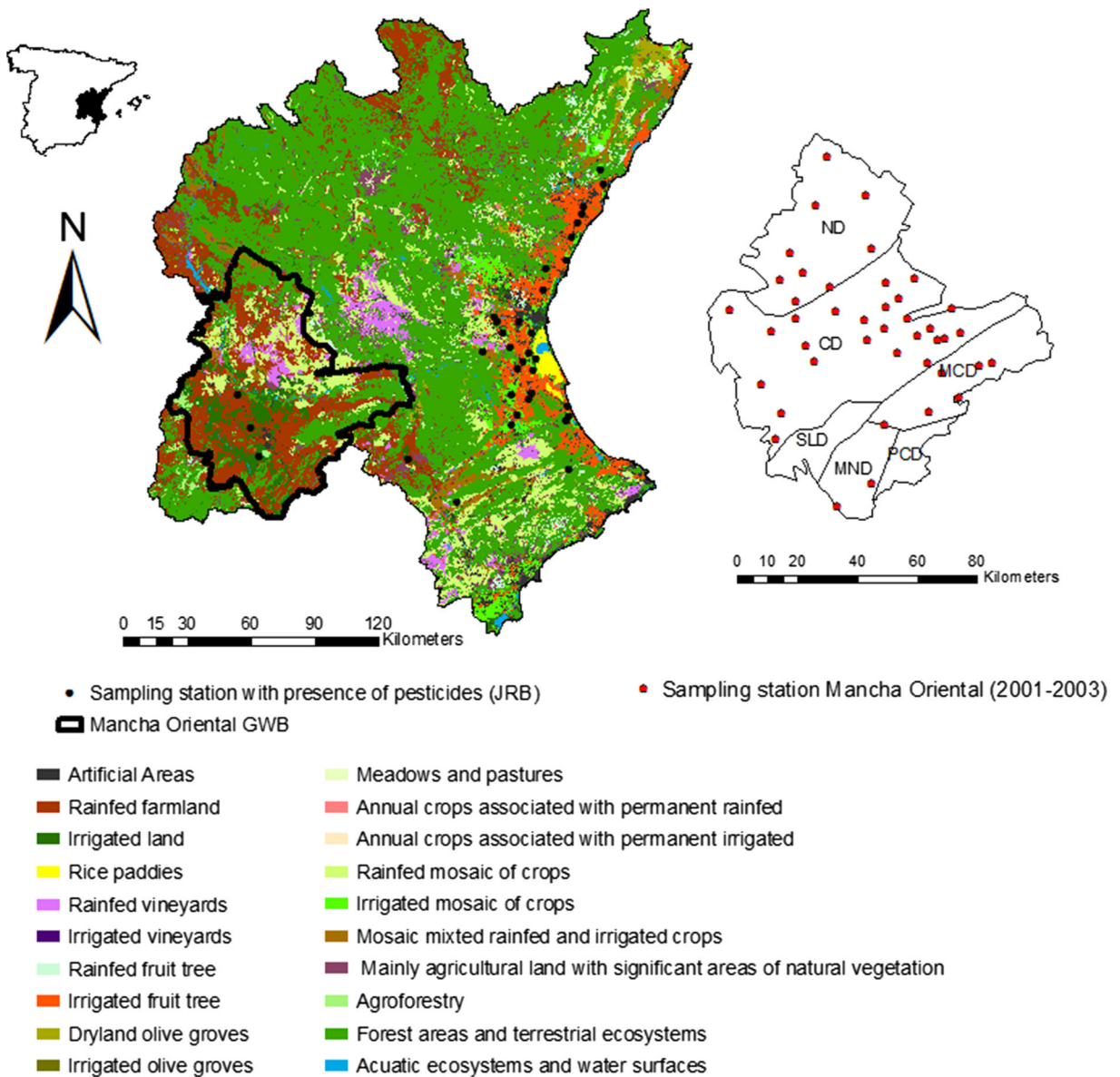
The Júcar Basin Authority (JBA) is charged with controlling the chemical status of groundwater in this catchment. The Control Program for Protected Areas (CPPA) analyses inorganic and organic contaminants, (i.e. pesticides) and metals, and includes water bodies in which groundwater is used for water supply with an average volume of consumption greater than 100 m<sup>3</sup> per day (Article 7 of Directive 2000/06/EC). An additional program, the Operational Program for Pollution Control (OPPC) from diffuse sources, analyses both organic pollutants (pesticides) and nitrate. The objective of this work is to characterize groundwater contamination by pesticides and perform a preliminary approximation to the causes and factors that control the spatial and temporal distribution of pesticides in the Júcar River Basin (JRB) and the Mancha Oriental groundwater body.

## Methodology

### Study area

The JRB is located in the eastern Iberian Peninsula (Fig. 1) and comprises nine river basins covering an area of 42,989 km<sup>2</sup> as well as associated transitional and coastal waters (Júcar River Basin 2015). The WFD (Parliament and the Council of the EU 2000) defines a groundwater body (GWB) as a clearly differentiated volume of groundwater in an aquifer or aquifers, by which definition, the JRB has 90 GWBs (JBA, 2015). Predominant land use within the JRB is forest and seminatural areas (50.5%, Corine Land Cover 2000), followed by rainfed areas (35.5%) and then irrigated agricultural areas (10.5%). Urban and industrial areas cover a mere 2.8% of the territory, and just 0.7% is wetlands and water surfaces (Fig. 1). Therefore, irrigated areas comprise around 4520 km<sup>2</sup>, mainly in the Plana de Castellón, Valencia and the lower basin of the Turia River, the Mancha Oriental, the lower basin of the Júcar River and the valleys of Vinalopó and Monnegre.

Total water demand in the JRB is approximately 3230 hm<sup>3</sup>/year, with about 78% of that allocated to agriculture, 17% to urban and industrial needs connected to the water network) and 5% to industrial, recreational and livestock demands (JBA 2015). The total contribution of the Júcar River system to this demand is



**Fig. 1** Location of the sampling points (2010–2013) and main land uses in the JRB (source Corine Land Cover 2000). Hydrostructural domains defined in the Mancha Oriental GWB and sampling points (2001–2003)

3250 hm<sup>3</sup>/year, with 27% (890 hm<sup>3</sup>/year) coming from direct runoff and the remaining 73% (2360 hm<sup>3</sup>/year) from groundwater withdrawals (JBA 2015). These figures contrast with the distribution average for the rest of Spain, which is almost exactly the opposite (75% direct surface runoff and 25% groundwater withdrawals). These figures underscore the importance of groundwater resources for covering water demand in the JRB.

In order to gain a better perspective on the spatial-temporal evolution of pesticides, we examined samples

collected from the Mancha Oriental GWB in 2001–2003. The Mancha Oriental GWB in the SW JRB extends over an area of 7260 km<sup>2</sup>, making it the largest carbonate aquifer system in Spain (Fig. 1). This system supports about 1000 km<sup>2</sup> of irrigated land, and the groundwater supplies a population of 275,000 inhabitants. The Mancha Oriental GWB consists of six hydrostructural domains: Northern Domain (ND), Central Domain (CD), El Salobral-Los Llanos Domain (SLD), Moro-Nevazos Domain (MND), Pozocañada

Domain (PD) and Montearagón-Carcelén Domain (MCD) (Fig. 1). For a more detailed description of their geology and hydrogeology, see Sanz et al. (2009).

#### Groundwater analyses

The WFD was adopted in 2000. Articles 4 and 5 set the environmental objectives and the types of pressures and associated impacts to which the GWBs are subjected. Since the pressures and impacts must be analysed jointly, Article 8 describes the programs to be designed in order to both monitor and control GWB status. The available data were gathered from the JBA website. Groundwater analyses were carried out during spring and fall campaigns from 2010 to 2013. In this period, the JBA conducted 553 analyses in 77 and 82 data points from the CPPA and OPPC control programs, respectively.

In 2000–2003, a total of 332 samples were collected from 42 public wells randomly distributed in the Mancha Oriental GWB to obtain, insofar as possible, a representative sample of the study area. However, no sampling points were available from the SLD or in the PD for pesticide analysis (Fig. 1). Each sample was collected in a 1-L opaque glass container and analysed at the municipal laboratory of Albacete within 24 h, when possible. The analysis was carried out using a gas chromatography device coupled to a mass spectrometer (Varian Saturn 2000). A solid phase microextraction was used in 1.2 mL of sample and mixed with 0.12 g of sodium chloride, without any clean-up or preconcentration processes. Detection limits (dl) for the pesticides analysed were between 1 and 10 ng/L. In addition to pesticides, various chemical parameters were also analysed following the official standard methods for water analysis (APHA-AWWA-WPCF 1998). The parameters determined, the detection limits, the technique employed and the instruments necessary were pH (dl = 0.33, pH meter GLP21 Crison), conductivity (dl = 1.2  $\mu$ S/cm, GLP31/32 Crison) and total organic carbon (TOC) (dl = 0.30 mg/L, non-dispersive infrared spectrophotometry vario TOC cube Elementar). Chloride (dl = 0.93 mg/L), nitrate (dl = 0.5 mg/L), fluoride (dl = 0.005 mg/L) and sulphate (dl = 5.88 mg/L) were analysed by ion chromatography (DX 120 Vertex). Calcium (dl = 0.1 mg/L) and magnesium (dl = 0.1 mg/L) were determined by complexometric titration. Sodium (dl = 0.0002 mg/L) and potassium (dl = 0.0003 mg/L) were analysed by atomic absorption

spectroscopy (AA50-SIPS-10 Varian). Aluminium (dl = 3.79  $\mu$ g/L) and manganese (dl = 0.35  $\mu$ g/L) were determined by atomic absorption spectroscopy (graphite furnace, Varian 280Z). Copper (dl = 0.005 mg/L) and iron (dl = 0.005 mg/L) were analysed by fast sequential atomic absorption spectroscopy (Varian 240FS).

#### Land use and climate data

Raster layers of land uses from the Corine Land Cover (CLC) database were downloaded from the National Centre for Geographic Information (CNIG, its initials in Spanish; CNIG, 2014). The boundaries of the JBA and the raster layer of groundwater bodies were downloaded from geographic information system (GIS) resources available on the JBA Web site. The 2000 version of the CLC land use raster layer was chosen, because the 2006 version could not differentiate between irrigated and dry crops for several categories (e.g. fruit trees, olive groves, vineyards, etc.); the difference between the two versions only affects 0.58% of the area of agricultural land and so was not relevant. The advantages of being able to distinguish between irrigated and dry land was considered more useful than the benefits of having more current land use information, since the percentage of land occupied by irrigated crops may be a factor in the distribution of nitrate and pesticides in groundwater. This calculation was based on the creation of a circular buffer around each sampling station where the presence of a pesticide was detected, with a radius of 1000 m (McLay et al. 2001).

The isoconcentration maps of nitrate and pesticides were prepared with geostatistical methods. Since the sampling points were not very numerous and their distribution was not completely random, we chose the interpolation method of the inverse distance weighted (IDW), which is a local method based on weighted averages such as kriging; however, unlike kriging, the IDW does not require many points. The ArcMap (ESRI ArcMap™ 9.3) software was used for visualizing geographic information and the creation of maps. Principal component analysis (PCA) is a statistical technique based on either synthesizing information or dimension reduction (number of variables). Therefore, if a matrix is formed by N cases and N variables, the goal is to reduce their number while losing as little information as possible. PCA has already been successfully applied in groundwater pollution studies on agricultural activities by Melo et al. (2012), Ielpo et al. (2012), Olsen et al.

(2013) and Vonberg et al. (2014). We used natural logarithm transformation in order to achieve a normal distribution, and we standardized data by converting the standard normal value or “z” transform, resulting in a mean of zero and a standard deviation of one for each variable. Values below the quantification level are considered to be zero since (according to Olsen et al. 2013) they do not affect the PCA. The varimax rotation method was used to maintain orthogonal axes. The statistical analysis was performed using the statistical program SPSS statistics 19. The data processing was carried out using the ACCESS database, and all operations were calculated in the Excel program. The precipitation data for the period of 2001–2003 belong to the weather station at the Los Llanos airport, 5 km south of Albacete city. Meteorological data were downloaded from the Irrigation Advisory Service for Farmers (SIAR, its initials in Spanish) for the Castilla-La Mancha region (SIAR, 2015).

## Results and discussion

### Pesticide contents in JRB groundwater bodies: temporal evolution

From 2010 to 2013, pesticides were detected in 77 samples from the OPPC and CPPA programs. Under the OPPC, 314 samples were analysed, with 75 revealing at least one pesticide (24%). Moreover, a minimum of one pesticide was detected at each of 33 sampling stations belonging to 18 GWBs (Table 1). The most frequently detected pesticide was terbuthylazine (38 times), followed by bromacil and the metabolite desisopropylatrazine (DIA; 26), simazine (24) and the metabolite desethylatrazine (DEA; 18) (Table 2).

The threshold level for an individual pesticide was exceeded (100 ng/L) on 37 occasions at 19 sampling stations corresponding to 12 GWBs. This represents almost 9% of the samples from the OPPC. Furthermore, the maximum allowable level of 500 ng/L for the sum of all pesticides determined (Directive 2006/118/EC, European Parliament and Council of the EU, 2006) was exceeded at five sampling stations corresponding to five GWBs (Table 1). The pesticide that exceeded this limit most frequently was terbuthylazine, followed by bromacil and atrazine (Table 2).

Pesticides that exceeded concentrations of 100 ng/L were terbuthylazine (520 ng/L, spring 2010 campaign; 900 ng/L, spring 2011 campaign) in the Medio Palancia

GWB, followed by bromacil (460 ng/L, spring 2012 campaign; 480 ng/L, autumn 2012 campaign) in the Plana de Castellón GWB and pendimethalin (420 ng/L; autumn 2011 campaign) in the Buñol-Cheste GWB. Other pesticides found in concentrations above 100 ng/L were atrazine (max. 380 ng/L), chlorpyrifos (max. 290 ng/L), metolachlor (max. 230 ng/L), DIA (max. 210 ng/L), simazine (max. 180 ng/L), prometryn (max. 150 ng/L), DEA (max. 120 ng/L), trifluralin (max. 110 ng/L) and propazine (max. 100 ng/L) (Table 2). These maximum concentrations and the number of times legal concentrations were exceeded indicate that the Buñol-Cheste and Mancha Oriental GWBs have the worst chemical status (Fig. 2). It is noteworthy that two data points (08.129.CA806, Villena-Benejama GWB and 08.160.CA004, Mancha Oriental GWB), which belong to the CPPA, exceeded the legal levels for an individual pesticide concentration (Table 1).

The maximum concentrations in the JRB are lower (by up to three orders of magnitude) than those found in other European GWBs. In a study conducted at the European level, Loos et al. (2010) found the highest concentrations to be for *N,N'*-dimethylsulfamide (DMS) (52,000 ng/L), followed by chloridazon-desphenyl (13,000 ng/L) and bentazon (10,550 ng/L). Italy, according to data from Meffe et al. (2014), has recorded the maximum concentrations for the insecticide dieldrin (478,000 ng/L), simazine (221,000 ng/L) and terbuthylazine (29,050 ng/L). Pesticide concentrations in other Spanish river basins were also higher than those detected in this work. Jurado et al. (2012) found that the highest concentrations were for alachlor (9950 ng/L), metolachlor (5370 ng/L), malathion (3500 ng/L), atrazine (3450 ng/L), chlorfenvinphos (2500 ng/L), dimethoate (2300 ng/L), DEA (1980 ng/L), chlortoluron (1700 ng/L), simazine (1690 ng/L), parathion-methyl (1500 ng/L), terbuthylazine (1270 ng/L) and linuron (1010 ng/L). On the other hand, pesticides most often detected were triazine herbicides such as atrazine (and its degradation products such as DEA), simazine and terbuthylazine such as those encountered in the JRB. Bromacil, found in concentrations of up to 480 ng/L in the JRB, is not detected in significant concentrations or frequencies in other parts of Spain, because this herbicide is mainly used for citrus and pineapple cultivation, and its use was banned in December 2003 (EU Commission 2002).

The pesticide concentrations obtained in the region of Valencia (western JRB) in 2000 by Hernández et al. (2008) are within the range of those found in the JBA. DIA was the most frequently detected chemical (72%

**Table 1** Minimum (m) and maximum (M) concentrations of pesticides in GWBs and pesticides that exceeded the concentration of 100 ng/L during the period of 2010–2013

Groundwater body		Year				Total pesticides (ng/L)		Threshold values		Pesticides >100 ng/L
Station code	Site	2010	2011	2012	2013	m	M	tp>500 ng/L	ip>100 ng/L	
08.131.CA004	Liria-Casino	X	X		X	dl	260		X	Beta HCH
08.160.CA004 <sup>a</sup>	Villena-Benejama	X				dl	150		X	Prometryn
08.129.CA004	Mancha Oriental			X	X	dl	610	X	X	Atrazine (2), Desethylatrazine, Terbuthylazine (2), Metolachlor
08.129.CA806 <sup>a</sup>			X		X	dl	210		X	Atrazine
08.129.CA808			X			dl	97		X	
08.140.CA002	Buñol-Cheste		X	X	X	dl	710	X	X	Pendimethalin, Terbuthylazine, Chlorpyrifos (2)
08.140.CA003				X		130	170		X	Bromacil (2)
08.140.CA142				X	X	144	447		X	Atrazine, Bromacil
08.141.CA001	Plana de Valencia Norte		X	X	X	dl	340		X	Bromacil, Terbuthylazine
08.141.CA003					X	dl	13			
08.142.CA003	Plana de Valencia Sur			X	X	dl	142			
08.142.CA004					X	dl	87			
08.142.CA006					X	dl	101			
08.142.CA008			X		X	dl	91			
08.146.CA002	Almansa	X	X		X	dl	520	X	X	Atrazine (2), Metolachlor
08.130.CA002	Medio Palancia	X	X			dl	900	X	X	Terbuthylazine (2)
08.143.CA001	La Contienda		X		X	dl	77			
08.143.CA002				X			dl	130		X
08.149.CA001	Sierra de la Agujas		X	X	X	dl	560	X	X	Terbuthylazine (2), Simazine
08.149.CA004						X	dl	89		
08.164.CA002	Ondara-Denia		X			dl	60			
08.144.CA001	Sierra de Ave			X		dl	89			
08.144.CA003						X	dl	15		
08.148.CA002	Hoya de Xatíva			X		dl	177			
08.150.CA002	Barig			X	X	dl	230		X	Terbuthylazine, Trifluralin
08.151.CA001	Plana de Jaraco			X		dl	163		X	Propazine
08.151.CA077					X	X	dl	110		X
08.127.CA001	Plana de Castellón			X	X	dl	310		X	Bromacil (2)
08.127.CA003				X	X	dl	480		X	Bromacil (2)
08.127.CA592						X	44	56		
08.127.CA593						X	146	147		X
08.128.CA014	Plana de Sagunto			X		dl	112			
08.110.CA002	Plana de Oropesa				X	dl	37			

The fields marked with an X belong to those GWBs where a pesticide has been detected. Threshold values indicate whether pesticides exceed the levels set by European legislation for total pesticides (tp) and for individual pesticides (ip). Fields filled with grey indicate water samples that were not analysed. The number in parentheses after the name of the pesticide indicates the times that it exceeded the concentration of 100 ng/L

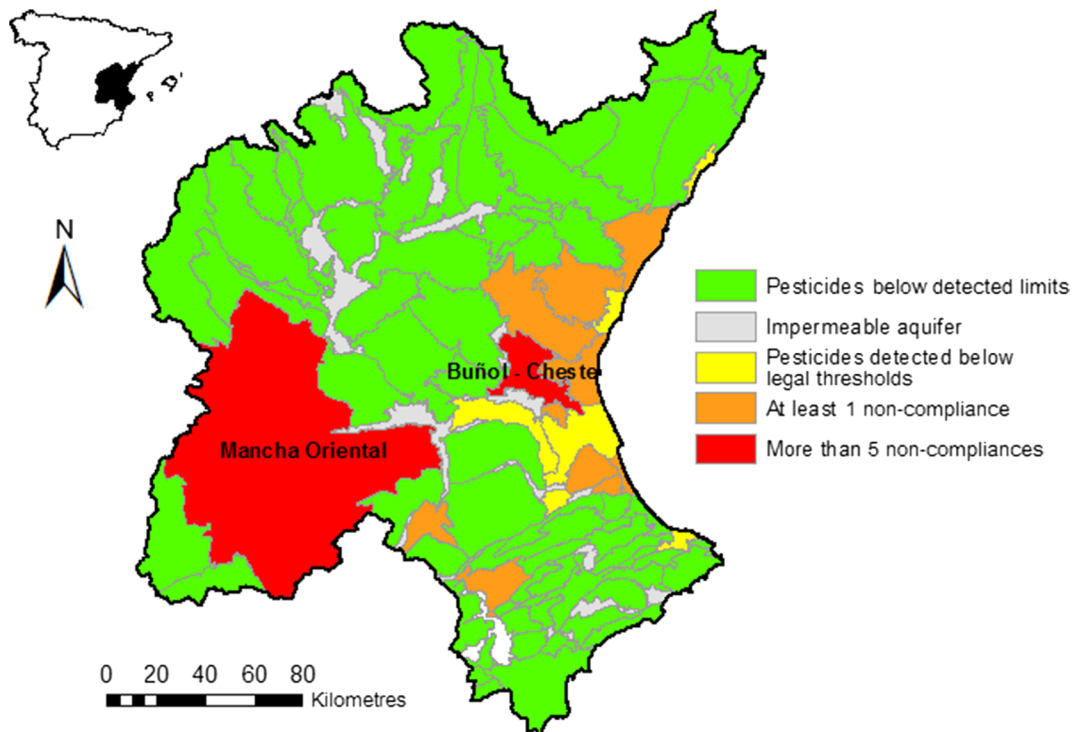
dl detection limit

<sup>a</sup> Sampling stations belonging to the control program of protected areas. Data source: JBA

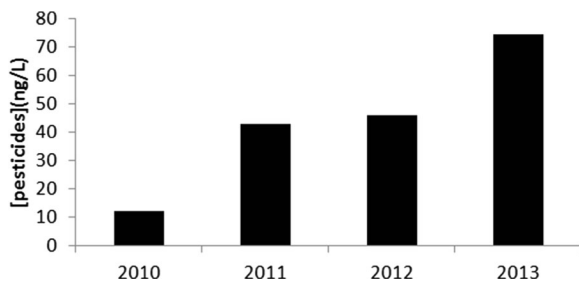
**Table 2** Number of times a pesticide was detected (NOD), minimum (m) and maximum (M) concentrations and times when the pesticide concentration exceeded the threshold value of 100 ng/L

Pesticide	NOD	m (ng/L)	M (ng/L)	>100 ng/L
Terbuthylazine	38	10.0	900	9
Bromacil	26	0.017	480	8
Pendimethalin	2	0.7	420	1
Atrazine	14	1.1	380	6
Chlorpyrifos	3	21.0	290	2
Alpha HCH	1	260.0	260	1
Metolachlor	6	0.9	230	2
Deisopropylatrazine	26	11.0	210	1
Simazine	24	11.0	180	2
Prometryn	2	1.1	150	1
Desethylatrazine	18	12.0	120	1
Trifluralin	3	63.0	110	2
Propazine	6	16.0	100	1
Diuron	11	11.0	50	0
Metalaxyl	2	16.0	22	0
Oxyfluorfen	4	0.9	11	0
Alachlor	1	1.1	1.1	0
Lindane	2	1.1	1.1	0

of samples). Simazine, terbuthylazine and carbendazim fungicide were detected in about 50% of the samples. Bromacil reached maximum values of 4500 ng/L, followed by terbumeton at 1540 ng/L, and 4-chloro-2-methylphenoxyacetic acid (MCPA) at 800 ng/L. In the 2003 campaign, a larger number of metabolites were analysed. The most common pesticide in groundwater was simazine, followed by desethyl terbumeton and 2-hydroxyterbuthylazine. Pesticides found in the highest concentrations were desethyl terbumeton (1620 ng/L), DEA (1420 ng/L) and terbumeton (1070 ng/L). It is worth noting that the metabolites of some triazine herbicides (simazine, terbumeton and terbuthylazine) were typically found in higher concentrations than their parent compounds. The fact that pesticides reached concentrations above legislated levels indicates an excessive use of chemicals or poor methods of pesticide application. In fact, it is estimated that only 0.1% of the pesticides applied reach the target pest (Pimentel and Levitan 1986). Therefore, to achieve a sustainable use of pesticides (European Parliament and Council of the European Union 2009), the implementation of EU Directive 2009/128/EC was encouraged.



**Fig. 2** Incidence of pesticide pollution in the JRB GWBs



**Fig. 3** Temporal evolution of mean pesticide concentrations between 2010 and 2013 in the JRB. Years 2010 and 2011 general sampling. Years 2012 and 2013 sampling focused on polluted zones

As for the temporal evolution, the mean concentrations of pesticides in GWBs increased from 12.38 ng/L in 2010 to 74.30 ng/L in 2013 (Fig. 3). This increase could be explained by higher pesticide applications since, according to the Spanish Association for Plant Protection (AEPLA, its initials in Spanish), the consumption of agricultural pesticides in Spain increased from 75,883 Mg in 2009 up to 95,760 Mg in 2013 (Aragon Statistics Institute, 2015). Another explanation could be the type of sampling design, from general sampling to determine areas with the highest concentrations (2010) to another directed towards areas with pollution problems due to pesticide campaigns (2012 and 2013).

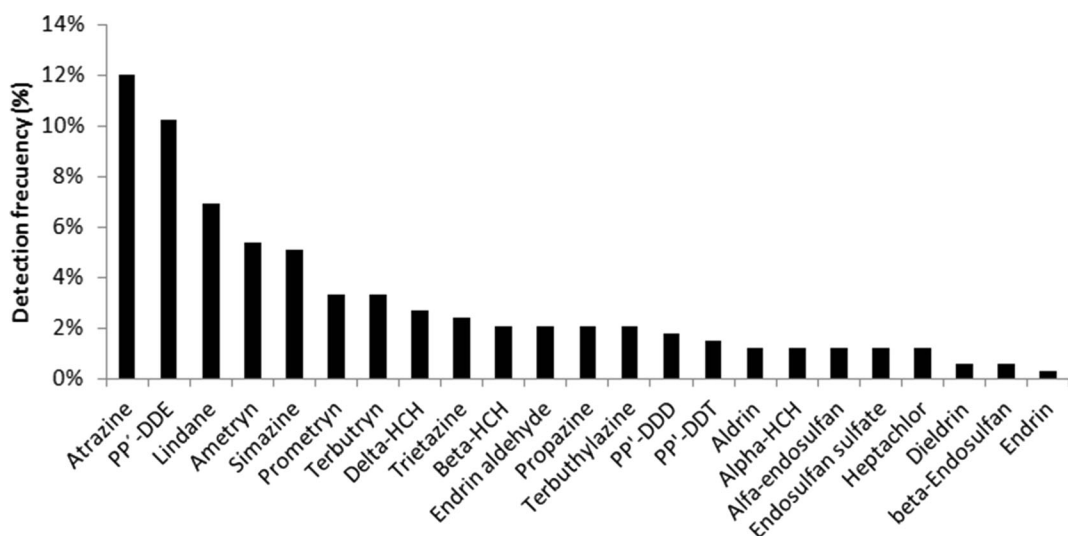
In order to gain a better perspective on pollution temporal trends, data from the 2010–2013 period and the 2001–2003 period from the Mancha Oriental GWB were compared. For the 2001–2003 period, 23 different pesticides were detected in 235 samples (70%) (Fig. 4). Based on the chemical structure and pest target of the

pesticides detected, they correspond to triazine herbicides and organochlorine insecticides. Most of the organochlorine insecticides found were banned in 1994 (Ministerio de Sanidad y Consumo, 1994) with the exception of lindane. The use and trading of the remaining pesticides detected were authorized or in the process of being regulated.

The average concentration of total pesticides in the Mancha Oriental GWB increased dramatically from 1.74 ng/L in 2001 up to 20.77 ng/L in 2003 (Fig. 5), although this evolution was not uniform in the groundwater body. In the Central Domain, for instance, the average pesticide concentration increased gradually, whereas in other hydrogeological domains, it reached a maximum in 2002 and decreased in 2003 (Fig. 5). From 2001 to 2003, there was an increase in the use of pesticides in Spain, from 102,912 Mg in 2000 to 113,734 Mg in 2003. It is noticeable that 2003 showed the highest concentrations of the temporal series from 2000 to 2013 (Aragon Statistics Institute 2015).

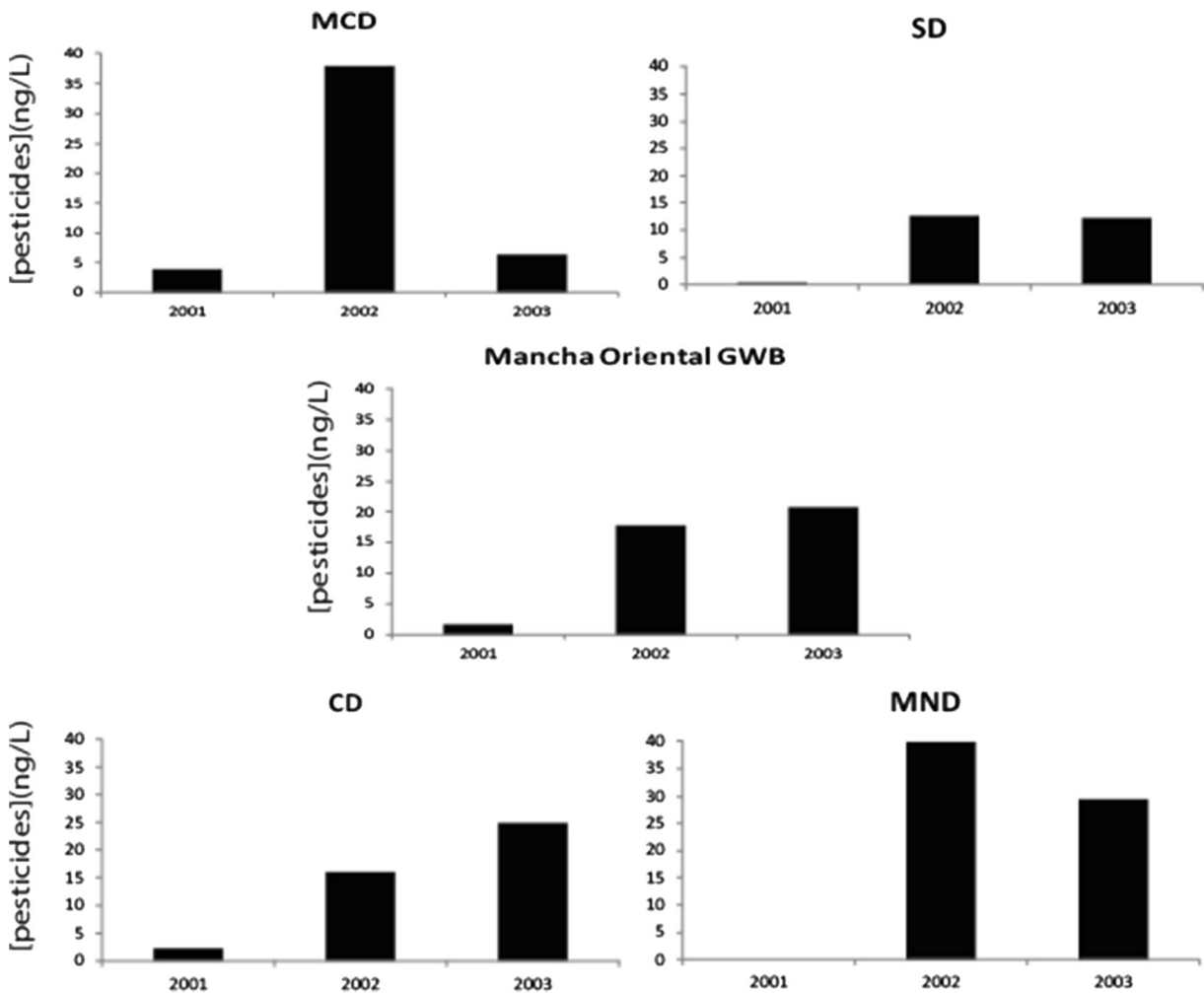
#### Factors affecting pesticide distribution in the JRB

Pesticide concentrations in groundwater depend on the vulnerability of the aquifer to pollution, which is largely determined by land use. In addition, aquifer recharge (precipitation pattern and irrigation return flows), depth to groundwater, geological characteristics of the medium, characteristics of the unsaturated zone, geomorphology and hydraulic properties (e.g. permeability) also impact aquifer vulnerability to pollution. In the case of



**Fig. 4** Pesticides detected in the Mancha Oriental GWB (2001–2003)





**Fig. 5** Temporal evolution of the mean pesticide concentration in the Mancha Oriental GWB hydrostructural domains. *MCD* Montearagón-Carcelén Domain, *SD* Septentrional Domain, *ND* North Domain, *CD* Central Domain, *MND* Moro-Nevazos Domain

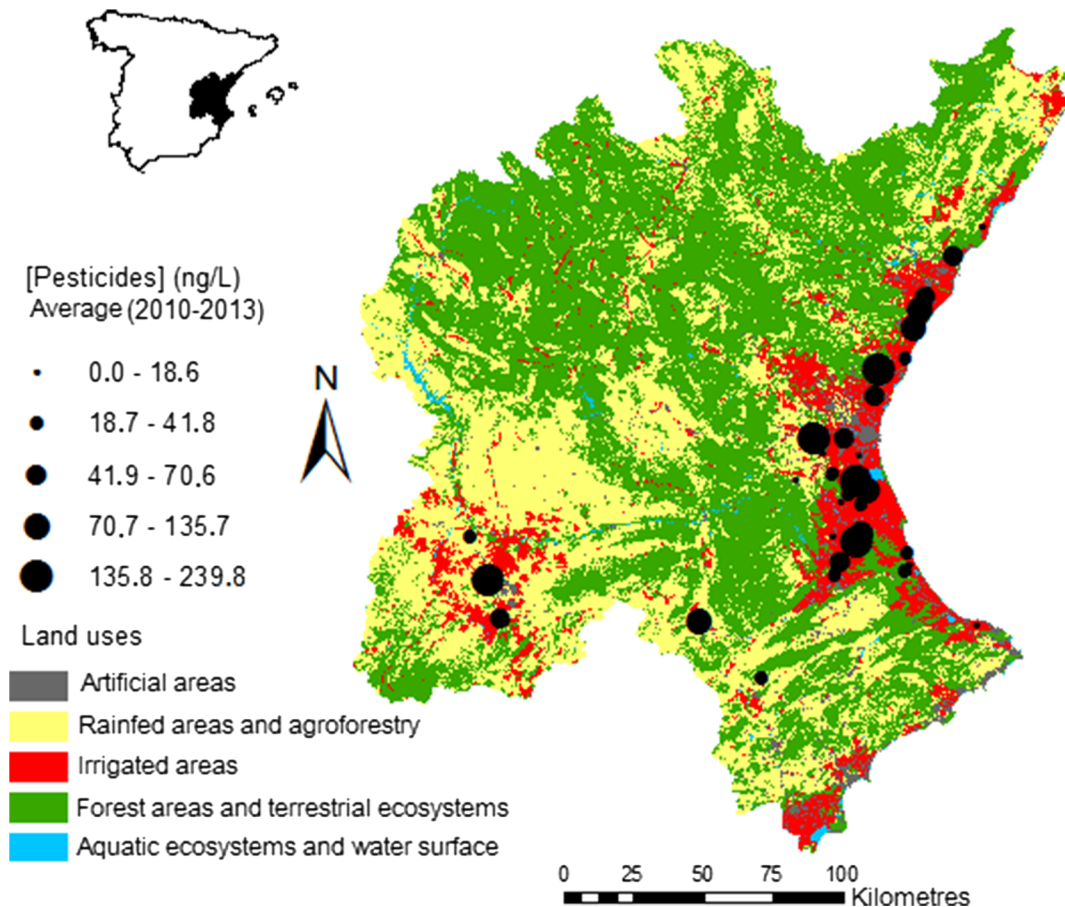
pesticides, it also depends on the pesticide’s capacity to reach the saturated zone, based on its physicochemical properties (Gavrilescu 2005; Åkesson et al. 2013).

*Land uses*

Irrigation is one of the land uses related to groundwater contamination by pesticides (Andrade and Stigter 2009; Sánchez et al. 2013; Köck- Schulmeyer et al. 2014). In the JBA, results indicate that most of the areas with pesticides detected correspond to agricultural land or nearby zones (Fig. 6). In more than 50% of the GWBs in which pesticides have been detected, the main land use corresponds to irrigated land. In the La Contienda, Barig, Sierra Ave, and Medio Palancia GWBs, forested

areas and terrestrial ecosystems cover most of the territory (Fig. 6). However, the maximum pesticide concentration (900 ng/L) is in the Medio Palancia GWB, which has a relatively small percentage of irrigated land (18%) (Fig. 7). This apparent anomaly could be explained by a medium that is more vulnerable to pesticide contamination since pollutants can reach the saturated zone of the aquifer through natural or artificial preferential flow paths (deteriorated wells) without going through the unsaturated zone and thereby circumventing the natural processes of contamination attenuation.

Adams and Thurman (1991) defined the ratio of DEA/atrazine (DAR) in order to characterize the transport of atrazine and its metabolite DEA. This ratio indicates the capacity of the unsaturated zone to cause



**Fig. 6** Land uses and average concentration of the sum of pesticides. Data source: JBA and Corine Land Cover 2000

atrazine desethylation due to biodegradation, which is the result of the metabolic activity of bacteria and fungi found in the soil. Its effectiveness depends on the interaction time of microorganisms with the contaminant in the unsaturated zone. Therefore, in the case of a homogeneous media, the atrazine could be metabolized in significant amounts by organisms, and the DAR would have values higher than 0.4 or even close to 1.0 (Adams and Thurman 1991; Goolsby et al. 1997). In contrast, when atrazine enters the saturated zone through heterogeneous systems with preferential flow paths, the contact time between atrazine and soil organisms could be shorter and, therefore, the DAR ratio would be less than 0.4 or 1.0. Thus, DAR can be employed to define the source of pollution (punctual versus diffuse). The calculated DAR ratio in some GWBs was found to be between 1.22 and 3.00 (average = 1.94;  $n = 14$ ; Table 3). The DAR indicates that the contamination probably comes from diffuse sources (Baran et al. 2008; Hildebrandt et al. 2008; Koch-Shulmeyer et al.

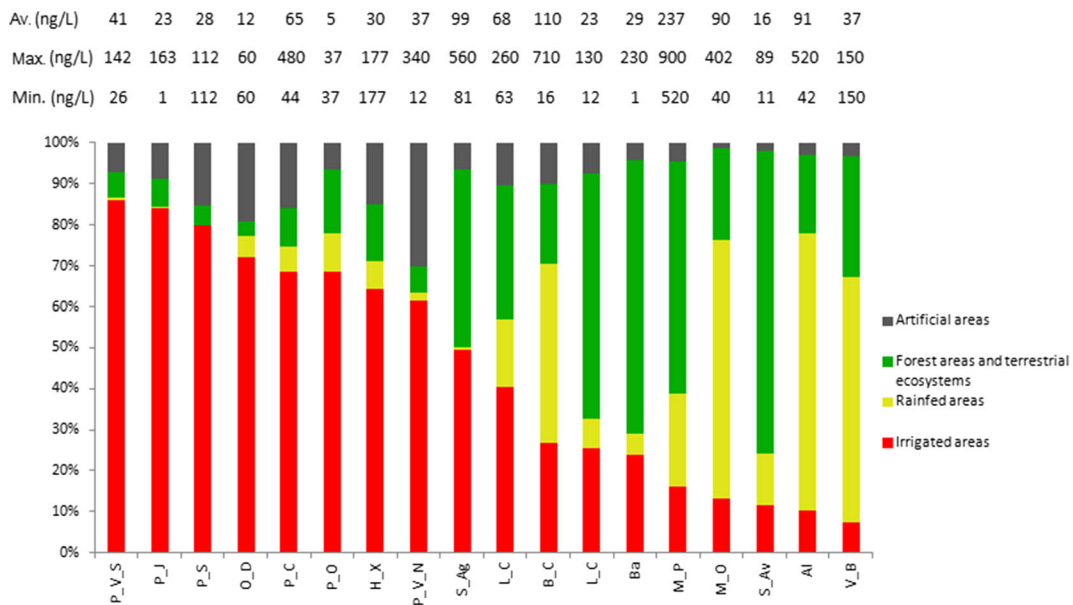
2014; Vonberg et al. 2014). Some values may have been underestimated, because atrazine was below the detection limit and, therefore, we chose the highest possible value below that limit for the calculation, resulting in the minimum possible ratio in that case. The GWBs where the DAR can be calculated have at least 50% of the land area occupied by agricultural activities, reaching nearly 90% in the Plana de Valencia Sur GWB.

#### *Pesticide persistence in groundwater*

The physical-chemical characteristics of pesticides also control the behaviour and distribution of these pollutants. Gustafson (1989) developed the Groundwater Ubiquity Score (GUS):

$$GUS = \left( \log t_{1/2} \right) \times (4 - \log K_{oc})$$

which considers the half-life ( $t_{1/2}$ , the time elapsed until the pesticide reaches half of its initial concentration) of a



**Fig. 7** Percentage occupied by different land uses in the groundwater bodies where pesticides were detected. Mean; *Max* maximum detected, *Min* minimum detected, *P\_V\_S* Plana Valencia Sur GWB, *P\_J* Plana Jaraco GWB, *P\_S* Plana Sagunto GWB, *O\_D* Ondara Denia GWB, *P\_C* Plana Castellon GWB, *P\_O* Plana

Oropesa GWB, *H\_X* Hoya Xativa GWB, *P\_V\_N* Plana Valencia Norte GWB, *S\_Ag* Sierra de las Agujas GWB, *L\_C* Liria Casinos GWB, *Ba* Barig GWB, *M\_P* Medio Palancia GWB, *M\_O* Mancha Oriental GWB, *S\_Av* Sierra Ave GWB, *Al* Almansa GWB, *V\_B* Villena Benejama GWB. Data source: Corine Land Cover 2000

pollutant in the saturated zone and the organic carbon partition coefficient ( $K_{oc}$ ), which indicates the adsorption capacity of the pesticide in the unsaturated zone. If the GUS is higher than 2.8, the pesticide has a high

leaching capacity, and a score lower than 1.8 indicates a low leaching capacity (Gustafson 1989).

The most common pesticides in the JRB GWBs are triazine herbicides (terbuthylazine, bromacil, simazine,

**Table 3** Values of the DAR

Sample station	GWB	Campaign	[Atrazine] (ng/L)	[DEA] (ng/L)	DAR
08.129.CA004	Mancha Oriental	SPR13	120	210	1.75
08.140.CA002	Buñol-Cheste	SPR13	9*	15	1.67
08.141.CA003	Plana de Valencia Norte	SPR13	9*	13	1.44
08.142.CA003	Plana de Valencia Sur	SPR13	9*	18	2.00
08.142.CA004	Plana de Valencia Sur	SPR13	9*	11	1.22
08.142.CA006	Plana de Valencia Sur	SPR13	9*	26	2.89
08.142.CA008	Plana de Valencia Sur	SPR13	9*	11	1.22
08.149.CA001	Sierra de la Agujas	SPR13	21	60	2.86
08.129.CA004	Mancha Oriental	AUT13	25	45	1.80
08.140.CA002	Buñol-Cheste	AUT13	9*	14	1.56
08.141.CA003	Plana de Valencia Norte	AUT13	9*	12	1.33
08.142.CA003	Plana de Valencia Sur	AUT13	9*	20	2.22
08.142.CA006	Plana de Valencia Sur	AUT13	9*	27	3.00
08.149.CA001	Sierra de la Agujas	AUT13	22	49	2.23

The concentration values with asterisks indicate samples in which atrazine was not detected above the quantification limit (9 ng/L). Data source: JBA

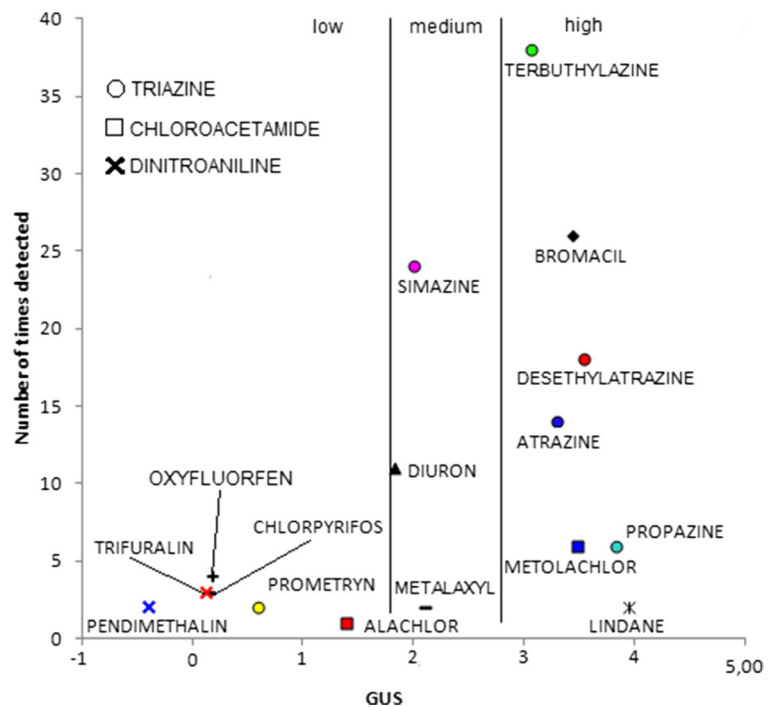
etc.), with a GUS above 2 (with the exception of prometryn) and, therefore, a high leaching capacity and higher detection rates in the aquifer. Pesticides with a GUS of under 1.8 were not detected as frequently (Fig. 8). However, lindane, propazine and metolachlor (3.95, 3.84 and 3.49, respectively) were not detected as expected when the GUS is applied. This is probably due to lindane being banned in 2001 (Commission of the European Communities, 2000), propazine and metolachlor in 2003 and atrazine and simazine in 2004. Exceptionally, in Spain, the use of atrazine and simazine were authorized until July 2007 for certain crops such as corn, accounting for their greater frequency (EU Commission 2004a, b). On the other hand, it is possible that the metabolite concentrations derived from metolachlor degradation are higher than the parent pesticide, but these concentrations have not been analysed for this work. Kolpin et al. (2000) noted that the degradation metabolites of atrazine and metolachlor are detected at higher frequencies and concentrations than their parent compounds. Lindane has a high GUS because its half-life is elevated despite having a high adsorption coefficient as well. This apparent contradiction can be explained by the likelihood that part of the lindane found was discharged into the environment before its ban, being retained in the unsaturated zone and slowly diffusing into the saturated zone of the

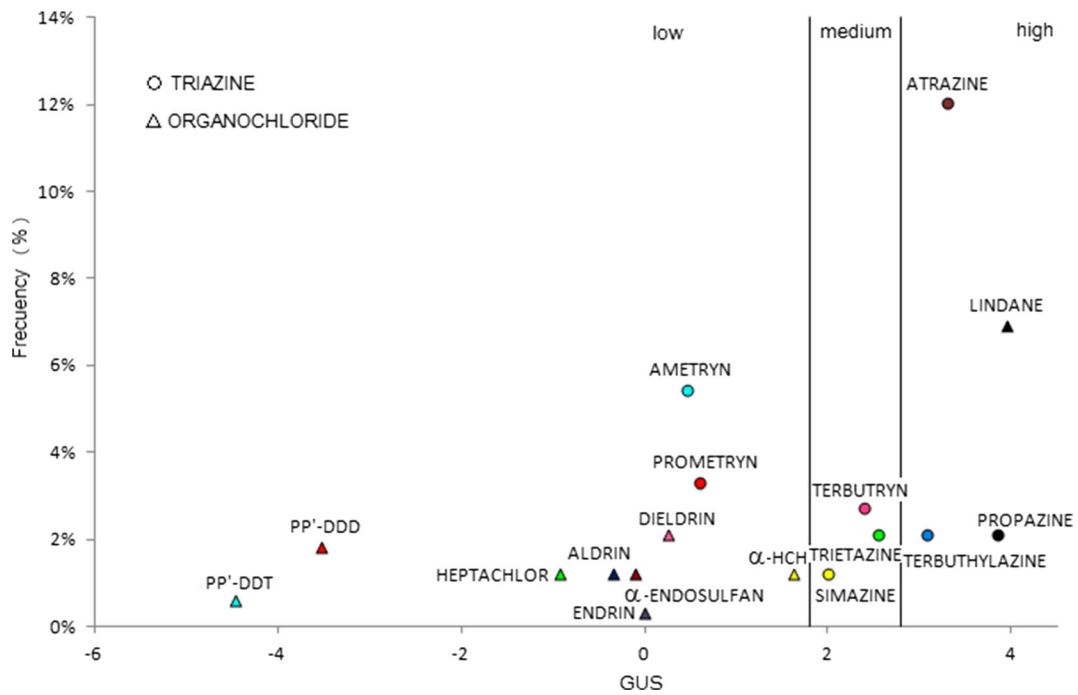
aquifer. As a result, this pollutant is not detected in significant quantities in groundwater.

In the Mancha Oriental GWB (2001–2003), pesticides (in this case, organochlorine insecticides) that have a GUS that is negative or under 1.8 also have a low frequency of detection (1.4% on average). Lindane and DDE (a metabolite of DDT) were exceptions, and their frequency of detection was higher (6.9 and 10.9% respectively, Fig. 9). Triazine herbicides tend to have a higher GUS (0.46–3.84) and a higher detection frequency as well (4.1%; Fig. 9). In this regard, although the determination coefficient between the GUS and the frequency of occurrence of pesticides in the Mancha Oriental GWB is not high ( $R^2 = 0.3$   $p$  value = 0.035;  $n = 16$ ), the sample distribution in Fig. 9 suggests a positive relationship. DDT and DDD (a DDT metabolite) have a low GUS (−4.47 and −3.53, respectively) and were not detected with the frequency of DDE (a DDT metabolite), which has been found with significant frequency (10% of the samples). Metabolites quite commonly have different physicochemical properties than the parent pesticide and may have a higher capacity to be transported to groundwater (Kolpin et al. 2000; Hernández et al. 2008).

The GUS is a preliminary attempt to predict which pesticides are most likely to be found in groundwater,

**Fig. 8** Number of time detected of pesticides vs GUS in JRB GWBs. Data source: Hertfordshire University (2015)



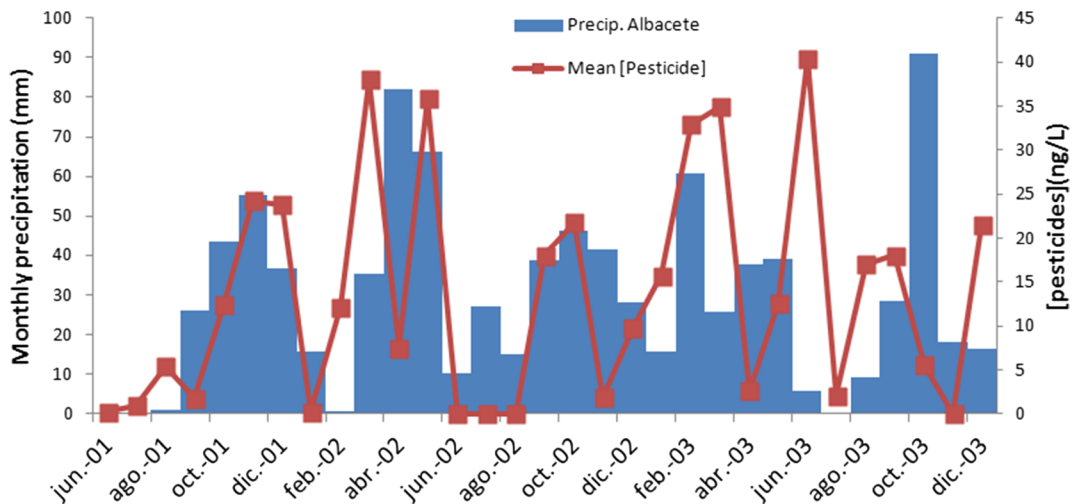


**Fig. 9** Frequency of detection of pesticides compared with the GUS in the Mancha Oriental GWB. Data source: Hertfordshire University (2015)

but it does have limitations. Since it is measured under controlled laboratory conditions, it does not take into account environmental vulnerability to pesticide pollution. Another limitation is the possibility of calculating negative values for pesticides with a short half-life or high absorption coefficients, which can cause misleading interpretations (Spadotto 2002).

*Distribution of precipitation and presence of pesticides in the Mancha Oriental GWB*

Visually, the meteorological data suggest that there is a temporal coincidence between pesticide concentrations in the groundwater of the Mancha Oriental GWB and total monthly precipitation since the highest mean



**Fig. 10** Evolution of mean pesticide concentrations and average monthly rainfall of the 2001–2003 period in the Mancha Oriental GWB

**Table 4** Results of principal component analysis (PCA)

	IP	OP
Variance (%)	46.98	23.45
EC	0.95	0.11
TOC	0.12	0.71
Nitrate	0.78	0.07
Chloride	0.92	0.02
Pesticides	0.00	0.80

IP inorganic pollution,  
OP organic pollution

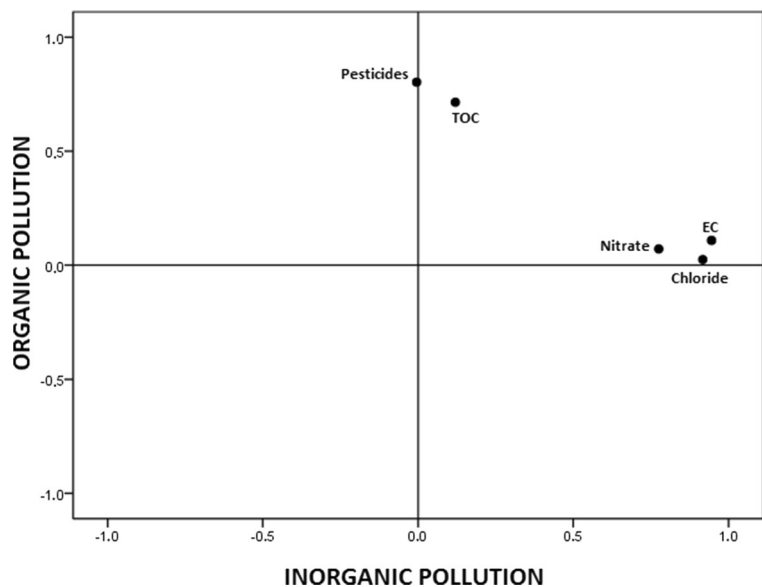
pesticide concentrations were recorded during the rainy months (or in the month immediately afterward) (Fig. 10). Results suggest that there were 2 cycles associated with different precipitation rates from June 2001 to May 2003. The minimum pesticide concentrations occurred during the dry seasons (June–September) and the maximum concentrations during the rainiest period (April–May 2002). In the study period (2001–2003), there have been seven precipitation events of over 20 mm (more than 5% of the annual precipitation) and two above 35 mm (approximately 10% of the annual precipitation). In addition, these events often occur in spring, coinciding with the implementation of pre-emergence treatments for most herbicides, and autumn when pesticide treatments are also applied for crops such as olives and almonds. However, there is no statistical correlation between the precipitation and the pesticide concentration variables ( $R^2 = 0.06$ ;  $p$  value = 0.16;  $n = 31$ ), perhaps because the rain station is not

sufficiently representative of the GWB, and/or because irrigation return flows are not considered. During the spring and summer, crop irrigation, which can constitute an important source of recharge, enhances pesticide transport to the saturated zone.

#### *Relationship between groundwater salinization and pollution by nitrate and pesticides*

Increasing values of electrical conductivity (EC) or chlorides are indicators of groundwater salinization (Vengosh 2003), with values above 2500  $\mu\text{S}/\text{cm}$  indicating seawater intrusion or other saline water sources (JBA 2015). The statistical technique of principal component analysis (PCA) was used to analyse the hydrochemical data, selecting the following variables: EC, TOC, nitrate, chloride and pesticides. The information was reduced to two main components (inorganic pollution (IP) and organic pollution (OP)) that account for 70.43% of the total variance (Table 4; Fig. 11). In the IP (46.98%), contamination by nitrate and related factors such as the EC, chloride concentrations and irrigation land use dominate. In the OP (23.45%), the factors that predominate are those associated with organic pollution such as TOC.

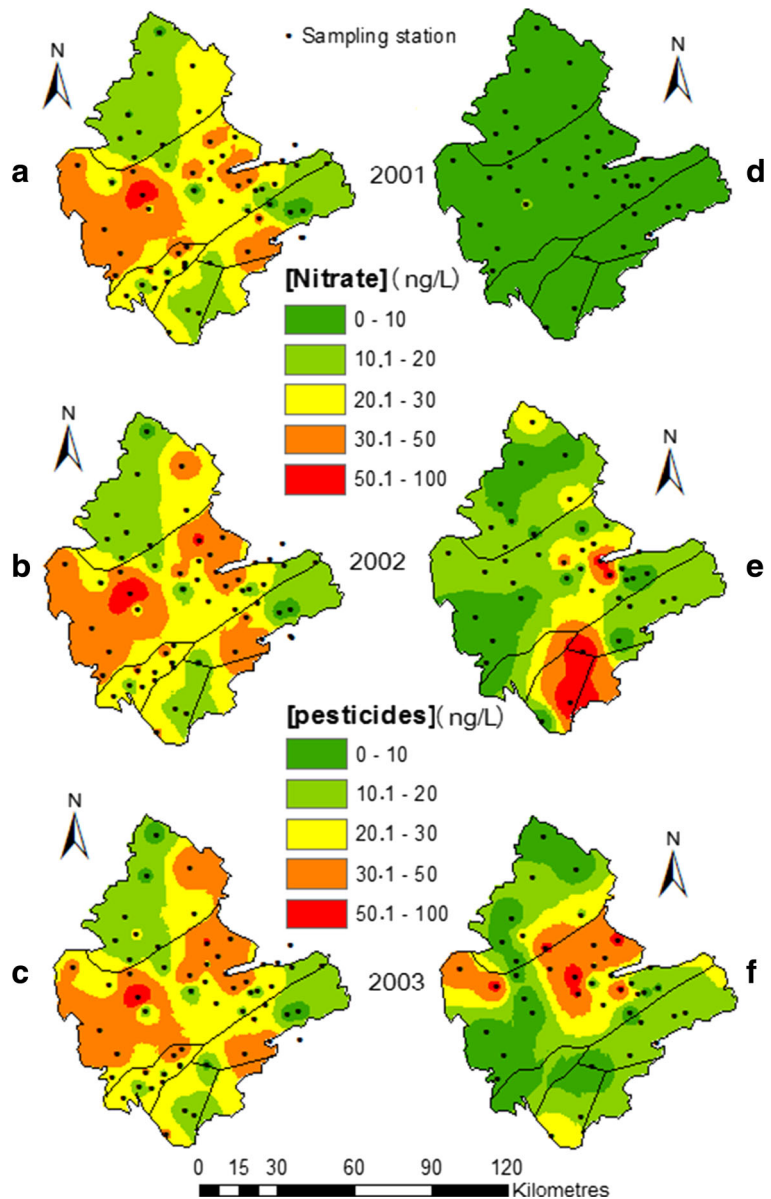
The use of groundwater resources for agricultural purposes may lead to increased concentrations of pollutants and salinity (Vengosh. 2003). Since only a small percentage of the water withdrawn is used by the plant, the remaining fraction evaporates or returns to the

**Fig. 11** Representation of the variables in the PC1 and PC2 axes

aquifer. Thus, aquifer recharge by irrigation return flows can enhance contaminant leaching in the soil. In fact, return is considered to contribute most to the diffuse pollution of surface water or groundwater bodies (Aragüés and Tanji 2003; Moratalla et al. 2011). In the case of pesticides, a similar trend would be expected; however, natural attenuation processes driven by biogeochemical degradation in the unsaturated zone can also occur. These processes can completely degrade pesticides before they reach the saturated zone, or pesticide contamination can be underestimated if the metabolites are not detected.

In the Mancha Oriental GWB, the spatial distribution and temporal evolution of average nitrate concentrations were similar for the 3 years, whereas pesticides were more heterogeneous (Fig. 12). In 2001, pesticide levels were low (0–10 ng/L), whereas in 2002 and 2003, the areas with higher pesticide concentrations tend to overlap the areas with higher nitrate levels in groundwater. Nonetheless, no statistical correlation was found between nitrate and pesticide for either 2002 ( $R^2 = 0.00$ ;  $p$  value = 0.95;  $n = 35$ ) or 2003 ( $R^2 = 0.00$ ;  $p$  value = 0.70;  $n = 35$ ).

**Fig. 12** Inverse distance weighted interpolation of the annual average concentration of nitrate (a–c) and pesticides (d–f) in the Mancha Oriental GWB in the period of 2001–2003



If pesticides and nitrate are agricultural in origin, the spatial and temporal distribution of their concentrations would be expected to be similar. One possible explanation for the lack of similarity is that nitrate is the final oxidation product of ammonium fertilizers, whereas pesticides may be affected by factors other than those that control the distribution and fate of nitrate. In any case, nitrate and pesticides were found in higher concentrations in areas with intensive agricultural irrigation, such as the Central Domain (Fig. 12).

## Conclusions

The groundwater bodies of the Júcar River Basin have different chemical states in relation to pesticide presence, and some of them do not reach good chemical status (Buñol-Cheste and La Mancha Oriental GWBs). The pesticide that most frequently exceeded this limit was terbuthylazine (9), followed by bromacil (8) and atrazine (6). Individual maximum concentrations (e.g. terbuthylazine with a concentration of 900 ng/L) are much lower than the highest in Europe (478,000 ng/L) and in other districts of Spain such as the Hydrographic Basin of Catalonia (9950 ng/L). In comparison to other regions in Spain, it is noteworthy that the Júcar River Basin shows significant concentrations and frequencies of bromacil due to the presence of citric crops.

Geographically, pesticide distribution corresponds with agricultural land or nearby areas. The highest average concentrations are found in areas with irrigated crops. These results are consistent with the DAR values obtained in this study, which indicate that the groundwater contamination is probably diffuse in origin. In general, pesticides that have a higher GUS are more likely to be found in groundwater, and triazine pesticides (terbuthylazine, simazine and atrazine) have been found more often. However, lindane, metolachlor and propazine have a high GUS but have not been detected as often as expected. This is probably due to lindane being banned in 2001, propazine and metolachlor in 2003 and atrazine and simazine in 2004.

Principal component analysis indicates that nitrate groundwater concentrations are positively correlated with chloride concentrations and electrical conductivity, whereas pesticides are positively correlated with total organic carbon contents. The relationship between nitrate concentration and conductivity can be explained by taking into account that major groundwater withdrawals mostly occur

in irrigated cropland. In these areas, irrigation return flows favour pollutant transport to the saturated zone. Therefore, there is a need for further knowledge of the processes that affect this type of pollution. This research is a starting point for studying groundwater pollution in more detail for understanding the factors that govern the distribution and fate of pesticides in groundwater.

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